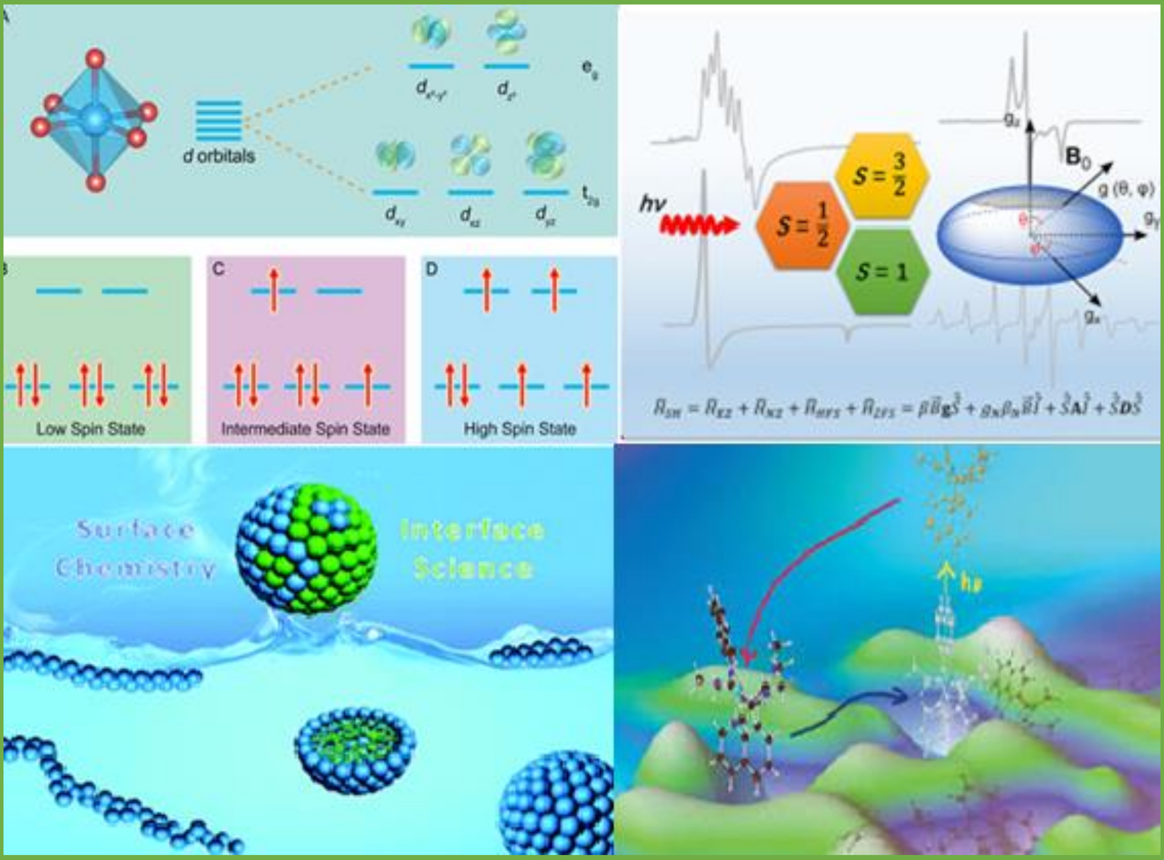
CHE (N)-301

B.Sc. Vth Semester

ADVANCE CHEMISTRY-I



DEPARTMENT OF CHEMISTRY
SCHOOL OF SCIENCES

UTTARAKHAND OPEN UNIVERSITY

HALDWANI, (NAINITAL)

UTTARKHAND-263139

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1.1 INTRODUCTION

The world of coordination chemistry is rich and complex, leading scientists to develop various theories to explain the unique bonding, color, and magnetic properties of metal complexes. While useful for explaining some complexes like [$Ni(CO)_4$] and [$Cr(CO)_6$] the EAN rule couldn't account for varying coordination numbers or explain many real-world behaviors.

To overcome these gaps, the Valence Bond Theory (VBT) was introduced, offering better insight into the geometry and bonding of complexes through orbital hybridization. However, VBT still couldn't explain the color and magnetic properties of these compounds. This led to the development of the Crystal Field Theory (CFT), which considers how ligand arrangement affects d-orbital energies unlocking explanations for electronic transitions, magnetism, and complex geometries. Each theory builds on the last, reflecting the evolving understanding of bonding in coordination chemistry.

1.2 OBJECTIVES

By the end of this unit, learners will be able to:

1. Understand the basic concepts of metal-ligand bonding in coordination compounds.
2. Recognize the limitations of Valence Bond Theory (VBT) in explaining complex bonding.
3. Explain the fundamental principles of Crystal Field Theory (CFT).
4. Identify and describe the factors that affect crystal field splitting energy (Δ).
5. Apply CFT to explain properties such as color, magnetic behavior, and stability of complexes.
6. Develop an understanding of Ligand Field Theory (LFT) as an improvement over CFT.
7. Gain a basic conceptual understanding of Molecular Orbital Theory (MOT) and its application to metal complexes.

1.3 LIMITATION OF VALANCE BOND THEORY

Valence Bond Theory (VBT), a hybridization-based model proposed by Linus Pauling, was one of the earliest attempts to explain metal-ligand bonding in coordination compounds. According to this theory, the bonding is purely covalent in nature, with metal atoms utilizing hybrid orbitals to accommodate ligands. However, despite its foundational role, VBT has several significant limitations that restrict its applicability in modern coordination chemistry. These are outlined below:

1. **Inability to Explain Stability Across Geometries and Coordination Numbers** VBT falls short in explaining the relative stability of different geometries and coordination numbers in transition metal complexes. For instance, it does not adequately clarify why **Co^{2+} (d^7)** can form both tetrahedral and octahedral complexes, while **Ni^{2+} (d^8)** typically forms only octahedral complexes, with tetrahedral forms being extremely rare.

2. **Distorted Geometry of Complexes Remains Unexplained**- The theory also fails to account for structural distortions. A key example is **Cu^{2+}**, which almost always forms **distorted octahedral complexes**, even when all six ligands are identical—something VBT cannot explain.

3. **No Explanation for Color in Complexes**- One of the most visible limitations of VBT is its inability to explain the **origin of color** in coordination compounds. Since it lacks a detailed description of d-orbital splitting, it cannot relate electronic transitions to the observed spectral properties.

4. **Ligand Strength and the Spectrochemical Series Not Addressed** VBT does not offer any framework to classify ligands as **strong field** or **weak field**, nor can it explain their position in the **spectrochemical series**. It provides no insight into how different ligands influence the electronic structure of the metal center.

5. **Inaccurate Magnetic Moment Predictions**- Magnetic moment (μ_s) is calculated in VBT using the spin-only formula:

$$\mu_s = \sqrt{n(n+2)} \text{ B.M.} \quad \text{(where } n \text{ = number of unpaired electrons)}$$

However, experimental values often exceed those predicted by this equation. VBT does not consider **orbital contributions** to magnetic moment, leading to discrepancies between theory and reality.

6. **Failure to Predict Actual Magnetic Behavior**- While VBT can estimate the number of unpaired electrons, it often misrepresents their relationship to the geometry and magnetism of complexes. For example, it predicts all square planar **Ni^{2+} (d^8)** complexes

(via **dsp^2 hybridization**) to be diamagnetic and all tetrahedral ones (via **sp^3 hybridization**) to be paramagnetic. Yet, **X-ray crystallography** and magnetic studies have shown that the same complex may exist in both **paramagnetic and diamagnetic** forms, a contradiction VBT cannot resolve.

7. **Incorrect Ionic vs Covalent Character Predictions**- According to VBT, **inner orbital (d^2sp^3)** octahedral complexes are covalent, whereas **outer orbital (sp^3d^2)** ones are ionic. However, many outer orbital complexes exhibit covalent behavior, and some predicted to be covalent behave ionically—again, beyond the explanatory power of VBT.

8. **No Insight into Reactivity or Activation Energies**- VBT does not provide any framework to understand the **reactivity trends** among inner orbital complexes (especially those involving **d^3, d^4, d^5, and d^6 ions**) or the differences in **activation energies** in similar complexes.

9. **Failure to Explain Kinetics of Complexes**- The theory offers no explanation for the **kinetic behavior** of coordination compounds. It cannot distinguish between **labile** and **inert** complexes or predict their rates of ligand substitution.

1.4 AN ELEMENTARY IDEA OF CRYSTAL FIELD THEORY

1.4.1 Introduction to Crystal Field Theory (CFT)

In light of the limitations associated with Valence Bond Theory (VBT), an alternative model known as Crystal Field Theory (CFT) was developed to explain bonding in transition metal complexes more effectively. This theory was originally proposed by Bethe and van Vleck to describe the bonding in ionic crystals. Later, in 1952, Hans Bethe and John Hasbrouck Van Vleck's ideas were extended by Van Vleck and F. A. Cotton to explain the nature of bonding in metal-ligand coordination complexes, giving rise to what we now refer to as CFT in coordination chemistry.

1.4.1.1 Fundamental Postulates of Crystal Field Theory

1. **Metal-Ligand Environment**- According to CFT, a central metal ion (CMI) in a coordination complex is surrounded by a specific number of ligands arranged in a geometric fashion (e.g., octahedral, tetrahedral, square planar).

2. **Nature of Ligands**- Ligands in coordination complexes are treated as **point charges** (if negatively charged) or as **point dipoles** (if neutral molecules like NH_3, H_2O, etc.).

   (a) *Negatively charged ligands* act as point charges.

   (b) *Neutral ligands* act as point dipoles, where the negatively charged pole of the dipole is directed toward the metal ion.

3. **No Orbital Overlap**- CFT assumes no orbital overlap between the metal ion and ligands. This implies that metal-ligand bonding has zero covalent character. Unlike VBT, CFT does not involve hybridization or sharing of electrons.

4. **Purely Electrostatic Interaction**- The interaction between the metal ion and ligands is 100% electrostatic. Ligands are attracted to the positive charge of the central metal ion via ionic forces. In the case of neutral ligands, their negative pole aligns toward the metal ion to create this attraction.

1.4.2 Crystal Field Theory for Octahedral Complexes

In octahedral complexes, six ligands symmetrically surround the central metal ion, positioned at the corners of an octahedron. This symmetrical arrangement directly influences the energy levels of the metal's d-orbitals.

Step I – Splitting of d-Orbitals in an Octahedral Field

The five d-orbitals of the central metal ion are initially degenerate (equal in energy). However, when ligands approach the metal ion in an octahedral geometry, electrostatic repulsion between the ligand electrons and the electrons in the metal's d-orbitals causes a splitting of these orbitals into two distinct energy levels:

1. **t_2g Set – Non-Axial Orbitals**- These include the d_{xy}, d_{yz}, and d_{zx} orbitals. These orbitals lie between the axes, hence experience less repulsion from incoming ligands. As a result, they remain at lower energy.
2. **eg Set – Axial Orbitals**- This set includes $d_{x^2-y^2}$ and dz^2 orbitals. These orbitals lie along the axes directly in the path of the approaching ligands leading to greater repulsion and, thus, higher energy.

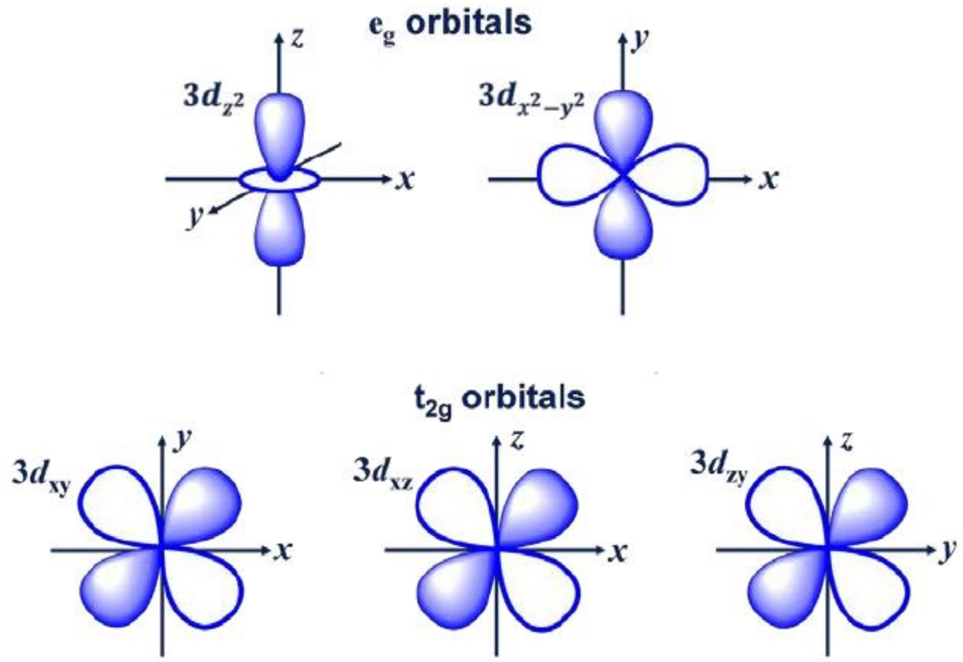


Figure 1.1: Different types of d-orbitals

This difference in energy between the t_2g and eg orbitals is known as the **crystal field splitting energy (Δ_o)** for octahedral complexes.

This elegant model of orbital splitting allows CFT to successfully explain several important properties of transition metal complexes, including (**Fig.1.1**):

- Color (due to d–d transitions),
- Magnetic behavior (based on electron configurations),
- High spin vs. low spin states,
- Ligand strength (via crystal field splitting values).

When a central metal ion (CMI) exists in isolation, all five of its d-orbitals possess the same energy and are said to be degenerate. However, when ligands approach the metal ion, their negative charge (or the negative end in the case of neutral ligands) creates electrostatic repulsion with the electrons present in the d-orbitals of the metal ion. This repulsion leads to a slight overall increase in the energy of all five d-orbitals. When six ligands surround the metal ion symmetrically in an octahedral geometry, the repulsion becomes directionally dependent, causing the initially degenerate d-orbitals to split into two distinct energy levels. Three orbitals $d_{x\gamma}$, dyz, and dz_x experience less repulsion as they lie between the axes and form the lower energy set, known as the *t_2g* orbitals. The remaining two orbitals $d_{x^2-\gamma^2}$ and dz^2 are oriented along the axes, directly facing the ligands, and thus experience greater repulsion, forming the higher energy *eg* set. This separation of energy levels is referred to as **crystal field splitting**, and the energy gap between the *t₂g* and *eg* orbitals is known as the **crystal field splitting energy (Δ_o)**. This concept is fundamental to understanding the electronic structure, magnetic properties, color, and stability of octahedral coordination complexes.

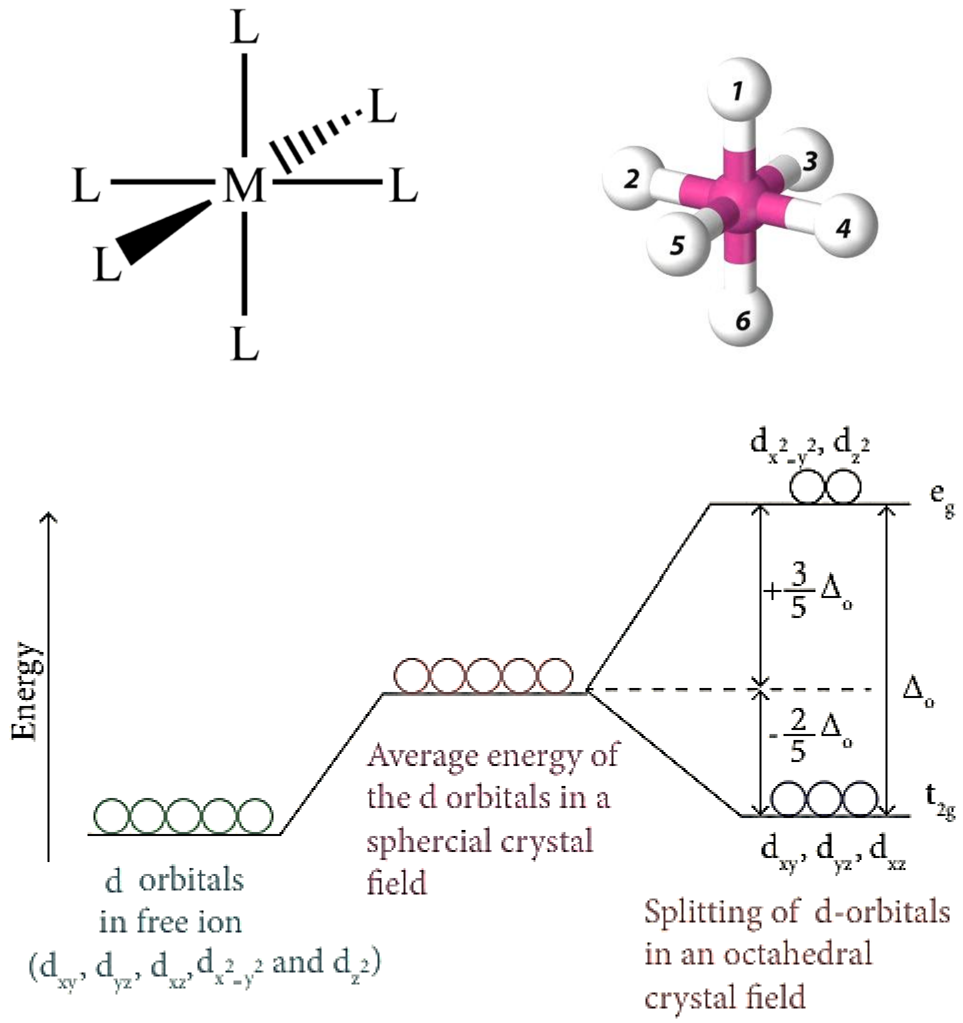


Figure 1.2: Crystal field splitting of d orbitals in octahedral complex

1.4.3 Crystal Field splitting for Tetrahedral Complexes

Tetrahedral complexes have a lower splitting energy (Δt) and an inverted crystal field splitting of d-orbitals when compared to octahedral complexes. The energy of the dz2 and dx2-y2 orbitals (e set) is lower than that of the dxy, dxz, and dyz orbitals (t2 set). This is because a tetrahedron's ligands are positioned between its axes, which increases the t2 set's repulsion.

Step 1: Shape and Splitting of the Five d-Orbitals

In any transition metal ion (called the central metal ion or CMI), there are five d-orbitals, and their energies are the same when the ion is isolated this is called a degenerate set.

But we can group these orbitals into two sets:

- **'e' set (axial orbitals):** These include the $dx^2–y^2$ and dz^2 orbitals. These point directly along the axes.
- **'t_2' set (non-axial orbitals):** These include dxy, dyz, and dxz orbitals. These lie between the axes and are often called the non-axial set.

These groupings help us understand how ligands interact with these orbitals based on their direction and orientation.

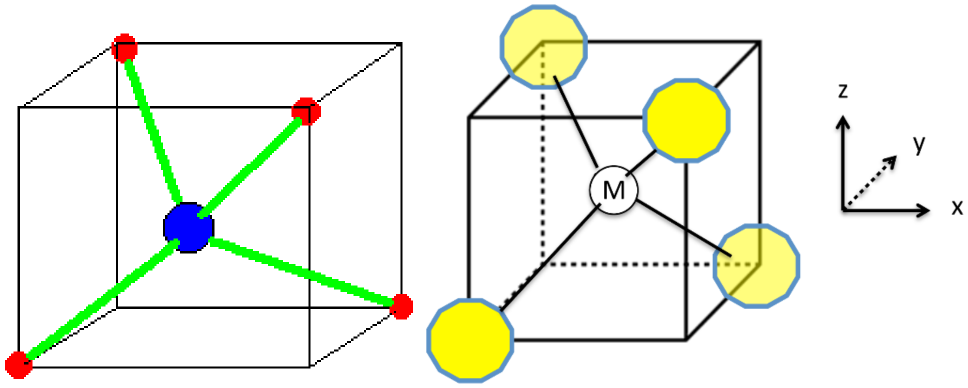


Figure 1.3: 3-D structure of the Tetrahedral complexes

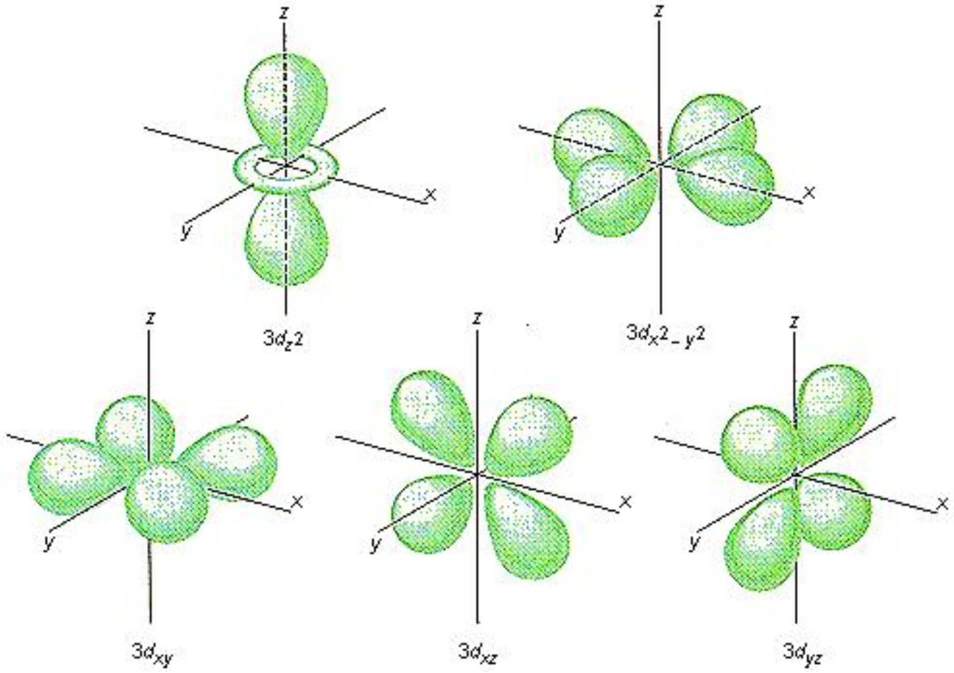


Figure 1.4: Orientation of orbitals of the Tetrahedral complexes

Step 2: Ligand Arrangement in Tetrahedral Complexes

In a tetrahedral complex, four ligands surround the metal ion. However, unlike octahedral complexes (where ligands approach along the axes), here ligands approach from the corners of a tetrahedron which means they come between the axes, not directly along them.

This is important because it affects which orbitals feel more repulsion due to the negatively charged ligands.

Step 3: Crystal Field Splitting in Tetrahedral Complexes

Here's where the magic happens crystal field splitting

- In the free ion (no ligands), all 5 d-orbitals have the same energy (degenerate).
- But when **4 ligands approach from non-axial directions**, they repel the electrons in the d-orbitals. This repulsion isn't equal for all orbitals:
  - t_2 orbitals (dxy, dyz, dxz) point more toward the ligands → they experience more repulsion → their energy increases.
  - e orbitals ($dx^2–y^2$, dz^2) are less affected as they point away → they experience less repulsion → their energy stays lower.

So, the orbitals **split into two sets**:

- Lower energy = e set
- Higher energy = t_2 set

This energy gap is called **crystal field splitting energy (Δt)** for tetrahedral complexes.

Step 4: How Electrons Fill These Orbitals (dn Configuration)

Let's say a metal ion has n d-electrons (dn configuration). These electrons will now fill the e and t_2 orbitals based on the energy difference (Δt).

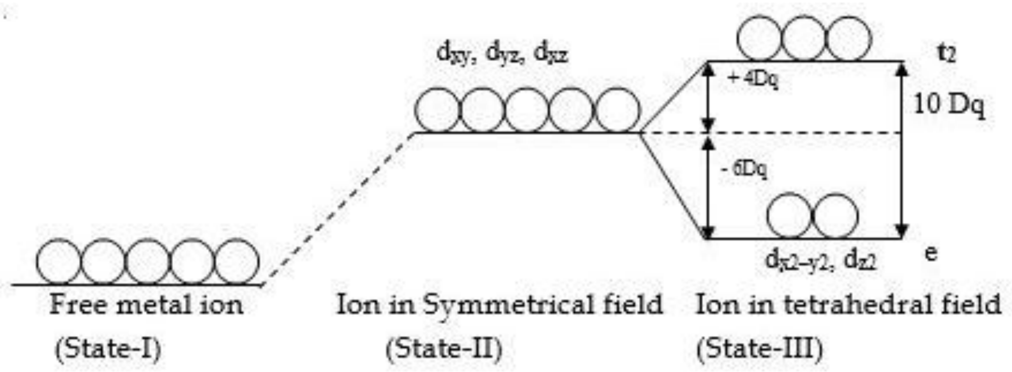


Figure 1.5: Splitting of the d-orbital of Tetrahedral complexes

Let's define:

- q = number of electrons in the e set (can be 1 to 4)
- p = number of electrons in the t_2 set (can be 1 to 6)

Now, the energy contribution of these electrons is:

- For each electron in the e set → energy decreases by -0.6 Δt→ So total decrease = -0.6 Δt × q
- For each electron in the t_2 set → energy increases by +0.4 Δt→ So total increase = +0.4 Δt × p

CFSE – Crystal Field Stabilization Energy;

$$\boxed{\mathbf{CFSE = (-0.6 \times q + 0.4 \times p)\, \Delta t}}$$

1.4.4 Crystal Field Splitting in Square Planar Complexe

Given that of the distinct ligand arrangement in square planar complexes, the crystal field splitting of d-orbitals differs greatly from that in octahedral or tetrahedral geometries. Four different energy levels were formed by the splitting of the d-orbitals, with the dz^2 orbital becoming more stable than in an octahedral field and the dx^2-y^2 orbital undergoing the most destabilization. This design favors d^8 electron complexes, which are frequently square planar.

Square planar complexes are formed when four ligands surround the central metal ion (CMI) in a flat square arrangement, like the four corners of a square on a tabletop. This shape is similar to an octahedral complex, except that the two ligands along the z-axis are missing. That's a crucial difference and it changes everything in terms of orbital energy.

1.4.4.1 d-Orbitals Split in Square Planar Geometry

In the free metal ion, all five d-orbitals are degenerate (have the same energy). But when ligands approach in a square planar fashion, the repulsion from these ligands is not equal across all d-orbitals, leading to a unique pattern of crystal field splitting.

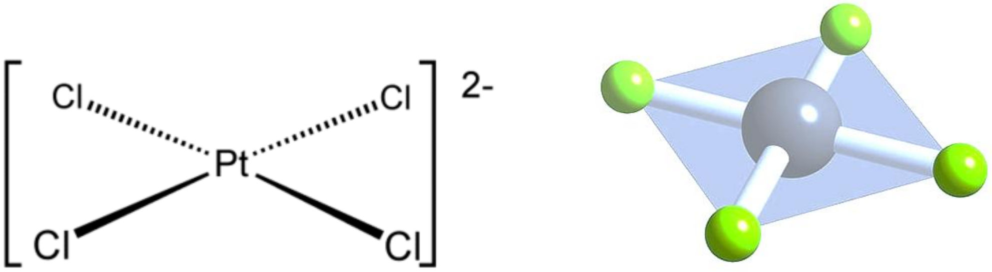


Figure 1.6 Structure of Square planer complexes

Let's break it down step by step:

1. Ligands approach along the x and y axes, but not along the z-axis. So, the orbitals that lie in the xy-plane feel strong repulsion, especially the one that points directly at the ligands.
2. Here's how the d-orbitals arrange from highest to lowest energy in square planar geometry:
    - Highest energy → **$dx^2–y^2$**, because this orbital lies directly along the x and y axes, exactly where the ligands are approaching — so it experiences the strongest repulsion.
    - Next highest → **dxy**, it also lies in the plane, but between the ligands, so it's slightly less affected than $dx^2–y^2$.
    - Middle → **dz^2,** even though it lies along the z-axis (where no ligands are present), it has a doughnut-shaped ring in the xy-plane, so it still feels some repulsion.
    - Lower energies → **dxz and dyz**, these orbitals are oriented between the z-axis and x/y-axes — and since there are no ligands along the z-axis, they experience minimal repulsion and remain at lower energy.

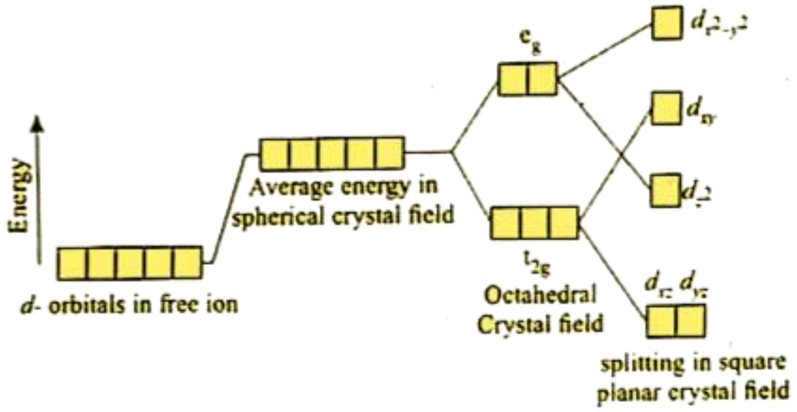


Figure 1.7 Splitting of the d-orbital in square planner complexes

Large Energy Gap: The most important feature of square planar splitting is the very large energy gap between $dx^2–y^2$ and the rest of the orbitals. In fact, this gap is so large that electrons prefer to pair up in the lower-energy orbitals rather than jump to the $dx^2–y^2$ orbital.

Why'd^8 Metal Ions Love Square Planar Geometry- Square planar complexes are most commonly formed by metal ions with a d^8 configuration (like Ni^{2+}, Pd^{2+}, Pt^{2+}).

- Because in a d^8 system, you have 8 d-electrons.
- These electrons can completely fill the four lower-energy d-orbitals (dxz, dyz, dz^2, and dxy).

- The $dx^2–y^2$ orbital remains empty, avoiding the high-energy cost.
- This results in a low-spin, highly stable complex.
- Square planar geometry = octahedral minus two ligands on the z-axis.
- Ligands repel d-orbitals most along x and y axes, especially the $dx^2–y^2$ orbital.
- Energy levels from high to low: $dx^2–y^2 > dxy > dz^2 > dxz \approx dyz$
- d^8 metals form square planar complexes easily due to a perfect match with available low-energy orbitals.

1.5 SPECTROCHEMICAL SERIES

Spectrochemical Series is an empirical arrangement of ligands in the order of their increasing ability to split the d-orbitals of a central metal ion in a coordination complex, based on Crystal Field Theory (CFT). It classifies ligands as weak field or strong field, depending on the magnitude of crystal field splitting energy (Δ) they produce. In other hand *spectrochemical Series is the order of ligands arranged according to their increasing crystal field splitting power, from weak field ligands to strong field ligands.*

spectrochemical Series as:

Weak end ←

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^- < F^- < Urea < OH^- < C_2H_5OH < C_2O_4^{2-} < < O_2^- < H_2O < NCS^- < gly < NH3 < py < en < Pn < SO_3^{2-} < NH_2OH < bpy < phen < NO_2^- < CH_3^- < C_6H_5^- < R_3P < CN^- < CO < NO$

→

Strong end

Strength	***Ligands***	***Splitting Power (Δ)***
Weak Field	I^-, Br^-, S^{2-}, $SCN^-(S)$, Cl^-	*Low (Δ small)*
Moderate	F^-, OH^-, H_2O, NO_2^-, $NCS^-(N)$, py, en	*Medium (Δ moderate)*
Strong Field	bipy, phen, CN^-, CO	*High (Δ)*

- *The greater the splitting power of a ligand, the stronger the field strength.*
- *Weak field ligands produce smaller crystal field splitting energy (Δ).*
- *The type of ligand determines the color and magnetic properties of the complex.*

- *Strong field ligands often cause pairing of electrons, leading to low-spin configuration.*
- *The series is mostly based on experimental observations, especially from electronic spectra*

1.5.1 Effect of Metal Ion on Crystal Field Splitting Energy (Δ_0)

When the ligand remains the same, even then the value of crystal field splitting energy (Δ_0) can vary depending on the nature of the central metal ion (CMI). If the metal ion has a higher positive charge, it pulls the ligands more strongly, resulting in greater d-orbital splitting. Similarly, transition metals from the 2nd and 3rd series (4d and 5d elements) generally show larger Δ_0 values compared to 3d metals. This is due to the greater radial extension and polarizability of their d-orbitals, which allow better overlap with ligands.

More positive charge on metal ion + Heavier transition series metal (4d or 5d) ⟶ Higher crystal field splitting energy (Δ_0)

1.5.1.1 Distribution of d^n Configuration in Octahedral Complexes

Now, the way d-electrons are distributed among the split d-orbitals depends on the relative magnitude of Δ_0 (splitting energy) and P (pairing energy).

- ***Case (a): When $\Delta_0 > P \rightarrow$ Strong Field Condition***

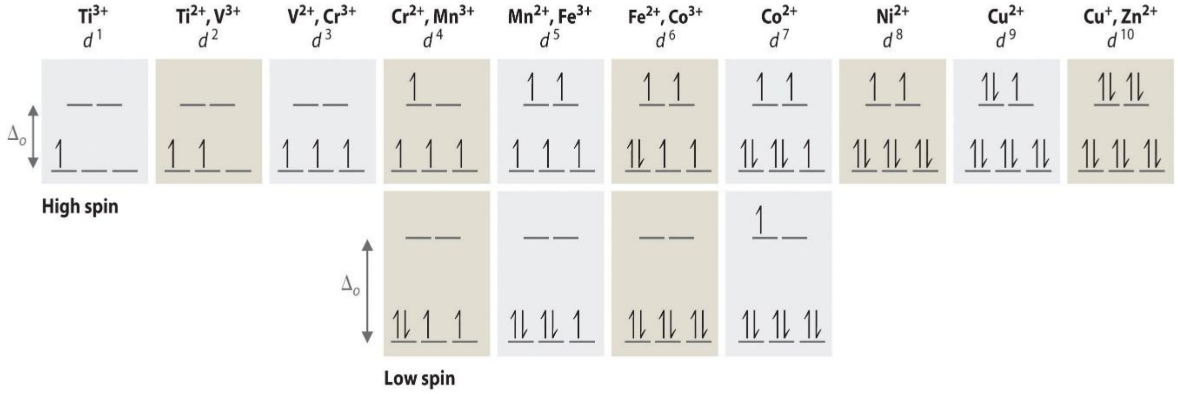
When an octahedral complex contains strong field ligands like CN^-, CO, or NO^+, the crystal field splitting (Δ_0) becomes larger than the pairing energy (P). Under this condition, it becomes energetically favorable for electrons to pair up in the lower-energy t_2g orbitals before occupying the higher-energy eg orbitals.

- Electrons prefer pairing in t_2g set (lower orbitals)
- Low-spin complexes are formed
- Results in fewer unpaired electrons
- Often leads to diamagnetic or weakly paramagnetic nature
- Common with ligands like CN^-, CO, NO^+, en, bipy, phen

Electron Configuration in Strong Field (Low Spin)

d^n Configuration	Electron Arrangement (Strong Field)	Spin Type
d^4	$t_2g^4\ eg^0$	Low spin
d^5	$t_2g^5\ eg^0$	Low spin

d^n Configuration	Electron Arrangement (Strong Field)	Spin Type
d^6	$t_{2}g^6\ eg^0$	Low spin
d^7	$t_{2}g^6\ eg^1$	Low spin
d^8	$t_{2}g^6\ eg^2$	Low spin



1.6 CRYSTAL FIELD STABILIZATION ENERGY (CFSE)

In octahedral coordination geometry, the five-degenerate d-orbitals of a transition metal ion split into two distinct sets due to the approach of ligands along the x, y, and z axes. This splitting leads to an overall energy change in the system, which is quantified as Crystal Field Stabilization Energy (CFSE).

Crystal field stabilization energy (CFSE) in octahedral complexes is the energy difference between the d-orbitals when they are split in an octahedral ligand field compared to their energy in a spherical field. This splitting arises because ligands interact with the d-orbitals of a metal ion, causing some orbitals to be stabilized (lower energy) and others to be destabilized (higher energy)

Crystal Field Splitting: When ligands surround a central metal ion in an octahedral geometry:

The **d-orbitals split** into two energy levels:

- **t_2g set**: Lower energy → d_{xy}, d_{yz}, d_{zx}
- **eg set**: Higher energy → $d_{x^2-y^2}, d_{z^2}$

Let the total number of electrons in the *dn* configuration be distributed as:

- **p** electrons in the **t_2g** orbitals (p ranges from 1 to 6)
- **q** electrons in the **eg** orbitals (q ranges from 0 to 4)

1. Energy Changes due to Electron Placement:

- Each electron in t_2g → energy decreases by 0.4 Δ_o
- Each electron in eg → energy increases by 0.6 Δ_o

Total Crystal Field Stabilization Energy (CFSE):

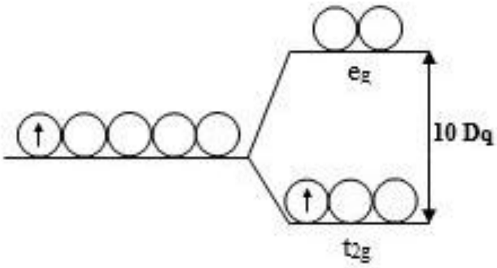
$$CFSE = (-0.4p + 0.6q)\,\Delta 0$$

Where:

- **Δ_o** = Octahedral crystal field splitting energy
- **p** = Number of electrons in t_2g
- **q** = Number of electrons in eg

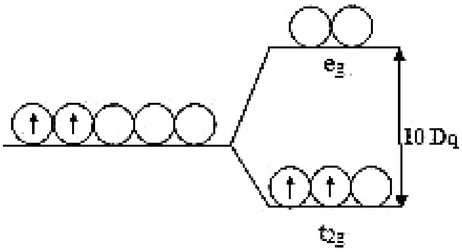
Calculation of CFSE for octahedral complexes

CFSE For d^1



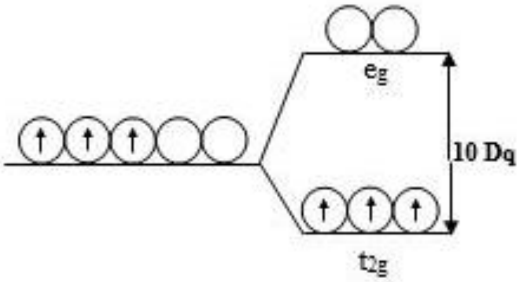
C.F.S.E . = x (-4Dq) + y (+6Dq) + P
C.F.S.E. = 1 x (-4Dq) + 0 x (+ 6Dq) +0
= -4Dq

CFSE For d^2



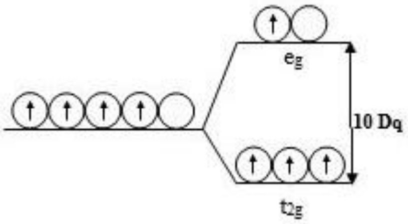
C.F.S.E. = x (-4Dq) + y (+6Dq) + P
C.F.S.E. = 2 x (-4Dq) + 0 x (+6Dq) +0
= -8Dq

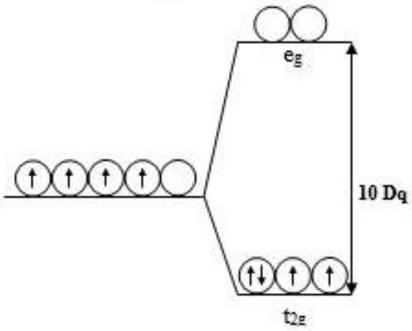
CFSE For d^3



C.F.S.E. = x (-4Dq) + y (+6Dq) + P
C.F.S.E. = 3 x (-4Dq) + 0 x (+ 6Dq) + 0
= -12Dq

CFSE For d^4 both high and low spin

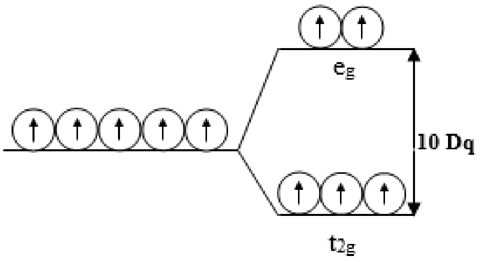


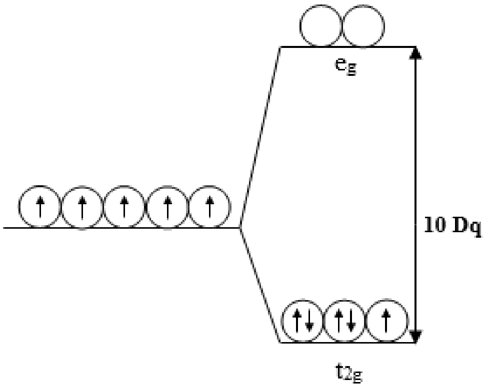


C.F.S.E. = x (-4Dq) + y (+6Dq) + P
C.F.S.E. = 3 x (-4Dq) + 1 x (+6Dq) +0
= -12Dq + 6Dq
= -6Dq

C.F.S.E. = x (-4Dq) + y (+6Dq) + P
C.F.S.E. = 4 x (-4Dq) + 0 x (+6Dq) + P
= -16Dq + P

CFSE For d^5 both high and low spin





C.F.S.E. = x (-4Dq) + y (+6Dq)+P
C.F.S.E. = 3 x (-4Dq) + 2 x (+6Dq) +0
= -12Dq + 12Dq
= 0 Dq

C.F.S.E. = x (-4Dq) + y (+6Dq) + P
C.F.S.E. = 5 x (-4Dq) + 0 x (+6Dq) + 2P
= -20Dq + 2P

1.6.1 Factors Affecting CFSE (Crystal Field Stabilization Energy)

CFSE tells us **how much stability** a metal complex gains due to the arrangement of d-electrons in split d-orbitals when surrounded by ligands.

1. **Charge on the Metal Ion-** A higher positive charge on the metal ion increases the electrostatic attraction between the metal and the ligands. This stronger attraction pulls the ligands closer, leading to greater splitting of the d-orbitals. As a result, the crystal field splitting energy (Δ_o) increases, which in turn increases the CFSE. For example, Fe^{3+} forms complexes with higher CFSE than Fe^{2+} due to its higher charge.

Example:

- **Fe^{2+}** vs **Fe^{3+}**:
  - Fe^{3+} has +3 charge, which pulls ligands closer than Fe^{2+} (+2).
  - So, Fe^{3+} complexes have higher CFSE than Fe^{2+}.

2. Nature of the Ligands- Ligands are not all the same — some create strong fields (big splitting), others create weak fields (small splitting). This is explained by the Spectrochemical Series, which ranks ligands from weak field to strong field:

$$\mathbf{I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < en < NO_2^- < CN^- < CO}$$

- **Strong field ligands** (like CN^-, CO): cause **large Δ_o** → higher CFSE
- **Weak field ligands** (like Cl^-, H_2O): cause **small Δ_o** → lower CFSE

Example:

- $[Fe(CN)_6]^{3-}$ has a strong field ligand (CN^-) → high CFSE
- $[Fe(H_2O)_6]^{3+}$ has a weaker ligand (H_2O) → lower CFSE

2. **Spin State of the Complex-** The spin state of a complex depends on the metal ion and the strength of the ligand. In high-spin complexes, electrons occupy higher energy orbitals first, resulting in more unpaired electrons and lower CFSE. This usually happens with weak field ligands. In contrast, low-spin complexes form when strong field ligands are present, causing electrons to pair in lower orbitals, leading to higher CFSE due to greater stabilization. Thus, high-spin → low CFSE, and low-spin → high CFSE.

(i) High-Spin Complex: Electrons occupy higher orbitals first (less pairing)

(ii) Low-Spin Complex: Electrons prefer to pair up in lower orbitals (more pairing)

Spin state depends on:

- The **metal ion**
- The **ligand strength**

Example:

For **d^6 metal ion (like Fe^{2+})**:

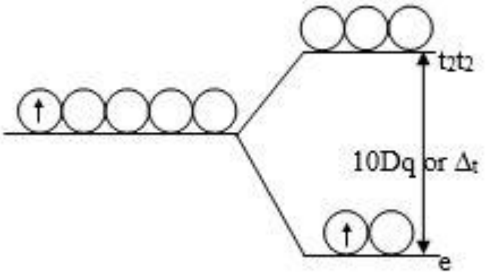
- With H_2O ligand (weak field) → $[Fe(H_2O)_6]^{2+}$ → High-spin
- With CN^- ligand (strong field) → $[Fe(CN)_6]^{4-}$ → Low-spin

So, $[Fe(CN)_6]^{4-}$ has higher CFSE than $[Fe(H_2O)_6]^{2+}$.

CFSE of the d1 to d10 tetrahedral complexes as follows;

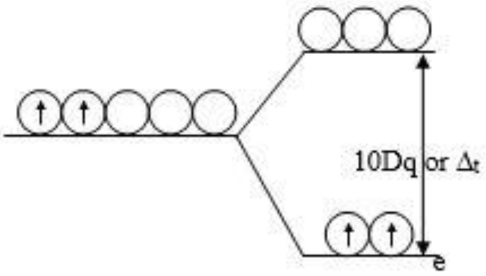
Weak field or Strong field, 10Dq < Pairing energy (P)

1)d^1



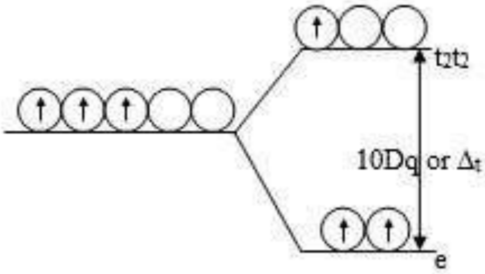
C.F.S.E. = x (- 6Dq) + y (+4Dq) +P
C.F.S.E = 1 x (-6Dq) + 0 x (+4Dq) +0
= - 6Dq

2) d^2



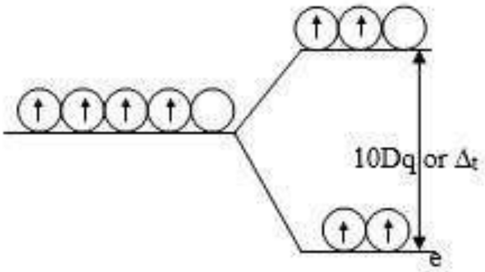
C.F.S.E. = x (- 6Dq) + y (+4Dq) + 0
C.F.S.E = 2 x (-6Dq) + 0 x (+4Dq) +0
= - 12Dq

3)d^3



C.F.S.E. = x (- 6Dq) + y (+4Dq) + P
C.F.S.E = 2 x (-6Dq) + 1 x (+4Dq) +0
= -12Dq + 4Dq= -12Dq + 8Dq
= - 8Dq

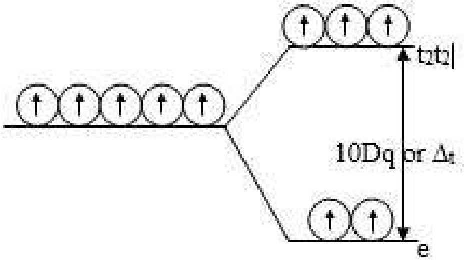
4) d^4



C.F.S.E. = x (- 6Dq) + y (+4Dq) +P
C.F.S. E= 2 x (-6Dq) + 2 x (+4Dq) +0

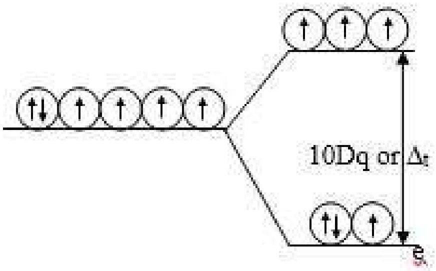
= - 4Dq

5)d^5



C.F.S.E. = x (- 6Dq) + y (+4Dq) +P
C.F.S.E = 2 x (-6Dq) + 3 x (+4Dq) +0
= -12Dq + 12Dq = -18Dq + 12Dq + P
= 0 Dq

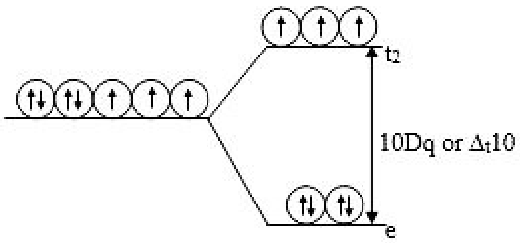
6) d^6



C.F.S.E. = x (- 6Dq) + y (+4Dq) +P
C.F.S. E= 3 x (-6Dq) + 3 x (+4Dq) + P

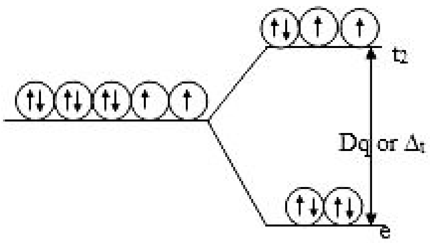
= - 6Dq + P

7)d^7



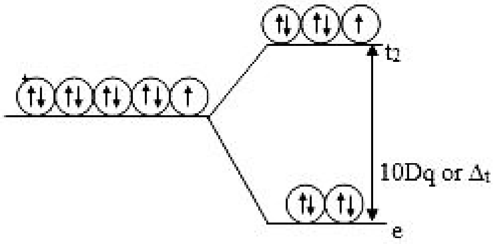
C.F.S.E. = x (- 6Dq) + y (+4Dq) + P
C.F.S.E = 4 x (-6Dq) + 3 x (+4Dq) + 2P
= -24Dq + 12Dq + 2P
= - 12Dq + 2P

8) d^8



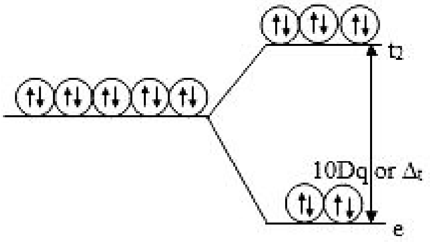
C.F.S.E. = x (- 6Dq) + y (+4Dq) + P
C.F.S. E= 4 x (-6Dq) + 4 x (+4Dq) + 3P
= -24Dq + 16Dq + 3P
= - 8Dq + 3P

9)d^9



C.F.S.E. = x (- 6Dq) + y (+4Dq) + P
C.F.S.E = 4 x (-6Dq) + 5 x (+4Dq) + 4P
= -24Dq + 20Dq + 4P
= - 4Dq + 4P

10) d^{10}



C.F.S.E. = x (- 6Dq) + y (+4Dq) + P
C.F.S.E = 4 x (-6Dq) + 6 x (+4Dq) + 5P
= -24Dq + 24Dq + 5P
= Dq + 5P

1.7 APPLICATIONS OF CRYSTAL FIELD THEORY (CFT)

Crystal Field Theory (CFT) is a powerful tool that helps chemists understand and predict many important properties of transition metal complexes. Let's explore how CFT explains magnetism, stability, and even the color of these fascinating compounds.

1. Magnetism in Complexes -CFT tells us that the magnetic behavior of a complex depends on whether the d-orbitals contain unpaired electrons or not.

- If unpaired electrons are present in the split d-orbitals, the complex is paramagnetic (it gets attracted to a magnetic field).
- If all electrons are paired, the complex is diamagnetic (not attracted to a magnetic field).

Let's understand this with examples:

(I) Complex: $[Co(F)_6]^{3-}$

- Electronic configuration of Co: $3d^7 4s^2$

- Oxidation state: $Co^{3+} \rightarrow 3d^6$
- Fluoride (F^-) is a **weak field ligand**, so the complex forms a **high-spin configuration**.

In this case:

- The d-orbitals split into t_2g and e_g
- The 6 electrons arrange themselves to maximize unpaired electrons.
- Result: 4 unpaired electrons → So, the complex is paramagnetic.

Magnetic moment (μ) is calculated using the formula:

$$\mu = \sqrt{n\,(n+2)} \quad \text{B.M.}$$

$$\sqrt{4\,(4+2)}$$

$$\mathbf{\mu = 4.9\ BM}$$

2. Stability of Complexes- Crystal Field Stabilization Energy (CFSE) plays a key role in determining the relative stability of different oxidation states of a metal under strong field or weak field conditions.

Let's take cobalt (Co) as an example:

Under Strong Field Ligands:

- Co(III) configuration: $t_2g^6\ eg^0$

  $CFSE = 6 \times (-0.4\ \Delta_o) + 3P = -2.4\ \Delta_o + 3P$

- Co(II) configuration: $t_2g^6\ eg^1$

  $CFSE = 6 \times (-0.4\ \Delta_o) + 1 \times (+0.6\ \Delta_o) + 3P = -1.8\ \Delta_o + 3P$

Co(III) is more stable in strong field ligands due to higher CFSE

Under Weak Field Ligands:

- **Co(III)** configuration: $t_2g^4\ eg^2$

  $CFSE = (4 \times -0.4\ \Delta_o) + (2 \times +0.6\ \Delta_o) + 1P = \mathbf{-0.4\ \Delta_o + 1P}$

- **Co(II)** configuration: $t_2g^5\ eg^2$

  $CFSE = (5 \times -0.4\ \Delta_o) + (2 \times +0.6\ \Delta_o) + 2P = \mathbf{-0.8\ \Delta_o + 2P}$

Co(II) is more stable under weak field ligands.

Higher CFSE = Greater Stability of the complex

3. Color of Complexes – One of the most beautiful applications of CFT is in explaining the **color** of transition metal complexes. When white light passes through a solution of a complex, the behavior of that light determines the observed color:

1. If all wavelengths pass through, the complex appears white.

2. If all wavelengths are absorbed, the complex appears black.
3. If some wavelengths are absorbed and others transmitted or reflected the complex appears colored.
4. The absorbed wavelengths must be in the visible range (4000 Å – 7000 Å) to produce color.

The mechanism which is responsible for the colour in the complexes can be defined by d- d transition phenomena. According to d-d transition phenomena, when the e^- present in the lower energy splatted set of d- orbitals of the CMI absorbs the radiation of any particular wavelength, then there occurs the transition of e^- to the higher energy splitted set of d- orbitals, which is known as d-d transition phenomena, that can be represented as: -

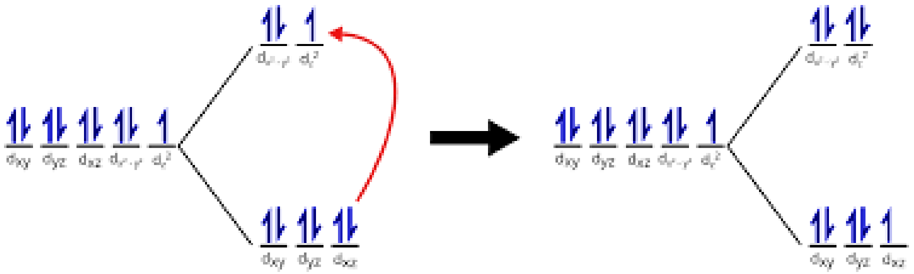


Figure 1.8 d-d transition

"When a complex absorbs electromagnetic radiation, the electrons in its ground state absorb that energy and move to a higher excited state. As the electrons return to their ground state, they release the absorbed energy. The color that the complex appears is not the one it absorbs, but its complementary color. For example, if a compound absorbs red light, it will appear green, which is the complementary color of red."

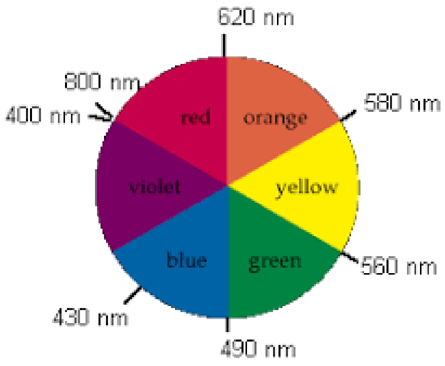


Figure 1.9 Color wheel

Color Depends on Which Wavelength Is Absorbed

For example:

Wavelength Absorbed	Color Seen (Complementary Color)
4000–4350 Å (violet)	Yellow-green
4800–4900 Å (blue)	Orange
5800–5900 Å (yellow)	Violet
6050–7000 Å (red)	Blue-green

When light hits a complex:

- Electrons in the lower-energy d-orbitals (t_2g) absorb energy.
- They jump to higher-energy orbitals (eg)
- This movement is called a d–d transition.
- The energy absorbed corresponds to a specific wavelength of light.
- The remaining (unabsorbed) wavelengths are what we actually see.

Only complexes with partially filled d-orbitals (like d^1 to d^9) show color.

- Complexes with d^0 or d^{10} configurations have no d–d transitions, so they appear colourless.

1.8 DETERMINATION OF THE SPINEL STRUCTURE

The compound $Mg^{2+}Al_2^{3+}O_4$ is known as mineral spinel. Based on this, all mixed metal oxides with the general formula $A^{2+}B_2^{3+}O_4$ are referred to as spinels, where the A^{2+} and B^{3+} cations may be the same or different.

In a spinel structure, the oxide ions (O^{2-}) form a cubic close-packed (ccp) lattice, creating two types of interstitial voids: tetrahedral and octahedral voids.

Spinels can be classified into two types based on the distribution of cations in these voids:

1. **Normal (Simple) Spinel-**: If all the A^{2+} cations occupy the tetrahedral voids and all the B^{3+} cations occupy the octahedral voids, the structure is called a normal spinel. It is represented as:

$$\mathbf{A^{2+}[B_2^{3+}]O_4}$$

2. **Inverse Spinel-:** If all the A^{2+} cations and half of the B^{3+} cations occupy the octahedral voids, while the remaining half of the B^{3+} cations occupy the tetrahedral voids, the structure is referred to as an inverse spinel. It is represented as:

$$B^{3+}[A^{2+}B^{3+}]O_4$$

The nature of a spinel (normal or inverse) can be determined by comparing the Crystal Field Stabilization Energy (CFSE) values of A^{2+} and B^{3+} cations in weak field octahedral and tetrahedral environments.

2.6.4.1 Spinel Structure of Mn_3O_4

To determine the spinel structure of Mn_3O_4, we first consider the electronic configurations of Mn^{2+} ($3d^5$) and Mn^{3+} ($3d^4$) ions in both octahedral and tetrahedral sites. The CFSE values under weak field conditions are:

Ion	CFSE in Octahedral Field	CFSE in Tetrahedral Field
Mn^{2+} ($3d^5$)	0	0
Mn^{3+} ($3d^4$)	$-0.9\ \Delta_o$	$-0.27\ \Delta_o$

Since Mn^{3+} has a significantly more negative CFSE in the octahedral field, it shows a preference for occupying the octahedral voids. Thus, Mn_3O_4 adopts a normal spinel structure:

$$Mn_3O_4 \rightarrow Mn^{2+}[Mn_2^{3+}]O_4$$

2.6.4.2 Spinel Structure of Fe_3O_4

Fe_3O_4 contains one Fe^{2+} ion and two Fe^{3+} ions. To determine its spinel structure, we analyze the distribution of Fe^{2+} ($3d^6$) and Fe^{3+} ($3d^5$) ions in octahedral and tetrahedral sites under weak field conditions:

Ion	CFSE in Octahedral Field	CFSE in Tetrahedral Field
Fe^{2+} ($3d^6$)	$-0.4\ \Delta_o$	$-0.27\ \Delta_o$
Fe^{3+} ($3d^5$)	0	0

Since Fe^{2+} shows a more negative CFSE in the octahedral field, it prefers to occupy octahedral sites, while Fe^{3+} ions are distributed between both types of voids. Therefore, Fe_3O_4 has an inverse spinel structure:

$$Fe_3O_4 \rightarrow Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$$

1.9 LIMITATIONS OF CRYSTAL FIELD THEORY (CFT)

While **Crystal Field Theory (CFT)** has been instrumental in explaining the electronic structures, colors, and magnetic properties of coordination compounds, it also has several limitations. These are outlined below:

1. **Neglect of Covalent Character**-: CFT considers only electrostatic (ionic) interactions between the metal cation and surrounding ligands. It does not account for covalent bonding or orbital overlap, which are significant in many coordination complexes.

2. **Failure to Explain Spectrochemical Series Completely**-: CFT cannot adequately explain why certain ligands (like CN^- and CO) produce a much stronger crystal field splitting than others (like Cl^- or F^-), as it does not consider π-backbonding or other covalent effects.

3. **Inability to Describe Metal-Ligand Bonding Mechanism**-: The theory does not provide any insight into how metal-ligand bonds are formed. It ignores the role of ligand orbitals in bond formation, which is addressed in more advanced theories like Ligand Field Theory or Molecular Orbital Theory.

4. **No Explanation for Spectral Intensities**-: CFT explains the energy of d-d transitions but does not explain their intensities. It cannot predict why some complexes are deeply colored while others are pale or colorless.

5. **Oversimplification of Geometry**-: The theory assumes perfect geometries (like ideal octahedral or tetrahedral), whereas actual complexes often show distortions due to factors like Jahn-Teller effect, steric hindrance, or electronic repulsion.

6. **Limited to d-Orbitals**-: CFT only considers the effect of the ligand field on the metal ion's d-orbitals and does not include s- or p-orbitals, which also play roles in bonding and properties of coordination compounds.

7. **Poor Prediction of Thermodynamic and Kinetic Properties**-: CFT cannot explain or predict the stability, reactivity, or substitution mechanisms of complexes. It gives no information about the kinetics of ligand exchange reactions.

1.10 LIGAND FIELD THEORY (LFT) AND MOLECULAR ORBITAL THEORY (MOT)

Crystal Field Theory (CFT) was originally developed to explain the behavior of electrons in metal complexes by treating the metal-ligand interaction as purely ionic (electrostatic). But real-life experimental evidence like electron spin resonance spectra shows that this interaction isn't purely ionic. Some of the metal's electrons are shared with or spread into ligand orbitals, showing that there is also covalent character in the bonding.

Ligand Field Theory (LFT) is an extension of Crystal Field Theory (CFT), refined to include the partial covalent nature of metal-ligand bonding. Evidence from electron spin resonance suggests that some electron density from metal ions diffuses into ligand orbitals, indicating the bonds are not purely electrostatic. When this overlap becomes significant, Molecular Orbital Theory (MOT) offers a better explanation. LFT thus serves as a bridge between purely electrostatic (CFT) and fully covalent (MOT) models. It is a parameter-based approach, relying on experimental data such as crystal field stabilization energy and Racah parameters derived from electronic spectra.

Molecular Orbital Theory (MOT) is an advanced bonding model that explains the covalent nature of metal-ligand interactions in coordination complexes. It goes beyond Crystal Field Theory by considering the overlap of atomic orbitals from the central metal ion (like 3d, 4s, 4p) with donor orbitals from ligands (such as NH_3). This overlap leads to the formation of molecular orbitals, which are categorized as bonding, antibonding, and nonbonding. Bonding molecular orbitals (BMOs) are lower in energy, while antibonding molecular orbitals (ABMOs) are higher in energy, and nonbonding orbitals remain unaffected. In octahedral complexes like $[Co(NH_3)_6]^{3+}$, bonding mainly occurs through σ-overlap, where ligand orbitals align directly with the metal's s, p, and eg-type d-orbitals (dz^2 and $dx^2{-}y^2$). The six ligand orbitals and compatible metal orbitals combine to form six BMOs and six ABMOs. Electrons donated by ligands fill the BMOs first, while the metal's d-electrons occupy the nonbonding t_2g orbitals (dxy, dxz, dyz). If needed, remaining electrons enter the antibonding eg* orbitals (LUMOs). In this model, the symmetry of the metal orbitals in octahedral geometry is important s-orbitals have a_1g symmetry, p-orbitals have t_1u symmetry, and d-orbitals split into eg and t_2g sets. Overall, MOT provides a more realistic picture of bonding in metal complexes by accounting for both orbital interactions and electron delocalization.

MOT takes bonding a step further. It assumes that:

- Atomic orbitals from ligands (like NH_3) and the valence orbitals of the metal (like 3d, 4s, 4p) combine (overlap) to form molecular orbitals.
- These orbitals are grouped as:
  - ❖ Bonding Molecular Orbitals (BMOs): lower in energy
  - ❖ Antibonding Molecular Orbitals (ABMOs): higher in energy
  - ❖ Nonbonding Orbitals: mostly unchanged

In an **octahedral complex** like **$[Co(NH_3)_6]^{3+}$**, bonding is dominated by **σ-overlap** (sigma bonding), meaning ligand orbitals align directly with metal orbitals for maximum overlap.

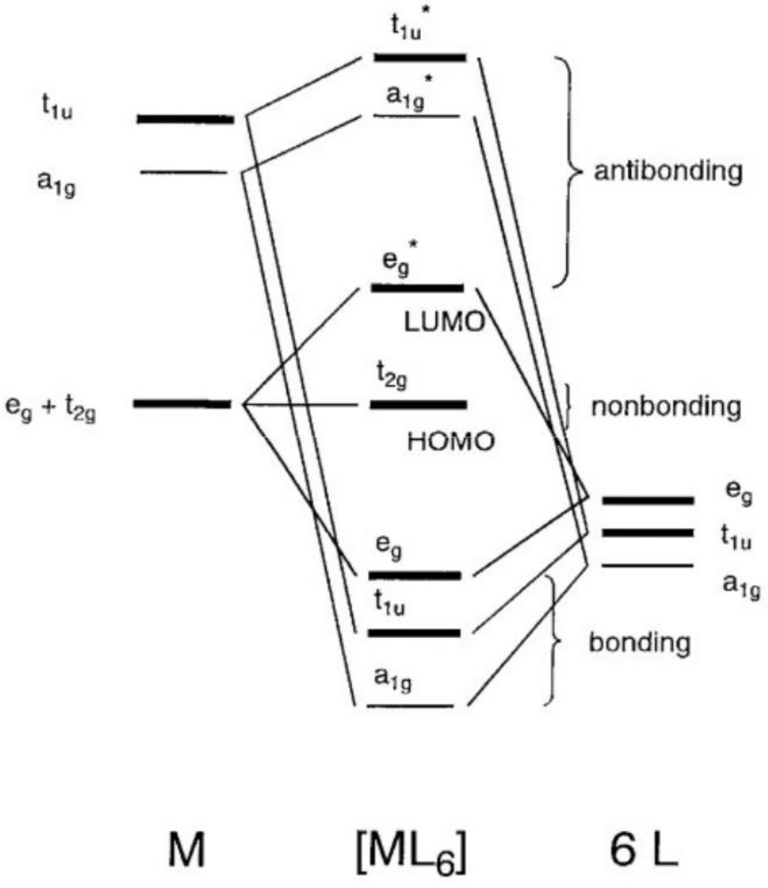


Figure 1.10 MOT of the octahedral complexes

Example: $[Co(NH_3)_6]^{3+}$ Complex

- The metal (Co^{3+}) uses its 3d, 4s, and 4p orbitals.
- The ligands (NH_3) each donate one pair of electrons through lone pairs.

- Together, the 6 ligand orbitals and metal orbitals combine to form:
    - ❖ 6 bonding molecular orbitals (BMOs)
    - ❖ 6 antibonding molecular orbitals (ABMOs)
- Electrons from ligands go into the BMOs.
- The metal's d-electrons go into the nonbonding t_2g orbitals and, if needed, into **antibonding eg* orbitals (LUMOs)**.

💡 Interesting Note: In octahedral symmetry:

- Metal s-orbital → a_1g symmetry
- Metal p-orbitals → t_1u symmetry
- Metal d-orbitals split into:
    - ❖ eg: (dz^2, $dx^2–y^2$) – point directly at ligands → bonding
    - ❖ t_2g: (dxy, dyz, dxz) – between ligands → nonbonding

1.11 SUMMARY

This unit introduces the bonding interactions between metal ions and ligands in transition metal complexes. It begins with the objectives and basic principles, followed by a discussion on the limitations of Valence Bond Theory, which fails to explain certain electronic and magnetic properties of complexes. To address these shortcomings, the Crystal Field Theory (CFT) is introduced, which explains the d-orbital splitting in various geometries and its impact on properties such as color and magnetism. The unit also discusses the factors influencing crystal field parameters, like the nature of the metal ion, the type of ligands, and geometry. Applications of CFT are covered in terms of electronic spectra and magnetic moments. However, since CFT considers only electrostatic interactions, its limitations are also highlighted. The unit concludes with an introduction to Ligand Field Theory (LFT), which incorporates covalent character into bonding, and Molecular Orbital Theory (MOT), which provides a more comprehensive and quantum mechanical explanation of bonding in metal complexes.

1.12 GLOSSARY

MOT	:	Molecular Orbital Theory
LFT	:	Ligand Field Theory
CFT	:	Crystal Field Theory
Δ_o	:	Delta Zero
CFSE	:	Crystal Field Stabilization Energy
BMOs	:	Bonding Molecular Orbitals
ABMOs	:	Antibonding molecular orbitals
LUMO	:	Lowest Unoccupied Molecular Orbital
HOMO	:	Highest occupied Molecular Orbital

1.13 REFERENCES

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6. https://people.wou.edu/~courtna/ch462/tmcolors.htm
7. https://www.vivekanandcollege.ac.in/uploads/dptchemistry/ppt/3%20molecular%20orbital%20theory.pdf.

1.14 SUGGESTED READING

1. J.D. Lee – *Concise Inorganic Chemistry*
    - Why? Excellent for understanding the basics of coordination chemistry, crystal field theory (CFT), and ligand interactions.
    - Useful Sections: Chapter on Transition Elements & Coordination Compounds.
2. F.A. Cotton, G. Wilkinson – *Advanced Inorganic Chemistry*

- Why? Gold standard for in-depth study of metal-ligand bonding theories like CFT, LFT, MOT.
- Level: Advanced (great for NET/JRF/GATE/University toppers).

3. Huheey, Keiter & Keiter – *Inorganic Chemistry: Principles of Structure and Reactivity*
   - Why? Very clear explanations of bonding, CFSE, spectrochemical series, and MOT.
   - Recommended for: Concept building + Competitive exams.
4. Shriver & Atkins – *Inorganic Chemistry*
   - Why? Modern approach with molecular orbital diagrams, symmetry-based bonding. Ideal for visual learners.
   - Bonus: Exercises at the end of each chapter for practice.
5. Gary L. Miessler, Paul Fischer – *Inorganic Chemistry* (especially for LFT & MOT)
   - Why? Best source for understanding Ligand Field Theory and Molecular Orbital Theory with energy level diagrams.
   - Clarity Level: High (often used in foreign universities too).
6. R.D. Madan – *Modern Inorganic Chemistry*
   - Why? Student-friendly language; good for university-level exams and quick revision.
   - Level: Undergraduate (B.Sc./M.Sc. level).
7. Baselo & Pearson – *Mechanisms of Inorganic Reactions*
   - Why? Useful for ligand substitution, complex stability, and kinetic aspects related to bonding.
   - Extra: Application-based understanding.

1.15 TERMINAL QUASTIONS

1. What is Crystal Field Stabilization Energy (CFSE)? Explain with an example.
2. Differentiate between high-spin and low-spin complexes with suitable examples.
3. Draw and explain the d-orbital splitting in an octahedral field.
4. Explain why $[Co(NH_3)_6]^{3+}$ is diamagnetic while $[CoF_6]^{3-}$ is paramagnetic.
5. Calculate the CFSE and number of unpaired electrons for a d^5 ion in:
   - (a) High-spin octahedral field
   - (b) Low-spin octahedral field
6. What is the spectrochemical series? How does it affect crystal field splitting?
7. Why is $[Ti(H_2O)_6]^{3+}$ purple while $[Sc(H_2O)_6]^{3+}$ is colourless? Explain with CFT.

8. Explain the crystal field splitting in a square planar complex with a diagram.
9. Calculate CFSE for the following:
   - (a) Strong field octahedral d^6
   - (b) Weak field tetrahedral d^5
10. Compare the magnitude of Δ in octahedral and tetrahedral complexes. Why is $\Delta_t < \Delta_o$?
11. Which complex has a higher Δ value: $[Co(H_2O)_6]^{2+}$ or $[Co(NH_3)_6]^{3+}$? Why?
12. Discuss the d-orbital splitting in a tetrahedral field. Why no 'g' subscripts here?
13. Write electronic configuration and calculate CFSE for $[Fe(CN)_6]^{3-}$ and $[Fe(H_2O)_6]^{3+}$.
14. What are outer orbital and inner orbital complexes? Give one example of each.
15. Why is Co^{3+} more stable in a strong field, but Co^{2+} more stable in a weak field?
16. Define crystal field splitting energy (Δ). How is it affected by ligands?
17. Calculate magnetic moment (spin-only) for a d^6 high-spin octahedral complex.
18. Why is the magnetic moment of $[Fe(CN)_6]^{3-}$ lower than that of $[Fe(H_2O)_6]^{3+}$?
19. Give three key limitations of Valence Bond Theory in explaining metal complexes.
20. How does ligand orientation cause d-orbital splitting in tetrahedral and octahedral fields?

UNIT-2 THERMODYNAMIC AND KINETIC ASPECTS OF METAL COMPLEXES

Table of Contents:

2.1 INTRODUCTION

The study of thermodynamic stability and reaction kinetics of coordination compounds is a cornerstone of coordination chemistry, with wide-ranging applications across various scientific and industrial fields. These include catalyst design in manufacturing processes, pharmaceutical research in drug development, analytical chemistry, and biochemical investigations of drug metabolism.

Understanding the stability and reactivity of coordination complexes is essential because it reveals how these compounds behave under varying environmental conditions, such as changes in temperature or pH. Notably, thermodynamic and kinetic stability represent two distinct yet complementary aspects of a complex's behavior.

Thermodynamic stability is governed by the equilibrium constant—a higher value indicates a more stable complex at equilibrium. In contrast, kinetic stability depends on the rate constant of a reaction, where a higher rate constant suggests a faster reaction. Together, these parameters offer critical insights into the design, function, and practical utility of coordination compounds in both natural and industrial processes.

2.2 OBJECTIVES

The primary objective of this unit is to develop a comprehensive understanding of the thermodynamic and kinetic stability of metal complexes, a fundamental aspect of coordination chemistry. This unit aims to:

- Introduce the basic concepts and distinctions between thermodynamic and kinetic stability in coordination compounds.
- Explore the theoretical foundations of thermodynamic stability, including equilibrium constants and their implications for complex stability.
- Explain the concept of kinetic stability and its dependence on reaction rates and mechanisms.
- Identify and analyze the key factors that influence the stability of metal complexes, including the nature of the central metal atom and the coordinating ligands.
- Examine the trans effect in square planar complexes and its significance in substitution reactions.

- Understand the mechanisms of nucleophilic substitution reactions in square planar complexes, including the nature of the transition state, energy profiles of exothermic and endothermic reactions, and the SN2 pathway.
- Investigate the factors that affect the SN2 reaction mechanism in square planar complexes.
- Provide a concise summary of key concepts and assess understanding through terminal questions and their corresponding answers.

By achieving these objectives, learners will gain a strong theoretical and practical foundation in the stability and reactivity of coordination complexes, equipping them for further studies and applications in inorganic chemistry, catalysis, and pharmaceutical sciences.

2.3 A BRIEF OUTLINE OF THERMODYNAMIC AND KINETIC STABILITY OF METAL COMPLEXES

In coordination chemistry, the stability of a complex formed in solution is very important. To understand this, chemists use two different concepts: **thermodynamic stability** and **kinetic stability**. This help explain how strong a complex is and how fast it reacts in solution.

2.3.1Thermodynamic Stability of Complexes

Thermodynamic stability refers to how strongly a complex is held together in a solution. It is measured using thermodynamic properties like bond energy and the formation constant (also called the stability constant). If a complex has a high formation constant, it is considered thermodynamically stable. This means the metal ion and ligands are strongly bonded and the complex does not easily break apart. On the other hand, a complex with a low formation constant is considered thermodynamically unstable because it is more likely to dissociate.

Based on thermodynamic stability, complexes are classified into:

- **Stable complexes** – have very high formation constants; they are strongly bonded and do not break easily in solution.

- **Unstable complexes** – have low formation constants; they are weakly bonded and can break apart easily.

2.3.2 Kinetic Stability of Complexes

Kinetic stability tells us how quickly or slowly a complex undergoes chemical changes, especially when one ligand is replaced by another. This type of stability is related to the rate of reaction. It is not about how strong the complex is, but how fast it reacts. A complex can be kinetically stable (inert) even if it is not thermodynamically stable, and vice versa.

Based on kinetic stability, complexes are divided into:

- **Inert complexes** – these undergo **ligand substitution reactions very slowly**; they are kinetically stable.
- **Labile complexes** – these undergo **ligand substitution reactions quickly**; they are kinetically unstable.

2.3.3 Relationship Between Thermodynamic and Kinetic Stability

Thermodynamic and kinetic stabilities are **not always related**. A complex may be very stable thermodynamically but still react quickly (kinetically labile), or it might be kinetically stable (inert) but thermodynamically unstable.

For example:

- The complex $[Hg(CN)_4]^{2-}$ has a very high formation constant (10^{42}), which makes it thermodynamically very stable. However, it can still undergo ligand exchange reactions easily, meaning it is kinetically labile.

$$[Hg(CN)_4]^{2-} + 4CN^{-} \rightarrow [Hg(CN)_4]^{2-} + 4CN-$$

- On the other hand, the complex $[Co(NH_3)_6]^{3+}$ does not react easily, so it is kinetically inert, but it has a low formation constant, which means it is thermodynamically unstable.

This proves that thermodynamic and kinetic stability are independent of each other.

2.3.4 Stepwise Formation of Complexes and Formation Constants

According to **J. Bjerrum**, metal complexes are not formed all at once. Instead, ligands attach to the central metal ion **step by step**, forming intermediate complexes before the final complex is formed. Each step has its own **stepwise formation constant**, which helps us understand how easily ligands bind to the metal.

M = Central metal

L = ligand

K = formation constant

Step-1

$$M + L \overset{K_1}{\rightleftharpoons} ML \quad K_1 = \frac{[ML]}{[M][L]} \quad \ldots\ldots\ldots\ldots\ldots\ldots 1$$

Step-2

$$ML + L \overset{K_2}{\rightleftharpoons} ML_2 \quad K_2 = \frac{[ML_2]}{[ML][L]} \quad \ldots\ldots\ldots\ldots\ldots\ldots 2$$

Step-3

$$ML_2 + L \overset{K_3}{\rightleftharpoons} ML_3 \quad K_3 = \frac{[ML_3]}{[ML_2][L]} \quad \ldots\ldots\ldots\ldots\ldots\ldots 3$$

Step-4

$$ML_{n-1} + L \overset{K_n}{\rightleftharpoons} ML_n \quad K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \quad \ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where K1, K2, K3,- - - Kn are the stepwise formation or stability constants for the complexes formed in the corresponding steps.

The equilibrium constants K_1, K_2, …, K_n are known as stepwise formation constants. On the other hand, the equilibrium constant for the overall reaction may be considered as

$$M + L \overset{\beta_1}{\rightleftharpoons} ML, \qquad \beta_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L \overset{\beta_2}{\rightleftharpoons} ML_2, \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$M + 3L \overset{\beta_3}{\rightleftharpoons} ML_3, \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

$$M + nL \overset{\beta_n}{\rightleftharpoons} ML_n, \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

where β_1, β_2, β_3, …, β_n are the equilibrium constants called as overall formation constants

Where βn = overall formation constant for MLn complex

Relationship Between Stepwise Formation Constant and Overall Formation Constant

To understand how **stepwise formation constants** relate to the **overall formation constant**, let's consider the formation of a complex **ML_3** by both stepwise and overall methods.

In the **stepwise formation method**, ligands attach to the metal ion one at a time, forming intermediate complexes step by step:

$$M + L \longrightarrow ML \quad K1 = \frac{[ML]}{[M][L]} \quad ---- (1)$$

$$ML + L \longrightarrow ML2 \quad K2 = \frac{[ML_2]}{[ML][L]} \quad - --- (2)$$

$$ML2 + L \longrightarrow ML3 \quad K3 = \frac{[ML_3]}{[ML_2][L]} \quad ---- (3)$$

According to overall formation method

$$M + 3L \longrightarrow ML_3 \quad \beta_3 = \frac{[ML_3]}{[M]\ [L]^3} \quad --- (4)$$

Dividing and multiplying the equation (4) by $[ML_2]$ $[ML]$

$$\beta_n = \frac{[ML_3]}{[M]\ [L]^3}\ \frac{[ML_2]}{[ML2]}\ \frac{[ML]}{[ML]}$$

or

$$\beta_3 = \frac{[ML_3]}{[ML_2][L]}\ \frac{[ML_2]}{[ML]\ [L]}\ \frac{[ML]}{[M][L]} \quad ---- (5)$$From eq, (1), (2), (3) & (5)

$$\boxed{\beta_3 = K_3 \times K_2 \times K_1}$$

where β_1, β_2, β_3, …, β_n are the equilibrium constants called as overall formation constants and K_1, K_2, K_3, …, K_n are the stepwise stability or formation constants. The products of stepwise constants are Ks and βs, are related to one another. For example, consider the product of stepwise formation constants K_1, K_2, K_3, …, K_n.

$$K_1 \times K_2 \times K_3 \times ......K_n = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]} \times ...... \frac{[MLn]}{[ML_{n-1}][L]}$$

$$= \frac{[ML_n]}{[M][L]^n} = \beta$$

The above equation indicates that the overall formation constant (β) is equal to the product of the stepwise formation constants K_1, K_2, K_3, …, K_n.

2.4 FACTORS AFFECTING THE STABILITY OF THE COMPLEXES

The stability of coordination complexes formed in solution depends mainly on **two important factors**:

- Nature of the Central Metal Ion (CMI)
- Nature of the Ligands

2.4.1 Nature of the Central Metal Ion (CMI)

Several properties of the central metal ion influence the stability of the complex it forms. Key factors related to the metal ion are:

- **Charge on the Metal Ion:** Metal ions with a higher positive charge and smaller size tend to form more stable complexes. This is because a smaller ion with a higher charge has a higher charge density (charge-to-size ratio), which attracts ligands more strongly, creating a tighter, more stable complex. In simple terms, the greater the positive charge on the metal ion, the stronger the attraction to the ligands and the more stable the complex.
- **Size of the Metal Ion:** As the size of the metal ion decreases, the stability of its complexes increases. For example, among divalent metal ions such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, the stability order follows the ***Irving-Williams*** series:

$$Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)$$

This is because the charge density increases as ionic radius decreases, up to Cu^{2+}, after which Zn^{2+} has a slightly larger radius and lower stability.

Electronegativity of the Metal Ion: Metal ions can be classified as:

Class 'a' metal: Electropositive metals like alkali and alkaline earth metals, and some transition metals with few d-electrons (e.g., Sc, Ti, V). These tend to form stable complexes with ligands containing electronegative atoms such as nitrogen, oxygen, or fluorine.

Class 'b' metals: Heavier metals like Rh, Pd, Ag, Pt, Au, Hg, and Pb, which have more d-electrons. These metals form more stable complexes with ligands that are π-acceptors, containing atoms like phosphorus, sulfur, arsenic, bromine, or iodine.

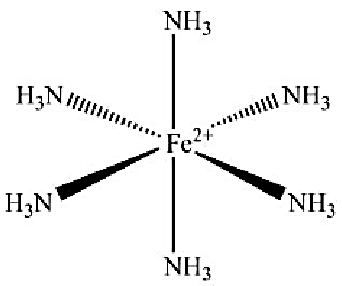
- **Chelate Effect:** The chelate effect refers to the increased stability of coordination complexes that contain chelating ligands—ligands that can attach to a central metal ion through two or more donor atoms, forming a ring-like structure. In simple terms, chelating ligands (like ethylenediamine or EDTA) "grab" the metal ion at multiple points, making the complex more stable than when the metal is bound to the same number of monodentate ligands (ligands that attach at only one point, like NH_3 or H_2O).

  Key Points:

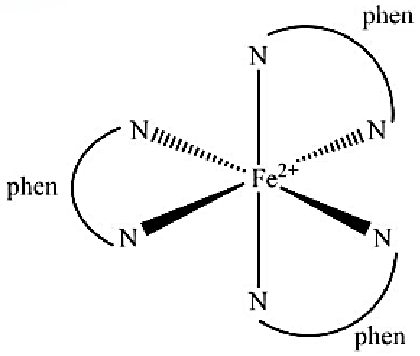
- Chelating ligands form ring structures with metal ions.
- These ring structures are more stable than similar complexes with single-point (monodentate) ligands.
- The increased stability is mainly due to entropy gain (more disorder) and stronger bonding.

Example: Compare these two complexes of Ni^{2+}:

- $[Ni(NH_3)_6]^{2+}$ (with 6 monodentate ligands)
- $[Ni(en)_3]^{2+}$ (with 3 bidentate ethylenediamine ligands forming 3 rings)
  The complex with chelating ligands ($[Ni(en)_3]^{2+}$) is much more stable due to the chelate effect.



$[Fe(NH_3)_6]^{2+}$ Non-chelate complex (Less stable)



$[Fe(phen)_3]^{2+}$ Chelate complex (More stable)

For instance, the stability constant (β_6) for Ni^{2+} with three ethylenediamine ligands is about 10^{10} times higher than with six ammonia ligands.

- **Steric Effect:** Less bulky Ligands (sterically unhindered) form more stable complexes than larger, bulky ligands. For example, ethylenediamine (en) forms more stable complexes than its bulky substituted derivatives.

- **Polarizing Power:** The greater the polarizing power of the metal ion (its ability to distort the electron cloud of the ligand), the higher the stability of the complex.

2.4.2 Nature of the Ligands

The properties of ligands also significantly affect complex stability. Important factors related to ligands include:

- **Size and Charge of the Ligand:** Smaller ligands with higher negative charge tend to form more stable complexes because they can approach the metal ion more closely and strongly. For example:

(a) Fluoride ions (F^-) form more stable complexes with Fe^{3+} than chloride (Cl^-), bromide (Br^-), or iodide (I^-) ions because fluoride is smaller and more negatively charged.
(b) Similarly, oxide ions (O^{2-}) form more stable complexes than sulfide ions (S^{2-}) due to their smaller size.

- **Basicity of the Ligand:** Ligands with stronger basic character (better electron donors) form more stable complexes because they donate electrons more effectively to the central metal ion. In other words, the stability of a complex increases with the ligand's basic strength.

2.5 TRANS EFFECT IN THE SQUARE PLANAR COMPLEXES

The **trans effect** is the influence that a ligand bonded to a metal center in a square planar complex (especially in Pt(II) complexes) has on the rate of substitution of the ligand trans (opposite) to it. In other words, it is the ability of a ligand to enhance the replacement of the ligand located directly opposite to it in the coordination plane. Ligands with a strong trans effect make it easier for the trans ligand to be substituted.

Some ligands have a stronger trans effect than others. When we arrange ligands in order from low to high trans effect strength, we get what's called the trans effect series.

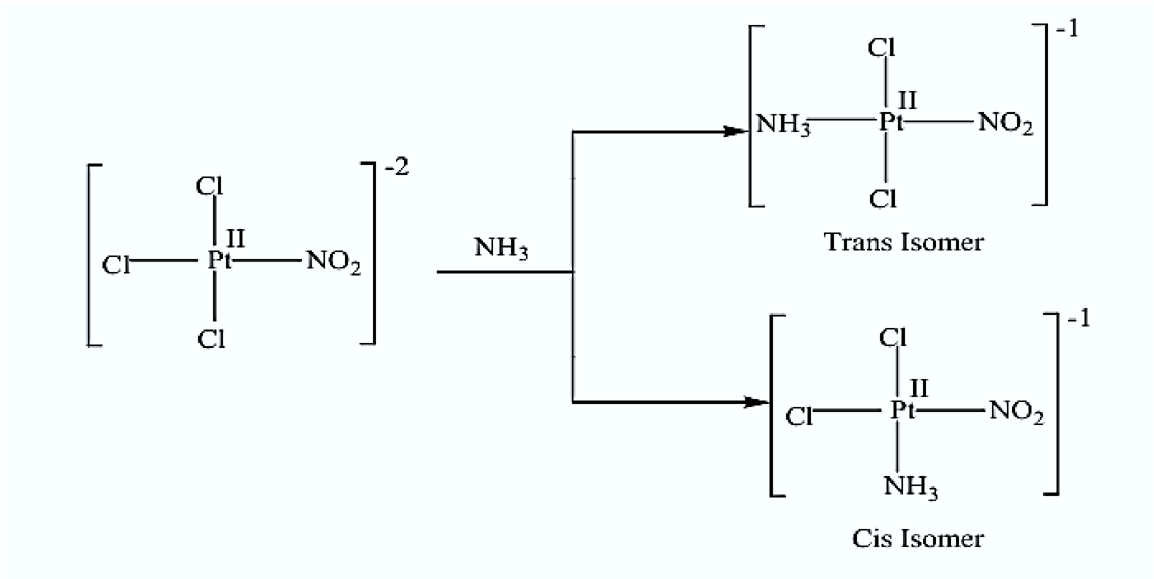
Here’s a simplified version of the **trans effect series** (from weak to strong):

H_2O, OH^- < NH_3, Pyridine < F^- < Cl^- < Br^- < I^-, SCN^-, NO_2^- < Urea (NH_2–CO–NH_2) < PR_3 < C_2H_4, CO, NO, CN^-

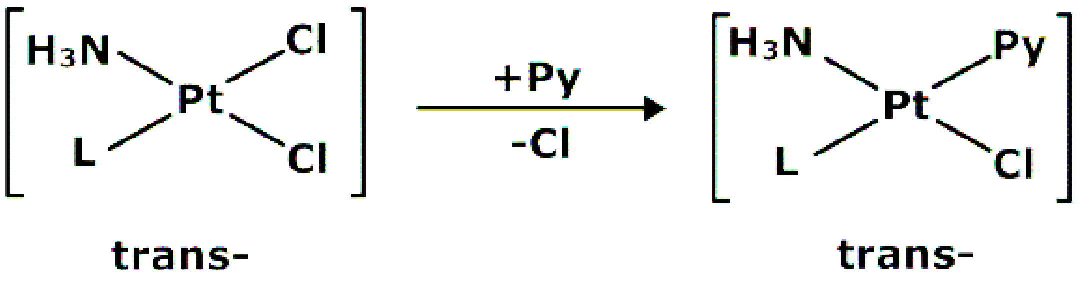
example:

When the complex ion $[Pt(Cl)_3(NO_2)]^{2-}$ reacts with NH_3, it can form two different isomers of $[Pt(Cl)_2(NO_2)(NH_3)]^-$ because NH_3 can attach in two ways, either trans to Cl^- or trans to NO_2^-.

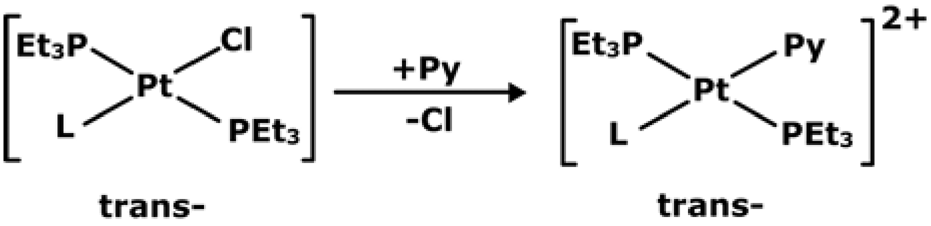
Since NO_2^- has a stronger trans effect than Cl^-, the NH_3 ligand prefers to attach opposite (trans to) NO_2^-, making that isomer more likely to form.



Trans effect is the ability of a group to direct substitution into its opposite trans position. The decrease of the rate of substitution in the trans Pt (II) complex is the decrease of the trans effect. For example,



The relative rates of various L-like C_2H_4> NO_2^-> Br->Cl- increase as the trans effect increases; however, activation energy decreases in the same way. The usual effect of trans effect on the rate has been observed in the following reactions.



In this reaction, L like H-> CH3-> C6H5- increases as the trans- effect of these ligands increases.

2.5.1 Theories of the trans effect phenomena

Trans effect phenomena in the Pt (II) square planar complexes can be explained by the two different types of concepts:

1. Polarisability Theory: According to the Polarisability Concept, in square planar platinum(II) complexes, when two different ligands are positioned opposite each other (in the trans positions), the ligand with higher polarisability tends to show a stronger trans effect. Polarisability refers to how easily a ligand's electron cloud can be distorted. A ligand with a highly polarisable (soft and flexible) electron cloud can form a stronger and more stable bond with the central metal atom (CMA), such as platinum.

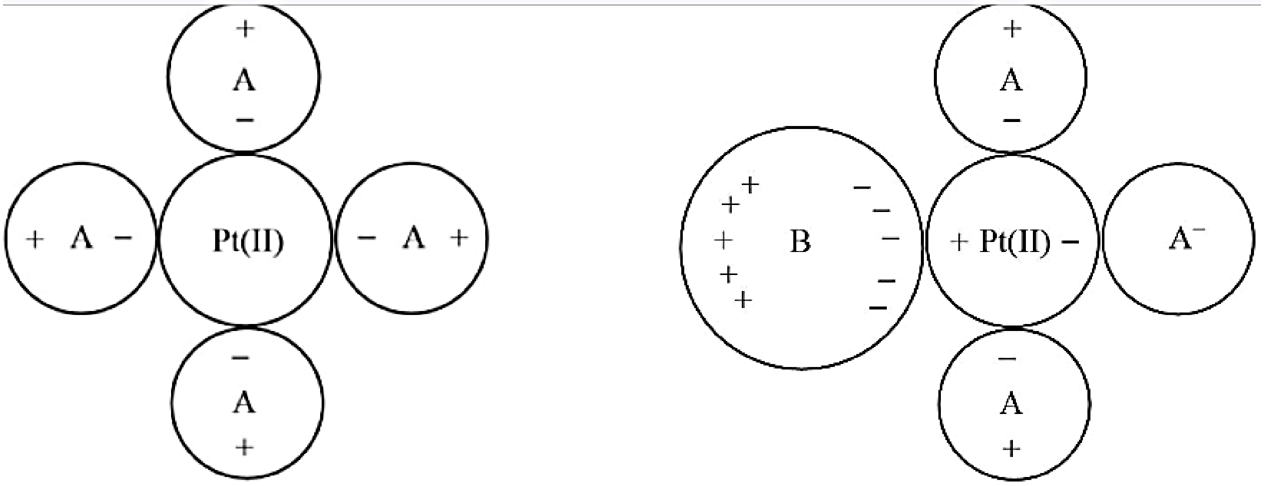


Figure 12. The effect of polarization in MA4 and MA3B complexes

Because of this stronger bond, the metal's electron density becomes unevenly distributed. This causes the bond to the ligand sitting opposite (trans) to weaken. As a result, that trans ligand becomes easier to remove or substitute during a reaction. So, the more easily a ligand can shift or stretch its electron cloud, the more power it has to "push out" the ligand on the opposite side.

In simple words, the polarisable ligand acts like a strong player in a tug-of-war — pulling the metal closer to itself and making it easier for the ligand on the other side to let go. This is why ligands with high polarisability, like phosphines (PR_3), carbon monoxide (CO), or cyanide (CN^-), are known to show very strong trans effects in Pt(II) complexes.

2. Pi-bonding theory: The trans effect is not about the size or bulkiness of ligands (steric factors), but rather about their electronic properties. In simple terms, it's the way a ligand's electronic nature influences how easily the ligand opposite to it (in the trans position) gets replaced in square planar Pt(II) complexes.

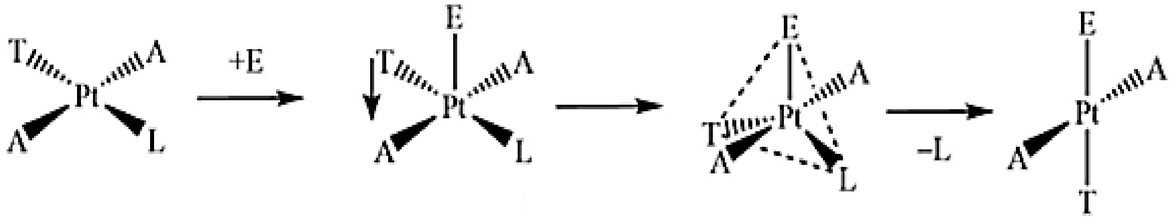
Let's take a look at the halide ions:

$$I^- > Br^- > Cl^- > F^-$$

This order shows that as we move from iodide to fluoride, the electronegativity increases, which makes the ligand a weaker σ-donor (sigma base). As a result, their ability to cause the trans effect also decreases. Fluoride, being the most electronegative, holds its electrons tightly and doesn't "help" in pushing out the ligand opposite to it.

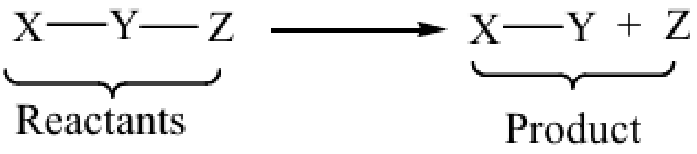
However, here's where it gets interesting: ligands like CO, C_2H_4, and PR_3 show an exceptionally strong trans effect, but they aren't great σ-donors. Instead, they are π-acceptor ligands that accept electron density back from the metal into their empty π* orbitals.

This means the trans effect is not only about strong σ-donation. It can also come from a ligand's ability to accept electron density via π-backbonding. So, a powerful trans-effect ligand is either a strong σ-donor or a good π-acceptor or sometimes, both.



2.6 NUCLEOPHILIC SUBSTITUTION REACTIONS OF SQUARE PLANAR COMPLEXES

Before diving into the mechanism of ligand substitution reactions in coordination compounds, it's important to understand some basic terms. One of the most crucial among them is the transition state, also known as the activated complex.



Let's consider the energy changes that happen during a chemical reaction. Suppose we have two reactants: X and Y–Z. At the beginning of the reaction, both X and Y–Z possess a certain amount of potential energy, represented as point (a) on an energy diagram. As the reaction progresses, the system absorbs energy and the Y–Z bond begins to weaken, leading to the formation of a high-energy, unstable state at point (b). This unstable arrangement of atoms is known as the transition state or activated complex.

After reaching this point, the system moves toward product formation. The bond between Y and Z breaks, and a new bond forms between X and Y, producing the final products X–Y and Z, represented by point (c) on the curve. As this happens, the potential energy is released in the form of kinetic energy, heat, or other types of energy.

There are two main types of reactions based on energy changes:

- **Exothermic Reaction**: In this type, the reactants start with **higher potential energy** than the products. As the reaction proceeds, **excess energy (ΔH)** is released, usually as **heat**. That's why the reaction feels warm.
- **Endothermic Reaction**: Here, the products have **more potential energy** than the reactants. To make the reaction happen, the system must **absorb energy (ΔH)** from its surroundings, often in the form of **heat**.

The **difference in energy** between the reactants and products is called the **reaction energy (ΔH)**. This value helps us understand whether a reaction is heat-releasing or heat-absorbing.

$$A + B{-}C \longrightarrow A{-}B + C$$

The molecule **A** approaches the compound **B–C** from the side opposite to **C**. As **A** draws closer to **B**, the bond between **B** and **C** begins to weaken and **C** gradually moves away. Eventually, the system reaches a stage where both **A** and **C** are loosely connected to **B**, positioned nearly at equal distances from it.

At this crucial moment, an intermediate structure known as **A...B...C** forms. This special configuration is called the **transition state** or **activated complex**, and it possesses the following key features:

1. The distances between **A–B** and **B–C** are slightly longer than those in a stable bond.
2. This complex is not a true molecule, as the bonds are only partially formed. It is a fleeting, imaginary structure that cannot be isolated or observed directly.
3. It represents the **highest energy state** along the reaction pathway — highly unstable and extremely short-lived. From this unstable transition state, the system proceeds to form the final products: **A–B** and **C**

$$\underset{\text{Reactant}}{A + B{-}C} \longrightarrow \underset{\text{Activated complex}}{A\text{------}B\text{------}C} \longrightarrow \underset{\text{product}}{A{-}B + C}$$

2.6.2 Energy changes in exothermic and endothermic reactions

The energy changes in exothermic and endothermic reactions are represented in Figure 2.1.

In the fascinating world of substitution reactions, several key terms help us understand how these processes unfold.

Substrate is the term used to describe the molecule that transforms a reaction. It is the reactant in which existing bonds are broken and new ones are formed, all as a result of the interaction with another species known as the reagent.

The species that initiates the chemical change by interacting with the substrate is called the **attacking reagent**. These reagents are crucial for driving the reaction forward and can be broadly classified into two categories: **electrophilic** and **nucleophilic reagents**.

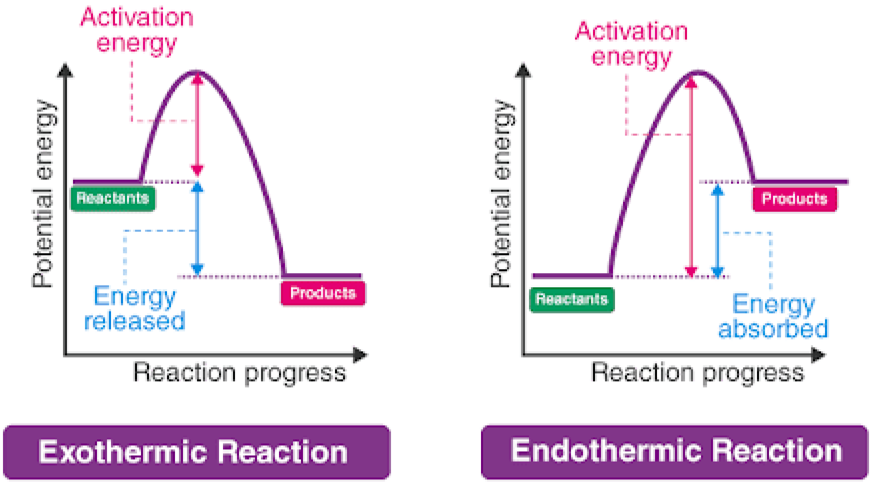


Fig. 2.2 Energy profile diagram

Electrophilic reagents, or **electrophiles** (from *the Greek words "electro," meaning "electron," and "philic," meaning "loving"*), are electron-deficient species that seek out electrons. In essence, they are attracted to regions of high electron density and act as electron pair acceptors. Electrophiles are often positively charged ions such as the carbonium ion, bromonium ion (Br^+), nitronium ion (NO_2^+), nitrosonium ion (NO^+), diazonium ion ($C_6H_5N_2^+$), bisulphonium ion (SO_2OH^+), and protons (H^+). Some electrophiles can also be neutral molecules like boron trifluoride (BF_3), aluminum chloride ($AlCl_3$), sulfur trioxide (SO_3), and ferric chloride ($FeCl_3$), all of which are classic Lewis acids.

On the other hand, **nucleophilic reagents**, or **nucleophiles** (*nucleo* meaning nucleus and *philic* meaning loving), are electron-rich species that are attracted to positive centers, particularly atomic nuclei. Because nuclei carry a positive charge, nucleophiles are typically negatively charged ions or neutral molecules with lone pairs of electrons. Examples include carbanions, halide ions like chloride (Cl^-), hydroxide ions (OH^-), and ammonia (NH_3).

2.6.3 Nucleoplhilic substitution reactions (SN2) in square planar complexes

In coordination chemistry, nucleophilic substitution reactions are key mechanisms through which ligands in metal complexes are replaced by other ligands. One important type is the bimolecular nucleophilic substitution reaction, commonly abbreviated as SN2, particularly observed in square planar complexes of transition metals.

Mechanism of SN2 in Square Planar Complexes

Square planar complexes typically involve **d^8 metal ions**, such as **Pt(II), Pd(II), or Ni(II)**. This metal centers coordinate with four ligands arranged in a square planar geometry. In an SN2-type substitution, one ligand (known as the *leaving group*) is replaced by an incoming ligand (the *nucleophile*), and the reaction follows a **concerted, one-step mechanism**.

The nucleophile approaches the metal center from a position trans to the leaving group, forming a five-coordinate transition state or intermediate. This intermediate often adopts a trigonal bipyramidal or square pyramidal geometry, although it is highly unstable and short-lived.

The incoming nucleophile and the leaving group are positioned opposite each other during the reaction, leading to inversion of configuration at the metal center. This stereochemical feature is a hallmark of SN2 mechanisms in general.

Key Features of SN2 in Square Planar Complexes

1. **Bimolecular Mechanism:** The rate of the reaction depends on the concentration of both the complex and the nucleophile:

$$\textbf{Rate=k[Complex][Nucleophile]}$$

This second-order rate law confirms the bimolecular nature of the reaction.

2. **Stereochemistry:** The reaction typically leads to inversion of configuration at the metal center, consistent with a direct backside attack by the nucleophile.
3. **Transition State: A five-coordinate transition state** is briefly formed. Depending on the system, this may resemble either a trigonal bipyramidal or square pyramidal geometry, but it rapidly collapses to give the substituted product.
4. **Typical Metal Centers:** SN2 mechanisms are commonly observed in low-spin d^8 metal ions like Pt(II), Pd(II), and Ni(II), due to their strong preference for square planar geometry.
5. **Ligand Effects:** The nature of the leaving group, the nucleophile, and other ligands around the metal center can influence the rate and outcome of the reaction. For example, good leaving groups (like halides or weakly bound ligands) and strong nucleophiles (like CN^- or NH_3) accelerate the substitution.

Example Reaction:

A classic example is the substitution of a chloride ligand in **$[PtCl_4]^{2-}$** with ammonia:

$$[PtCl_4]^{2-} + NH_3 \rightarrow [PtCl_3(NH_3)]^{-} + Cl^{-}$$

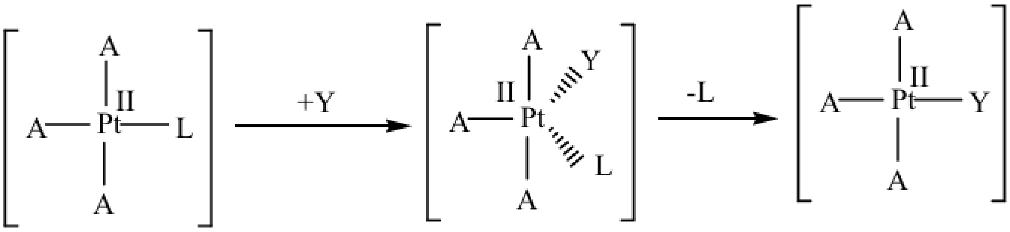
In this reaction:

- **$[PtCl_4]^{2-}$** is the square planar complex,
- **NH_3** is the nucleophile,
- **Cl^-** is the leaving group,
- The product is a new square planar complex with one ammonia ligand.

2.6.4 Factors affecting the SN2 reaction of square planar complexes

Some of the factors that can affect the rate of the SN2 reaction in the square planar complexes are given below:

1. ***Trans Effect:*** In the Pt(II) square planar complexes, with the increase in the trans effecting power of ligand (A) present in the trans position of leaving ligand (L), the rate of the SN2 reaction increases.



Where A = C_2H_4, NO_2^-, Br^-, Cl^-

L = F-

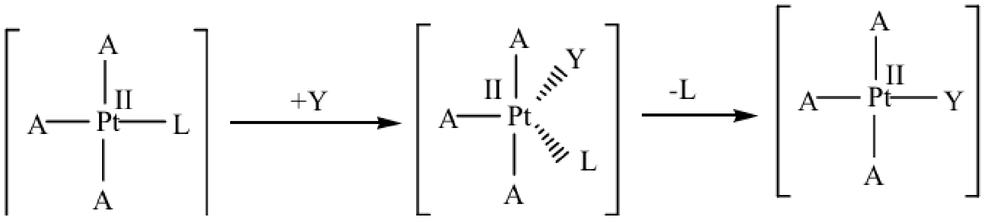
Trans effecting power of A = $C_2H_4 > NO_2^- > Br^- > Cl^-$

Rate of SN2 reaction = $C_2H_4 > NO_2^- > Br^- > Cl^-$

2. Nature of leaving ligand (L): With the increase the trans effecting power of the leaving ligand (L), its bonding with CMA becomes more and more stable, by which its rate of replacement decreases. Example:

Where A = C_2H_4

L = PR_3 , NO_2^-, Br^-, Cl^-, F^-



Trans effecting power of L = PR_3> NO_2^-> Br^-> Ci^-> F^-

Rate of SN2 reaction = $PR_3 > NO_2^- > Br^- > Cl^- > F^-$

3. **Solvent Effect:** According to the kinetic evidence of the SN2 reaction, it was observed that the SN2 reaction can also be affected by the solvent.

2.7 SUMMARY

This unit provides an in-depth exploration of the thermodynamic and kinetic stability of coordination complexes, key concepts in coordination chemistry with important applications in catalysis, pharmaceuticals, and analytical chemistry.

Thermodynamic stability refers to the overall energy favorability and bonding strength in complexes, typically measured by formation constants (stepwise K and overall β). A complex with high formation constants is more stable thermodynamically. This stability depends on factors such as metal ion charge, size, and electronegativity, as well as ligand properties like basicity, charge, and size.

In contrast, kinetic stability relates to the rate of ligand substitution. Complexes may be thermodynamically stable yet kinetically labile, or vice versa. The unit distinguishes between inert complexes (slow substitution) and labile complexes (fast substitution), emphasizing that thermodynamic and kinetic stabilities are not always correlated.

The stepwise formation of complexes is discussed, highlighting how ligands bind sequentially to metal ions, affecting the overall stability. The chelate effect is introduced as a key factor that increases stability through ring formation with multidentate ligands. Also covered is the trans effect, particularly in square planar complexes, which influences substitution patterns and rates.

Finally, the unit examines nucleophilic substitution reactions in square planar complexes, focusing on their associative (SN2-type) mechanism, energy profiles, and transition states.

Factors such as the trans effect, nature of the leaving group, and solvent effects are analyzed for their role in reaction kinetics.

2.8 REFERENCES

1. Huheey, J. E., Keiter, E. A., & Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*. Pearson Education.
2. Cotton, F. A., Wilkinson, G., Murillo, C. A., & Bochmann, M. *Advanced Inorganic Chemistry*. Wiley.
3. Miessler, G. L., & Tarr, D. A. *Inorganic Chemistry*. Pearson.
4. Greenwood, N. N., & Earnshaw, A. *Chemistry of the Elements*. Butterworth-Heinemann.

2.9SUGGESTED READING

1. Transition Metal Chemistry by M.J. Winter
2. Concise Coordination Chemistry by Gopalan and Ramalingam
3. Basic Concepts of Inorganic Chemistry by D.F. Shriver and P.W. Atkins
4. Research journals: Inorganic Chemistry, Dalton Transactions, Journal of Coordination Chemistry

2.10 TERMINAL QUESTIONS

A. Multiple Choice Questions (MCQs)

1. Which of the following is thermodynamically stable but kinetically labile?

   A. $[Co(NH_3)_6]^{3+}$ B. $[Hg(CN)_4]^{2-}$

   C. $[Ni(CN)_4]^{2-}$ D. $[Fe(CN)_6]^{3-}$

2. What is the correct order of kinetic stability (inertness) among the following?

   A. $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+}$ B. $Co^{3+} > Ni^{2+} > Fe^{2+} > Mn^{2+}$

   C. $Mn^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+}$ D. $Co^{2+} < Mn^{2+} < Ni^{2+} < Fe^{2+}$

3. The chelate effect increases stability because:
   A. It reduces entropy
   B. It forms rigid structures
   C. It increases entropy and bonding strength
   D. Chelating ligands are bulky
4. Which ligand shows the strongest trans effect?
   A. NH_3
   B. H_2O
   C. CN^-
   D. Cl^-
5. In SN2 substitution in square planar complexes, the nucleophile attacks:
   A. From the cis position
   B. From the front side
   C. From the trans position to the leaving group
   D. From any random position

B. True or False

1. Thermodynamically stable complexes always react slowly.
2. Kinetically inert complexes always have high formation constants.
3. The trans effect is purely a steric effect.
4. The formation constant (β) is the product of all stepwise formation constants.
5. A higher trans effect increases the rate of ligand substitution in square planar complexes.

C. Fill in the Blanks

1. The __________ effect is responsible for the increased stability of complexes formed with multidentate ligands.
2. The SN2 mechanism in square planar complexes proceeds through a __________ intermediate.
3. The unit for the rate constant in a bimolecular reaction is __________
4. Ligands like PR_3 and CN^- exhibit a strong __________ effect.
5. In an exothermic reaction, energy is __________ to the surroundings.

Long Answer Questions:

1. Differentiate between thermodynamic stability and kinetic stability of coordination complexes. Provide relevant examples and explain why these two types of stability are considered independent of each other.

2. Discuss in detail the factors affecting the stability of coordination complexes, with specific reference to the nature of the central metal ion and ligands. Include the roles of charge, size, chelate effect, and ligand basicity.
3. Explain the concept of the trans effect in square planar complexes. Discuss both Polarisability and Pi-bonding theories and illustrate how they account for the trans effect in Pt(II) complexes with suitable examples.
4. Describe the SN2 nucleophilic substitution mechanism in square planar complexes. Include an explanation of the transition state, stereochemistry, energy profile, and the influence of ligands and solvents.
5. Using the example of stepwise and overall formation constants, explain how metal-ligand complexes are formed. Derive the relationship between stepwise stability constants and overall formation constants.

Short Answer Questions:

1. What is meant by the chelate effect, and why do chelating ligands form more stable complexes than monodentate ligands?
2. List any four factors that influence the rate of SN2 reactions in square planar complexes.
3. Define the term 'transition state' in the context of nucleophilic substitution reactions and mention two key features of this state.
4. Why is $[Hg(CN)_4]^{2-}$ considered thermodynamically stable but kinetically labile?
5. Arrange the following ligands in order of increasing trans effect strength: Cl^-, NO_2^-, NH_3, PR_3.

ANSWER KEY

A. 1 B 2 B 3 C 4 C 5 D

B. 1 False 2 False 3 False 4 True 5 True

C. 1 Chelate 2 Five -Coordinate 3 $M^{-1}S^{-1}$ 4 True 5 Released

UNIT 3 : ELECTRON SPECTRA OF TRANSITION METAL-COMPLEXES

CONTENTS:

3.1. INTRODUCTION

Transition metal compounds display a wide variety of colours. A compound is coloured if it absorbs part of the visible light. When a sample absorbs visible light, the colour observed by us is the sum of the remaining colours that are reflected or transmitted by the sample and strikes our eyes. The colour of these compounds is due to the electronic transitions generated by the incident light, causing absorption at certain wavelengths which depend on the structure and bonding in the molecule. Based on Crystal Field Theory (CFT), Uultraviolet (UV)–Visible spectroscopy is used to evaluate the absorption properties of the transition metal complexes.

The electronic transitions in the transition metal compounds can be categorized into three classes: charge transfer, d–d transition and f–f transitions. Charge transfer bands occur when the excited electrons move either from a metal orbital to a ligand orbital (metal–to–ligand charge transfer – MLCT) or from a ligand orbital to a metal orbital (ligand–to–metal charge transfer – LMCT). MLCT transitions are more common than LMCT. d–d transitions occur when the excited electron moves from one d orbital to another d orbital of the metal and f-f transition occur when the excited electron moves from f orbital to f orbital of the same metal centre . The d-d or f-f transitions can further be classified as spin–allowed transition where the spin quantum number in the ground and excited states are the same while in the spin–forbidden transition, the spin state changes during the excitation.

3.2. OBJECTIVES

In this unit, our concern will be with the electronic spectra of transition metal complexes, mainly those of the first transition series. The energy required for the promotion of an electron from one orbital to another, the excitation of a molecule from its ground state to an electronic excited state, corresponds to absorption of light in the near-infrared, visible or ultraviolet regions of the spectrum. By going through this unit, you will be able to understand:

- Electronic transitions
- Selection rules for electronic transitions
- Term symbol
- Spectrochemical series
- Orgel diagrams

3.3. TYPES OF ELECTRONIC TRANSITIONS

When the Electromagnetic Radiation (EMR) is passed from the sample of the transition metal complexes, the transition of electron can occur by the absorption of certain EMR to give the electronic spectra.

Electronic transitions can be classified into two different types, which are given below (Figure 4.1):

1. **Allowed transitions:** The types of electronic transition which can generate the high intense spectra are known as allowed transitions.
2. **Forbidden transitions:** The types of electronic transition which can generate the low intense spectra are known as forbidden transitions.

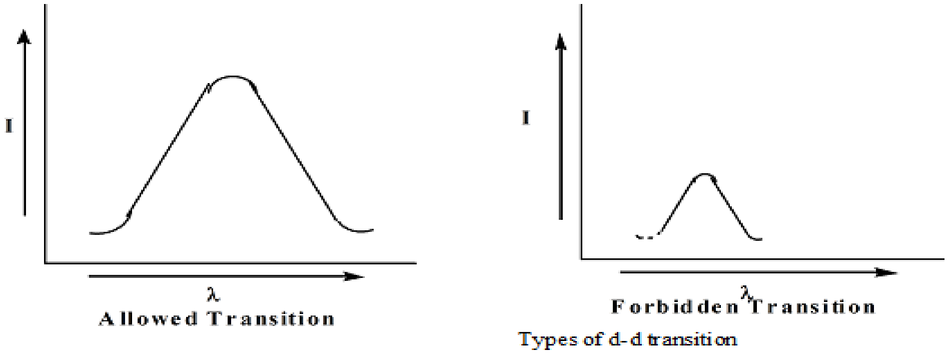


Figure 3.1

3.4. SELECTION RULE FOR d-d TRANSITION

To define the allowed or forbidden nature of electronic transitions, 2 different selection rules can be used which are given below:

3.4.1 Spin selection rule

According to the spin selection rule, all the electronic transitions in the transition metal complexes which does not involve the change in the spin multiplicity are called as spin allowed transitions while on the other hand all the electronic transitions which can involve the change in the spin multiplicity are known as spin forbidden transitions. therefore,

$\Delta S = 0$ (Allowed transition)

$\Delta S \# 0$ (Forbidden transition)

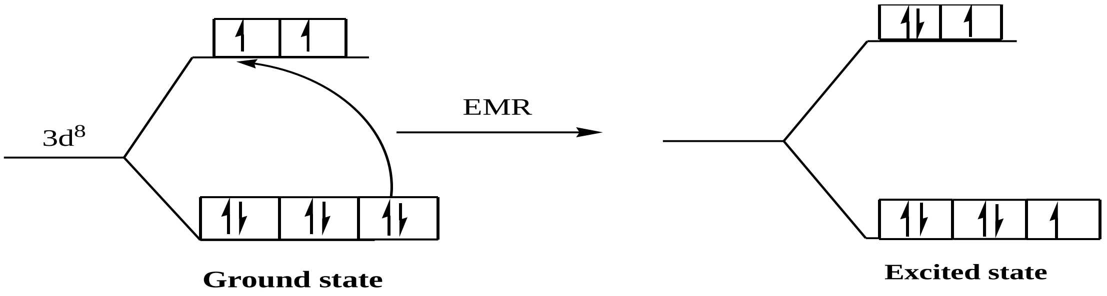
Example:

(i) $[Ni(H_2O)_6]^{+2}$ ion.

Ni – $3d^8, 4s^2$

Ni^{+2} –$3d^8, 4s^0$

According to CFT:



Spin multiplicity

$$\underbrace{\begin{matrix}\text{Ground state} & \qquad & \text{Excited state} \\ n + 1 = 3 & \qquad & (n + 1) = 3\end{matrix}}_{\Delta S = 0}$$

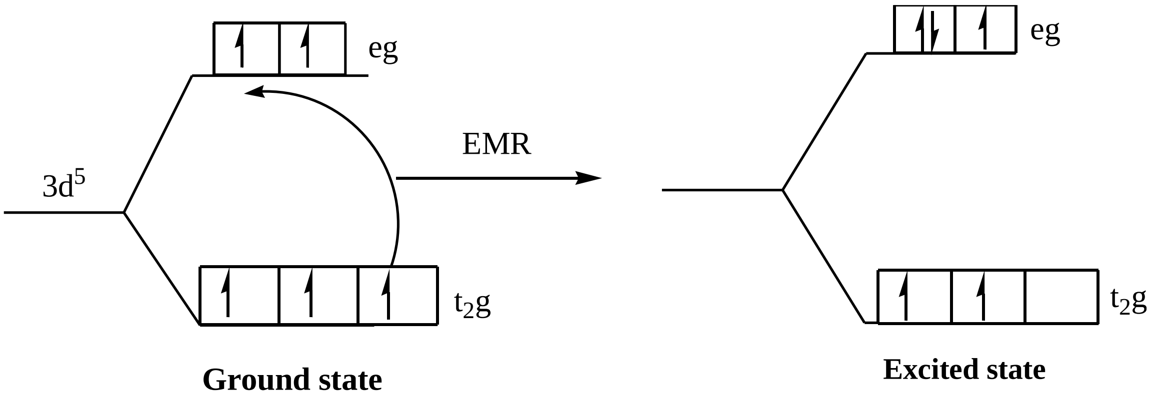
Allowed transition

(ii) $[Mn(H_2O)_6]^{+2}$ ion.

Mn - $3d^5, 4s^2$

Mn^{+2} - $4s^5, 4s^0$

According to CFT:



Spin multiplicity

$$\underbrace{\overset{\text{Ground state}}{n+1 = 6} \qquad\qquad \overset{\text{Excited state}}{(n+1) = 4}}_{\Delta S \# 0}$$

Forbidden transition

3.4.2. Laporte selection rule

According to the this rule, all the electronic transitions which occur from G (g) to U (u) (gerade to ungerade) or u to g orbitals, are known as Laporte allowed or symmetry allowed transitions while all the electronic transitions, which occur from g to g or u to u orbitals are known as Laporte forbidden transition or symmetry forbidden transition.

$$\left.\begin{array}{l} G \longrightarrow U \\ U \longrightarrow G \end{array}\right\} \text{Allowed} \qquad \left.\begin{array}{l} G \longrightarrow G \\ U \longrightarrow U \end{array}\right\} \text{Forbidden}$$

According to this selection rule all the d-d transition phenomena in the transition metal complexes bung forbidden.

Therefore, according to the Laporte selection rule, all the electronic transitions in which there does not occur any change in the orbital quantum no (l) value are known as Laporte forbidden transition while all the electronic transitions which involve certain change in the orbital quantum number are known as Laporte allowed transition.

$\Delta l = 0$ (Laporte forbidden transitions)

$\Delta l \# 0$ (Laporte allowed transitions)

Thus, according to this selection rule, it is observed that all the d-d transitions (g-g transitions) are Laporte forbidden. There are certain relaxations in Laoprte selection rule due to the possibility of certain extent of d-p mixing.

3.5. TERM SYMBOL AND SPECTROSCOPIC GROUND STATE TERM

In quantum mechanics, the term symbol is the energy level of a single or multi-electron atom which is deduced from total angular momentam quantum number including orbital quantum number and spin quantum number. The atomic term symbols can be calculated from L-S coupling (Russell-Saunders coupling or Spin-Orbit coupling) and the ground state term symbol is predicted by Hund's rules.

Russell- Saunder coupling (Spin orbital or L-S coupling)

Russell and Saunder have proposed a coupling scheme i. e. Russell- Saunder coupling to calculate the term symbol for the various electronic configurations, which involve the following qauantum numbers:

(1) Total orbital momentum quantum number or L term

Vector summation of the l values of the differfent electrons present in a particular configuration is known as total orbital angular momentum quantum number (L term) for the configuration.

Different symbols for the different L value can be written as:

L	=	0	1	2	3	4	5	6	7
Symbol	=	S	P	D	F	G	H	I	J

(2) Total spin momentum quantum number or S term

Vector summation of spin angular momentum quantum number of all electrons present in any configuration (s values) is known as total spin angular momentum quantum number or S term.

$$S = \frac{n}{2}$$

Where n is the number of unpaired electrons

(3) Total angular quantum number or J term

Vector summation of L and S terms for a particular electronic configuration is known as total angular quantum number or J term which arises due to L-S coupling. The values of J are

$$J = L - S, L-S-1, L-S-2 \text{ ...... upto } L + S$$

For less than half filled configuration

$$J = L - S$$

For a configuration which is more than half filled

$$J = L + S$$

(4) Spin multiplicity or M term

Total number of the possible spin orientations of the unpaired electrons in a particular configuration is known as spin multiplicity or M term.

$$M = n + 1$$
$$= 2S+1$$

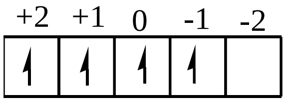
Where n = number of unpaired electrons

According to the above four different terms, term symbol for a particular configuration can be written as

$$^{M}L_{J}$$

For example for d^4 configuration

d^4 =



$$L = 2\ (D)$$

$$S = \frac{n}{2} = \frac{4}{2} = 2$$

For an electronic configuration less than half filled

$$J = L - S = 0$$

$$M = 4 + 1 = 5$$

So, the term symbol for d^4 configuration is $^{M}L_{J}$ = $^{5}\mathbf{D}_{0}$

Term symbol for the various d^n configuration, P^n configuration, S^n configuration can also easily determined:-

Hund's rule for ground state term

The calculation of term symbol for the ground state of an atom is relatively easy to using Hund's rules. Ground state term symbol corresponds to a state with maximum S and L values. Each electronic configuration except fully filled has large number of possible arrangements which are known as microstates which can be calculated as follow:

$$\text{Number of microstates} = \frac{n!}{r!\,(n-r)!}$$

Where n is maximum capacity (maximum number of electrons that can be accommodated in the orbital) of the particular configuration and r is number of electron in the configuration.

Out of the various possible electronic arrangements, one of the arrangement i.e. ground state electronic arrangement can be calculated with the help of different rule proposed by the Hund, which are given below:

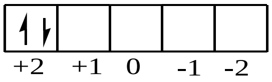
Rule 1: According to the Hund’s rule, out of the various electronic arrangements, the arrangement having the maximum value of spin multiplicity will be the ground state electronic arrangement.

Rule 2: If more than one electronic arrangement have the same value of spin multiplicity, than the electronic arrangement with higher L value will be the ground state electronic arrangement.

Rule 3: Among various the ground state electronic arrangements with different J values, if the electronic configuration is less than half filled, than the ground state term will be withleast J value while if the configuration is more than half filled, than the ground state term will be the term with maximum J value.

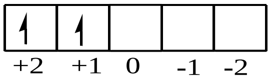
Example: Evaluation of ground state term symbol for d^2 configuration.

d^2 -



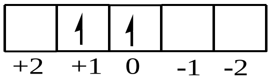
L = 4 (G)
S = 0
J = 4
M = 1

d^2 -



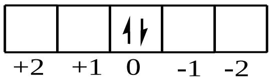
L = 3(F)
S = 1
J = 2,3,4
M = 3

d^2 -



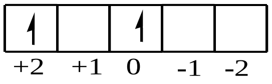
L = 1 (P)
S = 1
J = 0,1,2
M = 3

d^2 -



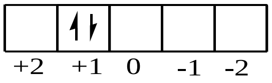
L = 0 (S)
S = 0
J = 0
M = 1

d^2 -



L = 2 (D)
S = 1
J = 1,2,3
M = 3

d^2 -



L = 2 (D)
S = 0
J = 2
M = 1

According to the Hund's rule, second arrangement will be the actual ground state electronic arrangement for d^2 configuration. Thus, the term symbol for d^2 configuration will be $^3F_2$.

3.6. SPECTROCHEMICAL SERIES

Order of ligands arranged according to the strength of ligand and arrangement of metal ions on the basis of oxidation number, group and its identity is called as spectrochemical series. Accordung to crystal field theory, ligands can change the difference in energy between the two sets of d orbitals (Δ_o) called the ligand-field splitting parameter for ligands or the crystal-field splitting parameter, which can be the cause of differences in color of similar type of metal-ligand complexes.

The spectrochemical series was first given in 1938 and was based on the results of absorption spectra of cobalt complexes. Spectrochemical series of the ligands from smaller value of Δ_o to larger value of Δ_o is given below.

O_2^{2-} < I^- < Br^- < S^{2-} < SCN^- < Cl^- < N^{3-} < F^- < NCO^- < OH^- < $C_2O_4^{2-}$ ≈ H_2O < NCS^- < CH_3CN < py (pyridine) < NH_3 < en (ethylenediamine) < bipy (2,2'-bipyridine) < phen (1,10-phenanthroline) < $NO2^-$ < PPh_3 < CN^- ≈ CO

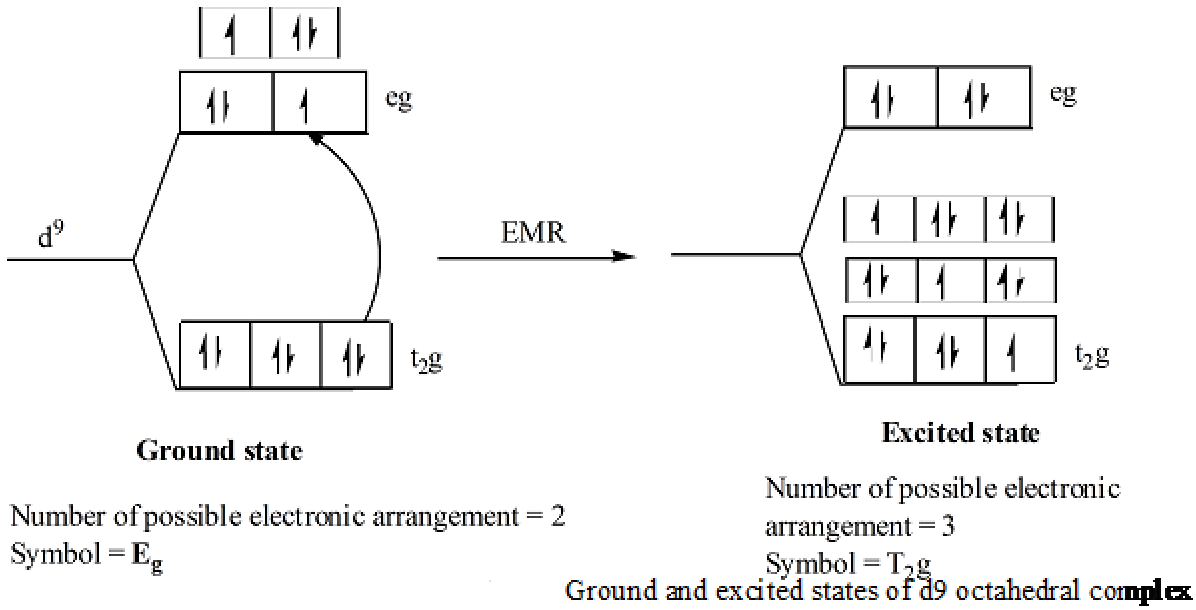
Ligands present on the left end of this spectrochemical series are generally known as weaker ligands and cannot cause pairing of electrons within 3d level and thus, form outer orbital octahedral complexes and are called as high spin ligands. While, ligands present at the right end of the series are stronger ligands which can form inner orbital octahedral complexes after forcible pairing of electrons within 3d level and hence, are called as low spin ligands.
The strong ligands in the spectrochemical series are also called as л-acceptor ligands while weak ligands are known as σ-donor ligands.

3*.7. ORGEL ENERGY LEVEL DIAGRAM FOR d^1 AND d^9 STATE*

Orgel diagrams are the correlation diagrams that represent the relative energies of electronic terms in transition metal complexes.These diagrams are firstly drown by Leslie Orgel. Orgel diagrams are drawn for only weak field complexes (i.e. high spin). These are the diagrams drawn between Δ_o. These diagrams are qualitative and no energy calculations can be carried out from these diagrams. In Orgel diagrams, only symmetry states with the highest spin *multiplicity* are used instead of all possible terms. With the help of Orgel diagrams, we can deduce the number of spin allowed transitions. In these diagrams, the gtound state term (atomic term) (P, D, or F) is located at the center of the diagram in the absence of ligand field while in presence of ligand field, the atomic term splits into molecular Mulliken terms. On the basis of the above discussion, Orgel diagram for the various d^n configuration of transition metal complexes, are discussed in this section.

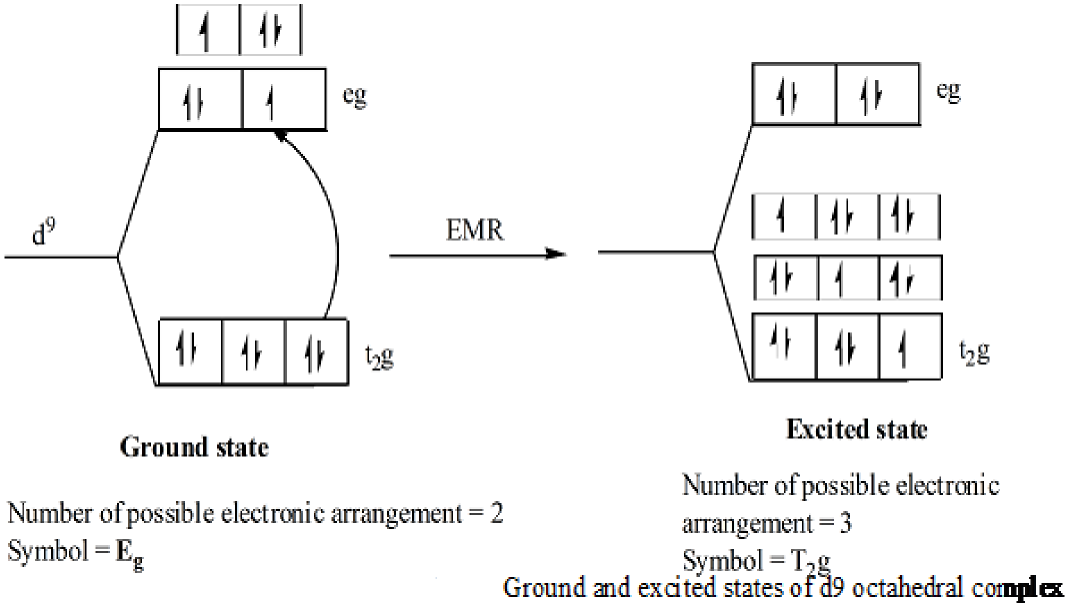
A. Orgel diagram for d^9 octahedral complexes

Orgel diagram of octahedral complexe with d^9 configuration can be drawn in the three different steps which are given below (Figure 4.2):



Ground and excited states of d9 octahedral complex

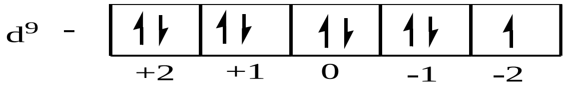
Step I:



Ground and excited states of d9 octahedral complex

Figure 3.2

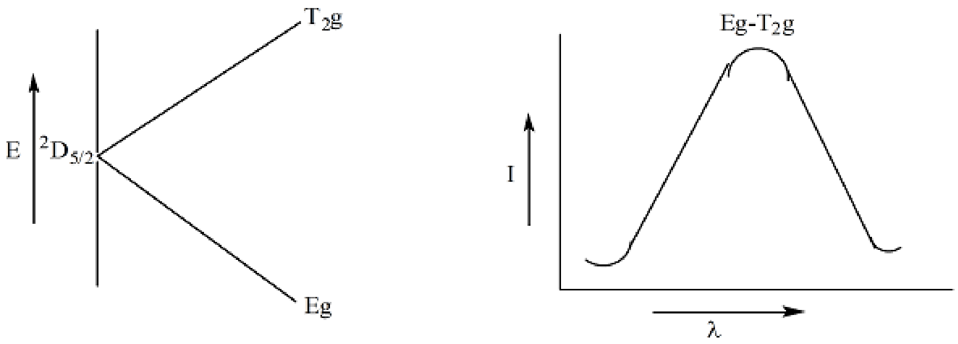
Step II:



L = 2 (D)
S = 1/2
J = 5/2
M = 2

So, the term symbol for d^9 configuration = $\mathbf{^2D_{5/2}}$

Step III: Formation of Orgel diagram (Figure 3.3).

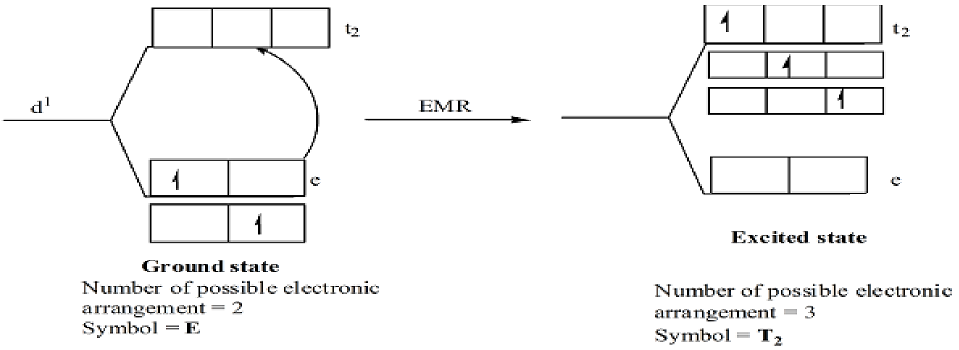


Orgel diagram and absoption spectra of d9 octahedral complex

Figure 3.3

B. Orgel diagram for the d^1 tetrahedral complexes: Orgel diagram for the d^1 configuration of tetrahedral complexe can be explained in the three different steps, is are givenin Figure 3.4 and Figure 3.5.

Step I:



Ground and excited states of d1 tetrahedral complex

Figure 3.4

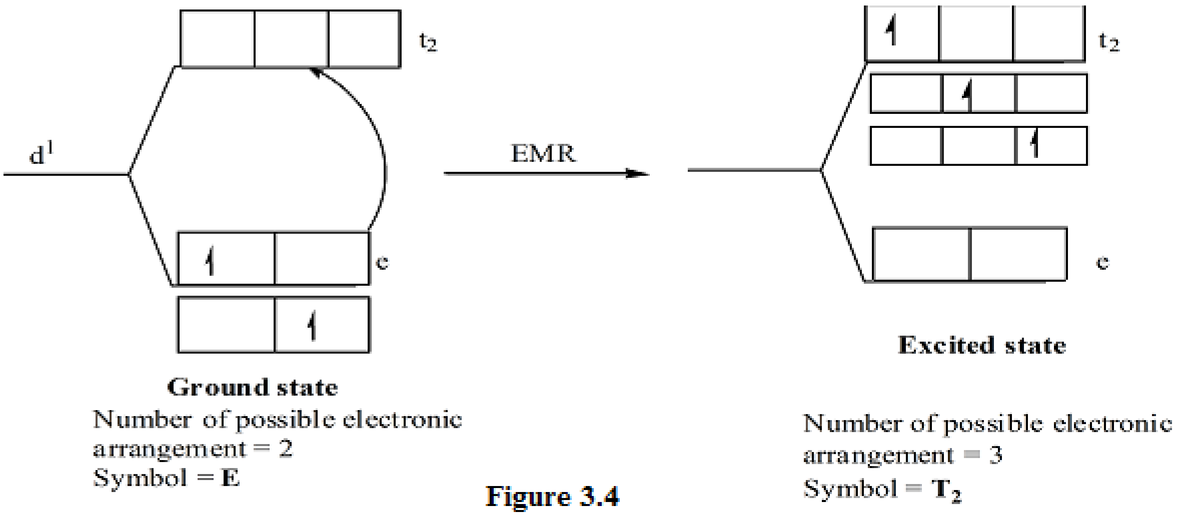
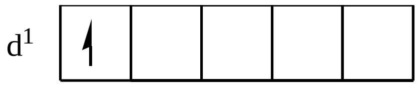


Figure 3.4

Ground and excited states of d1 tetrahedral complex

Step II:



L = 2(D)
S = 1/2
J = 3/2
M = 2

So, the term symbol for d^1 configuration = $^2\mathbf{D}_{3/2}$

Step III:

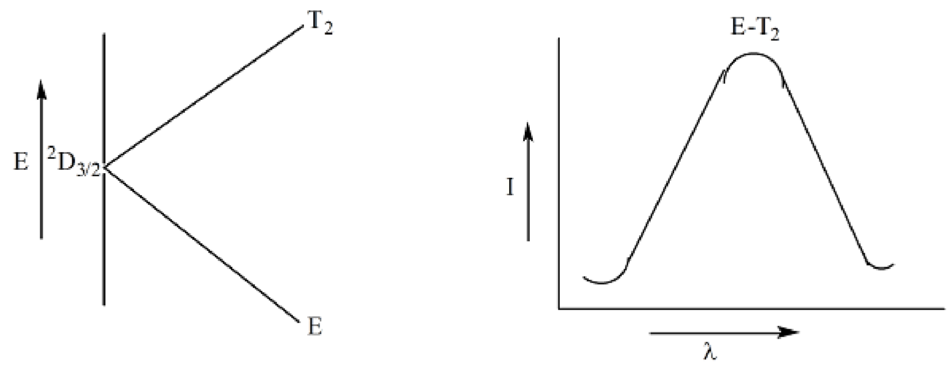


Fig. 35

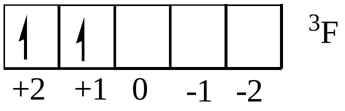
Orgel diagram and absoption spectra of d1 tetraheral complex

Thus, from the above, it can be concluded that d^n tetrahedral complexes and d^{10-n} octahedral complexes have same spectra while d^n tetrahedral complexes and d^{10-n} tetrahedral complexes or d^n octahedral complexes and d^{10-n} octahedral complexes have opposite spectra.

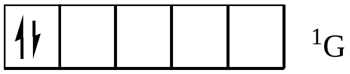
C. Orgel diagram for d^2 octahedral complexes

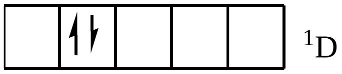
In the electronic spectra of d^2 configuration with octahedral ligand field, such as $[V(H_2O)_6]^{+3}$, it two peaks in the range of $1700 cm^{-1}$ and $2100 cm^{-1}$ are obtained which indicates that the d^2 configuration with octahedral field ligands can exhibit two types of the electronic transitions. According to Orgel, d^2 configuration has ground term symbol ^3F and various exited state term symbols like ^1S, ^1D, ^1G and ^3P. Out of these, only ^3P term (both having same multiplicity) symbol is used during the electronic transition because the electronic transitions from ground state to this excited state are allowed while the electron transitions from ground state to other excited states such as ^1S, ^1G and ^1D are spin forbidden. The Orgel diagram corresponding to this allowed transition for the d^2 configuration with octahedral field ligand can be given below.

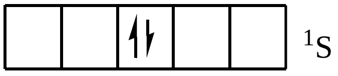
Ground state electronic arrangement for d^2 octahedral complexes is as follows:

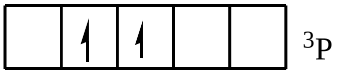


Exited state electronic arrangement for d^2 octahedral complexes is as follows:









Thus, according to the above discussion, the Orgel energy level diagram and spectra for d^2 configuration with octahedral field ligand can be represented as shown in Figure 3.6, 3.7.

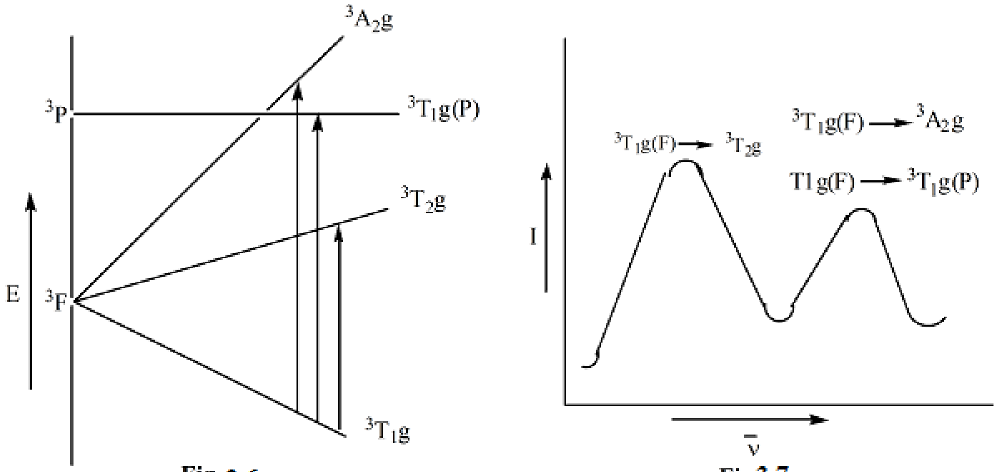


Fig. 3.6 Fig.3.7

Orgel diagram and absoption spectra of d^2 octahedral complex

D. Orgel energy level diagram for d^8 octahedral complexes

The spectra of octahedral complexes with d^8 configurationcontains different peaks which indicates that octahedral complexes like $[Ni(H_2O)_6]^{+2}$, have different types of the transitions (Figure 3.8 ,3.9).

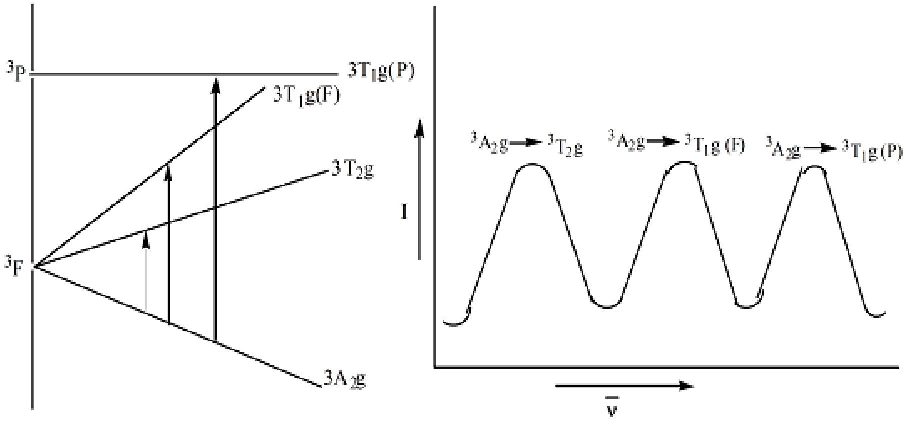


Fig.3.8 Fig3.9

Orgel diagram and absoption spectra of d^8 octahedral complex

3.8. TYPES OF THE ELECTRONIC TRANSITION

Transition metal complexes can exhibit two types of the electronic transitions

1. d- d transition
2. Charge transfer transition

1.d-d transition: In a d–d transition, an electron in a d orbital on the metal is excited to another d orbital of higher energy by a photon. In complexes of the transition metals, the d orbitals do not all have the same energy. In centrosymmetric complexes, d-d transitions are forbidden by the Laporte rule. According to Laporte rule states that, if a molecule is centrosymmetric, transitions within a given set of p or d orbitals will be forbidden. However, forbidden transitions become allowed if the center of symmetry is disrupted. Transitions that occur as a result of an asymmetrical vibration of a molecule are called vibronic transitions. Through such asymmetric vibrations, transitions that should be theoretically forbidden, such as a d-d transition, are weakly allowed.

d-d- Transition is the phenomena of excitation of the electrons of the splitted lower energy set of d-orbitals into the higher energy splitted set of d- arbitals by the absorption of electromagnetic radiation is known as phenomena.

Example: In the d^1 configuration containing octahedral complex i. E. [Ti $(H_2O)_6]^{+3}$ ion, the d-d transition phenomena is representedin Figure 3.8.

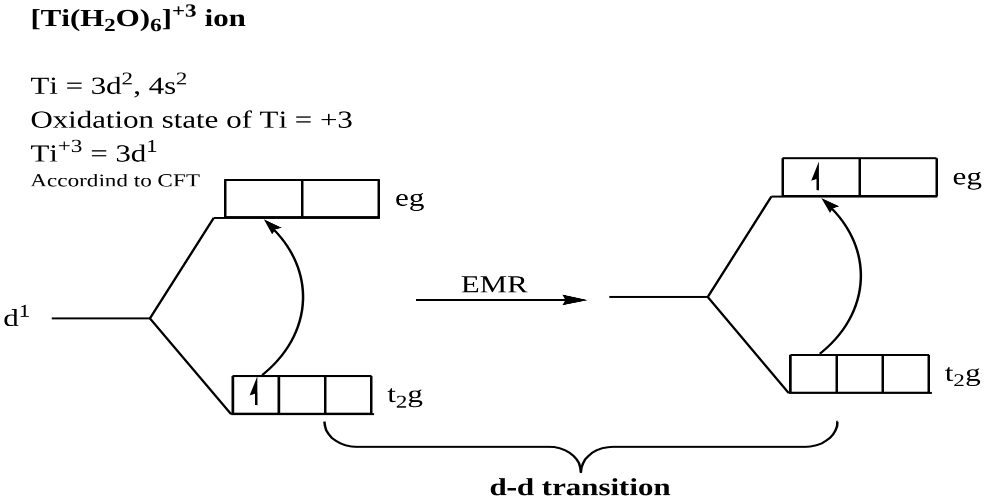


Figure 3.10 ,d-d Transition in$[Ti(H_2O)_6]^{+3}$

2.Charge transfer transition: In inorganic compounds, most of the charge-transfer complexes involve electron transfer between metal atoms and ligands. The charge-transfer bands of transition metal complexes result from shift of charge density between molecular orbitals (MO) that are predominantly metal like nature and those that are predominantly ligand like nature. If the transfer occurs from the MO with ligand character to the MO with metal-like charcater, the complex is called a ligand-to-metal charge-transfer (LMCT) complex and the transfer is LMCT. If the electronic charge shifts from the MO with metal character to the MO with ligand character, the complex is called a metal-to-ligand charge-transfer (MLCT) complex. Thus, oxidation of the metal center occurs as a result of MLCT, whereas a LMCT results in the reduction of the metal center.Depending on the direction of charge transfer, these are classified as either ligand-to-metal (LM) or metal-to-ligand (ML) charge transfer

(a) Ligand-to-metal charge transfer (LMCT)

LMCT complexes arise from the transfer of electrons from MO having ligand character to those having metal character. This type of transfer occurs when complexes have ligands with relatively high-energy lone pairs and if the metal has low-lying empty orbitals. In such complexes, metals have higher uncommon oxidation states or less number of d-electrons (even d^0). These conditions suggest that the acceptor metal level is available which is of low energy.

Consider a d^6 octahedral complex, such as $IrBr_6^{3-}$, whose t_{2g} orbitals are filled. As a result, an intense absorption peak is observed around 250 nm corresponding to a transition from ligand like σ MO to the empty e_g MO of metal like character. However, in case of $IrBr_6^{2-}$, a d^5 complex, two absorption peaks, one near 600 nm and another near 270 nm, are observed. This is because two transitions are possible, one to t_{2g} (that can now accommodate one more electron) and another to e_g. The 600 nm band corresponds to transition of electron from ligand orbital to the t_{2g} MO of metal and the 270 nm band correspond to transfer of electron from ligand MO to the e_g MO of the metal.

Charge transfer bands may also arise from transfer of electrons from nonbonding orbitals of the ligand to the e_g MO of metal.

Examples:

MnO_4^-: The permanganate ion with tetrahedral geometry is intensely purple coloured due to strong absorption involving charge transfer from MO of filled oxygen p orbitals to empty MO of manganese (VII).

CdS: The yellow color of cadmium sulphide is due to the transition of electrons from Cd^{2+} (5s) $\leftarrow S^{2-}$ (π).

HgS: It is red due to Hg^{2+} (6s) $\leftarrow S^{2-}$ (π) electronic transition.

(b) Metal-to-ligand charge transfer

Metal-to-ligand charge-transfer (MLCT) complexes arise as a result of transfer of electrons from MO with metal-like character to those with ligand-like character. These transitions are most common in complexes with ligands having low-lying π* orbitals, especially aromatic ligands. For these trasitions to occur, metal should have low oxidation state with sufficient number of electrons and should be relatively high in energy.

Examples:

i.Tris (2,2'-bipyridyl)ruthenium(II): This is a orange-colour complex due to MLCT.

ii.$W(CO)_4$(phen)

iii.$Fe(CO)_3$(bipy)

3.9. DISCUSSION OF THE ELECTRONIC SPECTRUM OF [Ti $(H_2O)_6]^{+3}$ COMPLEX ION

In $[Ti(H_2O)_6]^{+3}$ complex, Ti (III) has d^1 configuration and in an octahedral field, the configuration is t_{2g}^1. The t_{2g} level is triply degenerated due to the presence of single electron in the excited state (configuration being e_g^1), Jahn Teller distortion was observed in the abnsorption spectra of $[Ti(H_2O)_6]^{+3}$ ion (Figure 4.10). Due to tetragonal distortion, the ion was compressed along the z axis. The CFSE will be $2/3\delta_2$ larger than it would have been in a regular octahedron. The excited state (t_{2g}^0 e_g^1) splits due to Jahn Teller distortion. Therefore, the spectrum of the complex ion shows a shoulder as a result of this splitting (Figure 3.11) and seems to be comprised of two peaks: one from the ground state to the lower e_g level and the other to the upper e_g level (Figure 3.12).

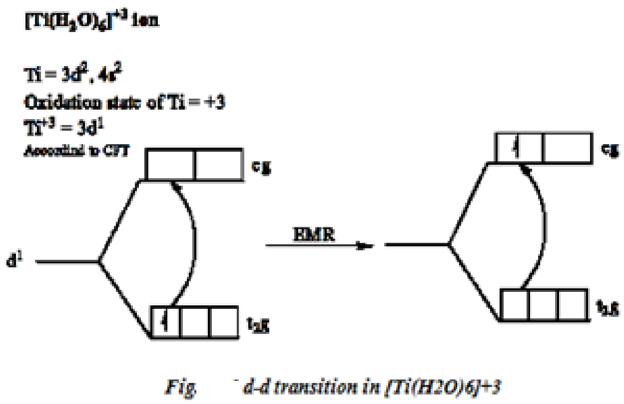


Figure 3.11

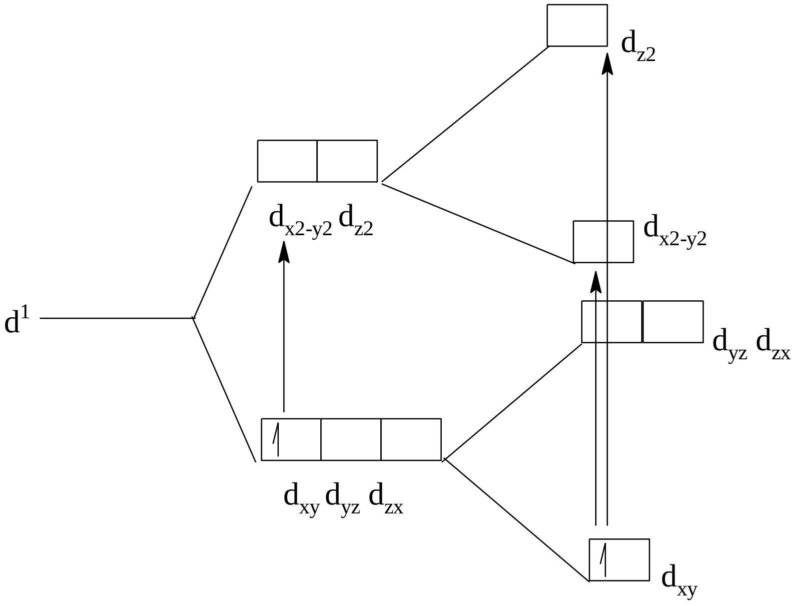


***Figure* 3.12.** *Transtitions in d^1 configuration due to Jahn Teller distortion*

3.10. SUMMARY

Electronic spectra of transition metal complexes help us to understand the structure and bonding in these complexes. A very special characteristic of transition metal complexes is that they exhibit colours of varying intensity of the visible region.

It has been established that colour of the complex compounds is because of d-d transition. The electrons excite from lower energy set of d orbital to high energy set of d orbitals. Energy from the visible range is absorbed by the transition metal complexes and the energy of complementary colour is transmitted. It is the transmitted radiation that from the colour of the substance.

3.11. TERMINAL QUESTIONS AND ANSWERS

A. Short Answer Type Questions

1. Why metal complexes are having colors?
2. If the transition is between one set of d-orbital to another set of d-orbital, only one color should be there for a complex. However, different colors are seen for different complexes. Why?
3. Why d-d transitions are weak as compared to CT transitions?
4. Calculate the term symbol for d^9 octahedral complex.
5. Differentiate between LS coupling and JJ coupling.
6. Why do tetrahedral complexes of an element give much more intense d-d spectra than its octahedral complexes?
7. Discuss the electronic spectra of $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ complexes.
8. What are spin multiplicity forbidden and Laporte forbidden transitions?
9. What are selection rules for electronic spectra?
10. Discuss the spectral features of Mn(II) in octahedral complexes of weak ligand fields.
11. Write briefly about L-S coupling.
12. Discuss the absorption spectra for Co(II) octahedral and Co (II) tetrahedral complexes.
13. Calculate the ground state terms with spin multiplicity for the following octahedral ions: Vi^{3+}, Ni^{2+}, Cu^{2+}
14. Discuss the Orgel diagram and absorption spectra for a d^8 ion.
15. Determine the ground state term symbol of anion with d^1 configuration.
16. Draw the energy level diagram for d^2 configuartion in tetrahedral and octahedral fields showing three possible transitions.

17. How does Hund's rule help to arrange the different spectroscopic terms in order of their increasing energies? How does it help to find the terms in ground state?
18. Discuss Russel-Saunders states for d^2 configurations.
19. Discuss the special features of electronic spectra of $[Ni(H_20)_6]^{2+}$ ion.
20. Discuss special features of electronic spectra of Cr(III) octahedral and Mn(II) octahedral complex ions.
21. Arrange the different spectroscopic terms of titanium with the help of Hund's rules.
22. State and explain the Laporte selection rule.
23. What are the two important limitations of Orgel diagrams?
24. Draw combined Orgel diagram for d^1 and d^9 octahedral complexes.
25. What are Orgel diagrams? What information is conveyed by these diagrams?
26. Give a detailed account of the selection rules of electronic spectra.
27. State and explain Hunds rule for assigning ground state spectroscopic term with suitable examples.
28. Why do tetrahedral complexes give much more intense d-d transition than octahedral complexes?
29. Calculate the term symbol for ground state of Cr.

B. OBJECTIVE TYPE QUESTIONS

1. Which metal complex ion is expected to be subject to a Jahn-Teller distortion?
   a. $[Cr(H_2O)_6]^{+3}$
   b. $[Cr(NH_3)_6]^{+2}$
   c. $[Cr(CN)_6]^{-3}$
   d. $[Cr(bpy)_3]$
2. A d^1 electron configuration corresponds to which of the following terms?
   a. ^2D
   b. ^1D
   c. ^2P

d. ^3P

3. How many microstates are possible for a d^2 configuration, including both weak and strong field limits?

a. 15
b. 45
c. 10
d. 90

4. The‘d-d’ transitions in an octahedral $[NiX_6]^{2+}$ complexes are:

a. Laporte forbidden but spin allowed
b. Laporte forbidden and spin forbidden
c. Laporte allowed and spin allowed
d. Laporte allowed but spin forbidden

5. Why does the absorption spectrum of aqueous $[Ti(OH_2)_6]^{3+}$ exhibit a broad band with a shoulder?

a. The ground state of $[Ti(H_2O)_6]^{3+}$ is Jahn-Teller distorted
b. The excited state of $[Ti(H_2O)_6]^{3+}$ undergoes a Jahn-Teller distortion
c. $[Ti(H_2O)_6]^{3+}$ is a d^2 ion and therefore there are two absorptions
d. $[Ti(H_2O)_6]^{3+}$ is partly reduced to $[Ti(H_2O)_6]^{2+}$ in aqueous solution and two absorptions which are close in energy are observed, one for each species

6. Ground state term for d^2 configuration is:

a. ^3F b. ^3P c. ^1G d. ^1S

7. For Laporte forbidden transitions,

a. $\Delta l = 0$ b. $\Delta S = 0$ c. $\Delta l = -1$ d. $\Delta l = \pm 1$

8. Mullikin symbol for spectroscopic term P in octahedral field is:

a. A_{1g} b. T_{1g} c. T_{2g} d. E_g

9. The ground state for $2p^3$ is:

a. $^4S_3$ b. $^3P_4$ c. $^4S_{3/2}$ d. $^2P_1$

10. The ground state term for p^6 is same for

a. d^{10} b. d^6 c. p^3 d. d^5

ANSWERS

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

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UNIT 4 : ISOMERISM OF COORDINATION COMPOUNDS

CONTENTS:

4.1 INTRODUCTION

Coordinate compounds, or complex compounds, are chemical compounds where a central metal atom or ion is bonded to a group of surrounding molecules or ions, called ligands**.** These ligands are typically electron-pair donors, and they form coordinate covalent bonds with the metal. In a coordination compound**,** the metal atom or ion (usually a transition metal) is at the center and is surrounded by ligands, which could be neutral molecules (like water or ammonia) or anions (like chloride or cyanide). These ligands donate electron pairs to the metal, forming a stable structure.

Isomerism in coordination compounds refers to the phenomenon where two or more coordination compounds have the same molecular formula but different structural arrangements, leading to distinct chemical and physical properties. This occurs due to the flexibility in the coordination of ligands around a central metal atom or ion, which can result in different spatial arrangements or bonding interactions.There are two main types of isomerism in coordination compounds: Structural isomerism,(Ionisation, Hydrate, Coordinate, Linkage, Coordinate position), Stereo isomerism (Geometrical, optical).
In the context of coordination compounds**,** VBT is used to explain the bonding between the central metal atom or ion and the ligands (which are electron-pair donors). The theory focuses on how the central metal atom uses its atomic orbital’s to overlap with the orbital’s of the ligands and form coordinate covalent bonds. This Unit in Valence Bond Theory (VBT) explaining the bonding in coordination compounds by describing the interaction between the central metal ion and the ligands using hybridization and orbital overlap concepts. However, for more detailed explanations of properties like the geometry, color, and stability of coordination compounds,

4.2 OBJECTIVES:

The main objectives of studying the isomerism of coordination compounds are:

- To Understanding Structural Variations.
- Classification of Isomers
- Predicting physical and chemical properties of isomers
- Distinguishing between different isomers by, chemical reactivity in order to determine their unique characteristics.
- These objectives are essential for a deeper understanding of coordination chemistry, which plays a critical role in various industrial, biological, and chemical processes.

- The Valence Bond (VB) Theory for transition metal complexes is essential for understanding the bonding, structure, and properties of coordination compounds.
- To critically analyze the limitations of VBT, especially in explaining some complex phenomena like ligand field effects**,** large splitting of d-orbitals**,** and color changes under different conditions, which led to the development of more advanced theories like Crystal Field Theory (CFT) and Molecular Orbital Theory (MOT)**.**

4.3 ISOMERISM OF COORDINATION COMPOUNDS

Compounds having same molecular formula but different structures and hence different physical and chemical properties are called isomers and this phenomenon is known as isomerism. A vast diversity of isomers can be produced by coordination compounds because of the many connections and structural configurations of the constituent atoms.

4.4. ISOMERISM IN COORDINATION COMPOUNDS

Coordinate compounds give rise to a wide variety of isomer due to different types of arrangements of ligands with the central metal ion through which different physical and chemical properties of the isomers. There are two principal types of isomerism in coordination compounds these are shown below:

Isomerism in Coordination compounds

A.Structural Isomerism

1. Ionisation Isomerism
2. Hydrate Isomerism
3. Coordination Isomerism
4. Linkage Isomerism
5. Coordination position Isomerism
6. Polymerization isomerism

B. **Stereo Isomerism**

1.Geometrical Isomerism

2.Optical Isomerism

4.5 STRUCTURAL ISOMERISM

Structural isomers are the isomers that have the same molecular formula, that differ in the bonding patterns and atomic organization. Structural isomerism is subdivided as below:

4.5.1 Ionisation Isomerism : The compounds which have same molecular formula but give different ions in solution are called ionization isomers. This isomerism arises due to interchange of groups within or outside the coordination sphere.This type of isomerism occurs when the counter ion in a coordination compound is itself a potential ligands.

For example: The compound $Pt(NH_3)_4Br_2Cl_2$,when dissolved in water gives two isomers:

i) $[Pt(NH_3)_4Br_2]Cl_2$

ii) $[Pt(NH_3)_4Cl_2]Br_2$

These two complexes differ only in the location of chloride and bromide ions (counter ions). Add silver nitrate ($AgNO_3$**)** to both solutions.

In the first compound, it will form a white precipitate **of** silver chloride (AgCl).

$$[Pt(NH_3)_4Br_2]Cl_2 \longrightarrow [Pt(NH_3)_4Br_2]^{+2} + 2Cl^- \xrightarrow{AgNO_3} \text{White precipitate}$$

In the second compound, the addition of silver nitrate will form a yellow precipitate of silver bromide (AgBr), confirming the presence of bromide ions.

$$[Pt(NH_3)_4Br_2]Cl_2 \longrightarrow [Pt(NH_3)_4Cl_2]^{+2} + 2Br^- \xrightarrow{AgNO_3} \text{Yellow precipitate}$$

Other example of ionization isomerism are:

- $[CoCl_2(NO_2)(NH_3)_4]NO_2$ and $[CoCl(NO_2(NH_3)_4]Cl$
- $[CoBr(NH_3)_5]SO_4$ and $[CoSO_4(NH_3)_5]Br$
- $[Ni(NH_3)_6]Cl_2$ and $[Ni(NH_3)_5Cl]Cl\cdot H_2O$

Factor affecting ionization isomerism:

This isomerism arise when ligands in a coordination compound can form different ions or exchange places between the coordination sphere and the ionic lattice. The factors affecting the formation of ionization isomers include:

a) **Ligands that can be neutral or anionic**: The ability of certain ligands to either remain in the coordination sphere or dissociate into the solution as counterions contributes to ionization isomerism. For example, chloride ions (Cl^-) can exist as both coordinated ligands and as counterions outside the coordination sphere.

b) Nature of Counterions

The nature and charge of the counterions in the crystal lattice play a significant role. For example, counterions like chloride (Cl^-), sulfate (SO_4^{2-}), and nitrate (NO_3^-) can interact with the metal-ligand complex in different ways, influencing whether they end up inside or outside the coordination sphere.

c) **Coordination Number and Geometry**:The coordination number and geometry of the central metal ion can influence which ligands are able to form bonds with the metal ion, and which remain outside as counterions. For example, a square planar complex might have different geometries and ligand interactions than an octahedral one, influencing ionization behavior.

d) **Solubility and Crystallization Conditions:**
Crystal packing can play a role. During crystallization, the ionization of the compound depends on the interaction between the metal-ligand complex and the solvent or crystallizing agents, which may favor different arrangements of ions.

4.5.2 Hydrate Isomerism:

In simpler terms, hydrate isomerism occurs when the coordination compound contains water molecules, and these water molecules can either be coordinated directly to the metal or be present as non-coordinated molecules within the crystal lattice.

In Hydrate Isomerism ,coordination compounds, the difference between the isomers lies in the distribution of water molecules. In this isomerism, some water molecules may be part of the coordination sphere (bound directly to the metal ion), while others may be present as free water molecules (also called "water of crystallization" or "crystallization water").

For example: $CrCl_3 .6H_2O$,may consider the following three isomers i.e.:

i) $[Cr(H_2O)_6]Cl_3$

ii) $[CrCl(H_2O)_5] Cl_2. H_2O$

iii) $[CrCl_2(H_2O)_4] Cl. 2H_2O$

- In first isomer, 6 water molecules are coordinated to the chromium ion when it treated with con. H_2SO_4does not lose the water molecules and $3Cl^-$ ion get precipitated with $AgNO_3$ and produce violet colour.
- In second isomers, 5 water molecules are coordinated to the chromium ion when it treated with con. H_2SO_4 it lose one water molecules and $2Cl^-$ ion get precipitated with $AgNO_3$ and produce green colour.
- In third isomers, 4 water molecules are coordinated to the chromium ion when it treated with con. H_2SO_4 it lose two water molecules and Cl^- ion get precipitated with $AgNO_3$ and produce dark green colour.

  Another example of hydrate isomerism are:

  - $[Co(NH_3)_5Cl]Cl\cdot 2H_2O$ and $[Co(NH3)_5.H_2O]Cl_2\cdot H2O$
  - $[CoCl(en)_2(H_2O)]Cl_2$ and $[CoCl_2(en)_2] Cl. H_2O$

Factor affecting Hydrate isomerism: In Hydrate isomerism the arrangement of water molecules in the complex can lead to different isomers. Several factors can influence hydrate isomerism:

a) Coordination Number of the Metal Ion: The coordination number refers to the number of ligand bonds formed with the central metal ion. A metal ion with a high coordination number (e.g., 6 or 8) will generally accommodate more water molecules as coordinated ligands, while a metal ion with a lower coordination number might have fewer coordinated water molecules.

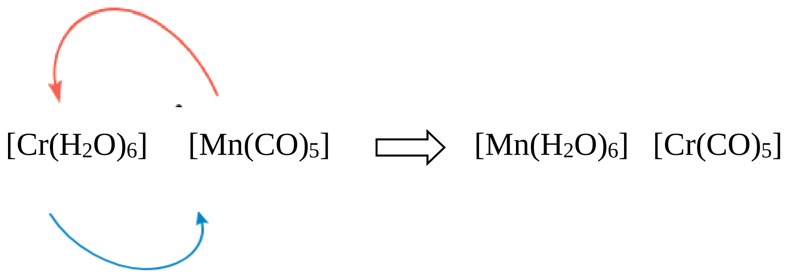
b) Size and charge of metal ion :Smaller and more highly charged metal ions tend to have a greater ability to coordinate water molecules. The charge density (ratio of charge to size) of the metal ion can affect how many water molecules can be attracted to the metal ion and how strongly they will bind.

c) Solvent Effects:The solvent in which the complex is dissolved can affect the hydrate isomerism. If the solvent interacts strongly with the metal or the water molecules in the complex, it could influence the distribution of coordinated and lattice water molecules. Solvents that can hydrogen bond with water, for instance, may alter the way water molecules are distributed in the crystal.

4.5. 3.Coordination Isomerism:

Coordination isomerism is a type of isomerism found in coordination compounds, where two or more coordination compounds have the same molecular formula but differ in the arrangement of ligands and/or metal ions. This type of isomerism is observed when the ligand exchange happens between the metal centers in a coordination complex. Coordination isomerism is generally seen in complexes where there are multiple metal centers and ligands that can be coordinated to either metal center. This can result in different isomers that have the same overall composition but differ in the identity of the metal-ligand interactions.

The example of coordination isomerism is in the following complex are:



$$[Cr(H_2O)_6]\quad [Mn(CO)_5] \Rightarrow [Mn(H_2O)_6]\quad [Cr(CO)_5]$$

These two are coordination isomers. In the first complex, chromium is coordinated with six water molecules, and manganese is coordinated with five carbon monoxide molecules. In the second isomer, manganese is coordinated with six water molecules, and chromium is coordinated with five carbon monoxide molecules.

Other examples of coordination isomerism are:

- $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
- $[Co(NH_3)_6]$ $[Cr(NO_2)_6]$ and $[Cr(NH_3)_6]$ $[Co(NO_2)_6]$

Factor affecting Coordination isomerism: Different arrangements of metal-ligand coordination. Several factors affect the occurrence and stability of coordination isomerism:

a) **Ligand Distribution**: The distribution of ligands between different metal ions in the complex determines the possibility of coordination isomerism. If ligands can be exchanged between metal ions, the different arrangements result in distinct isomers.
b) **Steric Hindrance**: The size of the ligands and the spatial arrangement around the metal ions can influence how easily ligands can be exchanged between the metal centers. Bulky ligands may hinder the transfer of ligands from one metal to another, affecting the formation of isomers.
c) **Exchangeable Ligands**: In a coordination complex, if the ligands are exchangeable between metal centers (e.g., due to low coordination strength or weak bonds with the metal), it increases the possibility of forming isomers by rearranging the ligand-metal assignments. This exchangeability is typically governed by the ligand's binding strength and how easily it can detach from one metal and attach to another.

4.5.4. Linkage isomerism:

In some ligands (ambidentate ligands) there are two atoms which can donate their lone pairs.For example, NO_2^- ion, the nitrogen atom as well as the oxygen atom can donate their lone pairs, give rise to linkage isomerism.This type of isomerism occurs in coordination compounds, when a ligand can coordinate to the central metal atom through **two different donor atoms.** The donor atoms can form different types of bonds with the metal, leading to different isomers. These isomers are known as **linkage isomers.**

Examples of linkage Isomerism: Nitrite ion (NO_2^-): The nitrite ion can bind to the metal in two different ways:

- Through the nitrogen atom (forming a nitro-complex, −NO2)
- Through the oxygen atom (forming a nitrito-complex, -ONO)

An example of linkage isomerism involving nitrite is:

$[Co(NH_3)_5(NO_2)]^{2+}$:Pentaamminenitrito-N cobalt(III)chloride,here nitrite is bound through the oxygen atom.

$[Co(NH_3)_5(ONO)]^{2+}$: Pentaamminenitrito-Ocobalt(III)chloride ,here nitrite is bound through the nitrogen atom.

Other example of linkage isomerism:

- $[Fe(CO)_5(SCN)]^{2+}$ (where SCN binds through sulfur)
- $[Fe(CO)_5(NCS)]^{2+}$[(where SCN binds through nitrogen)

Factors Affecting Linkage Isomerism:

Linkage isomerism occurs when a ligand can coordinate to a metal center through two different donor atoms, and several factors influence whether or not linkage isomerism will occur in a coordination compound. Below are the main factors that affect linkage isomerism:

a) **Flexibility of the Ligand**: The more flexible the ligand (i.e., the easier it is for the ligand to change the position of its donor atoms), the more likely linkage isomerism will occur. Ligands with a rigid structure are less likely to show linkage isomerism because the donor atom position is fixed.

b) **Steric Factors:**Steric hindrance can influence whether the metal prefers to bind through one donor atom or the other. If one donor atom is sterically hindered (i.e., its approach to the metal is obstructed by the size of the ligand or other groups attached to it), the ligand may prefer to bind through the other donor atom. This factor is particularly important when the metal ion is small or has specific spatial requirements for ligand coordination.

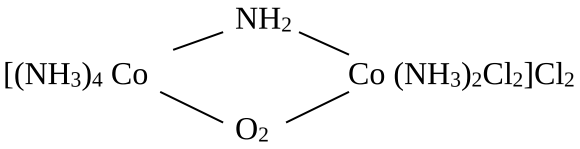
c) **Nature of the Metal Ion:** A highly charged metal ion tends to have a stronger attraction to donor atoms with high electron density, which may influence the coordination preference of the ligand.

d) **Geometry of the Complex**: The complex requires a specific geometric arrangement of the ligands (such as octahedral, tetrahedral, or square planar), the metal ion may favor the donor atom that leads to a more stable complex geometry.

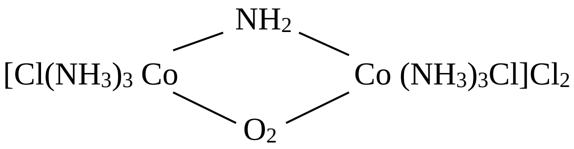
e)**Temperature and Concentration**: Higher temperatures may provide enough energy to overcome any steric or electronic preferences for one donor atom, allowing for the formation of both isomers. Additionally, the concentration of the ligand or metal may shift the equilibrium towards one isomer over another.

4.5.5.Coordination Position Isomerism : The difference in the position of ligands in a bridge complex causes a special type of coordination isomerism. This special type of isomerism is called co-ordination position isomerism. In polynuclear complexes, an interchange of ligands between the different metal nuclei gives rise to co-ordination positional isomerism.

The example of co-ordination position isomerism are:



Tetrammine cobalt (III)μ-amido- μsuperoxodiamminidichloridocobalt(III) chloride



Triamminechlorodocobalt (III)μ-amido- μsuperoxotriamminichloridocobalt(III) chloride

It will be seen in both isomers ammonia and chloride ligands are differently placed relative to the two cobalt atoms and superoxo O_2 and amido NH_2^- is bridging group.

4.5.6.Polymerization isomerization:

This type of certain complexes which molecular compositions that are multiples of simple complexes. The molecular formula of these compounds appears to be polymers of some simple, complex compound.

Example : $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_4]$, $[PtCl_4]$.are polymerization isomers and have same empirical formula but have molecular weight in the ratio of 1:2.

4.6.STEREOISOMERISM

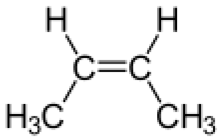
In stereoisomers are compounds that differ only in how their atoms are oriented in three-dimensional space. This contrasts with structural isomerism, where the connectivity of atoms differs.There are two main types of stereoisomerism:

4.6.1.Geometrical Isomerism (cis-trans isomerism):

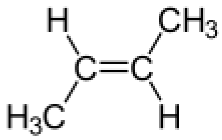
Geometrical isomerism is a type of stereoisomerism where molecules with the same molecular formula have different spatial arrangements of atoms or groups around a double bond or a ring structure. This type of isomerism arises due to the restricted rotation around certain bonds, typically **a** double bond (in alkenes) or a ring system (in cyclic compounds).There are two primary types **of** geometrical isomerism and this is typically seen in compounds that have a double bond (C=C) or in ring structures.

- **Cis isomer**: The substituent groups are on the same side of the double bond or ring.
- **Trans isomer**: The substituent groups are on opposite sides of the double bond or ring.

Example: In **but-2-ene**, there are two isomers:



cis



trans

- **Cis-but-2-ene**: Both methyl groups ($–CH_3$) are on the same side of the double bond.
- **trans-but-2-ene**: The methyl groups are on opposite sides of the double bond.

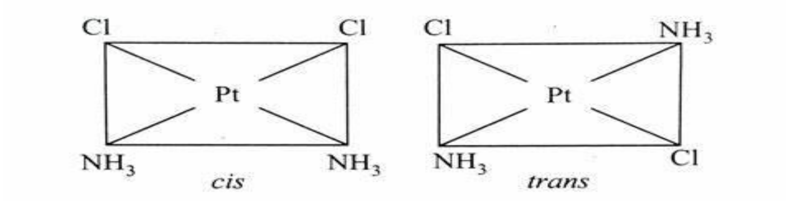
A much larger variety of geometrical isomerism is available in coordination compounds than even in organic compounds.This is due to different coordination numbers.Geometrical isomerism is not possible for complexes having coordination number 2and 3 because in these arrangements all the positions are adjacent to on another.Geometrical isomerism of compounds with coordination number 4 in square planer complexes and 6 octahedral complexes is most important and is describe below;

4.6.2.Geometrical isomerism in coordination number 4: (In square planer complex)

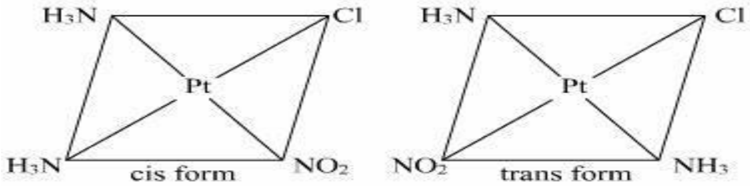
Geometrical isomerism arises in hetroleptic complexes due to ligands occupying different position around the central ion.In geometrical isomerism cis –trans isomers is not possible in tetrahedral complexes because all four ligands are adjacent to one another. However, cis- trans isomerism is very common amongst square planer complexes.Square planer complex of the type MA_2X_2, MA_2XY, MABXY, $M(AB)_2$ can exist as geometrical isomers, (Here, A, B are neutral ligands such as H_2O,NH_3,CO, NO,C_5H_5N,Whereas, X, Y are anionic ligands such as Cl^-,$NO2^-$, CN^-,SCN^- etc.

Example:

i)**MA_2X_2 Type**: Complexs of MA_2X_2 type can exist in cis and trans forms.In complex$[Pt(NH_3)_2Cl_2]$ existed two geometrical form and it must have a planar structure.

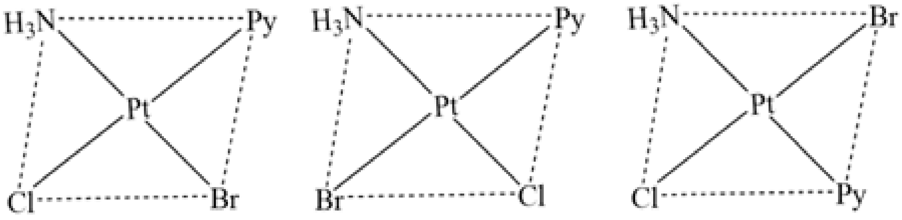


ii)MA_2XY Type: Complexes $[Pt(NH_3)_2ClNO_2]$ can exist in the following geometrical forms:



iii) MABXY Type: Square planer complexes MABXY shown three isomers.The structures of these isomers can be written by fixing the position of one ligands (say A) and placing the other ligands B, C,and D trans to it.

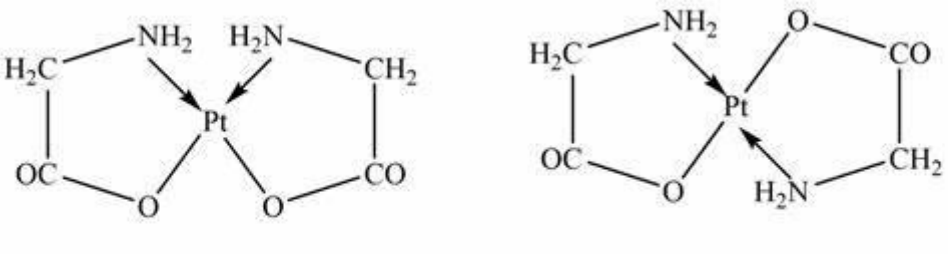
Example:$[Pt(py)(NH_3)(CI)(Br)]$



Three isomeric forms of [Pt(NH$_3$)(Py)Cl(Br)]

These can be written by fixing one ligands (NH$_3$) and then placing other ligands trans to it. Three isomers of the complex have actually been isolated and identified.

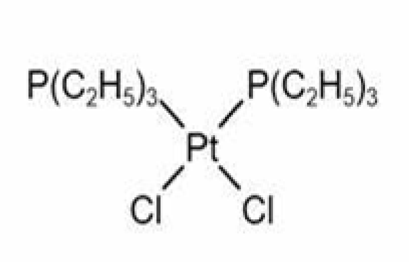
iv)M(AB)$_2$ Type: Geometrical isomers are also found in square planar complexes which have unsymmetrical bidentate ligands .**For example:**Complex [Pt(gly)$_2$] ,where gly stands for NH$_2$CH$_2$COO$^-$ exists in cis and trans forms.

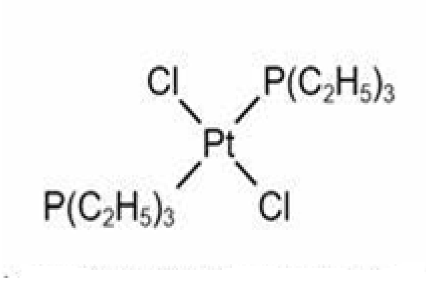


Cis form Trans form

v)Geometrical isomerism is also shown by bridged binuclear complexes of the type MA$_2$X$_4$.

For example : The complex [PtCl$_2$P(C$_2$H$_5$)$_3$]$_2$ exhibits geometrical isomers as:





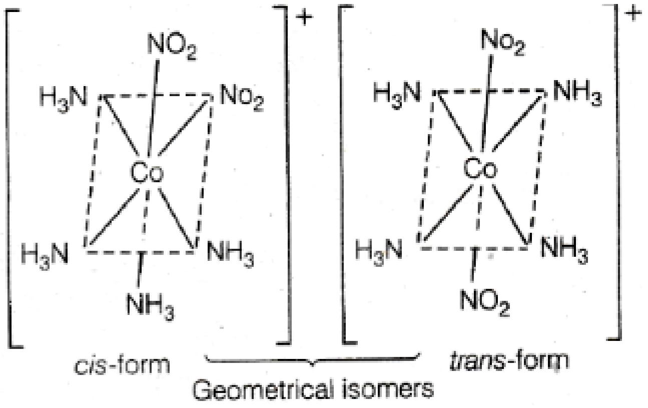
Cis-dichlorobis(triethylphosphine) trans-dichlorobis(triethylphosphine) platinum(II) platinum(II)

4.6.3.Geometrical isomerism in coordination number 6: (In Octahedral complex)

In coordination number six (6) shown octahedral geometry. The different type of octahedral complexes exhibiting following geometrical isomers are discuss below:

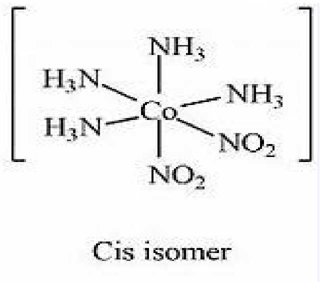
i)MA_2B_4 Type:MA_2B_4,/ MA_4B_2,type of octahedral complexs exist as cis-isomers(two monodentate ligands in 1,2 –position) and trans – isomers (two ligand in 1-6 –positions).

For example: MA_2B_4Complex , $[Co(NO_2)_2(NH_3)_4]^-$, dinitrotetraamminecobalt(III)ion, represent cis and trans isomers :

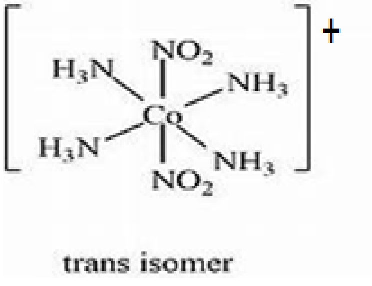


1, 2- dinitrotetraammine cobalt(III)ion 1, 6- dinitrotetraammine cobalt(III)ion

MA_4B_2 complex, $[Co(NH_3)_4(NO_2)_2]^+$, dinitrotramminecobalt(III)ion , cis and trans iomers represent as:

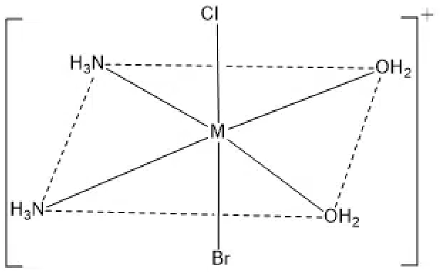


1, 2- dinitrotetrammine cobalt(III)ion

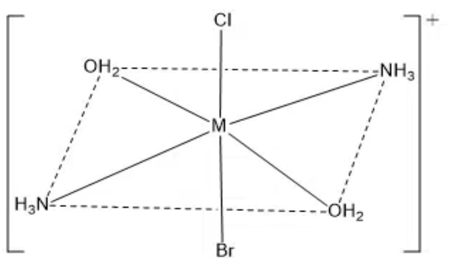


1, 6- dinitrotetrammine cobalt(III)ion

ii) MA$_4$BC Type:In complex **,** [Co(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$ ion is an important example of this type of complex. This ion has cis- and trans-isomers whose structures are shown in the figure below. In cis-form two NH$_3$ molecules have cis positions to each other, and in trans-form these ligands (i.e. two NH$_3$ molecules) have trans position with each other.



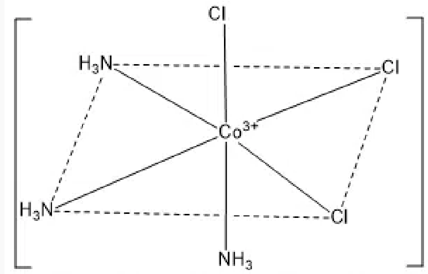
cis-isomer



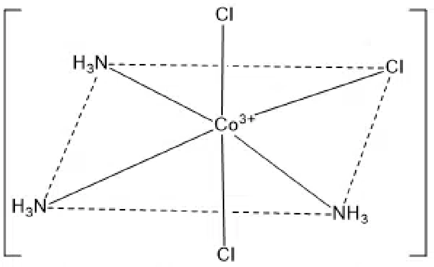
trans-isomer

iii) MA$_3$B$_3$ Type: All complex of this type exist in cis- and trans- isomers. [Co(NH$_3$)$_3$Cl$_3$], [Co(NH$_3$)$_3$(NO$_2$)$_3$], [Cr(H$_2$O)$_3$F$_3$], [Cr(NH$_3$)$_3$Cl$_3$] etc are important examples of octahedral complexes.When the three ligands (with same donor atoms) ar on the same triangular face of the octahedron, the compound is called facial or fac isomers . When the three ligands are on the same equatorial plane of the octahedron i.e around the meridian of the octahedron, the compound is called meridional or mer isomer. In the meridional isomer, the three ligands are at the three corners of a square plane, as illustrated below, whereas in the facial isomer, they are at the corners of a triangular face:

For example: cis- and trans- isomers of [Co(NH$_3$)$_3$Cl$_3$] :

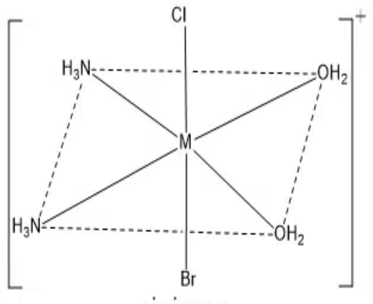


cis-isomer [1,2,3-isomer or facial isomer]

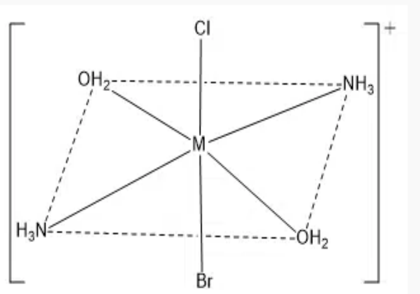


trans-isomer [1,2,6-isomer or meridional isomer]

iv) MA$_2$B$_2$CDType: It exist as two isomers. Where A,B,C, and D are monodentate ligands. for example; [Co(NH$_3$)$_2$(H$_2$O)$_2$ClBr]$^+$



cis-isomer

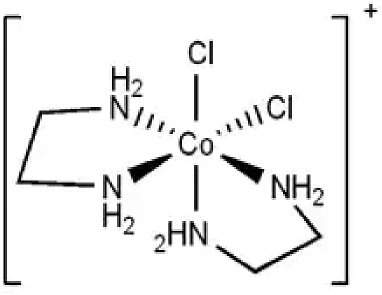


trans-isomer

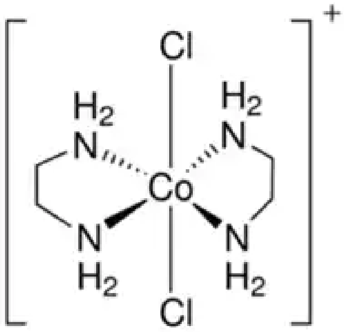
v) **MABCDEF Type:** In case of MABCDEF type complexes all the ligands are different. Theoretically it exist fifteen possible geometrical isomers, but actual practice it has been isolated only three different form of isomers.

vi) **M(AA)$_2$ a$_2$ Type:** In M(AA)$_2$ a$_2$ / M(AA)$_2$ ab complexes**,** AA is a symmetrical bidentate ligand such as ethylenediammine, and 'a' and 'b' is a monodentate ligand exists as cis and trans isomers. Example: $[Co(en)_2Cl_2]^+$ and $[Cr(gly)_2Cl_2]^+$, $[Co(en)_2Cl\ Br]^+$.

For example: Geometrical isomers of $[Co(en)_2Cl_2]^+$ ion.

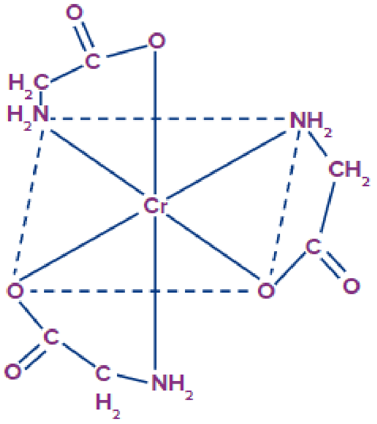


cis-isomer

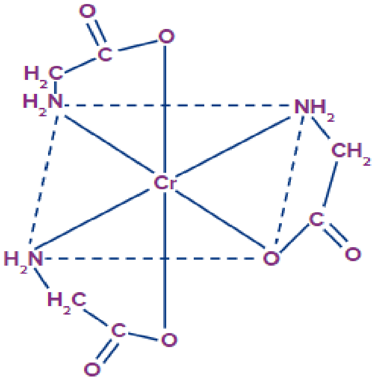


trans-isomer

vii) **M(AA)$_3$ Type:** Unsymmetrical bidentate ligands in octahedral complexes exhibit geometrical isomerism . For example:$[Cr(gly)_3]$ where: gly is $NH_2CH_2COO^-$ exists in cis and trans forms.



Cis- form
Trans-triglycinatochromium (III)



Trans- form
Trans-triglycinatochromium (III)

4.6.4.Optical isomerism: Optical isomers are those two compounds with the same chemical formula such that their mirror images are not superimposable on each other. Depending on the direction they rotate the plane of polarised light in a polarimeter, we have two forms of optical isomers. They are:

- **Dextro Isomer**: The isomers which rotates the plane of polarized light to the right or clockwise is called dextro rotator and designated as *d*.
- **Laevo Isomer**: The isomers which rotates the plane of polarized light to the left or anticlockwise is called laevo rotator and designated as *l*.
- Optically inactive isomers are those that cannot rotate the plane of polarized light. Such an isomer is known as meso, racemic, or dl-form

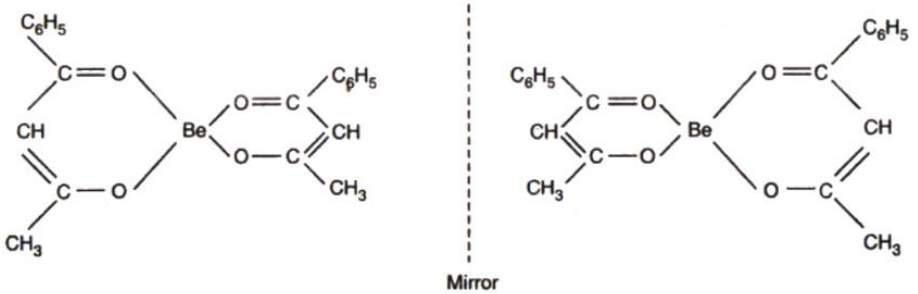
The essential requirement for a substance to show optical activity is that the substance should not have a plane of symmetry in its structure. The optical isomers have identical physical and chemical properties. They are differ only in the direction in which they rotate the plane of polarized light.

4.6.5.Optical isomerism in coordination number 4: Optical isomerism can still occur in coordination number 4, especially in **tetrahedral or square planar** geometries.

- In **square planar** complexes, optical isomerism is less common but still possible. Optical isomerism can occur in square planar complexes when the ligands are arranged asymmetrically, which again results in chirality. The geometry is flat, and the complex must be arranged in such a way that it lacks symmetry.

- In **tetrahedral** complexes (where the central metal is surrounded by four ligands), optical isomerism can occur when the ligands around the metal center are arranged in such a way that the complex is **chiral.** This usually happens when the ligands are different from each other. In a tetrahedral arrangement, the complex can be chiral and have two non-super imposable mirror images, which are optical isomers (enantiomers).

  For example:Complex of Be, B Cu(II),Zn (II) etc. containing unsymmetrical ligands have been resolved into optical isomers like bis (benzoylactonat)beryllium (II) complex.

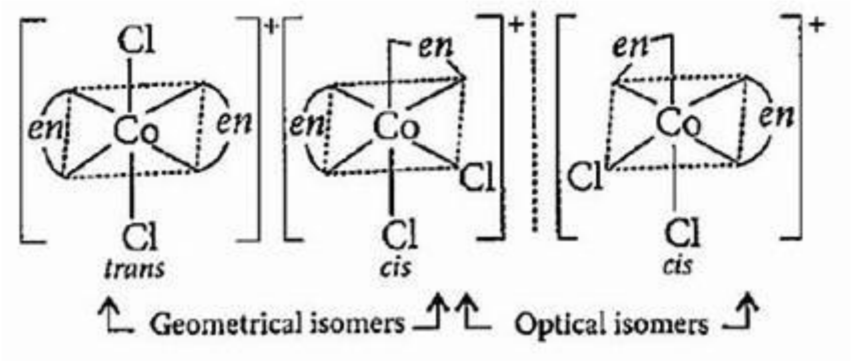


Optical isomers of bis (benzoylactonat)beryllium (II) complex

4.6.6.Optical isomerism in coordination number6: Optical isomerism in coordination number 6 , octahedral complex can occur when the ligands are arranged asymmetrically, resulting in two non-superimposable mirror image isomers, (**enantiomers**) are arises.some example of optical isomerism in coordination number six are given below:

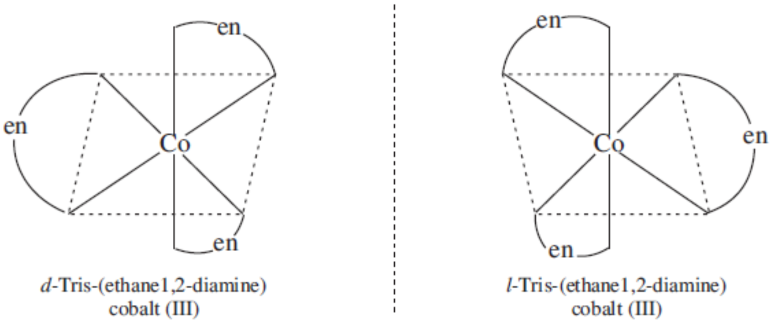
i)$M(AA)_2X_2$ Type:$M(AA)_2X_2$ / $M(AA)_2XY$: Such type of isomers shown geometrical and optical isomerism.The trans isomers don’t shown optical isomerism. This is because in this case is molecules shown plane of symmetry and cis form is unsymmetrical form d and l isomers.

For example: $[Co(en)_2Cl_2]^+$ cis-dichloridobis(ethylendiammine)cobalt(III) ion, three possible isomers are:



cis-dichloridobis(ethylendiammine)cobalt(III) ion

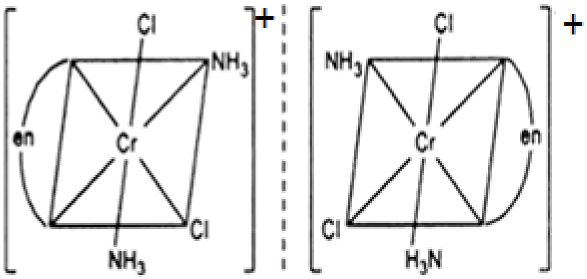
ii)M(AA)$_3$ Type: In this type **AA=** Bidentate ligands . such complexes exist as optical isomers because they form non- super imposable mirror images. The example of this type of isomerism are given below:[Co(en)$_3$]Cl$_3$



d-Tris-(ethane1,2-diamine) cobalt (III)

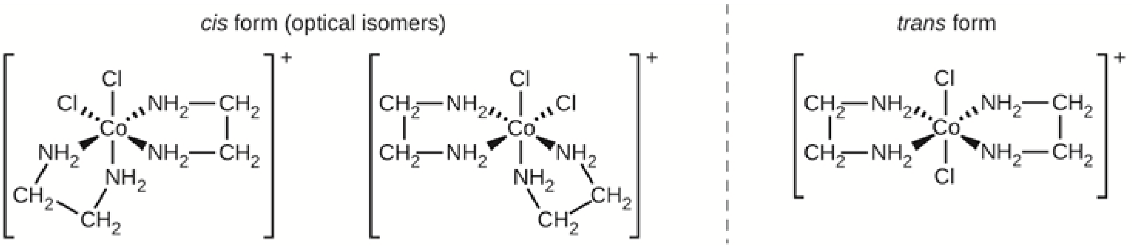
l-Tris-(ethane1,2-diamine) cobalt (III)

iii)M(AA)B$_2$C$_2$ Type: In this type of complexes containing only one bidentate ligands shown optical isomerism. For example: [CoCl$_2$(NH$_3$)$_2$(en)]$^+$ it exists d and l form.

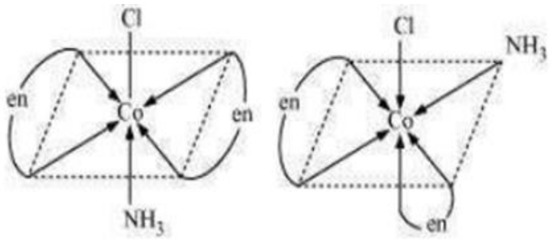


iv)M(AA)$_2$B$_2$ or M(AA)$_2$BC Type: In these complexes ,bidentate ligands (such as **AA**) are involved, which often create chelated rings around the metal and result in chiral centers. These optical isomers would differ in the way they interact with polarized light. Only the cis-form is unsymmetrical and can create two optical isomers, while trans isomers will be optically inactive because of the plane of symmetry.

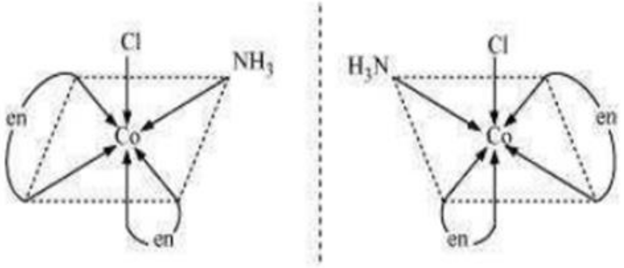
For example:[Co(en)$_2$Cl$_2$]$^+$ exists three isomers trans , optically inactive and in cis (*d*) and cis(*l*) isomers optically active (Non-superimposable mirror images) ,and trans [CoCl$_2$(en)$_2$]$^+$ isomers optically inactive (superimposable mirror images).



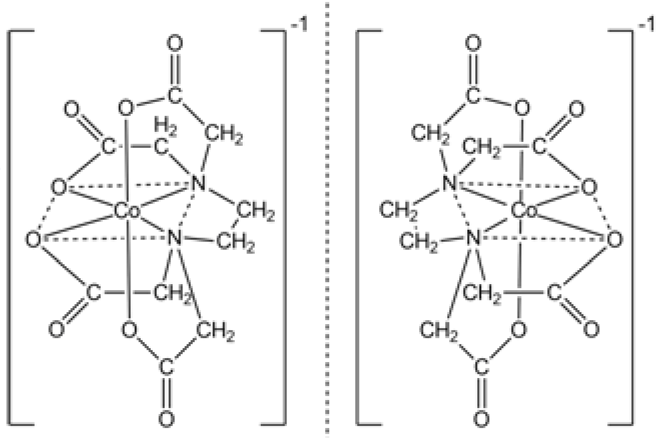
M(AA)B$_2$C$_2$ type example is [Co(en)$_2$NH$_3$Cl]$^{2+}$ shown three possible isomers i.e:



Trans Cis



v)The compound containing hexadentate ligand have also been resolved into optical isomers. For example: $[Co(EDTA)]^-$



d-form i-form

4.7 IMPORTANCE OF ISOMERISM

Isomerism is incredibly important in various scientific and industrial fields because it helps explain the diversity in the behavior, properties, and functions of molecules. Isomers are compounds with the same molecular formula but different arrangements or orientations of atoms, leading to distinct properties.In Geometrical isomerism due to restricted rotation around a bond, typically in compounds with double bonds or cyclic structures. It leads to different spatial arrangements of atoms or groups attached to the molecule. The significance of geometrical isomerism lies in the following aspects:

1.The orientation of substituent groups in geometrical isomers can significantly impact how molecules interact with biological systems. For example, fatty acids, vitamins, and hormones can exhibit different biological effects depending on whether they are in the **cis** or **trans** form. In biological systems, cis configurations tend to be more common, while trans configurations may have negative health effects (e.g., trans fats**).**

2. Geometrical isomerism plays a key role in determining the properties of materials like plastics and rubbers. For example, the cis and trans forms of polyisoprene (rubber) exhibit different elasticity and hardness, impacting their uses in products like tires and medical devices.

3. The cis and trans isomers often react differently in chemical reactions because of their distinct spatial arrangements. In certain reactions, affecting how they participate in organic synthesis and industrial processes.

Optical isomerism arises when molecules are chiral**,** meaning they are non-superimposable on their mirror images, similar to how your left and right hands are mirror images but cannot be aligned perfectly. Optical isomerism is important in the following ways:

1.Many natural compounds that contribute to the taste and aroma of foods are chiral. For example**,** L- and D- amino acids have distinct flavors and properties. The difference in chirality can influence the flavor profile of food and beverages, making optical isomerism significant in food chemistry and the fragrance industry.

2. In optical isomerism polarized light (using a polarimeter), we can determine the concentration and identity of chiral compounds. This technique is widely used for identifying substances in the lab, especially in chemistry and forensics.

3. Optical isomerism is critical in the pharmaceutical industry because enantiomers (pairs of optical isomers) can have vastly different biological effects. one enantiomer of a drug might be therapeutic, while the other might be toxic, inactive, or cause harmful side effects. Thalidomide is a notorious example where one enantiomer was helpful, while the other caused severe birth defects. The ability to synthesize and use only the active enantiomer is a key factor in drug design.

Both isomerisms are foundational for chemistry, biology, medicine, and industry, as they directly influence the behavior and properties of molecules.

4.8 VALENCE BOND THEORY OF TRANSITION METAL COMPLEX

Valence Bond (VB) theory in coordination compounds describes how metal-ligand bonds are formed using the concept of hybridization and orbital overlap. In the context of coordination compounds, VB theory provides a framework for understanding the nature of bonding and the geometry of the complexes.

Here are the key postulates of Valence Bond theory as applied to coordination compounds:

1. The central metal ion in a coordination compound typically has empty orbitals, which can overlap with the orbitals of the ligands **(**which can be atoms, ions, or molecules).
2. An equal number of new orbitals with equivalent energy are produced when the metal's appropriate atomic orbitals (s, p, and d) hybridize. These new orbitals are known as hybrid orbitals.The ligand's hybrid orbital position is determined by shape of the complex's.Such as : Square planer, Tetrahedral, Octahedral etc.
3. In Square planar geometry**:** $dx^2{-}y^2$ and s-orbitals hybridize

   Tetrahedral geometry: In some cases, the metal ion uses s,p, and d-orbitals for hybridization.

   Octahedral geometry:d-orbitals, s, and p-orbitals combine in hybridization.In octahedral inner (n-1)d orbital or the outer nd orbital used.for example: octahedral hyberidisation may be either $(n\text{-}1)d^2sp^3$/ nsp^3d^2.
4. The ligands donate lone pairs of electrons to the central metal atom or ion, forming coordinate covalent bonds.

5.The non bonding metal electrons present in the inner orbital’s do not take part in chemical bonding.

6. This theory can predict whether a complex will exhibit magnetic properties based on the number of unpaired / unpaired electrons in the metal's d-orbitals .In a complex, electron become unpaired is paramagnetic in nature whereas if it has paired electrons the complex is dimagnatic.The theory also aids in understanding the stability of complexes, as the type of metal-ligand bond affects the overall stability.

There are few example illustrate the valance bond theory are given below:

Example : Coordination Number 4:In Coordination 4 , square planer and tetrahedral complex is possible:

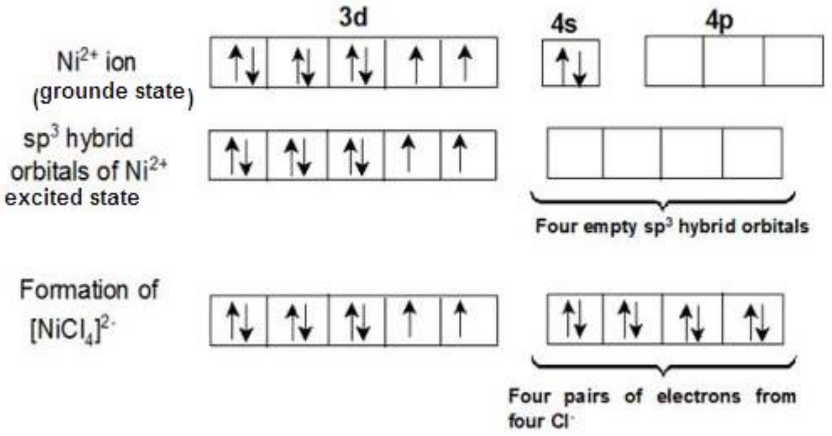
1.$[Ni(Cl)_4]^{2-}$: Ni in +2 Oxidation state has d^8 electronic configuration, and according to Hund’s rule this complex it will have two unpaired electrons.In case of $[Ni(Cl)4]^{2-}$, Cl^- ion is a weak field ligand. Therefore,it does not lead to the pairing of unpaired 3d electrons. Therefore , it undergoes sp^3 hyberidization occurs resulting in tetrahedral structure of the complex. Since there are 2 unpaired electrons, in this case it is paramagnetic in nature.

Nickel has the atomic number 28, so its ground-state electron configuration is:

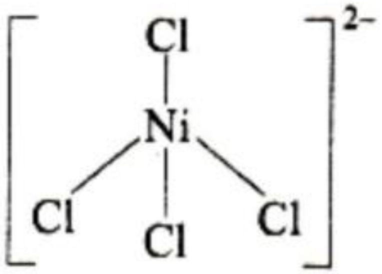
$$Ni:[Ar]3d^8 4s^2$$

For Ni^{2+}, two electrons are removed, typically from the 4s orbital and one 3d orbital, so the electron configuration of Ni^{2+} is:$[Ar]3d^8$

$Ni^{2+}$is surrounded by four chloride ions (Cl^-) as ligands.



The structure of $[Ni(Cl)_4]^{2-}$ is tetrahedral.



The magnetic moment of the complex is :

$$= \sqrt{n(n+2)} = \sqrt{2(2+2)} \quad \text{(where n = unpaired of electron)}$$

$$= 2.82 \text{ BM}$$

2.$[Ni(CN)_4]^{2-}$:

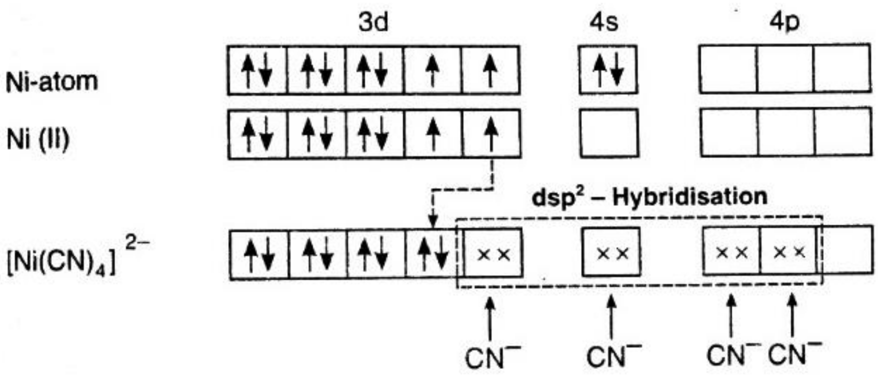
In $[Ni(CN)_4]^{2-}$, there is Ni^{2+} ion for which the electronic configuration in the valence shell is

Nickel has the atomic number 28, so its ground-state electron configuration is:

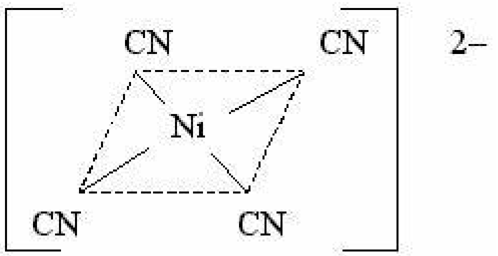
$Ni:[Ar]3d^8 4s^2$

For Ni^{2+}, two electrons are removed, typically from the 4s orbital and one 3d orbital, so the electron configuration of Ni^{2+} is:$[Ar]3d^8$

In presence of strong field CN^- ions, all the electrons are paired up. The empty 3d, 3s and two 4p orbitals undergo dsp^2 hybridization to make bonds with CN^- ligands in square planar geometry. Thus $[Ni(CN)_4]^{2-}$ is diamagnetic. It is said to be a low spin inner orbital complex.



The structure of $[Ni(CN)_4]^{2-}$ is square planar.



The magnetic moment of the complex is :

$$= \sqrt{n(n+2)} = \sqrt{0(0+2)} \quad \text{(n = no unpaired of electron)}$$

$$= 0 \text{ (zero)}$$

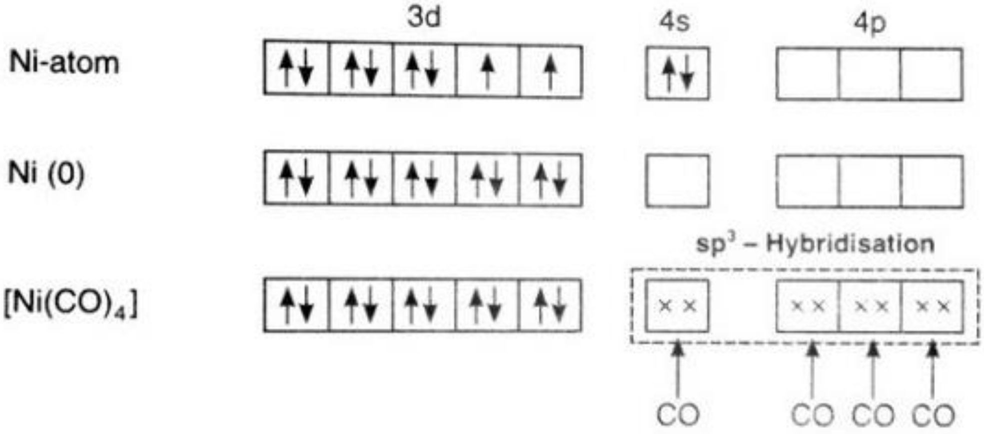
3.$[Ni(CO)_4]$:

In $[Ni(CN)_4]^{2-}$, there is Ni^{2+} ion for which the electronic configuration in the valence shell is

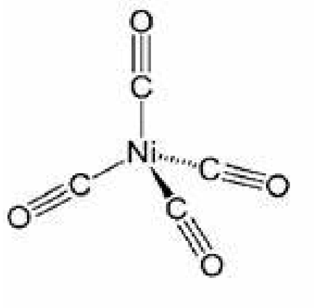
Nickel has the atomic number 28, so its ground-state electron configuration is:

Ni:[Ar]$3d^8 4s^2$

In $[Ni(CN)_4]^{2-}$ All of these 10 electrons are pushed into 3d orbitals and get paired up when strong field CO ligands approach Ni atom. The empty 4s and three 4p orbitals undergo sp^3 hybridization and form bonds with CO ligands to give $Ni(CO)_4$, with tetrahedral geometry.In complex all electron are paired complex is diamagnetic in nature.



The structure of $[Ni(CO)_4]^{2-}$ is tetrahedral.



The magnetic moment of the complex is :

$$= \sqrt{n(n+2)} = \sqrt{0(0+2)} \quad \text{(n = no unpaired of electron)}$$

$$= 0 \text{ (zero)}$$

Other example of Coordination number 4 are: $[FeCl_4]^-$, $[CoCl_4]^{-2}$,$[PtCl_4]^2$, $[Cu(NH_3)_4]^{2+}$, $[Ni(CO)_4]$ etc.

Example : Coordination Number 6:

A coordination number of 6 refers to a central atom or ion surrounded by six ligands (atoms, ions, or molecules) in a specific arrangement . It can be seen in the **octahedral geometry** where the central atom is at the center and the six ligands are positioned symmetrically around it. Some octahedral complex are:

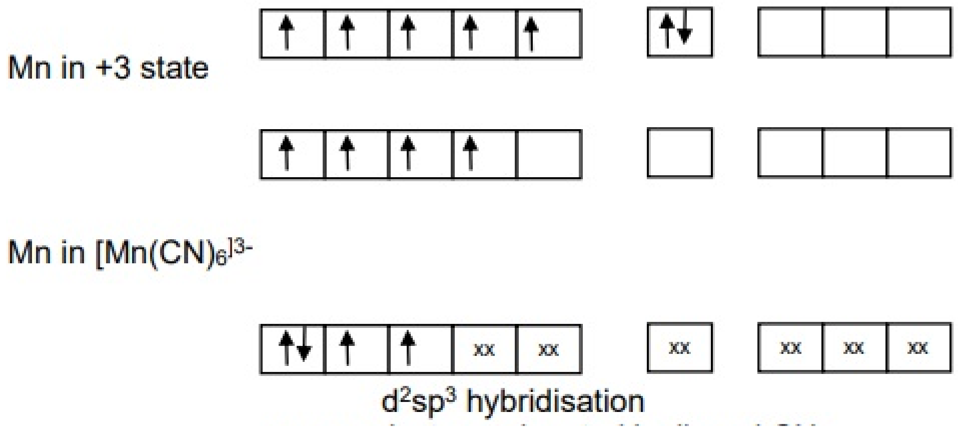
1.$[Mn(CN)_6]^{3-}$:

In $[Mn(CN)_4]^{3-}$, there is Mn^{3+} ion for which the electronic configuration in the valence shell is Mn has the atomic number 25, so its ground-state electron configuration is:

$$Mn\ :\ [Ar]3d^5 4s^2$$

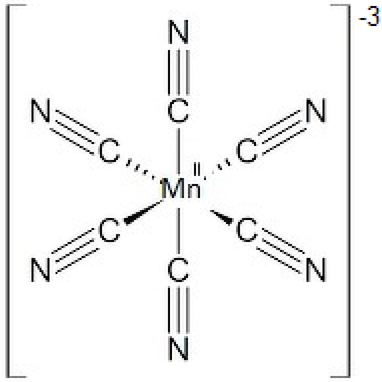
For Mn^{+3}, two electrons are removed, typically from the 4s orbital and one 3d orbital, so the electron configuration of Mn^{3+} is:$[Ar]3d^4$

In presence of strong field CN^- ions, the electrons are paired up. The empty two 3d, 3s and three 4p orbitals undergo d^2sp^3 hybridization to make bonds with CN^- ligands(strong ligands) in inner Octahedral geometry.



xx are electrons donated by ligands CN^-.

The Geometry of $[Mn(CN)_4]^{3-}$ is inner octahedral.



The magnetic moment the complex is :

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

$$= \sqrt{2(2+2)} \quad \text{(where n = unpaired of electron)}$$

$$= 2.82 \text{ BM}$$

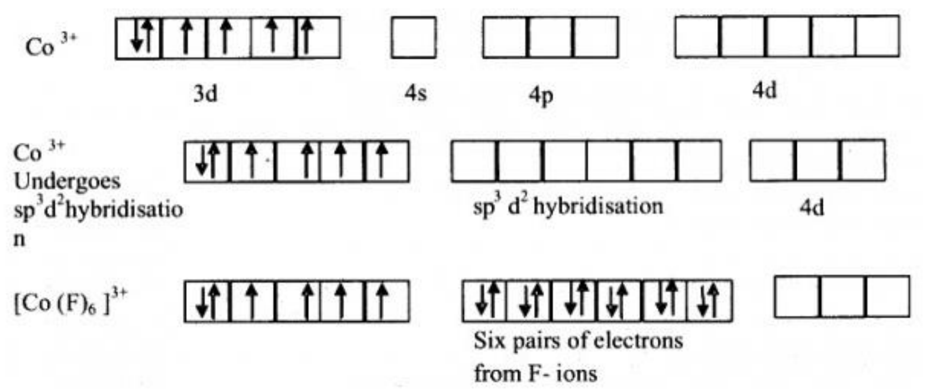
2. **$[Co(F)_6]^{3-}$:** In $[Co(F)_6]^{3-}$, there is Co^{3+} ion for which the electronic configuration in the valence shell is Co has the atomic number 27, so its ground-state electron configuration is:

Cobalt is in +3 oxidation state and has the electronic configuration $3d^6$.

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

For Co^{3+}, three electrons are removed, typically from the 4s orbital and one 3d orbital, so the electron configuration of Co^{3+} is:$[Ar]3d^5$

In presence of weak field F^- ions, the electrons are not paired up and the electron in 3d – orbital are not disturbed whereasthe outer 4d orbital's are used for hyberdisation. The empty two 4d, one 4s and three 4p orbitals undergo sp^3d^2 hybridization to make bonds with six F^- ligands(weakligands) in outer Octahedral geometry.Due to six pairs of electrons, each one form F^- ion are donated to the vacant hybrid orbitals forming Co-F bonds.



The above complex are paramaganic due to four (4) unpaired of electrons.

The magnetic moment the complex is :

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

$$= \sqrt{4(4+2)} \quad \text{(where n = 4 unpaired of electron)}$$

$$= 4.89 \text{ BM}$$

Other example of Coordination number 6 are: $[FeF_6]^{-3}$, $[Co(NH_3)_4]^{+3}$, $[Cr(NH_3)_6]^{3+}$, $[Co(CN)_6]^{-3}$, $[Ni(NH3)6]^{2+}$ etc.

Limitation of Valence Bond Theory : The **Valence Bond Theory (VBT),** though widely used for understanding coordination compounds, has several limitations in coordination chemistry:

1. The geometrical geometries of coordination complexes are not sufficiently explained by VBT, particularly when the complex contains more than four ligands. While VBT is capable of describing some basic geometries (such as octahedral or tetrahedral), it is unable to accurately anticipate the geometry in more complicated situations or when the geometry is distorted (such as square planar vs. tetrahedral in transition metal complexes).
2. A coordination compound's colour results from the d-d transitions. This theory does not provide a clear understanding of how these transitions occur? How coordination compounds shown colour ?
3. In VBT same complexes electrons pairs up against the Hund's rule wile in others the electronic configuration is not disturbed. This abnormality is not well explained by VBT.

4. VBT does not provide a framework for explaining spectroscopic data, such as absorption spectra, which require a more advanced understanding of the electronic structure of the complex.
5. This theory does not give any satisfactory explanation for the existence of inner orbital and outer orbital complexes.
6. It does not explain the relative energies of different structures.

While Valence Bond Theory provides an intuitive approach to understanding the basic bonding and geometrical properties of coordination compounds, its limitations, particularly in explaining magnetic properties, color, and the complexities of bonding interactions, have led to the development of more advanced theories .Which offer better explanations for many of the phenomena observed in coordination chemistry.

4.9 SUMMARY

In this unit learners studied different type of coordination isomerism. Coordination isomerism is important because it offers insight into how legends' interact with metal ions in a complex, leading to different physical, chemical, and biological properties. In Valance bond theory (VBT) ,ability to predict basic bonding characteristics, geometries,magnetic moment and magnetic properties of coordination compounds.

4.10 TERMINAL QUESTIONS AND ANSWERS

Section-A

Q.1 Long answered questions: Answer the following questions

1. What are isomerism? Explain each of the following isomerism in metal complexes:

i)Ionization ii) Linkage iii) Coordination iv) Hydrate

2.Define different kinds of optical isomerism in coordination compounds. Give one example of each kind of isomer.

3.How does Valance Bond Theory (VBT) explain the following complexes also explain its magnetic moments and magnetic behavior :

i) $[Ni(CN)_4]^{2-}$ ii) $[Ni(Co)_4]$

4.Discuss geometrical isomerism in octahedral complexes and optical isomerism in $[Co(en)3]^{3+}$, $[Co(en)(NH_3)_2Cl_2]^{+}$, $[Co(en)_2NH_3Cl]^{2+}$.

5. Define optical isomerism? In coordination number four (4) explain optical isomerism with suitable examples?

Section-B

1.Write the stereochemistry and magnetic behaviour of the following :

(atomic number : Mn = 25, Co = 27, Ni= 28)

i) K4[Mn(CN)6]
ii) $[Co(NH_3)_5Cl]Cl_2$
iii) $K_2[Ni(CN)_4]$

2. How many geometrical and optical isomerism are possible for the example $[Co(en)_2 Cl_2]^{+}$ ion explain with structures.

3**.**Discuss important postulates of valence bond theory of coordination compounds.

4.$[CoF_6]^{3-}$ is paramagnetic while $[Co(NH_3)_6]^{3-}$ is diamagnetic explain on the basis of VBT.

5.What is the difference between inner orbital and outer orbital complexes? Explain with examples.

6.Discuss the geometry of [$Cr(NH_3)_6$] ion by using V.B.T. and suggest whether this complex is inner orbital or outer orbital.

Section-C

Q.3 Multiple choice questions(MCQ)

1. Two or more compounds that have the same chemical formula, but different arrangement of atoms are called _______.

a) isotopes b) isotones

c) isomers d) allotropes

2. Which of the following is not a subdivision of structural isomerism?

a) Geometrical isomerism b) Linkage isomerism

c) Coordination isomerism d) Ionisation isomerism

3. Which of the following do not show geometrical isomerism? (Assume all ligands are unidentate)

a) Square planar [MXL_3] b) Square planar [MX_2L_2]

c) Octahedral [MX_2L_4] d) Octahedral [MX_3L_3]

4. Optical isomers are also known as __________

a) structural isomers b) facial isomers

c) meridional isomers d) enantiomers

5. The optical isomer that rotates the plane of polarised in the clockwise direction is called ______

a) trans b) dextro

c) mer d) laevo

6. In the coordination entity [$Co(NH_3)_3(NO_2)_3$], if all three N atoms of the amine ligands occupy adjacent positions at the corners of an octahedral face, the geometrical isomer formed is known as _______ isomer.

a) cis b) trans

c) fac d) mer

7. Which of the following compounds has a meridional isomer?

a) $[Fe(NO)_5Br]^+$ b) $[Al(CO)_3(NO_2)_3]$

c) $[K(NH)_3)_4(NO)_2]^+$ d) $[Fe(H_2O)_2(CO)_2(NO)_2]^{3+}$

8.The number of unpaired electron in $[NiCl_4]^{2-}$ are:

a) two b) Zero c) one d)four

9.The complexes $[Co(NH_3)_5NO_2]Cl_2$ and $[CO(NH_3)_5ONO]$ Cl_2 are the example of:

a) Linkage b)Geometrical

c) position d) coordination

10.Which of the following option are correct for $[Fe(CN)_6]^{3-}$ complex?

a) sp^3 b) dsp^2 c) d^2sp^3 d) sp^3d^2

11. The orbitals involved in hybridisation in $PtCl_4^{2-}$ is:

a) 6s, $6p_x$,$6p_y$,$6p_z$ b) 5s, $5p_x$, $5p_y$,$5p_z$

c) 6s, $6p_x$, $6p_y$, $5d_x{}^2$-y^2 d) 5s, $5p_x$, $5p_y$, $4d_x{}^2$-y^2

12. For $[Ni(CO)_4]$ and $K_2[Ni(CN)_4]$, which property is the same for the given pairs.

a)Oxidation state of central atom b) Magnetic moment

c) Electronic configuration d)Shape

13. Among the following aqua complex, a low spin complex is

a) $[Ti(H_2O)_6]^{3+}$ b) $[Co(H_2O)_6]^{3+}$

c) $[Co(H_2O)_6]^{2+}$ d) None of the above

14. A complex having _________ geometry can have more than one type of hybridisation.

a) tetrahedral b) square planar

c) trigonal bipyramidal d) octahedral

ANSWERS:

1. (c)	2. (a)	3. (a)	4. (d)	5. (b)	6. (c)	7. (a)
8. (a)	9. (a)	10. (c)	11. (c)	12. (b)	13. (b)	14. (d)

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UNIT: 5 REAGENT IN ORGANIC SYNTHESIS

CONTENTS:

5.1 INTRODUCTION

Organic synthesis relies on a diverse toolkit of reagents—compounds that initiate, drive, or modify chemical transformations. These reagents can be broadly classified by their primary function (e.g., oxidation, reduction, C–C bond formation, protection/deportation, coupling, catalysis), and within each category there exist numerous specific reagents tailored for particular substrates and conditions. Each reagent is selected based on its reactivity profile, selectivity, and compatibility with other functional groups in the molecule. By combining these reagents thoughtfully, synthetic chemists can construct complex organic molecules with high precision and efficiency.

5.2 OBJECTIVES

Objectives of this unit are to introduce students about the organic reagent from basic to advance level. By the end of this unit students will be able to define and classify various organic reagents based on their chemical role. This unit also describe the physical properties, uses, and handling precautions of common reagents and reaction outcomes and products based on reagent-substrate pairs.

5.3. REAGENT COMPOUNDS

Reagent compounds are chemicals used to bring about a chemical reaction in organic or inorganic chemistry. They are not the main focus of the reaction (like a reactant in synthesis), but they help initiate, speed up, direct, or complete the transformation of other compounds.

5.3.1. Definition

A reagent compound is a substance or compound that is added to a system to cause a chemical reaction, or to test if a reaction occurs.

5.3.2 Types of Reagent Compounds in Organic Chemistry:

Reagent Type	Function	Example Reagent Compounds
Oxidizing agents	Add oxygen or remove	KMnO4, $K_2Cr_2O_7$,

Reagent Type	Function	Example Reagent Compounds
	hydrogen/electrons	H_2O_2, OsO_4
Reducing agents	Add hydrogen or remove oxygen/electrons	$NaBH_4$, $LiAlH_4$, H_2 with Raney Ni
Halogenating Agents	Introduce halogen atoms	$SOCl_2$, PCl_5, NBS
Dehydrating agents	Remove water	H_2SO_4, P_2O_5
Acylating agents	Introduce acyl group (R–CO)	Acyl chloride (R–COCl), $SOCl_2$
Testing agents	Used in identification tests	$AgNO_3$ (for halides), Tollens' reagent

5.5. ACETYLENE (C_2H_2)

5.5.1Definition

- Acetylene, also calledethyne, is thesimplest alkynewith the formulaC_2H_2.
- It contains a triple bond between two carbon atoms.
- It is a colourless gas, highly flammable, and widely used in both organic synthesis and welding.

  The structure of acetylene is :

H–C≡C–H

Key Properties:

- It has acidic hydrogen atoms due to the sp-hybridized carbon.
- Can undergo addition reactions, substitution, and metal salt formation.

5.5.2. Main Reactions of Acetylene

1.Addition Reactions (Electrophilic Addition):

a) With Hydrogen (H_2) (Hydrogenation)

$$C_2H_2 + H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$$

Forms ethene, then ethane.

- Requires Ni, Pd, or Pt catalyst

With Halogens (Br_2 or Cl_2)

$$C_2H_2 + Br_2 \rightarrow C_2H_2Br_2 \rightarrow C_2H_2Br_4$$

- Forms dihalo- or tetrahalo-compounds.

With Hydrogen Halides (HX)

$$C_2H_2 + HBr \rightarrow CH_2{=}CHBr \rightarrow CH_3CHBr_2$$

Forms haloalkenes **or** dihalides depending on amount.

b)Formation of Metal Acetylides (with Ag $^+$ or Cu$^+$)

$$HC{\equiv}CH + AgNO_3/NH_3 \rightarrow AgC{\equiv}CAg\downarrow + NH_4NO_3$$

- Forms silver acetylide precipitate.
- Used as a test for terminal alkynes**.**

2. Substitution to Form Longer Carbon Chains

Acetylene can be deprotonated with a strong base like $NaNH_4$ to form an acetylide ion**:**

$$HC{\equiv}CH + NaNH_2 \rightarrow HC{\equiv}C{-}Na^+ + NH_3$$

Then, it reacts with alkyl halides:

$$HC{\equiv}C^- + R{-}Br \rightarrow HC{\equiv}C{-}R + Br^-$$

This is used to extend carbon chains in synthesis.

5.5.3. Summary Table:

Reaction Type	**Reagent/Condition**	**Product**
Hydrogenation	H_2 / Ni or Pd	Ethene → Ethane
Halogenation	Br_2 or Cl_2	Dihalo-/tetrahalo compounds
Hydrohalogenation	HCl, HBr	Vinyl halide or alkyl halide
Metal acetylide formation	$AgNO_3/NH_3$ or Cu^+	Silver or copper acetylide
Chain extension	$NaNH_4$ then R–X	Longer alkyne chain

Real-Life Example

Acetylene is commonly used in oxy-acetylene welding, where it burns with oxygen to produce a very hot flame.

5.6. AMMONIA

Ammonia (NH_3) is a simple nitrogen-containing compound that functions as a versatile reagent in both inorganic and organic chemistry. It behaves as:

- A Lewis base, due to its lone pair of electrons on nitrogen, allowing it to form coordinate bonds.
- A Bronsted-Lowry base**,** as it can accept protons (H^+).
- A nucleophile, in substitution and addition reactions.
- **A** ligand**,** forming coordination complexes with transition metal ions.

Ammonia's small size, basicity, and nucleophilic character make it a key reagent in synthesis and analysis.

5.6.1 Chemical reactions

1. Neutralization Reaction (with Acids)

Ammonia reacts with acids to form ammonium salts**.** This is a classic acid-base reaction.

Example: $NH_3 + HCl \rightarrow NH_4Cl$

Ammonia + Hydrochloric acid → Ammonium chloride

Here, NH_3 acts as a Brønsted base, accepting a proton to form NH_4^+.

2. Nucleophilic Substitution (with Alkyl Halides)

Ammonia reacts with alkyl halides to produce primary amines in a nucleophilic substitution (SN_2) reaction.

Example: $CH_3Cl + NH_3 \rightarrow CH_3NH_2 + HCl$

Methyl chloride + Ammonia → Methylamine + Hydrogen chloride

The nitrogen in NH_3 donates its lone pair to the carbon attached to the halide.

3. Formation of Coordination Complexes

Ammonia acts as a ligand, donating its lone pair to transition metal ions to form coordination compounds.

Example: $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$

Copper(II) ion + Ammonia → Tetraamminecopper(II) complex

This is common in qualitative analysis for detecting Cu^{2+} ions (deep blue solution).

4. Redox Reaction (with Halogens)

Ammonia can undergo redox reactions, particularly with halogens like chlorine, where it is oxidized to nitrogen gas.

Example: $2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$

Ammonia is oxidized from -3 oxidation state (in NH_3) to 0 (in N_2), and chlorine is reduced from 0 to -1.

5. Reaction with Metal Salts (Analytical Chemistry)

Ammonia is used in qualitative analysis to precipitate metal hydroxides.

Example: $Fe^{3+} + 3NH_3 + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3NH_4^+$

5.6.2 Applications of Ammonia Reagent

- Fertilizer production (as ammonium salts and urea)
- Analytical chemistry (qualitative and complexation tests)
- Industrial synthesis (e.g., nitric acid)
- Cleaning agents (aqueous ammonia solutions)

5.7. BAEYER'S REAGENT

Baeyer's reagent is a mild oxidizing agent commonly used to test for unsaturation(double or triple bonds) in organic compounds. It is an alkaline potassium permanganate solution. It is named after Adolf von Baeyer, a German chemist.

5.7.1 Chemical Composition

- $KMnO_4$ (potassium permanganate)in cold, dilute NaOH (sodium hydroxide)or just water.
- Colour: Purple (due to permanganate ion, MnO_4^-)

Use: It is a mild oxidizing agent, commonly used to test for unsaturationin organic compounds (i.e., carbon-carbon double or triple bonds).

5.7.2 General Reaction

1. **Reaction with alkenes (C=C):**

$3RCH{=}CH_2 + 2KMnO_4 + 4H_2O \rightarrow 3RCH(OH)CH_2OH + 2MnO_2\downarrow + 2KOH$

- Alkenes are oxidized to vicinal diols (glycols).
- Brown precipitate of MnO_4 is formed.

Example Reactions

1. Ethene with Baeyer's Reagent

$CH_2{=}CH_2 + [O] \rightarrow HO–CH_2–CH_2–OH$

- Ethene is oxidized to ethylene glycol.
- Purple colour of $KMnO_4$ disappears.

2. Cyclohexene with Baeyer's Reagent

$C_6H_{10}+2[O]\rightarrow C_6H_{10}(OH)_2$

- Cyclohexene forms cis-1,2-cyclohexanediol.

3. Terminal Alkynes

$RC\equiv CH + 4[O] \rightarrow RCOOH + CO2$

- Terminal alkynes get oxidized to carboxylic acids and carbon dioxide.

Use as a Test for Unsaturation

Baeyer's reagent is used qualitatively to detect unsaturation:

- **Positive test**: Purple colour disappears and a brownprecipitate (MnO_2) forms.
- **Negative test**: Purple colour remains (no reaction occurs with alkanes or aromatic compounds under mild conditions).

Limitations

- Baeyer's test can sometimes give false positives with certain oxidizable functional groups (e.g., aldehydes or phenols).
- Not all unsaturated compounds react equally fast or completely.

5.7.3 Summary Table

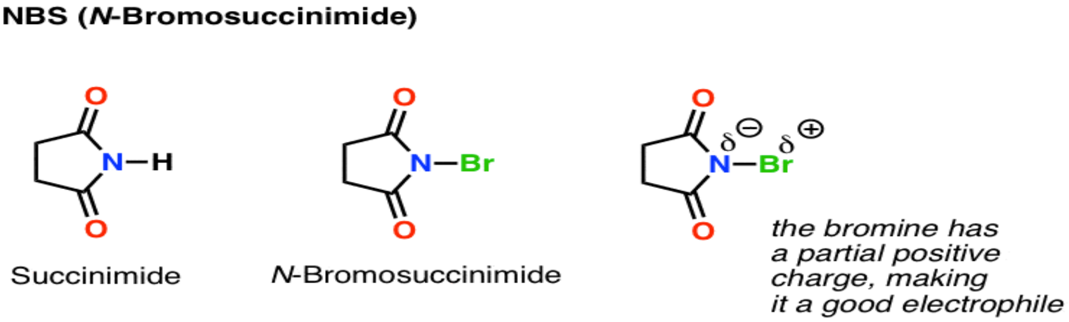
Compound Type	Reaction with Baeyer's Reagent	Observation
Alkene	Forms vicinal diol	Decolourization + MnO_4 ppt
Alkyne	Forms acids/CO_2	Decolourization + MnO_4 ppt
Alkane	No reaction	No change (purple remains)
Aromatic ring	Usually no reaction	No change under mild conditions

5.8. N-BROMOSUCCINIMIDE (NBS)

NBS (N-Bromosuccinimide) is a versatile brominating and oxidizing reagent widely used in organic synthesis. It is especially valued for its selective bromination and mild reaction conditions.

5.8.1. Structure of NBS:

- Chemical formula: **$C_4H_4BrNO_2$**
- Structural formula:



It consists of a succinimide ring with a bromine atom attached to the nitrogen.

5.8.2 Physical Properties:

- Appearance: White to light yellow crystalline powder
- Solubility: Soluble in organic solvents like CCl_4, CH_2Cl_2, and acetonitrile
- Acts as a source of electrophilic bromine (Br^+)

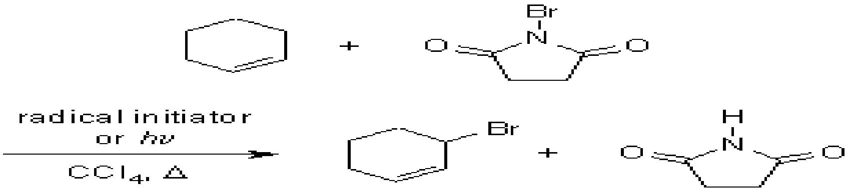
5.8.3. Reaction Schemes Involving NBS

1. Allylic Bromination (Wohl–Ziegler Reaction)

NBS is widely used for selective bromination at allylic positions via a radical mechanism.

General Reaction: $\text{Alkene+NBS} \xrightarrow{\text{hv or AIBN}} \text{Allylic Bromide}$

$$CH_2{=}CH{-}CH_3 + NBS \overset{hv}{\rightarrow} CH_2{=}CH{-}CH_2Br + \text{Succinimide}$$



Mechanism Overview:

i)Initiation:

- A radical initiator (light, heat, or AIBN) breaks NBS to release a **Br$^\bullet$** (bromine radical)**.**
- Alternatively, NBS reacts with trace HBr to generate Br_2, which then photolyzes into Br•.

ii)**Propagation:**

- Br• abstracts an allylic hydrogen from the alkene, forming an allylic radical**.**
- The allylic radical reacts with Br_2 (formed in situ from NBS + HBr) to form the allyl bromide and regenerate Br•.

iii)Termination:

- Two radicals combine to end the chain.

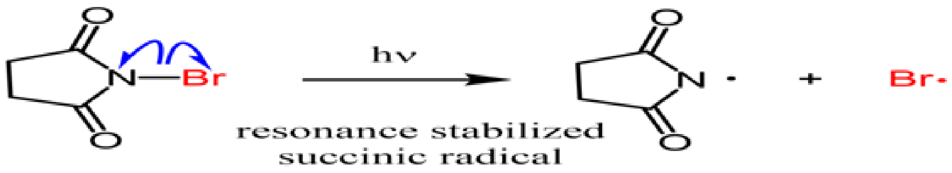
2. Benzylic Bromination

Similar to allylic bromination, NBS can selectively brominate benzylic positions.

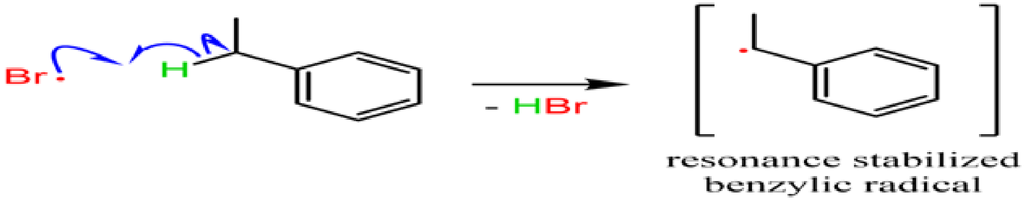
$$\textbf{Alkylbenzene} + \textbf{NBS} \xrightarrow{\text{hv or AIBN}} \textbf{Benzylic Bromide}$$

The mechanism of Benzylic Bromonation by NBS

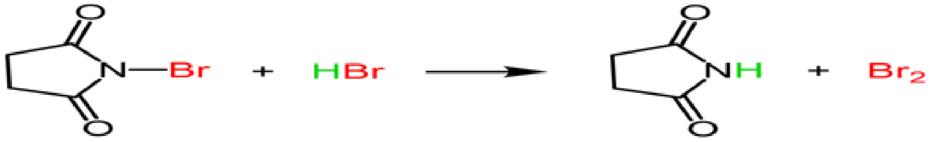
Step 1: A homolytic cleavage forms a Br free radical.



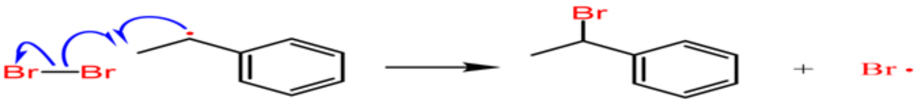
Step2: Br free radical abstracts a benzylic.



Step 3: NBS and HBr react to form Br_2.

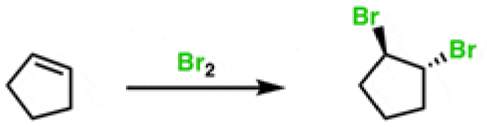


Step 4: The Benzylic radical react with Br_2



Allylic Bromide with NBS: How its works

When heated or treated with light in the presence of peroxides,bromine (Br_2)will replace certain hydrogen atom with Br (free radical bromination) especially hydrogen on tertiary carbons.Howerver bromine is not a great choice for during free radical bromination on allylic C-H bonds since it will simply add to the alkene.

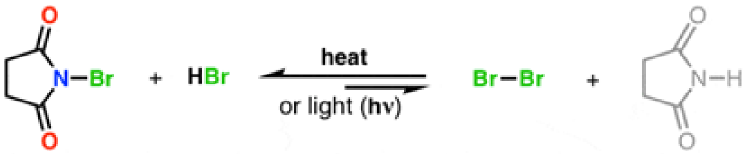


Not what we want in this case

(mixture of enantiomers)

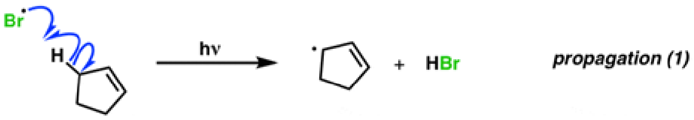
NBS is useful in that it provide a constant low concentration of Br_2

Detail: This is catalyzed by HBr trace amount of which are usually present in NBS

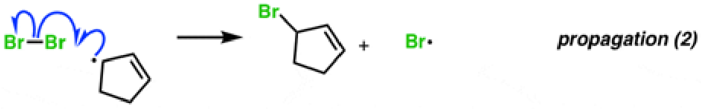


Once formed the Br_2 can then fragment homolytically.

Then the bromine radical can rip of a hydrogen from the allylic carbon.



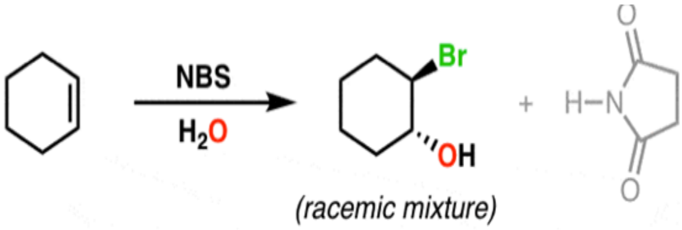
The allylic radical then react with Br_2 giving the desired product and regenrating the Br free radical.



3.Bromohydrin Formation From Alkenes using NBS

NBS can also serve as a replacement for Br_2 in formation of halohydrins.

Another common use for NBS: Formation of bromohydrins



5.9 *n-BUTYL LITHIUM*

n-Butyl lithium (n-BuLi) is a highly reactive organo lithium compound with the formula: C_4H_9Li

It is one of the most widely used strong bases and nucleophiles in organic synthesis, particularly in deprotonation, metalation, and nucleophilic substitution reactions.

5.9.1 Key Features

Structure:

Linear alkyl group (butyl) attached to lithium

$CH_3CH_2CH_2CH_2Li$

- **Physical state**: Colourless to pale yellow solution (in hexane or ether)
- **Air and moisture sensitive**: Reacts violently with water and oxygen

5.9.2 Chemical Properties

1. **Strong Base**:

   pKa of butane ≈ 50 → makes n-BuLi one of the strongest bases used in synthesis.
2. **Strong Nucleophile**:

   Can attack electrophilic centers like carbonyls or halogens.
3. **Organometallic Character**:

   The C–Li bond is highly polar, behaving as a carbanion (R^-).

5.9.3 Key Reactions of n-BuLi

1. Metalation / Deprotonation

n-BuLi removes a proton (H^+) from relatively acidic C–H groups (e.g., terminal alkynes, aromatics, or ketones):

$$RC{\equiv}CH + n\text{-}BuLi \rightarrow RC{\equiv}C{-}Li^+ + \text{Butane}$$

2.Nucleophilic Addition to Carbonyls

$$RCHO + n\text{-}BuLi \rightarrow RCHLiR \xrightarrow{H2O} RCH(OH)R'$$

3.Halogen–Lithium Exchange

n-BuLi reacts with alkyl or aryl halides to generate other organolithium reagents:

$$Ph\text{-}Br + n\text{-}BuLi \rightarrow Ph\text{-}Li + Bu\text{-}Br$$

4.**Directed Ortho-Lithiation**

Used to functionalize aromatic compounds selectively:

$$Ar\text{-}H + n\text{-}BuLi \rightarrow Ar\text{-}Li \xrightarrow{E+} Ar\text{-}E$$

5.9.4. Applications in Organic Synthesis

- Generation of carbanions for further C–C bond formation
- Precursor to Gilman reagents (organocuprates)
- Regioselective lithiation of heterocycles and aromatics
- Used in polymerizations and complex molecule synthesis

5.9.5 Safety Note

- Highly pyrophoric**:** ignites spontaneously in air.
- Must be handled under inert atmosphere (argon or nitrogen).

5.10. CHROMIC ACID (H_2CrO_4)

Chromic acid is a powerful inorganic oxidizing agent, commonly generated in situ by dissolving chromium trioxide (CrO_3) in aqueous sulfuric acid. It's most often used as Jones reagent (CrO_3/H_2SO_4 in acetone) for the oxidation of alcohols under mild conditions.

5.10.1. Composition & Preparation

Chromic acid (H_2CrO_4) is typically formed by dissolving chromium trioxide (CrO_3) in concentrated sulfuric acid (H_2SO_4)**:**

$$CrO_3 + H_2O \rightarrow H_2CrO_4$$

In aqueous solutions, chromic acid exists in equilibrium with dichromate($Cr_2O_7^{2-}$) and chromate (CrO_4^{2-}) ions, depending on the pH:

$$2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O$$

5.10.2. Chemical Reactions

1. Oxidation Reactions

a. Primary Alcohol to Carboxylic Acid

$$3CH_3CH_2OH + 2H_2CrO_4 \rightarrow 3CH_3COOH + 2Cr^{3+} + 4H_2O$$

b.Secondary Alcohol to Ketone

1. $3CH_3CHOHCH_3 + 2H_2CrO_4 \rightarrow 3CH_3COCH_3 + 2Cr^{3+} + 4H_2O$

In these reactions, Cr^{3+} in chromic acid is reduced to Cr^{3+} (green colour), while the organic substrate is oxidized.

2.Cleaning Reaction (Oxidation of Organic Residues)

This is a generalized representation of how chromic acid cleans organic contaminants:

$$C_xH_yO_z + H_2CrO_4 \rightarrow CO_2 + H_2O + Cr^{3+}$$

5.11. DIBORANE(B_2H_6)

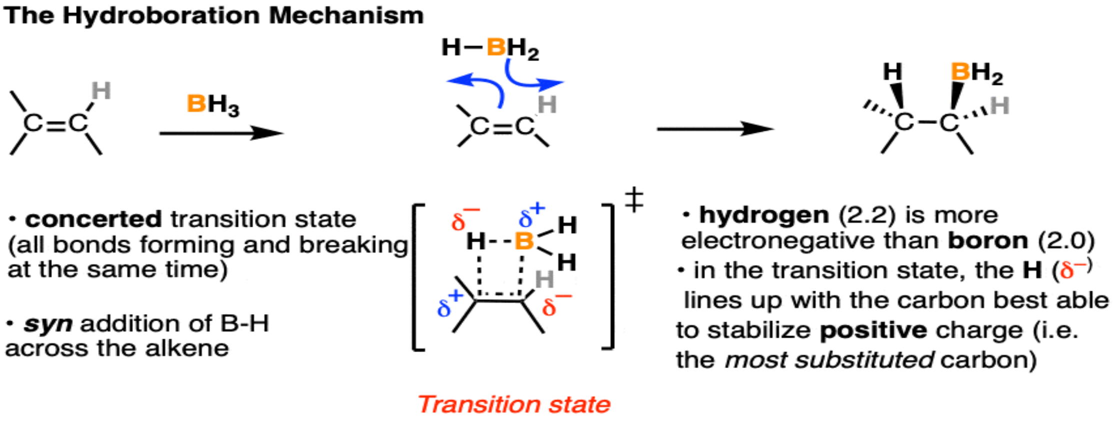
Diboraneis a versatile and powerful reagent in organic synthesis, especially known for its use in hydroboration reactions. Here's a concise but detailed overview of its role, reactivity, and applications:

5.11.1. Chemical Properties

- Molecular formula: B_2H_6
- Structure: Electron-deficient, featuring three-center two-electron (3c–2e) bonds
- Physical form: Colourless, toxic gas at room temperature, typically handled in ether solutions (e.g., THF)

5.11.2. Main Reactions involving Diborane

1.Hydroboration of Alkenes and Alkynes Reaction:



$$RCH{=}CH_2 + B_2H_6 \longrightarrow RCH_2CH_2BH_2$$

Mechanism:

Syn-addition of boron and hydrogen across the double bond.

- **Regioselectivity:** Anti-Markovnikov (boron attaches to less substituted carbon).
- **Stereoselectivity:** Syn addition (both B and H add to the same face).

Hydroboration-Oxidation of Alkenes:

- Hydroboration is an **addition** reaction between an alkene (olefin) and a a borane (neutral species containing a B-H bond). In hydroboration, a C-C pi bond is broken, and a C-H bond as well as a C-B bond is formed. Oxidation of the resulting organoborane with hydrogen peroxide (H_2O_2) then replaces the C-B bond with a C-OH bond.

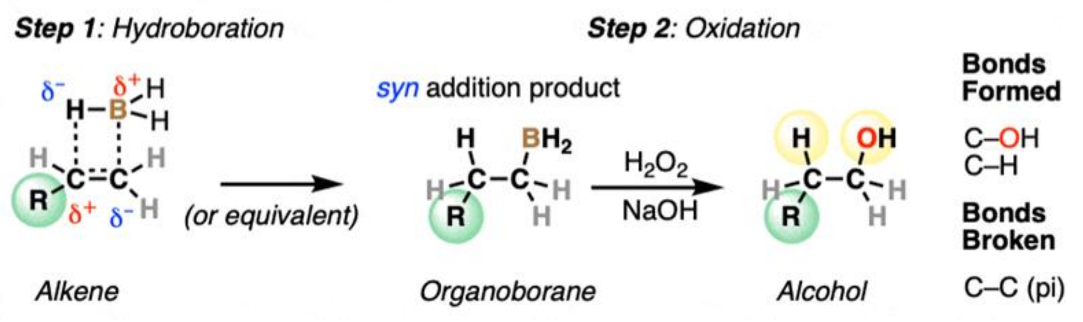
- The notable outcome of hydroboration-oxidation is formation of an alcohol on the least substituted carbon of the alkene ("anti-Markovnikov" regioselectivity. This contrasts with the "Markovnikov" selectivity for formation of alcohols from alkenes using acid-catalyzed hydration ($H_3O^{+)}$ or oxymercuration.

- Hydroboration is stereoselective for *syn* addition – that is,the H and B are delivered to the same face of the alkene. Oxidation of the C-B bond occurs with complete retention of stereochemistry.

$$RCH_2CH_2BH_2 \xrightarrow{NaOH/H2O2} RCH_2CH_2OH$$

Summary: Hydroboration –Oxidation Of Alkenes:

- In hydroboration a B-H bond adds across a C-C pi bond, resulting in formation of new C-B and C-H bonds.
- The bonds form on the same face of the alkene (synaddition) and hydrogen is delivered to the most substituted carbon (anti Markonikov regioselectivity)
- The resulting organoboranen is then oxidized (eg. With basic hydrogen peroxide), replacing C-B with C-OH with retention of configuration.



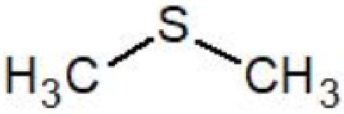
Note: That C-OH forms on the least substituted carbon "anti – Markovnikov"and BH_3 can perform hydroboration with up to three molar equivalents of alkene.

5.12. DIMETHYL SULFOXIDE (DMSO)

DMSO (Dimethyl sulfoxide)is an organosulfur compound with the formula:$(CH3)_2SO$

5.12.1. Key Properties of DMSO

Structure



5.12.2. Important Reactions

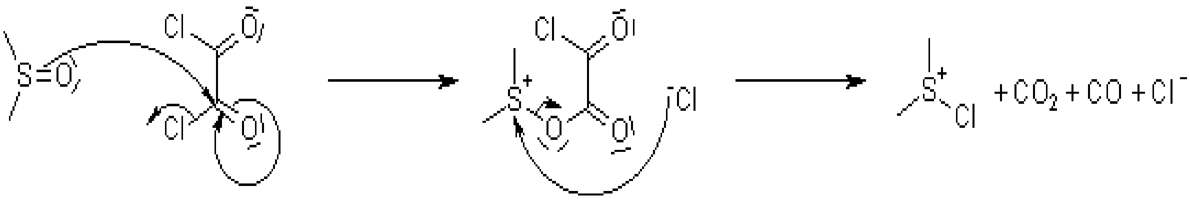
1. Swern Oxidation

- **Purpose**: Converts primary and secondary alcohols **to** aldehydes and ketones**.**
- **Reagents**: DMSO + Oxalyl chloride $(COCl)_2$ + Triethylamine (Et_3N)

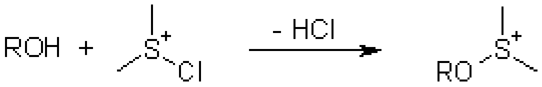
General Reaction:

$$R–CH_2OH + DMSO + (COCl)_2 + Et_3N \rightarrow R–CHO + CO + CO_2 + HCl$$

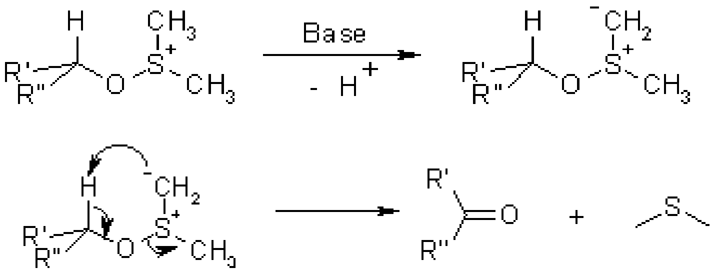
Advantage: Mild oxidation; no heavy metals used.



The reaction with an alcohol give at −78 °Cleads to an alkoxysulphonium ion



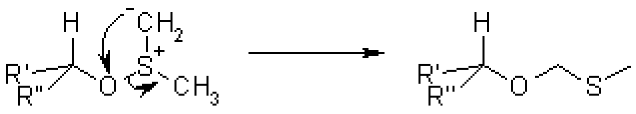
Deprotonation of this intermediate gives a sulphur ylide, which undergoes intramolecular deprotonation via a five-membered ring transition state and fragmentation to yield the product and DMS (odour).

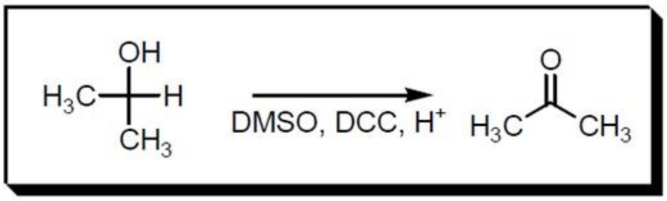


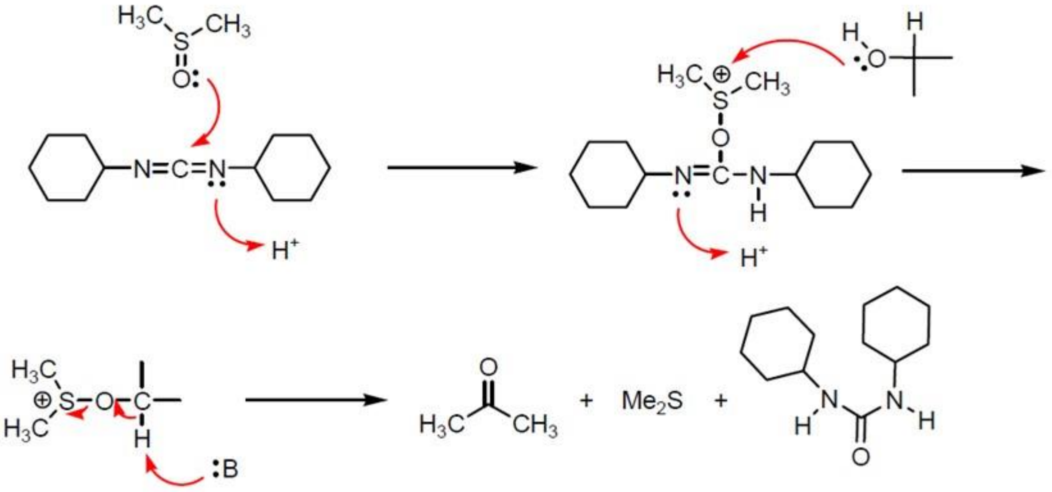
If the temperature is not kept near -78°C, mixed thio acetals may result:

1.**Moffatt Oxidation**

- Older method using DMSO + Dicyclohexylcarbodiimide (DCC).
- Also oxidizes alcohols to aldehydes/ketones.







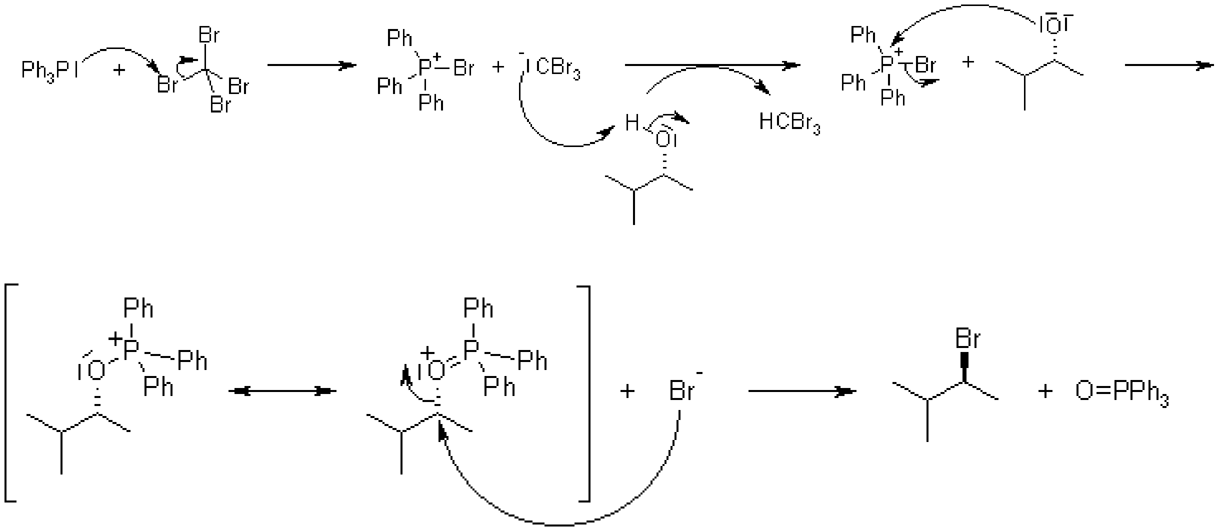
Mechanism of Moffatt Oxidation

The mechanisms of DMSO-based oxidation reactions all involve the activation of DMSO by electrophiles, making the sulfur atom an electrophilic center that can withstand the attack of alcohols. The mechanism of Moffatt oxidation involves several key steps:

- **Activation of DMSO**: DMSO is activated by a coupling reagent, typically DCC, to form a highly reactive sulfonium ion intermediate.
- **Nucleophilic Attack**: The alcohol, acting as a nucleophile, attacks the sulfur atom of the sulfonium ion, leading to the formation of an alkoxysulfonium ion.
- **Hydride Abstraction**: A base, such as pyridine or triethylamine, abstracts a hydride ion from the α-carbon of the alkoxysulfonium ion, generating a carbonyl compound and regenerating DMSO.

3. Appel Reaction (with DMSO as solvent)

Converts alcohols to alkyl halides using triphenylphosphine (PPh_3) and carbon tetrabromide (CBr_4).



4. Nucleophilic Substitution Reactions (S_N2)

DMSO is commonly used as a solvent in S_N2 reactions because it enhances the nucleophilicity of the nucleophile.Example:

$CH_3CH_2Br + NaCN \rightarrow CH_3CH_2CN$ (in DMSO)

5.12.3. Summary Table:

	Reagent Used	Product
Swern Oxidation	DMSO + $(COCl)_2$ + Et_3N	Alcohol → Aldehyde/Ketone
Moffatt Oxidation	DMSO + DCC	Alcohol → Aldehyde/Ketone
SN2 Reactions	DMSO as solvent	Promotes substitution
Appel Reaction	PPh_3 + CBr_4 (in DMSO)	Alcohol → Alkyl halide

5.13. HYDROGEN PEROXIDE (H_2O_2)

Formula: H_2O_2

Structure: H–O–O–H (contains a weak O–O bond)

Oxidation states:Oxygen in H_2O_2 has an oxidation state of **–1** (intermediate between 0 and –2).Acts as both an oxidizing and reducing agent, but mostly oxidizing in organic chemistry.

5.13.1. Important Reactions of H_2O_2

1.Oxidation of Alkenes to Epoxides

In presence of a **peracid** (like mCPBA), or using H_2O_2 + base + catalyst**.**

Example Reaction:

$$RCH{=}CH_2{+}H_2O_2 \xrightarrow{mCPBA} RCH(O)CH_2(\text{epoxide})$$

Mechanism (simplified for H_2O_2 and base):

Nucleophilic attack by alkene on the electrophilic oxygen of H_2O_2 (activated under basic conditions).
Concerted formation of a three-membered epoxide ring.

2.Oxidation of Sulfides to Sulfoxides/Sulfones

The oxidation of sulfides to sulfoxidesand **s**ulfone**s**is an important reaction in organic chemistry. It is used to make compounds that have biological and chemical uses**.** Different oxidizing agents like hydrogen peroxide (H_2O_2)**,** peracids**,** and imides are used for this reaction. The type of oxidant and the reaction conditions decide whether a **s**ulfoxideor a sulfone is formed**.**

$$R–S–R' + H_2O_2 \rightarrow R–S(=O)–R'(\text{sulfoxide}) \rightarrow R–SO_2–R'(\text{sulfone})\text{withexcess}H_2O$$

Mechanism:

- Electrophilic attack by H_2O_2 oxygen on sulfur.
- Formation of sulfoxide intermediate.
- Further oxidation gives sulfone.

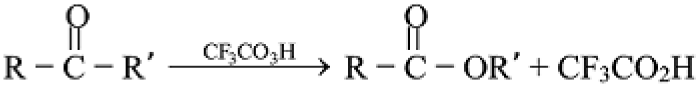
3.Hydroxylation of Alkenes

In the presence of $OsO_4 + H_2O_2$ or $KMnO_4 + H_2O_2$,alkenes give vicinal diols**.**

$$RCH = CH_2 + H_2O_2 \rightarrow RCH(OH)–CH_2OH_5.$$

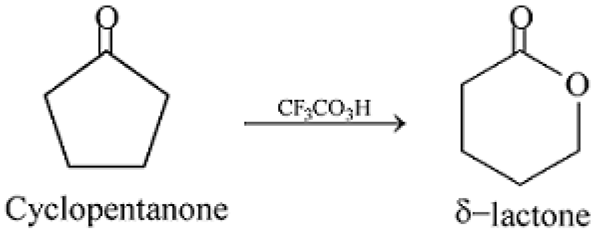
4.Baeyer-Villiger Oxidation

The Baeyer-Villiger oxidation is the oxidative cleavage of a carbon-carbon bond that is adjacent to a carbonyl functional group. This reaction is used to convert ketones to esters and cyclic ketones to lactones. It can be carried out with peroxy acids (also called peracid) like MCPBA, or with hydrogen peroxide and a Lewis acid. This reaction can be viewed as the insertion of O into one of the C-C bonds adjacent to the carbonyl functional group.



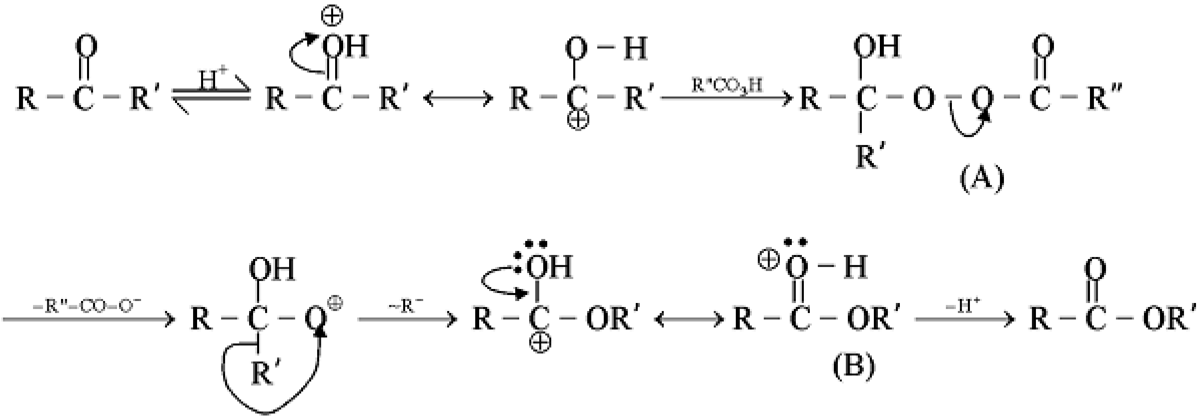
$$R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{CF_3CO_3H} R-\overset{\overset{O}{\|}}{C}-OR' + CF_3CO_2H$$

Cyclic ketones are converted to lactones with ring expansion.



Baeyer-Villiger Oxidation Mechanism

First of all the peroxyacid protonates the ketone and then peroxyacids undergoes nucleophilic attack on this protonated ketone to form a peroxide intermediate (A). This intermediate then undergoes loss of carboxylate anion and migration of a group from carbon to electron deficient oxygen to yield the protonated ester (B). This finally losses a proton to give an ester.



Application of group in Baeyer-Villiger Oxidation

The presence of electron releasing groups in the ketone and electron withdrawing groups in the peroxyacids increases the rate of reaction. In unsymmetrical ketones that group migrates which is more electron releasing, thus the migratory aptitude of alkyl groups is in the order 3° > 2° > 1° > CH_3.

Electron releasing substituents in the aryl group facilitate migration. The migratory order of aryl groups is p−anisyl > p−tolyl > phenyl > p−chlorophenyl > p−nitrophenol.

In case of alkyl aryl ketones, it is the aryl group which migrates (except in case of tert butyl groups).

5.14. *OSMIUM TETROXIDE*(OsO_4)

- Osmium tetroxide is a chemical reagent with the formula OsO_4**.**
- It is a toxic, strong oxidizing agent**.**
- Used in organic chemistry to add two hydroxyl (–OH) groups to alkenes

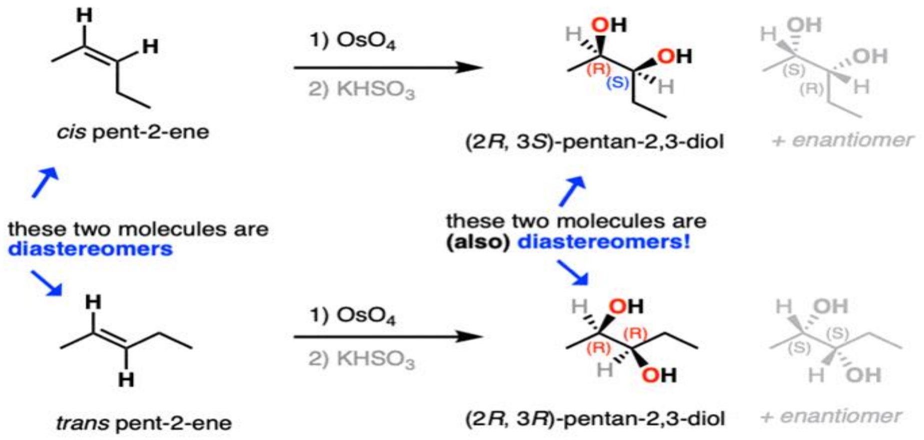
5.14.1. Important Reaction of OsO_4

Convert an alkene(C=C double bond) into a vicinal diol (two –OH groups on neighboring carbons).

$$RCH{=}CHR'+OsO_4+H_2O_2\rightarrow RCH(OH){-}CH(OH)R$$

Mechanism:

The dihydroxylation alkene with OsO_4 is an example of stereospecific reaction.



“A reaction is termed stereospecific is starting materials didffering only in their configuration are converted into steroisomeric products ‘’

- The alkene reacts with OsO_4.
- Two –OH groups are added to the same side (syn addition).

- Sometimes H_2O_2 (hydrogen peroxide) or NMO is added to regenerate OsO_4 (catalytic use).

  Notes:

  - OsO_4 is very toxic and expensive.
  - Often used in very small (catalytic) amounts with a co-oxidant like H_2O_2or NMO.
  - Produces cis-diols (both –OH on the same side of the double bond).

5.15. POTASSIUM DICHROMATE (K2Cr_2O_7)

- $K_2Cr_2O_7$ is an orange-coloured chemical.It is a strong oxidizing agent.
- Commonly used in acidic medium (with sulphuric acid, H_2SO_4).
- Often used to oxidize alcohols in organic chemistry.

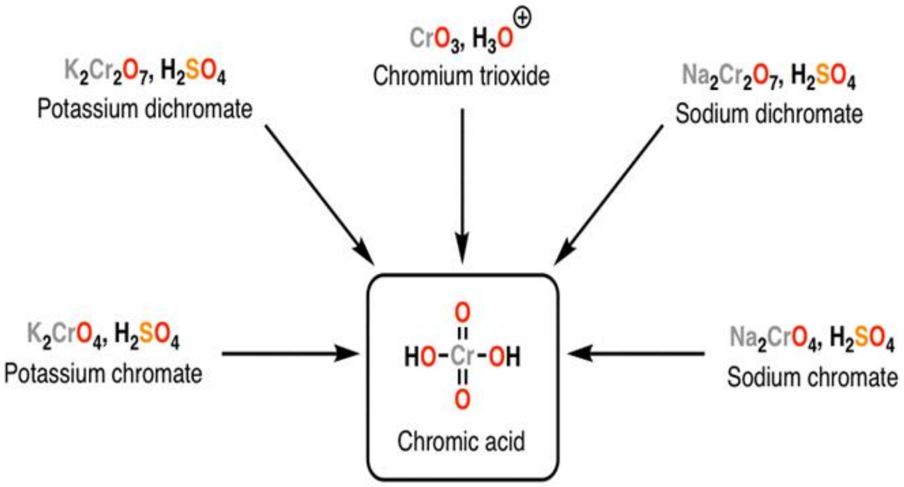
5.15.1. Important reactions of $K_2Cr_2O_7$

1. Oxidation of Primary Alcohols

$$R–CH_2OH + [O] \rightarrow R–COOH$$

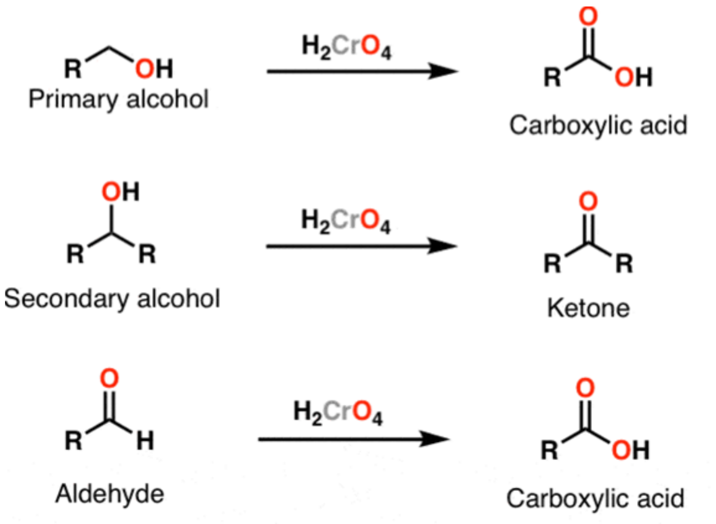
- Primary alcohol → Carboxylic acid
- Requires acidic $K_2Cr_2O_7$ (with H_2SO_4)

Note: Chromic Acid (H_2CrO_4) Is Equivalent to $K_2Cr_2O_7$ + H_2SO_4 (Among Other Combinations)All paths lead to Chromic acid:



Chromic acid is often made “in situ” (that , in the reaction flask)through the addition of acid to sources of chromium (such as chromate salts) . The large number of possible chromium sources (and acids) can make this confusing but it is chromic acid that is the active reagents.

Once deciphered , chromic acid is a fairly straightforward reagent. It oxidizes primary alcohols to carboxylic acid and secondary alcohols to ketones. It will also oxidize aldehydes to carboxylic acids.like:



Colour Change (Visual Test)

- Orange (Cr^{3+} in $K_2Cr_2O_7$) → Green (Cr^{3+})
- Used as a test for alcohols or aldehydes

5.15.2. Safety Note:

- $K_2Cr_2O_7$is toxic and carcinogenic
- Handle with care in a well-ventilated lab

5.16. POTASSIUM PERMANGANATE (KMNO4)

- $KMnO_4$ is a purple-coloured solid.
- It is a strong oxidizing agent.
- It works in acidic, neutral, or basic medium.
- Commonly used in organic chemistry to oxidize alkenes, alcohols, aldehydes, and side chains of aromatic compounds.

5.16.1. Chemical Reactions of $KMnO_4$

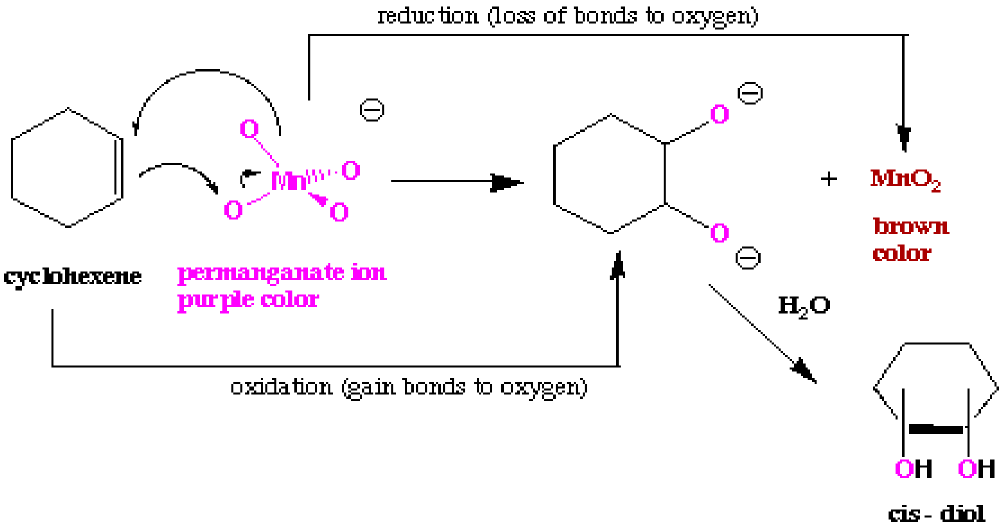
1. Oxidation of Alkenes to Diols

$$RCH = CHR' + KMnO_4 + H_2O \rightarrow RCH(OH){-}CH(OH)R'$$

- Alkenes become vicinal diols (two –OH groups on neighbouring carbons).
- This is a mild oxidation in cold dilute $KMnO_4$.
- Colour change: Purple → Brown (MnO_2)

Mechanism

Alkenes can be dihydroxylated using potassium permanganate. The method encompasses the reaction of an alkene with a cold, dilute solution of potassium permanganate under basic conditions to form a *cis*-diol along with a brown precipitate of manganese dioxide.



2. Oxidation of Alkenes to Carboxylic Acids (Strong Oxidation)

$$RCH = CH_2 + [O] \rightarrow R\text{–}COOH$$

- Strong/heat + concentrated $KMnO_4$.
- Breaks the double bond.
- Forms carboxylic acids or ketones, depending on the structure.

5.16.2. Oxidation of Alcohols and Aldehydes – Summary Table

Reaction Type	**Starting Compound**	**Oxidizing Agent (e.g.)**	**Product**	**Oxidation Outcome**	**Colour Change**
Primary Alcohol	RCH_2OH	$KMnO_4$/ $K_2Cr_2O_7$	RCOOH (Carboxylic acid)	Full oxidation	Purple → Brown /Orange→ Green
Secondary Alcohol	R_2CHOH	$KMnO_4$/ $K_2Cr_2O_7$	$R_2C=O$ (Ketone)	Partial oxidation	Purple → Brown /Orange→ Green

Reaction Type	**Starting Compound**	**Oxidizing Agent (e.g.)**	**Product**	**Oxidation Outcome**	**Colour Change**
Tertiary Alcohol	R_3COH	$KMnO_4$/ $K_2Cr_2O_7$	No reaction (generally)	No oxidation (no H on C)	Nocolour change
Aldehyde	R–CHO	$KMnO_4$/ K_2Cr_2O	R–COOH (Carboxylic acid)	Oxidized	Purple → Brown /Orange→ Green

5.16.3.Safety Tip:

- $KMnO_4$ is strong and can stain skin and clothes.
- Always use with care and proper lab protection

5.17. RANEY NICKEL (RANEY Ni)

- Raney Nickel is a finely divided form of nickel metal**.**
- It acts as a solid catalyst, especially for hydrogenation reactions**.**
- It is made by treating a nickel–aluminum alloy with sodium hydroxide (NaOH) to remove the aluminum, leaving porous nickel**.**
- It is often used in the presence of hydrogen gas (H_2)**.**

5.17.1 Chemical Reactions:

1. Hydrogenation of Alkenes and Alkynes

$$RCH = CH_2 + H_2 \xrightarrow{Raney\ Ni} RCH_2CH_3$$

Alkene or alkyne is converted into an alkane.Raney Ni helps add hydrogen atoms across double or triple bonds.

2.**Reduction of Nitro Compounds to Amines**

$$RNO_2 + 3H_2 \xrightarrow{Raney\ Ni} RNH_2 + 2H_2O$$

Nitro compound becomes a primary amine**.**

3.Desulfurization of Thio Compounds

$$R–S–R' + 2H \xrightarrow{Raney\ Ni} R–H + R'–H + H_2S$$

- Thioethers (or thioketones)lose sulfur to form alkanes or alkanes with hydrogen.

- This is useful for removing sulfur from organic molecules.

Notes: Raney Ni is pyrophoric (can catch fire in air when dry), so it's stored under liquid (e.g. alcohol or water)**.**It is reusable**,** but must be handled with care in the lab.

5.18.SILVER NITRATE ($AgNO_3$)

- $AgNO_3$ is a white crystalline compound.
- It is a source of silver ions (Ag^+)**.**
- Commonly used in inorganic tests and organic chemistry for detection and substitution reactions**.**

5.18.1. Reactions of Silver Nitrate

1. Test for Halide Ions (Cl^-, Br^-, I^-)

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$

- Silver nitrate reacts with halide salts to form precipitates of silver halides:
  - AgCl – white precipitate
  - AgBr – pale yellow
  - AgI – yellow

Used as a qualitative test to identify halides.

2.Detection of Alkyl Halides (SN1 reaction test)

$$R\text{–}Cl + AgNO_3(\text{inethanol}) \rightarrow R^+ + AgCl\downarrow + NO_3^-$$

- Tertiary alkyl halides react quickly with $AgNO_3$ in ethanol, forming a precipitate of AgCl.
- This is used to distinguish tertiary, secondary, and primary alkyl halides based on how fast the reaction occurs.

4. **Formation of Silver Acetylides (with Terminal Alkynes)**

$$RC\equiv CH + AgNO_3 + NH_3 \rightarrow RC\equiv CAg\downarrow + NH_4NO_3$$

Terminal alkynes react with Ag^+ in ammoniacal silver nitrate to form silver acetylide precipitates.

- Used as a test for terminal alkynes.

4.Tollens' Test (for Aldehydes)

$$RCHO + 2[Ag(NH3)_2]^+ + 3OH^- \rightarrow RCOO^- + 2Ag\downarrow + 4NH_3 + 2H_2O$$

- Tollens' reagent is made from $AgNO_3 + NH_3$ (to form $[Ag(NH_3)_2]^+$).
- Aldehydes reduce Ag^+ to metallic silver (Ag), forming a silver mirror.
- Ketones do not give this test.

Used to distinguish aldehydes from ketones.

5.18.2. Summary Table:

Reaction Type	Reactant	Observation	Use
Halide test	NaCl, NaBr, NaI	White/yellow precipitate	Test for halide ions
Alkyl halide substitution (SN1)	Tertiaryalkyl halide	AgCl precipitate	Distinguish alkyl halides
Alkyne test	Terminal alkyne	Silver acetylide (white ppt)	Detect terminal alkynes
Tollens' test	Aldehyde	Silver mirror forms	Identify aldehydes

5.19. SODIUM BOROHYDRIDE ($NaBH_4$)

- $NaBH_4$ is a white crystalline solid.
- It is a selective reducing agent.
- Commonly used in organic chemistry to reduce carbonyl compounds like aldehydes and ketones.
- It is milder than lithium aluminium hydride ($LiAlH_4$) and safer to handle.

5.19.1. Reactions of $NaBH_4$

1. Reduction of Aldehydes to Primary Alcohols

$$R–CHO + NaBH_4 \rightarrow R–CH_2OH$$

Aldehyde → Primary alcohol

2. **Reduction of Ketones to Secondary Alcohols**

$R_2C=O + NaBH_4 \rightarrow R_2CH–OH$

Ketone → Secondary alcohol

3. Reduction of Acid Chlorides and Imines

- $NaBH_4$ can reduce acid chlorides, imines, and schiff bases, though not as efficiently as $LiAlH_4$.

What $NaBH_4$ Does *Not* Reduce:

- Esters, amides, carboxylic acids, and nitriles are not reduced by $NaBH_4$.
- These require stronger reducing agents like $LiAlH_4$.

5.19.2. Summary Table:

Compound Type	**Reagent**	**Product**
Aldehyde (R–CHO)	$NaBH_4$	Primary alcohol (RCH_2OH)
Ketone ($R_2C=O$)	$NaBH_4$	Secondary alcohol (R_2CHOH)
Ester, acid, amide	✗ Not reactive	No reaction

5.20.THIONYL CHLORIDE ($SOCl_2$)

- Thionyl chloride is a colourless to pale yellow liquid.
- It is widely used in organic chemistry as a chlorinating agent.
- Formula: $SOCl_2$
- Reacts mainly with alcohols and carboxylic acids to replace –OH with –Cl.

5.20.1. Reactions of $SOCl_2$

1. Conversion of Alcohols to Alkyl Chlorides

$R–OH + SOCl_2 \rightarrow R–Cl + SO_2\uparrow + HCl\uparrow$

Alcohol → **Alkyl chloride**

- By-products: Sulfur dioxide (SO_2) andhydrogen chloride (HCl) gases
- Often used with pyridine to neutralize HCl and improve yield

✓ This reaction is useful for making alkyl halides from alcohols.

2. Conversion of Carboxylic Acids to Acyl Chlorides

$$R–COOH + SOCl_2 \rightarrow R–COCl + SO_2\uparrow + HCl\uparrow$$

Carboxylic acid → Acid chloride (acyl chloride)

✓ This is a key step in preparing acid chlorides for making amides, esters, or anhydrides.

5.20.2.Summary Table:

Reactant	Reagent	Product	Use
Alcohol (R–OH)	$SOCl_2$	Alkyl chloride (R–Cl)	To convert alcohols to halides
Carboxylic acid (R–COOH)	$SOCl_2$	Acid chloride (R–COCl)	To make acyl chlorides

Notes:

- Reactions release gaseous by-products (SO_2 and HCl), so they are done in a fume hood.
- Pyridine is often added as a base to absorb HCl.

5.21 SUMMARY

Organic reagents are chemical substances used to bring about specific transformations in organic compounds during chemical reactions. These reagents play a crucial role in the synthesis, modification, and analysis of organic molecules. They can act as oxidizing agents (e.g., chromic acid, PCC), reducing agents (e.g., sodium borohydride, lithium aluminium hydride), nucleophiles (e.g., Grignard reagents, organolithium compounds), electrophiles, or catalysts (e.g., Lewis acids like $AlCl_3$). Each reagent is chosen based on the desired chemical transformation, such as the addition, substitution, elimination, or rearrangement of functional groups. Proper selection and handling of organic reagents are vital in laboratory and industrial organic synthesis.

5.22. TERMINAL QUESTIONS

A.Multiple choice questions

1.What is the final product when a primary alcohol is treated with chromic acid under standard conditions?

a) Ketone

b) Aldehyde

c) Carboxylic acid

d) Ether

2.What observable colour change indicates a positive chromic acid test for alcohols?

a) Blue to red

b) Colourless to yellow

c) Orange to green

d) Pink to purple

3**.** What type of reaction occurs when n-BuLi is treated with a terminal alkyne (RC≡CH)?

a)Oxidation

b) Deprotonation

c) Esterification

d) Electrophilic substitution

4.What is Baeyer's reagent composed of?

a)Dilute nitric acid

b) Acidic potassium dichromate

c) Alkaline potassium permanganate solution

d) Aqueous bromine

5.In acidic medium, hydrogen peroxide oxidizes Fe^{2+} ions to:

a) Fe

b) Fe^{3+}

c)FeO

d) $Fe(OH)_3$

6. For Osmium tetroxide incorrect is :

a) Toxic

b) Produces cis-diols

c) Produces trans-diols

d) strong oxidizing agent

7. Which of the following is known as Jones reagent?

a) $KMnO_4$ in alkaline medium

b) CrO_3 in H_2SO_4

c) $K_2Cr_2O_7$ in acidic medium

d) $KMnO_4$ in H_2SO_4

8. Benzoic acid is obtained from the oxidation of _______ with alkaline $KMnO_4$ followed by treatment with mineral acid.

a) phenol

b) benzaldehyde

c) acetophenone

d) benzyl alcohol

9. Identify the most suitable reagent for the conversion of ethanal to acetic acid.

a) Alkaline $KMnO_4$, H_3O^+

b) Jones reagent

c) Tollen's reagent

d) $LiAlH_4$

10. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?

a) H2 (excess)/ Pt b) $LiAlH_4$ in ether

c) Fe and HCl d) Sn and HCl

B.Short Answer type question

1. What is observed when Baeyer's regent is added to an alkene?

2.Why is NBS preferred over Br_2 for selective bromination?

3. What colour change is observed when $K_2Cr_2O_7$ oxidizes an alcohol?

4. Writethe rection between ammonia and hydrochloric acid.

5.How is acetylene prepared from calcium carbide?

C.Long Questions:

Q.1.Dimethyl sulfoxide (DMSO) is widely used in organic synthesis. Explain its properties as a solvent and its role in SN2 reactions. Also, discuss any synthetic applications where DMSO is directly involved.

Q.2.Compare the oxidizing action of potassium permanganate ($KMnO_4$) and osmium tetroxide (OsO_4) on alkenes. How do their reaction conditions and products differ? Provide chemical equations.

Q.3.Discuss the mechanism and stereochemistry of hydroboration-oxidation of alkenes using diborane. Why is this method preferred for anti-Markovnikov alcohol synthesis?

Q.4.Write a detailed account of the use of reducing agents such as sodium borohydride ($NaBH_4$) and Raney nickel in organic chemistry. Compare their selectivity, reaction conditions, and types of reducible compounds.

Q.5.Explain the role of N-Bromosuccinimide (NBS) in organic synthesis. How does it differ from molecular bromine in reactivity? Illustrate with a suitable reaction mechanism.

ANSWERS:

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

5.23 REFERENCES AND FURTHER STUDIES

1."Advanced Organic Chemistry: Part B: Reaction and Synthesis" Francis A. Carey & Richard J. Sundberg
2."Strategic Applications of Named Reactions in Organic Synthesis" László Kürti and Barbara Czakó
3."Modern Methods of Organic Synthesis" W. Carruthers and Iain Coldham
4."March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure" Michael B. Smith & Jerry March
5."Organic Synthesis" (Series by The Royal Society of Chemistry)

BLOCK-II ORGANIC CHEMISTRY

UNIT6: ORGANOMATELLIC COMPOUND-I (Li AND Mg)

CONTENTS:

6.1 INTRODUCTION:

In this unit we will cover the general aspects of organomatallic compounds. In this unit you will be introduced to types of organomatallic compounds. Apert from the learning the defination, classification of organomatallic compounds; you are also going to learn about the structure and chemical reactions of Li and Mg organomatallic compounds.

6.2 OBJECTIVES/LEARNING OUTCOMES:

After studying this unit you should be able to

- Define the organomatellic compounds.
- Types of organomatellic compounds.
- Structure, preparation and chemical recations (properties) of lithium (Li) and magnisium (Mg) organomatellic compounds.
- Know the Grignard’s reagent and their chemical reactions.
- Differentiate between the reactivity, basicity, and stability of RMgX and RLi.
- Predict products of reactions involving these reagents with various electrophiles.

6.3 ORGANOMATELLIC COMPOUNDS:

Organometallic Compounds are a class of chemical compounds that contain at least one chemical bond between a carbon atom of an organic molecule/ group (Alkyl, Aryl etc.) and a metal, which can be a main-group element (Li, Mg, Al etc.) or a transition metal (Fe, Ni, Pd,Pt etc.). Organomatallic compounds have been used in various fields such as catalyst (hydrogenation, polymerizarion); organic synthesis like Grignard's reagent, organolithium, organocuperates used in the new carbon-carbon bond formation; precursoor for semiconductor in materials sciences and as drugs in medicinal chemistry.

6.4 ORGANOMAGNESIUM COMPOUND AND GRIGNARD'S REAGENT:

Organomagnesium compounds are organometallic compounds containing carbon magnesium (C–Mg) bond. The most common and important group of these are the Grignard reagents. Francois August Victor Grignard was an organic chemist who first introduced organomagnesium compounds, featuring a carbon-magnesium covalent bond, in 1899 and received the Nobel Prize in 1912. The Grignard reagent is a commonly utilized reagent for synthesizing various organic molecules that contain different functional groups.

6.4.1 Structure of Grignard reagents:

Grignard reagents are organomagnesium compounds with the general formula R–Mg–X, where R = alkyl, aryl, vinyl group (organic part) and X = halide (Cl, Br, or I rarely F). In the Grignard reagents the carbon-magnesium bond is polar covalent in wchich Carbon has a partial negative charge (δ^-) and magnesium has a partial positive charge (δ^+). In solution (e.g. ether solvents), Grignard reagents form complexes with the solvent due to coordination of Mg^{2+} with oxygen atoms.

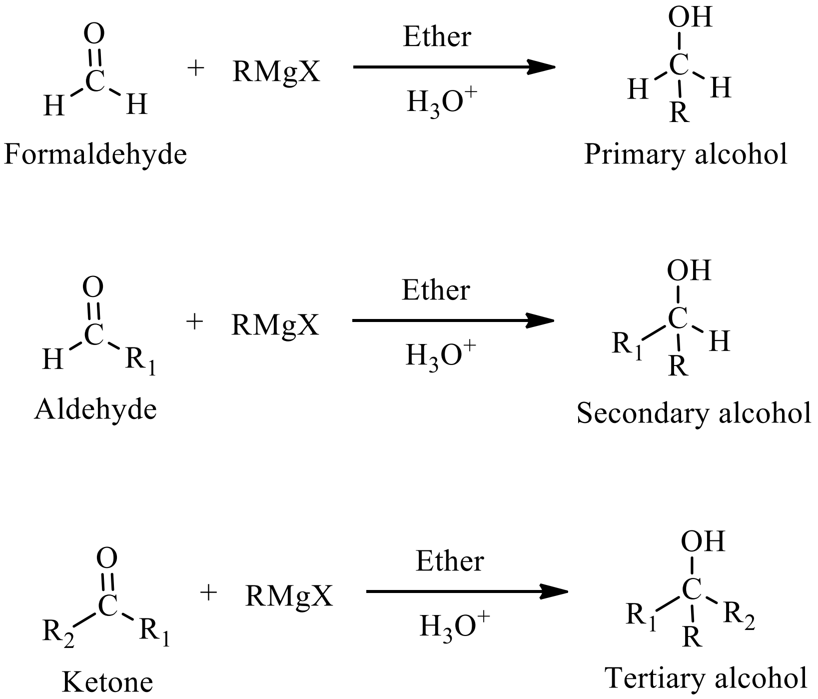
6.4.2 Preparation of Grignard reagents:

Grignard reagents are prepared by reacting alkyl/aryl halides (R-X) with magnesium metal (Mg) in dry ether (like diethyl ether or THF). The reaction condition must be moisture free (dry conditions) because Grignard reagent is usualyy colorless solution in the ether and highly reactive and unstable in water or air. The presence of ether acts as a solvent and stabilies the Grignard reagent.

$$\text{R-X} + \text{Mg} \xrightarrow[\text{Dry Ether}]{\Delta} \text{R-Mg-X}$$

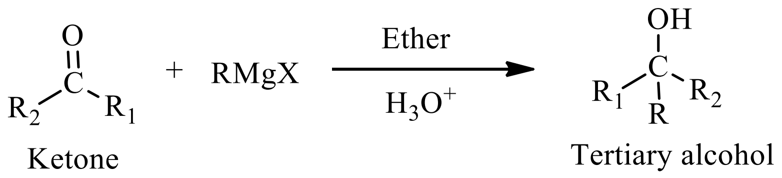
6.4.3 Chemical Reactions of Grignard reagents:

Grignard reagents are act as strong nucleophiles and bases due to the carbon-magnesium bond is highly polar and carbon bears a partial negative charges (act like cabranion) and readily attacks electrophilic centers. The addition reaction with carbonyl compounds Grignard reagent give the different product according to the carbonyl compounds (eg. aldehyde or ketone). For example formaldehyde (aldehyde) gives primary alcohol, other aldehyde give secondary alcohol while ketone gives tertiary alcohol (Scheme 6.1).



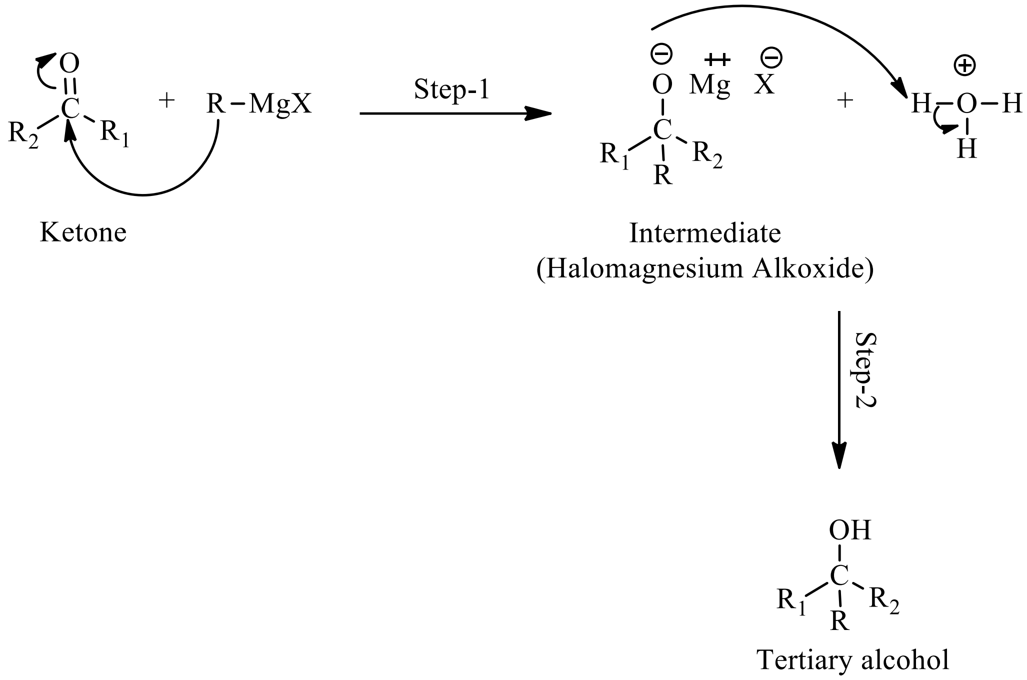
Scheme 6.1: Reactions of Grignard reagent with carbonyl compounds

A. Nucleophilic addtion reaction: The addition of Grignard reagents to carbonyl group is one of the most important methods for carbon-carbon bond formation. The reaction of Grignard reagent with carbonyl compounds is nucleophilic addition reaction and the mechanism (Scheme 6.2) occurs in the following steps:



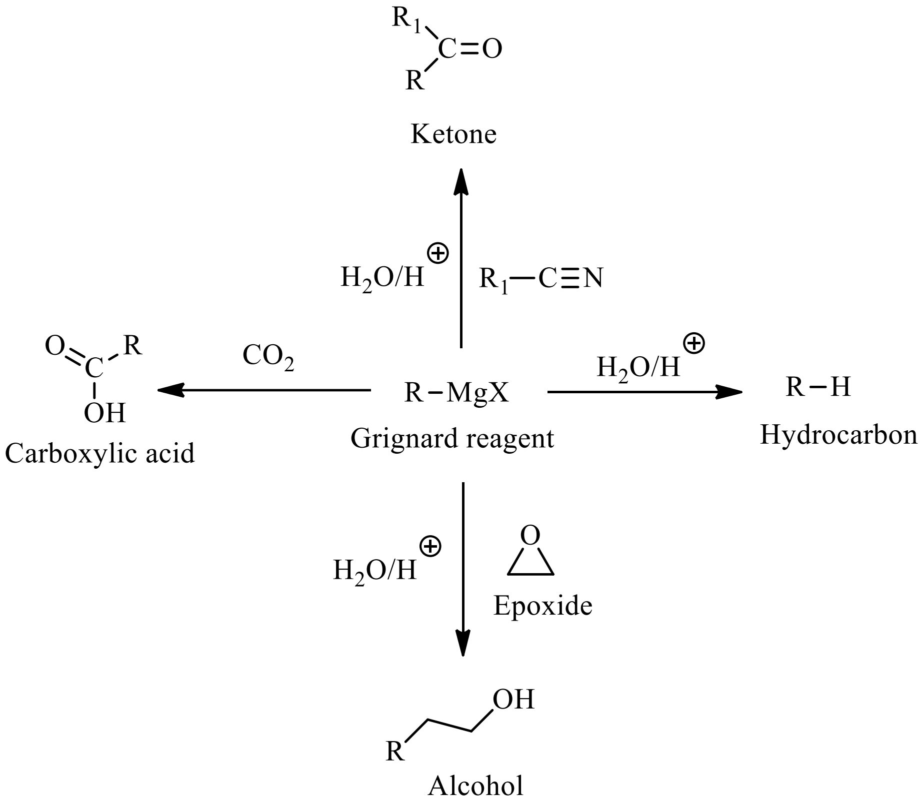
1. Nucleophilic attack of carbon atom of Grignard reagent to the electrophilic carbonyl carbon of aldehyde or ketone and pi (π) electrons of (C=O) bond shift to the oxygen atom.

2. In the next step intermediate (alkoxide) formed during the first step react with the H_3O^+ (acidic hydrolysis) to give the final product (alcohol). This step is known as protonation.



Scheme 6.2: Nucleophilic addition reaction mechanism of Grignard reagent with carbonyl compounds

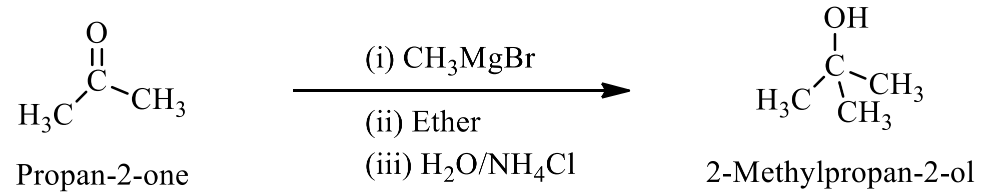
B. Summary of reactions with Grignard reagent: Grignard reagent reacts with different types of reagent such as carbon dioxide, water, ester, nitriles, and epoxide etc. to gives different end product. Here some examples shown in the scheme 6.3.



Scheme 6.3: Reaction of Grignard reagent with different reactant.

C. Some examples of Grignard reagent:

(i)



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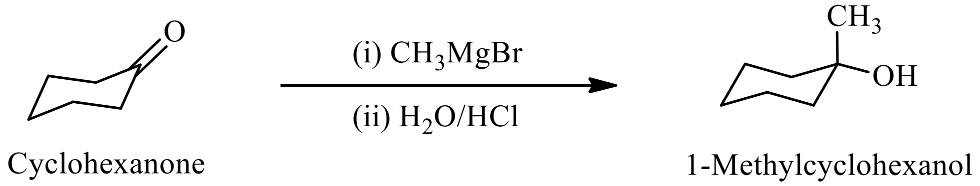

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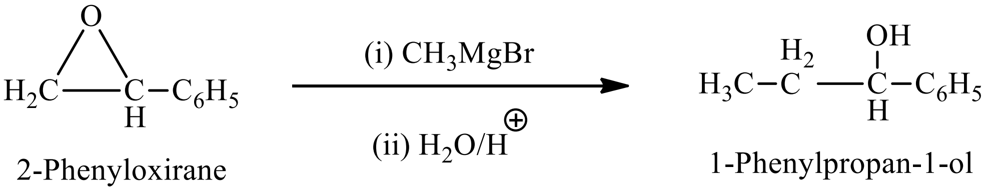

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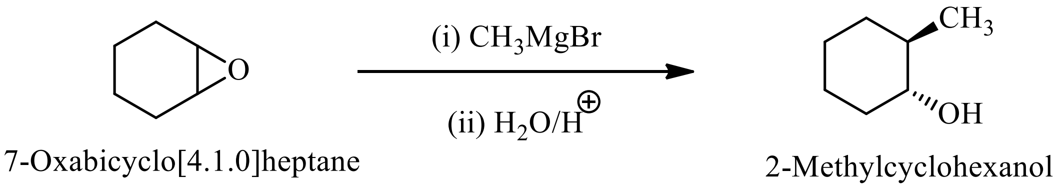


6.5 ORGANOLITHIUM COMPOUND:

Organolithium compounds are organometallic compounds containing carbon–lithium (C–Li) bonds with the general formula R-Li, where R is alkyl, aryl, vinyl etc. group. Among the nucleophilic reagents used in the organic synthesis organolithium compounds/ reagents are one of the most useful highly reactive nucleophillic reagents in organic synthesis due the polar C-Li bond. However, they need to be used with considerable caution because of their high reactivity and thermal instability.

6.5.1 Structure and nature of bond:

Organolithium compound is highly reactive, polymeric structure (dimers, tetramers, and hexamers) in solid and solution phase due to lithium-carbon-lithium (Li-C-Li) bridging and their structure can vary depending on the number of carbon atoms, solvent, and temperature. For example methyl lithium (CH_3-Li) exists in tetramer cubane like structure while n-butyl lithium (n-BuLi) exists in hexamer in non polar solvent (hexane) and in the polar solvent (THF) exist in tetramer. The C–Li bond is highly polar due to the large difference in electronegativity between carbon and lithium. In the carbon- lithium bond, carbon has δ^-

chage and lithium has δ^+ charge so the bond is largely ionic in character. They act as strong bases and nucleophiles in organic synthesis.

6.5.2 Preparation of organilithium compound:

Organolithium compounds are organometallic reagents where a carbon atom is directly bonded to lithium. Organolithium compounds are generally prepared by the reaction of an organohalide with metallic lithium in an aprotic solvent such as dry ether or hydrocarbon solvents.

i. Direct Metal-Halogen Exchange:

Organolithium compound are usually prepared by the reaction of alkyl halides (R-X) with lithium (Li) metal. The order of reactivity of the alkyl halides decreases in the following order RI > RBr > RCl.

$$R\text{-}X + 2Li \xrightarrow[\text{Ether } (C_2H_5)_2O]{\Delta} R\text{-}Li + LiX$$

Example:

$$C_2H_5\text{-}Br + 2Li \xrightarrow[\text{Ether } (C_2H_5)_2O]{\Delta} C_2H_5\text{-}Li + LiBr$$

ii. Transmetalation (Metal–Metal Exchange)

An existing organometallic reagent reacts with a lithium salt to give an organolithium compound.

$$R\text{-}MgX + 2Li \xrightarrow[\text{Ether } (C_2H_5)_2O]{\Delta} R\text{-}Li + Li\text{-}X$$

Example:

$$CH_3\text{-}MgBr + 2Li \xrightarrow[\text{Ether } (C_2H_5)_2O]{\Delta} CH_3\text{-}Li + Li\text{-}Br$$

iii. Lithium-Halogen Exchange

A common method for preparing vinyl, aryl, and alkynyl lithium compounds using an existing organolithium reage. The most common used n-butyllithium (n-BuLi) as exchange reagent.

$$\Delta$$

$$R\text{-}X + R_1\text{-}Li \xrightarrow[THF]{} R\text{-}Li + R_1\text{-}X$$

Example:

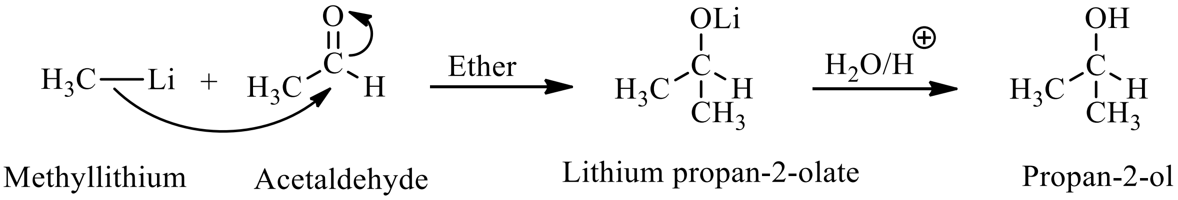
$$C_6H_5\text{-}Br + n\text{-}Bu\text{-}Li \xrightarrow[THF]{\Delta} C_6H_5\text{-}Li + n\text{-}Bu\text{-}Br$$

6.5.3 Chemical reactions of organilithium compound:

Organolithium compounds are highly reactive due the polar carbon-lithium (C-Li) bond. Reactivity depends on the solvent, temperature, and steric/electronic nature of the R (alkyl, aryl etc.) group. They give some important in nucleophilic additions, metalations, etc. reactions.

I. Reaction with carbonyl compounds:

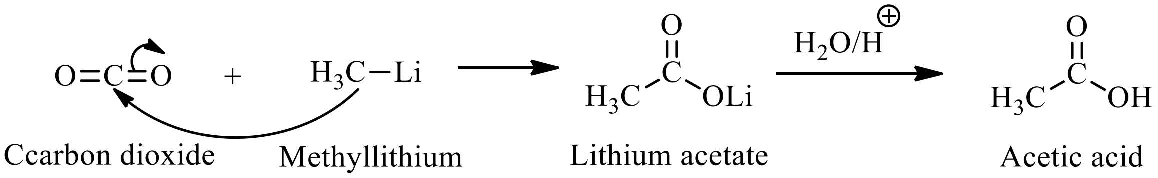
Organolithium reacts with carbonyl compounds as that of the Grignard reagents. Alkyllithium (RLi) react with carbonyl compound (aldehyde and ketone) to gives hydroxy compound (alcohol) as final product. In comparison to Grignard reagents, organolithium reagents are less susceptible to steric factors and react with hindered ketones to give the corresponding tertiary alcohols (Scheme 6.4).



Scheme 6.4: Reaction of organolithium compound with carbonyl compound.

II. Reaction with carbon dioxide:

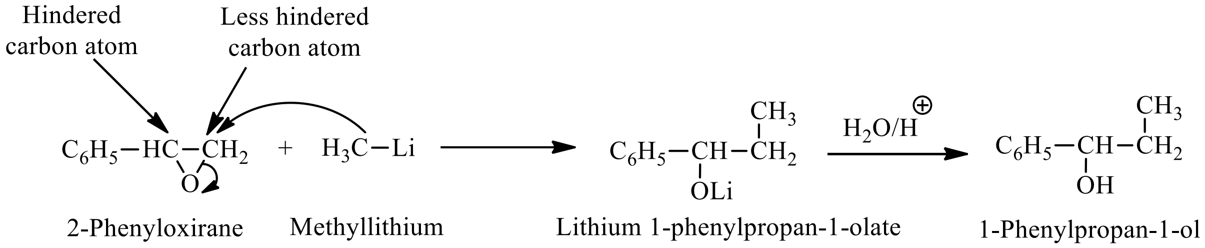
The excess of carbon dioxide (CO_2) react with organolitium compound to gives the carboxylic acid as product on hydrolysis (Scheme 6.5).



Scheme 6.5: Reaction of organolithium compound with carbon dioxide.

III. Reaction with epoxide:

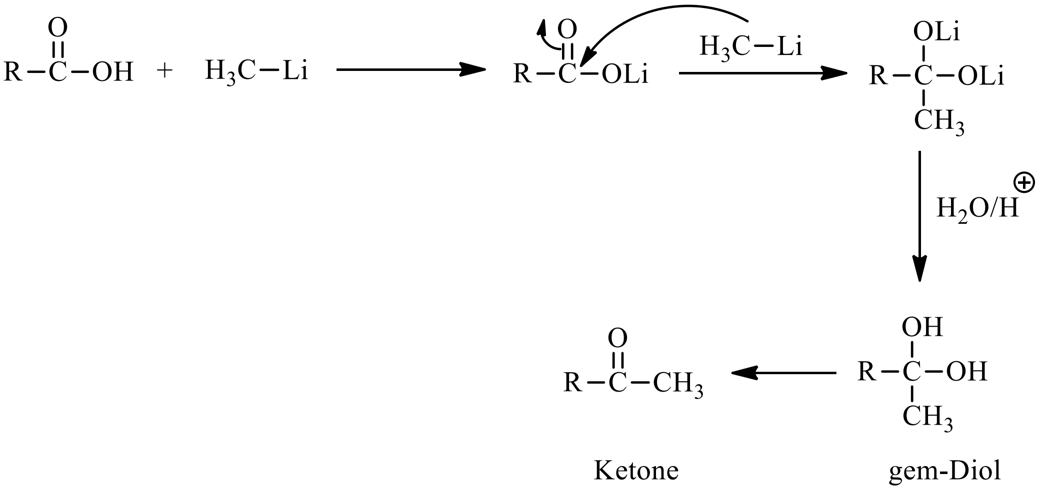
Epoxide (Oxirane) reacts with organolithium compound give the alcohol (hydroxy compound) as the final product. Organolithium compound behave as base so it may be attack less hindered carbon atom of the assymmetric (unsymmetrical) epoxide and proccede through SN^2 reaction (Scheme 6.6).



Scheme 6.6: Epoide ring opening reaction of organolithium compound

IV. Reaction with carboxylic acid:

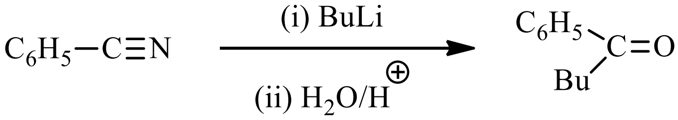
Carboxylic acid reacts with organolithium compound to gives the final product ketone. The reaction occurs in the excess ammount of organolithium compound and uopon the hydrolysis gem-diol formed, and the reaction procced further to gives ketone as final product (Scheme 6.7).



Scheme 6.7: Reaction of organolithium compound with carboxylic acid

V. Some examples of organolithium compound:

(i)



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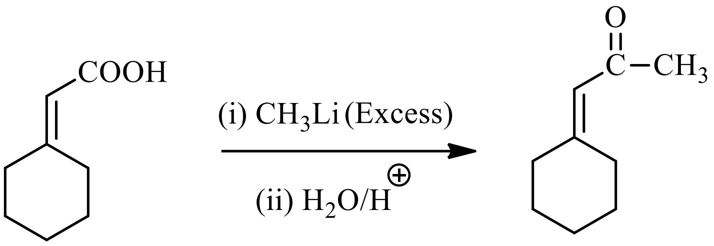

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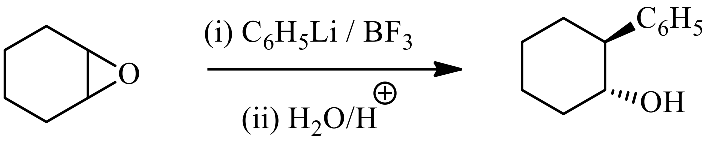

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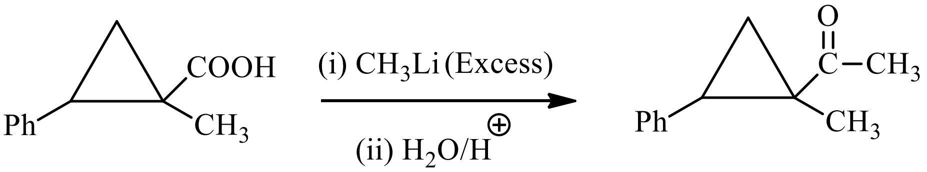

6.6 SUMMARY:

In this unit, we have learnt the following aspects of organomagnisium and organolithium compounds:

- Organometallic compounds are molecules containing a direct bond between a carbon atom of an organic group and a metal.
- The Grignard reagent is most common organomagnesium compound.
- Grignard and organolithium reagents play a vital role in organic synthesis as strong nucleophiles and bases, enabling the formation of C–C bonds.
- Grignard reagent prepared from alkyl/aryl halides and magnesium in dry ether and used fro the formation of alcohol, acid, hydrocarbons etc.
- Organolithium compound prepared from alkyl/aryl halides and lithium in dry ether/hydrocarbon solvents and highly polar covalent/ionic Li–C bond, aggregation in solution.
- Organolithium compound/ reagent stronger base and nucleophile than Grignard's reagent.
- Both the Grignard reagent and organolithium reagent are highly reactive; require anhydrous conditions.

6.7 BIBLIOGRAPHY:

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6.8 TERMINAL QUESTIONS:

A. Long-answer types questions

1. Describe the preparation of Grignard reagents. Explain the effect of reaction conditions (solvent, moisture, impurities) on their formation.
2. Discuss the general reactions of Grignard reagents with various classes of organic compounds (carbonyl compounds, epoxides, nitriles, CO_2).
3. Explain the mechanism of nucleophilic addition of Grignard reagents to carbonyl compounds.
4. Describe the reactions of organolithium compounds with carbonyl compounds and alkyl halides.

B. Multiple Choice Questions

1. Which of the following best describes a Grignard reagent?

A. RMgX
B. RLi
C. R_2Mg
D. R_2CuLi

Answer: A

2. Grignard reagents are prepared by reacting:

A. Alkyl halide with sodium in ether
B. Alkyl halide with magnesium in dry ether
C. Alkyl halide with lithium in pentane
D. Alkene with HCl in water

Answer: B

3. Which solvent is most suitable for organolithium reagent preparation?

A. Water
B. Ethanol
C. Diethyl ether or hexane
D. Acetic acid

Answer: C

4. Which of the following is NOT a correct statement?

A. Grignard reagents are strong nucleophiles and bases.
B. Organolithium reagents are stronger bases than Grignard reagents.
C. Both Grignard and organolithium reagents react violently with water.
D. Grignard reagents can be prepared in the presence of alcohol.

Answer: D

5. Which reaction is possible with a Grignard reagent?

A. $RMgX + CO_2 \rightarrow R–COOH$
B. $RMgX + R'–Cl \rightarrow R–R'$
C. $RMgX + H_2O \rightarrow R–H$
D. All of the above

Answer: D

7. Which compound is obtained from the reaction of CH_3MgBr with formaldehyde followed by acid work-up?

A. Methanol
B. Ethanol
C. Propanol
D. Butanol

Answer: B

8. Which statement about organolithium reagents is TRUE?

A. They can be used for lithium–halogen exchange.
B. They are less basic than Grignard reagents.
C. They are stable in water.
D. They are prepared in aqueous medium.

Answer: A

9. Which of the following is the correct order of basicity?

A. RLi > RMgX > NaOH
B. NaOH > RMgX > RLi
C. RMgX > NaOH > RLi
D. RLi > NaOH > RMgX

Answer: D

10. The most important condition for preparing Grignard reagent is:

A. Excess water in reaction mixture
B. Moisture-free conditions
C. Presence of dilute acid
D. Strong heating in open air

Answer: B

UNIT 7: ORGANOMATELLIC COMPOUND-II (Cu AND Zn)

CONTENTS:

7.1 INTRODUCTION:

In the previous unit-6 we learn about the structure, chemical reactions of the organomagnesium Compound, Grignard’s reagent and organolithium compound. In this unit you will be learn about the other to types of organomatallic compounds such as organocopper, organoinc and Gilman reagent. You are also going to learn about the structure and chemical reactions in detais of Cu and Zn organomatallic compounds/reagents.

7.2 OBJECTIVES/LEARNING OUTCOMES:

After studying this unit you should be able to

- Define the organocopper, organoinc and Gilman reagent.
- Structure, preparation and chemical recations of copper (Cu) and zinc (Zn) organomatellic compound.
- Know the Gilman reagent and their chemical reactions.
- Predict products of reactions involving these reagents.

7.3 ORGANOCOPPER COMPOUND AND GILMAN REAGENT:

Organocopper compounds are organometallic compounds in which a carbon atom is directly bonded to copper (C–Cu). They are important intermediates in organic synthesis for the carbon-carbon (C–C) bond formation. There are various types of organocopper compounds used but the most common and important class of organocopper compounds is Lithium diorganocuprates (R_2CuLi) known as Gilman reagents discovered by Henry Gilman.

7.3.1 Preparation of organocopper reagents (Gilman reagents):

Organocopper reagents (**Gilman reagent)** can be prepared by transmetallating the organolithium reagent and copper (I) salts

$$2RLi + CuX \longrightarrow R_2CuLi \text{ (Gilman Reagent) } + LiX$$

$$2CH_3Li + CuI \longrightarrow (CH_3)_2CuLi + LiI$$

7.3.2 Chemical Reactions of Gilman reagents:

The main reactions of Gilman reagent is substitution, ketone synthesis, conjugate adition reaction (1,4-addition), epoxide opening, and important for stereoselective and regioselective transformations. Gilman reagent is less reactive than Grignard (RMgX) and organolithium reagents (R-Li).

I. Substitution Reaction:

Gilman reagents (R_2CuLi) undergo nucleophilic substitution with alkyl halides (R'–X) to form a new C–C bond. R may be the alkyl, vinyl, allyl, and phenyl. This reaction is works well with primary alkyl halides while secondary and tertiary halides less reactive due to steric hindance. In the reaction mechanism carbon (R^-) bonded to copper acts as a nucleophile and it attacks the electrophilic carbon in R'–X (alkyl halide). After that the halogen (X^-) leaves, forming a new C–C bond in the final product hydrocarbon (Scheme 7.1).

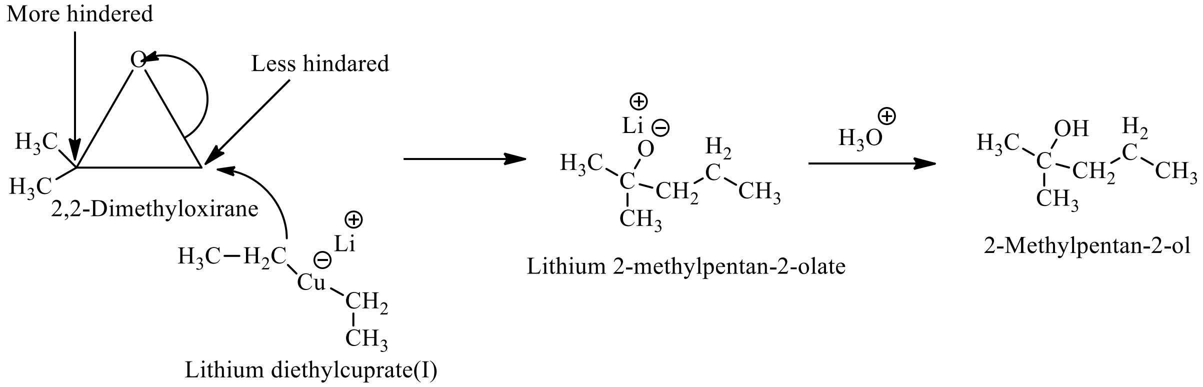
$$R_2CuLi + R'\text{-}X \longrightarrow R\text{-}R' + R\text{-}Cu + LiX$$

$$(CH_3)_2CuLi + C_2H_5Br \longrightarrow CH_3\text{-}C_2H_5 + CH_3Cu + LiBr$$

Scheme 7.1: Substitution reaction of Gilman reagent

II. Epoxide Ring-Opening by Gilman Reagents:

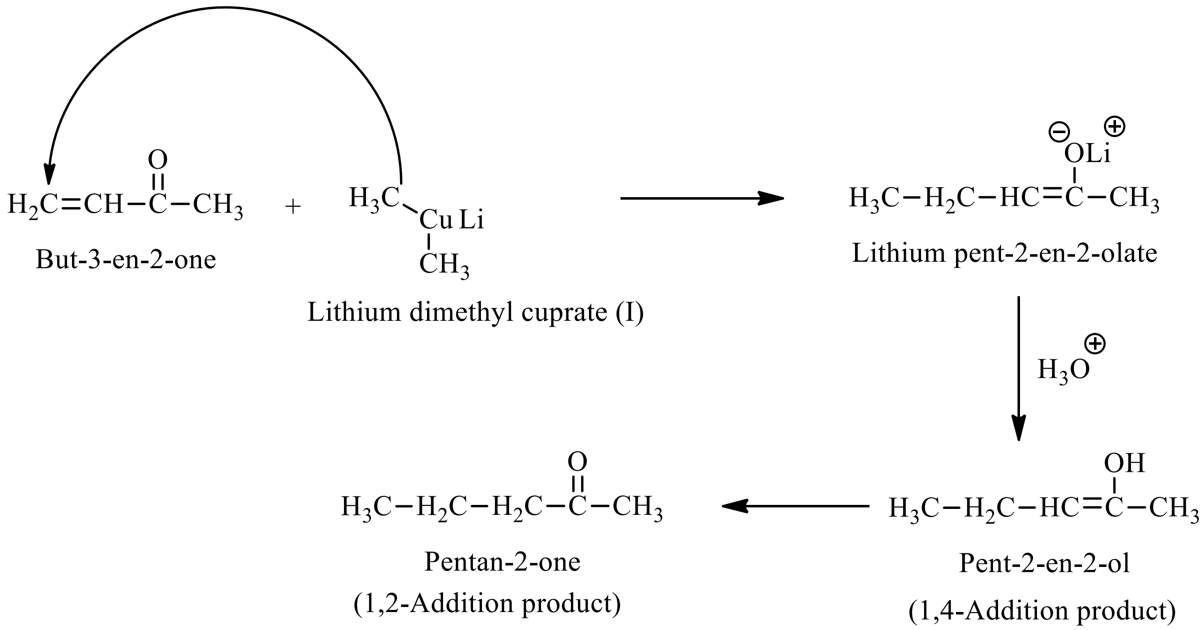
Gilman reagents (R_2CuLi) can open epoxide rings by nucleophilic attack, leading to the formation of an alcohol (after hydrolysis). The mechanism of this reactions involve by the SN^2 type nucleophilic attak of the carbon atom (R^-) bonded to copper attacks the less hindered carbon of the epoxide. This breaks the C–O bond, opening the ring and formed the alkoxide intermediate. After that the alkoxide is protonated to give the corresponding alcohol (Scheme 7.2).



Scheme 7.2: Epoxide Ring-Opening by Gilman Reagents

III. Conjugate addition reaction (Michael addition):

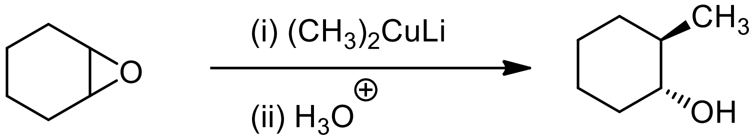
Gilman reagents (R_2CuLi) add to α,β-unsaturated carbonyl compounds at the β-carbon instead of the carbonyl carbon. This is called conjugate addition or 1,4-addition. The reaction is good example of regioselectivity because nucleophile attack occurs at the β-carbon (1,4-position), not the carbonyl carbon (1,2). The mechanisms of these reactions involve by the SN^2 type nucleophilic attak of the R group from R2CuLi attacks the β-carbon of the conjugated enone system. The shifts the double bond electrons toward the carbonyl oxygen and formed the enolate intermediate. After that the enolate is protonated to give the corresponding 1,4 addition product and this undergoes to give final saturated carbonyl compound as product. The reaction is 14, addtion reaction but the product is 1,2-addition product on carbon-carbon double bond (Scheme 7.3).



Scheme 7.3: Conjugate addition reaction (Michael addition)

IV. Some examples of Gilman reagent:

(i)



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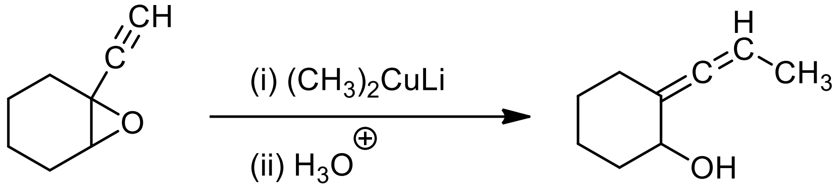
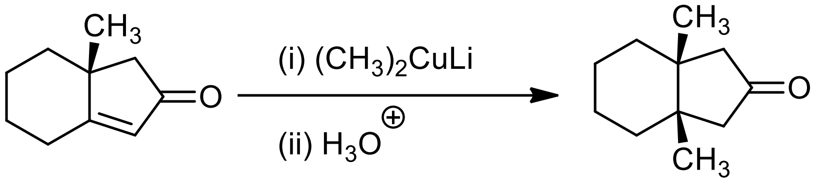


(iii)



7.4 ORGANOZINC COMPOUND:

Organozinc compounds/reagents are organometallic compounds containing a carbon–zinc bond (C–Zn). They are less reactive than Grignard (RMgX) and organolithium (RLi) reagents.Their mild reactivity makes them useful for reactions where selectivity is required. They have better functional group tolerance, which enables them to react with sensitive functional groups like ketones and esters without the need for protective groups. Organozinc reagent is utilized as a nucleophile in organic synthesis to produce C-C bonds through reactions such as the Simmons-Smith Reaction, Reformatsky and Negishi coupling.

7.4.1 Preparation of Organozinc Compound:

Organozinc halides and dialkyl/diorganozinc reagents are the common types of organozinc reahent. Organozinc halides are compounds of the form RZnX, where R is an organic group and X is a halogen. They are often easier to handle than other types of organozinc reagents. Dialkyl/Diorganozinc Reagents (R_2Zn) have two organic groups bonded to the zinc atom and are more reactive.

The most common and important method for the preparation of organozinc compound is the reaction between zinc and alkyl halide.

$$R\text{-}X + Zn \longrightarrow RZnX$$

$$CH_3I + Zn \longrightarrow CH_3ZnI$$

The organozinc compounds also prepared by the reaction of zinc halide with organolithium compounds.

$$\begin{tikzcd}R\text{-}Li + ZnX_2 \arrow[r] & RZnX \arrow[d, "R\text{-}Li"'] \\ & R_2Zn\end{tikzcd}$$

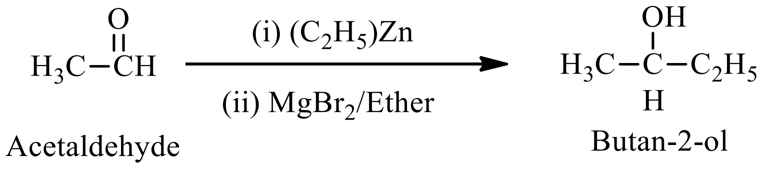
Scheme 7.4: Preparation of organozinc compounds

7.4.2 Chemical reactions of organozinc compound:

Organozinc reagents are milder nucleophiles compared to Grignard or organolithium reagents. They give some important in nucleophilic additions, cyclopropanation reactions.

I. Reaction with carbonyl compounds:

Organ zinc reagents (R–Zn–X) are less reactive than Grignard reagents or organolithium reagents, but they can react with carbonyl compounds under suitable conditions needs and activator like Lewis acid metal halides. Their milder reactivity makes them more chemoselective (less reactive functional groups remain unaffected). The organozinc reagents act as a nucleophile and add to the carbonyl carbon (electrophilic carbonyl carbon) and after hydrolysis it gives alcohol as product (Scheme 7.5).



$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}H \xrightarrow[\text{(ii) } MgBr_2/\text{Ether}]{\text{(i) } (C_2H_5)Zn} H_3C-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-C_2H_5$$

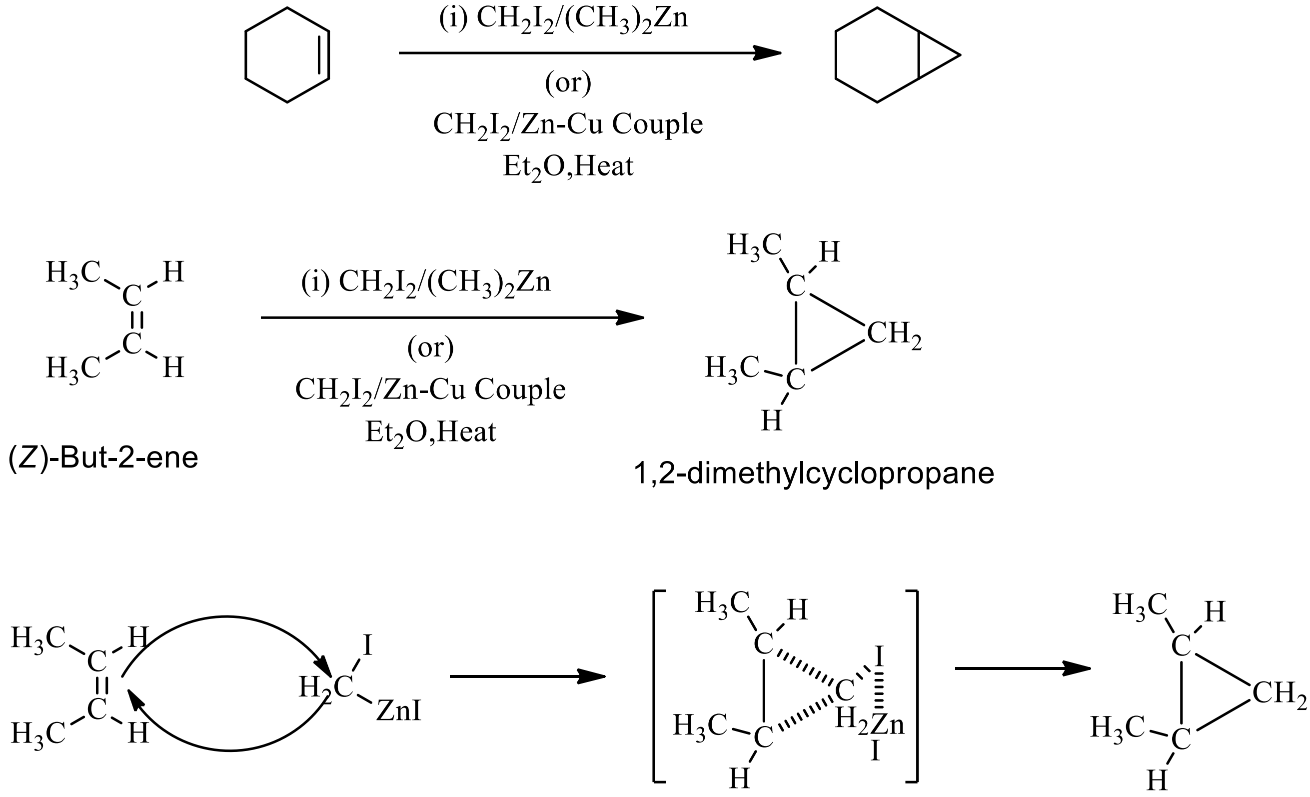
Scheme 7.5: Reaction of organozinc with carbonyl compound

II. Simmons Smith reaction:

The Simmons-Smith reaction is a method to convert an alkene into a cyclopropane using a zinc–carbenoid reagent (usually ICH_2ZnI). It is good example of Stereospecific (retains alkene geometry) reaction. It works well with alkenes, even in the presence of other functional groups.

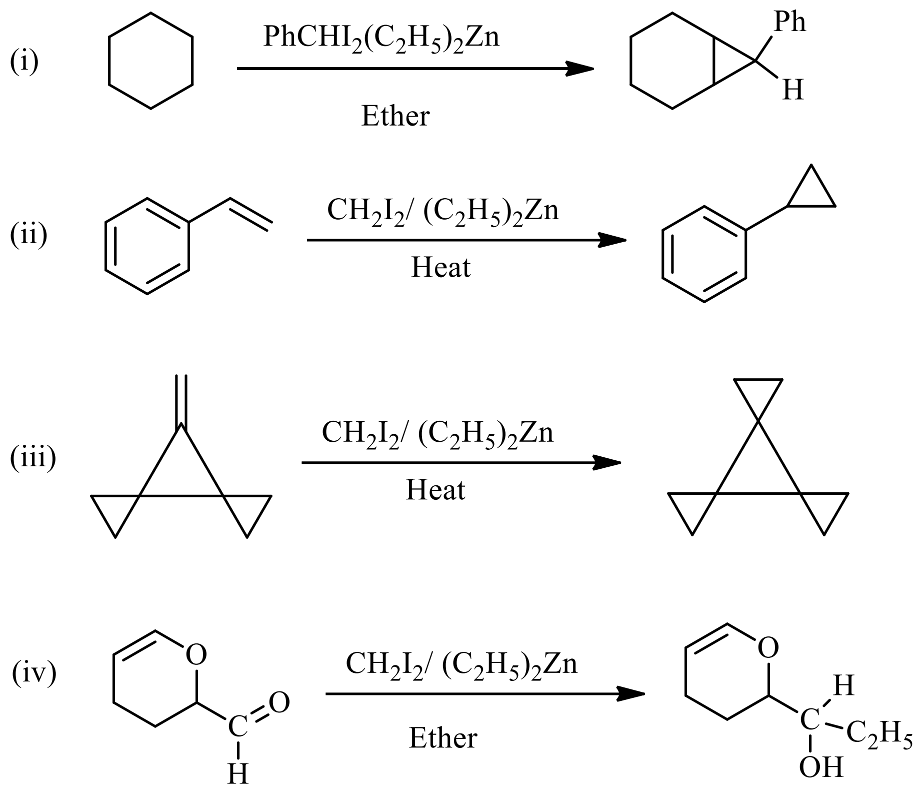
In the reaction CH_2I_2 reacts with activated coupled Zn-Cu to produce a zinc carbenoid (ICH_2ZnI). This behaves like a "carbene equivalent" (CH_2:). The carbenoid approaches the

C=C double bond and a concerted, syn-addition occurs both C–C bonds of the cyclopropane form simultaneously (Scheme 7.6).



Scheme 7.6: Simmons Smith reaction

III. Some examples of organozinc compound:



7.5 SUMMARY:

In this unit, we have learnt the following aspects of organocopper and organozinc compounds:

- Organocopper compounds are carbon-copper (C–Cu bond) compounds.
- The Gilman reagent (R_2CuLi) is most common organocopper compound.
- Gilman reagent give the main reaction like substitution, ketone synthesis, 1,4-addition, and epoxide opening.
- Organocopper reagents are milder and more selective than RLi and RMgX reagents.
- Organozinc reagents/compounds are the compounds that have carbon-zinc (C-Zn) bond.
- Organozinc compounds give the addition, cyclopropanation reaction.
- The Simmons–Smith reaction converts an alkene into a cyclopropane.

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7.7 TERMINAL QUESTIONS:

A. Long-answer types questions

1. Explain the chemical reactions of organozinc compounds with suitable examples
2. Discuss the chemical reactions of organocopper compounds with suitable examples.
3. Explain chemical reactivity of Gilman reagents.
4. What is the Simmons Smith reaction? Describe the role of organozinc compounds in this reaction.

B. Multiple Choice Questions

1. Which organometallic compound is commonly used in the Reformatsky reaction?

A) RLi
B) RMgX
C) R_2Zn
D) RZnX

Answer: D

2. The reaction of ethyl iodide with zinc in dry ether produces:

A) C_2H_5MgI
B) C_2H_5ZnI
C) C_2H_5Li
D) C_2H_6

Answer: B

3. Organocopper reagents are also known as:

A) Grignard reagents
B) Gilman reagents
C) Wittig reagents
D) Carbanions

Answer: B

4. Organozinc compounds are generally:

A) Highly reactive and unstable
B) Less reactive and more selective
C) Stable in water
D) Explosive

Answer: B

5. Which of the following reactions involves the use of organozinc reagents and palladium catalysts?

A) Wurtz reaction
B) Reformatsky reaction
C) Negishi coupling
D) Friedel–Crafts acylation

Answer: C

6. Which is the correct formula of a Gilman reagent?

A) R_2Mg
B) R_2Zn
C) R_2CuLi
D) RCuX

Answer: C

7. Which of the following reagents will perform 1,4-conjugate addition to α,β-unsaturated ketones?

A) RMgBr
B) RLi
C) R_2CuLi
D) RZnX

Answer: C

8. What is the oxidation state of Cu in Gilman reagents?

A) 0
B) +1
C) +2
D) –1

Answer: B

BLOCK-III PHYSICAL CHEMISTRY

UNIT -8 SURFACE CHEMISTRY

CONTENTS:

8.1OBJECTIVES

After studying this Unit, you will be able to:

- Describe interfacial phenomenon and its significance;
- Define adsorption and classify it into physical and chemical adsorption;
- Explain mechanism of adsorption;
- Explain adsorption results on the basis of Freundlich adsorption isotherms and Langmuir's absorption isotherm;

- Explain Charge on the colloidal particle and size of the colloidal particleExplain Perrin's method of determination of the Avogadro's number.

8.2 INTRODUCTION

Surface chemistry is the branch of Physical Chemistry that occursat the surfaces or interfaces. The interface or surfaceis represented by separating the bulk phases by ahyphen or a slash. For example, the interface betweena solid and a gas may be represented by solid-gasor solid/gas. Due to complete miscibility, there is nointerface between the gases. The bulk phases thatwe come across in surface chemistry may be purecompounds or solutions. The interface is normally afew molecules thick but its area depends on the sizeof the particles of bulk phases. Many importantphenomena, noticeable amongst these beingcorrosion, electrode processes, heterogeneouscatalysis, dissolution and crystallization occur atinterfaces. The subject of surface chemistry findsmany applications in industry, analytical work anddaily life situations.

8.3 SOME COMMON TERMS USED IN SURFACE CHEMISTRY

a) **Adsorption:** As like to the liquid surface, there occur certain unbalance residual forces at the surface molecules of the solid substances. Thus the tendency of the surface molecules of the solid substances to attract the molecules of the other substances at the surface to minimize the unbalanced residual forces is known as adsorption phenomena.Example When the gases like NH_3, Cl_2, SO_2 etc. comes in the contact of charcoal then there occurs the adsorption of the gases at the charcoal surface.

In the adsorption phenomena two types of the species are involved:

a. **Adsorbent:** That substance which attracts the molecules of the other substance at its own surface will be called as adsorbent.

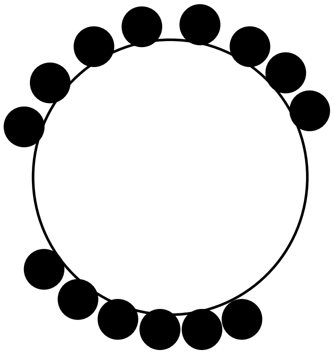
b. Generally solid substance can be used as a adsorbent in the adsorption phenomena. **Adsorbate:** That substances of which molecule are adsorbed at the surface of the adsorbent will be called as adsorbate.

Mostly gaseous molecule can behave as an adsorbate in the adsorption phenomena.

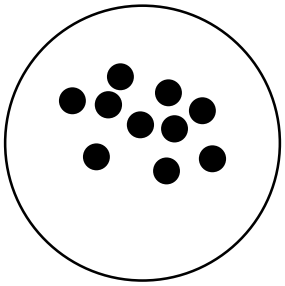
b) **Absorption:** The process of attracting the molecules of the other substance in the inner bulk is known as absorption phenomena.Example: When the NH_3ngas comes in the contact of H_2O then the NH_3 is absorbed by the H_2O to form the NH_4OH.

A. **Sorption:** When both the adsorption and absorption phenomena take place simultaneously, than such type of the process is known as sorption.

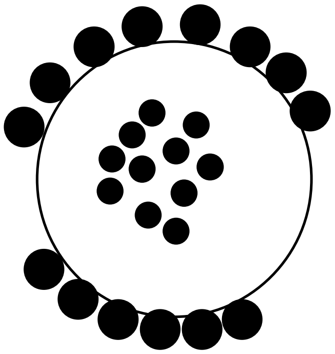
Representation of the adsorption, absorption and sorption process can be given as:



Adsorption



Absorption



Sorption

8.4 *TYPES OF ADSORPTION*

Depending on the force of attraction between the adsorbate and adsorbent surface the adsorption can be divided in to two different types, which are given below:

1. **Physical adsorption:** Such type of the adsorption phenomena in which there occur a weak Van der Waal attraction force between adsorbate and adsorbent surface is known as physical adsorption.
2. **Chemical adsorption:** Such type of the adsorption phenomena in which there occur a strong chemical bonding between the adsorbate and adsorbent surface is known as chemical adsorption.

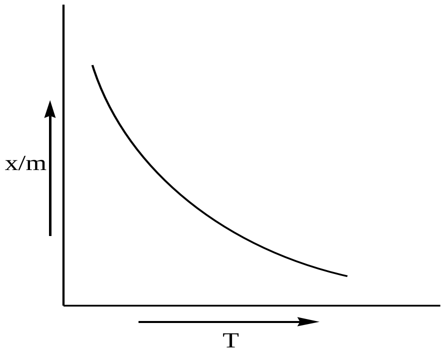
8.5 DIFFERENCE BETWEEN THE PHYSICAL AND CHEMICAL ADSORPTION

Properties	Physical adsorption	Chemical adsorption
Specificity	Physical adsorption does not having the specificity	Chemical adsorption has specificity

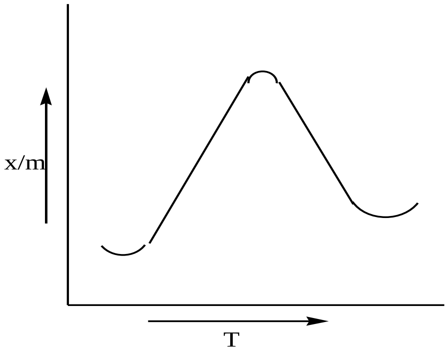
Force of attraction	In the physical adsorption there occur weak Vander waal force of attraction between the adsorbate and adsorbent.	In the chemical adsorption there occur strong chemical bonding between the adsorbate and adsorbent.
Enthalpy of adsorption	In the physical adsorption there occur very low enthalpy of adsorption(4-40KJ/mol)	In the chemical adsorption there occurs very high enthalpy of adsorption (40-400KJ/mol).
Activation energy	Physical adsorption required negiliziable activation energy value.	Chemical adsorption requires certain activation energy value.
Reversibility	Due to the weak Van der waal force of attraction between the adsorbate and adsorbent, the physical adsorption having reversible nature.	Due to the stronger chemical bonding between the adsorbate and adsorbent the chemical adsorption having irreversible nature.
Effect of temperature	With the increase in the temperature, the extent of physical adsorption is decreases.	With the increase in the temperature, the extent of chemical adsorption is initially increase and finally decreases.

8.6 ADSORPTION ISOBAR

At a constant pressure the graph plotted between the x/m(extent of adsorption) and temperature T is known as adsorption isobar. For the physical and chemical adsorption, the adsorption isobar can be represented as:



Adsorption isobar in physical adsorption



Adsorption isobar in physical adsorption

Where χ = Amount of the adsorbate at the adsorbentor m = Surface mass of the adsorbent.

Explanation: Physical adsorption require negligible amount of the activation energy due to which the physical adsorption can occur at the complete adsorbent surface at the very low temperature without providing the energy and with the increase in the in the temperature there occur the desorption by which the value of x as well as x/m will be decreases with the increase in the Temperature. While on the other hand chemical adsorption require a certain amount of activation energy due to which when the temperature increases then the increased temperature can provide the required activation by which the chemical adsorption is increases with the increase in the temperature but after a certain time interval when the complete adsorbent surface is adsorbed then the increase temperature can provide a certain amount of energy to cause the desorption by which the chemical adsorption is decreases.

8.7 ADSORPTION ISOTHERM

At the constant temperature the graph plotted between the extents of adsorption (x/m) and pressure (P) is known as adsorption isotherm.

There are some different types of the adsorption isotherm which can be defined as:

8.8.1Freundlich and Langmuir adsorption isotherm:

A. Freundlichadsorption isotherm: In 1909 Freundlich has been proposed an empirical equation to define the effect of pressure on the adsorption of gases molecules at the solid surface, which is known as Freundlich absorption isotherm.

According to the Freundlich adsorption isotherm equation;

$$\frac{\boldsymbol{x}}{\boldsymbol{m}} \propto P^{\frac{1}{n}} \text{or} \frac{\boldsymbol{x}}{\boldsymbol{m}} \propto K^{\frac{1}{n}}$$

x/m = Extent of adsorption, P = Pressure, n = integer

Where K, n = constant variable

Test of the Freundlich absorption isotherm: According to the Freundlich absorption isotherm;

$$\frac{\boldsymbol{x}}{\boldsymbol{m}} \propto K^{\frac{1}{n}} \ldots\ldots\ldots\ldots\ldots \quad (1)$$

Taking the Log of the this equation

$$\ln \frac{x}{m} = \ln K\, P^{1/n}$$

$$\ln \frac{x}{m} \ = \ln K + \ln P^{1/n}$$

$$ln \frac{x}{n} = \ln K + \frac{1}{n} \ln P$$

Or

$$\ln \frac{x}{m} = \ \frac{1}{n} \ln P + lnK \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

Compare equation number (2) with state line equation

Y = m x + C

Then,

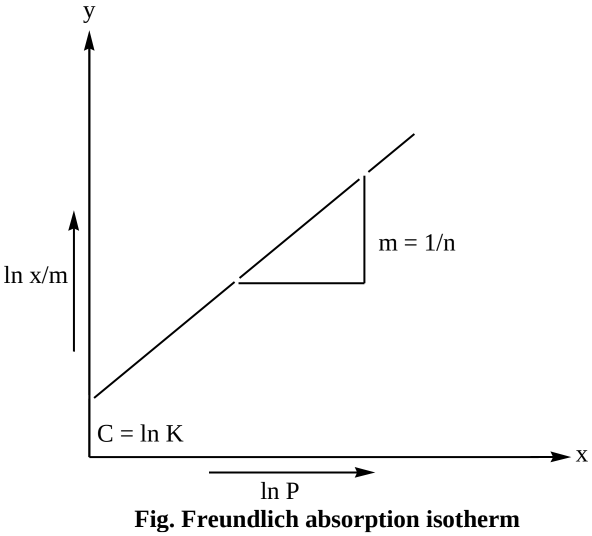


Fig. Freundlich absorption isotherm

Fig 8.1

Limitations of Freundlich adsorption isotherm:

1) Limitations of Freundlich adsorption isotherm equation is an empirical equation which does not having the mathematical proof.
2) Limitations of Freundlich adsorption isotherm equation cannot completely applicable at very low or high pressure.

Langmuir adsorption isotherm:

After the failure of Langmuir adsorption isotherm equation Langmiur has been proposed isotherms which define the adsorption of the gases molecule at the solid surface which is known as Langmuir adsorption isotherm.

Some of the postulates related with the Langmuir adsorption isotherm are given below.

1) According to the Langmuir when the gases molecule comes in the contact of solid surface then initially there occurs the formation of unimolecular layer at the solid surface. Bimolecular or multimolecular layer can also be formed at the solid surface by the Vander Waal attraction force but Langmiur does not consider the formation of bimolecular or multimolecular layer.
2) According to the langmiur when the gases molecules comes in the contact of solid surface then two types of the opposing process can occur at the solid surface which are known as adsorption (condensation) and desorption (evaporation). Initially rate of the condensation being very high and rate of vaporization being very low but with the passes of time rate of condensation being decreases and rate of evaporation is increases, after a certain time interval both become equal to each other, this condition is known as adsorption equilibria.

   Thus at the adsorption equilibria

Rate of condensation = Rate of evoporation

Derivation:

Suppose total surface area of adsorbent = 1 cm^2

Surface area already covered = θ cm^2

Remaining surface area for adsorption = $(1-\theta)$ cm^2

Number of gases molecules striking at the surface = n

Fraction of the molecules adsorbed at the surface = α

No. of adsorbing molecule = $n\alpha$

Then,

Rate of condensation = $(1-\theta)\, n\, \alpha$

Rate of evaporation $\propto \theta$

$= K\theta$

At adsorption equilibria,

Rate of condensation = Rate of evaporation

$(1-\theta)\, n\, \alpha = K\theta$

$n\alpha - n\,\alpha\theta = K\theta$

$n\alpha = K\theta + n\alpha\theta$

$n\alpha = \theta(K + n\alpha)$

$\theta = n\alpha/K + n\alpha$

$\frac{1}{\theta} = K + n\alpha/\, n\alpha$

$\frac{1}{\theta} = \frac{k}{n\alpha} + 1$

Since according to postulates of kinetic gas theory;

$n \propto P$

$n = \beta P$

so

$$\frac{1}{\theta} = \frac{K}{\alpha\beta P} + 1$$

$\frac{K}{\alpha\beta} = \frac{1}{K'}$

,Then

$\frac{K}{\theta} = \frac{1 + K'P}{K'P}$

$\theta = \frac{K'P}{1+K'P}$…………………….. (1)

Accordingto Langmiur,

$\frac{x}{m} \propto \theta$

$\frac{x}{m} = K_2\, \theta$…………………………. (2)

Putting θ from equation (1) to (2)

$\frac{K}{m} = \frac{K_2 K\prime P}{1+K\prime P}$ ………………………..(3)

Case I: If P = very high

Then K'P>>> 1 or 1+K'P ~K'P

So $\frac{x}{m} = K_2\ (Constant)$

Case II: If P = very low

1>>> K'P

Or 1+K'P ~1

so$\frac{x}{m} = K_2 K^{'} P/1$

or$\frac{x}{m} \propto P$

Case III: At the average pressure range,

Langmiur adsorption isotherm equation behaves as like to Freundlich adsorption isotherm i.e.

$$\frac{x}{m} \propto P^{1/n}$$

According to Langmiue diagrammatic representation of all the above three different cases can be given as:

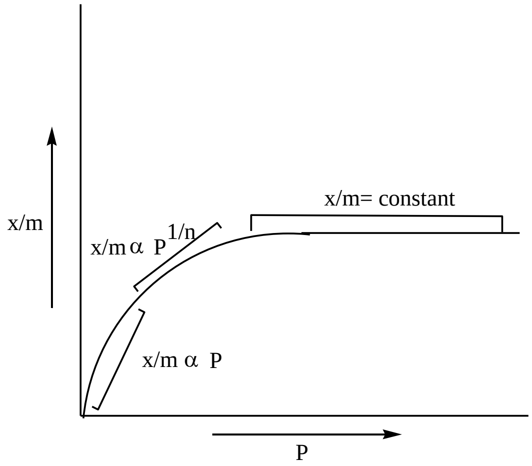


Fig. Langmiur adsorption isotherm

Fig. 8.2

8.8 CHARGES ON THE COLLOIDAL PARTICLES

The particles of a colloidal solution possess a definite electrical charge, either positive or negative. Due to the presence of the same charge, they repel each other and do not combine to form larger particles. This keeps them dispersed in the medium, and hence, a colloidal solution is stable.Based on the nature of the charge on the colloidal particles, colloidal solutions are classified as positively charged or negatively charged sols.

Hydrated metallic oxides, like $Al_2O_3.xH_2O$, $Fe_2O_3.xH_2O$ and $Cr_2O_3.xH_2O$, and basic dyes like methylene blue, form positively charged sols.

Starch solution, metal sols like copper sol and gold sol, metal sulphide sols and acid dyes like Congo red, are examples of negatively charged sols.

A list of some common sols with the natureof charge on their particles is given below:

Positively charged sols	**Negatively charged sols**
Hydrates of metallic oxides, e.g., $Al_2O_3.xH_2O$, $CrO_3.xH_2O$ and $Fe_2O_3.xH_2O$, etc.	Metals, e.g., copper, silver, gold sols.
Hemoglobin (blood)	Acid dye stuffs, e.g., eosin, congo red sols.
Oxides, e.g., TiO_2 sol.	Sols of starch, gum, gelatin, clay, charcoal, etc.

The electrical charge on colloidal particles may be due to several reasons. These include electron capture by the colloidal particles during electro-dispersion of metals, preferential adsorption of ions from the solution, and the formation of an electrical double layer.

The combination of two layers of opposite charges around a colloidal particle is called the "Helmholtz electrical double layer."

The presence of equal or similar charges on colloidal particles is highly responsible in providing stability to the colloidal solution,because the repulsive forces between charged particles having samecharge prevent them from aggregating when they comecloser to one another.

8.9 SIZE OF THE COLLOIDAL PARTICLES

A colloidal dispersion comprises a collection of small particles, droplets, or bubblesof one phase, having at least one dimension between about 1and 1000 nm, anddispersed in a second phase. Either or both phases may be in gas, liquid, solid orsupercritical phase states.

Simple colloidal dispersions are two-phase systems, comprising a dispersed phaseof small particles, droplets or bubbles, and a dispersion medium (or dispersingphase) surrounding them. Although the classical definition of colloidal species(droplets, bubbles, or particles) specifies sizes of between one nanometer and onemicrometer, in dealing with practical applications the upper size limit is frequentlyextended to tens or even hundreds of micrometers. For example, the principles ofcolloid science can be usefully applied to emulsions whose droplets exceed the 1 mmsize limit by several orders of magnitude. At the other extreme, the field of nano-technology is pushing the lower size limit for organized structures below 1 nm. Togive some idea of the sizes involved here, the diameter of a human blood cell isabout 7500 nm (7.5 mm) that of an individual hemoglobin molecule is about2.8 nm, while that of an oxygen molecule is about 0.16 nm.

8.10 PERRIN'S METHOD OF DETERMINATION OF THE AVOGADRO'S NUMBER

According to the Perrin's method when the substance is dissolved in the medium like H_2O then molecules of the substance in the medium can behave as a gas molecule and concentration of the molecules at the lower level in the medium being higher than the concentration in the upper level due to the gravitational force.

The value of potential energy for the molecule at the two different height as well as potential energy difference between these two levels can be given as:

$E_1 = mgh_1$

$E_2= mgh_2$

$E = mg (h_2-h_1)$

For N_A number of molecules,

$$E = N_A\, mg\, (h_2-h_1)\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

According to Boltzmann vertical distribution law,

$$\frac{n2}{n1} = e^{-E/RT} \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Taking log of this equation

$$loge\frac{n2}{n1} = loge\ e^{-E/RT}$$

$$loge\frac{n2}{n1} = -\frac{E}{RT}\text{..................(3)}$$

Putting E from equation (1) to (2)

$$loge\frac{n2}{n1} = -NAmg\frac{h2 - h1}{RT}$$

If the density of medium and species are e and e' respectively,

Then,

$$loge\frac{n2}{n1} = NAmg\frac{h2 - h1}{RT}\left(1 - \frac{e}{e'}\right)$$

$$ln\frac{n2}{n1} = NAmg\frac{h2 - h1}{RT}(e - e'/e')$$

Since m/e'= V

$$ln\frac{n2}{n1} = NAmg\frac{h2 - h1}{RT}(e - e')$$

Or

$$\boldsymbol{\frac{RT}{NA}ln\frac{n2}{n1} = Vg\frac{h2-h1}{RT}(e' - e)}\textbf{.............(4)}$$

If all the variables being given than the value of N_A can be calculated by the above equation and its value comes approx equal to the 6.023 x 10^{23} and known as Avogadro number.

8.11 SUMMARY

Adsorption is the phenomenon of attracting and retaining the molecules of asubstance on the surface of a solid resulting into a higher concentration on thesurface than in the bulk. The substance adsorbed is called as adsorbate and thesubstance on which adsorption takes place is called adsorbent. In Physical Adsorption (physisorption),adsorbate is attracting to the adsorbent by weak force (Van der Waals forces), and in chemical Adsorption (chemisorptions), adsorbate is attracting to the adsorbent by strong chemical bond (like covalent bond, ionic bond etc.). Almostall solids substance adsorbs gases. The extent of adsorption of a gas on a solid depends uponnature of gas, nature of solid, surface area of the solid, pressure of gas andtemperature of gas. The relationship between the extent of adsorption (x/m) andpressure of the gas at constant temperature is known as adsorption isotherm.

In this Chapter we talk about the phenomenon of Adsorption and its type i.e. Physisorption and Chemisorption. The factors on which the extent of adsorption of a gas on a solid are also given. Freundulich and Langmiur Adsorption Isotherm is also discussed under these factors.

8.12 TERMINAL QUESTIONS

A. Objective type Questions:

1. At the equilibrium position in the process of adsorption ___________.
    - (i) $\Delta H > 0$
    - (ii) $\Delta H = T\Delta S$
    - (iii) $\Delta H > T\Delta S$
    - (iv) $\Delta H < T\Delta S$
2. The term ‘Sorption’ stands for
    - (i) Absorption
    - (ii) Adsorption
    - (iii) Both adsorption and Absorption
    - (iv) Desorption
3. Extent of physisorption of a gas increases with ___________.
    - (i) Increase in temperature.
    - (ii) Decrease in temperature.
    - (iii) Decrease in surface area of adsorbent.
    - (iv) Decrease in strength of Van der Waals forces.
4. Which one of the following is **not** applicable to the phenomenon of adsorption?
    - (i) $\Delta H > 0$
    - (ii)$\Delta G < 0$
    - (iii) $\Delta S < 0$
    - (iv) $\Delta H < 0$
5. Which of the following is **not** a favorable condition for physical adsorption?
    - (i) High pressure

(ii) Negative ΔH

(iii) Higher critical temperature of adsorbate

(iv) High temperature

6. Physical adsorption of a gaseous species may change to chemical adsorption with _______
   (i) Decrease in temperature
   (ii) Increase in temperature
   (iii) Increase in surface area of adsorbent
   (iv) Decrease in surface area of adsorbent

7. In physisorption adsorbent does not show specificity for any particular gas because ____
   (i) Involved van der Waals forces are universal.
   (ii) Gases involved behave like ideal gases.
   (iii) Enthalpy of adsorption is low.
   (iv) It is a reversible process.

8. Which of the following is an example of absorption?
   (i) Water on silica gel
   (ii) Water on calcium chloride
   (iii) Hydrogen on finely divided nickel
   (iv) Oxygen on metal surface

9. On the basis of data given below predict which of the following gases shows least adsorption on a definite amount of charcoal?

Gas	CO_2	SO_2	CH_4	H_2
Critical temp./K	304	630	190	33

   (i) CO_2
   (ii) SO_2
   (iii) CH_4
   (iv) H_2

10. For Freundilich isotherm a graph of log x/m is plotted against log P. The slope of the line and its y-axis intercept, respectively corresponds to
   (i) 1/n, k
   (ii) log 1/n, k
   (iii) 1/n, log k

(iv) log 1/n, log k

B. Short Answer Type Questions:

1) Write any two characteristics of Chemisorption.
2) Why does physisorption decrease with the increase of temperature?
3) Why are powdered substances more effective adsorbents than theircrystalline forms?
4) Distinguish between the meaning of the terms adsorption and absorption. Give one example of each.
5) What is the difference between physisorption and chemisorption?
6) Give reason why a finely divided substance is more effective as an adsorbent.
7) What is an adsorption isotherm? Describe Freundlich adsorption isotherm.
8) Why is adsorption always exothermic?
9) Discuss the effect of pressure and temperature on the adsorption of gases on solids.
10) What is adsorption?
11) What is desorption?
12) What are adsorbate and adsorbent? Give an example.
13) Give two examples for adsorption.
14) Give differences between adsorption and absorption.
15) What is the effect of temperature on physical and chemical adsorption?
16) Mention any two applications of adsorption.
17) What happens to ΔH, ΔS and ΔG during the process of adsorption?
18) Write any three differences between two types of adsorption of gases on solids.
19) What are the applications of adsorption in chemical analysis?

C. Long Answer Type Questions:

1. Define the term with examples- a. Adsorption, Absorption and Sorption.

2. Discuss briefly Langmuir's adsorption isotherm

3. What is the difference between physical adsorption and chemical adsorption?

4. Discuss in detail Perrin's method for the determination the size of colloidal particles.

5. Derive the expression for Freundlich adsorption isotherm

8.13 ANSWER

1. ii, 2.iii, 3. ii, 4. i, 5. iv, 6. ii, 7. i, 8. ii, 9. iv10. Ii

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UNIT- 9 ELEMENTARY QUANTUM MECHANICS

CONTENTS:

9.1 INTRODUCTION

The concepts and formulation of quantum mechanics are not elementary in the sense that they are easily understood. They are based on the outcome of considerable theoretical research supported by experimental evidence. The quantum mechanical approach to physical problems cannot be explained in simple non-mathematical terms.

Simple and elegant mathematical techniques have been used to elucidate the physical concepts. There are two approaches to quantum mechanics. One is to follow the historical development of the theory from the first indications that the whole fabric of classical mechanics and electrodynamics should be held in doubt to the resolution of the problem in the work of Planck, Einstein, Heisenberg, Schrodinger, and Dirac. The other is to stand back at a point late in the development of the theory and to see its underlying theoretical structure. The first is interesting and compelling because the theory is seen gradually emerging from confusion and dilemma. We see experiment and intuition jointly determining the form of the theory and, above all, we come to appreciate the need for a new theory of matter. The second, more formal approach is exciting and compelling in a different sense: there is logic and elegance in a scheme that starts from only a few postulates, yet reveals as their implications are unfolded, a rich, experimentally verifiable structure.

9.2 OBJECTIVES

In this chapter you will learn the following:

- The inadequacy of classical mechanics
- Birth of quantum mechanics
- Basic formalism of quantum mechanics
- Introduction to quantum mechanical operators

9.3 BLACK BODY RADIATION

Black-body radiation is the thermal electromagnetic radiation within or surrounding a body in thermodynamic equilibrium with its environment, or emitted by a black body (an opaque and non-reflective body). It has a specific spectrum and intensity that depends only on the body's temperature, which is assumed for the sake of calculations and theory to be uniform and constant. The thermal radiation spontaneously emitted by many ordinary objects can be approximated as black-body radiation. A perfectly insulated enclosure that is in thermal equilibrium internally contains black-body radiation and will emit it through a hole made in its wall, provided the hole is small enough to have negligible effect upon the equilibrium.

A black-body at room temperature appears black, as most of the energy it radiates is infrared and cannot be perceived by the human eye. Because the human eye cannot perceive color at very low light intensities, a black body, viewed in the dark at the lowest just faintly visible temperature, subjectively appears grey (but only because the human eye is sensitive only to black and white at very low intensities - in reality, the frequency of the light in the visible range would still be red, although the intensity would be too low to discern as red), even though its objective physical spectrum peaks in the infrared range. When it becomes a little hotter, it appears dull red. As its temperature increases further it eventually becomes blue-white.

Although planets and stars are neither in thermal equilibrium with their surroundings nor perfect black bodies, black-body radiation is used as a first approximation for the energy they emit. Black holes are near-perfect black bodies, in the sense that they absorb all the radiation that falls on them. It has been proposed that they emit black-body radiation (called Hawking radiation), with a temperature that depends on the mass of the black hole.

Equations for Black-body radiation

1. Planck's law of black-body radiation

Planck's law states that

$$B_\nu(T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

Where,

B_ν (T) is the spectral radiance (the power per unit solid angle and per unit of area normal to the propagation) density of frequency ν radiation per unit frequency at thermal equilibrium at temperature T;h is the Planck constant;c is the speed of light in a vacuum;k is the Boltzmann constant;ν is the frequency of the electromagnetic radiation and T is the absolute temperature of the body.

2. Wien's displacement law

Wien's displacement law states that the black body radiation curve for different temperatures peaks at a wavelength inversely proportional to the temperature. The shift of that peak is a direct consequence of the Planck radiation law which describes the spectral brightness of black body radiation as a function of wavelength at any given temperature. However, it had been discovered by Wilhelm Wien several years before Max Planck developed that more general equation, and describes the entire shift of the spectrum of black body radiation toward shorter wavelengths as temperature increases.

Formally, Wien's displacement law states that the spectral radiance of black body radiation per unit wavelength peaks at the wavelength λ_{max}given by:

$$\lambda_{max} = \frac{b}{T}$$

Where T is the absolute temperature in Kelvin; b is a constant of proportionality called Wien's displacement constant, equal to $2.8977729(17) \times 10^{-3}$m·K or more conveniently to obtain wavelength in micrometers, b ≈ 2900 μm·K.

Wien's displacement law shows how the spectrum of black-body radiation at any temperature is related to the spectrum at any other temperature. If we know the shape of the spectrum at one temperature, we can calculate the shape at any other temperature. Spectral intensity can be expressed as a function of wavelength or of frequency.

Planck's law was also stated above as a function of frequency. The intensity maximum for this is given by

$$\upsilon_{max} = T \text{ x } 58.8 \text{ GHz/K}$$

9.4 PLANCK'S RADIATION LAW

Planck's law describes the spectral density of electromagnetic radiation emitted by a black body in thermal equilibrium at a given temperature T (Fig9.1).The spectral radiance of a body, Bν, describes the amount of energy it gives off as radiation of different frequencies. It is measured in terms of the power emitted per unit area of the body, per unit solid angle of emission, per unit frequency. Planck showed that the spectral radiance of a body for frequency ν at absolute temperature T is given by

$$B_\nu(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{k_B T}} - 1}$$

Where, $k_B$is the Boltzmann constant, the Planck constant and c isthe speed of light in the medium, whether material or vacuum. The spectral radiance can also be measured per unit wavelength λ instead of per unit frequency. In this case, it is given by;

$$B_\lambda(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

The law may also be expressed in other terms, such as the number of photons emitted at a certain wavelength, or the energy density in a volume of radiation. The SI units of $B_\nu$are $W \cdot sr^{-1} \cdot m^{-2} \cdot Hz^{-1}$, while those of B_λ are $W \cdot sr^{-1} \cdot m^{-3}$.

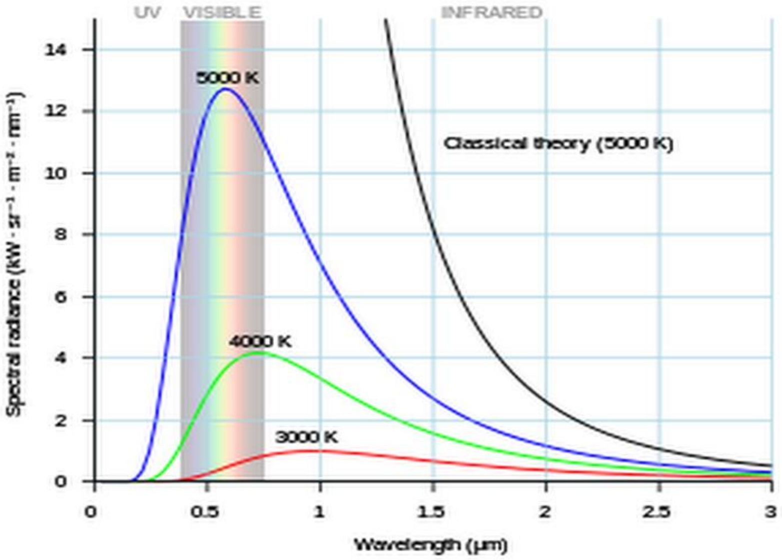

Fig 9.1: Planck's law (colored curves) accurately described black body radiation and resolved the ultraviolet catastrophe (black curve).

9.5 PHOTOELECTRIC EFFECT

The photoelectric effect is a phenomenonin which electrically charged particles are released from or within a material when it absorbs electromagnetic radiation. In a broader definition, the radiant energy may be infrared, visible, or ultraviolet light, X rays, or gamma rays; the material may be a solid, liquid, or gas; and the released particles may be ions (electrically charged atoms or molecules) as well as electrons. in 1887 by the German physicist Heinrich Rudolf Hertz.Further research showed that the photoelectric effect represents an interaction between light and matter that cannot be explained by classical physics, which describes light as an electromagnetic wave. One inexplicable observation was that the maximum kinetic energy of the released electrons did not vary with the intensity of the light, as expected according to the wave theory, but was proportional instead to the frequency of the light. Consideration of these unexpected behaviours led Albert Einstein to formulate in 1905 a new corpuscular theory of light in which each particle of light, or photon, contains a fixed amount of energy, or quantum, that depends on the light’s frequency. In particular, a photon carries an energy E equal to hf, where f is the frequency of the light and h is the universal constant that the German physicist Max Planck derived in 1900 to explain the wavelength distribution of blackbody radiation that is, the electromagnetic radiation emitted from a hot body. The relationship may also be written in the equivalent form $E = hc/\lambda$, where c is the speed of light and λ is its wavelength, showing that the energy of a photon is inversely proportional to its wavelength.

9.5.1 Theory of Photoelectric Effect

In order to study the effect, a metal plate and collecting electrode are placed in a volume. A variable source of potential difference is placed across the electrodes. A sensitive current measuring device is placed in series with the collector. Light is allowed to strike the surface and the current at the collector is noted as a function of the potential difference. According to the above discussion the following conclusion can be obtained;

1) If the frequencyof the light is constant, the photoelectric current increases with increasing intensity of the light.
2) The photoelectrons are released within less than 10^{-9} sec after the surface is illuminated by the light. The emission is essentially instantaneous with illumination.
3) For a given photosensitive surface, the emission of the photoelectrons takes placeonly if the frequency of the light is equal to a greater than a certain minimum frequency υ_o, sometimes called the threshold frequency. The value of $\upsilon_o$is different for different materials.

4) The maximum kinetic energy (k_{max}) of the photoelectrons is independent of the intensity of incident radiation (I).
5) The maximum kinetic energy (k_{max})of the photoelectrons depends on the frequency of the incident light.
6) The relationship between k_{max} and $\upsilon_o$is linear.

Explanation of photoelectric effect:

According to the quantum theory, the radiation consists of energy packets known as photon or quanta of energy hυ, where h is Planck's constant and υ is frequency of the incident light. When a photon of energy hυ falls on the metal surface its energy is used in two ways:

1) A part of its energy is used in ejecting the electrons just out of the surface; the energy depends on the metal and is called as work function (ϕ_0).
2) The rest part of the energy is used up in imparting the kinetic energy ½ $h\upsilon^2$ to the ejected electrons, thus-

$$h\upsilon = \phi_0 \ + \frac{1}{2}m\upsilon^2$$

$$\phi_0 \ = h\upsilon_0$$

Where, υ_0 = Threshold frequency

$$h\upsilon = h\upsilon_0 + \frac{1}{2}m\upsilon^2$$

$$h\upsilon \ - h\upsilon_0 \ = + \frac{1}{2}m\upsilon^2 \ (KE)$$

$$KE \ = h\ (\upsilon - \ \upsilon_0 \ )$$

We know that;

$$\upsilon = \frac{c}{\lambda}$$

$$KE \ = h\ (\frac{c}{\lambda} - \ \frac{c}{\lambda_0})$$

Where,λ_0= Threshold wavelength

$$KE \ = h\upsilon\ (\frac{1}{\lambda} - \ \frac{1}{\lambda_0})$$

$$KE \ = h\upsilon\ (\frac{\lambda_0 - \lambda}{\lambda\lambda_0})$$

9.6 BOHR'S MODEL OF THE HYDROGEN ATOM AND ITS DEFECTS

Bohr's model of the Hydrogen atom started from the planetary model, but he added one assumption regarding the electrons, what if the electronic structure of the atom was quantized? Bohr’s suggested that perhaps the electron could only orbit the nucleus in specific orbit or shells with a fixed radius.Only those shells with a radius provided by the equation below were allowed, and it was impossible for electrons to exist between these shells. Mathematically, the allowed value of the atomic radius is given by the equation

$$r(n)=n^2\times r(1)$$

Where n is a positive integer and r(1) is the smallest allowed radius for the hydrogen atom also known as the Bohr’s radius. The Bohr’s radius has a value of $r(1)=0.529\times10^{-10m}$.

By applying his postulates and the classical laws of physics Bohr workout on various expressions for uni-electronic species like H, $H^{+,}$ $Li^{+,\ -}$, these expressions are given for radius of nth orbit velocity and energy of an electron which is revolving around the nth orbit. He also derived an expression for the frequency (ʋ)andwavelength (λ)of the spectral line estimated when an electron falls from a high energy orbit to low energy orbit.

Expression for the Radius of nth Orbit of Hydrogen Atom and Hydrogen like Species:

Let us consider Hydrogen like species whose atomic number equal to **Z**;suppose an **ē**ofcharge **e** is revolving around the nucleus and its charge on the nucleus is equal to **Ze**; suppose **n** is equal to distance between the revolving electron and nucleus in the mass of electron and **v** is the velocity of the electron. Now the revolving electron is being acted upon simultaneously by the two types of forces:

1. Electrostatic Force of Attraction (centripetal force): This force exists between the nucleus and the electron which is revolving around the nucleus, this force of attraction tends to attract the electron towards the nucleus.

This force is equal to Ze^2/r^2
While in SI system this force is equal to

$$=\frac{1}{4\pi\in o}\text{x}\frac{ze^2}{r^2}$$

Whereε_0 is a constant called permittivity of medium and its value is, 8854x 10^{12} $J^{-1}C^2m^{-1}$

2. Force of Repulsion (Centrifugal Force): This force acts outwards from the nucleus and hence tries to keep the revolving electron away from its orbit. In both systems of units, this force is equal to

$$\frac{mv^2}{r}$$

Both the above forces work on opposite direction w.r.t the electron revolving around the nucleus. Then from the above two assumptions, it is clear that these forces must be equal.

Bohr's Radius (r_H): The radius of the first orbit when is equal to one (n-1)ofH-atom (Ե - 1) is known as Bohr's radius which is represented as (r_H), the value can be calculated as:

(a) **In c.g.s System:** we know that in c.g.s system the value of $r_n$is given by:

$$r_n = \frac{h^2}{4\pi^2 me^2} x \frac{n^2}{z}$$

If the value ofn=1(for $(r_1)_H$andz = 1,putting it in the above equation we get;

$$(r_1)_H = \frac{h^2}{4\pi^2 me^2} x \frac{(1)^2}{1}$$

Putting the value of h = 6.626x10^{-27} ergs, π = 3.14, m = 9.108 x10^{-28}g, e = 4.8x10^{-10}esu

$$(r_1)_H = \frac{6.626 \times 10-27 \text{ ergs}^2}{(4.3.14)^2 \times (9.108 \times 10^{-28})^2 \times (4.8 \times 10^{-10}\ esu)^2}$$

$$(r_1)_H = 0.529 \text{x} 10^{-8}$$

Or

$$(r_1)_H = 0.529\ \text{A}^{\circ}$$

The value of Bohr's Radius for hydrogen atom is 0.529 A°.

Defects of Bohr's Model:

- Bohr's model doesn't work well for complex atoms.
- It couldn't explain why some spectral lines are more intense than others.
- It could not explain why some spectral lines split into multiple lines in the presence of a magnetic field.
- The Heisenberg's uncertainty principle contradicts Bohr's idea of electrons existing in specific orbits with a known radius and velocity.

Although the modern quantum mechanical model and the Bohr model may seem vastly different, the fundamental idea is the same in both. Classical physics isn’t sufficient to describe all the phenomena that occur on an atomic level. But, Bohr was the first to realize the quantization of electronic shells by fusing the idea of quantization into the electronic structure of the hydrogen atom and was successfully able to explain the emission spectra of hydrogen as well as other one-electron systems.

9.7 COMPTON EFFECT

In 1923,A. M. Compton found that when X- Rays of high energy are allowed to fall on solid matter like carbon block or some other light elements, an electron is ejected from the carbon block and X-Rays are scattered from their original path. In this process a proton from the incident X-Ray collides while the loosely bound electron in the carbon block. After receiving an impact from the photon, the electronwhich was initially at restgain some velocity and hence moves below the direction of incident X-Rays while the photon is deflected above.According to the above discussion we see that X-Rays are scattered from their original path and as a result collision takes place between photon which is moving and electron at rest. It has been found that scatteredX-Rays have longer wavelength than the incident X-Rays (Fig 9. 2).

If the wavelength of incident X-Ray and scattered X-Ray are λ and λ' respectively then hc/λ and hc/λ’ are the energy associated with the photon of incident and scattered reflect respectively thus the decrease is energy is equal to-

$$\frac{hc}{\lambda} - \frac{hc}{\lambda'}$$

Then this energy $\frac{hc}{\lambda} - \frac{hc}{\lambda'}$is transmitted to the electron at rest and therefore the electron gains some velocity and move from its path in this process.

“*This phenomenon in which there is a change in the wavelength of the scattered X-Ray is called as Compton effect*”.

The angle through which the incident X-Rays are deflected from their original path is known as angle of scattering and is denoted by **ɵ.**

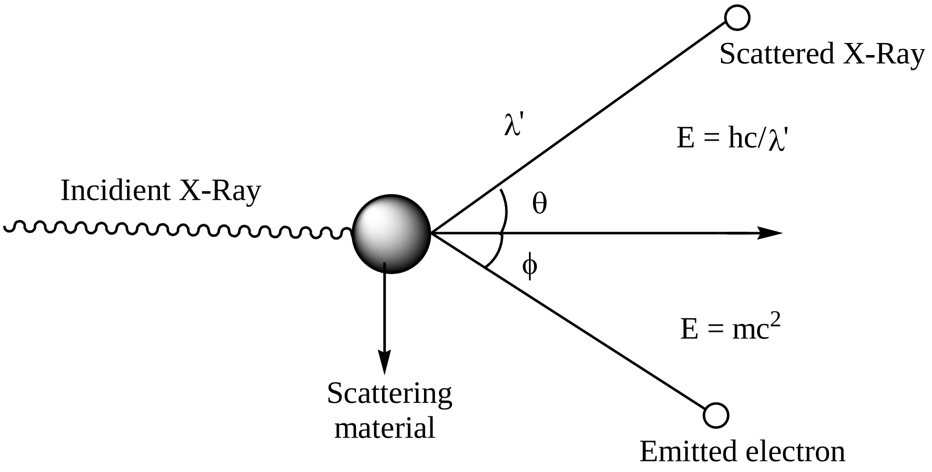

Fig2: Compton Effect of X-Ray Photons

By applying the conservation of energy and momentum and by assuming that the X-Ray is composed of photon each of which has energy equal to hυ. Compton shows that the wavelengthλ' of the scattered X-Ray and the wavelength λ of incident X-Ray are related to each other by the relation.

$$\lambda - \lambda' = \frac{h}{mc}(1 - Cos\theta)$$

Where h is the Planck's constant, m is the rest mass of the electron and c is the velocity of light.

The difference in λ and $\lambda'$is called Compton wavelength shift and is denoted by Δλ.

$$\lambda - \lambda' = \frac{h}{mc}(1 - Cos\theta)\text{……………..(1)}$$

$$\{1\text{-cos } \theta = \frac{2\sin^2\theta}{2}\}$$

$$\Delta\lambda = \frac{h}{mc}\frac{2\sin^2\theta}{2}$$

$$\Delta\lambda = \frac{2h}{mc}\frac{\sin^2\theta}{2}\text{……………….(2)}$$

In equation (1) $\frac{h}{mc}$ = constant = 0.2424 x 10^{-11} m or 0.2424 A^0

From the above relation following cases are obtained:

Case -1 When $\theta = 0^0$

$$\Delta\lambda = \frac{h}{mc}1 - Cos\ 0^0$$

$$\Delta\lambda = 0$$

Case -2 When $\theta = 90^0$

$$\Delta\lambda = \frac{h}{mc}1 - Cos\ 90^0 = 0.2424A^0$$

Case -2 When $\theta = 180^0$

$$\Delta\lambda = \frac{h}{mc} 1 - Cos\,180^0 = 0.4848A^0$$

9.8 de-BROGLIE HYPOTHESIS

Einstein in 1905 suggested that light shows dual character, i.e. particle as well as wave nature. de-Broglie in 1923 extended Einstein's view and said that all the forms of matter like electrons, protons, neutrons, atoms, molecules, etc. also show dual character, he further said that wavelength (λ) of the moving particles of mass m and velocity vis given by

$$\lambda = \frac{h}{mv}$$

Where, h = Planck 's constant

m = mass of electron

υ = velocity of electron

This equation is called as de-Broglie's wave equation and λ is called de-Broglie's wavelength.

Derivation of de-Broglie's equation:

We know that the energy (E) of a photon is given by E = hv ………. (1)

$$\text{i.e } \upsilon = \frac{c}{\lambda}$$

Putting the value of υ in equation number (1)

$E = h\frac{c}{\lambda}$………. (2) (According to Planck's Quantum theory).

According to Einstein's equation

$E = mc^2$ …………. (3)

Here, **c =** velocity of light

λ = wave length

m **=** mass of proton

On combining the above equation (2) and (3) we get

$$mc^2 = h\frac{c}{\lambda}$$

$$mc = \frac{h}{\lambda}$$

$$h = \lambda mc$$

$$\lambda = \frac{h}{m\times c} \ldots\ldots\ldots\ldots\ldots (4)$$

Thus, for another particle moving with a velocity **υ** then,

$$\lambda = \frac{h}{m \times v}$$

We know that m x v = ρ

$$\lambda = \frac{h}{\rho} \ldots\ldots\ldots (5)$$

Where ρ = momentum of the particles.

The equation (4) is known as de-Broglie's wave equation.

Experimental verification of de-Broglie's wave equation:

If an electron of charge**e**is accelerated by an applied potential, **v** (ES units), i.e. kinetic energy (KE) is given by:

$$KE = V_e \ldots\ldots\ldots (1),$$

Also, the magnitude of KE of an electron moving with a velocity **υ** is also given by;

$$KE = \frac{1}{2} mv^2 \ldots\ldots\ldots (2)$$

On combining these two relations we have,

$$KE = V_e = \frac{1}{2} mv^2$$

Or

$$\upsilon = \sqrt{ve/m}$$

Now on putting the value of **υ** obtained as above in de- Broglie's equation –

$$\lambda = \frac{h}{mv}$$

We get, $\lambda = \frac{h}{\sqrt{\frac{2ve}{m}}}$

On putting the value of h = 6.624x10^{-34} Js, e = 1.602 × 10^{-31} kg, the above equation becomes

$$\lambda = \frac{12.26}{\sqrt{V\ volts}}\ A^{0\circ} \text{ (de- Broglie's equation)}$$

If a potential difference of 10 volts is applied the wavelength **λ** of the e^- wave emerging out would be equal to 3.877 A^0. Similarly, if the potential difference is varied between 10 and 10000 volts, **λ**would vary between 3.877 A^0 and 0.1226 A^0. It is well-known that X- Rays have the wavelength in this range.

9.9 HEISENBERG'S UNCERTAINTY PRINCIPLES

According to this principle it is not possible to determine simultaneously and precisely both the position and momentum (or velocity) of a microscopic moving particle like electron, proton etc. Thus from the above discussion Heisenberg gives a mathematical treatment which can be expressed as:

$$\boxed{\Delta x\ X \Delta p \geq \frac{h}{4\,\pi}} \ldots\ldots.(1)$$

Where Δx = uncertainty position, Δp = uncertainty momentum and h = Planck's constant, the sign≥ means that the product of Δx and Δp is equal and greater than $\frac{h}{4\,\pi}$ but never less than$\frac{h}{4\,\pi}$.

The above equation shows Δx andΔp is inversely proportional to each other which means thatΔx is very small,Δp would be large.

Similarly if an attempt is made to measure the momentum (velocity) of the particle exactly, the uncertainty in the measurement of its position becomes large.

So the equation (1) can be written as:

$$\Delta x\ X \Delta p = \frac{h}{4\,\pi} \ldots\ldots.(2)$$

We know that, Δp = m X Δv;

Where m = mass of moving particle,

Δ v = change in velocity

The equation (2) is also written as

$$\Delta x \text{ X } m \text{ X } \Delta v = \frac{h}{4\,\pi}$$

$$\Delta x \text{ X } \Delta v = \frac{h}{4\,\pi m}$$

9.10 SCHRODINGER WAVE EQUATION (WITH DERIVATION)

In quantum mechanics, the Schrödinger equation is a mathematical equation that describes the changes over time of a physical system in which quantum effects, such as wave–particle duality, are significant. The equation is a mathematical formulation for studying quantum mechanical systems. It is considered as central result in the study of quantum systems and its derivation was a significant landmark in developing the theory of quantum mechanics. It was named after Erwin Schrödinger, who derived the equation in 1925 and published it in 1926, forming the basis for his work that resulted in Schrödinger being awarded the Nobel Prize in Physics in 1933. The equation is a type of differential equation known as a wave-equation, which serves as a mathematical model of the movement of waves.

The equation can be given as:

$$\frac{\delta^2\,\varphi}{\delta x^2}+\frac{\delta^2\,\varphi}{\delta y^2}+\frac{\delta^2\,\varphi}{\delta z^2})\frac{8\pi^2 m}{h^2}\,(E-V)\varphi=0$$

$$\left(\frac{\delta^2}{\delta x^2}+\frac{\delta^2}{\delta y^2}+\frac{\delta^2}{\delta z^2}\right)\varphi\ \frac{8\pi^2 m}{h^2}\,(E-V)\varphi=0$$

$$\boldsymbol{\nabla^2\,\varphi+\frac{8\pi^2 m}{h^2}\,(E-V)\varphi=0}$$

Where ∇ = Laplacian operator

φ = Wave function which gives the amplitude of wave around the nucleus of any point

m = Mass of particle

Derivation of the Schrodinger wave equation:

According to wave length relationship de- Broglie

$$\lambda=\frac{h}{mu}\ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

Let us consider the wave equation of the stationary wave associated with the particle in term of the certain Cartesian axis at any time can be given as:

$$\varphi = \varphi^0 \ Sin \ 2\pi\vartheta t \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Since the differential wave equation of motion can be written in classical way as follow-

$$\frac{\delta^2 \varphi}{\delta t^2} = u^2 \left(\frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2}\right)\varphi$$

$$\frac{\delta^2 \varphi}{\delta t^2} = u^2 \ \nabla^2\varphi \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (3)$$

Now differentiating equation (2) with respect to‘t’

$$\frac{\delta \ \ \varphi}{\delta t} = \varphi^0 Cos \ 2\pi\vartheta t . 2\pi\vartheta$$

We know that $\frac{\delta}{\delta t} \ Sin \ x \ = Cos \ x = \ -Sin \ x$

$$\frac{\delta \ \ \varphi}{\delta t} = -\varphi^0 2\pi\vartheta . Cos \ 2\pi\vartheta t \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (4)$$

Double differentiating of equation (4),

$$\frac{\delta^2 \varphi}{\delta t^2} = \ -\varphi^0 2\pi\vartheta \ Sin 2\pi\vartheta t . 2\pi\vartheta$$

$$\frac{\delta^2 \varphi}{\delta t^2} = \ -\varphi^0 4\pi^2 \vartheta^2 . Sin 2\pi\vartheta t$$

From equation (2)$\varphi = \varphi^0 Sin 2\pi\vartheta t$, on putting the value of $\varphi^0 2\pi Sin 2\pi\vartheta t = \lambda$i in equation (2)

$$\frac{\delta^2 \varphi}{\delta t^2} = \ -4\pi^2\vartheta^2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (5)$$

$$\vartheta = \frac{v}{\lambda} \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (6)$$

Putting the value of ϑ equation (5)

$$\frac{\delta^2 \varphi}{\delta t^2} = \ -\frac{4\pi^2 \vartheta^2}{\lambda^2}\varphi \ \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (7)$$

Equating the equation (3) and (7)

$$u^2 \ \nabla^2\varphi = \ -\frac{4\pi^2 u^2}{\lambda^2}\varphi$$

$$\nabla^2\varphi = \ -\frac{4\pi^2}{\lambda^2}\varphi \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Now putting the value of equation (1) to (8)

$$\nabla^2\varphi = -\frac{4\pi^2 m^2u^2}{h^2}\varphi \text{.........................(9)}$$

We know that, $E = KE + V$

$$E = \frac{1}{2}m\vartheta^2 + V$$

$$(E - V) = \frac{1}{2}m\vartheta^2$$

$$2(E - V) = m\vartheta^2$$

Multiplying by m on both side,

$$2m(E - V) = m^2\vartheta^2 \text{......................(10)}$$

Putting the value of $m^2\vartheta^2$ in equation (9)

$$\nabla^2\varphi = -\frac{4\pi^2\, 2m\,(E - V)}{h^2}\,\varphi$$

$$\boxed{\boldsymbol{\nabla^2\,\varphi + \frac{8\pi^2 m}{h^2}\,(E - V)\varphi = 0}}\textbf{.............. (11)}$$

Equation (11) is known as time independent wave equation of Schrodinger.

9.11 PHYSICAL INTERPRETATION OF THE WAVE FUNCTION

In Schrodinger's wave equation, wave function φ represents the amplitude of the spherical wave. According to the theory of propagation of light and sound waves, the square of the amplitude of the wave is proportional to the intensity of sound and light. A similar concept, modified to meet the requirement of uncertainty principle, has been developed for the physical interpretation of wave function φ.

This may be stated as the probability of finding an electron around the nucleus. It is proportional to the square of the function φ^2 at that point. If wave function φ is imaginary, φ φ* become a real quantity where φ* is complex conjugate of φ. This quantity represents the probability φ^2 as a function of x, y and z coordinate of the system, and it varies from one space region to another. Thus, the probability of finding an electron around the nucleus is different in different region.

In Schrodinger wave equation, the symbol φ represents the amplitude of the spherical wave. For hydrogen atom, Schrodinger wave equation gives the wave function of the electron situated at a particular distance ‘r’, so that:

$$\varphi = C_1 e - C_2 r$$

Where, C_1 and C_2 are constants. The square of the amplitude (φ^2) is proportional to the density of the wave. The wave of energy or the cloud of negative charge is denser in some part than others. Max Born proposed the wave equation on the basis of probabilities. The space characteristic of an electron is best described in term of distribution function given by,

$$D = 4\pi^2 \varphi 2$$

The numerical value of ‘D’ denotes the probability or chance of finding the electron in a shell of radius r and thickness dr, or volume $4\pi r^2\, dr$.

9.12 OPERATOR

Operators are commonly used to perform a specific mathematical operation on another function. The operation can be to take the derivative with respect to a particular term, or to multiply, divide, add or subtract a number or term with regard to the initial function. Operators are commonly used in physics, mathematics and chemistry, often to simplify complicated equations such as the Hamiltonian operator, used to solve the Schrödinger equation.The result of an operator on a function gives another function.

(Operator) x (Function) = Another function

9.12.1 Hamiltonian Operator:

From the fundamental wave equation of Schrodinger:

$$\nabla^2\varphi + \frac{8\pi^2 m}{h^2}(E - V)\varphi = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (1)$$

The potential energy $v = \frac{q_1\ q_2}{r}$

$$v = \frac{e-(-e)}{r} = -e^2/r$$

Putting the value of v in equation 1-

$$\nabla^2\varphi + \frac{8\pi^2 m}{h^2}\left(E - \frac{e^2}{r}\right)\varphi = 0$$

$$\nabla^2\varphi + \frac{8\pi^2 m}{h^2}E\varphi + \frac{e^2\varphi}{r} = 0$$

$$E\varphi + \frac{e^2\varphi}{r} = -\nabla^2\varphi \, X \, \frac{h^2}{8\pi^2 m}$$

$$E\varphi = -\nabla^2\varphi \, X \, \frac{h^2}{8\pi^2 m} - \frac{e^2\varphi}{r}$$

$$E\varphi = (-\nabla^2 \frac{h^2}{8\pi^2 m} - \frac{e^2}{r})\varphi$$

We know that,

$$(-\nabla^2 \frac{h^2}{8\pi^2 m} - + \frac{e^2}{r})\varphi = H\varphi$$

Since,

$$\boxed{\boldsymbol{E\varphi = H\varphi}}$$

Where, Hφ is called as Hamiltonian operator. In this equation, φ is called Eigenfunction and E is called Eigenvalue.Such an equation is, therefore, called Eigenvalue equation. Thus for Schrodinger wave equation, we can write as given:

(Energy operator) x (wave function) = (energy) x (wave function)

9.12.2 Laplacian operator:

This is a very common operator used in quantum mechanism. It is represented by $\nabla^2$and is defined as:

$$\nabla^2 = \frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2}$$

Schrodinger wave equation;

$$\frac{\delta^2\varphi}{\delta x^2} + \frac{\delta^2\varphi}{\delta y^2} + \frac{\delta^2\varphi}{\delta z^2} + \frac{8\pi^2 m(E - V)}{h^2}\varphi = 0$$

The above equation may also write as:

$$\boxed{\boldsymbol{\nabla^2\varphi + \frac{8\pi^2 m(E - V)}{h^2}\varphi = 0}}$$

9.13 POSTULATES OF QUANTUM MECHANICS

The postulates of quantum mechanism which can generate the derivation of Schrodinger wave equation are given as:

1.The state of a quantum mechanical system is completely specified by a function ψ (r,t) that depends on the coordinates of the particles and time. This function, called the wave function or state function, has the important property thatψ^*(r,t) ψ(r,t) dtis the probability that the particle lies in the volume element dt located at r at time t.

The wave function must satisfy certain mathematical conditions because of this probabilistic interpretation. For the case of a single particle, the probability of finding it somewhere is 1, so that we have the normalization condition

$$\int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)\, d\tau = 1$$

It is customary to also normalize many particle wave functions to 1. The wave function must also be single valued, continuous, and finite.

2. To each observable quantity in classical mechanics, like position, velocity, momentum, energy etc., there is a corresponding certain mathematical operator in quantum mechanics, the nature of which depends upon the classical expression for the observable quantity. Some common operators occurring in quantum mechanics are collected in given Table 1.

Table 1: Physical observables and their corresponding quantum operators

Observable Name	**Observable Symbol**	**Operator Symbol**	**Operator operation**
Position	R	$\hat{\mathbf{r}}$	Multiply by r
Momentum	P	$\hat{\mathrm{p}}$	$-i\hbar\left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	T	$\hat{T}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	V(r)	$\hat{V}(\mathbf{r})$	Multiply by V(r)
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\mathbf{r})$
Angular momentum	l_x	$\hat{l}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	l_y	$\hat{l}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	l_z	$\hat{l}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

3. If ψ is a well-behaved function for the given state of a system and A is a suitable operator for the observable quantity, then the operation on ψ by the operator A gives ψ multiplied by a constant value of the observable property i.e.,

$$\hat{A}\Psi = a\Psi$$

This postulate covers the central point of quantum mechanics, the values of dynamical variables can be quantized (although it is still possible to have a continuum of Eigenvalues in the case of unbound states). If the system is in an eigenstate of Â with Eigen value **a**, then any measurement of the quantity (A) will yield (a).

4. If a system is in a state described by a normalized wave function ψ, then the average value of the observable corresponding to Â is given by-

$$< A >= \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau$$

5. The wave function or state function of a system evolves in time according to the time dependent Schrödinger equation-

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi}{\partial t}$$

6. The total wave function must be antisymmetric with respect to the interchange of all coordinates of one fermion with those of another. Electronic spin must be included in this set of coordinates.

9.14 SCHRODINGER WAVE EQUATION FOR HYDROGEN LIKE ATOM

We know that in case of Hydrogen atom, one proton, one electron, and the electrostatic (Coulomb) potential that holds them together. The potential energy in this case is simply;

$$V = -\frac{e^2}{4\pi\varepsilon_0 r}$$

This is the attractive potential between charges of +e and -e separated by a distance r.

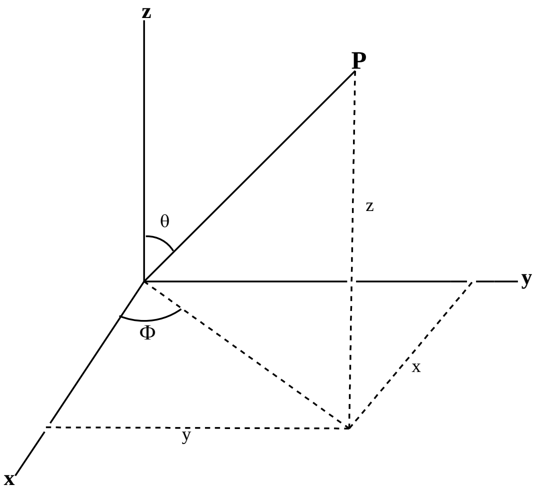

Fig3: spherical polar coordinates, r is the length of the radius vector from the origin to a point (xyz)

(a) Wave equation in Cartesians coordinates (x, y, z):

On putting $V = -\frac{e^2}{r}$in Schrodinger wave equation, we get:

$$\left(\frac{\delta}{\delta x^2}+\frac{\delta}{\delta y^2}+\frac{\delta}{\delta z^2}\right)\varphi \; \frac{8\pi^2 m}{h^2}\;(E+\frac{e^2}{r})\varphi = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

This is Schrodinger wave equation for H atom in Cartesian coordinates (x, y, z). In this equation the wave function ψ is a function of x, y and z.

(b) Wave equation in polar coordinates (r, θ, ϕ):

When three Cartesians coordinates (x, y, z) appearing in equation (1) are converted in to polar coordinates (r, θ, ϕ) with the help of relations z = r cos θ, y = r sin θ sin ϕ and x = r sin θ cos ϕ, equation (1) gets converted in to given equation (2) which is Schrodinger wave equation for H atom in polar coordinates.

$$\left[\frac{\delta}{\delta r}\left(r^2\frac{\delta}{\delta r}\right)+\frac{1}{sin\theta}\frac{\delta}{\delta\theta}\left(sin\theta\frac{\delta}{\delta\theta}\right)+\frac{1}{sin^2\theta}\frac{\delta^2}{\delta\phi^2}\right]\varphi+\frac{8\pi^2 mr^2}{h^2}\left(E+\frac{e^2}{r}\right)\varphi = 0 \ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

In equation (2) φ is a function of polar coordinates (r, θ, ϕ) instead of Cartesians coordinates (x, y, z).

Solution of Schrodinger wave equation for H- atom:

In the above Schrodinger wave equation for H -atom in polar coordinates is written as:

$$\left[\frac{\delta}{\delta r}\left(r^2\frac{\delta}{\delta r}\right)+\frac{1}{sin\theta}\frac{\delta}{\delta\theta}\left(sin\theta\frac{\delta}{\delta\theta}\right)+\frac{1}{sin^2\theta}\frac{\delta^2}{\delta\phi^2}\right]\varphi+\frac{8\pi^2 mr^2}{h^2}\left(E+\frac{e^2}{r}\right)\varphi = 0 \ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

The value of ψ appearing in the above equation can be made only when ψ is written in the form-

$$\Psi(r, \theta, \phi) = R(r)\,\Theta(\theta)\,\Phi(\phi) \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \text{(2)}$$

In the equation (2), R(r) is a function which depends on r only but is independent of the other two polar coordinates *viz*., θ and ϕ. Θ (θ) is a function which depends on θ and is independent of r and ϕ. Same way Φ (ϕ) is a function which is dependent on ϕ only but is independent of r and θ.

In the above equation (2), the function R(r) is called radial wave function while the other two wave functions viz., Θ (θ) and Φ (ϕ) are called angular wave function. Ψ(r, θ, ϕ) is called complete or total wave function.

When we assume Ψ(r, θ, ϕ) equal to R(r) Θ (θ) Φ (ϕ) in equation (1), this equation is converted in to a complicated equation. This equation is divided into following three equations which are given below.

(a)

$$\frac{1}{R}\cdot\frac{\delta}{\delta r}\left(r^2\frac{\delta R}{\delta r}\right)+\frac{8\pi^2 m r^2}{h^2}\left(E+\frac{e^2}{r}\right)=l\,(l+1)$$

The above equation is a function of r only and on solution gives the value of R(r). When this equation is solved for R(r), we get many values of R(r). The value of R(r) beside dependingon r also depends on two constants *n* and *l*. R(r) is, therefore, generally written as $R_{n,\,l}(r)$, n and l are called quantum numbers since they represent the quantization of definite physical properties about the electron in the atom.

The values of radial wave function, $R_{n,\,l}$for 1s, 2s and 2p states for hydrogen atom are given below:

For 1s state (n = 1, l = 0), $R_{1,0}$ or $R_{1s} = [Z/a_0]^{3/2}\ e^{-\sigma/2}$

For 2s state (n = 2, l = 0), $R_{2,0}$ or $R_{2s} = 2^{-3/2}\ [Z/a_0]^{3/2}\ (2-\sigma)\ e^{-\sigma/2}$

For 2p state (n = 2, l = 1), $R_{2,1}$ or $R_{2p} = 2^{-1} \times 6^{-1/2}\ [Z/a_0]^{3/2}\ \sigma \times e^{-\sigma/2}$

Where, a_0 = Bohr's radius, Z = atomic number and $\sigma = Zr/n\,a_0$

(b) $$\frac{\sin\theta}{\Theta}\frac{\delta}{\delta\theta}\left(sin\theta\ \frac{\delta\Theta}{\delta\theta}\right)+\ l(l+1)sin^2\theta=m^2$$

This equation is a function of Θ only and on solution gives the value of Θ (θ). When this equation is solved for Θ (θ), we get many values of Θ (θ). Each value of Θ (θ) beside depending on the angle θ, also depends on two constant *l* and *m*. Θ (θ) is, therefore, generally represented as $\Theta_{l,\,m}$ (θ). The value of *m* depends on the value of *l*. For a given value of *l, m* =

0, ± 1, ± 2….. ± *l*. Thus, m has (2*l* + 1) values for a given value of *l*, m is called magnetic quantum number.

If the values of *l* and *m* are known for a given orbital, the value of the angular wave function, $\Theta_{l,\,m}$ for that orbital can be written as given below:

(i) $\Theta_{0,0}(l = 0, m = 0) \; = \frac{1}{\sqrt{2}}(s - orbitals)$

(ii) $\Theta_{1,0}(l = 1, m = 0) \; = \sqrt{\frac{3}{2}}\cos\theta;\; \Theta_{1,\pm1}\; (l = 1, m = \pm1) = \sqrt{\frac{3}{2}}sin\theta \;\; (p - orbitals)$

$$\Theta_{2,0}(l = 2, m = 0) \; = \sqrt{\frac{5}{8}}(3\,cos^2\theta - 1$$

(iii) $\Theta_{2,\pm1}(l = 2, m = \pm1) \; = \sqrt{\frac{15}{4}}(sin\theta\; cos\theta)$ (d -orbitals)

$$\Theta_{2,\pm2}(l = 2, m = \pm2) \; = \sqrt{\frac{15}{16}}sin^2\theta$$

(c)$\frac{1}{\Phi}.\frac{\delta^2\Phi}{\delta\emptyset^2} = m^2$

This equation is a function of m only and on solution gives the value of Φ (∅), we get many values of Φ (∅). Each value of Φ (∅) depending on angle ∅ and also depends on the constant *m*. Hence the angular wave function Φ (∅) is also represented as $\Phi_m(\emptyset)$ or Φ_m.

9.15 INTERPRETATION OF QUANTUM NUMBERS

The three quantum numbers which arise in a natural way during search of acceptable solution of the Schrodinger wave equation may be express as follow:

n =1, 2, 3, …………..

l = 0, 1, 2,…………...

m_1 = 0, ±1, ±2……….., ±*l*

We can interpret these quantum numbers in the following way:

To interpret *n*, we note that according to the Schrodinger's theory of uni-electronic species, the total energy of the bound states of the atom can have only following values:

$$E_n = -\frac{2\pi^2 \mu Z^2 e^4}{n^2 h^2}$$

These Eigen values depend only on the quantum number n, are the same as obtained by old quantum theory. They are in excellent agreement with experiment. Thus n quantizes the total energy of the atom. Hence n is called the total or principal quantum number.

To explain *l, we consider the radial wave equation*

$$\frac{1}{R} \cdot \frac{\delta}{\delta r}\left(r^2 \frac{\delta R}{\delta r}\right) + \frac{8\pi^2 m r^2}{h^2}\left(E + \frac{e^2}{r}\right) = l\,(l+1)$$

$$\frac{1}{r^2} \cdot \frac{\delta}{\delta r}\left(r^2 \frac{\delta R}{\delta r}\right) + \left[\frac{8\pi^2 m}{h^2}\big(E + V(r)\big) - \frac{l(l+1)}{r^2}\right] R = 0$$

The total energy E of the atom consist of the kinetic energy K and potential energy V of its electron. The kinetic energy K has two parts K_{radial}due to electron motion towards or away from the nucleus and $K_{orbital}$ due to the motion around the nucleus. Thus

$$E = K_{radial} + K_{orbital} + V\,(r)$$

Putting the value of E in the radial equation, we obtained,

$$\frac{1}{r^2} \cdot \frac{\delta}{\delta r}\left(r^2 \frac{\delta R}{\delta r}\right) + \left[\frac{8\pi^2 m}{h^2}\left(E_{radial} + K_{orbital} - \frac{h^2}{8\pi^2 \mu}\frac{l(l+1)}{r^2}\right)\right] R = 0$$

This radial equation is concerned only with the radial motion of the electron, hence it must be free from$K_{orbital}$. This is possible only when the last two terms cancel out each other, i.e when

$$K_{orbital} = \frac{h^2}{8\pi^2 \mu}\frac{l(l+1)}{r^2}$$

Since the quantum number *l* is restricted to the values 0, 1, 2,……..(*n*-1), the electron can have only discrete values of the angular momentum. Thus like total energy E, the orbital angular momentum is also quantized and this quantization is described by *l*. Hence *l* called the orbital quantum number. The representation for the angular momentum is identical to that obtained in Bohr-Somerfield theory.

The interpretation of m_1 comes when the atom is placed in an external magnetic field. We know that an electron revolving around the nucleus is a minute counter loop and behave like a magnetic dipole in an external magnetic field. Its magnetic moment and its potential energy depend upon the magnetic moment and its orientation with respect to the field. But the magnitude and direction of the magnetic moment depends upon the magnitude and direction of the angular momentum of the electron which, therefore, determine the magnetic potential energy. As we see that the direction of the angular momentum is quantized with respect to an external magnetic field. If the field is along the z-axis, the component of angular momentum in this direction is:

$$l_z = m_l \frac{h}{2\pi}$$

Where m_1 are the values 0, ±1, ±2,…….±*l*. Thus, m_1 describe the quantization of the orientation of angular momentum in a magnetic field and hence the quantization of the magnetic energy of the electron. Hence m_1 is called the magnetic quantum number.

Thus each of the eignfunctions of one electron atom is specified by three quantum numbers *n*, *l* and m_l; in which *n* determines the total energy, *l* determine the angular momentum and m_l determine the z- component of the angular momentum of the electron. But for a given value of *n*, there are various possible values of *l* and m_l.

9.16 SUMMARY

In this chapter the historical development of quantum mechanics has been discussed several effects like photoelectric, Compton, black body radiation, Heisenberg Uncertainty principle. The postulates of quantum mechanics along with the basic terms involved are also discussed. The Schrödinger’s wave equation has been derivedand the properties and its physical significance also are given indetail. Schrodinger wave equation has been applied to several simple systems andalso being solved to get wave function and the respective energy values. The quantum numbersare also described.

9.17 TERMINAL QUESTIONS

1. What is black body? Discuss the energy distribution for black body radiation at different temperatures.

2. Discuss photoelectric effect.
3. What do you understand by de Broglie hypothesis?
4. State and explain Heisenberg's uncertainly principle. Derive the equation forit. Write its applications also.
5. Discuss Compton Effect. Write its physical significance.
6. What are operators? Discuss the algebra of operators.
7. Write a brief note on physical significance of ψ and ψ^2.
8. Write the Schrödinger wave equation for hydrogen atom in spherical polarcoordinates.Separate the variables of this equation to expression forindividual one.
9. How do the three quantum numbers follow from the solution of Schrodinger wave equation?
10. Derive the Plank's radiation law. How can it be verified experimentally?
11. Explain briefly de-Broglie hypothesis related to the dual nature of matter. Derive de-Broglie wave equation.
12. What are the main postulates of Bohr's atomic model?
13. State and explain Heisenberg's Uncertainty principle.
14. What is an operator? Give the types of operators.
15. Write a short note on:
    a) Compton effect
    b) Black body radiation
    c) Wien's Displacement law
    d) Photoelectric effect
    e) Heisenberg's Uncertainty principle

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UNIT 10: PHOTOCHEMISTRY

CONTENT

10.1 INTRODUCTION

Photochemistry is the branch of chemistry that deals with the chemical effects of light. It focuses on reactions and processes that occur when molecules absorb photons and transition to electronically excited states. These excited molecules often exhibit unique reactivity that is fundamentally different from their ground-state behaviour, enabling a wide range of chemical transformations that cannot be achieved through thermal processes alone.

At the core of photochemistry lies the interaction between electromagnetic radiation (typically ultraviolet or visible light) and matter. When a molecule absorbs light, it gains energy and transitions from its ground electronic state (S_0) to a higher excited singlet (S_1, S_2, …)or triplet (T_1)state. These excited states can undergo various pathways such as fluorescence, phosphorescence, internal conversion, intersystem crossing, or chemical reactions like bond breaking, rearrangement, or redox processes.

Two fundamental principles govern photochemistry:

1. **The Grotthuss–Draper law**, which states that only absorbed light can initiate a photochemical change.

2. **The Stark–Einstein law**, which establishes that each absorbed photon can activate one molecule, defining the basis for quantum yield.

Photochemical reactions are often highly selective, can proceed under mild conditions, and provide routes to green and energy-efficient chemical synthesis. This makes photochemistry essential in diverse fields such as:

- Photosynthesis in biology,
- Photodynamic therapy in medicine,
- Solar energy conversion and photo catalysis in environmental science,
- And photo polymerization in materials chemistry.

With growing interest in sustainable chemistry and light-driven technologies, photochemistry plays a pivotal role in modern science and innovation. This chapter will explore the principles, processes, mechanisms, and applications of photochemical reactions, providing a comprehensive foundation for further study and research.

10.2 OBJECTIVES

The objective of this chapter is to develop a fundamental and applied understanding of photochemistry, which explores the interaction between light and matter and the resulting chemical transformations. Specifically, this chapter aims to:

1. Introduce the principles of photochemistry, including the nature of electromagnetic radiation and how molecules absorb light to reach excited electronic states.
2. Explain the laws of photochemistry, such as the Grotthuss–Draper Law and the Stark–Einstein Law, which govern photon absorption and molecular excitation.
3. Describe photophysical processes including fluorescence, phosphorescence, internal conversion, and intersystem crossing using tools like the Jablonski diagram.
4. Define and interpret quantum yield, and explain its significance in measuring the efficiency of photochemical processes.

10.3 DIFFERENCE BETWEEN THERMAL AND PHOTOCHEMICAL PROCESSES:

Feature	Thermal Process	Photochemical Process
Initiation Energy Source	Supplied as heat (thermal energy)	Supplied as light (photons, usually UV or visible)
Mechanism	Molecules gain kinetic energy; reactions occur when thermal energy overcomes the activation energy barrier	Molecules absorb photons and get excited to higher electronic states, initiating reactions
Activation	Follows Arrhenius equation: Rate $\propto \exp(-Ea/RT)$	Depends on absorption of photons (quantized energy: $E = h\nu$)
Reaction Conditions	Requires high temperatures (often hundreds of °C)	Can proceed at room temperature or lower under appropriate light source
Type of Reactions	Mostly ground-state reactions	Involves excited-state species (e.g., singlet or triplet states)
Selectivity	Often less selective; side reactions common at high T	Often more selective, depending on wavelength and molecular absorption

Feature	Thermal Process	Photochemical Process
Energy Efficiency	Thermal energy may heat entire system—often less efficient	Photons target specific transitions—can be energy-efficient if well-tuned
Examples	Combustion, decomposition of $CaCO_3$ to CaO and CO_2, Haber process	Photosynthesis, photopolymerization, Photochemical smog formation, Photo chlorination of methane
Quantum Yield	Not defined (energy supplied continuously)	Quantum yield important: number of molecules reacted per photon absorbed
Intermediate Species	Typically thermal intermediates (ions, radicals)	Often involves radicals or excited states formed by photon absorption

Table 10.1

10.4 LAWS OF PHOTOCHEMISTRY:

Photochemistry deals with chemical reactions initiated by absorption of light**.** Two foundational laws govern the principles of how light energy initiates chemical change:

10.4.1 Grotthuss–Draper law (First Law of Photochemistry) :

Statement:

"Only the light that is absorbed by a substance can cause a photochemical change."

Implications:

- Light that is reflected or **t**ransmitted cannot induce photochemical reactions.
- Absorption of light is the first necessary condition for a photochemical reaction.
- The efficiency of a photochemical process depends on how well the reacting molecules absorb photons at specific wavelengths.

When light falls on a body, a part of it is reflected, a part of it is transmitted and the rest of it absorbed. It is only the absorbed light which is reflective is bringing about a chemical reaction.

This law, however does not imply that the absorbed light must always result into chemical reactions. The absorbed light may simply bring about phenomena such as fluorescence, phosphorescence etc. Similarly the absorbed light energy e.g. in case of potassium permanganate solution, the light energy is absorbed strongly but no chemical product is produced.

Example: In photosynthesis, only the chlorophyll-absorbed wavelengths (like red and blue light) contribute to the reaction—green light is mostly reflected and hence not effective**.**

10.4.2. Stark–Einstein Law(Second Law of Photochemistry or Law of Photochemical Equivalence)

Statement:

"For each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction."

Mathematically:

One mole of photons (1 Einstein) → activates one mole of molecules (ideally)

Implications:

- This law establishes a 1:1 stoichiometric relationship between the number of absorbed photons and the number of molecules undergoing reaction**,** in the primary photochemical step**.**
- It applies mainly to the primary quantum event (e.g., excitation or bond cleavage), not necessarily to the overall yield of the reaction.

If v is the frequency of the absorbed radiation, then energy absorbed by each reacting atom or molecule is one quantum i.e. hv where h is Plank's constant. The energy absorbed by one mole of the reacting molecule is given by

The energy absorbed by one mole of the reacting molecule is given by

$$E=Nhv \qquad \text{……..}(i)$$

Where N is the Avogadro's number Putting $v = \frac{c}{\lambda}$,

we can write, $$E=Nh\frac{c}{\lambda} \qquad \text{…………..}(ii)$$

Where c is the velocity of light and λ is the wave length of the absorbed radiation.

The energy possessed by one mole of photons or the energy absorbed by one mole of the reacting molecule is called one Einstein.

10.4.3 Summary Table:

Law	Name	Key Concept	Condition

Law	Name	Key Concept	Condition
1st Law	Grotthuss–Draper Law	Only absorbed light can initiate a reaction	Absorption of light is essential
2nd Law	Stark–Einstein Law	One photon → one molecule excited (per quantum event)	Based on quantum theory

10.5 JABLONSIKI DIAGRAM

The Jablonski Diagram is a graphical representation that illustrates the electronic states of a molecule and the transitions between them due to absorption**,** emission, and non-radiative processes**.**

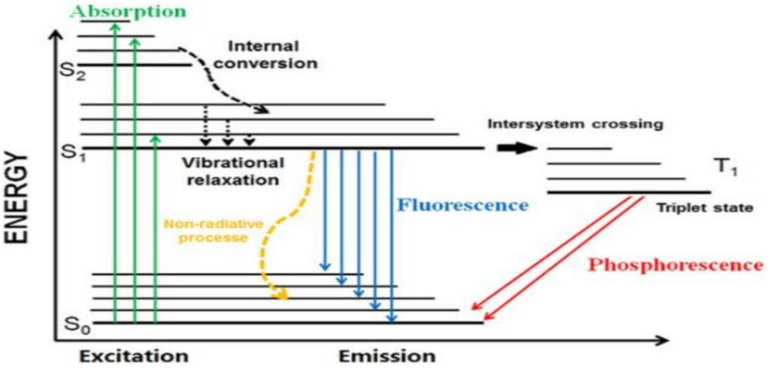

Figure 10.1 Joblonski Energy diagram

Axes of the Jablonski Diagram

- **Y-axis**: Energy (Increasing upward)
- **X-axis**: Not quantitative—Just separates states/processes visually

Electronic States

- **S_0**: Ground singlet electronic state (all electrons paired)
- **S_1, S_2**: Excited singlet states (short-lived, electrons still paired)
- **T_1**: First excited triplet state (electrons unpaired with parallel spins)

10.5.1 Key Photo-physical and Photochemical Processes

Process	Description	Type

Process	Description	Type
Absorption	Molecule absorbs a photon and is excited from S_0 to S_1 or S_2	Radiative
Internal Conversion (IC)	Non-radiative transition between singlet states (e.g., $S_2 \rightarrow S_1$)	Non-radiative
Fluorescence	Emission of a photon from $S_1 \rightarrow S_0$	Radiative (fast, 10^{-9} to 10^{-7} s)
Intersystem Crossing (ISC)	Transition from singlet to triplet state ($S_1 \rightarrow T_1$)	Non-radiative spin-forbidden, but possible
Phosphorescence	Emission of a photon from $T_1 \rightarrow S_0$	Radiative (slow,$10^{-3}$to seconds)
Vibrational Relaxation (VR)	Loss of vibrational energy within an electronic state	Non-radiative

Important Points

- Fluorescence occurs within nanoseconds and stops almost immediately after the light source is removed.
- Phosphorescence occurs much later and can be seen even after the excitation source is removed.
- Intersystem crossing (ISC) is more efficient in molecules with heavy atoms or aromatic rings.

10.6 FLUORESCENCE

There are certain substance which when exposed to light or certain radiations absorb and then immediately or instantaneously start re-emitting the energy. Such substances are called fluorescent. Obviously the absorption of energy results into the excitation of the electrons followed immediately by the jumping back of the excited electrons to the lower level. As a result, the absorbed energy is emitted back.

Fluorescence starts as soon as the substance is exposed to light and the fluorescence stop as soon as the light is cut off.

10.6.1 Mechanism:

- A molecule absorbs light and is promoted from the ground state (S_0) to an excited singlet state (S_1).
- After brief vibrational relaxation to the lowest vibrational level of S_1, it returns to the ground state S_0 by emitting a photon.
- This emission is spin-allowed, so it happens very quickly—typically within10^{-9} to 10^{-7} seconds.

Key Features:

- Short-lived, stops immediately after the light source is removed.
- The emitted light is usually of longer wavelength (lower energy) than the absorbed light (this is called the Stokes shift).
- Common in fluorescent dyes, minerals, and biological markers.

10.7. PHOSPHORESCENCE

Definition:

There are certain substances which continues to glow for sometimes even after the external light is cut off. Such substances are called phosphors or phosphorescent substances and the phenomenon is called phosphorescence.

10.7.1 Mechanism:

- A molecule absorbs light and reaches the excited singlet state (S_1).
- It undergoes intersystem crossing (spin change) to a triplet excited state (T_1).
- From T_1, it eventually relaxes back to the singlet ground state (S_0) by emitting a photon, but this triplet-to-singlet transition is spin-forbidden and thus slow.

Key Features:

- Long-lived emission (microseconds to minutes or more).
- Continues after the light source is removed (glow-in-the-dark).
- Often seen in luminous paints, organic crystals, and inorganic phosphors.

10.8 NON-RADIATIVE PROCESSES

These are processes where energy is lost without emitting light. Instead, it is dissipated as heat or transferred to other molecules.

10.8.1Internal Conversion (IC)

Definition:

A non-radiative transition between two electronic states of the same spin multiplicity (e.g., from S_2 to S_1 or from S_1 to S_0).

Mechanism:

- After excitation to a higher excited singlet state (e.g., S_2), the molecule relaxes to a lower excited singlet state (e.g., S_1) without emitting a photon**.**
- Energy is released internally as heatthrough vibrational energy dissipation.

Key Features:

- Very fast (femto seconds to picoseconds).
- Common in systems with closely spaced electronic states**.**
- Competes with fluorescence; more internal conversion → less fluorescence**.**

10.8.2 Intersystem Crossing (ISC)

Definition:

A non-radiative transition between electronic states of differentspin multiplicity, usually from singlet (S_1)totriplet (T_1)**.**

Mechanism:

- Electron undergoes a spin flip during transition.
- Facilitated by spin–orbit coupling**,** more likely in molecules with heavy atoms or certain structural features.

Key Features:

- Slower than IC but still fast (picoseconds to nanoseconds).
- Leads to phosphorescence or non-radioactive decay from T1.
- Competes with fluorescence, quenching it in some cases.

10.8.3 Summary Table

Process	**Type**	**Transition**	**Time Scale**	**Emits Light?**	**Spin Allowed?**
Fluorescence	Radiative	$S_1 \rightarrow S_0$	$10^{-9} – 10^{-7}$ s	Yes	Yes
Phosphorescence	Radiative	$T_1 \rightarrow S_0$	10^{-3} s to minute	Yes	No

Process	**Type**	**Transition**	**Time Scale**	**Emits Light?**	**Spin Allowed?**
Internal Conversion	Non-radiative	$S_2 \rightarrow S_1$ or $S_1 \rightarrow S_0$	10^{-14}–10^{-12} sec	No	Yes
Intersystem Crossing	Non-radiative	$S_1 \rightarrow T_1$	10^{-12}–10^{-9} sec	No (but leads to phosphorescence)	No

10.9 QUANTUM YIELD

Definition:

The quantum yield (Φ) of a photochemical process is the efficiency with which absorbedphotonscause a particular event—such as a chemical reaction, fluorescence, or phosphorescence.

$$\boxed{\Phi = \frac{\text{Number of molecules reacting or undergoing the process}}{\text{Number of photons absorbed}}}$$

Hence quantum efficiency may be defined as the number of moles reacting per Einstein of the light absorbed.

10.9.1 Interpretation:

- **Φ = 1**: Every photon absorbed causes one molecular event — ideal efficiency**.**
- **Φ > 1**: One photon triggers a chain reaction (e.g., radical polymerization, Cl_2–H_2 photoreaction).
- **Φ < 1**: Not all absorbed photons lead to the desired process — due to energy loss**,** non-radiative decay**,** or quenching**.**

10.9.2 Factors Affecting Quantum Yield:

1. Nature of the molecule(structure, electronic configuration)
2. Solvent and temperature
3. Presence of quenchers(e.g., O_2 quenching phosphorescence)
4. Competing processeslike internal conversion or intersystem crossing
5. Light intensity and wavelength

Example:

In the photodissociation of chlorine gas**:**

$$\mathbf{Cl_2 + h\nu \rightarrow 2Cl^{\cdot}}$$

Each Cl radical can initiate further chain reactions with H_2, so the quantum yield can be much greater than 1**.**

10.9.3 Experimental Determination:

Quantum yield is determined by comparing the number of molecules undergoing the process (measured chemically or spectroscopically) to the number of photons absorbed (measured using actinometry or light intensity calibration).

10.9.4 Why is Quantum Yield Important?

- Measures efficiency of photochemical reactions.
- Helps in mechanistic understanding**.**
- Guides design in photodynamic therapy**,** solar energy conversion**,** fluorescence imaging, and photo-catalysis**.**

10.10 PHOTOSENSITIZED REACTIONS

Definition:

A photosensitized reaction is a type of photochemical process in which a photosensitizer absorbs light and then transfers its excitation energy to another molecule (the reactant**),** whichthen undergoes a chemical transformation.

In Short

The photosensitizer initiates a reaction in another substance without itself being consumed.

10.10.1 Mechanism Overview

1. Photosensitizer (Sens) absorbs light:

$$\text{Sens} + h\nu \rightarrow \text{Sens}^*$$

2. Excited photosensitizer transfers energy or electrons:

Energy transfer to a reactant:

$$\text{Sens}^* + \text{Reactant} \rightarrow \text{Reactant}^* + \text{Sens}$$

10.11 SUMMARY

Photochemistry is a vital area of chemistry that explores the chemical and physical changes that occur when molecules absorb light energy**.** Unlike thermal reactions that rely on heat, photochemical processes are initiated by electromagnetic radiation, typically in the ultraviolet (UV) or visible regions of the spectrum. The absorption of photons excites molecules to higher electronic states, leading to a range of unique and highly specific chemical behaviours.

10.11 TERMINAL QUESTIONS

A. Multiple choice questions

1.Which law of photochemistry states that only absorbed light can bring about a chemical change?

a) Stark–Einstein Law b) Planck's Law

c)Grotthuss–Draper Law d) Lambert–Beer Law

2.The unit of quantum yield is:

a)Mole/litre b) Joule/mol

c)It has no unit (dimensionless) d) Watt/second

3.In a Jablonski diagram, which process represents a non-radiative transition between singlet states?

a)Fluorescence b)Phosphorescence

c) Internal Conversion d)Intersystem Crossing

4. The reactions which are caused by heat and in absence of light is called _____

a) Photochemical reactions b) Dark reactions

c) Reversible reaction d) Reversible photochemical reaction

5. Ozone is formed by ______ dissociation of molecular oxygen into individual oxygen atoms.

a) Photochemical b) thermochemical

c) thermal d) Ionic

6. Which of the following are the principle laws of photochemistry?

a) Grothus-Draper and Stark-Einstein law b) Raoult's and Dalton's law

c) Raoult's and Henry's law d) Lambert's and Beer's law

7. In _____ reactions, molecules absorbing light do not themselves react but induce other molecules to react.

a) Photosensitized
b) Thermal
c) Irreversible
d) Dark

8. Which of the following is an example of photochemical reaction?

a) Decomposition of HCl
b) Decomposition of ammonia
c) Formation of NaOH
d) Photosynthesis

9. In photochemical reactions, absorption of _____ radiations takes place.

a) radio
b) ultraviolet and visible
c) only visible
d) visible and x-rays

10. Which of the following is an incorrect statement?

a) Photochemical reactions are caused by absorption of ultraviolet only.

b) When a molecules or atom in the ground state (S_0) absorbs light , one electron is exited to higher orbital level.

c)It is possible for the excited state S1 to undergo spin inversion.

d) First step in photochemistry is excited state (Photoexcitation).

11. Classification of photochemical reaction on the basis of quantum efficiency can be done into ______ categories.

a) 2
b) 3
c) 4
d) 5

12. When two or more molecules are decomposed per photon, the reaction has ______ quantum yield.

a) high
b) low
c) unpredictable
d) variable

13. Which of the following is the condition for high and low quantum yield?

a) The reactivity of the molecules should be temperature dependent

b) All the reactant molecules should be in the different energy state

c) The molecules in the activated state should be largely unstable and decompose to form the products

d) quantum field=1

14. Decomposition of HI has quantum yield _______ .

a) 1
b) 2
c) 0
d) 4

B.Long Questions:

Q.1.Define quantum yield and write its formula.

Q.2.Name two laws of photochemistry and briefly state them.

Q.3.What is the role of a photosensitizer in photochemistry?

Q.4.Describe the Jablonski diagram and explain the photo-physical processes it represents.

Q.5.Describe fluorescence and phosphorescence in detail. What conditions favour each process, and how do they differ in terms of timescale, spin states, and its applications?

Q.6.Write down difference between Thermal and photochemical reaction?

ANSWERS:

1. (c)	**2.(c)**	**3.(c)**	**4.(b)**	**5.(a)**	**6. (a)**	**7.(a)**	**8.(d)**	**9.(b)**
10.(a)	**11.(b)**	**12.(a)**	**13.(c)**	**14.(b)**				

10.12 REFERENCES AND FURTHER STUDIES.

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2. K. K. Rohatgi & R. S. Singh – An Introduction to Photochemistry
3. Peter Atkins & Julio de Paula – Atkins' Physical Chemistry
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UNIT- 11: DILUTE SOLUTION AND COLLIGATIVE PROPERTIES

CONTENTS:

11.1 INTRODUCTION

A homogenous mixture of two or more compounds (chemical species) is known as solution. Homogenous solution whose composition and properties are uniform throughout the mixture are furthersubdivided into real (non-ideal) solutions (particle size: < 1 nm) and colloids (particle size: 1-500 nm). The solutions are of different type but in this chapter, we will discuss only solutions in which solid getsdissolved in liquid. The solid is referred to as the soluteand the liquid as the solvent**.** Generally, the component that is present in the largest quantity is known as solvent. Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called solutes. Solutions form in part because of intermolecular forces. The particles of the solute interact with the particles of the solvent through intermolecular forces like London dispersion force, dipole-dipole interaction, H-bonding and ion-dipole interaction.

For the solvent and solute to mix, we must overcome all of the solute–solute attractive forces or some of the solvent–solvent attractive forces. These processes are endothermic, for example when some compounds, such as NaOH, dissolve in water, a lot of heat is released making container hot. In cases where some of the energy to do this comes from making new solute–solvent attractions, which is exothermic, for example when compounds, such as NH_4NO_3, dissolve in water, heat is absorbed from the surroundings resulting cold container. When the solute-to-solvent attractions are weaker than the sum of the solute-to-solute and solvent-to-solvent attractions, the solution will form whereas the energy difference seems small enough to be overcome by the increase in entropy from mixing.A solute will dissolve in a solvent if it has a similar structure to the solvent i.e. *like dissolve like*. Polar molecules and ionic compounds will be more soluble in polar solvents. Nonpolar molecules will be more soluble in nonpolar solvents.

11.2 OBJECTIVES

At the end of the chapter, we will be able to understand

1. The classification of solutions into ideal and non-ideal behavior
2. Expression of solution concentration like normality, molarity, molality etc
3. Activity and activity coefficient
4. Colligative properties of solution
5. Molecular weight determination by using colligative properties

11.3 IDEAL AND NON-IDEAL SOLUTION

An ideal solution is that which is formed by dissolving such a small amount of the non-volatile solute in the solvent that there is no absorption or evolution of heat. In ideal solutions, the solute–solvent interactions are equal to the sum of the broken solute–solute and solvent–solvent interactions. Any solvent that obeys Raoult’s law and solute that obeys Henry’s law is called an ideal solution (Fig 11.1).

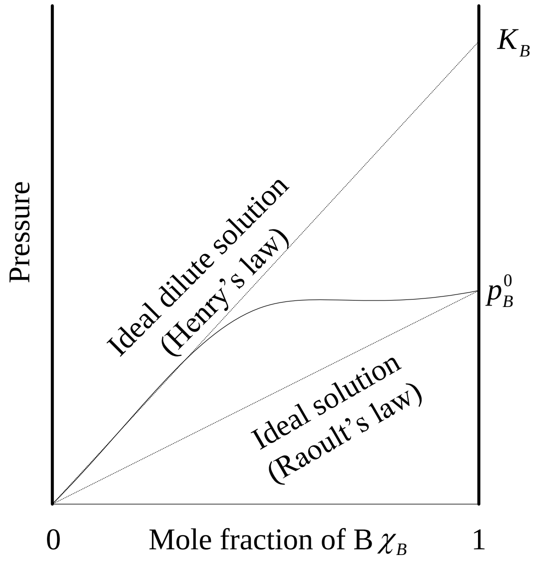

Fig 11.1: Behavior of an ideal solution.

Ideal solutions includespecies of the non-interacting components and very dilute solutions having no electrolyte/ions, e.g. mixtures of similar compounds (benzene + toluene). In other words, there are no energetic interactions between molecules of different species. At constant temperature and pressure, there is ideal entropy of mixingthat contributes to the total entropy, due to the presence of different components. Ideal solutions are valid in the very dilute limit, where there is one major component and the concentrations of all other species are very small. Ideal solution does not form azeotropic mixture (Azeotropes are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature, for example ethanol-water mixture). For ideal solutions, there is no change in volume on mixing and no change in enthalpy, resultingin no internal energy change.

$$\Delta_{mix}V = 0; \Delta_{mix}H = 0$$
$$\Delta_{mix}U = \Delta_{mix}H - P\Delta_{mix}V = 0$$

If the solute–solvent interactions are stronger or weaker than the broken interactions of solute-solute and solvent-solvent, such solution is said to benon-ideal. Any solvent that does not obeys Raoult's law and solute that does not obey Henry's law is called a non-ideal solution. For non-ideal solution, the volume of solution will change after mixing and there is enthalpy change, resulting in internal energy change.

$$\Delta_{mix}V \neq 0; \Delta_{mix}H \neq 0$$
$$\Delta_{mix}U \neq \Delta_{mix}H - P\Delta_{mix}V \neq 0$$

11.4 METHODS OF EXPRESSING CONCENTRATIONS OF SOLUTIONS

Composition of a solution can be described by expressing its concentration. The solution can be expressed either qualitatively or quantitatively. For example, qualitatively low amount of solute is dissolved in a solvent is known as dilute solution. Concentrated solutions are such solutions in which high amount of solute is dissolved in a solvent. These terms will not tell us whether a solution is saturated, unsaturated, or supersaturated. The concentration of solutions may be expressed in the following common sets of units.

1. **Molarity:**The molarity of a solution is the number of moles of solute present in one litre of the solution. It is expressed by 'M'.

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

2. **Molality:** The molality is defined as the number of moles of the solute present in one kg of solvent. It is denoted by 'm'. It does not depend on temperature.

$$\text{Molality}=\frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

3. **Normality:** The normality is the number of equivalents of solute present in one litre of solution. It is expressed by 'N'.

$$\text{Normality}=\frac{\text{Number of equivalent of solute}}{\text{Volume of solution in litre}}$$

4. **Mole fraction:** The ratio of the number of moles of the component (solute or solvent) to the total number of moles of the solution is known as mole fraction of the component. It is represented by 'x'. It is unit less quantity and does not depend on temperature.

$$\text{Mole fraction of component}\left(solute\ or\ solvent\right)=\frac{\text{Number of moles of component}}{\text{Total number of moles of component}}$$

If x_1 and x_2 represent the mole fraction of the solute and solvent respectively, we have,

$$x_1=\frac{n_1}{n_1+n_2}\ and\ x_2=\frac{n_2}{n_1+n_2}$$

It can be given that

$$x_1+x_2=1$$

Where, n_1 and n_2 are the number of moles of the solute and the solvent respectively.

5. **Mole percentage:** Itis the percentage of moles of one component in the total moles of all the components of the solution. It does not depend on temperature.

   Mole %= mole fraction × 100%

6. **Parts per million:** When solute is present in trace amount than concentration is expressed in parts per million (ppm).

$$\text{Parts per million}=\frac{\text{number of parts of the component}}{\text{Total number of parts of the all component of solution}}\times 10^{6}$$

11.5 ACTIVITY AND ACTIVITY COEFFICIENT

Strong interionic electrostatic attraction of ionic concentrations in solution is experimentally observed less than they actually are. The term 'activity' is the apparent value of concentration and effective concentration of ion in solution that can be written as follows,

$$a = \gamma c$$

Where"a" is the activity of the ion and γ is the activity coefficient.

Activities of pure solids/liquids can also be derived by chemical potential. Chemical potential, a partial molar quantity, diffuses from high to low potential.For any non-ideal solution, the chemical potential for the solute (or solvent) is given by

$$\text{Chemical Potential } \equiv \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}$$

$$\mu_i = \mu^o + RT \ln a_i$$

For multi-components:

$$G = f(P,T,n_i)$$

n_i is sum of moles of components

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_j} = \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j}$$

Chemical potential for pure solids and pure liquids

$$0 = RT \ln a_i$$

or $a_i = 1$

The chemical potential of a real gas is written in terms of its fugacity as follows,

$$\mu_J = \mu^o + RT \ln f_i$$

Activity Coefficient

The activity coefficient (γ) relates the activity to the concentration terms of interest. It can be defined as the ratio between effective and actual concentration of the ion in solution. Thus,

$$\gamma = \frac{\text{effective concentration}}{\text{actual concentration}} = \frac{a}{c}$$

The activity coefficient 'γ' is always less than one and it approaches one at infinite dilution.

11.6 DILUTE SOLTIONS

A **dilute solution** refers to a solution in which the concentration of the solute (the substance being dissolved) is low compared to the solvent (the substance doing the dissolving). In simpler terms, it's a solution where only a small amount of solute is present relative to the amount of solvent.

For example, if you dissolve a small amount of sugar in a large amount of water, the sugar-water mixture is considered a dilute solution.

In dilute solutions:

- The solute is less concentrated.
- More solvent is used in comparison to solute.
- The solution appears lighter or less intense in color or taste (depending on the solute).

11.7 COLLIGATIVE PROPERTIES

Colligative properties(Greek *colligatus* = Collected together) are properties whose value depends only on the number of solute particles (invariably taken as non-volatile) contained in a known volume of a given solvent, and do not depend on the identity or nature (i.e. chemical composition or constitution) of the solute. Value of these properties depends on the concentration of the solution. This means that when considering the impact of solute on a colligative property, 1 mole of sugar≡ 1 mole Na^+ ≡ 1 mole O_2^- ≡ 1 mole urea does exactly the same thing. The difference in the value of the property between the solution and the pure substance generally related to the different attractive forces and solute particles occupying solvent molecules positions. The various colligative properties are:

1. Lowering of Vapour Pressure
2. Osmotic Pressure
3. Elevation of Boiling Point
4. Depression of Freezing Point

They are properties of only dilute solutions which are supposed to behave ideal solutions.

11.8 RAOULT'S LAW

Henry's Law: At constant temperature, solubility of a gas in a liquid is directly proportional to the partial pressure of gas present above the solution, OR

At constant temperature, the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

Mathematically,

$$p \propto x \; ; \; p = K_H \, x.$$

Where K_H is Henry's law constant and depends on the nature of the gas. This law is used when solution turns into vapour phase.

Raoult's Law: F. Raoult a French chemist proposed a study of vapour pressures of binary solutions of volatile liquids at a constant temperature and gave a law, which is known as Raoult's Law.

The partial vapour pressure of a volatile solvent above a solution at any temperature is equal to its normal vapour pressure, P°, multiplied by its mole fraction in the solution.

$$P_{\text{solvent in solution}} = \chi_{\text{solvent}} \cdot P^{\circ}$$

Because the mole fraction is always less than one, the vapour pressure of the solvent in solution will always be less than the vapour pressure of the pure solvent.

Suppose a binary solution contain n_A mole of volatile liquid A and n_B moles of a volatile liquid B, if p_A and p_B are partial pressure of two liquids, then, according to Raoult's law,

$$p_A = \chi_A p_A^0 \qquad and \qquad p_B = \chi_B p_B^0$$

In other terms Raoult’s law can be expressed as*the vapour pressure of a liquid in a solution is directly proportional to the mole fraction of that liquid in the solution*.

$$P \propto \chi$$

The law is obeyed perfectly by an *ideal solution*. An ideal solution is a solution of A and B in which the intermolecular forces between A and A molecules, B and B molecules, and A and B molecules are all the same, then, according to Dalton’s law of partial pressure, the total vapour pressure P is given by (Fig 11.2).

$$P_{total} = p_A + p_B = p^\circ_A \chi_A + p^\circ_B \chi_B$$

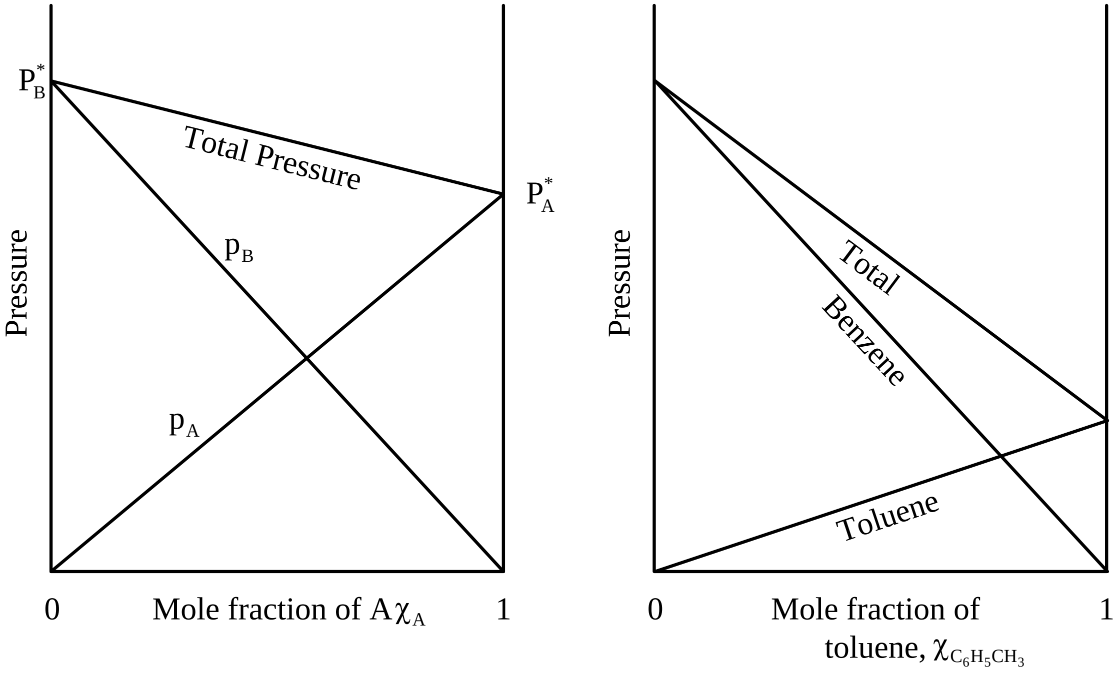

Fig11.2: Raoult's law interpretation

The total vapour pressure and partial vapour pressure of an ideal binary mixture depends on the vapour pressure on mole fractions of the components. For example, benzene and toluene behave almost ideally which follow Raoult’s law over the entire composition range.

Systems that deviate from Raoult’s law

(A) Positive deviation

A system in which mixing is energetically not favorable in liquid phase, so vapour pressure will be higher than expected by Raoult's Law. It can be shown by such system that forms a minimum boiling point azeotrope,i.e. the azeotropic mixture has a boiling point lower than either of the two pure components. Total vapour pressure is greater for an ideal solution. Change in enthalpy and volume of solution after mixing A and B will be higher than before i. e. ΔHmixing > 0 and ΔVmixing > 0. Solute-solvent (A-B) intermolecular forces are weaker than solute-solute (A-A) and solvent-solvent (A-B) interaction e.g. CS_2-acetone (Fig 3).

(B) Negative deviation

A system in which mixing is energetically favorable in liquid phase, so vapour pressure will be lower than expected by Raoults. It can be shown by such system that forms a maximum boiling point azeotropei.e. the azeotropic mixture has a boiling point higher than either of the two pure components. Total vapour pressure is smaller than for an ideal solution. Change in enthalpy and volume of solution after mixing A and B will be lower than before i. e. ΔHmixing < 0 and ΔVmixing < 0. Solute-solvent (A-B) intermolecular forces are stronger than solute-solute (A-A) and solvent-solvent (A-B) interaction e.g. $CHCl_3$-acetone and ethanol-water (Fig 11.3).

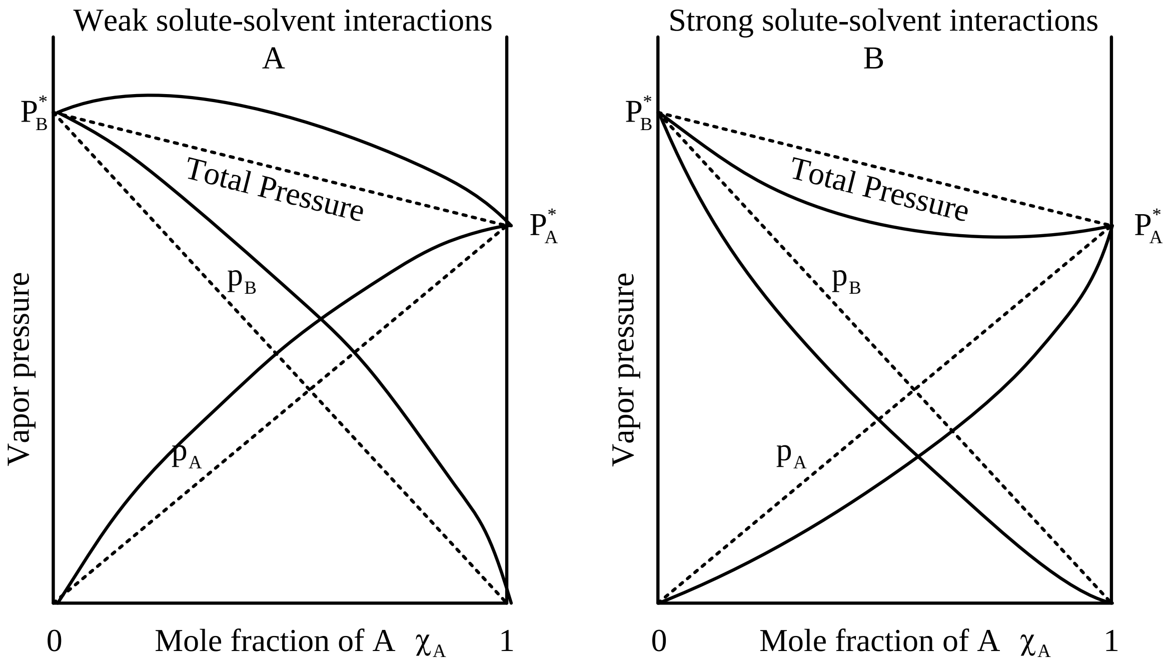

Fig11.3: Deviations from Raoult's Law (A) Positive deviation (B) Negative deviation

11.9 RELATIVE LOWERING OF VAPOUR PRESSURE MOLECULAR WEIGHT DETERMINATION

Vapour pressure is the pressure exerted by a vapour that is in dynamic equilibrium with solid or liquid at a given temperaturein a closed system. The vapour pressure of a solvent above a solution is lower than the vapour pressure of the pure solvent. In solution, the solute particles replace some of the solvent molecules at the surface and the pure solvent establishes liquid vapour equilibrium. Addition of a non-volatile solute into the solution reduces the rate of vapourization, decreasing the amount of vapour.Since a molecular non-volatile solute has zero vapour pressure than volatile solute. From Raoult’s law, the total vapour pressure of the solution is,

$$P_{solution} = P°_{solvent}\chi_{solvent} = (1 - \chi_{solute})P°_{solvent}$$

Since $\chi_{solvent} + \chi_{solute} = 1$

$$\Delta P = P°_{solvent} - P_{solution} = \chi_{solute}P°_{solvent} = \left(\frac{n_{solute}}{n_{solvent} + n_{solute}}\right)P°_{solvent}$$

$$\frac{\Delta P}{P°_{solvent}} = \frac{n_{solute}}{n_{solvent} + n_{solute}}$$

If we consider dilute solutions then $\frac{\Delta P}{P°_{solvent}} \cong \frac{n_{solute}}{n_{solvent}}$

Therefore, the lowering of the vapour pressure in a *dilute solution of a non-volatile solute is directly proportional to the amount of the solute dissolved in a definite amount of solvent.*

The difference between the vapour pressure of the pure solvent and the vapour pressure of the solvent in solution is called the vapour pressure lowering.

$$\text{Lowering of vapor pressure } (\Delta P) = P°_{solvent} - P_{solution} = \chi_{solute}.P°_{solvent}$$

This lowering of vapour pressure relative to the vapour pressure of the pure solvent is termed as the **Relative lowering of Vapour pressure.** Thus,

$$\text{Lowering of vapor pressure}\left(\frac{\Delta P}{P°_{solvent}}\right) = \frac{P°_{solvent} - P_{solution}}{P°_{solvent}} = \chi_{solute} = \frac{n_{solute}}{n_{solute} + N_{solvent}}$$

Determination of Molecular Weight

The molecular mass of a non-volatile solute can be determined by measuring the lowering of vapour pressure $P^\circ_{solvent} - P_{solution}$ produced by dissolving a known weight of it in a known weight of the solvent.

If in a determination *w* grams of solute are dissolved in *W* grams of the solvent, *m* and *M* are molecular masses of the solute and solvent respectively, we have:

No. of Moles of solute (*n*) = $\frac{w}{m}$

No. of Moles of solvent (*N*) = $\frac{W}{M}$

Substituting these values in Raoult's law Equation,

$$\frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = \frac{n_{solute}}{n_{solute} + N_{solvent}} = \frac{w/m}{w/m + W/M}$$

For very dilute solution, the number of moles (molecules) of solute (*w*/*m*), is very small, it can be neglected in the denominator. The equation can now be written as,

$$\frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = \frac{n_{solute}}{n_{solute} + N_{solvent}} = \frac{wM}{mW}$$

Knowing the experimental value of $\frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}}$, and the molecular mass of the solvent (*M*), the molecular weight of solute (*m*) can be calculated.

Example: The vapour pressure of pure benzene at a certain temperature is 640 mmHg. A non-volatile non-electrolyte solid weighing 2.175 g is added to 39 g of benzene. The vapour pressure of the solution is 600 mmHg. What is the molecular weight of the solid substance?

Solution: As we know,

$$\frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = \frac{n_{solute}}{n_{solute} + N_{solvent}}$$

Given that: $P^O_{solvent}$ = 640 mmHg, $P^O_{solution}$ = 600 mmHg

$$n_{solute} = \frac{2.175}{M_{solute}}; N_{solvent} = \frac{39}{78} = 0.5 \left(\text{No. of moles} = \frac{\text{Wt. in gram}}{\text{Molecular weight}} \right)$$

$$\left(\text{M}_{\text{solute}} \text{ is the mol. wt. of the solute} \right)$$

$$\therefore \frac{640-600}{640} = \frac{2.175/M}{2.175/M + 0.5}; M = 65.25$$

Example: 1.20 g of a non-volatile organic substance was dissolved in 100 g of acetone at 20°C. The vapour pressure of the solution was found to be 182.5 torr. Calculate the molar mass of the substance (vapour pressure of acetone at 20°C is 185.0 torr).

Solution: We know that

$$\frac{P^{\circ}_{solvent} - P_{solution}}{P^{\circ}_{solvent}} = \frac{wM}{mW}$$

Substituting values, we have

$$\frac{(185.0\text{-}182.5)\,\text{torr}}{185.0\,\text{torr}} = \frac{(1.20\text{g})(58\,\text{g mol}^{-1})}{(\text{m})(100\text{g})}$$

$$\text{m} = 51.51\,\text{g mol}^{-1}$$

11.10. OSMOSIS, LAW OF OSMOTIC PRESSURE, AND ITS MEASUREMENT

The process of spontaneous movement of a solvent from low solute concentration to high solute concentration across a semipermeable membrane is called osmosis. The semipermeable membrane permits passage of some components of a solution. Because solvent can freely move from one side to another, the solvent chemical potential on the left must equal that on the right. There is movement in both directions across the membrane, the fluid levels in the arms becomes uneven. Eventually, the pressure difference between the arms stops osmosis.

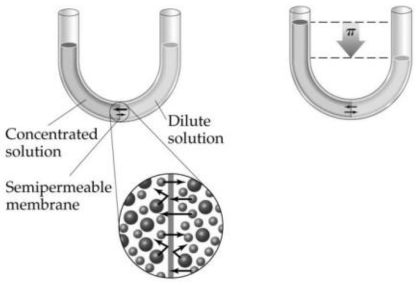

Fig11. 4: Osmosis and osmotic pressure

Osmotic pressure is the pressure required to stop osmosis.Osmotic pressure is a colligative property as it

depends on the number of solute molecules and not on their identity (Fig 11.4). For dilute solutions, it has been found experimentally that osmotic pressure is proportional to the molarity, C of the solution at a given temperature T, thus,Osmotic Pressure $\propto$ molar concentration at a given temperature T

$$\text{Or } \Pi = C\,RT$$

Here Π is osmotic pressure and R is gas constant.

Isotonic solutions: Two solutions, with the same osmotic pressure separated by a semipermeable membrane at a given temperature, are known to be **isotonic solutions**. Isotonic solutions have same molar concentrations.

Hypertonic and Hypotonic Solutions: When such solutions are separated by semipermeable membrane where no osmosis occurs between them. Solution of lower osmotic pressure is termed as a **hypotonic solution** and higher osmotic pressure is termed as **hypertonic solutions**.

11.11 DETERMINATION OF MOLECULAR WEIGHT FROM OSMOTIC PRESSUREAND ITS MEASUREMENT

The osmotic pressure of the solution can bewritten as follows,

$$\Pi = (n/V)\,RT$$

Here V is volume of a solution in litres containing n moles of solute. If w grams of solute, of molar mass M is present in the solution, then n=w / M and we can write,

$$\Pi V = \frac{wRT}{M}$$

$$or\ M = \frac{wRT}{\Pi V}$$

Thus, knowing the quantities w, T, Π and V we can calculate the molar mass of the solute.

Determination of Osmotic Pressure:

Following methods are used for the measurement of osmotic pressure,

1. Pfeffer’s method: Pfeffer gave a direct method to measure osmotic pressure of solution. Here a porous pot (A) containing membrane of copper ferrocyanide in its wallis cemented to a glass tube (B) containing solution and attached to manometer (M). The porous pot is kept in pure solvent. The osmotic pressure exerted by the solution is given by the manometer (Fig 11.5). The method is of historical interest only and has been given off.

   There are few disadvantages of this method:

   a. The osmotic pressure developed in dilute solution is very great and bursts the semipermeable membrane used.
   b. It takes a long time to register the final osmotic pressure.

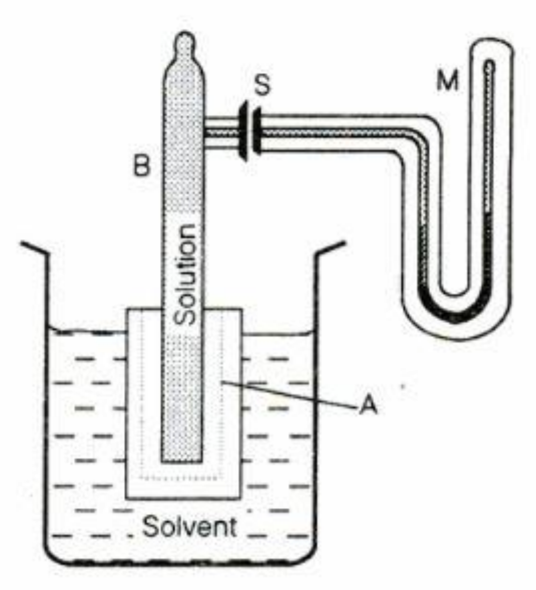

Fig 11.5: Pfeffer’s method

2. Morse and Frazer’s method: An improvement was made by H.N. Morse and J.C.W. frazer along with their collaborators. They prepared sophisticated semipermeable membranes of copper ferrocyanide by using an electric current. This made the membranes tougher and they were capable of withstanding high pressures without leakage. The apparatus as shown in Fig 11.6, has two chambers. Chamber 1 has semipermeable membrane deposited on its wall is filled with water. Tube 2 is also filled with water. Chamber 3 is filled with solution. When osmosis begins, solvent flows from 1

to 3 increasing the hydrostatic pressure in vessel 3. This hydrostatic pressure developed is equal to osmotic pressure, which is measured by a manometer attached to 4.

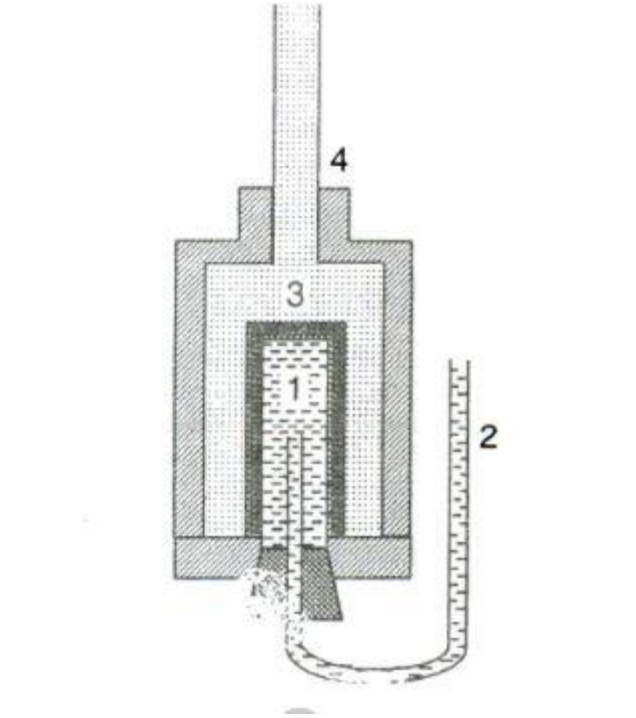

Fig 11.6: Frazer's Osmotic pressure apparatus.

3. Berkeley and Hartley's method: Berkeley and Hartley (1904-1909) employed the technique of applying external pressure on the solution just enough to prevent osmosis. The osmometer used by them is illustrated in Fig 11.7. A porcelain tube with copper ferrocyanide membrane deposited in its walls is enclosed in a metallic jacket. The tube is fitted with a reservoir of pure solvent (water) at one end and a capillary tube at the other. Mechanical pressure can be applied on the solution with a piston connected to a pressure gauge.

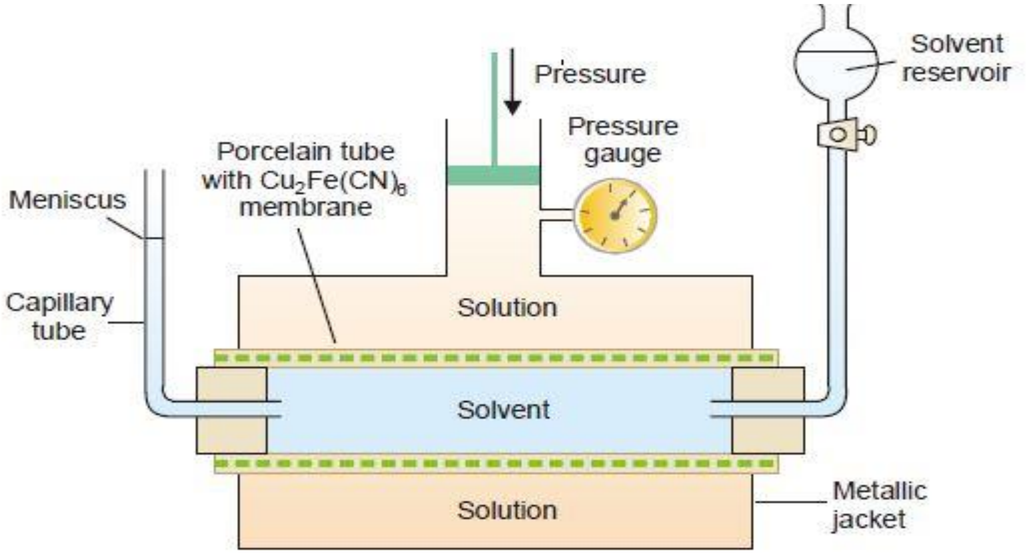

Fig 11.7: Berkeley's and Hartley's Osmometer

The inner porcelain tube is filled with pure solvent and the jacket with the solutionwhose osmotic pressure is to be determined. The level of the solvent meniscus in the capillary tubewill tend to move down as solvent flows into the solution across the membrane. Pressure is thenapplied through the piston so that the meniscus becomes stationary. It indicates that osmosis hasbeen stopped and now the pressure recorded by the pressure gauge gives the osmotic pressure ofthe solution.

Example: What is the molar mass of a protein if 5.87 mg per 10 mL gives an osmotic pressure of 2.45 torr at 25 °C?

Solution: Given that**:** 5.87 mg protein; 10.0 mL solution; $\Pi = 2.45$ torr; $T = 25$ °C

Need to find:molar mass of protein (g/mol) we know that,

$\Pi = CRT$, $T(\mathrm{K}) = T(°\mathrm{C}) + 273.15$, $R = 0.08206 \mathrm{atm \cdot L/mol \cdot K}$

M = mol/L, 1 mL = 0.001 L, MM=g/mol, 1atm =760 torr

$T(\mathrm{K}) = 25 + 273.15 = 298$ K

$$C = \Pi / RT$$

$$C = \frac{2.45\,torr \Big/ 760\,torr/atom}{(0.08206\,\frac{atm\,L}{mol\,K})(298\,K)}$$

$$C = 1.318\times10^{-4}\,M$$

$$10mL\times\frac{1L}{0.001mL}\times\frac{1.318\times10^{-4}M\ protein}{1L} = 1.318\times10^{-6}\,mol\ protein$$

$$molar\ mass = \frac{5.87\times10^{-3}\,g}{1.318\times10^{-6}\,mol} = 4.45\times10^{3}\ g/mol$$

Example: Calculate the osmotic pressure of a decinormal solution of cane sugar at 0 ^{0}C.

Solution:

$$\frac{n}{V} = \text{molar concentration} = 0.1M$$

$$R = 0.082\,\text{lit.atom/K/mole}; T = 273K$$

$$\text{we have, } p = \frac{n}{V}RT$$

$$p = 0.1\times0.082\times273$$

$$= 2.24\,atm.$$

Example: A solution of 1.73 g of 'A' in 100 cc of water is found to be isotonic with a 3.42 % (wt./vol.) solution of sucrose ($C_{12}H_{22}O_{11}$). Calculate the molecular weight of A.

($C_{12}H_{22}O_{11}$=342)

Solution: We have known that the isotonic solutions have the same molar concentration (i.e. moles/lit.)

Let the molecular weight of A be M.

$$\text{Moles of A} = \frac{1.73}{M}$$

$$\therefore \text{molar conc. of A (moles/litre)} = \frac{1.73}{M}\times\frac{1000}{100} = \frac{17.3}{M}$$

$$\text{Molar conc. of sucrose} = \frac{3.42}{342}\times\frac{1000}{100} = 0.1$$

$$\therefore \qquad \frac{17.3}{M} = 0.1; M = 173$$

Example: Calculate the molecular weight of cellulose acetate if its 0.2 (wt./vol.) solution in acetone (sp. Gr. 0.8) shows an osmotic rise of 23.1 mm against pure acetone at 27 ^{0}C.

Solution: 0.2 % solution means 0.2 g of cellulose acetate dissolved in 100 ml of solution.

Osmotic pressure=2.31 cm acetone

$$\text{p} = 2.31\times\frac{0.80}{13.6}\text{cm of Hg} = 0.136\,\text{cm of Hg}$$

$$\text{p} = \frac{0.136}{76}\,atom\,(1\,\text{atom} = 76\,\text{cm of } Hg)$$

Suppose M is the molecular weight of cellulose acetate.

$$n = \frac{0.2}{M}, V = 100\,mL = 0.1\,lit.atom/K/mole\; and\; T = 273+27 = 300\,K$$

$$Now, \qquad p = \frac{n}{V}RT$$

$$\therefore \qquad \frac{0.136}{76} = \frac{0.2/M}{0.1}\times 0.082\times 300$$

$$\text{M} = 27{,}500$$

11.12 ELEVATION OF BOILING POINT AND DEPRESSION OF FREEZING POINT

Freezing-Point Depression

When a substance freezes, the particles of the solid take on an orderly pattern. The presence of a solute in water disrupts the formation of this pattern. As a result, more kinetic energy must be withdrawn from a solution than from the pure solvent to cause the solution to solidify. The freezing point of a solution is lower than the freezing point of the pure solvent. Therefore, the melting point of the solid solution is lower.The difference in temperature between the freezing point of a solution and the freezing point of the pure solvent is called the **freezing-point depression**(Fig 11. 8).The magnitude of the freezing-point depression is proportional to the number of solute particles dissolved in the solvent and does not depend upon their identity.

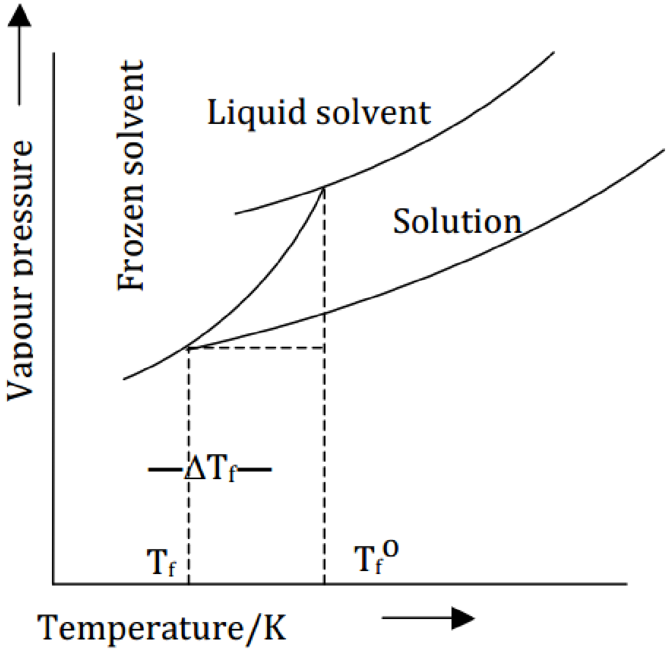

Fig11.8:Relation between temperature and vapour pressure

Freezing-Point Depression (ΔT_f):

It is directly proportional to the molal concentration of solute particles.

Depression in freezing point $\propto$ molal concentration (m)

$T^{\circ}_{f} - T_f = \Delta T_f \propto$ m or $\Delta T_f = K_f . m$

Where T°_{f} is the freezing point of the pure solvent and T_f is the freezing point of the solution. The proportionality constant, K_f is called the freezing point depression constant. The value of K_f (unit = °C/m) depends on the solvent. K_f is the molal freezing-point depression constant or cryoscopic constant of the solvent, which is defined as the depression in freezing point produced when 1 mol of the solute is dissolved in 1000 g of the solvent.

K_f may also be calculated from the following equation

$$K_f = \frac{RT^2}{1000 l_f}$$

Where T is the freezing point of the solvent and l_f is the latent heat of fusion per gram of solvent. The value of $K_f$for some substances can be seen from table 1.

Boiling-Point Elevation

The boiling point of a substance is the temperature at which the vapour pressure of the liquid phase equals the atmospheric pressure. After adding a non-volatile solute, to a liquid solvent decreases the vapour pressure of the solvent. Because of the decrease in vapour pressure, additional kinetic energy must be added to raise the vapour pressure of the liquid phase of the solution to atmospheric pressure and initiate boiling. The boiling of water increase by 0.512 ^{0}C for every mole of particles that the solute forms when dissolved in 1000 g of water.The boiling point of a solution is higher than the boiling point of the pure solvent for a non-volatile solute.The difference in temperature between the boiling point of a solution and the boiling point of the pure solvent is the **boiling-point elevation**(Fig 9).

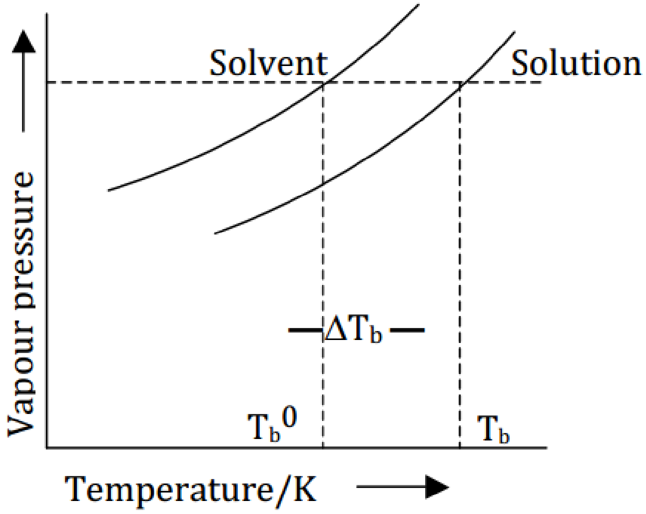

Fig9:Relation between temperature and vapour pressure

Boiling-Point Elevation (ΔT_b):

The difference between the boiling point of the solution and boiling point of the pure solvent is directly proportional to the molal concentration of solute particles.

Elevation in b.p $\propto$ molal concentration (m)

$$\Delta T_b \propto m$$

Or $$T_b - T^\circ_b = \Delta T_b = K_b . m$$

Where T_b is the boiling point of the solution and T°_b is the boiling point of the pure solvent. The proportionality constant, K_b is called the molal boiling point elevation constant or ebullioscopic constant of the solvent. The value of K_b (unit= °C/m) depends on the solvent. K_b may be calculated from the equation,

$$K_b = \frac{RT^2}{1000\,l_v}$$

Where T is boiling point of the solvent and l_v is the latent heat of vapourization per gram of the solvent. The value of $K_b$for some substances can be seen from table 1.

Example: How many grams of ethylene glycol, $C_2H_6O_2$, must be added to 1.0 kg H_2O to give a solution that boils at 105 °C?

Solution:

Given that: 1.0 kg H_2O, T_b = 105 °C

We need to find out mass $C_2H_6O_2$ in g

$\Delta T_b = m \bullet K_b$, K_b H_2O = 0.512 °C/m, BP_{H2O} = 100.0 °C

Molar mass, $C_2H_6O_2$ = 62.07 g/mol, 1 kg = 1000 g

$$(105.0 - 100.0\,^oC) = (m)(0.512\,^oC/m)$$

$$m = 9.77\,m$$

$$1.0\,kg\,H_2O \times \frac{9.77\,mol\,C_2H_6O_2}{1.0\,kg\,H_2O} \times \frac{62.07\,g\,C_2H_6O_2}{1\,mol\,C_2H_6O_2} = 6.1\times10^2\,g\,C_2H_6O_2$$

Example: Benzyl acetate is one of the active components of oil of jasmine. If 0.125 g of the compound is added to 25.0 g of chloroform ($CHCl_3$), the boiling point of the solution is 61.82 °C. What is the molar mass of benzyl acetate?

Solution:

$$\Delta T_f = K_f \times m_{solute}$$

$$m_{solute} = \frac{\Delta T_f}{K_f}$$

$$\Delta T_{bp} = 61.82\text{ °C} - 61.70\text{ °C} = 0.12\text{ °C}$$

$$m_{\text{benzyl acetate}} = \frac{\Delta T_{bp}}{K_{bp}} = \frac{0.12\text{ °C}}{\frac{3.63\text{ °C}}{m}} = 0.033\,m$$

$$\frac{0.033\ \text{mol benzyl acetate}}{1\ \text{kg CHCl}_3} \times 25.0\ \text{g CHCl}_3 \times \frac{1\ \text{kg}}{10^3\text{g}} = 8.3\times10^{-4}\ \text{mol}$$

$$\frac{0.125\ \text{g benzyl acetate}}{8.3\times10^{-4}\ \text{mol benzyl acetate}} = 150\ \text{g/mol}$$

Table 1: Molal Boiling-Point-Elevation constants (K_b) and Molal Freezing-point-Depression Constants (K_f) for some common substances

Substance	**K_b [(°C.kg)/mol]**	**K_f [(°C.kg)/mol]**
Benzene (C_6H_6)	2.53	5.12
Camphor ($C_{10}H_{16}O$)	5.95	37.7
Chloroform ($CHCl_3$)	3.63	4.70
Diethyl ether ($C_4H_{10}O$)	2.02	1.79
Ethyl alcohol (C_2H_5OH)	1.22	1.99
Water (H_2O)	0.51	1.86

11.13 ABNORMAL MOLAR MASS

We have already discussed solute of ideal solution which neither undergoes association and dissociation during formation of solutions. Ionic compounds produce multiple (dissociation) solute particles like cation and anion for each formula unit, the experimentally determined molar mass is always lower than the true value. However, in low dielectric constant solvents, molecules of acetic acid dimerize in benzene due to hydrogen bonding. In this case, the number of particles is reduced due to dimerization (association). The molar mass calculated, on the basis of this behavior abnormal results are obtained. Such a molar mass that is either lower or higher than the expected or normal value is called as abnormal molar mass.

In order to account for such abnormal results, in 1880 van't Hoff introduced the theoretical van't Hoff factor, i is the ratio of moles of solute particles to moles of formula units dissolved. This factor 'i' is defined as;

$$\text{i}=\frac{\text{observed magnitude of any colligative property}}{\text{noraml magnitude of the same colligative property}}$$

$$=\frac{\text{normal molecular weight}}{\text{observed mol. weight}}\quad\begin{Bmatrix}\text{as colligative properties and mol.wt.}\\\text{are inversely related}\end{Bmatrix}$$

‘i’ can also be calculated as

$$\text{i}=\frac{\text{moles of solute particles after dissociation/association}}{\text{moles of solute particle originally taken}}$$

$$=\frac{\text{observed molality}}{\text{calculated molality}}$$

The measured van’t Hoff factors are generally less than the theoretical due to abnormal behavior of ion in solution. Therefore, the measured van’t Hoff factors often cause colligative properties to be lower than we expect.

The equation of colligative properties of electrolyte solutions modifies after inclusion of van’t Hoff factors.

$$\text{Lowering of vapor pressure}=\frac{P^\circ_{solvent}-P_{solution}}{P^\circ_{solvent}}=i.\frac{n_{solute}}{n_{solute}+N_{solvent}}$$

Osmotic pressure: $\Pi = i\,C\,RT$

Boiling-Point Elevation (ΔT_b): ΔT_b = i. K_b .m

Freezing-Point Depression (ΔT_f): ΔT_f = i. K_f .m

11.14 DEGREE OF DISSOCIATION AND ASSOCIATION OF SOLUTE

The value of van’t Hoff factor ‘i’ depends upon degree of dissociation. For non-electrolytes the value of i is one, for weak electrolytes, it ranges as n >*i* > 1 and *i* = n for strong electrolytes. As a solution is made more dilute, the value of "*i*" for strong electrolytes approaches "n" (the whole number expected on the basis of complete dissociation).

The **degree of dissociation** is the fraction of an electrolyte which is dissociated into ions in aqueous solution. The degree of dissociation is represented by α .Suppose 1 mole of an electrolyte is capable of forming “n” ions on complete dissociation. If the degree of dissociation be α , the total number of particles in solution is:

$$\begin{array}{ll} A_n \longrightarrow nA & \\ 1mole & 0 \\ 1-\alpha & \alpha n \end{array}$$

Number of un-dissociated molecule: =1- α

Number of ion produces = α n

$\therefore$ Total number of particle = 1- α + α n

Hence, weak electrolytes do not dissociate completely and therefore their degree of dissociation can be expressed according to the following equation:

$$i = \frac{\text{Actual number of particles}}{\text{Number of particle for undissociation}}$$

$$i = \frac{1-\alpha+\alpha n}{1}$$

$$i - 1 = \alpha(\text{n}-1)$$

$$\alpha = \frac{i-1}{n-1}$$

$$\%\,\text{dissociation} = \frac{i-1}{n-1} \times 100$$

Where "i" is the van’t Hoff factor and "n" is the number of ions per formula unit of the electrolyte.

The **degree of association** is the fraction of an electrolyte, which is associated in aqueous solution. Suppose one mole of an electrolyte is capable of associating “n” ions on complete association. If the degree of association be α , the total number of particles in solution are:

$$\begin{array}{ll} nA \longrightarrow A_n & \\ 1mole & 0 \\ 1-\alpha & \alpha/n \end{array}$$

Number of un-associated molecule = 1- α

Number of ion produces = α /n

$\therefore$ Total number of particle = 1- α + α /n

The degree of association can be expressed according to the following equation:

$$i = \frac{\text{Actual number of particles}}{\text{Number of particle for unassociation}}$$

$$i = \frac{1-\alpha+\alpha/n}{1}$$

$$i-1 = \alpha(1/n - 1)$$

$$\alpha = n\left(\frac{i-1}{1-n}\right)$$

$$\%\,\text{association} = n\left(\frac{i-1}{1-n}\right)\times 100$$

Example: 20.27 g of benzene containing 0.2965 g of benzoic acid (mol. wt. = 122) freezes at 0.317^0 below the freezing point of pure benzene. If benzoic acid exists as dimer in benzene, find its degree of association. K_f for benzene is 5.12^0C m^{-1}.

Solution:

$$Molality\,(\text{calculated}) = \frac{0.2965/122}{20.27}\times 1000$$
$$= 0.12\,mole/1000g.$$

$$Molality\,(obseved)\,\frac{\Delta T_f}{K_f} = \frac{0.317}{5.12} = 0.0619\,mole/1000g$$

$$\therefore \qquad i = \frac{Molality\,(obseved)}{Molality\,(\text{calculated})} = \frac{0.0691}{5.12} = 0.5158$$

Since benzoic acid exists as dimer in benzene, we have

$$\begin{array}{lcc} \text{moles before association} & 1\,mole & 0 \\ & 2C_6H_5COOH \longrightarrow & (C_6H_5COOH)_2 \\ \text{moles after association} & 1-\alpha & \frac{\alpha}{2}\,(\alpha = \text{degree of association}) \end{array}$$

$$\therefore \qquad i = \frac{1-\alpha+\frac{\alpha}{2}}{1} = 0.5158$$

$$\alpha = 0.9684\,or\,96.84\%$$

Example: A 0.01 m aqueous solution of $K_3[Fe(CN)_6]$ freezes at -0.062 ^{0}C. What is the apparent percentage of dissociation? (K_f for water = 1.86)

Solution: we have,

$$\Delta T_f = m \times K_f$$

$$= 0.01 \times 1.86$$

$$i.e.\ (\Delta T_f)_{\text{normal}} = 0.0186^0$$

$$and\ (\Delta T_f)_{\text{observed}} = 0.062^0 \text{(given)}$$

$$\therefore \quad i = \frac{\text{observed colligative property}}{\text{normal colligative property}}$$

$$= \frac{0.062}{0.0186}$$

Now suppose α is the degree of dissociation of $K_3[Fe(CN)_6]$

Thus,

$\text{moles before dissociation} \quad 1mole \quad 0 \quad 0$

$$K_3[Fe(\text{CN})_6] \longrightarrow 3K^+ + [Fe(\text{CN})_6]^{3-}$$

$\text{moles after dissociation} \quad 1-\alpha \quad 3\alpha \quad \alpha \quad (\alpha = \text{degree of dissociation})$

$$\therefore \quad i = \frac{1-\alpha+3\alpha+\alpha}{1} = \frac{0.062}{0.0186}$$

$$\alpha = 0.78\ or\ 78\%$$

Example: A decimolar solution of potassium ferrocyanide is 50% dissociated at 300 K. Calculate the osmotic pressure of the solution. (R=8.314 $JK^{-1}mol^{-1}$)

Solution:

$\text{moles before dissociation} \quad 1mole \quad 0 \quad 0$

$$K_4[Fe(\text{CN})_6] \longrightarrow 4K^+ + [Fe(\text{CN})_6]^{4-}$$

$\text{moles after dissociation} \quad 1-\alpha \quad 4\alpha \quad \alpha \quad (\alpha = \text{degree of dissociation})$

$$\therefore \quad i = \frac{1-\alpha+4\alpha+\alpha}{1} = 1+4\alpha = 1+4\times0.5 = 3$$

$$\text{Observed osmotic pressure} = icRT$$

$$= 3 \times (0.1 \times 10^3) \times 8.314 \times 300$$

$$= 7.4826 \times 10^5\ pascal\ (\text{N/ m}^2)$$

11.15 SUMMARY

Formation of solution takes place when some interactive forces like all of the solute–solute attractive forces or some of the solvent–solvent attractive forces overcome. Based on interactions, solutions are categorized into two ways ideal and non-ideal (real) solutions. An ideal solution is that mixture of solute and solvent where there is no absorption or evolution of heat.For non-ideal solution, there is change in volume on mixing and there is enthalpy change, resulting in internal energy change. These solutions obey and disobey Raoult's and Henry law respectively.

Raoult's law: $P_{\text{solvent in solution}} = \chi_{\text{solvent}} \cdot P^\circ$

The colligative properties of solution whose value depends only on the number of non-volatile solute particles contained in a known volume of a given solvent. They do not depend on the chemical composition or constitution of the solute. They are Lowering of Vapour Pressure, Osmotic Pressure, Elevation of Boiling Point and depression of Freezing Point.

$$\text{Lowering of vapor pressure} = \frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = \frac{n_{solute}}{n_{solute} + N_{solvent}}$$

Osmotic pressure: $\Pi = C\,RT$

Boiling-Point Elevation (ΔT_b): $\Delta T_b = K_b\,.m$

Freezing-Point Depression (ΔT_f): $\Delta T_f = K_f\,.m$

Molecular weight of solute, non-electrolyte can easily be calculated with the help of mathematical formulas of these properties. Dissociation/association constant plays a very important role for association and dissociation of molecules in solution, which show abnormal molar mass. The measured van't Hoff factors often cause colligative properties to be lower than we expect.

The equation of colligative properties of electrolyte solutions modifies after inclusion of van't Hoff factors.

$$\text{Lowering of vapor pressure} = \frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = i.\frac{n_{solute}}{n_{solute} + N_{solvent}}$$

Osmotic pressure: $\Pi = i\,C\,RT$

Boiling-Point Elevation (ΔT_b): $\Delta T_b = \text{i. } K_b\,.m$

Freezing-Point Depression (ΔT_f): $\Delta T_f = \text{i. } K_f\,.m$

11.16 ERMINAL QUESTIONS

A.Long Questions:

Q1. Calculate the molarity of water.

Q2. An aqueous solution of urea has freezing point of -0.52℃. Predict the osmotic pressure of the same solution at 37℃. Assume that the molar concentration and the molality are numerically equal. (K_f=1.86)

Q3. A solution of urea has a boiling point of 100.18℃. Calculate the freezing point of the same solution. Molal constants for water K_f and K_b are 1.86 and 0.512 respectively.

Q4. Calculate the molecular weight of a substance. 10 g of which in 1 litre of solution exerts an osmotic pressure of 81 mmHg at 27 K.

Q5. A solution containing 2.56 g sulphur in 100 g CS_2 gave a freezing point lowering of 0.383 K. Calculate the molar mass of sulphur molecules. Given K_f of CS_2 = 3.83 K Kg mol^{-1}.

Q6.100 g of water has 3g of urea dissolved in it. Calculate the freezing point of the solution. K_f for water = 1.86 K kg $mol^{–1}$, molar mass of urea = 60 g $mol^{–1}$, freezing point of water = 273.15 K (0°C).

Q7. Human blood has osmotic pressure of 7.2 atm at body temperature of 37°C. Calculate the molar concentration of solute particles in blood.

Q8. Vapour pressure of benzene is 200 mm of Hg. 2g of a non-volatile solute in 78 g benzene has vapour pressure of 195 mm of Hg. Calculate the molar mass of the solute. Molar mass of benzene = 78 g mol^{-1}.

Q9. 500 g of water containing 27 g of a non-volatile solute will boil at 100.156°C. Calculate the molar mass of the solute. Given boiling point of water = 100°C, K_b = 0.52 K kg mol^{-1}.

Q10. The vapour pressure of ether (mol. mass = 74) is 442 mmHg at 293 K. If 3g of a compound A are dissolved in 50 g of ether at this temperature, the vapour pressure falls to 426mm Hg. Calculate the molecular mass of A. Assume that the solution of A in ether is very dilute.

Q11. 18.2 g of urea is dissolved in 100 g of water at 50°C. The lowering of vapour pressure produced is 5 mm Hg. Calculate the molecular mass of urea. The vapour pressure of water at 50°C is 92 mm Hg.

Q12. A current of dry air was passed through a solution of 2.64 g of benzoic acid in 30.0 g of ether ($C_2H_5OC_2H_5$) and then through pure ether. The loss in weight of the solution was 0.645 g and the ether 0.0345 g. What is the molecular mass of benzoic acid?

Q13. A stream of dry air was passed through a bulb containing a solution of 7.50 g of an aromatic compound in 75.0 g of water and through another globe containing pure water. The loss in mass in the first globe was 2.810 g and in the second globe, it was 0.054 g. calculate the molecular mass of the aromatic compound. (mol. mass of water = 18)

Q14. In an experiment, air was drawn successively through a solution of sugar (38.89 g per 100 g water) and distilled water, and then through anhydrous calcium chloride. It was found that the water lost was 0.0921 g and calcium chloride tubes gained 5.163 g. Find the molecular mass of the sugar. (Mol mass of H_2O = 18)

Q15. The boiling point of a solution containing 0.20 g of a substance X in 20.00 g of ether is 0.17 K higher than that of pure ether. Calculate the molecular mass of X. Boiling point constant of ether per 1 Kg is 2.16 K.

Q16. Acetone boils at 56.38°C and a solution of 1.41 grams of an organic solid in 20 grams of acetone boils at 56.88°C. If K for acetone per 100 g is 16.7, calculate the mass of one mole of the organic solid.

Q17. In a Cottrell determination, 22 g of benzene was used as solvent. The readings on the differential thermometer before and after adding 0.586 g of naphthalene (mol mass= 128), were 1.262 and 1.799 respectively. In a separate experiment, using the same amount of benzene but this time adding 0.627 g of an organic compound *X*, the temperature readings were 1.269 and 1.963. Calculate the molecular mass of *X*.

Q18. 0.440 g of a substance dissolved in 22.2 g of benzene lowered the freezing point of benzene by 0.567°C. Calculate the molecular mass of the substance. (K_f= 5.12°C mol^{-1})

Q19. 1.250 g of naphthalene was dissolved in 60 cm^3 of benzene and freezing point of the solution was found to be 277.515 K, while that of benzene 278.495 K. Density of benzene =0.880 g cm–3, K_f=5.1 K per 1000 g benzene. Calculate the molecular mass of naphthalene.

Q20. A solution of 0.124 g of a substance, *X*, in 25.0 *l* of ethanoic acid (acetic acid) has a freezing point 0.324°C below that of the pure acid 16.6°C. Calculate the molecular mass (relative molecular mass) of *X*, given that the specific latent heat of fusion of ethanoic acid is 180.75 J g^{-1}

Q21. A sample of camphor used in the Rast method of determining molecular masses had a melting point of 176.5°C. The melting point of a solution containing 0.522 g camphor and 0.0386 g of an unknown substance was 158.8°C. Find the molecular mass of the substance. $K_f$of camphor per kg is 37.7.

Q22. A solution containing 1.5 g of barium nitrate in 0.1 kg of water freezes at 272.720 K. Calculate the apparent degree of dissociation of the salt. *Kb*= 1.86 Molecular mass of $Ba(NO_3)_2$ = 261

Q23. Find the degree of ionization for HF (hydrofluoric acid) in 0.100 m aqueous solution, if the freezing point of the solution is – 0.197°C. ($K_f$for water = 1.86°C).

Q24. Phenol (C_6H_5OH) associates in water to double molecules. When 0.6677 g of phenol is dissolved in 35.5 g of water; it depresses the freezing point by 0.215°C. Calculate the van’t Hoff factor and the degree of association of phenol. Molal depression constant of water =1.85°C $mole^{-1}$.

B.Short Questions:

1.Write relationship between relative lowering of vapour pressure and osmotic pressure .Deduce Raoult’s law from it.

2.What is the cause of elevation in boiling point? Explain clearly with the help of vapour-pressure temperature curve.

3.Brefly explain at least five different methods of expressing the concentration of a solution.Which out of these are preferred and why?

4.Define osmotic pressure. How is it determined by Berkeley Hartley’s method and Morse and Frazer’s method.

5.Briefly explain Van't Hoff theory of dilute solutions. How it is used in the determination of degree of association and degree of dissociation of a solute?

6.Define positive and negative deviation in Raoult's law. Give at least two examples of each of them.

7.Explain with the help of vapour pressure- temperature diagram the cause for the depression in freezing point.

8. write a short notes on:

a) Dilute solution b) Activity coefficient c) Colligative properties

C.Multiple choice Questions:

1. Which of the following is not an example of an Ideal solution?

a) Benzene + Toluene b) n-Hexane + n-Heptane

c) Ethyl alcohol + Water d) Ethyl bromide + Ethyl chloride

2. Which of the following is false regarding Non-Ideal solutions?

a) They do not obey Raoult's law b) $\Delta V_{mixing} \neq 0$

c) $\Delta H_{mixing} = 0$ d) They form azeotropes

3. Which of the following is an example of a non-ideal solution showing positive deviation?

a) Acetone + Carbon disulphide b) Chlorobenzene + Bromobenzene

c) Chloroform + Benzene d) Acetone + Aniline

4. Which of the following is a colligative property?

a) Relative lowering of fluid pressure b) Decrease in boiling point

c) Decrease in freezing point d) Change in volume after mixing

5. What are the properties arising due to varying concentrations of solute in a given solvent, irrespective of the nature of solute with respect to the solvent?

a) Colligative properties b) Intensive properties

c) Extensive properties d) Solute properties

6. Which of the following is a colligative property?

a) Relative lowering of fluid pressure b) Decrease in boiling point

c) Decrease in freezing point d) Change in volume after mixing

7. When a non-volatile solute is added to a solvent what is the difference in vapor pressure expressed as a faction of original vapor pressure equal to?

a) Mole fraction of solute in vapor phase b) Mole fraction of solvent in vapor phase

c) Mole fraction of solute in liquid phase d) Mole fraction of solvent in liquid phase

8. What are colligative properties useful for?

a) Determining boiling and melting temperature b) Determining molar mass

c) Determining equivalent weight d) Determining van't Hoff factor

9. A pair of solution bears the same osmotic pressure. What is this pair of solutions called?

a) Hypertonic b) Hypotonic

c) Isotonic d) Osmolarity

10. What is a necessary condition for osmosis to take place?

a) Semi-permeable membrane b) Same concentration of solvent

c) High temperature d) Pressure greater than osmotic pressure

11. Which is the most appropriate method for determining the molar masses of biomolecules?

a) Relative lowering of vapor pressure b) Elevation of boiling point

c) Depression in freezing point d) Osmosis

12. What is the value of the Van't Hoff factor (i) for solutes that dissociate in water?

a) > 1 b) < 1 c) = 0 d) Not defined

13. Which of the following aqueous solutions should have the least boiling point?

a) 1.0 M KOH b) 1.0 M $(NH_4)_2SO_4$

c) 1.0 M K_2CO_3 d) 1.0 M K_2SO_4

14. Which of the following concentration determine techniques gives a more accurate value?

a) Molarity b) Molality

c) Formality d) Normality

Answers :

A.Long Questions:

1.55.55 M	**2.** 7.1 atm	**3.** 0.654^0	**4.** 207.99	**5.** 256 g mol^{-1}	**6.** 272.22 or -0.93°C	**7.** 0.2828 M	**8.** 80 g mol^{-1}
9. 180 g	**10.** 123	**11.** 57.05	**12.** 122	**13.** 93.6	**14.** 385	**15.**	**16.** 235 *g*

mol^{-1}						127.81	
17. 106	**18.** 178.9	**19.** 123	**20.** 59.09	**21.** 157	**22.** 81 or 81%	**23.** 0.06 or 6%	**24.** 0.838 or 83.8%

C. Multiple choice Questions:

1. (a)	**2.** (c)	**3.** (a)	**4.** (c)	**5.** (a)	**6.** (c)	**7.** (c)
8. (b)	**9.** (c)	**10.** (a)	**11.** (d)	**12.** (a)	**13.** (a)	**14.** (b)

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UNIT- 12 :THERMODYNAMICS III

CONTENTS

12.1. INTRODUCTION

At the end of the chapter, we will be able to understand basic concept of evolution of third law of thermodynamics, Planck, Einstein and Nernst formulation to understand entropy behavior when temperature approaches to absolute zero. Nernst heat theorem and residual entropy are also covered in this section. Calculation of absolute entropy with the help of third law of thermodynamics is also a part of this chapter.

12.2 OBJECTIVES

Thermodynamics introduces new concepts of energy of content and entropy. The second law, the third law and the rest of thermodynamics can also be introduced on the basis of the adiabatic accessibility principle. The third law represents a statement which physically is related to the second law but logically is independent of the second law. Though it does not contain new concept, but it is limited to certain extinct on the value of the entropy of crystalline solids.

The third law of thermodynamics has evolved from the Nernst theorem – the analysis of an entropy change in a reacting system at temperatures approaching absolute zero. The existing statements tend to be derived from the ideas expressed by Planck, Nernst or Einstein and can be classified accordingly.The most common formulation of the third law of thermodynamics belongs to Max Planck stated below;

Planck formulation: When temperature falls to absolute zero, the entropy of any pure crystalline substance tends to a universal constant (which can be taken to be zero).

$S \rightarrow 0$ as $T \rightarrow 0$

Entropy selected according to $S = 0$ at $T = 0$ is called absolute. This is not consistent with understanding the laws of thermodynamics as being the most fundamental and universally applicable principles of nature. This formulation does not comment on entropy of other substances at $T = 0$ and thus is not universally applicable.The Planck formulation necessitates validity of two statements of unequal universality: the Einstein statement and the Nernst theorem.

Einstein statement: As the temperature falls to absolute zero, the entropy of any substance remains finite.

$S(T) \rightarrow S(0)$, as $T \rightarrow 0$

The limiting value S may depend on parameter, which is presumed to remain finite at $T \rightarrow 0$. Considering expression for the entropy change in a constant volume heating process

$$S = \int_0^T \frac{C_V}{T} dT$$

Vanishing heat capacity

$C_V \rightarrow 0$ at $T \rightarrow 0$

The statement is attributed to Einstein, who was first to investigate entropy of quantum systems at low temperatures and to find that the heat capacities should vanish at absolute zero; this implies that S is finite at $T \rightarrow 0$.

Nernst-heat theorem: The entropy change of a system in any reversible isothermal process tends to zero as the temperature of the process tends to absolute zero.

$\Delta S \rightarrow 0$ as $T \rightarrow 0$

The Nernst theorem implies that

$$\left(\frac{\partial S}{\partial x}\right)_T \rightarrow 0 \; as T \; \rightarrow 0$$

The x is presumed to remain finite at $T \rightarrow 0$. The significance of this equation is that the entropy change of a reaction tends to approach zero and that the difference between the heat capacities of products and reactants also tends to approach zero as the temperature is towards the absolute zero.

12.3 STATEMENT AND CONCEPT OF RESIDUAL ENTROPY

Ludwig Boltzmann in 1877, proposed a formula $S = k \ln W$ *(entropy is a logarithmic function of W)*. Where S is entropy, $W$is the number of ways of arranging the components of a system having equivalent energy, and $k$is the Boltzmann constant = R/N_A (R = universal gas constant, N_A = Avogadro's number) = 1.38 x 10^{-23} *J*/K. According to the Boltzmann formula, the entropy is zero if there is only one accessible microstate (W= 1). In most cases, W= 1 at T= 0K because there is only one way of achieving the lowest total energy: put all the molecules into the same, lowest state. Therefore, S= 0 at T= 0K, in accord with the third law of thermodynamics. In certain cases, though, W may differ from 1 at T= 0K. A system with relatively few equivalent ways to arrange its components (smaller *W*) has relatively less disorder and low entropy. A system with many equivalent ways to arrange its components (larger *W*) has relatively more disorder and high entropy. This is the case if there is no energy advantage in adopting a particular orientation even at absolute zero. For instance, for a diatomic molecule AB there may be almost no energy difference between the arrangements...AB AB AB...and...BA AB BA..., so W> 1 even at T= 0K. If S> 0 at T= 0K we say that the substance has a **residual entropy**. Ice has residual entropy of 3.4 J K^{-1} mol^{-1}. It seems from the arrangement of the H bonds between neighboring water molecules: a given O atom has two short O—H bonds and two long O···H bonds to its neighbors, but there is a degree of randomness in which two bonds are short and which two are long. We, thus, conclude that entropies of substance like H_2, D_2, CO, NO, H_2O etc. are not zero at absolute temperature. These entropies are called residual entropies.

Example: In the solid state at 0 K, nitric oxide is capable of existing in two orientations, viz., NONO and NOON, which have practically equal probabilities. Calculate the molar entropy of NO at 0 K.

Solution: At 0 K, the probability of orientation of one molecule of NO is, 2. Thus, W=2. Hence, from the Boltzmann equation, for one mole, i.e., for Avogadro's number of molecules,

$$
\begin{aligned}
S &= k\ln W, \text{with } W = 2^{N_A}, \text{We find that} \\
S &= k\ln 2^{N_A} = N_A k\ln 2 = R\ln 2 \\
&= (8.314\, JK^{-1}mol^{-1})(2.303)(0.3010) \qquad (\because \log_{10} 2 = 0.3010) \\
&= 5.74\, JK^{-1}mol^{-1}
\end{aligned}
$$

12.4 THIRD LAW OF THERMODYNAMICS

It is interesting that the Nernst principle and the Einstein statement can be combined to produce the following formulation of the third law:

Nernst (Nernst-Einstein) formulation: A thermodynamic state with zero absolute temperature cannot be reached from any thermodynamic state with a positive absolute temperature through a finite isentropic process limited in time and space, although the entropy change between these states is finite.This statement implies that

$0 < \Delta S < \infty$ when $0 < T < \infty$

Or, possibly in some cases, $S(T) = S(0)$ but the isentropic process connecting these states need an infinite time for its completion.

For substances in internal equilibrium, undergoing an isothermal process, the entropy change goes to zero as T (in K) goes to zero. This is third law of thermodynamics. Mathematically,

$$\lim_{T \to 0} \Delta S = 0$$

The law is valid for pure substances and mixtures. This is the third law of thermodynamics. The entropy of any perfect crystal is 0 J/ (K mole) at 0 K (absolute zero). Due to the third law, we are able to calculate absolute entropy values. This value equals the entropy increase in a substance upon raising its temperature from 0 K to the specified temperature.

Standard Molar Entropies (S^o)

Standard states: 1 atm for gases; 1 *M* for solutions; pure substance in its most stable form for solids and liquids. **Units:** J/mol/K at 25 °C.

Predicting relative S^o values of a system

S^o increases with increase in temperature of the system and also increases as more ordered phase changes to a less ordered phase. S^o of a dissolved solid or liquid is usually greater than S^o of the pure solute. However, the extent depends on the nature of the solute and solvent. A gas becomes more ordered when it dissolves in a liquid or solid. In similar substances, increase in mass relate directly to entropy. In allotropic substances, increase in complexity (e.g., bond flexibility) relate directly to entropy.

12.5 UNATTAINABILITY OF ABSOLUTE ZERO

Nernst-unattainability principle:

According to Nernst unattainability principle, "any thermodynamic process cannot reach the temperature of absolute zero by a finite number of steps and within a finite time".

The Nernst principle implies that an isentropic process cannot start at any small positive T and finish at absolute zero when volume and other extensive parameters remain limited, i.e.

$\Delta S > 0$ when $T > 0$

Close to zero Kelvin, the molecular motions have to be treated using quantum mechanics still it is found that quantum ideal gases obey the third law.

A perfect crystal has zero entropy at a temperature of *absolute zero*. The third law leads to absolute values for the entropies of substances. Absolute zero is a temperature that an object can get arbitrarily close to, but never attain. Temperatures as low as 2.0×10^{-8} K have been achieved in the laboratory, but absolute zero will remain ever elusive.

12.6 NERNST HEAT THEOREM

Walther Nernst (Nobel Prize in Chemistry 1920) had investigated heat capacities and heats of reaction at progressively lower temperatures. Nernst theorem holds good only in the case of pure solids. Considering thermodynamic potential, from the Gibbs-Helmholtz relation we have

$$\Delta G = \Delta H - T\Delta S \quad \ldots\ldots\ldots\ldots 1$$

According to reciprocal relations

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P \left(\text{from second law of thermodynamics}\right)$$

Putting the value in eq. 1

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\Delta G - \Delta H = T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

Where ΔG and ΔH are the change in free energy and change in enthalpy for any chemical reaction.

Experimentally, it was found that the value of $\partial(\Delta G)/\partial T$ decreases with decreasing temperature (Fig 1). Nernst had noticed that, at progressively lower temperatures, the change in enthalpy and the change in the Gibbs function during a chemical reaction become more and more equal. And the rate of change of the Gibbs function with temperature becomes less and less as the temperature is lowered. He suggested that the value of $\partial(\Delta G)/\partial T$ become equal to zero when temperature reaches absolute zero. This implies that chemical reactions at a temperature of absolute zero take place with no change of entropy. This is known as **Nernst heat theorem**.

At the absolute temperature (T=0),

$$\lim_{T\to 0}\Delta G = \lim_{T\to 0}\Delta H$$

$$\lim_{T\to 0}\left(\frac{\partial \Delta G}{\partial T}\right)_P = \lim_{T\to 0}\left(\frac{\partial \Delta H}{\partial T}\right)_P = 0$$

Where $\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$ (from second law of thermodynamics) and $\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P$ (Kirchhoff's law)

ΔS and ΔC_P are the entropy change of the reaction and difference in the heat capacities of the products and the reactants.

From above equations, we can conclude that,

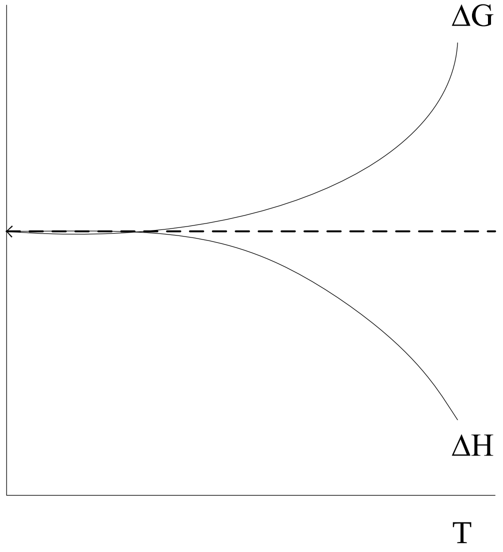

Figure 1 variation of ΔG and ΔH with change in temperature

$$\lim_{T\to 0}\Delta S = 0$$

and

$$\lim_{T\to 0}\Delta C_P = 0$$

These equations predict that the change in entropy and the difference between the heat capacities of products and reactants tends to approach zero as the temperature is lowered to absolute zero. This also indicates that the heat capacities of products and reactants in solid state are same.

The Nernst formulation of the Third Law:

"All reactions in a liquid or solid in thermal equilibrium take place with no change of entropy in the neighborhood of absolute zero."

12.7 EVALUATION OF ABSOLUTE ENTROPY FROM HEAT CAPACITY DATA

Third Law Entropy Calculations

The entropy of a perfect gas increases when it expands isothermally. The change in entropy of a substance accompanying a change of state at its transition temperature is calculated from its enthalpy of transition. The increase in entropy when a substance is heated is expressed in terms of its heat capacity. The entropy of a substance at a given temperature is determined from measurements of its heat capacity from T=0 upto the temperature of interest, allowing for phase transitions in that range, especially upto 15°C. It is difficult to measure heat capacities near T=0 K. Theoretically assume that the heat capacity is proportional to T^3 when T is low which is known as Debye extrapolation. $C_p$is measured down to as low a temperature as possible. That fit determines the value of a, and the expression $C_{p,m} = aT^3$ is assumed valid down to T= 0 K.

The Debye 'T-cubed' law says that the heat capacity at constant volume for metals is $C_V = aT^3 + bT$ and for nonmetals heat capacity changes to $C_V = aT^3$. This equation is valid to ≈ 15 K, Above 15 K, the heat capacity data are usually available.

Entropy change of phase transition

For a phase change or transition between 0 – T₁, we add in the appropriate entropy change.Consider a system and its surroundings at the normal transition temperature, T_{trs}, the temperature at which two phases are in equilibrium at one atm pressure.

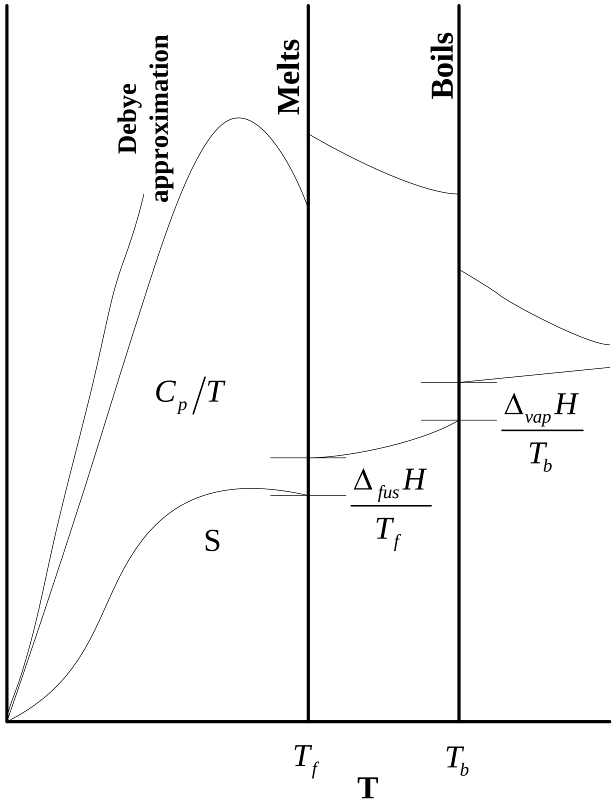

Figure 2 The variation of Cp /T with Temperature

Entropy of phase transition $\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$

A comparable change in volume occurs (with an accompanying change in the number of accessible microstates) when any liquid evaporates and becomes a gas. Hence, all liquids can be expected to have similar standard entropies of vapourization, known as Trouton's rule.

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T_b}$$

Entropy change on heating

For any system (constant pressure heating), we can write the following for the entropy change between two temperatures 0 and T₁. Entropy variation with constant pressure (when C_p is independent of T in the temperature range of interest):

$$\Delta S = \int_0^{T_1} \frac{C_p}{T} dT$$

The calculation of change in entropy between two temperature T_1 and T_2

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT = C_p \int_{T_1}^{T_2} \frac{dT}{T} = C_p \ln \frac{T_2}{T_1}$$

Heat Capacities at Low Temperatures

The variation of *Cp*/*T* with the temperature for a sample is used to evaluate the entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed (Fig 2).

The absolute entropy of metal at certain temperature $S_m(T)$, is equal to the sum of all entropy change during above calculated way.

$$S_m(T) = S_m(0) + \int_0^{T_f} \frac{C_{p,m}(s,T)}{T} dT + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}(l,T)}{T} dT + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_{p,m}(g,T)}{T} dT$$

Where $C_{p,m}(s, T)$, $C_{p,m}(l, T)$ and $C_{p,m}(g, T)$ are the heat capacities of metal at certain temperature at constant pressure when system is solid, liquid and gas respectively, $\Delta_{fus}H$ and $\Delta_{vap}H$ are change of enthalpy of system that undergoes phase transition and vapourization to attain gaseous state respectively. Thereactions involving only solids and liquids depend on the entropy values of the substances. Entropy values are absolute; the elements have non-zero entropy values, e.g., for H_2 (g), $\Delta_f H°$ = 0 kJ/mole, S° = 130.58 J/(K mole). Table 1 gives the absolute entropy of nitrogen gas at 25 °C determined by the procedure outlined above.

Table 1 Determination of Absolute Entropy of N_2 at 25 °C

S. No.	**Calculation**	**$S_m^o/(JK^{-1}mol^{-1})$**
1.	Debye extrapolation	1.92
2.	Integration from 10K to 35.61K	25.25
3.	Phase transition at 35.61 K	6.43
4.	Integration from 35.61K to 63.14K	23.38

5.	Fusion at 63.14K	11.42
6.	Integration from 63.14K to 77.32K	11.41
7.	Vapourization at 77.32K	72.13
8.	Integration from 77.32K to 298.15K	39.20
9.	Correction for gas imperfection	0.92
Total		**192.06**

S_m^o (298.15K) = S_m^o (0K)+192.1 $JK^{-1}mol^{-1}$

Absolute entropies of some of the elements and compounds in their standard states at 25℃, calculated from third law of thermodynamics, are given in table 2.

Table 2 Standard absolute entropies of elements and compound at 25℃

Substance	**S_m^o ($JK^{-1}mol^{-1}$)**	**Substance**	**S_m^o ($JK^{-1}mol^{-1}$)**
Graphite, C(s)	5.70	Diamond, C(s)	2.40
Sucrose, $C_{12}H_{22}O_{11}$(s)	360.20	Iodine, I_2 (s)	116.10
Benzene, C_6H_6 (l)	173.30	Water, H_2O (l)	69.90
Mercury, Hg (l)	76.00	Bromine, Br_2 (l)	153.97
Methane, CH_4 (g)	186.30	Carbon dioxide CO_2 (g)	213.70
Hydrogen, H_2 (g)	130.70	Helium, He	126.20
Ammonia, NH_3 (g)	192.40	Water, H_2O (g)	188.74

Example: A certain solid at 4.2 K: $C_{p,m} = 0.43\ J\ K^{-1}\ mol^{-1}$. What is its S_m at that Temperature?

Solution: We know that

$$S_m(T) = S_m(0) + \int_0^T \frac{C_{p,m}(\mathrm{s},T)}{T} dT = S_m(0) + \int_0^T \frac{aT^3}{T} dT$$

$$= S_m(0) + a\int_0^T T^2 dT = S_m(0) + \frac{1}{3}aT^3 = S_m(0) + \frac{1}{3}C_{p,m}(T)$$

$$S_m(T) = S_m(0) + 0.14 JK^{-1}mol^{-1}$$

12.8 SUMMARY

Nernst heat theorem has relevance to understand the third law of thermodynamics. According to Nernst heat theorem when temperature is lowered to absolute zero, the value of ΔG and ΔH closely approaches to each other and become equal. At progressively lower temperatures, the change in enthalpy and the change in the Gibbs function during a chemical reaction become more and more equal. He suggested that the value of $\partial(\Delta G)/\partial T$ become equal to zero when temperature reaches absolute zero. This implies that chemical reactions at a temperature of absolute zero take place with no change of entropy. This is known as Nernst heat theorem. Now we can conclude that, $\lim_{T\to 0} \Delta S = 0$ and $\lim_{T\to 0} \Delta C_P = 0$. *For substances in internal equilibrium, undergoing an isothermal process, the entropy change goes to zero as T (in K) goes to zero. This is third law of thermodynamics.* Mathematically,

$$\lim_{T\to 0} \Delta S = 0$$

According to the Boltzmann formula, S = k lnW, the entropy is zero if there is only one accessible microstate (W= 1). A system with relatively few equivalent ways to arrange its components (smaller *W*) has relatively less disorder and low entropy. A system with many equivalent ways to arrange its components (larger *W*) has relatively more disorder and high entropy.

It was found that entropies of substance like H_2, D_2, CO, NO, H_2O etc. are not zero at absolute temperature. These entropies are called residual entropies.The absolute entropy of metal at certain temperature, $S_m(T)$, is equal to the sum of all entropy changes during above calculated way.

$$S_m(T) = S_m(0) + \int_0^{T_f} \frac{C_{p,m}(s,T)}{T} dT + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}(l,T)}{T} dT + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_{p,m}(g,T)}{T} dT$$

Where $C_{p,m}$(s, T), $C_{p,m}$(l, T) and $C_{p,m}$(g, T) are the heat capacity of metal at certain temperature at constant pressure when system is solid, liquid and gas respectively, $\Delta_{fus}H$ and $\Delta_{vap}H$ are change of enthalpy of system that undergoes phase transition and vapourization to attain gaseous state respectively. For reactions involving only solids and liquids depends on the entropy values of the substances.

12.9TERMINAL QUESTIONS

A.Long Questions:

Q1. C_V for uranium metal is 3.04 $JK^{-1}mol^{-1}$at 20 K. Calculate the absolute entropy of the metal in $JK^{-1}mol^{-1}$ at 20 K.

Q2. The heat capacity, C_P (in $JK^{-1}mol^{-1}$) of a substance is given by the following equations:

$$C_P(s) = 16.74\times10^{-5}T^3\,(0 < T < 50K)$$
$$C_P(s) = 20.92\,(50 < T < 150K)$$
$$C_P(l) = 25.10\,(150 < T < 400K)$$

At the melting point (150 K), $\Delta H_f = 1255.2\, J\, mol^{-1}$. Calculate the absolute entropy of the substance in the liquid state at 300 K.

Q3. Show that the entropy of any substance at very low temperature (0<T<20K), where Debye's relation for heat capacities is valid and one-third of the molar heat capacity.

Q4. Define Nernst heat theorem and the concept of residual entropy.

Q5. How you evaluate of absolute entropy from heat capacity data?

B. Multiple Choice Questions:

1. Which of the following laws was expressed by Nernst?

a)The first law of thermodynamics b)The second law of thermodynamics

c)Third law of thermodynamics d)None of the above

2. The third law of Therodynamices:

a) Introduce the principle of increase of entropy

b) Throws light on concept of internal energy

c) establishes a concept of temperature

d)Defines the absolute zero of entropy

3.Which of the following statement " It is impossible by any means , to reduce any system to the absolute zero of temperature in a finite number of operations"?

a) Clausius statement of second law b) Kelvin- Planck's statement of II law

c) Fowler – Guggenheim statement of IIi law d) Carnot theorem.

4.Which of following is residual entropy of a substance:

a) Entropy of solid equal to 0 at T= 0 b) Entropy of solid equal to 0 at T= 273K

c) Entropy of solid greater than 0 at T= 273K d) Entropy of solid greater than 0 at T=0K

5.Unit of Standard Molar Entropies is:

a) J/mol/K b) J/K c) J mol / K d) mol K / J

ANSWERS: A. Ans1. 1.01 $JK^{-1}mol^{-1}$ **Ans2.** 55.73 $JK^{-1}mol^{-1}$**B.**

1.(c)	**2.** (d)	3. (c)	4. (d)	5. (a)

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BLOCK -IV: LABORATORY WORK

UNIT 13: LABORATORY HAZARDS AND SAFETY PRECAUTIONS

CONTENTS:

13.1 INTRODUCTION

In the laboratory it is require great care and attention in order to avoid safety hazards occures due to delicate lab instrument, open flames, hazardus 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 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 are applicable 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 burn with acid , wash it with ammonium hydroxide, while in case of concentrated H_2SO_4 wash affected part with Barium chloride solution and then with cold water and apply burnol.
- If the skin burn due to the concentrated/ stong alkali (base), washed it with acetic acidand 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, it is likely that a burn will 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

It is essential that learners are monitored consistently in the laboratory. The teacher must be physically present in the duration of the experiment, focusing on the students throughout.

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.

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UNIT-14 INORGANIC EXERCISE: INORGANIC SYNTHESIS

CONTENTS:

*14.*1 INTRODUCTION

Inorganic synthesis is a fundamental area of chemistry focused on the preparation and characterization of inorganic compounds. This branch of chemistry not only provides insights into the behavior and reactivity of metals and non-metals but also serves as the foundation for advancements in materials science, catalysis, and coordination chemistry. The laboratory component of inorganic synthesis emphasizes the development of practical skills such as precise measurement, controlled reaction conditions, and crystallization techniques essential for obtaining pure compounds.

This syllabus covers the synthesis and crystallization of a variety of inorganic compounds, including both simple salts and coordination complexes. Compounds such as cuprous chloride, potash alum, chrome alum, ferrous oxalate, ferrous ammonium sulfate, tetraamminecopper(II) sulfate, and hexaamminenickel(II) chloride are synthesized and studied for their unique chemical properties, crystal structures, and applications. The crystallization process, a critical part of purification, will be highlighted to emphasize its importance in achieving analytical-grade substances.

14.2 OBJECTIVE

The primary objectives of this course are to:

1. Introduce students to fundamental techniques in inorganic synthesis and crystallization.
2. Enable students to prepare and purify selected inorganic compounds through laboratory methods.
3. Develop proficiency in handling laboratory equipment, reagents, and procedures safely and effectively.
4. Foster an understanding of the chemical principles underlying the formation and properties of various salts and coordination compounds.
5. Illustrate the importance of crystallization as a purification technique and teach students how to obtain well-formed crystals.
6. Encourage careful observation, data recording, and analytical thinking in the laboratory environment.

14.3 SYNTHESIS OF CUPROUS CHLORIDE

Objective: To prepare cuprous chloride ($CuCl$) by reducing cupric chloride ($CuCl_2$) using sulphurous acid (H_2SO_4) or sodium bisulfite ($NaHSO_4$) in an acidic medium.

Chemicals Required:

Chemical	**Quantity**
Cupric chloride ($CuCl_2 \cdot 2H_2O$)	10 g
Concentrated hydrochloric acid (HCl)	20 mL

Chemical	Quantity
Sodium bisulfite ($NaHSO_4$) or sulphurous acid	~5 g or 20 mL
Distilled water	As required
Ice	Small amount

Apparatus Required: Beakers (250 mL), Glass rod, Measuring cylinder, Filter paper and funnel, Bunsen burner or hot plate, Ice bath, Wash bottle

Procedure: First, about 10 grams of cupric chloride ($CuCl_2 \cdot 2H_2O$) is dissolved in 20 mL of concentrated hydrochloric acid (HCl) in a 250 mL beaker. Distilled water is then added to make the total volume approximately 100 mL. The solution is stirred thoroughly until all the solid dissolves, forming a greenish-blue solution. In a separate container, prepare a fresh solution of the reducing agent by dissolving 5 grams of sodium bisulfite ($NaHSO_4$) in 20 mL of distilled water (alternatively, 20 mL of sulphurous acid can be used). This reducing agent solution is slowly added to the cupric chloride solution with continuous stirring. A white precipitate of cuprous chloride (CuCl) begins to form. The reaction mixture can be gently heated, if necessary, to complete the reduction process; however, it should not be boiled. Stirring is continued until the evolution of sulfur dioxide gas stops and precipitation is complete. The mixture is then cooled in an ice bath to aid crystallization. The white precipitate is filtered using filter paper, washed first with cold dilute HCl to remove impurities, and then with cold distilled water. Finally, the product is dried between filter papers or in a desiccator. The white cuprous chloride (CuCl) obtained should be stored in a dark, airtight container, as it is sensitive to air and light and can oxidize to form green cupric chloride ($CuCl_2$).

Chemical Reaction:

$$2CuCl_2 + SO_2 + 2H_2O \longrightarrow 2CuCl\downarrow + H_2SO_4 + 2HCl$$

Or using sodium bisulfite:

$$2CuCl_2 + NaHSO_3 + H_2O \longrightarrow 2CuCl\downarrow + NaHSO_4 + 2HCl$$

Results:

Colour: white crystalline precipitate

Yields: 80 %

14.4SYNTHESIS OF POTAS ALUM

Objective: To prepare potash alum by the aluminium sulphate and potassium sulphate in the presence of dilute sulphuric acid, followed by crystallization.

Chemicals Required:

Chemical	Quantity
Aluminium sulphate ($Al_2(SO_4)_3$)	10 g
Potassium sulphate (K2SO$_4$)	2-3 g
Dilute sulphuric acid (H_2SO_4)	5 mL
Distilled water	As required

Apparatus Required: Beakers (250 mL), Glass rod, Measuring cylinder, Funnel and filter paper, Hot plate or Bunsen burner, Crystallizing dish, Ice bath or cooling setup

Procedure: Take about 10 grams of aluminium sulphate ($Al_2(SO_4)_3$) in a 250 mL beaker and dissolve it in a minimum amount of hot distilled water (approximately 50 mL). Stir the solution well using a glass rod. In a separate beaker, dissolve 2–3 grams of potassium sulphate (K_2SO_4) in about 20–30 mL of hot distilled water. Once both salts are fully dissolved, mix the two solutions in a clean beaker. Add about 5 mL of dilute sulphuric acid (H_2SO_4) to the combined solution to prevent hydrolysis of the aluminium salt and to aid in crystallization. Heat the mixture gently if necessary, and stir to ensure complete mixing. Then filter the hot solution if any insoluble impurities are present. Transfer the clear hot solution to a crystallizing dish and allow it to cool slowly at room temperature. After some time, transparent, octahedral crystals of potash alum ($KAl(SO_4)_3\cdot 12H_2O$) will start forming. For better crystallization, place the dish in an ice bath. Once crystallization is complete, the crystals are filtered, washed with a small amount of cold distilled water, and dried between filter papers.

Chemical Reaction:

$$Al_2(SO_4)_3+K_2SO_4+24H_2O\rightarrow 2KAl(SO_4)_2\cdot 12H_2O\downarrow$$

Results:

Colour:colourless crystals of potash alum ($KAl(SO_4)_3·12H_2O$)

Yields: ……………

14.5 SYNTHESIS OF CHROME ALUM

Objective: To synthesize chrome alum ($KCr(SO_4)_2·12H_2O$ from potassium dichromate ($K_2Cr_2O_7$) and potassium and sulfate ions.

Chemicals Required (Materials Used):

Potassium dichromate	:	10 g
Concentrated sulfuric acid	:	20 mL
Ethanol (C_2H_5OH)	:	5 mL (reducing agent)
Potassium sulfate	:	5 g
Distilled water	:	as required
Ice	:	for cooling

Apparatus Used: Beaker (250 mL), Glass rod, measuring cylinder, Bunsen burner or hot plate, Funnel, Filter paper, Conical flask, Ice bath, Watch glass

Procedure: To begin the synthesis of chrome alum, about 10 grams of potassium dichromate ($K_2Cr_2O_7$) is dissolved in 50 mL of distilled water in a beaker. Then, 5 mL of ethanol is added slowly while stirring, which acts as a reducing agent. To this mixture, 10 mL of concentrated sulfuric acid (H_2SO_4) is carefully added dropwise with constant stirring, as the reaction is highly exothermic. The solution is then gently heated until it turns green, indicating the reduction of hexavalent chromium (Cr^{6+}) to trivalent chromium (Cr^{3+}). After the mixture is slightly cooled, about 5 grams of potassium sulfate (K_2SO_4) are added and stirred until completely dissolved. An additional 10 mL of concentrated sulfuric acid is added to ensure the solution is sufficiently acidic to facilitate crystal formation. The solution is then allowed to cool to room temperature and subsequently placed in an ice bath for 1 to 2 hours to promote crystallization. Finally, the dark violet chrome alum crystals that form are filtered, washed with cold distilled water, and dried on a watch glass or filter paper at room temperature.

Chemical Reaction:

Step 1 – Reduction of Cr^{6+} to Cr^{3+}:

$$K_2Cr_2O_7+4H_2SO_4+3C_2H_5OH\rightarrow 2Cr_2(SO_4)_3+3CH_3COOH+K_2SO_4+5H_2O$$

Step 2 – Formation of Chrome Alum:

$$Cr_2(SO_4)_3+K_2SO_4+24H_2O\rightarrow 2KCr(SO_4)_2\cdot 12H_2O$$

Results:

Color: Crystals appear dark violet or purple Chrome alum crystals ($KCr(SO_4)_2\cdot 12H_2O$)

Yields: …….

14.6 SYNTHESIS OF FERROUS OXALATE

Objective: To prepare ferrous oxalate ($FeC_2O_4\cdot 2H_2O$) by the reaction of ferrous sulfate with oxalic acid.

Chemicals Required (Materials Used):

Ferrous sulfate crystals ($FeSO_4\cdot 7H_2O$)	10 g
Oxalic acid ($H_2C_2O_4\cdot 2H_2O$)	5 g
Distilled water	as required

Apparatus Used: Two beakers (100 mL or 250 mL), Glass rod, measuring cylinder, Filter paper, Funnel, watch glass, Balance, Burner or hot plate (optional for heating water).

Procedure: To begin the synthesis, 10 grams of ferrous sulfate crystals ($FeSO_4\cdot 7H_2O$) are dissolved in about 50 mL of warm distilled water in a clean beaker with constant stirring. In a separate beaker, 5 grams of oxalic acid ($H_2C_2O_4\cdot 2H_2O$) are dissolved in 30–40 mL of warm distilled water. Once both solutions are completely dissolved, the oxalic acid solution is added slowly to the ferrous sulfate solution with continuous stirring. A light-yellow precipitate of ferrous oxalate begins to form immediately. The reaction mixture is allowed to stand undisturbed for about 15 to 20 minutes to complete the precipitation. The precipitated ferrous oxalate is then filtered using filter paper and a funnel, and washed thoroughly with cold distilled water to remove any soluble impurities. Finally, the product is dried by spreading it on a watch glass and allowing it to dry at room temperature or in a desiccator.

Chemical Reaction:

$$FeSO_4+H_2C_2O_4 \rightarrow FeC_2O_4\downarrow+H_2SO_4$$

Results:

Colour: Light yellow crystalline precipitate

Yields: ………….

14.7 SYNTHESIS OF FERROUS AMMONIUM SULPHATE

Objective: To synthesize ferrous ammonium sulphate hexahydrate $(NH_4)_2Fe(SO_4)_2\cdot6H_2O$,commonly known as **Mohr's salt**, by reacting ferrous sulfate with ammonium sulfate in the presence of dilute sulfuric acid.

Chemicals Required (Materials Used):

Ferrous sulfate	:	10 g
Ammonium sulfate	:	7 g
Dilute sulfuric acid	:	5 mL
Distilled water	:	as required

Apparatus Used: Beaker (250 mL), Glass rod, measuring cylinder, Bunsen burner or hot plate, Funnel, Filter paper, Conical flask, Ice bath, Watch glass.

Procedure: To synthesize Mohr's salt, first, 10 grams of ferrous sulfate ($FeSO_4\cdot7H_2O$) is dissolved in 50 mL of warm distilled water in a beaker with constant stirring. To this solution, 5 mL of dilute sulfuric acid is added to prevent the oxidation of ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}). In a separate beaker, 7 grams of ammonium sulfate$(NH_4)_2Fe(SO_4)_2\cdot6H_2O$ is dissolved in about 30 mL of distilled water. This ammonium sulfate solution is then slowly added to the ferrous sulfate solution while stirring continuously. The combined solution is heated gently to ensure complete dissolution and then allowed to cool slowly at room temperature. After that, the solution is placed in an ice bath to promote the crystallization of

Mohr’s salt. Once the light green crystals begin to form, they are collected by filtration, washed with a small amount of cold distilled water, and finally dried on a watch glass at room temperature.

Chemical Reaction:

$$FeSO_4+(NH_4)_2SO_4+6H_2O\rightarrow(NH_4)_2Fe(SO4)_2$$

Results:

Yields: …….

14.8 SYNTHESIS OF FERROUS AMMONIUM SULPHATE

Objective: To prepare tetraamminecopper (II) sulphate monohydrate, $[Cu(NH_3)_4]SO_4{\cdot}H_2O$] by the reaction of copper (II) sulphate with aqueous ammonia.

Chemicals Required:

Copper(II) sulphate pentahydrate : 5 g
Concentrated aqueous ammonia : 10–15 mL
Distilled water : As required
Ethanol : Small amount

Apparatus Used: Beaker (100 mL), Glass rod (for stirring), Measuring cylinder, Funnel, Filter paper, Conical flask, Ice bath, Dropper, Balance (to weigh $CuSO_4{\cdot}5H_2O$)

Procedure: First, about 5 grams of copper(II) sulfate pentahydrate is weighed and dissolved in approximately 20 mL of distilled water in a 100 mL beaker, with constant stirring to ensure complete dissolution. Then, concentrated aqueous ammonia is added dropwise to the blue solution using a dropper. Initially, a light blue precipitate of copper(II) hydroxide [$Cu(OH)_2$] forms. As more ammonia is added, the precipitate gradually dissolves, forming a deep royal blue solution. This color change indicates the formation of the tetraamminecopper(II) complex $[Cu(NH_3)_4]^{2+}$The solution is then gently heated, if necessary, to concentrate it slightly — care is taken not to boil it. After that, the solution is allowed to cool to room temperature and then further cooled in an ice bath to facilitate crystallization.

After some time, deep blue crystals of tetraamminecopper(II) sulfate monohydrate begin to form. These crystals are collected by filtration using filter paper and a funnel. The crystals are then washed with a small amount of cold ethanol or distilled water to remove impurities. Finally, the crystals are dried by pressing them between filter papers or placing them in a desiccator. In this way, pure crystals of tetraamminecopper(II) sulfate monohydrate are obtained.

Chemical Reactions:

1. **Initial precipitation:**

$$Cu^{2+}(aq)+2OH^{-}(aq)\rightarrow Cu(OH)2(s)$$

2. **Formation of the complex:**

$$Cu(OH)_2(s)+4NH_3(aq)\rightarrow [Cu(NH_3)_4]_2{}^{+(}aq)+2OH^{-}(aq)$$

3. **Final product formation:**

$$[Cu(NH_3)_4]^{2+(}aq)+SO_4{}^{2-}(aq)+H_2O(l)\rightarrow [Cu(NH_3)_4]SO_4\cdot H_2O(s)$$

Result:

- **Appearance:** Deep blue crystalline solid
- **Yield:**………..

14.8 SYNTHESIS OF HEXAAMMINENICKEL(II) CHLORIDE

Objective: To synthesize **hexaamminenickel(II) chloride**, a coordination complex of nickel with ammonia ligands.

Chemicals Required:

Nickel(II) chloride hexahydrate	:	2.0 g
Concentrated aqueous ammonia	:	10–15 mL
Ethanol	:	10 mL
Distilled water	:	As required
Ice	:	For cooling

Apparatus Used: Beaker (100 mL), Glass rod, Dropper or pipette, Measuring cylinder, Buchner funnel and filter paper, Vacuum filtration setup (or gravity filtration if vacuum is not available), Watch glass, Weighing balance, Ice bath setup.

Procedure: To begin the preparation of hexaamminenickel(II) chloride, about 2.0 grams of nickel(II) chloride hexahydrate ($NiCl_2·6H_2O$) is dissolved in 10 mL of distilled water in a clean 100 mL beaker. The solution is stirred until the salt dissolves completely, forming a light green solution. The beaker is then placed in an ice bath to maintain the solution's cold temperature during the subsequent steps. Concentrated aqueous ammonia is added slowly to the cold nickel chloride solution with constant stirring. As ammonia is added, the color of the solution gradually changes to a deep bluish-violet, indicating the formation of the $[Ni(NH_3)_6]^{2+}$ complex. Ammonia is added in excess to ensure complete complexation and to maintain the coordination environment.

After the addition of ammonia is complete, around 10 mL of ethanol is added slowly to the cold mixture. Ethanol helps reduce the solubility of the complex in water, which promotes crystallization. The solution is then allowed to stand in the ice bath for 30 to 60 minutes to allow the bluish-violet crystals of hexaamminenickel(II) chloride to form. Once crystallization is complete, the solid product is collected by vacuum filtration (or gravity filtration if a vacuum is not available). The crystals are washed with a small amount of cold ethanol to remove any impurities or residual ammonia. Finally, the product is allowed to dry on a watch glass, after which the dry bluish-violet crystals of $[Ni(NH_3)_6]Cl_2$ are obtained.

Chemical Reaction:

$$NiCl_2·6H_2O+6NH_3 \rightarrow [Ni(NH_3)_6]Cl_2+6H_2O$$

Results:

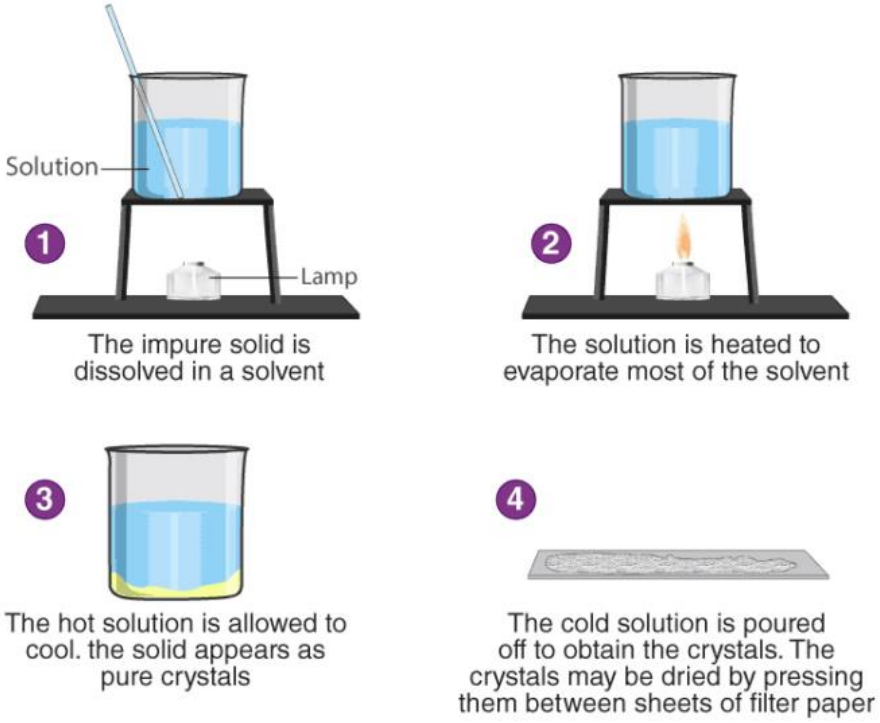
- **Colour:**bluish-violet crystals
- **Yield:**………………

14.9 CRYSTALLIZATION OF COMPOUNDS

Crystallization is a purification technique used to separate a solid compound from its impurities and obtain it in a pure, solid crystalline form. It is one of the most elegant and visually satisfying processes in chemistry.

What is Crystallization?

Crystallization is the process in which a solid forms from a solution and organizes itself into a crystal structure. During this process, the atoms or molecules arrange themselves in a highly ordered and repeating pattern, forming beautiful, well-defined crystals.



How Does It Work?

1. **Dissolving the compound**: First, the impure compound is dissolved in a suitable hot solvent (like water or ethanol) to make a solution.
2. **Cooling the solution**: The solution is slowly cooled. As it cools, the solubility of the compound decreases.
3. **Crystal formation**: When the solution becomes saturated, the pure compound begins to come out of solution and forms crystals, leaving impurities behind in the solution.

4. **Collection**: These crystals are then filtered, washed, and dried to obtain the pure compound.

14.10 SUMMARY

This unit provides a detailed exploration of inorganic synthesis with a strong focus on laboratory methods for preparing and purifying various inorganic compounds. It introduces essential synthetic techniques, including controlled reactions, precise measurements, and, especially, crystallization — a key method of purification. Compounds synthesized include cuprous chloride, potash alum, chrome alum, ferrous oxalate, Mohr's salt, tetraamminecopper(II) sulfate, and hexaamminenickel(II) chloride. Each synthesis is supported by objectives, required chemicals and apparatus, step-by-step procedures, chemical reactions, and observations. The unit concludes with a discussion on the principles and stages of crystallization.

14.11EFERENCES

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3. Shriver, D. F., Atkins, P., & Langford, C. H. *Inorganic Chemistry*, Oxford University Press, 1994.
4. University practical chemistry lab manuals and standard synthesis protocols.
5. Housecroft, C. E., & Sharpe, A. G. *Inorganic Chemistry*, 4th Ed., Pearson Education, 2012.

14.12 SUGGESTED READING

- Cotton, F. A., & Wilkinson, G. *Advanced Inorganic Chemistry*.
- Miessler, G. L., Fischer, P. J., & Tarr, D. A. *Inorganic Chemistry*, 5th Ed.
- Banwell, C. N., & McCash, E. M. *Fundamentals of Molecular Spectroscopy* – for characterization insights.
- Atkins, P. *Physical Chemistry* – helpful for thermodynamic and crystallization concepts.

- GL Squires, *Practical Physics* – supports lab safety and measurement understanding.

14.13 TERMINAL QUESTIONS

1. Define inorganic synthesis and its significance in chemistry.
2. Why is crystallization an essential technique in inorganic synthesis?
3. Explain the role of ligands in the formation of coordination compounds.
4. What precautions must be taken while synthesizing air-sensitive compounds like CuCl?
5. Write the balanced chemical reaction for the synthesis of potash alum.
6. Compare the use of ethanol and ammonia in the synthesis of transition metal complexes.
7. Describe the redox reaction involved in the synthesis of chrome alum.
8. How would you purify a compound that is soluble in cold water but crystallizes at low temperatures?
9. If green crystals appear instead of white during CuCl synthesis, what might have gone wrong?
10. Suggest ways to increase the yield of Mohr’s salt in a laboratory experiment.

UNIT 15: ORGANIC EXERCISE AND ORGANIC SYNTHESIS

CONTENTS:

15.1 INTRODUCTION

Organic compounds, due to their immense diversity in structure and functional groups, exhibit a wide range of physical and chemical properties. Identifying and separating them from mixtures is a fundamental aspect of organic chemistry, particularly in laboratory practices, natural product isolation, pharmaceuticals, and forensic analysis.

- **Qualitative Analysis**: Identifies the nature, type, elements, and functional groups in chemical substances.
- **Quantitative Analysis**: Determines the percentage composition of elements in a sample.

15.2 OBJECTIVES

The main objective of this chapter is to develop a clear understanding of the basic principles and techniques involved in organic synthesis and identification of organic compounds. It aims to familiarize students with common laboratory reactions such as halogenation, acetylation, sulphonation, oxidation, and nitration, along with their mechanisms, conditions, and safety requirements. The chapter emphasizes the importance of accurate measurement, proper handling of chemicals, and adherence to safety practices. It also focuses on separation and purification methods like crystallization, distillation, solvent extraction, and chromatography to obtain pure compounds. Through practical experiments, students learn to analyze, identify, and confirm functional groups, relate theoretical knowledge to practical applications, and develop skills for working safely and efficiently in a laboratory environment.

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, and they may be miscible (completely mix) or immiscible (do not mix completely)**.**

15.3.1 Types of Organic Compounds

1.Acids

2.Phenols

3.Bases

4.Neutral Compounds

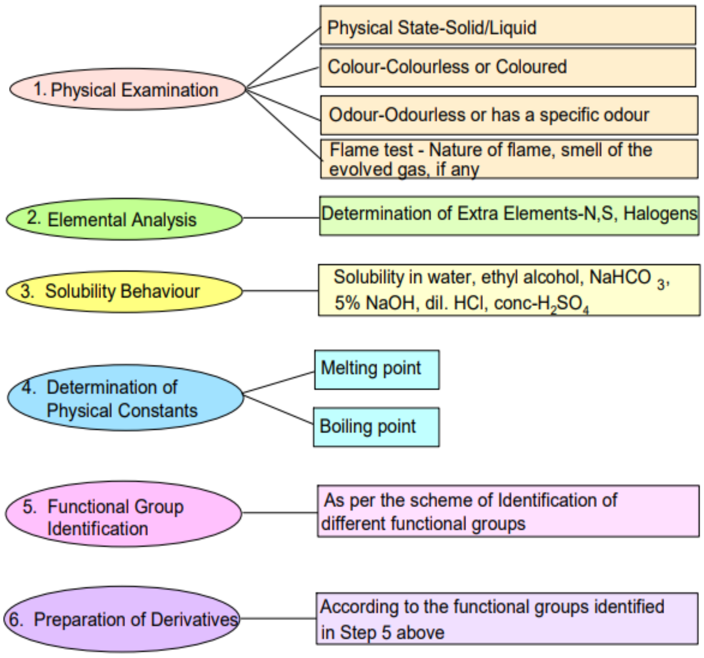
15.3.2 General Methodology:

Step	Process	Chemical Principle	Outcome
1	Mixture of X (neutral) and HA (acidic)	Initial binary mixture	Both compounds are together
2	Treat with base (NaOH or $NaHCO_3$)	Acid (HA) reacts with base to form water-soluble salt (Na^+A^-)	X remains unreacted, Na^+A^- formed
3A	Extract X with organic solvent	X is neutral and organic-soluble	X is separated into organic layer
3B	Na^+A^- dissolves in aqueous layer	Salt is water-soluble	Remains in aqueous layer
4A	Remove organic solvent	Solvent evaporated to get solid/liquid X	Pure X obtained
4B	Add dil. HCl to aqueous layer	Na^+A^- converts back to HA (acid)	Precipitation or separation of HA
5	Extract HA using organic solvent	HA is now organic-soluble	Separate into organic layer
6	Remove organic solvent	Solvent evaporated	Pure HA obtained

After that the two pure compounds obtained from the mixture are separately analysed by following the usual scheme of identification of organic compounds.

Similarly, we can separate of a basic (BH and a neutral compound Y),

15.3.3. Steps for Qualitative Analysis



15.4. SOME PROCEDURES INVOLVED AND CORRELATING THE OBSERVATIONS WITH IDENTIFICATION

Physical Examination

(a) Physical State: Observe whether the compound is solid or liquid. As generally, you may be provided with a mixture of solid compounds, therefore, the separated compounds will be solids. So, you have to look for its nature as crystalline or amorphous.

(b) Colour

The colour of the compound may indicate some likely classes as follows.

i)If a compound is colourless-it may be an aldehyde or a ketone, an alcohol, an ester, a carboxylic acid or an ester. Carbohydrates are also colourless and so are the simple hydrocarbons.

ii)Some compounds which are actually colourless, turn into pinkish or reddish coloured due to slow oxidation by air. The examples of such compounds being amines and phenols etc.

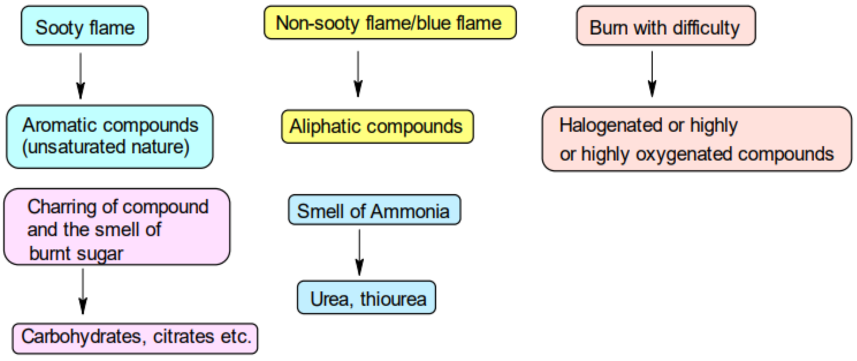
iii)Some typical yellow coloured compounds being iodoform, nitro compounds, quinones etc. However, p-nitroso compounds are greenish yellow is colour.

iv)Compounds having red-orange colour are azo compounds, napthaquinones etc.

(c) Odour

Odour of a compound sometimes gives an important indication about its nature. You know that esters have fruity smell and alcohols and chloroform are also sweet smelling. Acetic acid smells like vinegar and the odour of cinnamaldehyde is like that of cinnamon. Benzaldehyde has an odour like bitter almonds and phenols have a typical phenolic odour. Some aldehydes, carboxylic acids and acid halides have pungent odour while amines have fish like smell.

(d)Flame test also known as ignition test involves heating a small amount of the compound on a nickel spatula over a low flame. The colour of the flame and the odour, if any, is observed which indicates the following.



Elemental Analysis

The elements carbon, hydrogen, and oxygen are assumed to be present in an organic compound. But, the presence of elements-nitrogen sulphur and halogens can be checked by first converting them into ionisable inorganic substances which can then be determined by the methods of qualitative inorganic analysis. For this purpose, Lassaigne's test is very commonly used in the laboratory.

Solid-Solid Mixtures

- Separate components using chemical methods (e.g., $NaHCO_3$ for acids, NaOH for phenols).
- Recrystallize components for purification.

15.5ORGANIC SYNTHESIS BINARY MIXTURE OF ORGANIC COMPOUNDS

A binary mixture of organic compounds usually refers to two organic substances present together, such as a neutral compound and an acidic compound, or an acidic and a basiccompound.Example: A mixture of benzoic acid (acidic) and naphthalene (neutral), or aniline (basic) and phenol (acidic).

15.5.1 Determination of Nature:

The natures of binary mixture of organic compound are of three types.

a) Solid-Solid

b) Solid-Liquid

c) Liquid-Liquid.

Each of these can be either homogeneous or heterogeneous.

The solid-solid mixture and liquid – liquid mixture is identified directly by observation of the physical state of the mixture.

In order to identify the solid – liquid mixture, a small quantity of mixture is placed on a watch glass and is evaporated. If the liquid part gets evaporated and solid residue is left behind then the given mixture belongs to solid – liquid type.

If no solid residue is left behind, it is liquid – liquid type.

15.6. TYPE DETERMINATION OF WATER INSOLUBLE MIXTURE

1	Mixture + 10% $NaHCO_3$ solution (Shake well and filter)	One component is soluble with effervesces of CO_2 and reprecipitated by adding HCl to the filtrate	Acid Present
		Insoluble	Acid absent
2	Mixture or Residue +10% NaOH solution Shake well and filter)	One component is soluble and reprecipitated by adding conc. HCl to filtrate	Phenol present
		Insoluble	Phenol absent
3	Mixture or Residue + dil. HCl Solution (Shake well and filter)	One component is soluble and reprecipitated by adding 10% NaOH solution to filtrate	Base present
		Insoluble	Base absent
4	Mixture or residue +10 % $NaHCO_3$ or 10% NaOH or dil. HCl Solution	Insoluble	Neutrals present

15.6.1. Type determination for *water miscible* (solution) substance.

Test	Observation	Inference
a) Add few drops on litmus paper	a)Blue litmus turn red b)Red litmus turns	Acid or phenol present
	blue	Base present
	c)No change on either litmus	Neutral present
Distinguish between acid and phenol Substance+4 drops of 10 % $NaHCO_3$	Effervesces of CO_2	Acid is present
	No Effervesces of CO_2	Phenol is present

Conclusion: Type of given Binary mixture is …….+……..

Use simple distillation to separate volatile and non-volatile components.

15.6.2Tests for Organic Compounds

Water-Soluble Substances

- **Litmus Test**: Acid turns blue litmus red; base turns red litmus blue; neutral shows no change.
- **$NaHCO_3$ Test**: Effervescence indicates acid; no effervescence indicates phenol.

Water-Insoluble Substances

- **$NaHCO_3$ Test**: Effervescence confirms acid.

- **NaOH Test**: Solubility confirms phenol.
- **HCl Test**: Solubility confirms base.

Purification Methods

1. **Crystallization**: Dissolve in hot solvent, cool to form crystals, and filter.
2. **Sublimation**: Heat solid to vaporize and collect pure crystals.
3. **Distillation**: Separate liquids based on boiling points.

Detection of Elements

1. **Carbon & Hydrogen**: Heat with cupric oxide; CO_2 turns lime water milky, water droplets confirm hydrogen.
2. **Nitrogen, Sulfur, Halogens**: Sodium fusion test converts elements into ionic forms for detection.

Functional Group Tests

Acids (-COOH)

- **$NaHCO_3$Test**: Effervescence confirms carboxylic acid.
- **Esterification Test**: Fruity smell confirms acid.

Phenols (-OH)

- **NaOH Test**: Solubility confirms phenol.
- **$FeCl_3$ Test**: Blue/green/violet coloration confirms phenol.

Neutral Compounds

- **Aldehydes**: Tollen’s test (silver mirror), Fehling’s test (red precipitate).
- **Ketones**: Sodium nitroprusside test (red color), 2,4-DNP test (yellow/red precipitate).
- **Alcohols**: Sodium metal test (hydrogen gas evolution), Lucas test (cloudy precipitate).
- **Hydrocarbons**: Confirm by absence of other tests and physical constants.

Physical Constants

1. **Melting Point**: Temperature at which solid turns to liquid.

2. **Boiling Point**: Temperature at which vapor pressure equals atmospheric pressure.

Conclusion

The organic compound can be classified based on:

1. **Acidity/Basicity**: Acidic, Phenolic, Basic, Neutral.
2. **Saturation**: Saturated or Unsaturated.
3. **Structure**: Aliphatic or Aromatic.
4. **Elements**: C, H, O, N, S, Halogens.

This simplified guide provides a step-by-step approach to analyzing and identifying organic compounds.

15.7 EXERCISE

AIM: To separate and identify the components, A (Acidic) and B (Neutral) of a binary mixture of organic compounds.

THEORY:

The mixtures of an acidic compound and a neutral compound can be separated using solvent extraction. The two immiscible phases containing one aqueous phase and another and organic compound are taken in which the two components of the mixture get distributed. The two phases are then separated and individual compounds are obtained. An acidic compound, for example, a carboxylic acid is acidic in nature as indicated by its solubility in alkali and its reaction with sodium hydrogen carbonate. The sodium salt of the carboxylic acid is a soluble in water. Thus, the binary mixture on treatment with dilute sodium hydrogen carbonate will allow the carboxylic acid to pass into the aqueous phase as sodium carboxylate. The neutral compound could then be extracted by using an organic solvent such as dichloromethane by solvent extraction. The two layers i.e. are then separated and the evaporation of the solvent yields pure neutral compound. The acidic compound present in the aqueous medium can be recovered from its sodium salt by acidification by 6 M HCl and then by extracting the carboxylic acid so obtained using the organic solvent. The two compounds are then separately identified as given in the procedure.

REQUIREMENTS :

Apparatus	Quantity
China dish	1
Test tubes	6

Beaker	(100 mL) 1
Water bath	1
Filtration funnel	1
Filter paper	1
Chemicals	Quantity

Chemicals	**Qauntity**
$NaHCO_3$	……….
Sodium metal	…….
Conc. H_2SO_4	…….
$AgNO_3$	……
Dil. HNO_3	……..
Sodium nitroprusside	…..
PCl_5 ….	….
Ammonia solution	…..

PROCEDURE :

Record in the table below the details for separation of the two components of the mixture. Since it is a mixture of known compounds, e.g. benzoic acid and benzophenone, their separation can be recorded in the following table according to the steps listed in Sec.1.2.

Experiment step	Observation	Inference
1		
2		
3		
4		
5		

A.dentification of individual compounds :

A.Acidic Compound: Since the acidic compound is the benzoic acid, some of the observations have been filled in the table below. Rest of the observations and inferences are to be filled by you after performing the actual experiment.

Experiment step	Observation	Inference
1. Preliminary tests		
State		
Colour		
Flame Test		
2.M.P		

3.Solubility Test		
Water		
Hot water		
Dilute HCl		
Dilute $NaHCO_3$		
Dilute NaOH		
4.Test for extra elements		
Preparation of Lassigne Extract		
Test For Nitrogen	1 mL L.E.+2g $FeSO_4$, boil and acidify with H_2SO_4	Nitrogen absent
Test For Sulphur	1 mL L.E. + sodium nitroprusside	Sulphur absent
Test Forhalogen	2 mL L.E. + 2 M HNO3 + aq. AgNO3	Halogen absent
5. Test for carboxylic acid		
Sodium Bicarbonate Test	Brisk effervescences observed	-COOH group present.

B.Identification of Neutral Compound:

Fill in the following details for compound B which is benzophenone.

Experiment step	Observation	Inference
1. Preliminary tests		
State		
Colour		
Flame Test		
2.M.P		
3.Solubility Test		
Water		
Hot water		
Dilute HCl		
Dilute $NaHCO_3$		
Dilute NaOH		
4.Test for extra elements		
Preparation of Lassigne Extract [*1]		
Test For Nitrogen	1 mL L.E.+2g $FeSO_4$, boil and acidify with H_2SO4	Nitrogen absent
Test For Sulphur	1 mL L.E. + sodium nitroprusside	Sulphur absent
Test Forhalogen	2 mL L.E. + 2 M HNO_3 + aq. $AgNO_3$	Halogen absent
5. Test for aldehyde		
i)Tollens Test[*2]		
ii) Fehlings Test[*3]		

RESULT

The following compounds were indentified to be present in the given mixture of known compounds. 1. Acidic Compound = Benzoic acid

Melting Point observed = ………

Melting Point observed = ………

1. Neutral Compound = Benzophenone

Melting Point observed = ……… Melting Point observed = ………

15.8. ORGANIC SYNTHESIS

15.8.1 INTRODUCTION

Organic synthesis is the process of creating complex organic molecules through a series of chemical reactions, starting from simpler organic or inorganic compounds.

15.8.2 Goals of Organic Synthesis:

- Formation of new chemical bonds (C–C, C–N, C–O, etc.)
- Transformation of functional groups (e.g., converting alcohols to aldehydes)
- Designing new molecules for medicines, materials, or research
- Reproducing natural compounds (e.g., vitamins, hormones)
- Common Reactions in Organic Synthesis:
- Substitution reactions (SN1, SN2)
- Addition reactions (alkenes, alkynes)
- Elimination reactions (E1, E2)
- Oxidation & Reduction reactions
- Rearrangement reactions
- Coupling reactions (e.g., Suzuki, Heck)
- Condensation reactions (e.g., aldol condensation)

15.9 NITRATION

Nitrationis the introduction of a nitro group (–NO_2) into an aromatic or aliphatic compound using concentrated nitric acid (HNO_3)**,** often in the presence of concentrated sulfuric acid (H_2SO_4) as a catalyst.

SYNTHESIS OF NITROBENZENE FROM BENZENE

AIM

To synthesize nitrobenzene ($C_6H_5NO_2$) by the nitration of benzene (C_6H_6) using mixed acid (conc. HNO_3 and conc. H_2SO_4).

Chemicals Required

Reagent	Quantity
Benzene (C_6H_6)	5 mL
Concentrated HNO_3 (≈ 16 M)	3 mL
Concentrated H_2SO_4 (≈ 18 M)	6 mL
Distilled Water	As required
Sodium bicarbonate ($NaHCO_3$) solution	20 mL
Crushed Ice	As required
Anhydrous $CaCl_2$	2–3 g

Apparatus Required : Conical flask (100 mL),Beaker (250 mL),Ice bath,Separating funnel,Stirring rod,Thermometer, Measuring cylinder ,Distillation setup ,Dropper or burette ,Fume hood

Procedure:

1.Preparation of Nitrating Mixture:

- In a beaker placed in an ice bath, add:
- 3 mL concentrated nitric acid (HNO_3)
- Slowly add 6 mL concentrated sulfuric acid (H_2SO_4)dropwise with continuous stirring.
- Maintain temperature below 10 °C during mixing.

2.Nitration Reaction:

- In a 100 mL conical flask placed in the same ice bath:
- Add the 9 mL nitrating mixture.
- Using a dropper, add 5 mL benzene slowly, keeping the temperature at 0–5 °C.
- Stir the mixture gently for 30–45 minutes, allowing it to warm slowly to room temperature (not above 50 °C).

3.Quenching the Reaction:

- Pour the entire mixture into a beaker containing crushed ice (approx. 50 g).
- Stir well to precipitate the organic product.

4.**Separation and Washing:**

- Transfer to a separating funnel.
- Separate the lower organic layer (nitrobenzene).
- Wash sequentially with:
- Distilled water (20 mL).
- $NaHCO_3$ solution (20 mL)to neutralize remaining acids.
- Distilled water (2 × 10 mL) to remove salts.

5. Drying and Purification:

- Dry the organic layer with anhydrous calcium chloride (2–3 g)for 15–20 minutes.
- Decant and distill the product to collect pure nitrobenzene (b.p. ≈ 210 °C).

Observation:

Observation	**Inference**
Yellow oily liquid formed	Nitrobenzene formed

Observation	**Inference**
Almond-like odor	Characteristic of nitrobenzene
Effervescence during washing with $NaHCO_3$	Neutralization of acid by base

Chemical Reaction:

$$C_6H_6+HNO_3\xrightarrow{H2SO4}C_6H_5NO_2+H_2O$$

Precautions:

- Handle benzene and nitrobenzene in a fume hood (both are toxic and carcinogenic).
- Maintain low temperature during mixing to avoid runaway reactions.
- Use gloves, goggles, and a lab coat.

15.10 HALOGENATION

Halogenation is a process in organic synthesis where a halogen atom (Cl, Br, I, or F) is introduced into an organic molecule by replacing a hydrogen or another atom/group.

Example: Bromination of Alkene (Addition Reaction)
AIM: To prepare 1,2-dibromocyclohexane by halogenation of cyclohexene using bromine in CCl_2**,** and observe the addition reaction across the double bond**.**
Reaction:

$$C_6H_{10}+Br_2\rightarrow C_6H_{10}Br_2$$

Materials Required:

Reagent / Apparatus	**Quantity / Specification**
Cyclohexene	1.0 mL (approx. 0.85 g)
Bromine solution (Br_2 in CCl_4, 5% w/v)	5 mL
Carbon tetrachloride (CCl_4)	As solvent (5 mL if preparing Br_2 solution)
Test tubes	2
Pipette	5 mL
Dropper	1
Ice bath	Optional (for temperature control)
Fume hood	Mandatory due to bromine vapors
Gloves, goggles, lab coat	Safety equipment

Procedure Preparation of Bromine Solution (if not already prepared): In a fume hood, dissolve 0.5 mL of bromine in 9.5 mL of carbon tetrachloride (CCl_4) to make 5% Br2 solution.

- Store in a stoppered amber bottle.

Main Reaction:

- Take 1.0 mL of cyclohexene in a clean dry test tube.
- Add 5 mL of 5% bromine solution in CCl_4 to the test tube dropwise with continuous shaking.
- Observe the decolorization of the reddish-brown bromine.
- Continue adding bromine solution until colour persists, indicating the completion of reaction.
- (Optional) Place the reaction tube in an ice bath if the reaction appears vigorous.
- After the addition is complete and colour has faded, the product (1,2-dibromocyclohexane) may separate as an oily layer.

Observation:

Step	Observation
1	Bromine solution is reddish-brown
2	On adding to cyclohexene, color disappears
3	Final mixture shows pale oily product

Chemical Equation: Cyclohexene + $Br_2 \rightarrow$ 1,2-dibromocyclohexane

Confirmatory Test: Sodium bisulfite can be used to destroy excess bromine.

Add a few drops of $NaHSO_3$ solution**;** if no reddish color returns, bromine is consumed.

RESULT:

1,2-Dibromocyclohexane was successfully synthesized by halogenation of cyclohexene. The disappearance of bromine color confirmed the completion of addition reaction**.**

Precautions:

- Perform all steps in a well-ventilated fume hood.
- Avoid direct contact with bromine(corrosive and toxic).
- Carbon tetrachloride is toxic—do not inhale**.**
- Wear protective gloves, goggles, and a lab coat**.**

15.11 ACETYLATION

Synthesis of Acetanilide by Acetylation of Aniline

Theory: Acetylation is an organic reaction where **an** acetyl group (–$COCH_3$) **is** introduced into an organic compound. This reaction typically involves an amine or alcohol reacting with aceticanhydride $(CH_3CO)_2O$ or acetyl chloride (CH_3COCl).

In this experiment, aniline ($C_6H_5NH_2$) reacts with acetic anhydride to form acetanilide ($C_6H_5NHCOCH_2$)**.** This is a nucleophilic substitution reaction where the hydrogen of the –NH_2 group is replaced by an acetyl group.

Chemical Reaction:

$$C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3 + CH_3COOH$$

Materials Required

Chemical	Quantity
Aniline ($C_6H_5NH_2$)	2.0 mL (~2.0 g)
Acetic anhydride	3.0 mL (~3.0 g)
Glacial acetic acid	5.0 mL
Ice-cold distilled water	As required

Apparatus	Description
Test tubes/beakers	For mixing and heating
Measuring cylinder	10 mL
Glass rod, funnel, filter paper	For filtration
Bunsen burner or hot plate	Gentle heating

Procedure:

- In a 250 mL beaker**,** take 2.0 mL of aniline and add 5.0 mL of glacial acetic acid**.**
- Mix thoroughly and add 3.0 mL of acetic anhydride slowly while stirring.
- Heat the reaction mixture gently on a water bath for 10–15 minutes**.**
- Cool the mixture and pour it into 50 mL of ice-cold distilled water while stirring.
- A white crystalline solid of acetanilide will precipitate.
- Filter the solid using Buchner funnel or filter paper**.**
- Wash the solid with cold water to remove unreacted acetic acid or aniline.
- Recrystallize the crude product from hot water to purify.
- Dry the purified acetanilide and note its melting point (expected: ~114 °C).

Observation:

Step	Observation
1	Aniline and acetic acid mixed well
3	Slight warming, reaction begins
4	White solid begins to form
6	Crystals collected by filtration
9	Dry, white crystalline product

Result

Acetanilide was successfully synthesized by acetylation of aniline using acetic anhydride. The melting point of the purified sample was found to be ___ °C (fill your result), confirming its identity.

Precautions:

- Handle aniline carefully; it is toxic and may cause skin irritation.
- Carry out the reaction in a fume hood**.**
- Add acetic anhydride slowly to prevent excessive heat.
- Use cold water to quench the reaction and precipitate the product.

15.12 SULPHONATION

Synthesis of Benzenesulphonic Acid by Sulphonation of Benzene

Aim : To synthesize benzenesulphonic acid by the sulphonation of benzene using fuming sulfuricacid (oleum) and understand the electrophilic aromatic substitution mechanism.

Theory : Sulphonation is an electrophilic aromatic substitution (EAS) reaction in which a sulphonic acid group (–SO_3H) is introduced into an aromatic ring using concentrated sulfuric acid(H_2SO_4) or oleum (H_2SO_4 + SO_3)**.** The sulphonation of benzene involves the reaction of benzene with SO_3 (from oleum) to form benzenesulphonic acid ($C_6H_5SO_3H$)**.** It is reversible and typically requires heating.

Chemical reaction : $C_6H_6 + SO_3 \rightarrow C_6H_5SO_3H$ (SO_3 is present in oleum)

MATERIALS REQUIRED:

Reagent / Apparatus	**Quantity**
Benzene	2.0 mL (~1.74 g)
Fuming sulfuric acid (oleum)	5.0 mL
Concentrated H_2SO_4	5.0 mL (optional, for dilution)
Ice	As needed
Distilled water	As needed
Beakers, test tubes	For mixing and reaction
Dropper, glass rod	For handling reagents
Fume hood	Mandatory for benzene and oleum
Gloves, goggles, lab coat	For safety

PROCEDURE

- In a dry test tube or small conical flask, take 2.0 mL of benzene.
- Carefully add 5.0 mL of fuming sulfuric acid (oleum)dropwise with constant stirring.
- Mix thoroughly and heat gently on a water bath at 50–60 °C for 30 minutes.
- Cool the mixture and slowly pour it into a beaker containing crushed ice (50–100 g).
- Stir the mixture well. A clear aqueous solution of benzenesulphonic acid will form.
- Optionally, neutralize a small portion with NaOH and test with pH paper to check acidity.
- The product can be isolated(if desired) by neutralizing with NaOH to form sodium benzenesulphonate, and evaporating the solution to obtain crystals.

OBSERVATION

Step	Observation
1	Benzene is colorless and has a sharp odor
2	Mixing with oleum leads to an exothermic reaction
3	Heating enhances the reaction
4	On pouring into ice, a clear acidic solution forms

RESULT

Benzenesulphonic acid was successfully synthesized by sulphonation of benzene using oleum. The acidic aqueous product confirms the formation of a sulphonated compound.

PRECAUTIONS

- Benzene is carcinogenic; handle only in a fume hood.
- Oleum is highly corrosive; add it carefully to avoid splashing.
- Use gloves, goggles, and lab coat throughout the experiment. Do not inhale vapors of benzene or sulfuric acid.

15.13 OXIDATION

Synthesis of benzoic acid by oxidation of benzyl alcohol using potassium permanganate ($KMnO_4$)

Aim: To prepare benzoic acid by the oxidation of benzyl alcohol using alkaline potassium permanganate ($KMnO_4$)as an oxidizing agent.

Theory: Oxidation in organic synthesis involves the increase in oxidation state of a compound, usually by increasing the number of C–O bonds or decreasing the number of C–H bonds. In this experiment, benzyl alcohol ($C_6H_5CH_2OH$) is oxidized to benzoic acid (C_6H_5COOH) using alkaline potassium permanganate**,** which acts as a strong oxidizing agent.The purple color of $KMnO_4$ fades to brown due to the formation of MnO_4, confirming the reaction.

Chemical Reaction: $C_6H_5CH_2OH + [O] \xrightarrow{KMnO4} C_6H_5COOH + H_2O$

Materials Required:

Chemical	Quantity
Benzyl alcohol	2.0 mL (~2.1 g)
Potassium permanganate ($KMnO_4$)	5.0 g
Sodium hydroxide (NaOH)	2.0 g
Distilled water	100 mL (total)
Concentrated HCl	Few mL (to acidify)
Ice	As required
Apparatus	**Specification**
Beakers, conical flask	250 mL
Bunsen burner or water bath	Gentle heating
Glass rod, filter paper, funnel	Filtration

Procedure:

- In a 250 mL conical flask, dissolve 2.0 g of NaOH and 5.0 g of $KMnO_4$ in 100 mL distilled water to prepare an alkaline $KMnO_4$ solution.
- Add 2.0 mL of benzyl alcohol to the solution.
- Heat the mixture gently on a water bath or Bunsen burner for 30–40 minutes with continuous stirring.
- During the reaction, the purple color of $KMnO_4$ disappears and brown precipitate of MnO_4 forms.
- After cooling, acidify the mixture with concentrated HCl dropwise until it becomes acidic (check with litmus paper). This precipitates benzoic acid.
- Filter the precipitated benzoic acid, wash with cold water, and dry.
- Recrystallize the crude product from hot water for purification.
- Record the melting point of the final product (Benzoic acid m.p. ≈ **122 °C**).

Observations:

Step	Observation
3	$KMnO_4$ color fades, brown MnO_4 precipitates

Step	Observation
5	On acidification, white benzoic acid precipitates
7	Pure crystals of benzoic acid obtained

Result: Benzoic acid was successfully synthesized by oxidation of benzyl alcohol using $KMnO_4$. The melting point of the purified sample was found to be **____ °C**, close to the standard value of 122 °C**.**

Precautions:

- $KMnO_4$ is a strong oxidizer—handle carefully.
- Heat the reaction mixture gently to avoid decomposition.
- Always add HCl slowly; the reaction is exothermic.
- Use gloves, goggles, and lab coat.

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