Unit - I
Molecular structure and Theories of Bonding

Terms and Definitions involved

Orbitals - They represent the probability of finding an electron in any one place. They correspond to different energies. So an electron in an orbital has definite energy. Orbital’s are best described with quantum mechanics.

Atomic Orbitals – the region in space just outside the nucleus of the atom where the probability of finding the electrons is at the highest (95%).

Molecular Orbitals – formed as a result from the overlap of two atomic orbitals, wherein a pair of electrons occupying.

Electron Density – a measure of the probability of finding an electron in an orbital.

Wave Function – mathematical description of the volume of space occupied by an electron having a certain amount of energy.

A node in an orbital – is the place where a crest and a trough meet.

- Electrons in atoms treated as waves effectively than as compact particles in circular or elliptical orbits. Such particles like electrons, atoms or molecules do not obey Isaac Newton’s Law but rather obeys a different kind of mechanics called quantum mechanics.
- According to quantum mechanics, we cannot determine precisely the paths that electrons follow as they move about atomic nuclei (HEISENBERG UNCERTAINTY PRINCIPLE). Because of this, scientists resort to statistical approach and speak of the probability of finding an electron within specified region in space (ATOMIC ORBITAL).
- So, quantum numbers are used to designate the electronic arrangements in all atoms (ELECTRONIC CONFIGURATIONS) and play important roles in describing the energy levels and the shapes of orbital’s that describe the distributions of electrons in space.
  1. Principal quantum number (n) – It indicates the main shell of the atomic orbital. K,L,M,N……..Shell .The values are positive integers n = 1,2,3,4,5……..∞.It is the crude index of average distance between the electron and the nucleus
  2. Azimuthal quantum number (Angular momentum quantum number ) – For the given value of n the shape of the orbital can be determined by Azimuthal quantum number L may have all integral valus from 0 to n-1 which represents energy sub shells s,p,d,f……
3. Magnetic Quantum number (m) – It explains the direction of orbitals in the space. For each L value, the value of m may between $+L, (+L-1), 0, (-L+1), -L$

4. Spin Quantum Number (s) – Orientation of electron in the orbital can be understood

**Shape of S Orbitals**

**Shape of P Orbitals**

**Molecular Orbital Theory** - The goal of molecular orbital theory is to describe molecules in a similar way to how we describe atoms, that is, in terms of orbitals, orbital diagrams, and electron configurations. Bonding between atoms occurs when they come into close enough proximity for their orbitals to overlap. Thus, when two atoms are brought close enough together to permit overlap of their orbitals, their electron pair and go into a single orbital encompassing both nuclei.

**Constructive and Distructive approch of atomic orbitals**

- As two atoms form a bond, they interact very much like waves on a body of water.
- When two waves are traveling in the same directions and one overtakes the other the amplitude of the new wave is greater than the amplitude of either of the two that created it. In contrast, when two waves travel in opposite directions, and they meet, their amplitudes cancel each other.
- A pair of electrons encompassing two or more nuclei is said to occupy a MOLECULAR ORBITAL.
- As with atomic orbitals, a molecular orbital may not contain more than two electrons.
- The molecular orbital represents a lower energy state for the system than do two separate atomic orbitals at the characteristic internuclear distance.
- Energy is liberated during the overlap, and a stable covalent bond is formed.
- Orbital Mixing: When atoms share electrons to form a bond, their atomic orbitals mix to form molecular bonds. In order for these orbitals to mix they must:
  - Have similar energy levels,
  - Overlap well,
  - Be close together.

**Molecular Orbital Diagrams**
1. Electrons preferentially occupy molecular orbitals that are lower in energy.
2. Molecular orbitals may be empty, or contain one or two electrons.
3. If two electrons occupy the same molecular orbital, they must be spin paired.
4. When occupying degenerate molecular orbitals, electrons occupy separate orbitals with parallel spins before pairing.

Although molecular orbitals form from inner (core) electrons as well as valence electrons, many molecular orbital diagrams include only the valence level.
**Pi (\(\pi\)) molecular orbitals** – In a \(\pi\) molecular orbital, the electron density is concentrated above and below the line joining the two nuclei of the bonding atoms. The electrons in it are called \(\pi\) electrons and the bond is referred to as \(\pi\) bond. A double bond is one \(\sigma\) bond and one \(\pi\) bond, a triple bond consists of one \(\sigma\) bond and two \(\pi\) bonds.

A \(\pi\) molecular orbital may be formed by the sideways overlap of the Two pz atomic orbitals. **Combination of four parallel 2p atomic orbitals gives two \(p\)-bonding MOs and two \(p\)-antibonding MOs. These are represented in the diagrams**
Crystal Field Theory

With this theory, the bonding between the central metal atom and the ligands is completely ignored. The ligands are viewed simply as mere point charges. One focuses on the valence $d$ orbitals of the central transition metal atom and examines how the relative energies of the $d$ orbitals change upon introduction of external negative point charges (the ligands). Thus, it is necessary to go back and examine the various $d$ orbitals.

Octahedral geometry

In the figure below, an octahedral field created by six point charges is assumed:

If the distribution of the point charges is spherical then all $d$ orbitals will be affected in the same manner. All of the $d$ orbitals will rise in energy. In an octahedral arrangement, the point charges approach the metal atom along the Cartesian $x$, $y$ and $z$ axes. Thus, the orbitals that lie along these axes ($d_{z^2}$ and $d_{x^2-y^2}$) should rise in energy by a greater amount compared to the orbitals that do not lie exactly along the $x$, $y$ and $z$ axes ($d_{xy}$, $d_{xz}$, $d_{yz}$).

The $d$ orbitals in the presence of an octahedral field can be described by the energy diagram.

Square planar geometry

This should be similar to the octahedral case. In fact, one can imagine slowly removing the point charges along the $z$ axis until they are completely gone. The figure below shows the correlation diagram:

Based on the energies of the $d$ orbitals for a square planar complex, one would predict that this arrangement would be quite popular for $d^8$ species.
Tetrahedral geometry

Imagine the metal atom inside a cube with its $d_{z^2}$ and $d_{x^2-y^2}$ orbitals pointing at the center of the cube faces. In a tetrahedral arrangement, the point charges approach via the four opposite corners of the cube. The orbitals $d_{xy}$, $d_{xz}$, and $d_{yz}$ are pointing towards the center of the cube edges (These are closer to the corner). Therefore,

Subjective Questions

1. Draw the π Molecular Orbital diagram of Butadiene.
2. Outline the salient features of Crystal Field splitting for Tetrahedral Complexes
3. Outline the factors affecting magnitude of crystal field splitting of d-orbital’s
4. Outline the salient features of Crystal Field splitting for Octahedral Complexes
5. Draw the Molecular Orbital energy level diagram of $N_2$

Objective Questions

1. Which one of following statement is false [ ]
   a) Octahedral crystal field the d- electrons on a metal ion occupy the eg set of orbitals before they occupy the t2g set of orbitals
   b) Low spin complexes contain strong field ligands
c) Diamagnetic metal ions cannot have an odd no. of electrons

d) Low spin complexes can be paramagnetic

2. Select the correct IUPAC name for \([\text{Co(NH}_3\text{)}_6\text{]}^{3+}\) [ ]
a) Hexammonia cobaltate (III) ion c) Hexa ammine cobalt (III) ion
b) Hexammonia cobalt (III) ion d) Hexa ammine cobalt (III) ion

3. The ------- sphere is enclosed in brackets in formulaes for complex species , & it include the central metal ion plus the co-ordinated groups [ ]
a) Ligand b) Donar c) Oxidation d) Co-ordination

4. In co-ordination chemistry, the donor atom of a ligand is [ ]
a) A lewis acid b) Central metal atom
c) The atom in the ligand that shares an electron pair with the metal
d) Counter ion

5. The filling of molecular orbital takes place according to [ ]
a) The Aufbau Principle b) Pauli Exculsion Principle

6. Arrange the following molecules in decreasing bond length. [ ]
a) \(\text{O}_2 > \text{O}^{2-} > \text{O}^{2+} > \text{O}_2^{2-}\) b) \(\text{O}_2^{2-} > \text{O}^{2-} > \text{O}_2 > \text{O}^{2+}\)
c) \(\text{O}_2^{2-} > \text{O}^{2-} > \text{O}^{2+} > \text{O}_2\) d) \(\text{O}^{2-} > \text{O}^{2+} > \text{O}_2^{2-} > \text{O}_2\)

7. Which of the following molecule does not exist due to its zero bond order? [ ]
a) \(\text{H}_2^+\) b) \(\text{He}_2^+\) c) \(\text{He}_2\) d) \(\text{H}_2^-\)

8. Antibonding molecular orbitals are produced by [ ]
(a) Constructive interaction of atomic orbitals.
(b) Destructive interaction of atomic orbitals.
(c) The overlap of the atomic orbitals of two negative ions
(d) all of these
UNIT II
Water and its treatment

Hard water
Water which does not produce lather with soap solution, but produces white precipitate (scum) is called hard water.

\[
2\text{C}_{17}\text{H}_{35}\text{COONa} + \text{Ca}^{++} \rightarrow (\text{C}_{17}\text{H}_{35}\text{COO})\text{Ca} + 2\text{Na}^{+}
\]
Sodium soap Soluble Hard salt Calcium Soap – Water Insoluble

Soft water
Water, which produces lather, readily with soap solution is called soft water.
This is due to the absence of Ca and Mg salts.

Hardness:
Hardness is caused by the soluble salts of calcium, magnesium, iron, manganese, sodium, sulphate, chlorides and nitrates.

Types of hardness
Depending upon the types of dissolved salts present in water, hardness of water can be classified into two types:

- Temporary Hardness
- Permanent Hardness

Temporary Hardness (or) Carbonate Hardness (CH) (or) Alkaline Hardness
Temporary hardness is caused by a combination of calcium and magnesium bicarbonate ions in the water. It can be removed by

- boiling water
- by the addition of lime (Ca(OH)\text{2})

Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon coving.

\[
\text{Ca (HCO3)2} \rightarrow \text{CaCO3} \downarrow + \text{H2O} + \text{CO2}
\]
\[
\text{Mg (HCO3)2} + 2\text{Ca(OH)2} \rightarrow \text{Mg (OH)2}\downarrow + 2\text{CaCO3}\downarrow + 2\text{H2O}
\]

Permanent Hardness (or) Non – Carbonate Hardness (NCH) (or) Non – alkaline

Hardness
It is usually caused by the presence of calcium and magnesium sulphates and /or chlorides which become more soluble as the temperature rises. It can be removed by chemical treatment of water.
**Expression of hardness in terms of equivalents of CaCO₃**
The concentration of hardness producing salts are usually expressed in terms of an equivalent amount of CaCO₃. CaCO₃ is chosen as a standard because,
i) Its molecular weight (100) and equivalent weight (50) is a whole number, so the calculations in water analysis can be simplified.
ii) It is the most insoluble salt that can be precipitated in water treatment.

If the concentration of hardness producing salt is \(x\) mgs/lit, then

\[
\text{Amount} \times \frac{100}{\text{M.Wt of hard salt}} = \text{equivalent to CaCO₃} \times X
\]

**Units of Hardness**
1. Parts per million (ppm)
2. Milligrams per litre (mg/lit)
3. Clarke’s degree (oCl)
4. French degree (oFr)

**Relationship between various units**
1 ppm = 1 mg/lit = 0.10 Fr = 0.070 Cl

**Estimation of hardness by EDTA method:**
EDTA is Ethylene Diamine Tetra Acetic Acid.

Since EDTA is insoluble in water, its disodium salt is used as a sequestering or complexing agent.

**Basic Principle:**
When hard water comes in contact with EDTA, at pH 9-10, the Ca⁺² and Mg⁺² forms stable, color less complex with EDTA.
To the hard water sample the blue colored indicator Eriochrome Black-T (EBT) is added along with the buffer solution. EBT forms an unstable, wine red complex with Ca\(^{+2}\) and Mg\(^{+2}\) :

\[
\text{Ca}^{+2} + \text{Mg}^{+2} + \text{EBT} \rightarrow \left\{ \text{Ca – EBT} + \text{Mg - EBT} \right\}
\]

unstable, wine red coloured complex

The wine red coloured [Ca – EBT, Mg-EBT] complex is titrated with EDTA, where EDTA replaces EBT from [Ca – EBT+ Mg – EBT] complex and forms stable, colourless [Ca – EDTA] [Mg-EDTA] complex releasing the blue coloured indicator EBT into water. Hence the colour change at the end point is wine red to blue colour.

[Ca – EBT ] [ Mg – EBT] + EDTA \rightarrow [Ca – EDTA] [ Mg – EDTA] + EBT

Unstable wine red complex stable, colourless complex blue

**Portable water**

Water free from contaminants or water that safe for human consumption is called **Portable Water**.

The standards recommended for drinking water are as follows

1) It should be colorless and clear, good taste.
2) Turbidity should be less than 10 ppm
3) Its ph should be in the range of 7.0-8.5
4) Its total hardness should be less than 125 ppm
5) It should be free pathogenic bacteria
6) It should be free from objectionable dissolved gasses like H\(_2\)S
7) It should be free from metals such as lead ,arsenic ,chromium and Mn.
8) It’s chloride ,flourides and sulphate contents should be less than 250 ppm ,1.5 ppm and 250 ppm respectively.

**TREATMENT OF MUNICIPAL WATER**

The treatment of water for drinking purposes mainly includes the removal of suspended impurities, colloidal impurities and harmful pathogenic bacteria.
**Disinfection:** is the process of elimination of most pathogenic micro organisms (excluding bacterial spores on inanimate objects).

The following are the methods adopted for sterilization and disinfection.

a) Chlorination: the process of utilizing chlorine as a powerful disinfectant is called chlorination. There are three types of chlorinating reagents.

By passing chloramines:

\[ \text{Cl}_2 + \text{NH}_3 \rightarrow \text{ClNH}_2 + \text{HCl} \]

\[ \text{ClNH}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_3 \]

By bleaching power:

\[ \text{CaOCl}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{Cl}_2 \]

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} \]

Chlorination:

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} \]

**BREAK POINT CHLORINATION /FREE – RESIDUAL CHLORINATION:**

The amount of chlorine required to kill bacteria and to remove organic matter is called **Break point chlorination.**

The water sample is treated with chlorine and estimated for the residual chlorine in water and plotted a graph as shown below which gives the break point chlorination.
ADVANTAGES OF BREAK-POINT CHLORINATION:
(i) It oxidizes completely organic compounds, ammonia and other reducing compounds
(ii) It removes color in water, due to the presence of organic matters
(iii) It destroys completely (100%) all the disease-producing bacteria.
(iv) It prevents the growth of any weeds in water.

Boiler Feed water Treatment:
Internal conditioning OR Internal treatment OR Boiler compounds
It involves the removal of scale forming substance by adding chemicals directly into the boiler. These chemicals are also called boiler compounds.

Carbonate conditioning
Scale formation can be avoided by adding Na$_2$CO$_3$ to the boiler water. It is used only in low pressure boilers.
CaSO$_4$ + Na$_2$CO$_3$ $\rightarrow$ CaCO$_3$ + Na$_2$SO$_4$

Phosphate conditioning
Scale formation can be avoided by adding sodium phosphate. It is used in high pressure boilers.
3CaSO$_4$ + 2 Na$_3$PO$_4$ $\rightarrow$ Ca$_3$(PO$_4$)$_2$ + 3Na$_2$SO$_4$
Generally 3 types of phosphates are employed.
□ Trisodium phosphate – Na$_3$PO$_4$ (Too alkaline) – used for too acidic water.
□ Disodium hydrogen phosphate - Na$_2$HPO$_4$ (weakly alkaline) - used for weakly acidic water.
□ Sodium dihydrogen phosphate - NaH$_2$PO$_4$ (acidic) – used for alkaline water.

Calgon conditioning
Calgon is sodium hexa meta phosphate Na$_2$[Na$_4$(PO$_3$)6]. This substance interacts with calcium ions forming a highly soluble complex and thus prevents the precipitation of scale forming salt.
2CaSO$_4$ + Na$_2$[Na$_4$(PO$_3$)6]$\rightarrow$ Na$_2$[Ca$_2$(PO$_3$)6] + 2 Na$_2$SO$_4$.

External conditioning
Demineralization or Ion Exchange Process
In this process, ions present in water are removed by ion-exchange resins.
Ion exchange resins are high molecular weight insoluble, cross-linked, organic polymers which are capable of exchanging cations and anions form water.
These are styrene – divinyl benzene copolymers.
Acidic and basic functional groups attached to these resins are responsible for the iron exchange property of resins
Principle: when hard water is passed through cation exchange resin, H$^+$ ions are replaced by cations present in water.
2RH$^+$ + Ca$^{2+}$ $\rightarrow$ R$_2$Ca + 2H$^+$
When water is passed through anion exchange resin, OH⁻ ions are replaced by anions present in hard water.

\[
2\text{ROH} + \text{SO}_4^{2-} \rightarrow \text{R}_2\text{SO}_4 + 2\text{OH}^-
\]

\[
\text{ROH} + \text{Cl}^- \rightarrow 2\text{RCl} + \text{OH}^-
\]

\[
\text{ROH} + \text{HCO}_3^- \rightarrow \text{RHCO}_3 + \text{OH}^-
\]

The H⁺ and OH⁻ ions released will combine to form water.

When all the H⁺ ions of cation exchange resin and OH⁻ ions of anion exchange resin are replaced, the resins are said to be exhausted.

**Regeneration:** Regeneration of exhausted cation exchange resin and anion exchange resin are carried out by passing dil. HCl and dil. NaOH solution respectively into the bed and washing with distilled water.

\[
\text{R}_2\text{Ca} + 2\text{H}^+ \rightarrow 2\text{RH} + \text{Ca}^{+2}
\]

\[
\text{R}_2\text{SO}_4 + 2\text{OH}^- \rightarrow 2\text{ROH} + \text{SO}_4^{2-}
\]

**Desalination of Brackish water**

Brackish water: water containing high concentrations of dissolved salts with a salty taste is called brackish water, which contains about 3.5% of dissolved salts. This water cannot be used for domestic and industrial purpose, unless the dissolved salts are removed by desalination.

**Reverse osmosis**
**Principle:**
If a pressure higher than the osmotic pressure is applied on the concentrated side, solvent flows in reverse direction i.e. from higher concentrated region to lower concentrated region. Hence this method is called reverse osmosis.
Mostly the membranes are made of cellulous acetate, polyamide and polyamide sulphone

**Polymers**

**Advantages**
1. The water obtained by this process is used for high pressure boilers
2. Due to low capital cost and operational cost, it is used to convert brackish water to drinking water
3. It removes ionic and non-ionic, colloidal and organic matter from water
4. The life time of membrane is high.

**SHORT ANSWER QUESTIONS**

1. How calgon treatments prevent scale formation in boilers?
2. Give the definitions’ for the common units used for the expression of hardness?
3. Give reason, in the deionization process, water is usually first passed through the cation exchanger and then through the anion exchanger.
4. How caustic soda causing boiler corrosion explain.
5. What happens when temporary hard water is boiled? (Give equations)
6. What is sedimentation with coagulation? (Give equations)

**Objective Questions**

1. The purification of brackish water is carried through the following process. [ ]

2. One part of CaCO₃ equivalent hardness per 10⁵ parts of water is also called as [ ]
   a. Degree Clarke   b. ppm.   c. Degree French   d. Mg/L.

3. Boiler corrosion caused by using highly alkaline water in boiler is called [ ]
   a. Corrosion   b. boiler corrosion   c. caustic embrittlement   d. erosion.

4. Caustic embrittlement can be avoided by using [ ]
   a. Sodium phosphate   b. hydrogen   c. ammonium hydroxide   d. sedum sulphate.
5. The soft loose and slimy precipitate formed within the boiler is called
   a. Scale  b. sludge.  c. embrittlement  d. coagulation.

1. Presence of residual _______________ in boiler water causes caustic embrittlement.

2. __________ causes the flow of solvent from lower concentration to higher concentration, which is separated by a semi permeable membrane.

11. Sodium aluminate is used as ____________ during purification of water.

12. Anion exchange resins are regenerated by using ________________.

13. Best method of removing hardness of water is ________________ process.
UNIT-III

ELECTROCHEMISTRY & CORROSION

Galvanic cell or Voltaic cell
It is a simple device of producing electrical energy by chemical reaction, e.g., Daniel cell. Such a cell is also known as Electrochemical cell.

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \text{ (oxidation)} \]
\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \text{ (reduction)} \]
In the above cell Zn-electrode is anode and Cu-electrode is cathode.

Electrolytic cell
It is a device used for converting electrical energy into chemical energy.

Electrode potential (E)
The tendency of an electrode to lose or gain electrons, when it is in contact with its own ions.

Reduction potential is the tendency of an electrode in a half cell to gain electrons and oxidation potential is the tendency of an electrode in a half cell to lose electrons.

Standard electrode potential (E°)
It is the electrode potential of a metal in contact with its ions when the concentration of ions is 1M (1 molar).
E.M.F. of a cell
It is defined as the potential difference between the two terminals of the cell when no current is drawn from it.

Reference electrodes:
These are the electrodes whose potential is constant and independent of the composition of the contacting solution.
The most widely used are saturated calomel electrodes ($G = +0.246$ V) and the silver-silver chloride electrode ($e = +0.222$ V).

**Calomel electrode:**
This electrode consists of mercury, mercurous chloride and a solution of saturated KCl.
The cell is represented as; $\text{Pt, Hg, Hg}_2\text{Cl}_2 / \text{KCl(sat)}$
Mercury is placed at the bottom of the electrode. Mercury is covered by a paste of mercurous chloride and a solution of saturated KCl is introduced above the paste. A platinum wire sealed in to a glass tube serves to make electrical contact of the electrode with the circuit.
If the electrode acts as anode, the electrode reaction will be;
$$2\text{Hg} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{e}^-$$
If the electrode acts as cathode the electrode reaction will be;
$$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$$
The electrode potential can be written as
$$E = E^\circ - 0.0591/2 \log[\text{Cl}^-]_2 \text{ or } E = E^\circ - 0.0591 \log[\text{Cl}^-]$$
The electrode potential depends on the concentration of chloride ion.
Glass electrode:
It is an electrode, which produces current in response to a specific ion present in the solution. This electrode is otherwise known as ion selective electrode.
A glass membrane electrode consists of thin walled glass bulb containing AgCl coated Ag electrode or platinum wire in 0.1M HCl. There is an equilibrium exist between H\(^+\) ions of solution and Na\(^+\) ions of glass. For a particular type of glass the electrode potential depends on the concentration of H\(^+\) ions. This can be represented as; AgCl, Ag, HCl (0.1M)/Glass or Pt, HCl (0.1M)/Glass
If this electrode acts as anode, the electrode reaction will be;
\[
\frac{1}{2} H_2 \rightarrow H^+ + e^- \\
\]
If this electrode acts as cathode, the electrode reaction will be;
\[
H^+ + e^- \rightarrow \frac{1}{2} H_2 \\
\]
The electrode potential can be written as;
\[
E = E^\circ_g - 0.0591 \log[H^+] \quad \text{(oxidation potential)} \\
E = E^\circ_g + 0.0591pH \\
\]

Determination of pH with the help of glass electrode:
The electrode is dipped into the solution where pH is to be determined and is usually combined with a reference electrode—generally calomel electrode—to form a complete cell. The potential of the glass electrode varies linearly with pH. Solution of unknown pH
\[
E_{cell} = E_R - E_L \\
E_{cell} = E_{calomel} - E_{glass} \\
E_{cell} = +0.2422 - (E^\circ_g - 0.0591 \log[H^+]) \\
E_{cell} = +0.2422 - E^\circ_g - 0.0591pH \\
pH = +0.2422 - E^\circ_g - E_{cell} / 0.0591 \\
\]

Potentiometric Titrations:
A titration in which concentration change is followed by potential change is called a potentiometric titration. Two electrodes are required to measure the potential of the test solution. The potential of one electrode should be constant while that of the other should change with concentration of the test species. The former is called reference electrode and the latter is called an indicator electrode which is different for different types of titrations. For a redox titration (Fe\(^2+\) Vs Cr\(^6+\)), calomel electrode is used as a reference electrode and platinum is used as an indicator electrode. The two electrodes are connected to a potentiometer.
There are three types of potentiometric titrations:
1) Redox titrations
2) Precipitation titrations
3) Acid-base titrations

**Electrochemical series**

The electrode potentials of various electrodes are arranged in the order of increasing standard reduction potentials with respective to hydrogen scale. This arrangement is known as electrochemical series.

**Importance of electrochemical series:**

**Calculation of standard EMF of a cell:**
The standard EMF of a cell can be calculated using the standard reduction potentials of right hand side and left hand side electrodes from the emf series.

\[
E^\circ_{\text{cell}} = E^\circ_{R} - E^\circ_{L}
\]

**Relative ease of oxidation and reduction:**

Higher the value of standard reduction potential, greater is the tendency to get reduced. For example, in the electrochemical series, fluorine has high positive value of reduction potential (+2.87 V) and is reduced. Lower the value of standard reduction potential, greater is the tendency to get oxidized. In the electrochemical series, lithium has the lower negative reduction potential value (-3.05 V) and is oxidized.

**Predicting spontaneity of a reaction:**
The spontaneity of a reaction can be determined from the standard emf of the cell.

If the emf of a cell is positive, the reaction is spontaneous. If it is negative, the reaction is non spontaneous.

\[
E^\circ_{\text{cell}} = E^\circ_{R} - E^\circ_{L} = + \text{ive (spontaneous)}
\]

\[
E^\circ_{\text{cell}} = E^\circ_{R} - E^\circ_{L} = - \text{ive (non spontaneous)}
\]

**Displacement behaviour of hydrogen:**

If zinc electrode is immersed in H2SO4 solution, it displaces hydrogen from acid solution.

\[
\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2
\]

If silver electrode is immersed in H2SO4 solution, it will not displace
BATTERIES

- Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage.
- A device which converts chemical energy to electrical energy is called battery.
- Usually in the term applied to a group or two or more electric cells, connected together electrically in series.
- Batteries are commercial electrochemical cells.
- Batteries are 3 types
  1. Primary cells
  2. Secondary cells
  3. Fuel cells

Primary cells:

- These are disposable batteries, which are designed to use once and discard.
- Cannot be recharged
- The cell reaction is not reversible; hence when all the reactants are converted into products, no more electricity is produced and the cell becomes dead and cannot be used after that. (the reactants are not return back to reactants by application of current)
- These batteries are used as a source of DC power.
- These cells are convenient to use and inexpensive.
- Used in ordinary gadgets like torch lights, watches and toys.
- Ex: Leclanche cell, Lithium cells and alkaline cells.

Lithium battery

- Lithium is the lightest of metals and it can float on water.
- The electrochemical properties of lithium are excellent and it is also a highly reactive material.

These properties gives Lithium the potential to achieve very high energy and power densities in high-density battery applications such as automotive and standby power.

Lithium batteries are primary batteries in which lithium metal (or) lithium compound acts as a Anode. A lithium cell can produce voltage from 1.5 V to about 3 V based on the types of materials used.

There are two types of lithium-based batteries available.
1. Lithium batteries

2. Lithium-ion batteries

   In lithium batteries, a pure lithium metallic element is used as anode. These types of batteries are not rechargeable. Lithium cells can be classified as follows

   a. Lithium cells with solid cathodes
   b. Lithium cells with liquid cathodes

**Lithium cells with solid cathodes:** These systems may have solid or liquid electrolyte

Lithium manganese dioxide is widely used as a solid cathode lithium cell

Cathode is $\text{MnO}_2$ & anode is lithium

$\text{MnO}_2$ should be heated above 300°C to remove water

This i very important to improve the efficiency of the cell

Anodic and cathodic reactions are as follows

Anodic reaction: $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$

Cathodic reaction: $\text{Li}^+ + \text{e}^- + \text{MnO}_2 \rightarrow \text{LiMnO}_2$

Net reaction: $\text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2$

The electrolyte is a mixture of propylene carbonate and 1,2 – dimethoxy ethane

**Applications**

1. The cylindrical cells are used in fully automatic cameras
2. The coin cells are widely used in electronic device such as calculators and watches

**Lithium cell with liquid cathode**

Eg: Lithium sulphur dioxide cell
The co-solvents used are either acrylonitrile propylene carbonate or mixture with of the two or 50% by volume of SO₂

Cell reaction represents as follows

\[ 2\text{Li} + 2\text{SO}_2 \rightarrow \text{Li}_2\text{SO}_4 \]

The second type of this cathode is Lithium Thionyl Chloride cells

It consists of a high – surface area carbon cathode

Thionyl chloride acts as the electrolyte solvent and the active cathode the reactions of cell represented as follows

Anodic reaction: \[ \text{Li} \rightarrow \text{Li} + e^- \]

Cathodic reaction: \[ 4\text{Li} + 4e^- + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{SO}_2 + \text{S} \]

Net reaction: \[ 4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{SO}_2 + \text{S} \]

Due to the nature of reaction Li – thionyl chloride cells possess very high energy density

Reactions involve two electrons per thionyl chloride

The SO₂ liberated as product is a liquid under the internal pressure of the cell

No- co solvent is required for the solution as thinly chloride is a liquid having moderate vapour pressure

**Applications**

1. Li-SOCl₂ cells are used on electronic circuit bonds for supplying fixed voltage for memory prediction
2. These cells are also used for military and space applications
3. These cells are also used in medical device such as neuro – stimulators, drug delivery systems
Secondary cells:

- These are rechargeable batteries, which are designed to be recharged and used multiple times.
- The cells in which the cell reaction is reversed by passing direct current in opposite direction.
- The secondary batteries can be used through a large number of cycles of discharging and charging.
- They are used as source of dc power used to supply large, short term repetitive power requirements such as automotive and airplane batteries.
- These batteries have very large capacitance and long periods of low current rate discharge.
- The cell reaction is reversible; the reactants are return back to reactants by application of current
- These batteries are used as a source of DC power.
- EX: Lead acid storage cell (Lead accumulator)

Lead accumulator or Lead storage battery:

- A storage cell can operate both as a voltaic cell and as an electrolytic cell.
- When operating as a voltaic cell, it supplies electrical energy and as a result eventually becomes rundown, when being recharged; the cell operates as an electrolytic cell.
- This storage cell has the great advantage of working both as an electrolytic cell and as a voltaic cell.
- It has lead anode and PbO\textsubscript{2} cathode and dilute H\textsubscript{2}SO\textsubscript{4} acts as electrolyte.
- These all are placed in a plastic container as shown in diagram.
- A number of lead plates (-ve plates) are connected in parallel and a number of lead dioxide plates (+ve plates) are also connected in parallel.
- The lead plates fit in between the lead dioxide plates. The plates are separated from adjacent one by insulators like wooden strips, rubber or glass fibre.
- The entire combination is immersed in 20% dilute H\textsubscript{2}SO\textsubscript{4} corresponding specific gravity of 1.2

- **During Discharge:**
  - In the discharged state:
    - Both the anode and cathode become lead (II) sulfate (PbSO\textsubscript{4}) and the dilute H\textsubscript{2}SO\textsubscript{4} is changed into water.
    - Electrons move from cathode to anode through bulb.
The cell reactions are

At anode: \[ \text{Pb (s) + H}_2\text{SO}_4 (aq) \rightarrow \text{PbSO}_4 (s) + 2\text{H}^+ (aq) + 2\overline{e} \]

At cathode: \[ \text{PbO}_2 (s) + \text{H}_2\text{SO}_4 (aq) + 2\text{H}^+ (aq) + 2\overline{e} \rightarrow \text{PbSO}_4 (s) + 2\text{H}_2\text{O} (l) \]

Net reaction: \[ \text{Pb (s) + PbO}_2 (s) + 2\text{H}_2\text{SO}_4 (aq) \rightarrow 2\text{PbSO}_4 (s) + 2\text{H}_2\text{O} (l) + \text{energy} \]

- **During Charging:**
  - In the charged state:
    - Cell has anode of lead (Pb) and cathode of lead oxide (PbO₂) and dilute H₂SO₄
    - Electrons move from anode to cathode.
    - The cell reactions are
      - At anode: \[ \text{PbSO}_4(s) + 2\text{H}^+ (aq) + 2\overline{e} \rightarrow \text{Pb(s) + H}_2\text{SO}_4 (aq) \]
      - At cathode: \[ \text{PbSO}_4(s) + 2\text{H}_2\text{O} (l) \rightarrow \text{PbO}_2(s) + \text{H}_2\text{SO}_4 (aq) + 2\text{H}^+ (aq) + 2\overline{e} \]
      - Net reaction: \[ 2\text{PbSO}_4 (s) + 2\text{H}_2\text{O} (l) \rightarrow \text{Pb (s) + PbO}_2 (s) + 2 \text{H}_2\text{SO}_4 (aq) \]

- **Applications:**
  - Lead storage batteries are used in cars, motor cycles, Lorries to start the engine.
  - They are also used in invertors for electric supply in telephone exchanges, railway trains, hospitals and houses.

**Advantages:**
1. It has relatively constant potential i.e. 12V
2. It is portable and inexpensive.
3. When electricity is being drawn from the cell, to start the car it acts as a voltaic cell, when the car is running, the cell is being recharged as an electrolytic cell.

**Lithium-ion battery (Li-ion Battery)**

Li-ion batteries are secondary batteries.

- The battery consists of an anode of Lithium, dissolved as ions, into a carbon.
- The cathode material is made up from Lithium liberating compounds, typically the three electro-active oxide materials, like Lithium Cobalt-oxide (LiCoO$_2$).

![Li-Ion battery Principle](image)

**Construction**

- Li-ion cell has a four-layer structure.
- A positive electrode made with Lithium Cobalt Oxide has a current collector made of thin aluminum foil – **cathode**
- A negative electrode made with specialty carbon has a current collector of thin copper foil – **anode**
- A **separator** is a fine porous polymer film.
- An **electrolyte** made with lithium salt in an organic solvent.

**Working**

- The traditional batteries are based on galvanic action but Lithium ion secondary battery depends on an "intercalation" mechanism.
• This involves the insertion of lithium ions into the crystalline lattice of the host electrode without changing its crystal structure.

• These electrodes have two key properties. One is the open crystal structure, which allow the insertion or extraction of lithium ions and the second is the ability to accept compensating electrons at the same time. Such electrodes are called intercalation hosts.

• The chemical reaction that takes place inside the battery is as follows, during charge and discharge operation:

\[ \text{Charge} \]
\[ \text{LiCoO}_2 + C_6 \rightarrow \text{Li}_x\text{CoO}_2 + C_6\text{Li}_x \]

\[ \text{Discharge} \]

• During charging, lithium in positive electrode material is ionized and moves from layer to layer and inserted into the negative electrode.

• During discharge Li ions are dissociated from the anode and migrate across the electrolyte and are inserted into the crystal structure of the host compound of cathode.

• At the same time the compensating electrons travel in the external circuit and are accepted by the host to balance the reaction.

• The process is completely reversible. Thus the lithium ions pass back and forth between the electrodes during charging and discharging.

• Because of this reason, the lithium ion batteries are called ‘Rocking chair, ‘Swing’ cells.

• A typical Li-ion battery can store 150 watt-hours of electricity in 1 kilogram of battery as compared to lead acid batteries can store only 25 watt-hours of electricity in one kilogram.

Corrosion
It is the gradual deterioration of metals by chemical, electrochemical or biochemical interaction with the environment.

Causes of Corrosion
Metals occur in nature as their oxides, sulphides carbonates etc. The chemically combined state is thermodynamically more stable. When we extract a metal from its ore, the metal is in a higher energy state, which is thermodynamically unstable. So it tries
to go back to the stable state by chemical or electrochemical interaction with the environment.

**Consequences or effects of Corrosion**
1. Efficiency of the machine decreases.
2. Plant has to be shut down due to failure.
3. Product is contaminated.
4. The toxic products of corrosion cause health hazards.
5. There is a necessity to over design to allow for corrosion.

**Classification or Theories of Corrosion**
I. Dry or Chemical Corrosion
II. Wet or Electrochemical Corrosion

**Dry or Chemical Corrosion**
It is due to the attack on metal surface by atmospheric gases like O₂, SO₂, H₂S etc. (e.g.) Tarnishing of silver by H₂S.
There are three types of dry or chemical corrosion.
1) Oxidation Corrosion
2) Corrosion by Hydrogen
3) Liquid Metal Corrosion

**Wet (or) Electrochemical Corrosion**
It occurs under the following conditions.
(i) When two dissimilar metals or alloys are in contact with each other in presence of an aqueous solution or moisture.
(ii) When the metal is exposed to an electrolyte with varying amounts of oxygen.

**Factors influencing corrosion**
1. Nature of the metal
   (i) **Position in emf series**
   Metals above hydrogen in the electrochemical series corrode easily because they have negative reduction potential. When two metals are in contact, the more active metal with a higher negative potential corrodes.
   (ii) **Areas of anode and cathode**
   Corrosion will be severe if the anodic area is smaller and cathodic area is larger. The larger cathodic area demands more electrons. So the anodic area corrodes faster.
   (iii) **Purity**
   100% pure metal will not corrode. (e.g.) Pure Zn does not corrode. If the metal has trace amount of impurity, it corrodes. (e.g.) Zinc metal with iron or copper impurity forms an electrochemical cell. The base metal Zn acts as anode and corrodes.
   (iv) **Over Voltage**
   Corrosion rate is inversely proportional to the over voltage of the metal in a
corrosive surroundings. (e.g.) The hydrogen over voltage of Zn in 1M H2SO4 is 0.7V. So the rate of corrosion is low. But when some Cu impurity is present, the over voltage is reduced and corrosion rate increases.

(v) **Nature of the Film**
Nature of film formed on the metal surface determines extent of corrosion.
(e.g.) In the case of alkali and alkaline earth metals, the oxide film formed is porous. The corrosion continues. In the case of heavy metals, the oxide film is non-porous. The film acts as a protective layer.

(vi) **Nature of corrosion product**
If the corrosion product is soluble in the corroding medium, corrosion rate is faster. Similarly if the corrosion product is volatile (e.g. MoO3), corrosion will be more.

2. **Nature of Environment**
(i) **Temperature**
Increase of temperature increases corrosion rate because the rate of diffusion of ions increases.

(ii) **Humidity**
Rate of corrosion is more, if humidity of environment is high. Moisture acts as solvent for O2, CO2 etc, to produce electrolyte necessary for formation of corrosion cell.

(iii) **Corrosive gases**
Acidic gases like CO2, SO2, H2S etc, produce electrolytes and increase corrosion.

(iv) **Presence of suspended particles**
Particles like NaCl, (NH4)2SO4 along with moisture are powerful electrolytes and increase rate of corrosion.

(v) **Effect of pH**
Generally in alkaline medium, the rate of corrosion is less compared to acidic medium.

**Types of Corrosion:**
**Galvanic corrosion**
When two different metals are in contact with each other in presence of aqueous solution or moisture, galvanic corrosion takes place. The metal with more negative electrode potential acts as anode. Metal with less negative electrode potential acts as cathode.
In the Zn-Fe couple as shown in the figure, zinc with more negative electrode potential, dissolves in preference to iron. Zn acts as anode and Fe as cathode.
Example:
Steel screw in a brass marine hardware easily undergoes corrosion. Iron has $E_0 = -0.44\text{V}$. For Cu $E_0 = +0.34\text{V}$. Iron corrodes in preference to Cu.

Prevention
Galvanic corrosion is minimized by providing an insulation between the two metals.

Water line corrosion
Let us consider metal tank partially filled up with water. The metal area above water line is exposed to higher concentration of oxygen (cathode) than the metal below water level. The metal less exposed to O2 acts as anode and corrodes. This is called water line corrosion.

Pitting Corrosion
It is the localized attack resulting in the formation of a hole due to corrosion.
Example: Metal area covered by a drop of water, sand, dirt etc. The area covered by the drop or dirt acts as anode and corrodes. The uncovered area exposed to air or O2 acts as cathode. The rate of corrosion is more if the cathodic area is larger and anodic area is smaller. Thus more material is removed from the same area and a pit is formed.
At anode: Iron is oxidized to Fe\(^{+2}\)
\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-
\]
At cathode: O\(_2\) is reduced to OH\(^-\).
\[
\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- 
\]
Overall reaction:
\[
\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe(OH)}_2
\]

Cathodic Protection:

Sacrificial anodic protection
Here the metal to be protected is made cathode by connecting it to a more active metal (anodic metal) called sacrificial anode. Only the more active metal will be corroded, protecting the parent metal. Since the anodic metal is sacrificed, the method is called sacrificial anodic protection. Mg, Zn are used as sacrificial anodes.

Applications
i) Protection of buried pipelines, cables
ii) Protection of ships and boats
iii) Calcium metal is used to minimize engine corrosion
iv) Magnesium sheets are inserted into domestic water boilers to prevent rust formation.

b) Impressed current cathodic protection method
Here an impressed current is applied in an opposite direction to annul the corrosion current. Thus the corroding metal is converted to cathode from anode. The negative terminal of battery is connected to the metal to be protected. The positive terminal is connected to an inert electrode like graphite. The anode is buried in a ‘back-fill’ (containing a mixture of gypsum, coke breeze and sodium sulphate) to increase electrical contact.

Applications:
i) Protection of tanks, transmission line towers, underground water pipes, oil pipe line, ships etc.
Limitations
i) It is costly
ii) It fails when current is switched off.

PROTECTIVE COATINGS
Metal surface is covered by a protective coating to prevent corrosion. The coating acts as a physical barrier between the metal surface and the environment. The coating gives a decorative appeal and also imparts hardness, oxidation resistance and thermal insulation to the surface. The main types of coating are:
1) Metallic coating
2) Chemical conversion coating
3) Organic coating
4) Non-metallic coating

PAINTS
Paint is a mechanical dispersion of one or more fine pigments in a medium (thinner + vehicle). When a paint is applied to metal surface, the thinner evaporates. The vehicle undergoes slow oxidation to form a pigmented film.

Constituents of Paint
Pigment
Vehicle
Thinner
Drier
Filler
Plasticizer
Antiskinning agent

Metallic Coating
Electroplating or Electro-deposition
It is the deposition of coat metal on the base metal by passing direct current through an electrolytic solution of a soluble salt of the coat metal.
The base metal to be electroplated acts as cathode. The coat metal or an inert electrode forms anode. The electrolyte is a soluble salt of coat metal.

**Objectives or uses or applications of Electroplating:**
i) To enhance resistance to corrosion of base metals.
ii) To give a decorative appearance.
iii) To enhance resistance to chemical attack.
iv) To improve hardness and wearing resistance.
v) To obtain polished surface.

**Theory**
If the coating metal itself forms the anode, the concentration of electrolyte bath does not change during electrolysis. The metal ions deposited on the cathode are replenished continuously by dissolution of the anode.

**Electroless nickel plating**
The various steps are:

**Step I : Pretreatment and activation of the surface:**
The surface to be plated is degreased by using organic solvents or alkali and then accompanied by acid treatment.
i) The surface of stainless steel is activated by dipping in hot solution of 50% H₂SO₄.
i) Mg alloy surface is activated by giving a thin coating of zinc and copper over it.
iii) Al, Cu, Fe, brass etc, do not require activation.
iv) Plastic, glass etc, are activated by dipping in a solution of SnCl₂/HCl and then in PdCl₂ solution. On drying a thin layer of palladium is formed on the surface.

**Step II : Preparation of plating bath:**
The plating bath consists of:
i) Coating Metal : A solution of NiCl₂ 20g/lit.
ii) Reducing agent : Sodium hypophosphite 20g/lit.
iii) Exaltant to accelerate coating rate and complexing agent : Sodium succinate 15g/lit.
v) Buffer to maintain pH at 4.5 : Sodium acetate 10g/lit.

**Uses of Nickel Plating**
i) For decorative coating of jewellery, decorative items and automobile spares
ii) For coating of polymers for decorative purpose.
iii) For electronic appliances.

**Advantages of electroless plating over electro plating**

i) Electricity is not necessary
ii) Complicated parts are uniformly coated
iii) Plastics, glass etc, are easily coated
iv) Good mechanical, chemical and magnetic properties are obtained.

**SHORT ANSWER QUESTIONS**

1. Why efficiency of fuel cell is greater than other energy devices?
2. Write the chemical reactions involved in Methanol- Oxygen fuel cell.
3. What is electrode potential? Write the Nerst equation for the electrode potential?
4. Define reference electrode? Why does electrochemical cell stop working after some time?
5. Why glass electrode cannot be used for solution of pH above 9.0?

**Objective Questions:**

1. Corrosion of Zn containing an impurity of Cu is called ________________ corrosion.
2. The principle in electroplating is [ ]
   a) electrolysis  b) oxidation  c) reduction  d) anodisation
3. The metal which is protected by its own oxide layer [ ]
   A) Cu  B) Cu  C) Au  D) Al
4. Calomel electrode is constructed using __________ solution.
5. __________ of the cells which do not store energy.
6. Corrosion is an example of [ ]
   A) Oxidation  B) Reduction  C) Electrolysis  D) Erosion
7. Specific conductivity of an electrolyte is calculated by the __________
8. Specific conductance is expressed in ______________ units.
9. The units or resistivity are __________
10. The chemical composition of the corrosion product of iron is __________
Unit – IV: Stereochemistry, Reaction Mechanism and synthesis of drug molecules

Structural Representations of Organic Compounds

➢ **Structural formula** (skeletal formula) refers to the illustration of a compound which shows the arrangement of the atoms inside it.

![Structural formula of normal butane](image1)

*Skeletal formula of dichloroacetic acid*

**Wedge and Dash Representation**

**Saw-Horse Projection**

*Structure of Methane ethane*

![Wedge and Dash Representation](image2)

*staggered and eclipsed conformations of ethane*

Isomers are compounds that have the same chemical formula, but the atoms in the
compound are arranged differently. Two isomers will therefore have different properties.

Configurational isomers

- **Chiral compound** – a compound that is optically active (achiral compound will not rotate light). An object without symmetry is CHIRAL

**Enantiomers** - Nonsuperposable mirror images, or chiral molecules which are mirror images

**Diastereomers** - Stereoisomers which are not enantiomers (or mirror images).
**Optical activity** - The ability of chiral substances to rotate the plane of polarized light by a specific angle.

*Dextrorotatory* - Ability of chiral substances to rotate the plane of polarized light to the right.

*Levorotatory* - Ability of chiral substances to rotate the plane of polarized light to the left. *Specific rotation* - The measured angle of rotation of polarized light by a pure chiral sample under specified standard conditions (refer to textbook for a description of these).

*Racemic mixture, racemic modification, or racemate* - A mixture consisting of equal amounts of enantiomers. A racemic mixture exhibits no optical activity because the activities of the individual enantiomers are equal and opposite in value, thereby canceling each other out.

**Absolute configuration**: (Actual arrangement of substituents in space)

An absolute configuration refers to the spatial arrangement of the atoms of a chiral molecular entity (or group) and its stereochemical description e.g. R or S, referring to Rectus, or Sinister, respectively.
Conformation analysis of n-butane.

Nucleophilic substitution reactions: Nucleophilic substitution reactions occur when an electron-rich species, the nucleophile, reacts at an electrophilic saturated C atom attached to an electronegative group (important), the leaving group; the positive or partially positive atom is referred to as an electrophile. The whole molecular entity of which the electrophile and the leaving group are part is usually called the substrate. The most general form of the reaction may be given as the following:

Nuc: + R-LG → R-Nuc + LG:

**SN1 and SN2 Reactions**

*SN1 Reaction (Rate-Limiting Step)*

\[
\text{Transition state} \rightarrow [\text{Reaction}] \rightarrow \text{Products}
\]

*SN2 Reaction*

\[
\text{Transition state} \rightarrow [\text{Reaction}] \rightarrow \text{Products}
\]
Addition of HBr to propene. Markownikoff and anti Markownikoff’s additions.

The main difference between Markovnikov and Anti Markovnikov rule is that Markovnikov rule indicates that hydrogen atoms in an addition reaction are attached to the carbon atom with more hydrogen substituents whereas Anti Markovnikov rule indicates that hydrogen atoms are attached to the carbon atom with the least hydrogen substituents.

Grignard additions on carbonyl compounds:

The Grignard reaction (pronounced /ɡriɲar/) is an organometallic chemical reaction in which alkyl, vinyl, or aryl-magnesium halides (Grignard reagents) add to a carbonyl group in an aldehyde or ketone. The Grignard reagent functions as a nucleophile, attacking the electrophilic carbon atom that is present within the polar bond of a carbonyl group.

Elimination reactions:

Dehydro halogenation of alkylhalides.

Saytzeff rule.
Oxidation of alcohols using KMnO₄

Oxidation is an important process and has played an important role in organic synthesis.

Oxidation of alcohols with Potassium permanganate: Primary and secondary alcohols are readily oxidized by permanganate ion both in acidic and basic medium.

Oxidation of alcohols using Chromic acid

All paths lead to chromic acid

Chromic acid is often made “in situ” (that is, 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 reagent.

Once deciphered, chromic acid is a fairly straightforward reagent. It oxidizes primary alcohols to carboxylic acids and secondary alcohols to ketones. It will also oxidize aldehydes to carboxylic acids.
Reduction of carbonyl compounds using LiAlH₄ & NaBH₄.

\[
\begin{align*}
\text{cyclobutanone} + \text{LiAlH}_4 & \rightarrow \text{cyclobutanol} \\
4\text{CH}_3\text{O} - \text{CH} = \text{O} + 4\text{CH}_3\text{OH} + \text{NaBH}_4 & \rightarrow \text{p-methoxybenzyl alcohol}
\end{align*}
\]

Hydroboration of olefins.

The general form of the hydroboration of alkenes mechanism is as follows:

Structure, synthesis and pharmaceutical applications of Paracetamol and Aspirin.

Paracetamol is used to treat many conditions such as headache, muscle aches, arthritis, backache, toothaches, colds, and fevers.

Aspirin

Analgesic: Relieves pain without anesthesia or loss of consciousness

Antipyretic: Reduces a fever

Anti-inflammatory: Lowers inflammation when used in higher doses
SHORT ANSWER QUESTIONS

1. Differentiate Enantiomers & diastereomers.
2. What is a racemic mixture and how it can be resolved?
3. What conditions are present to determine whether a reaction will be Substitution or elimination?
4. What is Markownikov’s rule? Justify the Markownikov’s addition of HBr to isobutylene.
5. Using a Grignard reagent of your own choosing (not necessarily CH3CH2MgBr), how would you make a sample of the alcohol 2-methylpropan-2-ol?
6. Why NaBH₄ is less reactive than LiAlH₄?

OBJECTIVE ANSWER QUESTIONS

1. Stereoisomers that are exact mirror images of one another are called _____.
   a. Diastereomers
   b. Enantiomers
   c. Constitutional isomers
   d. Geometrical isomers

2. Which statement regarding stereoisomers is correct?
   a. A stereoisomer of a drug typically has the same effect and potency as the original.
   b. Most biological molecules have at least one stereoisomer.
   c. A pair of stereoisomers can easily convert between the two structures.
   d. All statements are correct.

3. Hexane and 3-methylpentane are examples of:
   a. enantiomers.
   b. stereoisomers.
   c. diastereomers.
   d. constitutional isomers.

4. (2R,4S)–2,4–Dichloropentane and (2S,4R)-2,4-dichloropentane are:
   a. enantiomers
   b. diastereomers
   c. identical
   d. conformational isomers
   e. constitutional isomers
5. Which of the following molecules is achiral?

a. (2R,3R)-2,3-Dichloropentane  
b. (2R,3S)-2,3-Dichloropentane  
c. (2S,4S)-2,4-Dichloropentane  
d. (2S,4R)-2,4-Dichloropentane  
e. Two of these

Fill in the blanks

1) N-acetyl-para-aminophenol is the chemical name of ________
2) The infinity of intermediate conformations are called ________
3) Conversion of an aldehyde to an alcohol is known as ________
4) The products of the reaction of a carboxylic acid and an alcohol would be ________
5) Molecules which are not superposable on their mirror images are called ________
6) ________ reaction at a saturated carbon is concerted.
7) Secondary alcohols on oxidation always produces ________
8) LiAlH₄ and NaBH₄ are both capable of ________ aldehydes and ketones to the corresponding alcohol.
9) ________ & ________ are the precursors of aspirin.
10) ________ Rule implies that base-induced eliminations (E₂) will lead predominantly to the olefin in which the double bond is more highly substituted
Unit – V: Spectroscopic techniques and applications

Spectroscopy is the measurement and interpretation of electromagnetic radiation which is absorbed or emitted by atoms of a sample.

**Spectroscopy Principle:** Every sample has molecules consisting of some functional groups by which they may incur color or some nature to absorb light of specific wavelength. This wavelength at which sample absorbs to a greater extent is called as λ max.

When the light beam is passed on to the sample, the electrons in the molecules absorb energy in the light and go for excited state. During this transition, some of the light energy is absorbed while the remaining light falls on the photo-electric detector.

**Qualitative spectroscopy:** This is the technique to know the type of sample molecule thereby one can tell what the sample is and its chemical nature after comparing the obtained analysis curve peaks with that of the standard sample.

**Quantitative spectroscopy:** This is a method to determine the exact concentration of a substance in a given sample.

**Selection Rules for Electronic Spectra of Transition Metal Complexes.**

The Selection Rules governing transitions between electronic energy levels of transition metal complexes are:

1. \( \Delta S = 0 \) The Spin Rule

2. \( \Delta l = +/- 1 \) The Orbital Rule (Laporte)

The first rule says that allowed transitions must involve the promotion of electrons without a change in their spin.

The second rule says that if the molecule has a centre of symmetry, transitions within a given set of p or d orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden.

**Types of transition**

1. Charge transfer, either ligand to metal or metal to ligand. These are often extremely intense and are generally found in the UV but they may have a tail into the visible.

2. d-d, these can occur in both the UV and visible region but since they are forbidden transitions have small intensities.
**Vibrational spectroscopy** Vibrational spectroscopy is concerned with vibrational transitions due to absorption and emission of electromagnetic radiation. The vibrational energies of the molecule can be studied by infrared and Raman spectroscopy. The IR and Raman spectroscopic methods often furnish the complementary types of information. For a complete vibrational analysis, both methods should necessarily be used. The gross selection rule for vibrational transitions is that the electric dipole moment of the molecule must change in the course of the vibrational motion.

Selection rules for pure rotational spectra

A molecule must have a transitional dipole moment that is in resonance with an electromagnetic field for rotational spectroscopy to be used. *Polar* molecules have a dipole moment. A transitional dipole moment not equal to zero is possible.

The conservation of the angular momentum is fundamental for the selection rules that allow or prohibit transitions of a linear molecule:

\[
\Delta J = \pm 1 \quad \Delta M_J = 0, \pm 1
\]

**Basic concepts of Nuclear magnetic resonance Spectroscopy:** Nuclear Magnetic Resonance (NMR) spectroscopy is an analytical chemistry technique used in quality control and research for determining the content and purity of a sample as well as its molecular structure.

The principle behind NMR is that many nuclei have spin and all nuclei are electrically charged. If an external magnetic field is applied, an energy transfer is possible between the base energy to a higher energy level (generally a single energy gap). The energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its base level, energy is emitted at the same frequency.
Chemical shift

The precise resonant frequency of the energy transition is dependent on the effective magnetic field at the nucleus. This field is affected by electron shielding which is in turn dependent on the chemical environment. Chemical shift $\delta$ is usually expressed in parts per million (ppm) by frequency, because it is calculated from:

$$\delta = \frac{v_{\text{sample}} - v_{\text{ref}}}{v_{\text{ref}}}$$

where $v_{\text{sample}}$ is the absolute resonance frequency of the sample and $v_{\text{ref}}$ is the absolute resonance frequency of a standard reference compound, measured in the same applied magnetic field $B_0$. Since the numerator is usually expressed in hertz, and the denominator in megahertz, $\delta$ is expressed in ppm.

**FACTORS AFFECTING CHEMICAL SHIFT**

- Local diamagnetic shielding ($\sigma_{\text{dia}}$)
- Non-spherical paramagnetic shielding ($\sigma_{\text{para}}$)
- Magnetic anisotropy of neighboring groups ($\sigma_N$)
- Ring current effects ($\sigma_R$)
- Electric field effects ($\sigma_e$)
- Intermolecular interactions e.i. H-bonding & solvent effects ($\sigma_i$)

$$\sigma = \sigma_{\text{dia}} + \sigma_{\text{para}} + \sigma_N + \sigma_R + \sigma_e + \sigma_i$$

**Magnetic Resonance Imaging**

It is a medical imaging technique and diagnostic tool in radiology based on the Nuclear Magnetic Resonance (NMR).

**MRI scanner**

It is composed of: a magnet which produces a very powerful uniform magnetic field $B_0$ (1.5T - 11T, note that the earth magnetic field is around 60 microT) shim coils to make $B_0$ homogeneous gradient coils that make the magnetic field linearly vary across the imaging volume. This determines the plane of imaging Radio Frequency (RF) transmission system.

**How does it work?**

- An MRI machine uses a powerful magnetic field to align the magnetization of some atoms in the body.
• radio frequency fields systematically alter the alignment of this magnetization
• This causes the nuclei to produce a rotating magnetic field detectable by the scanner
• This information is recorded to construct an image of the body.

Main pros

non-invasive and 3D
no ionizing radiations
very good spatial resolution (1mm isotropic for anatomy) anatomy,
functional and physiological state of the internal organs
both healthy and pathological tissues

SHORT ANSWER QUESTIONS

1. IR spectra is often characterised as molecular finger prints. Justify

2. What property of nuclei is involved in NMR spectroscopy

3. $^{13}$C has nuclear spin ; while $^{12}$C doesnot have nuclear spin

4. What is selection rule?

5. What is chemical shift?

6. How many normal modes of vibrations are possible for a) Ethane b) Benzene

OBJECTIVE ANSWER QUESTIONS

1. What is the relationship between wavelength and wavenumber ?

   a) Wavenumber = $\frac{1}{\text{wavelength}}$ in centimeters
   b) Wavenumber = $\frac{1}{\text{wavelength}}$ in nanometers
   c) Wavelength in nanometers = $\frac{1}{\text{wavenumber}}$

2. For a molecule to absorb IR, why must the molecule's vibrations cause fluctuations in the dipole moment of the molecule?

   a) Because a change in dipole moment lowers the energy required for electronic transitions
   b) Because for absorption to occur, the radiation must interact with the electric field caused by changing dipole moment
c) Because fluctuations in the dipole moment allow the molecule to deform by bending and stretching

3. Vibration Spectroscopy is associated with
a) overall movement of molecules along with three axes
b) spinning of molecules about the axes
c) vibrations within a molecule such as stretching and bending

4. Presence of impurities in a sample can be detected in IR spectra by
a) spectra shows extra absorption bands
b) spectra shows deficient absorption bands
c) spectra shows no absorption bands

5. The number of signals in the NMR spectrum indicates
a) types of carbons in the compound
b) types of protons in the compound
c) types of isotopes in the compound

**Fill in the blanks**

1. ___________ employs NMR of protons to produce proton density maps (or images) of the human body.

2. NMR is particularly concerned almost exclusively with the nuclear spin associated with ______

3. According to MOT, the interaction of atomic orbitals leads to the formation of ______ & _______ MOs.

4. UV-Vis Spectra usually carried out by _____ & ______ values.

5. Franck-Condon principle states that ___________