**Atomic Structure - II**

1. **___** would have the maximum de Broglie wavelength?
   a) Proton  
   b) Neutron  
   c) α - particle  
   d) β - particle.

2. de Broglie equation is
   a) \( \lambda = \frac{mv}{h} \)  
   b) \( \lambda = hmv \)  
   c) \( \lambda = \frac{hv}{m} \)  
   d) \( \lambda = \frac{h}{mv} \)

3. Dual character of an electron was explained by
   a) Bohr  
   b) Heisenberg  
   c) de Broglie  
   d) Pauli.

4. \( E_n = -\frac{313.6}{n^2} \), if the value of \( E_n = -34.84 \) to which value \( n \) corresponds to
   a) 4  
   b) 3  
   c) 2  
   d) 1

5. Energy levels of molecular orbitals have been determined experimentally by
   a) Spectroscopic studies  
   b) X-ray diffraction  
   c) Crystallographic studies  
   d) none of these.

6. If the energy of an electron in the second Bohr orbit of H-atom is -E, what is the energy of the electron in the Bohr's first orbit?
   a) 2E  
   b) -4E  
   c) -2E  
   d) 4E.

7. In a molecule eight electrons are present in bonding molecular orbital and four electrons are present in anti-bonding molecular orbital. Its bond order is
   a) 3  
   b) 1  
   c) 2.5  
   d) 2.

8. Inter-molecular hydrogen bonding is present in
   a) HF  
   b) H₂O  
   c) ethanol  
   d) all of these. /  
   a) o-nitrophenol  
   b) salicylic acid  
   c) o-hydroxy benzaldehyde  
   d) hydrogen fluoride.

9. Intramolecular hydrogen bonding is present in
   a) o-nitrophenol  
   b) m-nitrophenol  
   c) p-nitrophenol  
   d) p-aminophenol  
   /  
   a) o-nitrophenol  
   b) m-nitrophenol  
   c) p-nitrophenol  
   d) p-hydroxy benzaldehyde  
   /  
   a) o-nitrophenol  
   b) m-nitrophenol  
   c) p-nitrophenol  
   d) none of these.

10. Molecular orbital with the least energy is
    a) \( \sigma 1s \)  
    b) \( \sigma^* 1s \)  
    c) \( \pi 2py \)  
    d) \( \pi^* 2py \)

11. Number of **spherical nodes** in 2s orbital is
    a) 1  
    b) 2  
    c) 3  
    d) 4.

12. The bond order of nitrogen molecule is
    a) 2.5  
    b) 3  
    c) 2  
    d) 4.

13. The bond order of oxygen molecule is
    a) 2.5  
    b) 1  
    c) 3  
    d) 2.

14. The circumference of the circular orbit of an electron is an integral multiple of its
    a) frequency  
    b) momentum  
    c) mass  
    d) wavelength.

15. The **hybridisation** / The nature of hybridisation in IF₇ molecule is
    a) sp³d  
    b) sp³d²  
    c) sp³  
    d) sp³d³.

16. The hybridisation in CO₃²⁻ ion is
    a) sp²  
    b) sp³  
    c) sp  
    d) sp³d.

17. The hybridisation in SF₆ molecule is
18. The hybridisation in SO₄²⁻ ion is
   a) sp³  b) sp³d  c) sp³d²  d) sp³d³.
19. The hybridisation involved in XeF₆ is
   a) sp³d³  b) sp³d²  c) sp³d  d) sp³.
20. The momentum of a particle which has de-Broglie wavelength of 1 Å (h = 6.626 x 10⁻34 kgm²s⁻¹) is
   a) 6.63 x 10⁻²³ kgms⁻¹  b) 6.63 x 10⁻²⁴ kgms⁻¹
   c) 6.63 x 10⁻³⁴ kgms⁻¹  d) 6.63 x 10⁻³⁴ kgms⁻¹
21. Which of the following particles having same kinetic energy?
   a) α-particle  b) proton  c) β-particle  d) neutron
22. Which one of the following experiments confirmed the wave nature of electron?
   a) G.P. Thomson's gold foil experiment  b) Black body radiation
   c) Photoelectric effect  d) Millikan's oil-drop experiment.
23. Water exists in liquid state. This is due to
   a) high boiling point  b) low boiling point  c) freezing point is zero  d) hydrogen bond.
24. The hybridisation in ICl₄⁻ ion is
   a) sp³  b) sp³d  c) sp³d²  d) sp³d³

**Periodic Classification - II**

1. Among the following which has higher electron affinity value?
   a) Fluorine  b) Chlorine  c) Bromine  d) Iodine.
2. Among the following which has the maximum ionisation energy?
   a) Alkali metals  b) Alkaline earth metals  c) Halogens  d) Noble gases.
3. Effective nuclear charge Z* is given by the equation / can be calculated using the formula
   a) Z* = Z - S  b) Z* = Z + S  c) Z* = S - Z  d) Z = Z* - S.
4. Noble gases have _____ electron affinity
   a) High  b) Low  c) Zero  d) Very low.
5. On moving down a group, the radius of an ion
   a) decreases  b) increases  c) first increases and then decreases  d) remains a constant/
   a) decreases  b) increases  c) no change  d) all of these.
6. The bond length of Cl₂ molecule is
   a) 0.74 Å  b) 1.44 Å  c) 1.98 Å  d) 2.28 Å
7. The electron affinity of an atom is
   a) directly proportional to its size  b) inversely proportional to its size
   c) independent of its size  d) none of these.
8. The metal having maximum electron affinity is
   a) sodium  b) calcium  c) gold  d) silver.
9. The order of ionisation energy is
   a) s<p<d<f  b) s > p > d > f  c) s>d>p>f  d) s<d<p<f.
10. The scale which is based on an empirical relation between the energy of a bond and the electronegativities of bonded atoms is that of
   a) Pauling   b) Mulliken   c) Sanderson   d) Alfred Rochow.
11. When $\text{XA} \gg \text{XB}$, A - B bond is
   a) polar covalent   b) non-polar covalent   c) ionic   d) metallic
12. In a molecule eight electrons are present in bonding molecular orbital and four electrons are present in anti-bonding molecular orbital. Its bond order is
   a) 3   b) 1   c) 2.5   d) 2
13. Water exists in liquid state. This is due to
   a) high boiling point   b) low boiling point   c) freezing point is zero   d) hydrogen bond

**p - Block Elements - II**

1. Among the halogen acids, the weakest acid is
   a) HI   b) HBr   c) HCl   d) HF.
2. An element is burnt in limited supply of air to give an oxide A, which on treatment with water gives an acid B. Acid B on heating gives acid C which gives yellow precipitate with silver nitrate solution. Oxide A is
   a) $\text{P}_2\text{O}_3$   b) SO2   c) CO2   d) NO2.
3. An element which belongs to group 14 is soft in nature, does not react with pure water, but dissolves in water containing dissolved air. Then the element is
   a) C   b) Ge   c) Pb   d) Ti.
4. Inert gas used in beacon lights for safety of air navigation is
   a) Helium   b) Argon   c) Neon   d) Xenon.
5. The compound used as smoke screen is
   a) $\text{PCl}_3$   b) $\text{PCl}_5$   c) $\text{PH}_3$   d) $\text{H}_3\text{PO}_3$.
6. The compound used to arrest the bleeding is
   a) $\text{K}_2\text{SO}_4$   b) Potash alum   c) $\text{Al}_2(\text{SO}_4)_3$   d) $\text{KI}$.
7. The compound with garlic odour is
   a) $\text{P}_2\text{O}_3$   b) $\text{P}_2\text{O}_5$   c) $\text{H}_3\text{PO}_3$   d) $\text{H}_3\text{PO}_4$.
8. The general electronic configuration of carbon family is
   a) $\text{n}^2\text{n}^2\text{n}^3$   b) $\text{n}^2\text{n}^3$   c) $\text{n}^2\text{n}^1$   d) $\text{n}^2\text{n}^4$.
9. The lightest gas which is non-inflammable is
   a) He   b) H2   c) N2   d) Ar.
10. The metalloid among the following is
    a) Pb   b) P   c) Ge   d) Sn.
11. The noble gases are unreactive because they
    a) have same number of electrons   b) have an atomicity of one
    c) are gases with low density   d) have stable electronic configuration
12. The shape of $\text{PCl}_5$ is
    a) Bipyramidal   b) Trigonal bipyramidal   c) Linear   d) Tetrahedral.
13. The shape of $\text{XeF}_4$ is
A.MOORTHY.MSc,B.Ed...  8754706647

14. The toxic element of Boron family is
   a) Boron  b) Indium  c) Thallium  d) Gallium.
15. Which of the following does not belong to group 14?
   a) C  b) Si  c) Ga  d) Pb
16. Which of the following has the property of etching on glass?
   a) HI  b) HF  c) HBr  d) HCl.
17. Which of the following shows negative oxidation state only?
   a) Br  b) F  c) Cl  d) I
18. Which of the following is the second most abundant element in earth’s crust?
   a) Carbon  b) Silicon  c) Germanium  d) Tin.

- Block Elements

1. A metal which precipitates gold from its aurocyanide complex is
   a) Cr  b) Ag  c) Pt  d) Zn.
2. Bordeaux mixture contains
   a) AgNO₃ + HNO₃  b) ZnSO₄ + H₂SO₄  c) CuSO₄ + Ca(OH)₂  d) KMnO₄ + HCl
3. Copper is extracted from
   a) Cuprite  b) Copper glance  c) Malachite  d) Copper pyrites.
4. Ferrochrome is an alloy of
   a) Cr, C, Fe, N  b) Cr, Co, Ni, C  c) Fe, C  d) Cr, Ni, Fe.
5. Formation of coloured ions is possible when compounds contain
   a) paired electrons  b) unpaired electrons  c) lone pair of electrons  d) none of these
6. If the magnetic moment value is 5.92 BM, the number of unpaired electrons is
   a) 5  b) 3  c) 4  d) 6
7. K₂Cr₂O₇ reacts with KI and dilute sulphuric acid and liberates
   a) O₂  b) I₂  c) H₂  d) SO₂
8. Paramagnetism is the property of
   a) paired electrons  b) completely filled electronic sub-shells  c) unpaired electrons  d) completely vacant electronic sub-shells.
9. Silver obtained from silver coin is purified by fusion with
   a) AgNO₃  b) HNO₃  c) H₂SO₄  d) borax.
10. Silver salt used in photography is
    a) AgCl  b) AgNO₃  c) AgF  d) AgBr.
11. Spitting of silver can be prevented by covering the molten metal with a thin layer of
    a) borax  b) charcoal  c) sand  d) silver bromide.
12. The catalyst used in the manufacture of polythene is
    a) V₂O₅  b) Fe  c) Mo  d) TiCl₄.
13. The chemical composition of slag formed during the smelting process in the extraction of copper is
    a) Cu₂O + FeS  b) FeSiO₃  c) CuFeS₂  d) Cu₂S + FeO.
14. The colour of Purple of Cassius is
   a) purple (or) red b) blue c) bluish green d) apple green

15. The correct electronic configuration of copper atom is
   a) 3d^{10} 4s^{2} b) 3d^{10} 4s^{1} c) 3d^{8} 4s^{2} d) 3d^{5} 4s^{2}

16. The general outer electronic configuration of d block elements is
   a) (n-1)d^{10} ns^{2} b) (n-1)d^{10} ns^{1} c) (n-1)d^{9} ns^{2} d) (n-1)d^{5} ns^{1}

17. The ion with maximum number of unpaired electrons is / Which of the following has the maximum number of unpaired electrons?
   a) Mn^{2+} b) Ti^{3+} c) V^{3+} d) Fe^{2+}

18. The metal used in galvanising iron sheets is
   a) chromium b) zinc c) copper d) silver.

19. The number of unpaired electrons in Ti^{3+} is 1. Its magnetic moment in BM is
   a) 1.414 b) 2 c) 1.732 d) 3

20. The outer(most) electronic configuration of chromium is
   a) 3d^{6} 4s^{0} b) 3d^{5} 4s^{1} c) 3d^{4} 4s^{2} d) 3d^{3} 4s^{2} 4p^{1}

21. The reagent which is added first in the separation of silver from silver coin is
   a) conc. sulphuric acid b) conc. hydrochloric acid c) conc. nitric acid d) Aqua regia.

22. The substance used in making ruby-red glass and high class pottery is
   a) colloidal silver b) purple of Cassius c) ruby silver d) ruby copper

23. The transition element showing maximum oxidation state is / Which transition element shows the highest oxidation state?
   a) Sc b) Ti c) Os d) Zn.

24. The transition element with the lowest atomic number is
   a) scandium b) titanium c) zinc d) lanthanum.

25. When excess of KCN is added to an aqueous solution of copper sulphate, it gives / Which compound is formed when excess of KCN is added to an aqueous solution of copper sulphate?
   a) Cu(CN)_{2} / Cu2(CN)_{2} b) K_{2}[Cu(CN)_{6}] c) K[Cu(CN)_{2}] d) Cu_{2}(CN)_{2} + (CN)_{2}

26. Which of the following compounds will not give positive Chromyl Chloride Test?
   a) CuCl_{2} b) C_{6}H_{5}Cl c) ZnCl_{2} d) HgCl_{2}.

27. Which of the following is wrong statement regarding K_{2}Cr_{2}O_{7}?
   a) Oxidising agent b) Used in tanning industry c) Soluble in water d) Reduces ferric sulphate to ferrous sulphate.

28. Which of the following ions will give colourless aqueous solution?
   a) Ni^{2+} b) Cu^{+} c) Cu^{2+} d) Fe^{2+}.

29. Which of the following pairs have almost equal radii?
   a) Mo, W b) Y, La c) Zr, Hf d) Nb, Ta.

30. Which one of the following will have maximum magnetic moment?
   a) 3d^{2} b) 3d^{8} c) 3d^{7} d) 3d^{9}.

31. The most malleable and ductile of all metals is
   a) silver b) gold c) copper d) zinc.
**f - Block Elements**

1. _____ is used in gas lamp material / The compound / oxide used in gas lamp material is
   a) MnO2  
   b) CeO2  
   c) N2O5  
   d) Fe2O3

2. ------ form(s) oxocations / Elements that form oxocations are
   a) Lanthanides  
   b) Actinides  
   c) Noble gases  
   d) Alkali / base metals.

3. _____ is the oxidation state of U in UF6.
   a) +6  
   b) +4  
   c) +3  
   d) 0.

4. According to Fajan’s rule, decrease in size of Ln$^{3+}$ ion in Ln(OH)3
   a) increases the covalent character  
   b) decreases the covalent character  
   c) increases the basic character  
   d) increases the ionic character

5. Alloys of Lanthanides are called as
   a) Misch metals  
   b) Metalloids  
   c) Plate metal  
   d) Actinides.

6. Among the Lanthanide elements, with the increase in atomic number the tendency to act as reducing agent
   a) increases  
   b) decreases  
   c) no change  
   d) none of these.

7. Ceria / CeO2 is used in
   a) toys  
   b) tracer bullets  
   c) gas lamp material  
   d) none of these.

8. Lanthanide contraction is due to
   a) perfect shielding of 3d electron  
   b) imperfect shielding of 3d electron  
   c) perfect shielding of 4f electron  
   d) imperfect shielding of 4f electron.

9. Maximum oxidation state exhibited by Lanthanides is / The maximum oxidation state exhibited by Lanthanide is
   a) +3  
   b) +4  
   c) +6  
   d) +7 /  
   a) +1  
   b) +3  
   c) +2  
   d) +4 /  

10. Oxidation state exhibited by lanthanides is / The (most) common oxidation state of lanthanides is
    a) +2  
    b) 1  
    c) +3  
    d) +4 /  
    a) +2  
    b) +3  
    c) +4  
    d) +6.

11. The elements in which extra electron enter (n - 2) f orbital are
    a) s-block elements  
    b) p-block elements  
    c) d-block elements  
    d) f-block elements.

12. The fuel used in nuclear power plant is
    a) Copper  
    b) Lead  
    c) Uranium  
    d) Radium.

13. The isotope / Which is used as a power source in long mission space probes is
    a) U-235  
    b) Pu-235  
    c) Pu-238  
    d) U-238.
a) Uranium-235  

b) Uranium-238  
c) Plutonium-238  
d) Mish metal.

14. The long mission space probes use as power source....

a) Pu  
b) Pm  
c) Th  
d) U.

15. The radioactive element of lanthanide is

a) Cerium  
b) Promethium  
c) Gadolinium  
d) Lutetium

16. The radioactive lanthanide is / Which of the following is a radioactive lanthanide

a) terbium  
b) lutetium  
c) promethium  
d) gadolinium. /

a) Pu  
b) Ac  
c) T'h  
d) Pm.

17. ThO2 / Thoria is used in

a) toys  
b) tracer bullets  
c) gas lamp material  
d) dyeing cotton.

18. Which is used in gas lamp materials?

a) Ceria  
b) Thoria  
c) Misch metal  
d) Both (a) & (b)

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**Coordination Compounds**

1. \([\text{FeF}_6]^{4-}\) is paramagnetic because

a) F\(^-\) is a weaker ligand  
b) F\(^-\) is a stronger ligand  
c) F\(^-\) is a flexidentate ligand  
d) F\(^-\) is a chelating ligand.

2. An example of a bidentate (chelating) ligand is

a) NO\(^2-\)  
b) NO\(^3-\)  
c) en  
d) SO\(^4-\) / / 

a) Cl\(^-\)  
b) en  
c) NO\(^2-\)  
d) I\(^-\)

3. An example of a chelating ligand is

a) Chloro  
b) Bromo  
c) en  
d) NO\(^2-\) / nitro.

4. An example of ambidentate ligand is

a) Cl\(^-\)  
b) NO\(^2-\)  
c) H2O  
d) NH3.

5. In \([\text{Fe(CN)}_6]^{4-}\) / \([\text{Fe}^{II}(\text{CN})_6]^{4-}\) the central metal ion is

a) Fe  
b) Fe\(^{2+}\)  
c) Fe\(^{3+}\)  
d) (CN)\(^-\)

6. The co-ordination number of Cr (III) in \([\text{Cr(H}_2\text{O)}_4\text{Cl}_2]\)Cl . 2H2O is

a) 3  
b) 4  
c) 6  
d) 2.

7. The coordination number of Ni (II) in \([\text{Ni(CN)}_4]^{2-}\) is

a) 2  
b) 4  
c) 5  
d) 6.

8. The coordination number of Nickel in the complex ion \([\text{NiCl}_4]^{2-}\) is

a) + 1  
b) +4  
c) +2  
d) +6.

9. The geometry of \([\text{Fe(CN)}_6]^{4-}\) is

a) Tetrahedral  
b) Square Planar  
c) Octahedral  
d) Triangular

10. The geometry of \([\text{Ni(CN)}_4]^{2-}\) is

a) Tetrahedral  
b) Square Planar  
c) Triangular  
d) Octahedral

11. The type of isomerism found in the complexes \([\text{Pt(NH}_3)_4][\text{CuCl}_4]\) & \([\text{PtCl}_4][\text{Cu(NH}_3)_4]\) is

a) ionization isomerism  
b) co-ordination isomerism
c) linkage isomerism  d) ligand isomerism.

12. Which of the following is cationic complex?
   a) K₄[Fe(CN)₆]
   b) [Cu(NH₃)₄]²⁺
   c) K₃[Cr(C₂O₄)₃] / [Cr(C₂O₄)₃]³⁻
   d) K₃[Fe(CN)₆].

13. The type of isomerism found in the complexes [Co(NO₂)(NH₃)₅]SO₄ and [Co(SO₄)(NH₃)₅]NO₂
   a) Hydrate isomerism
   b) Coordination isomerism
   c) Linkage isomerism
   d) Ionisation

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**Nuclear Chemistry**

1. ⁹²U²³⁵ Nucleus absorbs a neutron and disintegrates into ⁵₄Xe¹³⁹, ³⁸Sr⁸⁴ and X. What is X?
   a) 3 neutrons
   b) 2 neutrons
   c) α – particle
   d) β – particle.

2. After 24 hours 0.125 g of the initial quantity of 1 g of a radioactive isotope is left out / is left out.
   The half-life period is
   a) 24 hours
   b) 12 hours
   c) 8 hours
   d) 16 hours
   a) 0.8 hours
   b) 8 hours
   c) 100 hours
   d) 80 hours

3. Find out the missing: In a reaction ⁵B⁸ → ⁴Be⁸ + ?
   a) α-particle
   b) β -particle
   c) electron capture
   d) positron.

4. Half life period of a radioactive element is 1500 years. Find the value of disintegration constant in terms of second.
   a) 0.1465 × 10⁻¹⁰ sec⁻¹
   b) 0.2465 × 10⁻¹⁰ sec⁻¹
   c) 0.1465 × 10⁻⁸ sec⁻¹
   d) 0.3645 × 10⁻¹⁰ sec⁻¹

5. Half-life period of a radioactive element is 100 seconds. Its average life period is
   a) 100 seconds
   b) 50 seconds
   c) 200 seconds
   d) 144 seconds.

6. In nuclear reaction ------- is / are balanced on both sides.
   a) mass
   b) number of atoms
   c) mass number
   d) atomic number and mass number

7. Loss of β – particle is equivalent to
   a) increase of one proton only
   b) decrease of one neutron
   c) loss of proton / increase of one neutron only / none of these
   d) both (a) and (b).

8. Radioactivity is due to
   a) Stable electronic configuration
   b) Stable nucleus
   c) Unstable nucleus
   d) Unstable electronic configuration.

9. The isotope of which element is used in nuclear fission reaction?
   a) Barium
   b) Lead
   c) Uranium
   d) Caesium.

10. The most penetrating radiations are
    a) α rays
    b) β rays
    c) γ rays
    d) all are equally penetrating

11. The reaction ⁵B⁸ → ⁴Be⁸ takes place due to
    a) α -decay
    b) β-decay
    c) electron capture
    d) positron decay.

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12. When $^7\text{N}\,^{15}$ is bombarded with a proton it gives $^6\text{C}\,^{12}$ and
   a) $\alpha$- particle  b) $\beta$- particle  c) neutron  d) proton
13. Which of the following is used as neutron absorber in nuclear reactors?
   a) Water  b) Deuterium  c) Uranium  d) Cadmium
14. Which one of the following particles is used to bombard $^{13}\text{Al}\,^{27}$ to give $^{15}\text{P}\,^{30}$ and a neutron?
   a) $\alpha$-particle  b) Deuteron / $\beta$-particle  c) Proton  d) Neutron.

**Solid State - II**

1. An example for metal deficiency defect is
   a) NaCl  b) AgCl  c) FeS  d) CsCl
2. An ion leaves its regular site and occupies a position in the space between the lattice sites. This defect is called as
   a) Schottky defect  b) Frenkel defect  c) impurity defect  d) vacancy defect.
3. In a simple cubic cell, each point on a corner is shared by
   a) one unit cell  b) two unit cells  c) eight unit cells  d) four unit cells.
4. In Bragg's equation 'n' represent
   a) number of moles  b) Avogadro number  c) quantum number  d) order of reflection.
5. Rutile is
6. Semiconductors which exhibit conductivity due to the flow of excess negatively charged electron are called
   a) superconductors  b) $n$-type semiconductors  c) p-type semiconductors  d) insulators.
7. The Bragg's equation is
   a) $\lambda = 2d \sin \theta$  b) $nd = 2 \lambda \sin \theta$  c) $2 \lambda = nd \sin \theta$  d) $n \lambda = 2d \sin \Theta$.
8. The co-ordination number of ZnS is
   a) 3  b) 4  c) 6  d) 8.
9. The crystal structure of CsCl is
    a) simple cube  b) face-centred cube  c) body-centred cube  d) edge-centred cube.
10. The number of chloride ions present per unit of CsCl
    a) 6  b) 8  c) 1  d) 4
11. The number of close neighbours in a body centred cubic lattice of identical sphere is
    a) 6  b) 4  c) 12  d) 8.
12. The size of the anion in Frenkel defect crystal is
    a) larger than the cation  b) smaller than the cation  c) equal in size with cation  d) both are larger in size.
13. The total number of atoms per unit cell in bcc is
   a) 1  b) 2  c) 3  d) 4.

14. Crystal lattice with coordination number four is
   a) CsCl  b) ZnO  c) BN  d) NaCl

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**Thermodynamics - II**

1. According to Trouton's rule, the value of change in entropy of vaporization is
   a) 21 cal. deg⁻¹ mole⁻¹  b) 12 cal. deg⁻¹ mol
   c) 21 kcal. deg⁻¹ mole⁻¹  d) 12 kcal. deg. mol⁻¹.

2. All the naturally occurring processes proceed spontaneously in a direction which leads to
   a) decrease of entropy  b) increase in enthalpy
   c) increase in free energy  d) decrease of free energy.

3. Change in Gibbs free energy is given by
   a) \( \Delta G = \Delta H + T\Delta S \)  b) \( \Delta G = \Delta H - T\Delta S \)
   c) \( \Delta G = \Delta H \times T\Delta S \)  d) \( \Delta G = T\Delta S - \Delta H \)

4. Entropy (S) and the entropy change (\( \Delta S \)) of a process
   a) are path functions  b) are state functions
   c) are constants  d) have no values.

5. Entropy is a ______ function.
   a) state  b) path  c) exact  d) inexact.

6. For the reaction \( 2\text{Cl}(g) \rightarrow \text{Cl}_2(g) \), the signs of \( \Delta H \) and \( \Delta S \) are respectively
   a) +, -  b) +, +  c) -, -  d) -, +.

7. Free energy (G) and the free energy change (\( \Delta G \)) correspond to the
   a) system only  b) surrounding only  c) system and surrounding  d) all of these.

8. \( \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \). In this process the entropy,
   a) remains constant  b) decreases  c) increases  d) becomes zero.

9. If \( \Delta G \) for a reaction is negative, the change is
   a) spontaneous  b) non-spontaneous
   c) reversible  d) irreversible / 
   a) spontaneous  b) non-spontaneous
10. In an adiabatic process which of the following is correct?
   a) \( q = w \)
   b) \( q = 0 \)
   c) \( \Delta E = q \)
   d) \( P \Delta V = 0 \)

11. In which of the following processes / the process is always non-feasible?
   a) \( \Delta H > 0, \Delta S > 0 \)
   b) \( \Delta H < 0, \Delta S > 0 \)
   c) \( \Delta H > 0, \Delta S < 0 \)
   d) \( \Delta H < 0, \Delta S < 0 \).

12. Standard free energies of formation of elements are taken as
   a) positive
   b) negative
   c) zero
   d) all of these

13. The amount of heat exchanged with the surrounding at constant temperature and pressure is called
   a) \( \Delta E \)
   b) \( \Delta H \)
   c) \( \Delta S \)
   d) \( \Delta G \).

14. The amount of heat exchanged with the surroundings at constant pressure is called
   a) \( \Delta E \)
   b) \( \Delta H \)
   c) \( \Delta S \)
   d) \( \Delta G \).

15. The entropy change (\( \Delta S(\text{fusion}) \)) involved in the process of \( \text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l) \) at 0°C and 1 atm pressure involving \( \Delta H(\text{fusion}) = 6008 \text{ J mol}^{-1} \) is
   a) 22.007 J mol\(^{-1}\) K\(^{-1}\)
   b) 22.007 J mol\(^{-1}\) K\(^{-1}\)
   c) 220.07 J mol\(^{-1}\) K\(^{-1}\)
   d) 2.2007 J mol\(^{-1}\) K\(^{-1}\).

16. The entropy change involved in the process water (liq) to water (vapor, 373K) involving \( \Delta H_{\text{vap}} = 40850 \text{ J mol}^{-1} \) at 373 K is
   a) 120 J mol\(^{-1}\) K\(^{-1}\)
   b) 9.1 x 10\(^{-3}\) J mol\(^{-1}\) K\(^{-1}\)
   c) 109.52 J mol\(^{-1}\) K\(^{-1}\)
   d) 109.52 J mol\(^{-1}\) K\(^{-1}\)

17. The network obtained from a system is given by
   a) \( w - P \Delta V \)
   b) \( w + P \Delta V \)
   c) \( -w + P \Delta V \)
   d) \( -w - P \Delta V \).

18. The percentage efficiency of a heat engine that operates between 127°C and 27°C is
   a) 20%
   b) 50%
   c) 100%
   d) 25%.

19. Thermodynamic condition for irreversible spontaneous process at constant T and P is
   a) \( \Delta G < 0 \)
   b) \( \Delta S < 0 \)
   c) \( \Delta G > 0 \)
   d) \( \Delta H > 0 \).

20. When a liquid boils, there is
   a) an increase in entropy
   b) a decrease in entropy
   c) an increase in heat of vaporization
   d) an increase to free energy.

21. Which of the following does not result in an increase in the entropy?
   a) Rusting of iron
   b) Crystallisation of sucrose from solution
   c) Vaporisation of camphor
   d) Conversion of ice to water.

22. Which one of the following is a state function?
   a) \( q \)
   b) \( \Delta q \)
   c) \( w \)
   d) \( \Delta S \).

23. In SI unit 1 eu is
a) 41.84 EU  

b) 4.184 EU  

c) 418.4 EU  

d) 4184 EU  

24. The entropy change for the following process possessing $\Delta H$ (transition) as 2090 J.mol$^{-1}$

1 mole Sn ($\alpha$, 13°C) $\rightleftharpoons$ 1 mole Sn ($\beta$, 13°C) is

a) 22.007 J mol$^{-1}$ K$^{-1}$  

b) 7.307 J. mol$^{-1}$ K$^{-1}$  

c) 0.314J mol$^{-1}$ K$^{-1}$  

d) 109.52 J mol$^{-1}$ K$^{-1}$

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**Chemical Equilibrium - II**

1. $2\text{H}_2\text{O}(g) + 2\text{Cl}_2(g) \rightleftharpoons 4\text{HCl}(g) + 5\text{O}_2(g)$, the value of $K_p$ and $K_c$ are related as

a) $K_p = K_c$  

b) $K_p > K_c$  

c) $K_p < K_c$  

d) $K_p = K_c = 0.$

2. For a homogenous gaseous reaction at 600K $4\text{NH}_3(g) + 5\text{O}_2(g) \rightleftharpoons 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$ the equilibrium constant $K_c$ has the unit

a) (mol dm$^3$)$^{-1}$  

b) mol dm$^3$  

c) (mol dm$^3$)$^4$  

d) (mol dm$^3$)$^{-2}$

3. For an endothermic equilibrium reaction, if $K_1$ and $K_2$ are the equilibrium constants at T1 and T2 temperatures respectively and if T2 is greater than T1, then

a) $K_1 < K_2$  

b) $K_1 > K_2$  

c) $K_1 = K_2$  

d) None/

a) $K_1$ is less than $K_2$  

b) $K_1$ is greater than $K_2$  

c) $K_1$ is equal to $K_2$  

d) None of these.

4. Forward reaction takes place, when

a) $Q < k_c$  

b) $Q > k_c$  

c) $Q = k_c$  

d) $k_c = 1/Q$

5. $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$ The equilibrium constant $K_c$ for this reaction is 16. $K_p$ value is

a) 1/16  

b) 4  

c) 64  

d) 16.

6. If the equilibrium constant for the formation of a product is 25, the equilibrium constant for the decomposition of the same product is

a) 25  

b) 1/25  

c) 5  

d) 625.

7. If the equilibrium constants of the following reactions $2\text{A} \rightleftharpoons \text{B}$ is $K_1$ and $\text{B} \rightleftharpoons 2\text{A}$ is $K_2$, then

a) $K_1 = 2K_2$  

b) $K_1 = 1/K_2$  

c) $K_2 = (K_1)^2$  

d) $K_1 = 1/K_2^2$

8. In a reaction $2\text{O}_3 \rightleftharpoons 3\text{O}_2$ the value of $K_c$ is

a) $[\text{O}_3]^3 / [\text{O}_2]^2$  

b) $[\text{O}_2]^2 / [\text{O}_3]^3$  

c) $[\text{O}_2]^3 / [\text{O}_3]^2$  

d) $[\text{O}_3] / [\text{O}_2]$
9. In the equilibrium \( \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \), in the manufacture of ammonia by Haber’s process, the maximum yield of ammonia will be obtained with the process having:
   a) low pressure and high temperature  
   b) low pressure and low temperature  
   c) high temperature and high pressure  
   d) high pressure and low temperature.

10. In the Haber process the yield of ammonia is greater
   a) at high pressure  
   b) at low pressure  
   c) at high temperature  
   d) in absence of catalyst.

11. In the reversible reaction \( 2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2 \), \( K_p \) is
   a) greater than \( K_c \)  
   b) less than \( K_c \)  
   c) equal to \( K_c \)  
   d) 0 / zero.

12. In the synthesis of \( \text{NH}_3 \) between \( \text{N}_2 \) and \( \text{H}_2 \) reaction the unit of \( K_c \) is
   a) \( \text{lit}^2 \text{mol}^{-2} \)  
   b) \( \text{atm}^{-2} \)  
   c) \( \text{lit atm}^{-1} \)  
   d) \( \text{atm}^{-1} \).

13. State of a chemical equilibrium is
   a) dynamic  
   b) stationary  
   c) both (a) and (b)  
   d) none of these.

14. The equilibrium constant for the reaction \( 2\text{A} \rightleftharpoons \text{B} \) is 25 mol\(^{-1}\) dm\(^3\) at 900 K. What is the equilibrium constant for the reaction \( \text{B} \rightarrow 2\text{A} \) in dm\(^{-3}\) mol at the same temperature?
   a) 25  
   b) 625  
   c) 0.04  
   d) 0.4.

15. The fraction of total moles of reactant dissociated is called
   a) dissociation equilibrium  
   b) degree of association  
   c) degree of dissociation  
   d) dissociation constant.

16. The maximum yield of ammonia by Haber’s process is
   a) 78%  
   b) 97%  
   c) 37%  
   d) 89%.

17. The optimum temperature used in contact process for the manufacture of \( \text{SO}_3 \) is
   a) 400°C to 450°C  
   b) 1800°C to 2700°C  
   c) 500°C to 550°C  
   d) 350°C to 450°C.

18. The rate constant of forward and reverse reactions are \( 8 \times 10^{-5} \) and \( 2 \times 10^{-4} \) respectively. The value of \( K_c \) is
   a) 0.04  
   b) 0.02  
   c) 0.2  
   d) 0.4.

19. The relationship between \( K_p \) and \( K_c \) for the equilibrium \( 2\text{H}_2\text{O}(g) + 2\text{Cl}_2(g) \rightleftharpoons 4\text{HCl}(g) + \text{O}_2(g) \) is
   a) \( K_p = K_c \)  
   b) \( K_p = K_c(\text{RT})^2 \)  
   c) \( K_p = K_c(\text{RT}) \)  
   d) \( K_p = K_c(\text{RT})^{-2} \).

20. Two moles of ammonia gas are introduced into a previously evacuated 1.0 dm\(^3\) vessel in which it partially dissociates at high temperature. At equilibrium 1.0 mole of ammonia remains. The equilibrium constant \( K_c \) for the dissociation is
   a) 27 / 16 (mole dm\(^{-3}\))\(^2\)  
   b) 27 / 8 (mole dm\(^{-3}\))\(^2\)  
   c) 27 / 4 (mole dm\(^{-3}\))\(^2\)  
   d) none of these.

21. When \( \Delta n_g \) in a homogenous gaseous equilibrium is positive, then
   a) \( K_p = K_c \)  
   b) \( K_p > K_c \)  
   c) \( K_c > K_p \)  
   d) \( K_p = 2K_c \)  
   a) \( K_p = K_c \)  
   b) \( K_p < K_c \)  
   c) \( K_c > K_p \)  
   d) \( K_p = K_c/2 \).
22. Which of the following gaseous equilibria is favoured by increase in temperature?

a) \( N_2O_4 \rightleftharpoons 2NO_2; \Delta H = +59 \text{ kJ mol}^{-1} \)

b) \( N_2 + 3H_2 \rightleftharpoons 2NH_3; \Delta H = -22 \text{ kcal mol}^{-1} \)

c) \( 2SO_2 + O_2 \rightleftharpoons 2SO_3; \Delta H = -47 \text{ k cal mol}^{-1} \)

d) Both (b) and (c).

23. Which one of the following has negative value for \( \Delta n_g \)?

a) \( H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \)

b) \( PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \)

c) \( 3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \)

d) \( 2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g) \).

24. In an equilibrium reaction, \( Q < k_c \) then

a) forward reaction is favoured

b) reverse reaction is favoured

c) both forward and reverse reaction is favoured

d) none of these

25. In which of the following gaseous reactions \( K_p < K_c \)?

a) \( PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \)

b) \( H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \)

c) \( N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \)

d) \( CO(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \).

26. The equilibrium constant \( K_c \) for the reaction \( A(g) \rightleftharpoons B(g) \) is \( 2.5 \times 10^{-2} \). The rate constant of forward reaction is \( 0.05 \text{ sec}^{-1} \). Therefore, the rate constant of reverse reaction is

a) \( 2 \text{ seconds}^{-1} \)

b) \( 0.2 \text{ seconds}^{-1} \)

c) \( 2 \text{ minutes}^{-1} \)

d) \( 0.2 \text{ minutes}^{-1} \)

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**Chemical Kinetics - II**

1. 50% of a first order reaction is completed in 20 minutes. The time required for 75% completion is

a) 60 minutes 

b) 10 minutes 

c) 40 minutes 

d) 80 minutes.

2. Decomposition of nitrogen pentoxide in CCl4 is an example for

a) second order reaction

b) third order reaction

c) zero order reaction 

d) first order reaction.

3. For a reaction \( Ea = 0 \) and \( k = 4.2 \times 10^5 \text{ sec}^{-1} \) at 300 K, the value of \( k \) at 310 K will be

a) \( 4.2 \times 10^5 \text{ sec}^{-1} \)

b) \( 8.4 \times 10^5 \text{ sec}^{-1} \)

c) \( 8.4 \times 10^5 \text{ sec}^{-1} \)

d) \( 4.2 \times 10^5 \text{ sec}^{-1} \) / unpredictable.

4. For a reaction: \( aA \rightarrow bB \), the rate of reaction is doubled when the concentration of \( A \) is increased by four times. The rate of reaction is equal to

a) \( k [A]^a \)

b) \( k [A]^{1/2} \)

c) \( k [A]^{1/a} \)

d) \( k [A] \)

5. Half-life period of a first order reaction is 20 min. The time taken for the completion of 99.9% of the reaction is

a) 20 min 

b) 2000 min 

c) 250 sec 

d) 200 min.

6. Hydrolysis of an ester by dilute HCl is an example for

a) zero order reaction 

b) first order reaction 

c) second order reaction

d) pseudo first order reaction.
7. If the activation energy is high then the rate of the reaction is
   a) high   b) moderate   c) low         d) cannot be predicted.
8. In a first order reaction the concentration of the reactant is increased by 2 times. The rate of the reaction is increased by
   a) 2 times   b) 4 times   c) 10 times   d) 6 times.
9. Reactions in which the reacting molecules react in more than one way yielding different set of products are called
   a) consecutive reactions   b) parallel reactions
   c) opposing reactions   d) chain reactions
10. The excess energy which a molecule possesses to become active is known as
     a) kinetic energy   b) potential energy
     c) activation energy   d) threshold energy.
11. The first order rate constant of a reaction is $0.0693 \text{ min}^{-1}$. Then the time required for 50% completion of a reaction is
    a) 10 min   b) 1 min   c) 100 min   d) 50 min.
12. The half-life period of a first order reaction is 10 minutes. The rate constant is
    a) $6.93 \times 10^2 \text{ min}^{-1}$   b) $0.693 \times 10^{-2} \text{ min}^{-1}$
    c) $6.932 \times 10^{-2} \text{ min}^{-1}$   d) $69.3 \times 10^{-1} \text{ min}^{-1}$
13. The sum of the powers of the concentration terms that occur in the rate equation is called
    a) molecularity   b) order
    c) rate   d) rate constant.
14. The $t_{1/2}$ of a first order reaction is 100 minutes. The rate constant of the reaction is
    a) $6.93 \times 10^4 \text{ min}^{-1}$   b) $0.693 \times 10^{-1} \text{ min}^{-1}$
    c) $6.93 \times 10^{-3} \text{ min}$   d) $69.3 \times 10^{-2} \text{ min}$
15. The unit of zero order rate constant is
    a) $\text{sec}^{-1}$   b) $\text{mol lit}^{-1} \text{ sec}^{-1}$
    c) $\text{mol sec}^{-1}$   d) $\text{lit}^2 \text{ sec}^{-1}$.
16. Arrhenius equation is
    a) $k = \frac{Ae}{RT}$   b) $k = \frac{Ae^{-RT}}{Ea}$
    c) $k = \frac{Ae^{-Ea}}{RT}$   d) $k = Ae^{Ea/RT}$

**Surface Chemistry**

1. (The phenomenon of) Tyndall effect is not observed in
   a) emulsion   b) colloidal solution
   c) true solution   d) suspension / none of these.
2. An emulsion is a colloidal solution of
   a) two solids   b) two liquids
   c) two gases   d) one solid and one liquid
3. An example of gel is
   a) paint   b) pumice-stone
   c) milk   d) curd.
4. An example of lyophilic colloid is
   a) sulphur in water   b) phosphorus in water
   c) starch   d) all of these
5. Argyrol is
   a) colloidal silver  b) colloidal antimony
   c) colloidal gold  d) milk of magnesia.

6. Catalyst used in Deacon's method of manufacture of chlorine is
   a) NO  b) CuCl2  c) Fe2O3  d) Ni.

7. Coconut charcoal has a great capacity of the -------- of gases.
   a) adsorption  b) absorption  c) desorption  d) all of these.

8. Colloidal medicines are more effective because
   a) they are clean  b) they are easy to prepare
   c) they are easily assimilated and adsorbed  d) the germs move towards them.

9. Colloids are purified by
   a) precipitation  b) Coagulation  c) Dialysis  d) Filtration

10. Curd is a colloidal solution of
    a) liquid in liquid  b) liquid in solid
    c) solid in liquid  d) solid in solid.

11. Decomposition of hydrogen peroxide is retarded in the presence of
    a) alcohol  b) glycerin
    c) Manganese dioxide, MnO2  d) Molybdenum, Mo.

12. Emulsifying agent is used for
    a) precipitation of an emulsion  b) coagulation of an emulsion
    c) stabilization of an emulsion  d) none of these.

13. Fe(OH)3 colloidal particles adsorb ______ ions
    a) Fe3+  b) Mg2+
    c) Ca2+  d) Cu2+

14. Fog is a colloidal solution of
    a) liquid in gas  b) gas in liquid
    c) gas in solid  d) solid in gas.

15. For chemisorption which is wrong?
    a) It is irreversible  b) It requires activation energy
    c) It forms multi(molecular) layers on absorbate  d) Surface compounds are formed.

16. In case of physical adsorption, there is desorption when
    a) temperature decreases  b) temperature increases
    c) pressure increases  d) concentration increases.

17. In the reaction between oxalic acid and potassium permanganate, in the presence of dil. H2SO4 acts as an auto catalyst
    a) K2SO4  b) MnSO4  c) MnO2  d) Mn2O3

18. Oil soluble dye is mixed with emulsion and emulsion remains colorless then, the emulsion is
    a) O/W  b) W/O  c) O/O  d) W/W

19. Smoke is a colloidal solution of
    a) gas in solid  b) solid in gas
    c) gas in liquid  d) liquid in gas.

20. The auto catalyst in the oxidation of oxalic acid by KMnO4 is
    a) K2SO4  b) MnSO4  c) KMnO4  d) CO2

21. The blue colour of the sky is due to
    a) Tyndall effect  b) Brownian movement
22. The catalyst used for the decomposition of KClO₃ is
   a) MnO₂   b) Cl₂   c) V₂O₅   d) Pt.

c) electrophoresis  d) electro-osmosis.

23. The colloid used for stomach disorder is
   a) colloidal silver   b) colloidal antimony   c) colloidal gold   d) Milk of Magnesia.

24. The decomposition of hydrogen peroxide in the presence of colloidal platinum is a/an
   a) positive catalysis   b) negative catalysis   c) auto-catalysis   d) induced catalysis.

25. The emulsifying agent used in O/W emulsion is
   a) long chain alcohols   b) lampblack   c) protein   d) glycerol

26. The function of FeCl₃ in the conversion of Fe(OH)₃ precipitate into a colloid is
   a) peptising agent   b) emulsifying agent   c) reducing agent   d) precipitating agent.

27. The iron catalyst used in the Haber's process is poisoned by / The iron catalyst used in the synthesis of ammonia in Haber's process is poisoned by
   a) Pt   b) H₂   c) H₂S   d) As₂O₃ /
   a) As₂O₃   b) V₂O₅   c) H₂S   d) Glycerine

28. The migration of colloidal particles under the influence of an electric field is known as
   a) electro-osmosis   b) electrolysis / hot dialysis   c) electrodialysis   d) electrophoresis.

29. The oxidation of sodium sulphite by air is retarded by
   a) MnO₂   b) H₂S   c) Alcohol   d) As₂O₃.

30. The platinum catalyst used in the oxidation of SO₂ in contact process is poisoned by
   a) arsenious oxide (As₂O₃)   b) vanadium pentoxide (V₂O₅)
   c) Ferric oxide (Fe₂O₃)   d) Cupric chloride (CuCl₂)

31. The sky looks blue due to
   a) adsorption   b) dispersion   c) reflection   d) scatter blue light

32. The Tyndall effect is associated with colloidal particle due to
   a) scattering of light   b) presence of charge   c) absorption / diffusion of light   d) reflection of light.

33. Which one is correct factor that explains the increase of rate of reaction by a catalyst?
   a) Shape selectivity   b) Particle size   c) Increase of free energy   d) Lowering of activation energy.

34. Which one of the following factors is false regarding catalyst?
   a) Small quantity is enough   b) Initiate the reaction   c) Remains unchanged in mass and chemical composition   d) Specific in its action.

35. Which type of colloidal is a sol?
   a) solid in liquid   b) liquid in solid   c) solid in solid   d) gas in solid.

**Electrochemistry – I**
1. Equivalent conductance of acetic acid at 25°C is 80 ohm⁻¹ cm² (gram equivalent)⁻¹ and at infinite
dilution is 400 ohm⁻¹ cm² (gram equivalent)⁻¹. The degree of dissociation is
a) 1  b) 0.2  c) 0.1  d) 0.3.
2. Faraday's laws of electrolysis are related to
   a) atomic number of the cation  b) atomic number of the anion
   c) equivalent weight of the electrolyte  d) speed of the cation.
3. For the titration between oxalic acid and sodium hydroxide, the indicator used is / The indicator
suitable for the titration of oxalic acid against NaOH is
a) potassium permanganate  b) phenolphthalein  c) litmus  d) methyl orange.
4. If 0.2 ampere can deposit 0.1978 g of copper in 50 minutes, how much of copper will be deposited
   by 600 coulombs?
   a) 19.78 g  b) 1.978 g  c) 0.1978 g  d) 197.8 g
5. Ostwald’s dilution law is applicable in the case / to the solution of
   a) CH₃COOH  b) NaCl  c) NaOH  d) H₂SO₄
6. The Indicator used in the titration of ammonium hydroxide with hydrochloric acid is
   a) KMnO₄  b) Methyl orange  c) Phenolphthalein  d) Litmus.
7. The pH of a solution containing 0.1N NaOH solution is
   a) 1  b) 10⁻¹  c) 13  d) 10⁻¹³.
8. When 10⁻⁶ mole of a monobasic strong acid is dissolved in one litre of solvent, the pH of the
   solution is
   a) 6  b) 7  c) 4  d) less than 7
9. When one coulomb of electricity is passed through an electrolytic solution, the mass deposited on
   the electrode is equal to
   a) equivalent weight  b) molecular weight
   c) electrochemical equivalent  d) one gram.
10. When pH of a solution is 2, the hydrogen ion concentration in moles litre⁻¹ is
    a) 1 x 10⁻¹²  b) 1 x 10⁻⁴  c) 1 x 10⁻⁷  d) 1 x 10⁻²
11. When sodium acetate is added to (a solution of) acetic acid, the degree of ionisation of acetic
    acid
    a) increases  b) decreases  c) does not change  d) becomes unity / becomes zero.

**Hydroxy Derivatives**

1. A compound that undergoes bromination easily is
   a) benzoic acid  b) benzene  c) phenol  d) toluene.
2. Compound which is used as medicine for Asthma and Whooping cough is
   a) Benzyl acetate  b) Ethyl acetate  c) Benzyl benzoate  d) Benzyl formate.
3. Ethylene diamine forms glycol with
   a) nitrous acid  b) Na₂CO₃ solution  c) NaHCO₃ solution  d) Baeyer's reagent.
4. Order of reactivity of alcohol towards sodium metal is

a) primary < secondary > tertiary  

b) primary > secondary > tertiary

c) primary < secondary < tertiary  
d) primary > secondary < tertiary.

5. Oxidation of glycerol with bismuth nitrate gives
   a) meso-oxalic acid  
b) glyceric acid  
c) tartronic acid  
d) both (b) and (c).

6. The active component of dynamite is
   a) kieselghur  
b) nitroglycerine  
c) nitrobenzene  
d) trinitrotoluene

7. The characteristic odour of lower phenols is
   a) carbolic acid  
b) fruity  
c) oil of bitter almonds  
d) rotten fish

8. The compound that reacts fastest with Lucas reagent is / The reaction of Lucas reagent is fast with
   a) butan-1-ol  
b) butan-2-ol  
c) 2-methyl propan-1-ol  
d) 2-methyl propan-2-ol. / 
   a) 1-butanol  
b) 2-butanol  
c) 1-propanol  
d) 2-methyl-2-propanol.

9. The isomerism exhibited by 1-propanol and methoxy ethane is
   a) chain  
b) position  
c) functional  
d) metamerism.

10. The number of secondary alcoholic group(s) in glycerol is
    a) 1  
b) 2  
c) 3  
d) 0

11. The reaction of ethylene glycol with PI3 gives
    a) ICH2 CH2I  
b) CH2 = CH2  
c) CH2 = CHI  
d) ICH = CHI.

12. When phenol is distilled with zinc dust it gives
    a) benzaldehyde  
b) benzoic acid  
c) toluene  
d) benzene

**Ethers**

1. According to Lewis concept of acids and bases, ethers are
   a) acidic  
b) basic  
c) neutral  
d) amphoteric.

2. An organic compound C4H10O when heated with excess HI gives only one type of alkyl iodide. 
The Compound is
   a) diethyl ether  
b) methyl n-propyl ether  
c) methyl iso propyl ether  
d) n-butyl alcohol

3. Anisole on bromination yields
   a) m- bromoanisole  
b) o- bromoanisole  
c) o- & p- bromoanisole  
d) benzoic acid.

4. Diethyl ether behaves as a
   a) Lewis acid  
b) Lewis base  
c) Neutral compound  
d) Bronsted acid.

5. Diethyl ether can be decomposed with
   a) HI  
b) KMnO4  
c) NaOH  
d) H2O.

6. Ether is formed when alkyl halide is treated with sodium alkoxide. The / This method is known as
   a) Hoffmann's reaction  
b) Williamson’s synthesis  
c) Wurtz reaction  
d) Kolbe's reaction.

7. Ethers should not be evaporated to dryness because
   a) They form explosive peroxide  
b) they are insoluble in water  
c) they are inert  
d) they are lighter than water

8. Higher ethers can be prepared from lower members by the action of
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9. In the formation of oxonium salt when etherial oxygen reacts with strong mineral acid is called
a) electronation  b) protonation  c) deprotonation  d) dehydration.

10. Number of ether isomers possible for (the molecular formula) C_4H_10O is
a) 7  b) 5  c) 4  d) 3 /  d) four.

11. Oxygen atom of ether is
a) more / very reactive  b) replaceable  c) oxidizing  d) (comparatively) inert.

12. The compound mixed with ethanol to serve as substitute for petrol is
a) methoxy methane  b) ethoxy ethane  c) methanol  d) ethanal.

13. The IUPAC name of phenatole is
a) ethyl phenyl ether  b) methyl phenyl ether  c) diethyl ether  d) diphenyl ether (ethoxy benzene).

14. The preparation of diethyl ether by Williamson's synthesis is a / an /  Williamson's synthesis is an example of
a) nucleophilic addition reaction  b) electrophilic addition reaction  c) electrophilic substitution reaction  d) nucleophilic substitution reaction.

15. When ether is exposed to air for some time, an explosive substance produced is
a) peroxide  b) TNT  c) superoxide  d) gun cotton. / Oxide

16. When ethers are exposed to air for a long time, they form
a) peroxides  b) halides  c) oxides  d) superoxides.

17. When ethyl iodide is treated with dry silver oxide, it forms
a) ethyl alcohol  b) diethyl ether  c) silver ethoxide / silver methoxide  d) ethyl methyl ether

18. Which among the following is unsymmetrical ether?
a) C_6H_5-O-C_6H_5  b) C_2H_5-O-C_2H_5  c) CH_3-O-CH_3  d) C_6H_5-O-CH_3.

19. Which of the following produces ether, when heated with Conc. H_2SO_4 at 413 K?
   a) Organic acid  b) Aldehyde  c) Alcohol  d) Ketone.

20. Which one of the following ethers is used in perfumery?
   a) dimethyl ether  b) diethyl ether  c) ethyl methyl ether  d) methyl phenyl ether.

21. Which one of the following is simple ether?
   a) CH_3-O-C_2H_5  b) C_6H_5-O-C_2H_5  c) C_2H_5-O-C_2H_5  d) C_3H_7-O-C_2H_5

22. Zeisel's method of detection and estimation of alkoxy group in alkaloids involves the reaction of ether with
   a) HI  b) Cl_2  c) P  d) dil. HCl.

23. Intermolecular hydrogen bonds are not present in
   a) CH_3COOH  b) C_2H_5OC_2H_5  c) CH_3CH_2OH  d) C_2H_5NH_2

24. When diethyl ether reacts with chlorine in presence of sunlight gives
   a) α-chloro diethyl ether  b) α,α'-dichloro diethyl ether  c) perchloro diethyl ether  d) both (a) & (b)

25. Williamson's synthesis is an example of
Carbonyl Compounds

1. A Cyanohydrin of a compound X on hydrolysis gives lactic acid. X is
   a) HCHO   b) CH₃CHO   c) (CH₃)₂CO   d) C₆H₅CH₂CHO.

2. Aldol is
   a) 2-hydroxy butanol   b) 3-hydroxy butanol
   c) 3-hydroxy butanal   d) 2-hydroxy butanal.

Distillation

3. Calcium acetate + calcium benzoate → ?
   a) benzophenone   b) benzoic acid   c) acetophenone   d) phenyl benzoate

4. Compound which undergoes iodoform test is
   a) 1-pentanol   b) 2-pentanone   c) 3-pentanone   d) pentanal.

5. Concentrated solution of sodium acetate on electrolysis gives
   a) ethane   b) propane   c) methane   d) butane.

6. Hydrogenation of benzoyl chloride in the presence of Pd and BaSO₄ gives
   a) phenol   b) benzoic acid   c) benzyl alcohol   d) benzaldehyde.

7. Propanone is / Methyl ketones are (usually) characterised by
   a) Fehling’s solution   b) Iodoform test   c) Schiff’s test   d) Tollens reagent.

8. Oil of bitter almonds is
   a) nitrobenzene   b) benzaldehyde   c) methyl salicylate   d) aspirin.

9. Schiff’s reagent gives pink colour with
   a) acetone   b) acetaldehyde   c) ethanol   d) ether.
   a) acetone   b) acetaldehyde   c) ethyl alcohol   d) methyl acetate

10. Tertiary butyl alcohol can be prepared by the treating methyl magnesium iodide with
    a) formaldehyde (HCHO)   b) acetaldehyde (CH₃CHO)
    c) acetone (CH₃COCH₃)   d) carbon dioxide (CO₂)

11. The compound that does not answer iodoform test is
    a) acetophenone   b) isopropyl alcohol   c) 2-pentanol   d) benzophenone.

12. The compound that does not reduce Fehling solution is
    a) formaldehyde   b) acetaldehyde   c) benzaldehyde   d) propionialdehyde.

13. The compound that does not undergo Cannizzaro reaction is
    a) Formaldehyde   b) Acetaldehyde   c) Benzaldehyde   d) Trimethyl acetaldehyde

14. The compound used in the preparation of the tranquilizer sulphonal is
    a) acetone   b) acetophenone   c) isopropyl alcohol   d) glycol.

15. The compound used in the preparation of triphenyl methane dye is
    a) methanol   b) phenyl methanol   c) phenyl methanal   d) ethanol

16. The formation of a cyanohydrin with a ketone is an example of
    a) electrophilic substitution   b) nucleophilic addition
c) nucleophilic substitution  

17. Which of the following compounds is oxidised to give ethyl methyl ketone?
   a) 2-propanol  
   b) 2-pentanone  
   c) 1-butanol  
   d) 2-butanol

18. Conc. H2SO4

CH3COCH3 → the product is
   a) mesitylene  
   b) mesityl oxide  
   c) phorone  
   d) paraldehyde

**Carboxylic Acids**

1. Strongest acid among the following is
   a) ClCH2COOH  
   b) C13CCOOH  
   c) CH3COOH  
   d) Cl2CHCOOH

2. CH3CH(OH)COOH → X. The X is
   a) CH3COCOOH  
   b) CH3CH2COOH  
   c) CH3CHOHCHO  
   d) CH2(COOH)2

3. Ethylene dicyanide on hydrolysis (using acid) gives
   a) Oxalic acid  
   b) Succinic acid  
   c) Adipic acid  
   d) Propionic acid.

4. The acid that cannot be prepared from Grignard reagent is
   a) Formic acid  
   b) Acetic acid  
   c) Propionic acid / Butyric acid  
   d) Benzoic acid.

5. The acid which reduces Tollen’s reagent is
   a) acetic acid / benzoic acid  
   b) formic acid  
   c) oxalic acid

6. The compound found as / in some stony deposits in kidneys is
   a) potassium oxalate  
   b) oxalic acid  
   c) potassium succinate  
   d) calcium oxalate.

7. The isomerism exhibited by CH3CH2COOH and CH3COOCH3 is
   a) metamerism  
   b) functional isomerism  
   c) chain isomerism  
   d) position isomerism.

8. Which of the following is least acidic?
   a) C2H5OH  
   b) CH3COOH  
   c) C6H5OH  
   d) CICH2COOH

9. Which order of arrangement is correct in terms of the strength of the acid?
   a) CH3CH2COOH > CH3COOH < HCOOH < CICH2COOH  
   b) CICH2COOH < HCOOH < CH3COOH < CH3CH2COOH  
   c) CH3CH2COOH < CH3COOH < HCOOH < CICH2COOH  
   d) HCOOH > CH3CH2COOH < CH3COOH > CICH2COOH.

**Organic Nitrogen Compounds**

1. Aniline differs from ethylamine in its reaction with
   a) CH3I  
   b) CHCl3 and Caustic KOH  
   c) HNO2  
   d) CH3COC1

2. Aniline reacts with benzoyl chloride in the presence of sodium hydroxide and gives benzanilide. This reaction is known as
   a) Gattermann reaction  
   b) Sandmeyer’s reaction  
   c) Schotten-Baumann reaction  
   d) Gomberg-Bachmann reaction.

Cu2Cl2 / HCl
3. \( \text{C}_6\text{H}_5\text{N}2\text{Cl} \rightarrow \text{X} \); the compound X is
   a) \( \text{C}_6\text{H}_5\text{NH}2 \)  
   b) \( \text{C}_6\text{H}_5\text{NH}2\text{H} \)  
   c) \( \text{C}_6\text{H}_5\text{-C}_6\text{H}_5 \)  
   d) \( \text{C}_6\text{H}_5\text{Cl}. \)
   \( \text{NaNO}_2/\text{HCl} \)

4. \( \text{C}_6\text{H}_5\text{NH}2 \rightarrow \text{X} \). \( \text{X} \) is
   a) \( \text{C}_6\text{H}_5\text{Cl} \)  
   b) \( \text{C}_6\text{H}_5\text{NHOH} \)  
   c) \( \text{C}_6\text{H}_5\text{N}2\text{Cl} \)  
   d) \( \text{C}_6\text{H}_5\text{OH}. \)
   273 K

5. \( \text{CCl}_3\text{NO}_2 \) is used as
   a) explosive  
   b) dye  
   c) anaesthetic  
   d) sterilizing agent
   / Use of chloropicrin (\( \text{CCl}_3\text{NO}_2 \)) is
   a) soil sterilizing agent  
   b) organic synthesis  
   c) good solvent  
   d) antioxidant.

6. Conversion of benzene diazonium chloride to chlorobenzene is called
   a) Sandmeyer's reaction  
   b) Stephan's reaction  
   c) Gomberg reaction  
   d) Schotten-Baumann reaction.

7. Electrophile used in the nitration of benzene is
   a) hydronium ion  
   b) sulphonic acid  
   c) nitronium ion  
   d) bromide ion.

8. In nitroalkanes - NO2 group is converted to - NH2 group by the reaction with
   / The - NO2 group in nitro-alkane is converted into - NH2 group by the reagent
   / The nitro group can be reduced to primary amino group by
   a) \( \text{Zn} / \text{NH}_4\text{Cl} \)  
   b) \( \text{Zn dust} \)  
   c) \( \text{Sn} / \text{HCl} (\text{Sn} / \text{conc. HCl}) \)  
   d) \( \text{Zn} / \text{NaOH}. \)

9. Nitration of nitrobenzene results in
   a) o-dinitro benzene  
   b) 1,3,5-trinitro benzene  
   c) m-dinitrobenzene  
   d) p-dinitrobenzene.

10. Nitro-acinitro tautomerism is exhibited by
    a) nitromethane  
    b) nitrobenzene  
    c) chloropicrin  
    d) o-toluidine.

11. Nitromethane condenses with acetaldehyde to give
    a) nitropropane  
    b) 1-nitro-2-propanol  
    c) 2-nitro-1-propanol  
    d) 3-nitropropanol.

12. Organic compound that does not undergo diazotisation is
    a) m-toluidine  
    b) aniline  
    c) p-aminophenol  
    d) benzyamine.

13. Oxidation of aniline with acidified K2Cr2O7 gives
    a) p-benzoquinone  
    b) benzoic acid  
    c) benzaldehyde  
    d) benzyl alcohol

14. Primary amine acts as
    a) Electrophile  
    b) Lewis base  
    c) Lewis acid  
    d) Free radical

15. The basic character of amines is due to
    a) tetrahedral structure  
    b) presence of nitrogen atom  
    c) lone pair of electrons on nitrogen atom  
    d) high electronegativity of nitrogen.

16. The basic strength of amine is in the order of
    a) \( \text{NH}_3 > \text{CH}_3\text{NH}2 > (\text{CH}_3)2\text{NH} \)  
    b) \( (\text{CH}_3)2\text{NH} > \text{CH}_3\text{NH}2 > \text{NH}_3 \)  
    c) \( \text{CH}_3\text{NH}2 > (\text{CH}_3)2\text{NH} > \text{NH}_3 \)  
    d) \( \text{NH}_3 > (\text{CH}_3)2\text{NH} > \text{CH}_3\text{NH}2 \).

17. The compound most reactive towards electrophillic nitration is
    a) Methyl benzene / Toluene  
    b) Benzene  
    c) Benzoic acid  
    d) Nitrobenzene.
18. The compound that does not show tautomerism is
   a) nitrobenzene  b) nitromethane  c) nitroethane  d) 2-nitropropane.

19. The intermediate formed in the nitration of benzene is
   a) Arenium ion  b) Carbanion  c) Oxonium ion  d) Nitrite ion.

20. Nitrobenzene on electrolytic reduction in conc. Sulphuric acid, the intermediate formed is / The intermediate formed on electrolytic reduction of nitrobenzene in conc. H2SO4 is
   a) C6H5NH-NHC6H5  b) C6H5-NHOH  c) C6H5-N=N-C6H5  d) C6H5.HSO4 / all of these.

21. The isomerism exhibited by CH3-CH2-NO2 and CH3-CH2-O -N = O is
   a) position  b) chain  c) functional  d) tautomerism.

22. The isomerism exhibited by CH3-N=O and CH2=N-OH is
   ↓  ↓
   O  O
   a) position  b) chain  c) functional  d) tautomerism.

23. The nitrogen compound used in the preparation of sulpha drugs is
   a) methylamine  b) nitromethane  c) aminobenzene / aniline  d) nitrobenzene.

24. The organic compound that undergoes carbylamine reaction is
   a) (C2H5)2NH  b) C2H5NH2  c) (C2H5)3N  d) (C2H5)4N+I-

25. The product obtained when Nitro benzene is treated with Zn / NaOH is
   a) aniline  b) azoxy benzene  c) azo benzene  d) hydrazo benzene / N, N' - diphenyl hydrazine

26. The reaction between benzene diazonium chloride and benzene in the presence of NaOH is
   a) Perkin's reaction  b) Gattermann's reaction  c) Sandmeyer reaction  d) Gomberg-Bachmann reaction

27. The tertiary nitro compound is
   a) 2-nitropropane  b) 1-nitropropane  c) 1-nitro-2, 2-dimethyl propane  d) 2-nitro-2-methyl propane.

28. When aqueous solution of benzene diazonium chloride is boiled, the product formed is
   a) Benzyl alcohol  b) Benzene + N2  c) Phenol  d) Phenyl hydroxyl amine.

29. When nitromethane is reduced with Zn dust + NH4Cl we get
   a) CH3NH2  b) C2H5NH2  c) CH3NHOH  d) C2H5COOH.

30. Which among the following is a tertiary amine?
   a) (CH3)3-C-NH2  b) CH3 - CH (CH3) - NH - CH3  c) (CH3)2-N-C2H5  d) CH3-CH2- C (CH3) (C2H5) NH2

31. Which of the following compounds has the smell of bitter almonds?
   a) Aniline  b) Nitromethane  c) Benzene sulphonic acid  d) Nitrobenzene

32. Which of the following nitro-compounds behave as an acid in the presence of strong alkali?
   a) Primary  b) Secondary  c) Tertiary  d) both (a) and (b).

33. Which of the following will not undergo diazotisation?
   a) m-toluidine  b) aniline  c) p-amino phenol  d) benzyl amine.
34. Which of the following will not undergo Hoffman’s bromamide reaction?
   a) ethanamide   b) propanamide   c) methanamide   d) phenyl methanamide.

35. Which one of the following is a secondary amine?
   a) Aniline   b) Diphenyl amine   c) Secondary butyl amine   d) tertiary butyl amine.

36. Which of the following will not undergo diazotisation? / The compound which does not
    undergo diazotization reaction is
   a) m-toluidine   b) aniline   c) p-amino phenol   d) benzyl amine

37. Which one of the following is the most basic?
   a) ammonia   b) methylamine   c) diethylamine   d) aniline

38. Oil of mirbane is
   a) nitrobenzene   b) benzaldehyde   c) methyl salicylate   d) aspirin.

**Biomolecules**

1. A dipeptide does not have
   a) two peptide units   b) portions of two amino acids
   c) an amino / amido group   d) salt like structure.

2. Glucose forms ------------------ with acetic anhydride and sodium acetate
   a) di-acetate   b) tetra-acetate   c) penta-acetate   d) hexa-acetate.

3. Glucose is not oxidised to gluconic acid by
   a) Br2/H2O   b) Fehling solutions   c) Tollen’s reagent   d) Conc. HNO3

4. Glucose reacts with acetic anhydride in the presence of pyridine to give
   a) monoacetate   b) diacetate   c) penta acetate   d) no reaction

5. Important constituent of cell wall is
   a) Lipid   b) Cellulose   c) Protein   d) Vitamin

6. Inversion of sucrose refers to
   a) oxidation of sucrose   b) reduction of sucrose
   c) sucrose to glucose and fructose   d) polymerisation of sucrose.

7. Invert sugar is a mixture of equal amount of
   a) D (+) glucose and sucrose   b) D (-) fructose and sucrose
   c) D (+) glucose and D (-) fructose   d) sucrose and maltose.

8. ------------------is involved in the process of blood coagulation.
   a) Fats and oils   b) Cephalin   c) Glycolipids   d) Lecithins.

9. Mixture of equal molecules of D (+) glucose and D (-) fructose is called as
   a) Fruit sugar   b) Invert sugar   c) Cane sugar   d) Non-sugar.

10. Nucleic acid is made up of
    a) an organic base   b) a sugar unit   c) phosphoric acid   d) all of these.

11. Proteins are
    a) polypeptides   b) polyacids   c) polyphenols   d) polyesters.

12. Sorbitol and Mannitol are
    a) isomers   b) polymers   c) epimers   d) dimmers.
13. Sucrose contains glucose and fructose linked by
   a) C₁ – C₁  b) C₁ – C₂  c) C₁ – C₄  d) C₁ – C₆
14. The amino acid without chiral carbon is
   a) Alanine  b) Glycine  c) Proline  d) Thyrosine
15. The building block of proteins are
   a) α-hydroxy acids b) α-amino acids  c) β-hydroxy acids  d) β-amino acids
16. The most abundant carbohydrate is
   a) glucose  b) fructose  c) starch  d) cellulose
17. The optically inactive amino acid is
   a) Glysine  b) Alanine  c) proline  d) phenyl alanine
18. The precipitation of protein is called
   a) peptisation  b) denaturation  c) renaturation  d) none of these
19. The reducing sugar (of / among the following) is
   a) sucrose  b) cellulose  c) glucose  d) starch.
20. Ultimate product of hydrolysis of protein is
   a) aniline  b) aliphatic acid  c) amino acid  d) aromatic acid.
21. When starch is heated to 200°C - 250°C, the product is
   a) dextrin  b) caramel  c) barley sugar  d) cellulose.
22. Which is not true of amino acid?
   a) It forms Zwitter ion  b) Has Isoelectric point  c) Dual behavior  d) insoluble in NaOH solution.
23. An example for reducing disaccharide is
   a) Glucose  b) Fructose  c) Sucrose  d) Lactose
1. Apply molecular orbital theory to oxygen molecule.

1. The electronic configuration of oxygen atom (Z = 8) in the ground state is 1s2s2p4. Each oxygen atom has 8 electrons, hence, in O2 molecule there are 16 electrons.
2. The electronic configuration of O2 is:
   O2: KK (σ2s)2 (σ*2s)2 (σ2pz)2 (π2px)2 = (π2py)2 (π*2px)1 = (π*2py)1
   Here (σ1s)2 (σ*1s)2 part of the configuration is abbreviated as KK.
3. The molecular orbital energy level diagram of O2 molecule is:

4. The bond order of O2 can be calculated as follows:
   \[ N_b = 8 \quad \text{and} \quad N_a = 4 \]
   Bond order = \( N_b - N_a / 2 \)
   = 8 - 4 / 2 = 2
5. Nature of bond: A bond order of 2 means that a double bond is present in a molecule of oxygen.
6. Paramagnetic nature: Since two electrons in oxygen [(π*2px) & (π*2py)] are unpaired, it is paramagnetic in nature.
2. Derive / Define de Broglie's equation.

In case of a photon, if it is assumed to have wave character, its energy is given by

\[ E = h\nu \] (according to the Planck’s quantum theory) ...

Where, \( \nu \) is the frequency of the wave and

\( h \) is Planck’s constant.

If the photon is supposed to have particle character, its energy is given by

\[ E = mc^2 \] (according to Einstein equation) ...

Where, \( m \) is the mass of photon and

\( c \) is the velocity of light.

From equations 1 and 2, we get

\[ h\nu = mc^2 \]

But,

\[ \nu = c / \lambda \]

\[ h \cdot c / \lambda = mc^2 \]
or

\[ \lambda = h / mc \]

For any material particle like electron, we may write

\[ \lambda = h / mv \]
or

\[ \lambda = h / p \]

Where \( mv = p \) is the momentum of the particle.

The above equation is called de Broglie equation and ‘\( \lambda \)’ is called de Broglie wavelength.

3. Discuss Davisson and Germer’s experiment.

1. A beam of electrons obtained from a heated tungsten filament is accelerated by using a high positive potential.

2. When this fine beam of accelerated electron is allowed to fall on a large single crystal of nickel, the electrons are scattered from the crystal in different directions.

3. The diffraction pattern so obtained is similar to the diffraction pattern obtained by Bragg’s experiment on diffraction of X-rays from a target in the same way

4.

5. Since X-rays have wave character, therefore, the electrons must also have wave character associated with them.

6. Moreover, the wavelength of the electrons as determined by the diffraction experiments were found to be in agreement with the values calculated from de-Broglie equation.

7. From the above discussion, it is clear that an electron behaves both as a particle and as a wave i.e., it has dual character.
4. Explain the formation of N\textsubscript{2} / nitrogen molecule by using molecular orbital theory.

1. The electronic configuration of nitrogen atom (Z=7) in the ground state is 1s\(^2\)2s\(^2\)2p\(_x\)\(^1\)2p\(_y\)\(^1\)2p\(_z\)\(^1\). Therefore, the total number of electrons present in nitrogen molecule (N\textsubscript{2}) is 14.

2. The electronic configuration of N\textsubscript{2}:

\[\text{N}_2: \text{KK (}\sigma 2s^2 \text{)}2 (\sigma^* 2s^2)2 (\pi 2p_x)^2 = (\pi 2p_y)^2 (\sigma 2p_z)^2\]

Here (\sigma 1s\(^2\)) (\sigma^* 1s\(^2\)) part of the configuration is abbreviated as KK.

3. The molecular orbital energy level diagram of N\textsubscript{2} is:

4. The bond order of N\textsubscript{2} can be calculated as follows:

\[\text{Bond order} = \frac{N_b - N_a}{2} = \frac{8 - 2}{2} = 3\]

5. Nature of bond: A bond order of 3 means that a triple bond is present in a molecule of nitrogen.

6. Diamagnetic nature: Since all the electrons in nitrogen are paired, it is diamagnetic.

5. Give any five postulates of molecular orbital theory.

1. In a molecule, electrons are present in new orbitals called molecular orbitals.

2. Molecular orbitals are formed by combination of atomic orbitals of equal energies (in case of homonuclear molecules) or of comparable energies (in case of heteronuclear molecules).

3. The number of molecular orbitals formed is equal to the number of atomic orbitals undergoing combination.
4. Two atomic orbitals can combine to form two molecular orbitals. One of these two molecular orbitals one has a lower energy and the other has a higher energy. The molecular orbital with lower energy is called **bonding molecular orbital** and the other with higher energy is called **anti bonding molecular orbital**.

5. The **shapes of molecular orbitals** depend upon the shapes of combining atomic orbitals.

6. The bonding molecular orbitals are **represented by** σ (sigma), π (pi), δ (delta) and the antibonding molecular orbitals are represented by σ*, π*, δ*.

7. The molecular orbitals are filled in the increasing order of their energies, starting with orbital of least energy. (**Aufbau principle**)

8. A molecular orbital can accommodate only two electrons and these two electrons must have opposite spins. (**Paul's exclusion principle**)

9. While filling molecular orbitals of equal energy, pairing of electrons does not take place until all such molecular orbitals are singly filled with electrons having parallel spins. (**Hund’s rule**)

**6. The approximate mass of an electron is 10-27g. Calculate the uncertainty in its velocity. If the uncertainty in its position were of the order of 10-11m.**

- Mass of an electron, \( m = 10^{-27} \text{g} = 10^{-27} \times 10^{-3} \text{ kg} = 10^{-30} \text{ kg} \)
- Uncertainty in its position, \( \Delta x = 10^{-11} \text{m} \)
- Uncertainty in its velocity, \( \Delta v = ? \)

\[
\Delta x \cdot m \cdot \Delta v = \frac{h}{4\pi} \\
\Delta v = \frac{h}{4\pi \times \Delta x \cdot m} \\
\Delta v = 6.626 \times 10^{-34} / 4 \times 3.14 \times 10^{-11} \times 10^{-30} \\
\Delta v = 5.275 \times 10^{-6} \text{ m sec}^{-1}
\]

**9. A moving electron has 4.55 × 10-25 joules of kinetic energy. Calculate its wavelength (mass = 9.1 × 10-31 kg and h = 6.626 × 10-34 kg m2 s-1).**

Here we are given

- Kinetic energy i.e. \( 1 / 2 \text{ m} v^2 = 4.55 \times 10^{-25} \text{ J} \)
- Mass, \( m = 9.1 \times 10^{-31} \text{ kg} \)
- Planck’s constant, \( h = 6.626 \times 10^{-34} \text{ kg m2 s}^{-1} \)
- Wavelength, \( \lambda = ? \)

\[
1 / 2 \times (9.1 \times 10^{-31}) \cdot v^2 = 4.55 \times 10^{-25} \\
\text{Or} \quad v^2 = 4.55 \times 10^{-25} \times 2 / 9.1 \times 10^{-31} \\
\text{Or} \quad v = 103 \text{ m sec}^{-1} \\
\lambda = \frac{h}{m \cdot v} \\
\lambda = 6.626 \times 10^{-34} \text{ kg m2 s}^{-1} / 9.1 \times 10^{-31} \text{ kg} \times 103 \text{ m sec}^{-1} \\
\lambda = 7.2 \times 10^{-7} \text{ m}
\]
### Q.No 53 d - Block Elements

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Metal</th>
<th>Extraction of the Metal / Metallurgy</th>
</tr>
</thead>
</table>
| 1      | Copper, Cu | 1) **Chief ore**: Copper pyrites, CuFeS₂  
2) **Concentration**: By Froth floatation process  
3) **Roasting**: Volatile impurities S, P, As and Sb are removed as their oxides  
\[
\begin{align*}
S + O_2 &\rightarrow SO_2 \\
P_4 + 5O_2 &\rightarrow 2P_2O_5 \\
4As + 3O_2 &\rightarrow 2AsO_3 \\
\end{align*}
\]
Copper pyrites are partly converted into Sulphides of Cu & Fe  
\[
2CuFeS₂ + O₂ → Cu₂S + 2FeS + SO₂ \quad (\text{Major Reaction}) \\
2FeS + O₂ → 2 FeO + 2SO₂ \quad (\text{Minor Reaction})
\]
4) **Smelting**:  
\[
\begin{align*}
2FeS + 3O₂ &\rightarrow 2FeO + 2FeO + 2SO₂ \\
FeO + SiO₂ &\rightarrow FeSiO₃ \quad (\text{slag}) \\
2Cu₂S + 3O₂ &\rightarrow 2 Cu₂O + 2SO₂ \\
Cu₂O + FeS &\rightarrow Cu₂S + FeO \\
FeO + SiO₂ &\rightarrow FeSiO₃ \quad (\text{slag})
\end{align*}
\]
5) **Bessemerisation**:  
\[
\begin{align*}
2 Cu₂S + 3O₂ &\rightarrow 2 Cu₂O + 2 SO₂ \\
2 Cu₂O + Cu₂S &\rightarrow 6 Cu + SO₂ \\
\text{Blister copper contains 98% Copper}
\end{align*}
\]
6) **Purification**: Electrolytic Refining  
- **Anode (+)**: Impure Cu  
- **Cathode (−)**: Pure Cu  
- **Electrolyte**: CuSO₄ + dil. H₂SO₄  
On passing current, pure Cu is deposited at the Cathode. |
| 2      | Chromium, Cr | 1) **Chief ore**: Chromite (or) Chrome ore, FeO.Cr₂O₃  
2) **Concentration**: By Gravity separation process  
3) **Conversion of concentrated Chromite ore into Na₂Cr₂O₇ (Roasting)**  
\[
\begin{align*}
1000°C \\
4(FeO.Cr₂O₃) + 8Na₂CO₃ + 7O₂ \quad (\text{from air}) &\rightarrow 8Na₂CO₃ + 2Fe₂O₃ + 8CO₂ \\
\text{Soluble} &\quad \text{Insoluble}
\end{align*}
\]
4) **Conversion of Na₂Cr₂O₇ into Na₂Cr₂O₇**  
\[
\begin{align*}
2Na₂CrO₄ + H₂SO₄ &\rightarrow Na₂Cr₂O₇ + Na₂SO₄ + H₂O
\end{align*}
\]
5) **Conversion of Na₂Cr₂O₇ into Cr₂O₃ (Reduction of the dichromate)**  
\[
\begin{align*}
Na₂Cr₂O₇ + 3C &\rightarrow Na₂Cr₂O₄ + 3CO \\
Na₂Cr₂O₄ + H₂O &\rightarrow 2NaOH + Cr₂O₃
\end{align*}
\]
6) **Reduction of Cr₂O₃ into Cr**: Alumino thermic process  
**Diagram with labels**  
Cr₂O₃ is reduced with Al powder (3:1)  
**Ignition mixture**: BaO₂ + Mg powder |
The mixture is ignited by a piece of Mg ribbon
\[Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3 + 468.6 \text{ kJ (slag)}\]

<table>
<thead>
<tr>
<th>Element</th>
<th>3 Zinc, Zn</th>
<th>4 Silver, Ag</th>
<th>5 Gold, Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chief ore</td>
<td>Zinc blende, ZnS</td>
<td>Argentite (or) Silver glance, Ag₂S</td>
<td>Sulphide (or) Telluride ore.</td>
</tr>
<tr>
<td>Concentration</td>
<td>By Froth Floatation process</td>
<td>By Froth flotation process</td>
<td>By Froth flotation process</td>
</tr>
<tr>
<td>Roasting</td>
<td>2ZnS + 3O₂ (1200 \text{ K} \rightarrow 2ZnO + 2SO₂)</td>
<td>Treatment of the concentrated ore with NaCN: Mac Arthur Forrest’s Cyanide process</td>
<td>Volatile impurities S, As and Te are removed as their oxides.</td>
</tr>
<tr>
<td>Reduction</td>
<td>ZnO + C (1673 \text{ K} \rightarrow \text{Zn} + \text{CO})</td>
<td>4 (\text{Au} + 8\text{KCN} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{K[Au(CN)₂]} + 4\text{KOH})</td>
<td>Treatment of the concentrated ore with KCN: Mac Arthur Forrest Cyanide process</td>
</tr>
<tr>
<td>Purification</td>
<td>Electrolytic Refining</td>
<td>Electrolytic Refining</td>
<td>Electrolytic Refining</td>
</tr>
<tr>
<td>Anode (+)</td>
<td>Impure Zn</td>
<td>Impure Ag</td>
<td>Impure Au</td>
</tr>
<tr>
<td>Cathode (−)</td>
<td>Pure Zn</td>
<td>Pure Ag</td>
<td>Pure Ag</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>ZnSO₄ + dil. H₂SO₄</td>
<td>2Na[Ag(CN)₂] + Zn (\rightarrow) 2Ag↓ + Na₂[Zn(CN)₄]</td>
<td>AuCl₃ + 10 – 12% HCl</td>
</tr>
<tr>
<td></td>
<td>On passing current pure Zn gets deposited on the Cathode.</td>
<td>On passing electricity pure Ag gets deposited at the Cathode.</td>
<td>On passing current pure Au gets deposited at the Cathode.</td>
</tr>
</tbody>
</table>
1. Explain how potassium dichromate is extracted from chromite ore. Or How is potassium dichromate prepared from chrome iron ore?

   1. Conversion of chrome iron ore to sodium chromate
   
   \[
   4\text{FeO.Cr}_2\text{O}_3 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2
   \]

   2. Conversion of Na\text{2CrO}_4 to Na\text{2Cr}_2\text{O}_7

   \[
   2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}
   \]

   3. Conversion of sodium dichromate into potassium dichromate

   \[
   \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}
   \]

4. How is Cr\text{2O}_3 reduced to chromium by aluminothermic process? Or Explain aluminothermic process involved in the extraction of chromium.

Chromic oxide is mixed with powdered Aluminium in the ratio 3:1 and is placed in a large fire clay crucible. A mixture of barium peroxide and Mg powder is placed over this. The crucible is surrounded by sand which prevents loss of heat by radiation. The mixture is ignited by a piece of Mg ribbon. During this process a large amount of heat is liberated, in which Cr2O3 is reduced to chromium.

The molten chromium is collected in the crucible and aluminium oxide is removed as slag.

\[
\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3 + 468.6 \text{ kJ}
\]
Q.No 54-f - Block Elements

1. Compare / List the points of similarities and differences between lanthanides and actinides. Or Compare the properties of lanthanides and actinides. Or Write any five differences between lanthanides and actinides.

Points of Similarities:
Both show close resemblance because these involve filling of f-subshells.
Both have coloured ions, low electronegativity, high reactivity and show magnetic properties.

Points of differences:

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Lanthanides</th>
<th>Actinides</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Binding energies of 4f electrons are higher.</td>
<td>Binding energies of 5f electrons are lower.</td>
</tr>
<tr>
<td>2</td>
<td>Maximum oxidation state exhibited by lanthanides is +4 e.g. Ce4+</td>
<td>Due to lower binding energies they show higher oxidation states such as +4, +5 and +6. Uranium exhibits +6 oxidation state in UF6 and UO2Cl2</td>
</tr>
<tr>
<td>3</td>
<td>4f electrons have greater shielding effect.</td>
<td>5f electrons have poor shielding effect.</td>
</tr>
<tr>
<td>4</td>
<td>Most of their ions are colourless.</td>
<td>Most of their ions are coloured U3+ (red), U4+ (green) and UO22+ (yellow)</td>
</tr>
<tr>
<td>5</td>
<td>They are paramagnetic but magnetic properties can be easily explained.</td>
<td>They are also paramagnetic but their magnetic properties are very difficult to interpret.</td>
</tr>
<tr>
<td>6</td>
<td>They do not form complexes easily.</td>
<td>They have much greater tendency to form complexes.</td>
</tr>
<tr>
<td>7</td>
<td>Except promethium, they are non-radioactive.</td>
<td>All of them are radioactive.</td>
</tr>
<tr>
<td>8</td>
<td>Their compounds are less basic.</td>
<td>Their compounds are more basic.</td>
</tr>
<tr>
<td>9</td>
<td>They do not form oxocations.</td>
<td>They form oxocations such as UO22+, UO+, NpO2+, PuO2+.</td>
</tr>
</tbody>
</table>
2. Describe the extraction of lanthanides from monazite sand. Or How are lanthanides extracted from monazite sand?

The method used for extraction of lanthanides from monazite sand consists of the steps which have been shown in flow sheet.

- **Monazite sand**
- Heat 210°C with H₂SO₄ for several hours
- **Gray Mud**
- **Cold Water**
- **Unreacted monazite sand, SiO₂, TiO₂, ZrSiO₄, etc** (recycle sand)
- **Filtrate containing** (Ln³⁺, Th⁴⁺, H₂O⁻, HSO₄⁻, SO₄²⁻)
- **Neutralised acidity** to proper or added HF
- **Precipitate of ThPO₄** or **Precipitate of Th**
- **Filtrate containing lanthanide and phosphate ions**
- **NaOH or Oxalic acid**
- **Lanthanide hydroxides or Oxalates**

**Individual lanthanides are separated by** a suitable physical method.

The anhydrous fluorides and chlorides are heated under argon atmosphere in presence of calcium at 1270 K to get the individual metal.

The **pure metal is obtained by** heating the trifluorides of lanthanides in the presence of calcium and lithium.

3. Discuss the position of lanthanides in the periodic table

1. Position in the periodic table: Period Number - 6, Group Number - 3.
2. The 4f-block elements are located at the bottom of the periodic table and consist of metals only.
3. The Lanthanide series include fifteen elements i.e. lanthanum (57La) to lutetium (71Lu).
4. Lanthanum and Lutetium have no partly filled 4f- subshell but have electrons in 5d-subshell. Thus these elements should not be included in this series. However, all these elements closely resemble lanthanum and hence are considered together.
4. Mention the oxidation state and of uses of lanthanides.

Oxidation states of lanthanides
The common oxidation state exhibited by all the lanthanides is +3 (Ln3+) in aqueous solutions and in their solid compounds. Some elements exhibit +2 and +4 states as uncommon oxidation states.

La - +3
Ce - +3, +4, +2
Pr - +3, +4
Nd - +3, +4, +2

Uses of lanthanides
1. A pyrophoric alloy which contains cerium, lanthanum and Neodymium; iron; aluminium; calcium, carbon and silicon is used in cigarette lighters, toys, flame throwing tanks and tracer bullets.
2. Ceria (CeO2) and thoria (ThO2) are used in gas lamp materials.
3. Cerium salts are used in dyeing cotton, lead storage batteries and as catalyst.
4. Lanthanides are used in metallothermic reactions due to their extraordinary reducing property. Lanthanido - thermic processes can yield sufficiently pure Nb, Zr, Fe, Co, Ni, Mn, Y, W, U, B and Si.
5. Alloys of Lanthanides are known as mish - metals. The major constituents of mish-metals are Ce(45-50%), La(25%), Nd(5%) and small quantities of other lanthanide metals and Fe and Ca impurities. Mish-metals are used for the production of brands of steel like heat resistant, stainless and instrumental steels. Mg- alloys containing 30% mishmetal and 1% Zr are useful in making parts of jet engines.

5. What is lanthanide contraction? Discuss its causes and consequences. Or Bring out the consequences of lanthanide contraction. Or Discuss the consequences of lanthanide contraction. Or What are the consequences of lanthanide contraction?
The lanthanide contraction is due to the imperfect shielding of one 4f electron by another in the same sub shell. As we move along the lanthanide series, the nuclear charge and the number of 4f electrons increase by one unit at each step. However, due to imperfect shielding, the effective nuclear charge increases causing a contraction in electron cloud of 4f-subshell.

Consequences of lanthanide contraction
Important consequences of lanthanide contraction are given below.
1. Basicity of ions: Due to lanthanide contraction, the size of Ln3+ ions decreases regularly with increase in atomic number. According to Fajan’s rule, decrease in size of Ln3+ ions increase the covalent character and decreases the basic character between Ln3+ and OH- ion in Ln(OH)3.
Since the order of size of Ln3+ ions are: La3+ > Ce3+ .............. >Lu3+
2. There is regular decrease in their ionic radii.
3. Regular decrease in their tendency to act as reducing agent, with increase in atomic number.
4. Due to lanthanide contraction, second and third rows of d-block transition elements are quite close in properties.
5. Due to lanthanide contraction, these elements occur together in natural minerals and are difficult to separate.
6. Write the uses of Lanthanides and Actinides.

Use of Lanthanides
1. A pyrophoric alloy which contains cerium, lanthanum and Neodymium; iron; aluminium; calcium, carbon and silicon is used in cigarette lighters, toys, flame throwing tanks and tracer bullets.
2. Ceria (CeO₂) and thoria (ThO₂) are used in gas lamp materials.
3. Cerium salts are used in dyeing cotton, lead storage batteries and as catalyst.
4. Lanthanides are used in metalloceramic reactions due to their extraordinary reducing property. Lanthanido-thermic processes can yield sufficiently pure Nb, Zr, Fe, Co, Ni, Mn, Y, W, U, B and Si.
5. Alloys of Lanthanides are known as mish - metals. The major constituents of mish-metals are Ce(45-50%), La(25%), Nd(5%) and small quantities of other lanthanide metals and Fe and Ca impurities. Mish-metals are used for the production of brands of steel like heat resistant, stainless and instrumental steels. Mg- alloys containing 30% mishmetal and 1% Zr are useful in making parts of jet engines.

Uses of Actinides
1. U-235 is fissile, it is used as fuel in nuclear power plants and as a component in nuclear weapons.
2. Plutonium - 238 is used as a power source in long mission space probes.
Q.No 55 - Coordination Compounds

1. Explain the type of hybridisation, magnetic property and geometry for [Ni(CN)4]2– and [Ni(NH3)4]2+ using VB theory Or [Ni(CN)4]2– is diamagnetic whereas [Ni(NH3)4]2+ is paramagnetic. Explain (using VB theory). Or Apply VB theory to find out the geometry of [Ni(NH3)4]2+ and calculate its magnetic moment.

1) [Ni(NH3)4]2+

Nickel atom

Outer electronic configuration 3d8s2

Ni atom

\[
\begin{array}{c}
\text{Ni atom} \\
3d \\
\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \\
\text{Ni+2 ion} \\
4s \\
\uparrow \downarrow \\
4p \\
\end{array}
\]

Number of unpaired electrons = 2

\[\mu_s = \sqrt{2(2+2)}\]

Paramagnetic moment, \(\mu_s = 2.83\)BM

The molecule is paramagnetic.

Since the hybridisation is sp3, the geometry of the molecule is tetrahedral.

2) [Ni(CN)4]2–

Ni+2 ion

\[
\begin{array}{c}
\text{Ni+2 ion} \\
3d \\
\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \\
\text{CN-} \\
\end{array}
\]

The ligand CN- is a powerful ligand. Hence it forces the unpaired electrons to pair up in d orbitals.

Hence this complex ion does not contain unpaired electrons.

Paramagnetic moment, \(\mu_s = 0\)

The molecule is diamagnetic.

Since the hybridisation is dsp2 hybridization, the geometry of the molecule is square planar.

2. Apply V.B. theory for magnetic properties of [Fe(CN)6]4- and [FeF6]4- and explain the shape. Or In what way does [FeF6]4- differ from [Fe(CN)6]4-? Or Mention the type of
hybridisation, magnetic property and geometry of the following complexes using VB theory. Or Write the application of VB theory on the following complexes: i) [FeF6]4- ii) [Fe(CN)6]4+

1) Nickel atom
Outer electronic configuration 3d64s2

Fe atom

\[
\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}
\]

[Fe(CN)6]4+

\[
\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}
\]

The ligand CN- is a powerful ligand. Hence it forces the unpaired electrons to pair up in d orbitals.

Hence this complex ion does not contain unpaired electrons.

Paramagnetic moment, \(\mu_s = 0\)

The molecule is diamagnetic.

Since the hybridisation is d2sp3, the geometry of the molecule is Octahedral.

[FeF6]4-

Fe atom
Outer electronic configuration 3d64s2

\[
\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}
\]

\[
\begin{array}{c}
\downarrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\end{array}
\]

\[
\begin{array}{c}
x \\
x \\
x \\
x \\
x \\
x \\
x \\
\end{array}
\]

\[
\begin{array}{c}
x \\
x \\
x \\
x \\
x \\
x \\
x \\
\end{array}
\]

\[
\begin{array}{c}
x \\
x \\
x \\
x \\
x \\
x \\
x \\
\end{array}
\]

Number of unpaired electrons = 4

\[\therefore \mu_s = \sqrt{4(4+2)} = \sqrt{24}\]

Paramagnetic moment, \(\mu_s = 4.90\text{BM}\)

The molecule is paramagnetic.
Since the hybridisation is $sp^3d^2$, the geometry of the molecule is Octahedral.

Or

$[\text{FeF}_6]^{4–}$ differ from $[\text{Fe(CN)}_6]^{4–}$

S.No. 1. Diagrammatic electronic configuration of the complexes

<table>
<thead>
<tr>
<th>S.No.</th>
<th>$[\text{FeF}_6]^{4–}$</th>
<th>$[\text{Fe(CN)}_6]^{4–}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$sp^3d^2$ hybridisation</td>
<td>$d^2sp^3$ hybridisation</td>
</tr>
<tr>
<td>3</td>
<td>Number of unpaired electrons, $n = 4$</td>
<td>No unpaired electrons, $n = 0$</td>
</tr>
<tr>
<td>4</td>
<td>Paramagnetic</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>5</td>
<td>Paramagnetic moment, $\mu_s = 4.90$ BM</td>
<td>Paramagnetic moment, $\mu_s = 0$</td>
</tr>
<tr>
<td>6</td>
<td>$F^–$ is a weak ligand</td>
<td>$CN^–$ is a powerful ligand</td>
</tr>
</tbody>
</table>

3. Explain / Give / Write the postulates of Werner's theory. Or State the postulates of Werner's theory on co-ordination compound.

1) Every metal atom has two types of valencies
   i) Primary valency or ionisable valency
   ii) Secondary valency or non ionisable valency

2) The primary valency corresponds to the oxidation state of the metal ion.
The primary valency of the metal ion is always satisfied by negative ions.

3) Secondary valency corresponds to the coordination number of the metal ion or atom. The secondary valencies may be satisfied by either negative ions or neutral molecules.

4) The molecules or ion that satisfy secondary valencies are called ligands.

5) The ligands which satisfy secondary valencies must project in definite directions in space. So the secondary valencies are directional in nature whereas the primary valencies are non-directional in nature.

6) The ligands have unshared pair of electrons. These unshared pair of electrons are donated to central metal ion or atom in a compound. Such compounds are called coordination compounds.

4. Explain Co-ordination isomerism and ionisation isomerism with suitable examples.
Coordination isomerism: In a bimetallic complex, both complex cation and complex anion may be present. In such a case the distribution of ligands between the two coordination spheres can vary, giving rise to isomers called the coordination isomers. This phenomenon is called coordination isomerism.

Example:
\[ \text{[Co}^{\text{III}}(\text{NH}_3)_6] \text{[Cr}^{\text{II}}(\text{CN})_6] \quad \text{and} \quad \text{[Cr}^{\text{III}}(\text{NH}_3)_6] \text{[Co}^{\text{II}}(\text{CN})_6] \]

Ionisation isomerism: Coordination compounds having the same molecular formula but forming different ions in solution are called ionisation isomers. This property is known as ionisation isomerism.

Example:
\[ \text{[Co(NH}_3)_5\text{Br]}\text{SO}_4 \quad \text{[Co(NH}_3)_5\text{SO}_4]\text{Br} \]
The red-violet isomer yields sulphate ion and the red isomer furnishes bromide ion in solution.

5. For the complexes \( K_4[\text{Fe(CN)}_6] \), \( [\text{Cu(NH}_3)_4]\text{SO}_4 \) mention a) IUPAC names b) Central metal Ion c) Ligand d) Co-ordination number e) Charge on the complex ion f) Geometry of the complex g) Nature of complex

\( K_4[\text{Fe(CN)}_6] \)
- IUPAC names: Potassium hexacyanoferrate (II)
- Central metal Ion: Fe(II) / Fe\(^{2+}\) / ferrous ion
- Ligand: CN\(^-\), cyano
- Co-ordination number: 6
- Charge on the complex ion: –4
- Geometry of the complex: Octahedral
- Nature of complex: Anionic complex

\( [\text{Cu(NH}_3)_4]\text{SO}_4 \)
- IUPAC names: Tetraamminecopper (II) sulphate
- Central metal Ion: Cu(II)
- Ligand: NH\(_3\), ammine
- Co-ordination number: 4
- Charge on the complex ion: +2
- Geometry of the complex: Square planar
- Nature of complex: Cationic complex

6. How is chlorophyll important in environmental chemistry? Mention its function.

1. Chlorophyll is a magnesium - porphyrin complex. The magnesium is at the centre of the modified porphyrin ring septeon (corrin). The oxidation state of magnesium is +2(Mg\(^{2+}\)). The modified porphyrin acts as the ligand.
2. There are several kinds of chlorophyll that vary slightly in their molecular structure.
3. In plants, chlorophyll ‘a’ is the pigment directly responsible for the transformation of light energy to chemical energy.
4. Hence in plants, the green pigment chlorophyll helps photosynthesis.
5. The conversion of atmospheric carbondioxide and atmospheric moisture into carbohydrate and molecular oxygen in the presence of sunlight, by the plant is called as photosynthesis.
6. Chlorophyll acts as a light sensitisier in this important process.

\[ \text{Chlorophyll} \]
\[ \text{xCO}_2 + \text{yH}_2\text{O} \rightarrow \text{Cx(H}_2\text{O)}\text{y} + \text{O}_2 \]
Sunlight

7. In the coordination complex \([\text{Co(NH}_3)_6]\text{Cl}_3\) mention the following: a) IUPAC name of the complex b) Ligand c) Central metal ion d) Co-ordination number e) Nature of complex
8. Photosynthesis requires, in addition to chlorophyll, the help of four other metal complexes, a manganese complex, two iron complexes and a copper complex.

9. All oxygenated animals take molecular oxygen through haemoglobin and release CO₂. But chlorophyll helps in the conversion of atmosphere CO₂ into molecular oxygen which acts as a fuel for human cell.

a) IUPAC name of the complex - Hexaamminecobalt (III) chloride
b) Ligand - NH₃, ammine
c) Central metal ion - Cobalt(III)
d) Co-ordination number - 6
e) Nature of complex - Cationic complex

8. Mention the function of haemoglobin in natural process.
1. Haemoglobin in the red blood cells carries oxygen from the lungs to the tissues.
2. It delivers the oxygen molecule to myoglobin in the tissues.
3. When the oxygen has been released for cell respiration, haemoglobin loses its bright red colour and becomes purple.
4. It then combines with the waste carbon dioxide produced by the cells.
5. Deposits in the lungs so that the gas can be exhaled.

9. Explain hydrate and linkage isomerisms with suitable examples.

**Hydrate isomerism or Solvate isomerism**
The best known examples of this type of isomerism occurs for chromium chloride CrCl₃.6H₂O” which may contain 4, 5, (or) 6 coordinated water molecules.

1. [Cr(H₂O)₄Cl₂]Cl.2H₂O - Bright green
2. [Cr(H₂O)₅Cl]Cl₂.H₂O - grey-green
3. [Cr(H₂O)₆]Cl₃ - Violet

These isomers have very different chemical properties and on reaction with AgNO₃ to test for Cl⁻ ions, would find 1, 2, and 3 Cl⁻ ions in solution respectively.

**Linkage isomerism**
Linkage isomerism occurs with ambidentate ligands. These ligands are capable of coordinating in more than one way. The best known cases involve the monodentate ligands SCN⁻/NCS⁻ and NO₂⁻/ONO⁻

Example:
[Co(NH₃)₅ONO]Cl₂ the nitrito isomer - O attached - red colour
[Co(NH₃)₅NO₂]Cl₂ the nitro isomer - N attached - yellow colour

10. Explain the following terms: i) Neutral ligand  ii) chelates iii) coordination sphere.

i) Neutral ligand: The neutral ligands are named as such without any special name. But water is written as ‘aqua’ : Ammonia is written as ammine. Note that two m’s to distinguish from organic amine

CO-Carbonyl, NO-Nitrosyl, NH₂ - CH₂ - CH₂ - NH₂-ethylenediamine (en), Pyridine C₅H₅N.

ii) chelates: If a ligand is capable of forming more than one bond with the central metal atom (or) ion then the ring structures are produced which are known as metal chelates. Hence the ring forming group is described as chelating agents (or) polydentate ligands.
iii) coordination sphere: In a complex compound, it usually, central metal ion and the ligands are enclosed within square bracket is called as coordination sphere. This represents a single constituent unit. The ionisable species are placed outside the square bracket.

\[ \text{[M(L)\text{\textsuperscript{n}}]} \text{(n-) \ (or) \ (n+)} \]

\[ \text{[Fe(CN)\text{\textsuperscript{6}}]}^{4-}, \text{[Cu(NH\text{\textsuperscript{3}})\text{\textsuperscript{4}}]}^{2+} \]

These ions do not ionise to give the test for constituent ions

11. What are the postulates of valence bond theory?

5. The following table gives the coordination number, orbital hybridisation and spatial geometry of the more important geometries.

1. The central metal atom / ion makes available a number of vacant orbitals equal to its coordination number.

2. These vacant orbitals form covalent bonds with the ligand orbitals.

3. A covalent bond is formed by the overlap of a vacant metal orbital and filled ligand orbitals. This complete overlap leads to the formation of a metal ligand, \( \sigma \) (sigma) bond.

4. A strong covalent bond is formed only when the orbitals overlap to the maximum extent. This maximum overlapping is possible only when the metal vacant orbitals undergo a process called ‘hybridisation’. A hybridised orbital has a better directional characteristics than an unhybridised one.

<table>
<thead>
<tr>
<th>Coordination number</th>
<th>Types of hybridisation</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>sp</td>
<td>linear</td>
</tr>
<tr>
<td>4</td>
<td>sp(^3)</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>4</td>
<td>dsp(^2)</td>
<td>square planar</td>
</tr>
<tr>
<td>6</td>
<td>d(^2)sp(^3)</td>
<td>octahedral</td>
</tr>
<tr>
<td>6</td>
<td>sp(^3)d(^2)</td>
<td>octahedral</td>
</tr>
</tbody>
</table>

12. For the complex \( K_3[Cr(C_2O_4)_3].3H_2O \) mention
a) Name  
b) Central metal ion  
c) Ligand  
d) Coordination number  
e) Geometry

a) Name  
Potassium trioxalatochromate(III), trihydrate  
b) Central metal ion  
Chromium
c) Ligand: C₂O₄²⁻ / Oxalato  

d) Coordination number: 6 (3 bidentate ligands present)  

e) Geometry: Octahedral  

13. Write:  

a) IUPAC Name  
b) Central metal ion  
c) Ligand  
d) Coordination number  
e) Geometry of the complex [Co(en)₃]Cl₃  

a) IUPAC Name: Tris(ethylenediamine)cobalt(III) chloride  
b) Central metal ion: Co³⁺ / CoIII / Cobalt(III)  
c) Ligand: en / ethylenediamine / NH₂ - CH₂ - CH₂ - NH₂  
d) Coordination number: 6 (3 bidentate ligands present)  
e) Geometry of the complex: Octahedral  

14. For the complex [Co(NH₃)₃(NO₂)₃] Write the following:  

a) IUPAC Name  
b) Central metal ion  
c) Ligand  
d) Coordination number  
e) Geometry  

a) IUPAC Name: Triamminetrinitrocobalt(III)  
b) Central metal ion: Co³⁺ / CoIII / Cobalt(III)  
c) Ligand: NH₃ / ammine & NO₂⁻ / nitro  
d) Coordination number: 6 (3 + 3 unidentate ligands present)  
e) Geometry: Octahedral  

15. Mention the following for the complex [Co(NH₃)₄Cl₂]NO₂  

a) IUPAC Name  
b) Central metal ion  
c) Ligand  
d) Charge on the Co-ordination sphere  
e) Co-ordination number  

a) IUPAC Name: Tetraamminedichlorocobalt(III) nitrite  
b) Central metal ion: Co³⁺ / CoIII / Cobalt(III)  
c) Ligand: NH₃ / ammine & Cl⁻ / Chloro  
d) Charge on the Co-ordination sphere: + 3 / Cationic complex / Positive Charge  
e) Co-ordination number: 6 (4 + 2 unidentate ligands present)
SECTION-B

Q.No 57-Thermodynamics - II

1. Describe / Explain / Mention / Write the characteristics of free energy G.
   1. G is defined as \( (H - TS) \) where H and S are the enthalpy and entropy of the system respectively. \( T = \) temperature. Since H and S are state functions, G is a state function.
   2. G is an extensive property while \( \Delta G = (G_2 - G_1) \) which is the free energy change between the initial (1) and final (2) states of the system becomes the intensive property when mass remains constant between initial and final states (or) when the system is a closed system.
   3. G has a single value for the thermodynamic state of the system.
   4. G and \( \Delta G \) values correspond to the system only.

There are three cases of \( \Delta G \) in predicting the nature of the process.
   i) When, \( \Delta G < 0 \) (negative), the process is spontaneous and feasible;
   ii) \( \Delta G = 0 \), the process is in equilibrium and
   iii) \( \Delta G > 0 \) (positive), the process is nonspontaneous and not feasible.

5. \( \Delta G = \Delta H - \Delta S \).
   But according to I law of thermodynamics,
   \( \Delta H = \Delta E + P\Delta V \) and \( \Delta E = q - w. \)
   \( \therefore \Delta G = q - w + P\Delta V - T\Delta S \)
   But \( \Delta S = q / T \) and \( T\Delta S = q = \) heat involved in the process.
   \( \therefore \Delta G = q - w + P\Delta V - q = -w + P\Delta V \)
   or
   \( -\Delta G = w - P\Delta V = \) network.
   The decrease in free energy \( -\Delta G \), accompanying a process taking place at constant temperature and pressure is equal to the maximum obtainable work from the system other than work of expansion.
   This quantity is called as the “net work” of the system and it is equal to \( (w - P\Delta V) \).
   \( \therefore \) Net work = \( -\Delta G = w - P\Delta V. \)
   \( -\Delta G \) represents all others forms of work obtainable from the system such as electrical, chemical or surface work etc other than P-V work.

2. Give / State / Write the various statements of second law of thermodynamics.
   1. Kelvin – Planck statement of II law of thermodynamics
   It is impossible to construct an engine which operated in a complete cycle will absorb heat from a single body and convert it completely to work without leaving some changes in the working system.
   2. Clausius statement of II law of thermodynamics
   It is impossible to transfer heat from a cold body to a hot body by a machine without doing some work.
   3. Entropy statement of II law of thermodynamics
   A process accompanied by increase in entropy tends to be spontaneous.
   4. Efficiency of a machine can never be cent percent.
5. The heat Efficiency of any machine is given by the value of ratio of output to input energies. Output can be in the form of any measurable energy or temperature change while input can be in the form of heat energy or fuel amount which can be converted to heat energy. Thus, \[ \text{% efficiency} = \left( \frac{\text{output}}{\text{input}} \right) \times 100 \]

3. What are the characteristics of entropy?

1. The term ‘S’ entropy is evolved from the formulation of II law of thermodynamics as a thermodynamic state function.
2. Entropy change ‘\( \Delta S \)’ of a system under a process is defined as the constant equal to the ratio of the heat change accompanying a process at constant temperature to the temperature of the system under process. The process should be reversible at that temperature.
\[ \Delta S_{\text{rev}} = \frac{\Delta q_{\text{rev}}}{T(K)} \]
Heat, q is not a state function, But for a reversible process \( \Delta q = (q_2-q_1) \) divided by temperature (T) of the process is a state function.
3. A spontaneous process is accompanied by increase in the ‘disorder’ (or) ‘randomness’ of the molecules constituting the system. Entropy increases in all spontaneous processes. Hence entropy may be regarded as a measure of disorder (or) randomness of the molecules of the system.
4. When a system undergoes a physical (or) a chemical process, there occurs a change in the entropy of the system and also in its surroundings. This total change in the entropy of the system and its surroundings is termed as the entropy change of the universe brought about by the process. For an isothermal process (\( T = \text{constant} \)), the entropy change of the universe during an irreversible process is Zero.
The entropy of the universe increases in an irreversible process.
5. The energy of the universe remains constant although the entropy of the universe tends to a maximum.
6. For a spontaneous process, at constant T, \( \Delta S \) is positive (\( \Delta S > 0 \)).
   For an equilibrium process, \( \Delta S \) is zero.
   For a non spontaneous process, \( \Delta S \) is negative (\( \Delta S < 0 \)).
7. Units of entropy:
   The dimension of entropy are energy in terms of heat \( \times \) temperature\(^{-1} \).
   The entropy is expressed as calories per degree which is referred to as the entropy units (eu).
   Since entropy also depends on the quantity of the substance, unit of entropy is calories per degree per mole (or) eu. per mole.
   cgs units of entropy is cal.K\(^{-1} \) denoted as eu.
   The SI unit is JK\(^{-1} \) and denoted EU. 1 eu = 4.184 EU.
8. Entropy change is related to enthalpy change as follows:
For a reversible and isothermal process, \( \Delta S = \frac{\Delta q_{\text{rev}}}{T} \). Since \( \Delta H \) is the heat absorbed (or) evolved in the process at constant T and pressure P. \( \Delta S \) is also calculated from \( \Delta H \) as \( \Delta S = \frac{\Delta H}{T} \) where T is the temperature of the process involving \( \Delta H \), amount of enthalpy change, at constant pressure.
4. Define Trouton’s rule. What are the substances that deviate from this rule?
The heat of vaporisation (ΔHvap) in calories per mole divided by the boiling point of the liquid in Kelvin is a constant equal to 21 cal deg⁻¹ mole⁻¹ and is known as the entropy of vapourisation.

\[ \Delta S_{vap} = \Delta H_{vap} / T_b = 21 \text{ cal deg}^{-1} \text{ mole}^{-1} \]

Substances that deviate from this rule are:
1. Low boiling liquids such as Hydrogen and Helium which boil only a little above 0 K.
2. Polar substances like Water, Alcohol which form Hydrogen bonded liquids and exhibit very high boiling points as well as high ΔHvap.
3. Liquids such as Acetic acid whose molecules are partially associated in the vapor phase and possess very low entropy vaporization which is very much less than 21 cals / mol / deg.
Q.No 58-Chemical Equilibrium - II

1. Apply Le Chatelier's principle for the manufacture of SO3 by contact process and find the conditions for getting maximum yield of SO3.

Contact process involves the equilibrium reaction of oxidation of SO2 gas by gaseous oxygen in air to manufacture large quantities of SO3 gas.

\[ \text{V}_2\text{O}_5 \]

\[ 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \quad \Delta H^\circ = -47 \text{ kcal / mole} \]

**Effect of Pressure:**
The formation reaction of SO3 involves a decrease in the overall moles of the reactants. According Le Chatlier’s principle, when large pressure is applied, forward reaction is favoured. 700 atm - 1200 atm pressure is maintained on the 2 : 1 mole ratio mixture of pure SO2 and O2 gases in the reaction chamber.

**Effect of Temperature:**
SO3 production is an exothermic reaction. Hence, increase in temperature favours SO3 dissociation. However, lowering of temperature prolongs the time of attainment of equilibrium. Therefore, an optimum temperature at nearly 400°C to 450°C is maintained.

**Effect of Catalyst:**
The most widely used catalyst for SO3 production is porous vanadium pentoxide (V2O5). Presence of moisture deactivates the catalyst. Only dry and pure SO2 and O2 gases are used over the catalyst. Since oxidation of SO2 is a slow process, presence of V2O5 speeds up the equilibrium process and high yield of SO3 is achieved in a short period.

**Effect of Concentration:**
SO3 is the anhydride of H2SO4. Therefore, SO3 from contact process along with steam is used in oleum and H2SO4 manufacturing processes. The yield of SO3 is nearly 97%.

2. Apply Le Chatelier's principle to Haber's process for the manufacture of Ammonia.

Ammonia formation reaction is an equilibrium reaction.

\[ \text{Fe} \]

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \Delta H^\circ = -22.0 \text{ kcal / mole} \]

**Effect of Pressure:**
The forward reaction is accompanied by decrease in the number of moles of reactants. According to Le Chatlier’s principle, an increase in pressure favours such a reaction and shifts the equilibrium towards the product formation direction. Therefore, nearly 300-500 atm pressure is applied on 3 : 1 mole ratio of H2 : N2 gas mixture in the reaction chamber for maximum yield of ammonia.

**Effect of Temperature:**
The ammonia formation reaction is an exothermic reaction. According Le Chatlier’s principle, increase in temperature favours decomposition reaction of ammonia. However, at low temperature the time to reach the equilibrium becomes very long. Hence an optimum temperature close to 500°C-550°C is maintained.

**Effect of Catalyst:**
Iron catalyst is chosen to speed up the attainment of the equilibrium concentration of ammonia.
Effect of Concentration:
In order to maintain the equilibrium conditions, steam is passed to remove away the ammonia as and when it is formed so that the equilibrium remains shifted towards the product side. The maximum yield of ammonia is nearly 37%.

3. Derive the expression for $K_c$ and $K_p$ for formation of HI.
The formation of HI from H$_2$ and I$_2$ is an example of gaseous homogeneous equilibrium reaction. It can be represented as

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$$

In this equilibrium reaction, the number of moles of the products is equal to the number of moles of the reactants.

$$\Delta n_g = n_p - n_r = 2 - (1 + 1) = 2 - 2 = 0$$

∴ $K_p = K_c$

Derivation of $K_c$ in terms of $x$:
Let us assume ‘a’ and ‘b’ moles of H$_2$ and I$_2$ gases being present in ‘$V$’ litres of the reaction vessel. At equilibrium, let $x$ moles each of H$_2$ and I$_2$ react to form $2x$ moles of HI. Then, the equilibrium concentrations in moles litre of H$_2$, I$_2$ and HI in the reaction mixture will be $(a - x) / V$, $(b - x) / V$ and $2x / V$ respectively.

<table>
<thead>
<tr>
<th></th>
<th>H$_2$(g)</th>
<th>I$_2$(g)</th>
<th>HI(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial number of moles</td>
<td>a</td>
<td>b</td>
<td>0</td>
</tr>
<tr>
<td>Number of moles reacted</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Number of moles remaining at equilibrium</td>
<td>$(a - x)$</td>
<td>$(b - x)$</td>
<td>$2x$</td>
</tr>
<tr>
<td>Equilibrium concentration</td>
<td>$(a - x) / V$</td>
<td>$(b - x) / V$</td>
<td>$2x / V$</td>
</tr>
</tbody>
</table>

According to the law of mass action,

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x / V)^2}{((a - x) / V)(b - x) / V} = \frac{4x^2}{(a - x)(b - x)}$$

$x$ is also known as the extent of reaction.

Derivation of $K_p$ in terms of $x$:
Since $\Delta n_g = 0$, $K_p = K_c = 4x^2 / (a - x)(b - x)$

∴ $K_p$ and $K_c$ are equal in terms of $x$ values.

4. Derive the expressions for $K_c$ and $K_p$ for decomposition of PCl$_5$.
The dissociation equilibrium of PCl$_5$ in gaseous state is written as

$$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$$

For this reaction $\Delta n_g = np - nr = 1$ ∴ $K_p = K_c (RT) = (1 + 1) - 1 = 2 - 1$
Derivation of $K_c$ in terms of $x$:

Let ‘$a$’ moles of PCl$_5$ vapour be present in ‘$V$’ litres initially. If $x$ moles of PCl$_5$ dissociate to PCl$_3$ and Cl$_2$ gases at equilibrium at constant ‘$V$’ litres, then molar concentrations of PCl$_5$, PCl$_3$ and Cl$_2$ gases at equilibrium will be $a - x / V$, $x / V$ and $x / V$ respectively.

<table>
<thead>
<tr>
<th></th>
<th>PCl$_5$(g)</th>
<th>PCl$_3$(g)</th>
<th>Cl$_2$(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial number of moles</td>
<td>$a$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>Number of moles reacted</td>
<td>$x$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>Number of moles remaining at equilibrium</td>
<td>$a - x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
<tr>
<td>Equilibrium concentration</td>
<td>$(a - x) / V$</td>
<td>$x / V$</td>
<td>$x / V$</td>
</tr>
</tbody>
</table>

According to law of mass action,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(x / V)(x / V)}{(a - x) / V} = \frac{x^2}{V(a - x)}$$

$x$ is also known as $\alpha$ which represents the fraction of total moles of reactant dissociated.

$x = \frac{\text{Number of moles dissociated}}{\text{Total number of moles present initially}}$

If initially 1 mole of PCl$_5$ is present then

$$K_c = \frac{x^2}{(1 - x)V} = \frac{x^2P}{(1 - x)RT}$$

If the degree of dissociation is small compared to unity, then $(1 - x)$ is approximately equal to 1.0.

$$K_c = \frac{x^2}{V}$$

Or

$$x^2 = \frac{K \cdot V}{\sqrt{V}}$$

But $V \propto 1 / P$

$x \propto \sqrt{1 / P}$

Where $x$ is small, degree of dissociation varies inversely as the square root of pressure (or) varies directly as the square root of volume of the system.

Derivation of $K_p$ in terms of $x$:

<table>
<thead>
<tr>
<th></th>
<th>PCl$_5$(g)</th>
<th>PCl$_3$(g)</th>
<th>Cl$_2$(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial number of moles</td>
<td>$a$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>Number of moles reacted</td>
<td>$x$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>Number of moles remaining at equilibrium</td>
<td>$a - x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
<tr>
<td>Equilibrium concentration</td>
<td>$(a - x) / V$</td>
<td>$x / V$</td>
<td>$x / V$</td>
</tr>
</tbody>
</table>

$\therefore$ Total number of moles at equilibrium $= 1 - x + x + x = (1 + x)$

We know that, Partial pressure is the product of mole fraction and the total pressure.
Mole fraction is the number of moles of that component divided by the total number of moles in the mixture.

Therefore

\[ p_{PCl5} = \left( \frac{1 - x}{1 + x} \right) \cdot P \]
\[ p_{PCl3} = \left( \frac{x}{1 + x} \right) \cdot P \]
\[ p_{Cl2} = \left( \frac{x}{1 + x} \right) \cdot P \]

In terms of partial pressures of PCl5, PCl3 and Cl2 then

\[ \text{Kp} = \frac{p_{PCl3} \cdot p_{Cl2}}{p_{PCl5}} \]

Substituting the values of partial pressures in the above equation, we get

\[ \text{Kp} = \frac{x^2 \cdot P_2 \cdot (1 + x) \cdot x (1 + x / 1 - x) \cdot x}{1 / P} \]

When \( x < < 1 \), \( x^2 \) value can be neglected when compared to one i.e., \( (1 - x^2) = 1 \).

\[ \therefore \text{Kp} \approx x^2 P \]

5. Derive the relation \( \text{Kp} = \text{Kc}(RT)\Delta n_g \) for a general chemical equilibrium reaction. Or Derive a relation between (equilibrium constant) \( \text{Kp} \) and \( \text{Kc} \).

Consider a general chemical equilibrium reaction in which the reactants and products are in gaseous phases,

\[ aA + bB + cC + \ldots \rightleftharpoons lL + mM + nN + \ldots \]

Then,

\[ \text{Kp} = \frac{p_l^{p_l} \cdot p_m^{p_m} \cdot p_n^{p_n}}{p_a^{p_a} \cdot p_b^{p_b} \cdot p_c^{p_c}} \]

Where,

\( p \) is the partial pressure of the respective gases.

In terms of molar concentrations of reactants and products

\[ \text{Kc} = \frac{[L]^{l} \cdot [M]^{m} \cdot [N]^{n}}{[A]^{a} \cdot [B]^{b} \cdot [C]^{c}} \]

For any gaseous component ‘\( i \)’ in a mixture, its partial pressure ‘\( p_i \)’ is related to its molar concentration ‘\( C_i \)’ as \( C_i = p_i / RT \)

Since

\[ p_i = \frac{(n_i / V) \cdot RT}{[i]} \]

Where,

\( (n_i / V) = C_i \) = Number of moles of \( i \) per litre. \( V \) = Volume in litres.

Substituting concentration terms by partial pressures,

\[ \text{Kc} = \frac{(p_l / RT)^l \cdot (p_m / RT)^m \cdot (p_n / RT)^n}{(p_a / RT)^a \cdot (p_b / RT)^b \cdot (p_c / RT)^c} \]

\[ = p_l l \cdot p_m m \cdot p_n n / p_a a \cdot p_b b \cdot p_c c \cdot X \left( \frac{1}{RT} \right) (l + m + n + \ldots) - (a + b + c + \ldots) \]

\[ \text{Kc} = \frac{\text{Kp}}{(RT)\Delta n_g} \]

Or

\[ \text{Kp} = \text{Kc} (RT)\Delta n_g \]

Where,

\( \Delta n_g = (l + m + n + \ldots) - (a + b + c + \ldots) \)

\( \Delta n_g \) = Total number of stoichiometric moles of gaseous products, \( np - (\text{Minus}) \)
Total number of stoichiometric moles of gaseous reactants, \( n_r \).

6. Discuss the effect of temperature and pressure on the following equilibrium:

\[
\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \quad \Delta H = +59.0 \text{ kJ/mole.}
\]

**Effect of change of temperature**

A chemical equilibrium actually involves two opposing reactions. One favouring the formation of products and the other favouring the formation of reactants. If the forward reaction in a chemical equilibrium is endothermic (accompanied by absorption of heat) then the reverse reaction is exothermic (accompanied by evolution of heat).

Let us consider the example

\[
\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \quad ; \quad \Delta H = +59.0 \text{ kJ/mole}
\]

In this equilibrium, the reaction of the product formation (\( \text{NO}_2 \)) is endothermic in nature and therefore, the reverse reaction of reactant formation (\( \text{N}_2\text{O}_4 \)) should be exothermic. If the above equilibrium reaction mixture is heated then its temperature will be raised. According to Le Chatelier’s principle, the equilibrium will shift in the direction which tends to undo the effect of heat. Therefore, the equilibrium will shift towards the formation of \( \text{NO}_2 \) and subsequently dissociation of \( \text{N}_2\text{O}_4 \) increases. Therefore, generally, when the temperature is raised in a chemical equilibrium, among the forward and reverse reactions, the more endothermic reaction will be favoured.

Similarly, if the temperature of the equilibrium is decreased i.e., cooled, then the exothermic reaction among the forward and reverse reaction of the equilibrium will be favoured.

**Effect of change of pressure**

If a system in equilibrium consists of reactants and products in gaseous state, then the concentrations of all components can be altered by changing the total pressure of the system. Consider the equilibrium in the gaseous state such as

\[
\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)
\]

Increase in the total pressure of the system in equilibrium will decrease the volume proportionately. According to Le Chatelier’s principle, the change can be counteracted by shifting the equilibrium towards decreasing the moles of products. Hence, the reaction of combination of \( \text{NO}_2 \) molecules to \( \text{N}_2\text{O}_4 \) formation will be favoured.

7. The dissociation equilibrium constant of \( \text{HI} \) is \( 2.06 \times 10^{-2} \) at 458 K. At equilibrium the concentrations of \( \text{HI} \) and \( \text{I}_2 \) are 0.36 M and 0.15M respectively. What is the equilibrium concentration of \( \text{H}_2 \) at 458 K?

Dissociation equilibrium of \( \text{HI} \), \( 2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g) \)

Dissociation equilibrium constant of \( \text{HI} \), \( K_c = 2.06 \times 10^{-2} \)

Equilibrium concentration of \( \text{I}_2 \), \([\text{I}_2]\) = 0.15M

Equilibrium concentration of \( \text{HI} \), \([\text{HI}]\) = 0.36 M

Equilibrium concentration of \( \text{H}_2 \), \([\text{H}_2]\) = ?

\[
K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}
\]

\[
2.06 \times 10^{-2} = \frac{[\text{H}_2] \times 0.15}{(0.36)^2}
\]

\[
[\text{H}_2] = 2.06 \times 10^{-2} \times (0.36)^2 / 0.15
\]
Equilibrium concentration of H₂, \([H₂] = 1.78 \times 10^{-2} \text{ M}\)

8. Apply Le Chatelier’s principle for the following reaction \(\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})\) and discuss the effect of pressure and concentration on it.

Effect of pressure
If a system in equilibrium consists of reactants and products in gaseous state, then the concentrations of all components can be altered by changing the total pressure of the system.

Consider the equilibrium in the gaseous state such as \(\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})\)

Increase in the total pressure of the system in equilibrium will decrease the volume proportionately. According to Le Chatlier’s principle, the change can be counteracted by shifting the equilibrium towards decreasing the moles of products.

In this equilibrium reaction, the number of moles of the products is equal to the number of moles of the reactants.

Pressure has therefore no effect on the equilibrium

Effect of concentration
At the equilibrium conditions the reaction mixture contains both the reactant and product molecules, that is, \(\text{N}_2, \text{O}_2\) and \(\text{NO}\) molecules. The concentrations of reactant and product molecules are constant and remain the same as long as the equilibrium conditions are maintained the same.

If a change is imposed on the system by purposely adding \(\text{NO}\) into the reaction mixture then the product concentration is raised. Since the system possesses equilibrium concentrations of reactants and products, the excess amount of \(\text{NO}\) react in the reverse direction to produce back the reactants and this results in the increase in concentrations of \(\text{N}_2\) and \(\text{O}_2\).

Similarly if the concentration of reactants such as \(\text{N}_2\) and \(\text{O}_2\) are purposely raised when the system is already in the state of equilibrium, the excess concentrations of \(\text{N}_2\) and \(\text{O}_2\) favour forward reaction. Concentration of \(\text{NO}\) is raised in the reaction mixture.

In general, in a chemical equilibrium increasing the concentrations of the reactants results in shifting the equilibrium in favour of the products while increasing the concentrations of the products results in shifting the equilibrium in favour of the reactants.
Q.No 58 - Chemical Kinetics - II

1. A first order reaction is 75% completed in 100 minutes. What are the rate constant and half life period of the reaction?

\( t = 100 \) minutes  
\( a = 100 \)  
\( x = 75 \)  
\( (a - x) = (100 - 75) = 25 \)  
\( k = ? \)  
\( t^{1/2} = ? \)  
\[
\begin{align*}
k &= \frac{2.303}{t} \log_{10} \frac{a}{(a - x)} \\
k &= \frac{2.303}{100} \log_{10} \frac{100}{25} \\
&= \frac{2.303 \times 0.6021}{100} \\
&= 1.387 \times 10^{-2} \\
t^{1/2} &= \frac{0.693}{k} \\
t^{1/2} &= \frac{0.693}{1.387 \times 10^{-2}} \\
&= 49.96 \text{ minutes}
\end{align*}
\]

2. Compound A reacts by first order kinetics. At 25°C, the rate constant of the reaction is 0.45 sec\(^{-1}\). What is the half-life period of A at 25°C? What is the time required to have 12.5% unreacted A for first order reaction?

\[
\begin{align*}
t^{1/2} &= \frac{0.693}{k} \\
&= \frac{0.693}{0.45} \\
&= 1.54 \text{ secs}
\end{align*}
\]

<table>
<thead>
<tr>
<th>No. of ( t^{1/2} )</th>
<th>Amount unreacted from 100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50%</td>
</tr>
<tr>
<td>2</td>
<td>25%</td>
</tr>
<tr>
<td>3</td>
<td>12.5%</td>
</tr>
</tbody>
</table>

Time of three half-life periods = \( 3 \times 1.54 \)  
= 4.62 secs

3. Derive rate constant equation for first order reactions.

Consider the reaction  
\[
k1 \\
A \rightarrow \text{Products}
\]

**Rate of reaction**  
\[
\frac{-d[A]}{dt} = k1[A]  
\]

... (1)

Where, \( k1 \) is the rate constant of the first order reaction.

At the beginning of the reaction, time \( t' = 0 \), let the concentration of A be ‘a’ mol.lit\(^{-1}\).

After the reaction has proceeded for some time \( t' \), let the concentration of A that has reacted be \( x \) mol.lit\(^{-1}\).

The concentration of unreacted A remaining at time \( t' \) will be \( (a - x) \) mol.lit\(^{-1}\).

The rate of the reaction will be \( dx / dt \). For a first order reaction,

**Rate**  
\[
\frac{dx}{dt} = k1 (a - x)  
\]

... (2)

Upon integrating, equation (2) becomes,
\[ \int \frac{dx}{(a-x)} = k_1 \int dt \]
Which is, \(- \ln (a-x) = k_1 t + C \) \hspace{1cm} \text{(3)}

\( C \) = integration constant

At time, \( t = 0 \), \( x = 0 \).

Substituting \( t \) and \( x \) values in equation (3),
\[- \ln (a-0) = k_1 \times 0 + C \]
Or
\( C = - \ln a \).

Substituting \( C \) value in equation (3)
\[- \ln (a-x) = k_1 t - \ln a \]
Rearranging, \( k_1 = \frac{1}{t} \ln \frac{a}{a-x} \)
Or
\( k_1 = \frac{2.303}{t} \ln \frac{a}{a-x} \) \hspace{1cm} \text{(4)}

This equation is known as the \text{first order rate constant equation}.

4. \text{Discuss the characteristics of a first order reaction.}

1. When the concentration of the reactant is increased by \( n \) times, the rate of reaction is also increased by \( n \) times. That is, if the concentration of the reactant is doubled, the rate is doubled.

2. The \text{unit of rate constant of a first order reaction is sec}^{-1} \text{ or time}^{-1}.

\[ k_1 = \frac{\text{rate}}{(a-x)} = \frac{\text{mol. litre}^{-1} \text{sec}^{-1}}{\text{mol. litre}^{-1}} = \text{sec}^{-1} \]

3. The \text{time required to complete a definite fraction of reaction is independent of the initial concentration of the reactant.}

If \( t_{1/u} \) is the time of one \( u \) th fraction of reaction to take place then from equation
\[ k_1 = \frac{2.303}{t} \ln \frac{a}{a-x}, \]
\[ x = \frac{a}{u} \quad \text{and} \quad t_{1/u} = \frac{2.303}{k_1} \log \frac{a}{a-a} \]
\[ \therefore \quad t_{1/u} = \frac{2.303}{k_1} \log \left( \frac{u}{u-1} \right) \]

Since \( k_1 = \text{rate constant} \), \( t_{1/u} \) is independent of initial concentration \( a \).

5. \text{Explain the experimental determination of rate constant for the decomposition of hydrogen peroxide in aqueous solutions.}

Pt
\[ \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \]

The decomposition of \( \text{H}_2\text{O}_2 \) in aqueous medium in the presence of Pt catalyst follows a first order reaction. The progress of the reaction is followed by titrating equal volumes of the reaction mixture at regular time intervals against standard \( \text{KMnO}_4 \) solution.

Since volume of \( \text{KMnO}_4 \) used in the titration is a measure of concentration of undecomposed \( \text{H}_2\text{O}_2 \), volume of \( \text{KMnO}_4 \) consumed at \( t = 0 \) is \( V_0 \) which is proportional to \( a \), the initial concentration of \( \text{H}_2\text{O}_2 \).
Vt is the volume of KMnO4 consumed after time ‘t’ of the reaction. Vt is proportional to unreacted H2O2 which is similar to \((a - x)\).

Similarly \((Vo - Vt)\) is proportional to ‘x’; the concentration of H2O2 reacted in time interval ‘t’.

The first order rate constant ‘k1’ of the reaction is,

\[ k1 = 2.303/ \frac{t \log Vo}{Vt} \text{ sec}^{-1} \]

6. Explain the experimental determination of rate constant of acid hydrolysis of methyl acetate

The acid catalysed hydrolysis of an ester follows pseudo first order kinetics. The reaction can be represented as:

\[
H^+ + \text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}
\]

The overall rate of the reaction depends on the concentrations of reactants and also on the catalyst concentration.

Rate = \(k3 [\text{ester}] [\text{H}_2\text{O}] [H^+]\)

**Procedure**

1. Initially to a definite volume of (100 ml) hydrochloric acid (0.5 N), 10 ml of ester is added and the start of the reaction corresponds to time of addition of ester.
2. The rate of the reaction is followed by withdrawing a definite volume of the reaction mixture consisting of the ester and acid at various time intervals and arresting the further progress of reaction by adding ice. The whole cold mixture is titrated with standard NaOH (0.1 N) using phenolphthalein as the indicator.
3. Let the volume of alkali consumed at \(t = 0\) be \(Vo\) cc which is equivalent to the amount of hydrochloric acid present in the definite volume of the reaction mixture drawn out at regular intervals of time.
4. If \(Vt\) cc is the volume of alkali consumed for the same definite volume of the reaction mixture drawn out after reaction time ‘t’, then \((Vt - Vo)\) cc is equivalent to the acetic acid produced by the hydrolysis of ester in time ‘t’.
5. A final titration is done after about 8 hours or after refluxing the solution for 45 mins to complete the hydrolysis which is \(V\infty\) cc. \((V\infty - Vo)\) cc is equivalent to acetic acid produced from complete hydrolysis of ester.

**Calculations**

The initial concentration of ester = \(a \alpha (V\infty - Vo)\) cc

Concentration of ester reacted at ‘t’ = \(x \alpha (Vt - Vo)\) cc

Concentration of ester remaining at time ‘t’ = \((a - x) \alpha (V\infty - Vt)\)

\[
a / (a - x) = (V\infty - Vo) / (V\infty - Vt)
\]

The first order rate expression for the hydrolysis of ester can be written as

\[
k = 2.303 / t \log (V\infty - Vo) / (V\infty - Vt)
\]

By substituting \(Vt\) values for various ‘t’ values, \(k\) is determined. These values are found to be constant indicating \(k\) as the rate constant of the reaction.

7. Explain various types of complex reactions and give one example for each. Or Write notes on (i) consecutive reactions, (ii) parallel reactions and (iii) opposing reactions.

(i) Consecutive reactions
The reactions in which the reactant forms an intermediate and the intermediate forms the product in one or many subsequent reactions are called as consecutive or sequential reactions. In such reactions the product is not formed directly from the reactant. Various steps in the consecutive reaction are shown as below:

\[ k_1 \]
\[ A \rightarrow B \rightarrow C \]
\[ k_2 \]

A = reactant; B = intermediate; C = product.

Initially only the reactant A will be present. As the reaction starts, A produces an intermediate B through \( k_1 \) rate constant. As and when B is formed, it produces the product C through \( k_2 \) rate constant. After the completion of reaction only ‘C’ is present and concentrations of A and B will be zero.

**Example:** Saponification of a diester in presence of an alkali

\[ k_1 \]
\[ R'OOC-(CH_2)_n-COOR \rightarrow R'OOC-(CH_2)_n-COOH \]
\[ k_2 \]
\[ HOOC-(CH_2)_n-COOH \]

(ii) Parallel reactions

In these group of reactions, one or more reactants react simultaneously in two or more pathways to give two or more products. The parallel reactions are also called as side reactions.

The reactant A reacts to give products B, C, D separately by following three different reaction pathways involving different \( k_1, k_2, k_3 \) rate constants respectively. Among the many side reactions, the reaction in which maximum yield of the product obtained is called as the main or major reaction while the other reactions are called as side or parallel reactions.

**Examples:**

1. Bromination of bromobenzene:
2. Dehydration of 2-methyl-2-butanol

(iii) Opposing reactions

In opposing reactions, the products formed react back simultaneously to form the reactants. These reactions are also called as reversible reactions.

\[ A + B \rightleftharpoons C + D, \]

\[ k_f \]

\[ k_r \]

Examples:

1. Reaction between CO and NO2 gases

\[ \text{CO(g)} + \text{NO}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{NO(g)} \]

2. Isomerisation of cyclopropane to propene

3. Dissociation of hydrogen iodide in gas phase

\[ 2\text{HI(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{I}_2\text{(g)} \]
8. Give / State / Write the characteristics of order of a reaction.

1. The **magnitude of order of a reaction may be zero, or fractional or integral values.** For an elementary reaction, its order is never fractional since it is a one step process.
2. **Order of a reaction should be determined only by experiments.** It cannot be predicted in terms of stoichiometry of reactants and products.
3. **Simple reactions possess low values of order like** \( n = 0, 1, 2 \). Reactions with order greater than or equal to 3.0 are called complex reactions. Higher order reactions are rare.
4. Some reactions show fractional order depending on rate.
5. **Higher order reactions may be experimentally converted into simpler order (pseudo) reactions** by using excess concentrations of one or more reactants.

9. In the thermal decomposition of \( \text{N}_2\text{O} \) at 764°C, the time required to decompose half of the reactant was 263 seconds, when the initial pressure was 290 mm of Hg and 212 seconds at an initial pressure of 360 mm of Hg. What is the order of this reaction?

\[
\frac{t_1}{t_2} = \left( \frac{a_2}{a_1} \right)^{n-1}
\]

\[
263 / 212 = \left( \frac{360}{290} \right)^{n-1}
\]

\[
1.24 = (1.24)^{n-1}
\]

\[
n - 1 = 1
\]

\[
n = 1 + 1 = 2
\]

Hence, the reaction is of **second order.**

10. State the differences between simple and complex reactions.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Simple reactions</th>
<th>Complex reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Occurs in single step</td>
<td>Occurs in multi (or) many steps.</td>
</tr>
<tr>
<td>2</td>
<td>Overall order values are small. Total and pseudo order values lie between 0, 1, 2 and 3.</td>
<td>Overall order values are large and greater than 3.0. Sometimes fractional orders such as 1/2, 1/3, 3/2 etc. are seen.</td>
</tr>
<tr>
<td>3</td>
<td>No side reactions</td>
<td>Many side reactions are present.</td>
</tr>
<tr>
<td>4</td>
<td>Products are formed directly from the reactants</td>
<td>In some complex reactions products are not formed in steps directly involving the reactants.</td>
</tr>
<tr>
<td>5</td>
<td>Experimental rate constant values agree with the calculated values. Theories of reaction rates apply well on simple reactions.</td>
<td>Experimental overall rate constant values differ from the calculated values. Theories of reaction rates do not agree well on complex reactions.</td>
</tr>
</tbody>
</table>
Q.No 59 - Electrochemistry - II

1. Calculate the e.m.f of zinc-silver cell at 25°C when [Zn2+] = 0.10 M and [Ag+] = 10 M. (E°cell at 25°C = 1.56 volts). Or Calculate the e.m.f of the zinc-silver cell at 25°C. When [Zn2+] = 0.10 M and [Ag+] = 10 M, cell reaction is 2Ag+ + Zn ⇌ 2Ag + Zn2+; E°cell at 25°C = 1.56 V. Or Calculate the e.m.f of the cell having the cell reaction 2Ag+ + Zn ⇌ 2Ag + Zn2+; E°cell = 1.56 V at 25°C when concentration of Zn2+ = 0.1 M and Ag+ = 10 M in the solution.

The cell reaction in the zinc-silver cell would be: 2Ag+ + Zn ⇌ 2Ag + Zn2+

The Nernst equation for the above cell reaction may be written as:

Ecell = E°cell – RT / nF ln [Ag+]2 [Zn2+] / [Ag+]2 [Zn]

(Since concentrations of solids are taken as unity i.e., [M] = 1)

Ecell = E°cell – RT / nF ln [Zn2+] / [Ag+]2

Substituting the various values in Nernst equation, we have

Ecell = 1.56 – (2.303 x 8.314 x 298 / 2 x 96495) log 0.1 / 102

= 1.56 – 0.02957 log 10

= 1.56 – 0.0591 x log 10

= 1.56 + 0.0887

= 1.6487 volts

2. Calculate the e.m.f of the cell Zn | Zn2+(0.001 M) ||Ag+(0.1M) | Ag E°Ag/Ag+ = + 0.80 V, E°Zn/Zn2+= - 0.76V.

Step 1: Write the half-cell reactions of the anode and the cathode. Then add the anode and cathode half reactions to obtain the cell reaction and the value of Eo cell.

At Cathode: 2Ag+ + 2e– → 2Ag   Eo = + 0.80 V
At Anode: Zn → Zn2+ + 2e–   Eo = − 0.76 V

Cell reaction: 2 Ag+ + Zn ⇌ Zn2+ + 2Ag    Eo = 1.56 V

Step 2: K for the cell reaction = [Zn2+] / [Ag+]2

Substituting the values

n = 2 electrons

Eocell = 1.56 V

[Zn2+] = 0.001 M = 10−3 M

[Ag+] = 0.1 M = 10−1 M

in the Nernst equation and solving for Ecell, we have

Ecell = Eocell – 0.0591 / n log K

= 1.56 – 0.0591 / 2 log [Zn2+] / [Ag+]2

= 1.56 – 0.0591 / 2 log [10−3] / [10−1]2

= 1.56 – 0.02955 x log 10−1

= 1.56 + 0.02955

= 1.58955 V
3. Calculate the equilibrium constant for the following cell reaction \(2Ag^+ + Zn \rightleftharpoons Zn^{2+} + 2Ag\)

\[E^{\circ}_{Ag^+/Ag} = +0.80\text{ V, } E^{\circ}_{Zn^{2+}/Zn} = -0.76\text{ V.}\]

**Step 1:** Write the half-cell reactions of the anode and the cathode. Then add the anode and cathode half reactions to obtain the cell reaction and the value of \(E_{ocell}\).

At Cathode: \(2Ag^+ + 2e^- \rightarrow 2Ag\) \(E_o = +0.80\text{ V}\)

At Anode: \(Zn \rightarrow Zn^{2+} + 2e^-\) \(E_o = –0.76\text{ V}\)

Overall Cell reaction: \(2 \text{ Ag}^+ + \text{ Zn} \rightleftharpoons \text{ Zn}^{2+} + 2\text{ Ag}\) \(E_o = 1.56\text{ V}\)

**Step 2:** Substitute the values \(E_{cell} = 0\), \(n = 2\) & \(E_{ocell} = 1.56\text{ V}\) in the Nernst equation at equilibrium:

At equilibrium Cell potential, \(E_{cell} = 0\) and Reaction quotient, \(J = \text{Equilibrium constant, } K\)

\[0 = E_{ocell} – 0.0591 / nF \log K\]

The Nernst equation can be rearranged as:

\[nFE_{ocell} = 0.0591 \log K\]

\[\log K = nE_{ocell} / 0.0591\]

\[= 52.7919\]

\[K = \text{Antilog} 52.7919\]

\[= 6.19 \times 10^{52}\]

4. Calculate the standard e.m.f and standard free energy change of the following cell: \(Zn | Zn^{2+} || Cu^{2+} | Cu\)

\(E^{\circ}_{Zn^{2+}/Zn} = –0.762\text{ V, } E^{\circ}_{Cu^{2+}/Cu} = +0.337\text{ V.}\)

\(E_{ocell} = E_{oR} – E_{oL}\)

\[= +0.337 – (–0.762)\]

\[= +1.099\text{ V}\]

\(E_{ocell}\) is +ve. \(\therefore \Delta Go = –\) ve.

\(\therefore \Delta Go = – n \times F \times E_{ocell}\)

\(n = 2\) electrons

\(\therefore \Delta Go = – 2 \times 96495 \times 1.099\)

\[= –212096\text{ Joules}\]

\[= –212.096\text{ kJ.}\]

5. Derive Nernst equation (of reversible cell.)

The reaction occurring in a reversible cell is represented by the equation

\(A + B \rightleftharpoons C + D\)

The decrease in free energy, \(–\Delta G\), accompanying the process is given by

\[–\Delta G = – \Delta Go – RT \ln J\]

Where,
– $\Delta G_o$ is the decrease in free energy accompanying the same process when all the reactants and products are in their standard states of unit activity.

$J$ stands for the reaction quotient of the activities of the products and reactants at any given stage of the reaction.

Substituting the value of $J$, we have

$$-\Delta G = -\Delta G_o - RT \ln \frac{a_C \cdot a_D}{a_A \cdot a_B}$$

If $E$ is the E.M.F. of the cell in volts and the cell reaction involves the passage of ‘$n$’ faradays i.e., $nF$ coulombs, the electrical work done by the cell is in $nFE$ volt-coulombs or Joules.

Hence free energy decrease of the system, $-\Delta G$, is given by the expression

$$-\Delta G = nFE$$

$$nFE = -\Delta G_o - RT \ln \frac{a_C \cdot a_D}{a_A \cdot a_B}$$

$$E = E_o - RT / nF \ln \frac{a_C \cdot a_D}{a_A \cdot a_B}$$

is known as the Nernst equation

Where,

$E_o$ is the E.M.F. of the cell in which the activity, or as an approximation, the concentration of each reactant and each product of the cell reaction is equal to unity. $E_o$ is known as the standard E.M.F. of the cell.

Replacing activities by concentrations the Nernst equation may be written as

$$E = E_o - RT / nF \ln [C][D] / [A][B]$$

Replacing $[C][D] / [A][B]$ as equal to $K$, the equilibrium constant in the molar concentration units,

$$E = E_o - RT / nF \ln K$$

$$E = E_o - 2.303 \frac{RT}{nF} \log K$$

Where,

$E_o$ = Standard electrode potential
$R$ = Gas constant,
$T$ = Kelvin temperature
$n$ = Number of electrons transferred in the half-reaction
$F$ = Faraday of electricity
$K$ = Equilibrium constant for the half-cell reaction as in equilibrium law.

Substituting the values of $R$ (8.314 J K$^{-1}$ mol$^{-1}$), $F$ (96,495 coulombs) and $T$ at 25oC (273 + 25 = 298 K), the quantity $2.303 \frac{RT}{F}$ comes to be 0.0591.

Thus the Nernst equation can be written in its simplified form as

$$E = E_o - 0.0591 / n \log K$$

6. Determine the standard e.m.f of the cell and standard free energy change of the cell reaction. Zn, Zn$^{2+}$ || Ni$^{2+}$, Ni. The standard reduction potentials ($E^\circ$) of Zn$^{2+}$, Zn and Ni$^{2+}$, Ni half cells are –0.76 V and –0.25 V respectively.

$E_{cell} = E_oR - E_oL$

$$= -0.25 - (-0.76)$$

$$= +0.51 \text{ V}$$

$E_{cell}$ is $+ve$. ∴ $\Delta G_o = -ve$. 

The standard hydrogen half-cell or Standard Hydrogen Electrode (SHE) is selected for coupling with the unknown half-cell. It consists of a platinum electrode immersed in a 1 M solution of H\(^+\) ions maintained at 25°C. Hydrogen gas at one atmosphere enters the glass hood and bubbles over the platinum electrode. The hydrogen gas at the platinum electrode passes into solution, forming H\(^+\) ions and electrons.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So, SHE can be used as a standard for other electrodes.

The half-cell, whose potential is desired, is combined with the hydrogen electrode and the emf of the complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell. For example, it is desired to determine the emf of the zinc electrode, Zn | Zn\(^{2+}\). It is connected with the SHE. The complete electrochemical cell may be represented as:

\[
\text{Zn} \mid \text{Zn}^{2+} \parallel \text{H}^+ \mid \text{H}_2 (1 \text{ atm}), \text{Pt}
\]

The emf of the cell has been found to be \(-0.76\) V which is the emf the zinc half-cell. Similarly, the emf of the copper electrode, Cu\(^{2+}\) | Cu can be determined by pairing it with the SHE when the electrochemical cell can be represented as:

\[
\text{Pt, H}_2 (1 \text{ atm}) \mid \text{H}^+ \parallel \text{Cu}^{2+} \mid \text{Cu}
\]

The emf of this cell has been determined to be 0.34 V which is the emf of the copper half-cell.

\[
\text{E}_{\text{ocell}} = E_{\text{Cu/Cu}^{2+}} - E_{\text{SHE}} = 0.34 - \text{Zero} = 0.34 \text{ V}
\]

The two situations are explained as follows:

When it is placed on the right-hand side of the zinc electrode, the hydrogen electrode reaction is
2H+ + 2e− → H₂

The electrons flow to the SHE and it acts as the cathode.  
When the SHE is placed on the left hand side, the electrode reaction is  
H₂ → 2H+ + 2e−

The electrons flow to the copper electrode and the hydrogen electrode as the anode. Evidently, the SHE can act both as anode and cathode and, therefore can be used to determine the emf of any other half-cell electrode (or single electrode).

8. The e.m.f of the half cell Cu²⁺(aq) / Cu(s) containing 0.01M Cu²⁺ solution is + 0.301 V.  
Calculate the standard e.m.f of the half cell.  

\[ \text{e.m.f of the half cell, } E_{\text{Cu}^2+/\text{Cu}} = 0.301 \text{ V} \]

\[ \text{Cu}^2+ (\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu (s)} \]
\[ n = 2 \text{ electrons} \]
\[ [\text{Cu}^2+] = 0.01 \text{M} = 10^{-2} \text{ M} \]

Standard e.m.f of the half cell, \( E_{o\text{Cu}^2+/\text{Cu}} = ? \)

\[ \underline{ECu^2+/Cu} = E_{o\text{Cu}^2+/\text{Cu}} - 0.0591 / 2 \log [\text{Cu}^2+] \]
\[ 0.301 = E_{o\text{Cu}^2+/\text{Cu}} + 0.0591 / 2 \log [\text{Cu}^2+] \]

Or \[ \underline{EoCu_2+, Cu} = \text{Cu} + 0.0591 / 2 \log [\text{Cu}] / [\text{Cu}^2+] \]
\[ 0.301 = E_{o\text{Cu}^2+/\text{Cu}} + 0.0591 / 2 \log 10^{-2} \]

Or \[ \underline{EoCu_2+, Cu} = \text{Cu} + 0.0591 / 2 \log 1 / 10^2 \text{ M} \]
\[ 0.301 = E_{o\text{Cu}^2+/\text{Cu}} + 0.0591 / 2 \times (-2) \]

\[ 0.301 = E_{o\text{Cu}^2+/\text{Cu}} = 0.301 + 0.0591 \]
\[ = 0.3601 \text{ V} \]

9. Write an account on Cell terminology.  
1. Current is the flow of electrons through a wire or any conductor.  
2. Electrode is a metallic rod / bar / strip which conducts electrons into and out of a solution.  
3. Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit.  
   It has negative charge and is shown as (−) in cell diagrams.  
4. Cathode is the electrode at which reduction occurs. It receives electrons from the outer circuit. It has a positive charge and is shown as (+) in the cell diagrams.  
5. Electrolyte is the salt solution in a cell.  
6. Anode compartment is the compartment of the cell in which oxidation half-reaction occurs.  
   It contains the anode.  
7. Cathode compartment is the compartment of the cell in which reduction half-reaction occurs. It contains the cathode.  
8. Half-cell - Each half of an electrochemical cell, where oxidation occurs and the half where reduction occurs, is called the half cell.  
10. Derive the relation between e.m.f and free energy.  Or Establish a relation between free energy and e.m.f  Or Write a brief account on the relation between EMF and free energy.  
When a cell produces a current, the current can be used to do work – to run a motor, for instance.  
Thermodynamic principles can be employed to derive a relation between electrical energy and
the maximum amount of work, $W_{\text{max}}$, obtainable from the cell. The maximum amount of work obtainable from the cell is the product of charge flowing per mole and maximum potential difference, $E$, through which the charge is transferred.

$$W_{\text{max}} = -nFE$$  \hspace{1cm} (1)

Where,

- $n$ is the number of moles of electrons transferred and is equal to the valence of the ion participating in the cell reaction.
- $F$ stands for Faraday and is equal to 96,495 coulombs
- $E$ is the emf of the cell.

According to thermodynamics, the maximum work that can be derived from a chemical reaction is equal to the free energy ($\Delta G$) for the reaction,

$$W_{\text{max}} = \Delta G$$  \hspace{1cm} (2)

Therefore, from (1) and (2), we can write

$$\Delta G = -nFE$$  \hspace{1cm} (3)

Thus only when $E$ has a positive value, $\Delta G$ value will be negative and the cell reaction will be spontaneous and the e.m.f. of the cell can be measured.

Here $E$ refers to the Ecell.

Thus, the electrical energy supplied by the cell is $(nFE)$ equal to the free energy decrease ($-\Delta G$) of the cell reaction occurring in the cell.

11. Describe Daniel cell.

Daniel cell or a galvanic cell is an example of electrochemical cell.

The overall reaction taking place in the cell is the redox reaction given as

$$\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$$

This overall reaction is made of the summation of two half reactions such as oxidation half reaction and reduction half reaction.

The oxidation half reaction occurring at the zinc electrode in contact with the aqueous electrolyte containing Zn$^{2+}$, accumulates the electrons at the zinc rod.

$$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-$$

The reduction half reaction occurring at the copper electrode in contact with the aqueous electrolyte containing Cu$^{2+}$ ions receives the electrons from the zinc electrode when connected externally, to produce metallic copper according to the reaction as,

$$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}(s)$$

The decrease in the energy which appears as the heat energy when a zinc rod is directly dipped into the zinc sulphate solution, is converted into electrical energy when the same reaction takes place indirectly in an electrochemical cell.

The Daniel cell is also called as the voltaic cell. However for continuous supply of current for a long period, the two half cells each comprising the metal electrode and its aqueous electrolyte kept in separate containers and can be connected externally as below:
When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form $\text{Zn}^{2+}$ ions. The $\text{Cu}^{2+}$ ions in the cathode half-cell pick up electrons and are converted to Cu atoms on the cathode.

12. How is emf of a half cell determined?

The emf of the unknown half-cell $E_0$ is calculated by constructing a cell with standard half-cell. 

$$E_{\text{measured}} = E_R - E_L$$

If the standard half-cell acts as anode, the equation becomes $E_R = E_{\text{measured}}$ ($\because E_L = 0$)

If standard half-cell acts as cathode $E_L = -E_{\text{measured}}$ ($\because E_R = 0$)

The standard hydrogen half-cell or Standard Hydrogen Electrode (SHE) is selected for coupling with the unknown half-cell.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So, SHE can be used as a standard for other electrodes.

The SHE can act both as anode and cathode and, therefore, can be used to determine the emf of any other half-cell electrode (or single electrode).

13. Write IUPAC representation of a cell. Or Write notes on IUPAC convention of representation of a cell. Or Write the IUPAC conventions for writing cell diagram with examples.

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell. An electrochemical cell consists of two half-cells. Each half-cell is made of a metal electrode in contact with metal ion in solution.
IUPAC recommended the following conventions for writing cell diagram. We will illustrate these with reference to Zinc-Copper cell.

Cell Diagram

1. A single vertical line ( | ) represents a phase boundary between metal electrode and ion solution (electrolyte).

\[
\text{Zn} | \text{Zn}^{2+} \quad \text{Cu}^{2+} | \text{Cu}
\]

Anode half-cell  Cathode half-cell

It may be noted that the metal electrode in anode half-cell is on the left, while in cathode half-cell it is on the right of the metal ion.

2. A double vertical line ( || ) represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing.

Salt bridge

3. Anode half-cell is written on the left and cathode half-cell on the right.

4. In the complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between. The zinc-copper cell can now be written as

\[
\text{Zn} | \text{Zn}^{2+} \quad || \quad \text{Cu}^{2+} | \text{Cu}
\]

Anode half-cell  Cathode half-cell
5. The symbol for an inert electrode, like the platinum electrode is often enclosed in a bracket. Example

\[
\text{Mg} \mid \text{Mg}^{2+} \parallel \text{H}^+ \mid \text{H}_2 \text{(Pt)}
\]

Anode half-cell | Cathode half-cell

(6) The value of emf of a cell (E) is written on the right of the cell diagram. Thus a zinc-copper cell has emf 1.1 V and is represented as

\[
\text{Zn} \mid \text{ZnSO}_4 \parallel \text{CuSO}_4 \mid \text{Cu} \quad E = +1.1 \text{ V}
\]

Direction of electron flow \[\rightarrow\]

\[
\begin{align*}
\text{Anode half-cell} & \quad \underline{\text{Zn}(s)} \mid \text{Zn}^{2+}(aq) \parallel \text{Cu}^{2+}(aq) \mid \text{Cu}(s) \\
\text{Cathode half-cell} & \quad \underline{\text{Cu}(s)} \mid \text{CuSO}_4 \parallel \text{ZnSO}_4 \mid \text{Zn}
\end{align*}
\]

If the emf acts in the opposite direction through the cell circuit it is denoted as a negative value.

\[
\text{Cu} \mid \text{CuSO}_4 \parallel \text{ZnSO}_4 \mid \text{Zn} \quad E = -1.1 \text{ V}
\]

\[\leftarrow\] Direction of electron flow

The negative sign also indicates that the cell is not feasible in the given direction and the reaction will take place in the reverse direction only. The overall cell reaction for \(E = -1.1 \text{ V}\) of the Daniel cell is

\[
\text{Cu}(s) + \text{Zn}^{(aq)2+} \rightleftharpoons \text{Cu}^{(aq)2+} + \text{Zn}(s)
\]

The reversal of the cell current is accompanied by the reversal of direction of the cell reaction.

14. Write notes on single electrode potential.

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the single electrode potential. Thus in Daniel cell in which the electrodes are not connected externally, the anode \(\text{Zn} / \text{Zn}^{2+}\) develops a negative charge and the cathode \(\text{Cu} / \text{Cu}^{2+}\), a positive charge. The amount of the charge produced on an individual electrode determines its single electrode potential.

The single electrode potential of a half-cell depends on:

a. Concentration of ions in solution
b. Tendency to form ions and
c. Temperature.

Standard emf of a cell

The emf generated by an electrochemical cell is given by the symbol \(E\). It can be measured with the help of a potentiometer. When the emf of a cell is determined under standard conditions, it is called the standard emf. The standard emf may be defined as the emf of a cell with 1 M solutions of reactants and products in solution measured at 25°C. Standard emf of a cell is represented by
the symbol Eo. For gases 1 atm. pressure is a standard condition instead of concentration. For Zn-Cu voltaic cell, the standard emf, Eo is 1.10V.

\[
\text{Zn} \ | \ \text{Zn}^2+ (aq, 1M) \ || \ \text{Cu}^2+ (aq, 1M) \ | \ \text{Cu} \quad \quad \text{Eo} = 1.10 \text{ V}
\]

## Applications of Single electrode potential

### 1. Predicting Cell EMF:

The standard emf Eo, of a cell is the standard reduction potential of right-hand electrode (cathode) minus the standard reduction potential of the left-hand electrode (anode). That is, Ecell = Eright – Eleft

\[
= \text{Cathode potential} - \text{Anode potential}
\]

### 2. Predicting Feasibility of Reaction:

The feasibility of a redox reaction can be predicted with the help of the electrochemical series. The net emf of the cell reaction, Ecell, can be calculated from the expression

Ecell = Eocathode – Eoanode

In general, if Ecell = + ve, the reaction is feasible

Ecell = – ve, the reaction is not feasible.

### 3. Metal displacement: (Predicting whether a metal will displace another metal from its salt solution or not)

The metals near the bottom of the electrochemical series are strong reducing agents and are themselves oxidised to metal ions. On the contrary, the metal lying higher up in the series are strong oxidizing agents and their ions are readily reduced to the metal itself.

**Eg.** Zinc lying down below the series is oxidised to \( \text{Zn}^2+ \) ion, while copper which is higher up in the series is produced by reduction of \( \text{Cu}^2+ \) ion.

In general we can say that a metal lower down the electrochemical series can precipitate the one higher up in the series.

**Eg.** Silver cannot precipitate Cu from CuSO4 solution, since both metals have positions higher up in the series and are strong oxidising agents.
### SECTION-C

**Q.No 60-Ethers**

1. Discuss the isomerism in ethers. **Or** Discuss the isomerism exhibited by ethers.

**1. Functional Isomerism:**

Ethers are *functional isomers of alcohols* as both have the *same general formula* \( C_nH_{2n+2}O \) with different functional groups.

The \( C_2H_6O \) stands for both \( CH_3CH_2OH \) and \( CH_3–O–CH_3 \).

**Ethyl alcohol** | **Dimethyl ether**
---|---

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>Ethers</th>
<th>Alcohols</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_3H_8O )</td>
<td>( CH_3–O–CH_2–CH_3 ) Ethyl methyl ether</td>
<td>( CH_3CH_2CH_2OH ) n-Propyl alcohol ( OH )</td>
</tr>
<tr>
<td></td>
<td>( CH_3–O–CH_2–CH_3 ) Methyl-n-propyl ether</td>
<td>( CH_3–CH–CH_3 ) iso-Propyl alcohol</td>
</tr>
<tr>
<td>( C_4H_{10}O )</td>
<td>( CH_3CH_2–O–CH_2CH_3 ) Diethyl ether</td>
<td>( CH_3–CH_2–CH_2–OH ) n-Butyl alcohol ( CH_3 )</td>
</tr>
<tr>
<td></td>
<td>( CH_3–O–CH–CH_3 ) Methyl isopropyl ether</td>
<td>( CH_3–CH–CH_2OH ) iso-Butyl alcohol ( OH )</td>
</tr>
<tr>
<td></td>
<td>( CH_3–CH–CH_3 ) sec-Butyl alcohol</td>
<td>( CH_3–C–OH )</td>
</tr>
<tr>
<td></td>
<td>( CH_3–C–OH )</td>
<td>( CH_3 ) tert-Butyl alcohol</td>
</tr>
</tbody>
</table>

---

**Source:**

2. Metamerism:
It is a special isomerism in which molecules with same formula, same functional group, differing only in the nature of the alkyl group attached to oxygen.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{Methyl-n-propyl ether} & \quad \text{Diethyl ether} & \quad \text{Methyl isopropyl ether}
\end{align*}
\]

2. Distinguish between anisole and diethyl ether. Or Give the differences between anisole and diethyl ether. Or Distinguish between aromatic ethers and aliphatic ethers. Or Distinguish aliphatic and aromatic ethers.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Anisole</th>
<th>Diethyl ether</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Aromatic ether</strong></td>
<td><strong>Aliphatic ether</strong></td>
</tr>
<tr>
<td>1</td>
<td>Comparatively high boiling liquid</td>
<td>Volatile liquid</td>
</tr>
<tr>
<td>2</td>
<td>Used in perfumery.</td>
<td>Used as anaesthetic.</td>
</tr>
<tr>
<td>3</td>
<td>Not used as solvent.</td>
<td>Used as a solvent.</td>
</tr>
<tr>
<td>4</td>
<td>Cannot be used as a substitute for petrol.</td>
<td>Mixed with alcohol, used as a substitute for petrol.</td>
</tr>
<tr>
<td>5</td>
<td>Does not form peroxide easily.</td>
<td>Forms peroxide in air.</td>
</tr>
<tr>
<td>6</td>
<td>On heating with HI forms phenol and CH3I only.</td>
<td>It forms C2H5OH and C2H5I.</td>
</tr>
<tr>
<td>7</td>
<td>With nitrating mixture forms a mixture of ortho and para nitro anisoles.</td>
<td>Nitration does not take place.</td>
</tr>
</tbody>
</table>


1. Intermolecular dehydration of alcohol: When excess of ethyl alcohol is heated with con. H2SO4 or H3PO4, two molecules condense losing a molecule of water forming ether.

\[
\text{C}_2\text{H}_5 – \text{O} – \text{H} + \text{H} – \text{O} \rightarrow \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5 – \text{O} – \text{C}_2\text{H}_5 + \text{H}_2\text{O} \\
\text{con. H}_2\text{SO}_4
\]

2. Williamson’s synthesis: When ethyl bromide is heated with sodium or potassiummethoxide ether is prepared.

\[
\text{C}_2\text{H}_5\text{Br} + \text{NaOC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5 – \text{O} – \text{C}_2\text{H}_5 + \text{NaBr}
\]

3. From alkyl halides: By heating ethyl iodide with dry silver oxide ether is prepared.

\[
\Delta \quad \text{C}_2\text{H}_5 – \text{I} + \text{Ag}_2\text{O} + \text{I} \rightarrow \text{C}_2\text{H}_5 – \text{O} – \text{C}_2\text{H}_5 + 2\text{AgI}
\]

5. Give any two methods of preparation of anisole and explain the reaction of HI with anisole.

1. Williamson’s synthesis: When sodium phenoxide is heated with methyl iodide anisole is obtained.

\[
\text{C}_6\text{H}_5\text{O}^- \text{Na} + \text{I} – \text{CH}_3 \rightarrow \text{C}_6\text{H}_5 – \text{O} – \text{CH}_3 + \text{NaI}
\]
2. Using diazomethane: Phenol reacts with diazomethane gives anisole.
\[ \text{C}_6\text{H}_5 – \text{O} – \text{H} + \text{CH}_2 – \text{N}_2 \rightarrow \text{C}_6\text{H}_5 – \text{O} – \text{CH}_3 + \text{N}_2 \]

3. Manufacture of ether: Anisole is manufactured on large scale by reacting phenol with dimethyl sulphate in presence of sodium hydroxide.
\[ \text{NaOH} \]
\[ \text{C}_6\text{H}_5\text{OH} + (\text{CH}_3)\text{2SO}_4 \rightarrow \text{C}_6\text{H}_5 – \text{O} – \text{CH}_3 + \text{CH}_3\text{HSO}_4 \]

6. How do ethers react with HI? Give the significance of the reaction.
On treating with one equivalent of HI ether gets cleaved to form ethyl alcohol and ethyl iodide.
\[ \text{HI} \]
\[ \text{C}_2\text{H}_5 – \text{O} – \text{CH}_3 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{CH}_3 \]

With excess hot concentrated hydroiodic acid ether gives 2 moles of ethyl iodide.
\[ 2\text{HI} \]
\[ \text{C}_2\text{H}_5 – \text{O} – \text{C}_2\text{H}_5 \rightarrow 2\text{C}_2\text{H}_5\text{I} + \text{H}_2\text{O} \]

This reaction is used in the Zeisel’s method of detection and estimation of alkoxy (especially methoxy) group in natural products like alkaloids.

7. How does diethyl ether react with PCl₅, one equivalent of HI and excess of HI?

1. Phosphorous pentachloride cleaves the ether into ethyl chloride.
\[ \text{Cl} – \text{PCl}_3 – \text{Cl} \]
\[ \text{C}_2\text{H}_5 – \text{O} – \text{C}_2\text{H}_5 \rightarrow 2\text{C}_2\text{H}_5\text{Cl} + \text{POCl}_3 \]

2. On treating with one equivalent of HI ether gets cleaved to form ethyl alcohol and ethyl iodide.
\[ \text{HI} \]
\[ \text{C}_2\text{H}_5 – \text{O} – \text{CH}_3 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{I} \]

3. With excess hot concentrated hydroiodic acid ether gives 2 moles of ethyl iodide.
\[ 2\text{HI} \]
\[ \text{C}_2\text{H}_5 – \text{O} – \text{C}_2\text{H}_5 \rightarrow 2\text{C}_2\text{H}_5\text{I} + \text{H}_2\text{O} \]

8. How does diethyl ether react with the following reagents? a) O₂ / long contact b) dil. H₂SO₄ c) PCl₅.

a) Diethyl ether forms Diethyl peroxide by the action of air or oxygen.
\[ \text{O}\text{(O)} \]
\[ \text{C}_2\text{H}_5 – \text{O} – \text{C}_2\text{H}_5 \rightarrow (\text{C}_2\text{H}_5)\text{2O}_2 \]

b) Diethyl ether on boiling with water in presence dilute H₂SO₄ is hydrolysed to form ethyl alcohol.
\[ \text{H}_2\text{SO}_4 \]
\[ \text{C}_2\text{H}_5 – \text{O} – \text{C}_2\text{H}_5 + \text{H} – \text{O} – \text{H} \rightarrow 2\text{C}_2\text{H}_5\text{OH} \]

c) Phosphorous penta chloride cleaves the Diethyl ether into ethyl chloride.
\[ \text{Cl} – \text{PCl}_3 – \text{Cl} \]
\[ \text{C}_2\text{H}_5 – \text{O} – \text{C}_2\text{H}_5 \rightarrow 2\text{C}_2\text{H}_5\text{Cl} + \text{POCl}_3 \]

9. How are the following reactions effected? (i) diethyl ether with Grignard reagent (ii) diethyl ether with mineral acids (iii) ethyl methyl ether with excess hot conc. HI acid
(i) diethyl ether with Grignard reagent
An ether solution of Grignard reagent contains the following complex of ether. Thus the Grignard reagent is stabilised in dry ether.

\[
2 \text{C}_2\text{H}_5\text{O} - \text{C}_2\text{H}_5 + \text{CH}_3\text{MgI} \rightarrow \text{CH}_3\text{MgO(C}_2\text{H}_5)_2\text{MgI}
\]

(ii) diethyl ether with mineral acids
Strong mineral acids protonate the ethereal oxygen forming oxonium salts.

\[
\text{C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5 + \text{HCl} \rightarrow \left[\text{C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5 + \text{H}\right] + \text{Cl}^-
\]

\[
\text{C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5 + \text{H}_2\text{SO}_4 \rightarrow (\text{C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5)\text{HSO}_4^-
\]

(iii) Ethyl methyl ether with excess hot conc. HI acid
Ethyl methyl ether with excess hot concentrated hydroiodic acid, Methyl iodide and Ethyl iodide are formed.

\[
2\text{HI} \rightarrow \text{CH}_3 - \text{O} - \text{C}_2\text{H}_5 \rightarrow \text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{I} + \text{H}_2\text{O}
\]
Q.No 61-Carbonyl Compounds

1. Explain / Give the mechanism for Claisen Or Claisen-Schmidt reaction.

**Claisen or Claisen-Schmidt reaction:** Benzaldehyde reacts with aliphatic aldehydes or ketones in presence of NaOH forming α, β - unsaturated aldehyde or ketone.

\[
\text{NaOH} \\
\text{C}_6\text{H}_5 - \text{CHO} + \text{CH}_3 - \text{CHO} \rightarrow \text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{CHO} + \text{H}_2\text{O}
\]

Similarly,

\[
\text{NaOH} \\
\text{C}_6\text{H}_5 - \text{CHO} + \text{CH}_3 - \text{CO} - \text{CH}_3 \rightarrow \text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{CO} - \text{CH}_3 + \text{H}_2\text{O}
\]

**Mechanism:**
The carbanion formed from acetaldehyde or acetone brings forth a nucleophilic attack on the carbonyl carbon of Benzaldehyde. The aldol type of product undergoes β-elimination (of water).

**Step 1:** The carbanion is formed as the α-hydrogen atom is removed as a proton by the base.

\[
\text{CH}_3\text{CHO} \overset{\text{OH}^-}{\rightarrow} \text{CH}_2\text{CHO} + \text{H}_2\text{O}
\]

**Step 2:** The carbanion (Nucleophile) attacks the carbonyl carbon of Benzaldehyde.

**Step 3:** β-elimination of water.

\[
\text{C}_6\text{H}_5 - \text{CH} - \text{OH} \rightarrow \text{CH} - \text{CHO} - \text{H}_2\text{O} \rightarrow \text{CH} - \text{CHO} \rightarrow \text{CH} - \text{CH} = \text{CH} - \text{CHO} \rightarrow \text{C}_6\text{H}_5 - \text{CH} - \text{CH} = \text{CH} - \text{CHO}
\]

2. Explain / Write the mechanism of crossed aldol condensation (of acetone).

**Crossed aldol condensation:** When an aldehyde and a ketone with α-hydrogen atom react in presence of NaOH forming Aldol.

\[
\text{CH}_3 - \text{CO} - \text{CH}_3 + \text{CH}_3 - \text{CHO} \rightarrow \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CHO}
\]

**Mechanism:**

**Step 1:** The carbanion is formed as the α-hydrogen atom is removed as a proton by the base.

\[
\text{CH}_3 - \text{C} = \text{O} \overset{\text{OH}^-}{\rightarrow} \text{CH}_2 - \text{C} = \text{O} + \text{H}_2\text{O}
\]
Step 2: The carbanion attacks the carbonyl carbon of unionised ketone molecule.

Step 3: The alkoxide ion formed is protonated by water to give ‘Aldol’.

3. Explain the mechanism of aldol condensation in acetone.

Aldol condensation: When ketones with $\alpha$-hydrogen atom react in presence of NaOH forming Ketol.

$$\begin{align*}
\text{CH}_3 \text{O} \\
\text{CH}_3 \quad \| \\
\text{CH}_3 – \text{CO} – \text{CH}_3 + \text{CH}_3 – \text{CO} – \text{CH}_3 & \rightarrow \text{CH}_3 – \text{C} – \text{CH}_2 – \text{C} – \text{CH}_3 \\
& \quad \| \quad \text{OH}
\end{align*}$$

Mechanism:

Step 1: The carbanion is formed as the $\alpha$-hydrogen atom is removed as a proton by the base.

Step 2: The carbanion attacks the carbonyl carbon of another unionised ketone molecule.

Step 3: The alkoxide ion formed is protonated by water to give ‘Ketol’.
4. Explain the mechanism of aldol condensation of acetaldehyde. Or Discuss the mechanism involved in aldol condensation of acetaldehyde.

**Aldol condensation:** When aldehydes with α-hydrogen atom react in presence of NaOH forming Aldol.

\[
\begin{align*}
\text{CH}_3 - \text{C} - \text{O} & \quad \text{H}_2\text{O} \quad \text{Protonation} \\
\text{CH}_3\text{C} = \text{O} + \text{CH}_3 - \text{CHO} & \rightarrow \text{CH}_3 - \text{C} - \text{CH}_2 - \text{C} - \text{H} \\
& \quad \text{OH}
\end{align*}
\]

**Mechanism:**

Aldol condensation is catalysed by base. The carbanion generated is nucleophilic in nature. Hence it can bring about nucleophilic attack on carbonyl group.

**Step 1:** The carbanion is formed as the α-hydrogen atom is removed as a proton by the base.

\[
\begin{align*}
\text{CH}_3 - \text{C} = \text{O} & \quad \longrightarrow \quad \text{CH}_2 - \text{C} = \text{O} + \text{H}_2\text{O} \\
& \quad \text{OH}
\end{align*}
\]

**Step 2:** The carbanion attacks the carbonyl carbon of another unionised acetaldehyde molecule.

\[
\begin{align*}
\text{CH}_3 - \text{C} & \quad \longrightarrow \quad \text{CH}_3 - \text{C} - \text{O} \\
\text{CH}_2 - \text{CHO} & \quad \text{CH}_2 - \text{CHO} \\
& \quad \text{alkoxide ion}
\end{align*}
\]

**Step 3:** The alkoxide ion formed is protonated by water to give ‘Aldol’.

\[
\begin{align*}
\text{CH}_3 - \text{C} - \text{O} & \quad \text{H} - \text{OH} \quad \longrightarrow \quad \text{CH}_3 - \text{C} - \text{OH} + \text{OH} \\
\text{CH}_2\text{CHO} & \quad \text{CH}_2\text{CHO} \quad \text{Aldol}
\end{align*}
\]

6. Explain the mechanism of Cannizzaro reaction.
Cannizzaro reaction: Aldehydes without α-hydrogen atom when heated with concentrated NaOH involves self oxidation of one aldehyde molecule to carboxylic acid and self reduction of the other aldehyde molecule to a primary alcohol.

\[
\text{NaOH}
\]

\[
\text{C}_6\text{H}_5–\text{CHO} + \text{C}_6\text{H}_5–\text{CHO} \rightarrow \text{C}_6\text{H}_5–\text{COONa} + \text{C}_6\text{H}_5–\text{CH}_2–\text{OH}
\]

The mechanism involves the transfer of hydride ion from one molecule of benzaldehyde to the other molecule.

**Step 1:** Nucleophilic attack by OH – ion on carbonyl carbon

\[
\begin{align*}
\text{C}_6\text{H}_5–\text{CHO} + \text{OH}^– & \rightarrow \text{C}_6\text{H}_5–\text{C}–\text{O}^– \rightarrow \text{C}_6\text{H}_5–\text{C}–\text{O}^–
\end{align*}
\]

**Step 2:** Transfer of hydride ion from the anion to carbonyl carbon of another molecule.

\[
\begin{align*}
\text{C}_6\text{H}_5–\text{C}–\text{O}^– + \text{C}_6\text{H}_5–\text{C}=\text{O} & \rightarrow \text{C}_6\text{H}_5–\text{C}=\text{O} + \text{C}_6\text{H}_5–\text{C}–\text{O}^–
\end{align*}
\]

**Step 3:** The benzyloxide ion picks up the acidic proton from benzoic acid to give benzyl alcohol.

\[
\begin{align*}
\text{C}_6\text{H}_5–\text{C}=\text{O} + \text{C}_6\text{H}_5–\text{C}–\text{O}^– & \rightarrow \text{C}_6\text{H}_5–\text{C}=\text{O} + \text{C}_6\text{H}_5–\text{C}–\text{OH}
\end{align*}
\]

7. **Explain 'Popott's rule' with an example.**

During oxidation of unsymmetric ketones with oxidising agent which brings about the cleavage of C–C bond, the smaller alkyl group goes preferentially with the carbonyl group resulting in the carboxylic acids.
8. How is acetone converted to - i) mesityl oxide ii) mesitylene?

i) Acetone reacts with dry hydrogen chloride forms mesityl oxide.

\[
\text{CH}_3 - \text{CO} - \text{CH}_3 + \text{H}_2\text{CH} - \text{CO} - \text{CH}_3 \rightarrow (\text{H}_3\text{C})_2 - \text{C} = \text{CH} - \text{CO} - \text{CH}_3 + \text{H}_2\text{O}
\]

Mesityl oxide
4-methyl pent-3-ene-2-one

ii) In presence of Conc. H\textsubscript{2}SO\textsubscript{4} three molecules of acetone condense to give mesitylene (1, 3, 5 trimethyl benzene)

\[
3\text{CH}_3 - \text{CO} - \text{CH}_3 \rightarrow \text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{COOH} + 3\text{H}_2\text{O}
\]

9. Write notes on i) Perkin’s reaction and ii) Knoevenagal reaction iii) Stephen’s reaction.

i) Perkin’s reaction: When benzaldehyde is heated with sodium salt of acetic acid in presence of acetic anhydride, it forms Cinnamic acid.

\[
\text{C}_6\text{H}_5 - \text{CH} = \text{O} + \text{CH}_3 - \text{CO} - \text{O} - \text{CO} - \text{CH}_3 \rightarrow \text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{COOH} + \text{CH}_3 - \text{COOH}
\]

Acetic anhydride \(\Delta\) Cinnamic acid

Mechanism:

Sodium acetate is the base that generates a carbanion at the \(\alpha\)-carbon in the acetic anhydride. This brings forth nucleophilic attack on the carbonyl carbon forming \(\beta\)-hydroxy acid, water gets removed from this by \(\beta\)-elimination.
ii) Knoevenagal reaction: Benzaldehyde condenses with malonic acid in presence of pyridine forming cinnamic acid, pyridine is the basic catalyst here.

\[
\text{Pyridine} \quad \text{CO}_2 \\
\text{C}_6\text{H}_5 - \text{CH} = \text{O} + \text{H}_2\text{C} (\text{COOH})_2 \rightarrow \text{C}_6\text{H}_5 - \text{CH} = \text{C} (\text{COOH})_2 \rightarrow \text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{COOH}
\]

iii) Stephen’s reaction: Aldehyde can be prepared by the reduction of alkyl cyanide dissolved in ether with Stannous chloride and hydrochloric acid.

\[
\text{H} - \text{H} \quad \text{SnCl}_2 \\
\text{CH}_3 - \text{C} \equiv \text{N} \rightarrow \text{CH}_3\text{CH} = \text{NH} \cdot \text{HCl}
\]

Methyl cyanide HCl Iminimum hydro chloride

\[
\text{O} - \text{H}_2 \quad \text{Hydrolysis} \\
\text{CH}_3\text{CH} = \text{NH} \cdot \text{HCl} \rightarrow \text{CH}_3\text{CHO} + \text{NH}_4\text{Cl}
\]

10. Give the following reactions (i) Benzoin Condensation (ii) Knoevenagal reaction

(i) Benzoin Condensation:
When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide -- α - hydroxy ketone called benzoin is formed. Cyanide ion (CN–) is the specific catalyst in this reaction. Benzoin can be considered as dimer of benzaldehyde.

\[
\text{O} \quad \text{alc. KCN} \\
\text{C}_6\text{H}_5\text{CH} = \text{O} + \text{H} - \text{C} - \text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CHOH} - \text{C} - \text{C}_6\text{H}_5
\]

Benzoin

(ii) Knoevenagal reaction:
Benzaldehyde condenses with malonic acid in presence of pyridine forming cinnamic acid; pyridine is the basic catalyst here.

\[
\text{Pyridine} \quad \text{CO}_2 \\
\text{C}_6\text{H}_5\text{CH} = \text{O} + \text{H}_2\text{C} (\text{COOH})_2 \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{C} (\text{COOH})_2 \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CH} - \text{COOH}
\]

11. Write the differences between Acetaldehyde and Benzaldehyde Or

Compare Aliphatic aldehyde and Aromatic aldehyde

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Acetaldehyde CH₃CHO</th>
<th>Benzaldehyde C₆H₅CHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. With Fehling’s solution</td>
<td>Gives a Red precipitate.</td>
<td>No reaction</td>
</tr>
<tr>
<td>2. With Ammonia</td>
<td>Forms Simple Addition product</td>
<td>Forms Complex Condensation product</td>
</tr>
<tr>
<td>3. With Caustic soda</td>
<td>Undergoes Aldol condensation</td>
<td>Undergoes Cannizzaro reaction</td>
</tr>
<tr>
<td>4. With Primary amines</td>
<td>Does not form Schiff’s base</td>
<td>Forms Schiff’s base.</td>
</tr>
<tr>
<td>5. With Chlorine</td>
<td>Does not form Acetyl chloride</td>
<td>Forms Benzoyl chloride</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>6. Polymerisation</td>
<td>Undergoes Polymerisation</td>
<td>Does not polymerise</td>
</tr>
<tr>
<td>7. Electrophilic substitution</td>
<td>Does not undergo</td>
<td>Undergoes at the meta position</td>
</tr>
<tr>
<td>8. With Schiff’s reagent</td>
<td>Gives Pink colour in cold</td>
<td>Gives Pink colour</td>
</tr>
</tbody>
</table>

12. Write a note on i) Clemmenson reduction and ii) Knoevenagel reaction

i) **Clemmenson reduction**: Aldehydes and ketones can be reduced to Hydrocarbons by Zinc amalgam and Con. HCl.
This reaction proceeds by **electron addition to carbonyl carbon followed by protonation**. Zinc metal is the electron source.

In the absence of mercury, hydrogen gas will be evolved and the reduction is incomplete. This reduction is called **Clemmenson reduction**.

<table>
<thead>
<tr>
<th>Clemmenson reduction</th>
<th>HCHO</th>
<th>CH₃CHO</th>
<th>C₆H₅CHO</th>
<th>CH₃COCH₃</th>
<th>C₆H₅COCH₃</th>
<th>C₆H₅COC₆H₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn / Hg + Conc. HCl</td>
<td>←-----</td>
<td>&gt; C = O Group reduced to – CH₂ – Group to give Hydrocarbons ----→</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>CH₃CH₃</td>
<td>C₆H₅CH₃</td>
<td>CH₃CH₂CH₃</td>
<td>C₆H₅CH₂CH₃</td>
<td>C₆H₅CH₂C₆H₅</td>
</tr>
</tbody>
</table>

**ii) Knoevenagel reaction** : Benzaldehyde condenses with malonic acid in presence of pyridine forming cinnamic acid; pyridine is the basic catalyst here.

\[
\text{Pyridine} \quad \text{CO}_2 \\
\text{C}_6\text{H}_5\text{CH} = \text{O} + \text{H}_2\text{C(COOH)}_2 \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{C(COOH)}_2 \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CHCOOH}
\]

13. **Illustrate the reducing property of acetaldehyde with examples**

Because aldehydes are easily oxidised, they are reducing agents. The reduce Ammonical silver nitrate (Tollen’s reagent) to metallic Silver and Fehling’s solution (Copper sulphate, Sodium potassium tartrate) to red Cuprous oxide.

\[
\begin{align*}
\text{CH}_3\text{CHO} + 2\text{Ag}^+ + 3\text{OH}^- & \rightarrow \text{CH}_3\text{COO}^- + 2\text{Ag} + 2\text{H}_2\text{O} \\
\text{Acetaldehyde} & \quad \text{Acetate ion} \quad \text{Silver mirror} \\
\text{CH}_3\text{CHO} + 2\text{Cu}^{2+} + 5\text{OH}^- & \rightarrow \text{CH}_3\text{COO}^- + \text{Cu}^2\text{O} + 3\text{H}_2\text{O} \\
& \quad \text{Blue} \quad \text{Red precipitate} \\
& \quad \text{Cupric ion} \quad \text{Cuprous ion}
\end{align*}
\]

14. **Write the differences between acetaldehyde and acetone.**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Reactions</th>
<th>Acetaldehyde</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>With Fehling’s</td>
<td>Gives a red</td>
<td>Does not react.</td>
</tr>
<tr>
<td></td>
<td>solution</td>
<td>precipitate</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>With Tollen’s</td>
<td>Gives silver</td>
<td>No silver mirror.</td>
</tr>
<tr>
<td></td>
<td>reagent</td>
<td>mirror.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Oxidation</td>
<td>Gives acetic</td>
<td>Gives acetic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acid with</td>
<td>with loss of one Carbon atom.</td>
</tr>
<tr>
<td>4</td>
<td>Reduction with</td>
<td>Gives ethanol</td>
<td>Gives isopropyl alcohol</td>
</tr>
<tr>
<td></td>
<td>NaBH4</td>
<td>(primary</td>
<td>(secondary alcohol)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>alcohol)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>With NH₃</td>
<td>Simple</td>
<td>Forms complex ketonic amine.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>addition</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>product is</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>formed.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Iodoform reaction</td>
<td>Forms iodoform and formic acid.</td>
<td>Forms iodoform and acetic acid.</td>
</tr>
<tr>
<td>---</td>
<td>------------------</td>
<td>---------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>7</td>
<td>Polymerisation</td>
<td>Forms paraldehyde</td>
<td>Forms condensation products.</td>
</tr>
<tr>
<td>8</td>
<td>With Schiff’s reagent.</td>
<td>Pink colour appears in cold.</td>
<td>No pink colour in cold.</td>
</tr>
<tr>
<td>9</td>
<td>Warming with NaOH</td>
<td>A brown resinous mass.</td>
<td>No resinous mass</td>
</tr>
</tbody>
</table>
Q.No 62-Carboxylic Acids

1. Account for the reducing nature / property of formic acid.
   Formic acid is unique because it contains both an aldehyde group and carboxyl group also. Hence it can act as a reducing agent. It reduces Fehling’s solution, Tollen’s reagent and decolourises pink coloured KMnO₄ solution.

   ![Formic acid structure]

   In all cases formic acid is oxidised to CO₂ and water.

   \[
   \text{HCOOH} + \text{Ag}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{Ag} \text{ (Metallic Silver)}
   \]

   a) Formic acid reduces Tollen’s reagent (Ammoniacal silver nitrate solution) to metallic Silver.

   b) Formic acid reduces Fehling’s solution. It reduces blue coloured Cupric ions to red coloured Cuprous ions.

   \[
   \text{HCOO}^- + 2\text{Cu}^{2+} + 5\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{Cu}_2\text{O} + 3\text{H}_2\text{O} \\
   \text{(Blue)} \rightarrow \text{(Red)}
   \]

2. Bring about the following conversions a. Salicylic acid → aspirin b. Salicylic acid → methyl salicylate c. Lactic acid → lactide d. Benzoic acid → benzyl alcohol. Or How are the following conversions carried out? Or How to do the following conversions? i) Salicylic acid to aspirin ii) Salicylic acid to methyl salicylate iii) Lactic acid to lactide iv) Benzoic acid to benzyl alcohol.

   a) / i) Salicylic acid undergoes acetylation by heating with Acetic anhydride to form Aspirin.

   ![Acetylation reaction]

   b) / ii) Salicylic acid on heating with Methyl alcohol in presence of Conc. H₂SO₄ Methyl salicylate is formed.
c) / iii) By heating Lactic acid in presence of catalytic amount of Conc. H2SO4 Lactide - a cyclic diester - is formed.

![Chemical structure of Lactic acid and Lactide](image)

\[
\text{CH}_3\text{CHO} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH(OH)}\text{C} = \text{O} + 2\text{H}_2\text{O} \\
\text{Lactide}
\]

d) / iv) Lithium Aluminium hydride reduces Benzoic acid to Benzyl alcohol.

\[
\text{LiAlH}_4 \quad \text{LiAlH}_4 \\
\text{C}_6\text{H}_5\text{COOH} \rightarrow [\text{C}_6\text{H}_5\text{CHO}] \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OH}
\]

3. Discuss / Give / Write the mechanism of bromination of salicylic acid.

Reaction of Salicylic acid with Bromine water gives 2,4,6- Tribromo phenol.

\[
\text{OH} \xrightarrow{\text{Br}_2} [\text{OH}] \xrightarrow{\text{Br}_2} \text{Br} \text{OH} \\
\text{Br} \text{Br} \text{Br} \\
\text{2,4,6 Tribromo phenol}
\]

**Mechanism:** This reaction involves bromination with decarboxylation.
4. Distinguish between formic acid and acetic acid. **Or How do you distinguish formic acid from acetic acid?**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Formic acid</th>
<th>Acetic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HCOOH</td>
<td>CH₃COOH</td>
</tr>
<tr>
<td></td>
<td>Formic acid cannot be prepared by Grignard reagent since the acid contains only one carbon atom.</td>
<td>Acetic acid can be prepared by Grignard reagent</td>
</tr>
<tr>
<td>2</td>
<td>Formic acid <strong>does not undergo</strong> intermolecular dehydration on heating with P₂O₅.</td>
<td>Acetic acid <strong>undergoes</strong> intermolecular dehydration on heating with P₂O₅ <strong>forming</strong> acetic anhydride.</td>
</tr>
<tr>
<td>3</td>
<td>On dehydration with Conc. H₂SO₄ forms CO.</td>
<td>No reaction</td>
</tr>
<tr>
<td></td>
<td>Conc. H₂SO₄</td>
<td>HCOOH → H₂O + CO</td>
</tr>
<tr>
<td>4</td>
<td><strong>With PCl₅</strong> formic acid forms an unstable formyl chloride which decomposes to CO and HCl.</td>
<td><strong>With PCl₅</strong> acetic acid forms <strong>stable acetyl chloride.</strong></td>
</tr>
</tbody>
</table>
5. Explain the mechanism of Kolbe’s reaction Or Write the preparation of Salicylic acid with mechanism.

Salicylic acid can be prepared by heating Phenol with NaOH to get Sodium phenoxide.

\[
\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \xrightarrow{\Delta} \text{C}_6\text{H}_5\text{ONa}
\]

When Sodium phenoxide is heated with CO2 at 403 K under pressure Sodium salicylate is formed. This reaction is called ‘Kolbe’s reaction’.
Sodium salicylate is decomposed by dilute HCl. Salicylic acid is formed.

**Mechanism:** CO$_2$ is the electrophile in this reaction.

6. Explain the reactions of CH$_3$CONH$_2$ with i) P$_2$O$_5$ ii) Br$_2$ / NaOH and iii) hydrolysis by an acid.
   i) **Dehydration:** Heating with P$_2$O$_5$, CH$_3$CONH$_2$ forms Methyl cyanide.
   \[
   \text{CH}_3\text{CONH}_2 \rightarrow \text{CH}_3\equiv\text{N} - \text{H}_2\text{O}
   \]
   ii) **Hoffmann’s reaction:** CH$_3$CONH$_2$ reacts with Br$_2$ / NaOH forming Methyl amine.
   \[
   \text{CH}_3\text{CONH}_2 \rightarrow \text{CH}_3\text{NH}_2 + \text{CO}_2
   \]
   NaOH
   iii) **Hydrolysis:** Catalysed by an acid CH$_3$CONH$_2$ is hydrolysed to Acetic acid.
   \[
   \text{H}^+ \quad \text{CH}_3\text{CONH}_2 \rightarrow \text{CH}_3\text{COOH} + \text{NH}_3
   \]
   H$_2$O Acetic acid

7. Give the equation for the action of heat on a) Oxalic acid b) Succinic acid c) Formic acid.
   a) Oxalic acid on heating at 373 K – 378 K loses water of hydration. On further heating above 473 K it decomposes to Formic acid and Carbon dioxide.
   \[
   (\text{COOH})_2\text{.2H}_2\text{O} \rightarrow (\text{COOH})_2 + 2\text{H}_2\text{O}
   \]
   \[
   \text{COOH} \quad \xrightarrow{473K} \text{HCOOH} + \text{CO}_2
   \]
   b) Succinic acid on heating to 300°C loses a molecule of water to form Succinic anhydride.
c) Formic acid gets decarboxylated on heating above 433 K to give H2 + CO2
\[ \text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2 \]

8. Give the mechanism involved in the esterification of a carboxylic acid with alcohol. Or Write the mechanism of esterification reaction. Or Give the mechanism of esterification.
Carboxylic acid reacts with Alcohols in presence of mineral acid as catalyst and forms Esters.

\[ \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \]

**Mechanism:**
Protonation of the – OH group of the acid enhances the nucleophilic attack by alcohol to give the ester.

**Step 1:** Protonation of carboxylic acid.

**Step 2:** Attack by nucleophile.

9. How the following conversions are carried out / take place?
   i) Methyl acetate → ethyl acetate
   ii) Lactic acid → Pyruvic acid
   iii) Methyl cyanide → Acetamide
   iv) Succinic acid → succinimide.
i) In presence of a little acid, Methyl acetate is cleaved by Ethyl alcohol to form Ethyl acetate. This is called ‘Trans esterification’.

\[ H^+ + CH_3COOCH_3 + C_2H_5OH \rightarrow CH_3COOC_2H_5 + CH_3OH \]

ii) Mild oxidising agent like Fenton’s reagent, Fe2+/H2O2 forms Pyruvic acid with Lactic acid

\[ (O) \quad CH_3CH(OH)COOH \rightarrow CH_3COCOOH \]

\[ H_2O_2/Fe^{2+} \]

iii) Partial hydrolysis of Methyl cyanide with alkaline Hydrogen peroxide gives Acetamide

\[ CH_3C≡N \rightarrow CH_3CONH_2 \]

NaOH

iv) Succinic acid reacts with NH3 and forms Ammonium succinate. On strong heating Ammonium succinate forms Succinimide.

\[ \text{Succinic acid} + 2\text{NH}_3 \rightarrow \text{Ammonium succinate} \rightarrow \text{Succinimide} \]

10. How is benzoic acid obtained from a) C6H5CH2CH3 / Ethyl benzene b) Phenyl cyanide c) Carbon dioxide?

a) By oxidation: Ethyl benzene is oxidised by acidified KMnO4 or Potassium dichromate or alkaline KMnO4 gives Benzoic acid.

\[ C_6H_5CH_2CH_3 \rightarrow C_6H_5COOH \]

b) Hydrolysis: Phenyl cyanide is hydrolysed with aqueous acid to give Benzoic acid.

\[ C_6H_5CN \rightarrow C_6H_5CONH_2 \rightarrow C_6H_5COOH \]

H2O Benzamide H2O

c) From Grignard reagent: Carbonation of C6H5MgBr followed by hydrolysis gives Benzoic acid.

Or CO2 reacts with C6H5MgBr followed by hydrolysis gives Benzoic acid.

11. How is lactic acid manufactured in large scale? How can it be converted into cyclic diester?

Industrially Lactic acid is made by the Fermentation of solution of cane sugar or glucose.

1. To a dilute solution of cane sugar or glucose or maltose a little of sour milk or decayed cheese is added.
2. Temperature is maintained at 40 – 45°C for six days.
3. The *Bacillus aciditibacteri*um lacti, BAL brings forth fermentation.
4. Methyl glyoxal forms as *intermediate compound*.
5. Acid is removed by the *addition of CaCO₃* which precipitates Calcium lactate. It is filtered and *decomposed with dilute Sulphuric acid*.
6. The filtrate is *distilled under reduced pressure*.

\[
\text{H}_2\text{O} \\
\text{C}_{12}\text{H}_{22}\text{O}_{11} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6
\]

Cane sugar \hspace{2cm} Glucose \hspace{2cm} Fructose

\[
\text{BAL} \\
\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{CH}_3\text{COCHO} \rightarrow 2\text{CH}_3\text{CHOHCOOH}
\]

Methyl glyoxal \hspace{2cm} Lactic acid

**Formation of cyclic diester:**
By heating Lactic acid *in presence of catalytic amount of Conc. H}_2\text{SO}_4* Lactide - a cyclic diester - is formed.

\[
\begin{align*}
\text{CH}_3\text{CH(OH)COOH} & \quad \text{H}^+ \quad \text{CH}_3\text{CH(OH)COOH} \\
\text{Lactic acid} & \quad \text{Lactide}
\end{align*}
\]

12. **How is lactic acid synthesised from acetylene? How can it be converted into cyclic diester**

1. Acetylene is prepared by striking an Electric arc using Carbon electrodes in an atmosphere of Hydrogen.
2. This is passed through dilute Sulphuric acid containing Mercuric ion catalyst. Acetaldehyde is formed.
3. It is converted to Cyanohydrin on treatment with HCN,
4. which is then *hydrolysed* to get Lactic acid.

\[
\text{Electric arc} \quad \text{dil. H}_2\text{SO}_4 \quad \text{HCN} \quad \text{dil. HCl}
\]

\[
2\text{C} + \text{H}_2 \rightarrow \text{CH} = \text{CH} \rightarrow \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CH(OH)CN} \rightarrow \text{CH}_3\text{CH(OH)COOH}
\]

Arc \hspace{2cm} 1\% \text{HgSO}_4 \hspace{2cm} \text{Acetaldehyde cyanohydrin} \hspace{2cm} \text{Lactic acid}

13. **How is oxalic acid manufactured from sodium formate?**

Oxalic acid is made industrially by *heating Sodium formate to 673 K.* to get Sodium oxalate.

\[
\text{673 K}
\]

\[
2\text{HCOONa} \rightarrow \text{NaOOC} – \text{COONa} + \text{H}_2
\]
The Sodium oxalate thus formed is dissolved in water and Calcium hydroxide added to precipitate Calcium oxalate. The solution is filtered and the Calcium oxalate precipitate is treated with calculated quantity of dilute Sulphuric acid to liberate the Oxalic acid.

\[
\text{COONa} + \text{Ca(OH)}_2 \rightarrow \text{Ca} + 2 \text{NaOH}
\]

\[
\text{COONa} \quad \text{COO}\backslash
\text{COO}\backslash \quad \text{COOH}
\]

\[
\text{Ca} + \text{H}_2\text{SO}_4 \rightarrow + \text{CaSO}_4 \downarrow
\]

\[
\text{COO}\backslash \quad \text{COOH}
\]

Calcium sulphate precipitates and Oxalic acid is crystallised as the hydrate\((\text{COOH})_2\cdot\text{H}_2\text{O}\).

14. What happens when i) Oxalic acid is treated with \(\text{NH}_3\) ii) Benzoic acid is treated with \(\text{PCl}_5\)?

i) When Oxalic acid is treated with \(\text{NH}_3\) gives Ammonium oxalate first which then loses water molecule to give Oxamide.

\[
\text{COOH} + 2\text{NH}_3 \rightarrow \text{COONH}_4 \xrightarrow{\Delta} \text{CONH}_2 + 2\text{H}_2\text{O}
\]

Ammonium oxalate Oxamide

15. What happens when benzoic acid reacts with i) conc. \(\text{HNO}_3\) / Conc. \(\text{H}_2\text{SO}_4\) ii) \(\text{Cl}_2\) / \(\text{FeCl}_3\) iii) \(\text{PCl}_5\)?

i) Nitrination: When benzoic acid reacts with Conc. \(\text{HNO}_3\) / Conc. \(\text{H}_2\text{SO}_4\) \(\text{m}\text{- nitro benzoic acid is formed.}\)

\[
\text{COOH} \xrightarrow{\text{Conc. HNO}_3} \text{CON}_2
\]

\[
\text{COOH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{m-nitro benzoic acid}
\]

ii) Chlorination: When benzoic acid reacts with \(\text{Cl}_2\) in the presence of Anhydrous \(\text{FeCl}_3\) (a Lewis acid - a Catalyst) \(\text{m}\text{- chloro benzoic acid is formed.}\)

\[
\text{COOH} \xrightarrow{\text{Anhyd FeCl}_3} \text{Cl}
\]

\[
\text{COOH} \xrightarrow{\text{Anhyd FeCl}_3} \text{m-chloro benzoic acid}
\]
iii) When Benzoic acid reacts with Phosphorous pentachloride, \( \text{PCl}_5 \) Benzyol chloride is formed.
\[
\text{C}_6\text{H}_5\text{COOH} + \text{PCl}_5 \rightarrow \text{C}_6\text{H}_5\text{COCl} + \text{POCl}_3 + \text{HCl}
\]

16. What happens when lactic acid is i) treated with dilute \( \text{H}_2\text{SO}_4 \) ii) added to / treated with \( \text{PCl}_5 \) iii) oxidised with alkaline / acidified \( \text{KMnO}_4 \)?

i) With dil. \( \text{H}_2\text{SO}_4 \) Lactic acid dissociates to Acetaldehyde and Formic acid.
\[
\text{dil. } \text{H}_2\text{SO}_4
\]
\[
\text{CH}_3\text{CH}(_\text{OH})\text{COOH} \rightarrow \text{CH}_3\text{CHO} + \text{HCOOH}
\]

ii) With \( \text{PCl}_5 \) Lactic acid forms Lactyl chloride.
\[
\text{CH}_3\text{CH}(_\text{OH})\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{–CH}–\text{COCl}
\]

iii) With dilute alkaline or acidified \( \text{KMnO}_4 \) Lactic acid decomposes forming Acetaldehyde.
\[
\text{CH}_3\text{CH}(_\text{OH})\text{COOH} + (\text{O}) \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} + \text{CO}_2
\]

17. What happens when lactic acid is i) treated with dilute \( \text{H}_2\text{SO}_4 \) ii) heated alone iii) oxidised with Fenton’s reagent?

i) With dil. \( \text{H}_2\text{SO}_4 \) Lactic acid dissociates to Acetaldehyde and Formic acid.
\[
\text{dil. } \text{H}_2\text{SO}_4
\]
\[
\text{CH}_3\text{CH}(_\text{OH})\text{COOH} \rightarrow \text{CH}_3\text{CHO} + \text{HCOOH}
\]

ii) By heating Lactic acid in presence of catalytic amount of Conc. \( \text{H}_2\text{SO}_4 \) Lactide - a cyclic diester - is formed.

iii) Mild oxidising agent like Fenton’s reagent, \( \text{Fe}^{2+} / \text{H}_2\text{O}_2 \) forms Pyruvic acid with Lactic acid
\[
(\text{O})
\]
\[
\text{CH}_3\text{CH}(_\text{OH})\text{COOH} \rightarrow \text{CH}_3\text{COCOOH}
\]
\[
\text{H}_2\text{O}_2/\text{Fe}^{2+}
\]

18. Discuss the isomerism exhibited by carboxylic acid.

1. Chain isomerism:
This arises due to the difference in the carbon chain of alkyl group attached to carboxyl group.
CH₃

CH₃ – CH₂ – CH₂ – CH₂ – COOH  

3-Methyl butanoic acid

Pentanoic acid

2. Functional isomerism:

Carboxylic acids may be functional isomers of esters.

CH₃ – CH₂ – COOH  

and  

CH₃ – COOCH₃  

H – COOC₂H₅

Propanoic acid  

Methyl acetate  

Ethyl formate

19. Explain i) HVZ – reaction  ii) trans-esterification reaction  iii) Kolbe's electrolytic reaction

i) HVZ – reaction (Hell-Volhard Zelinsky reaction):

Halogenation of Carboxylic acid with Halogen and Phosphorous trihalide.  

Conversion of Carboxylic acid to α - bromo acid with Br₂ / PBr₃

H₂O

RCH₂COOH → RCH₂COBr → RCHBrCOBr → RCHBrCOOH

ii) Trans-esterification reaction:

In presence of a little acid, Methyl acetate is cleaved by Ethyl alcohol to form Ethyl acetate.

CH₃COOCH₃ + C₂H₅OH → CH₃COOC₂H₅ + CH₃OH

iii) Kolbe's electrolytic reaction:

Electrolysis of concentrated aqueous solution of Sodium salt of acids gives Hydrocarbon.

Electrolysis

CH₃ – COO – Na → CH₃

+  

CH₃ – COO – Na → CH₃ + 2CO₂ + 2Na

Sodium

Ethane

20. Explain the reactions of formation of aspirin, methyl salicylate and 2, 4, 6-tribromophenol from salicylic acid. Or How can salicylic acid be converted to i) Aspirin  ii) Methyl salicylate  iii) 2, 4, 6 tribromophenol? Or How do Salicylic acid react with the following? a) (CH₃CO)₂O  b) CH₃OH  c) Br₂ / H₂O

i) Salicylic acid undergoes acetylation by heating with Acetic anhydride to form Aspirin.

Acetyl salicylic acid  
or Aspiin

 ii) Salicylic acid on heating with Methyl alcohol in presence of Conc. H₂SO₄ Methyl salicylate is formed.
iii) Reaction of Salicylic acid with bromine water gives 2, 4, 6-Tribromophenol

21. How do Succinic acid react with the following? i) NaOH ii) NH3 iii) PCl5

i) With NaOH: Succinic acid gives two kinds of salts - Mono sodium succinate, Disodium succinate

\[
\begin{align*}
\text{CH}_2\text{COOH} & \xrightarrow{\text{+ NaOH}} \text{CH}_2\text{COONa} \\
\text{CH}_2\text{COOH} & \xrightarrow{\text{+ NaOH}} \text{CH}_2\text{COONa}
\end{align*}
\]

Succinic acid

Mono sodium succinate

Disodium succinate

ii) With NH3: Succinic acid forms Ammonium succinate. On strong heating it forms Succinimide

\[
\begin{align*}
\text{CH}_2 - \text{COOH} & \xrightarrow{\text{+ 2NH}_3} \text{CH}_2\text{COONH}_4 \\
\text{CH}_2 - \text{COOH} & \xrightarrow{\Delta} \text{CH}_2\text{COOH} / \text{NH}
\end{align*}
\]

Succinic acid

Ammonium succinate

Succinimide

iii) With PCl5: Succinic acid forms Succinoyl chloride

\[
\begin{align*}
\text{CH}_2 - \text{COOH} & \xrightarrow{\text{+ PCl}_5} \text{CH}_2\text{COCl} \\
\text{CH}_2 - \text{COOH} & \xrightarrow{\text{+ PCl}_3 + \text{H}_2\text{O}} \text{Succinoyl chloride}
\end{align*}
\]

22. Explain: i) Claisen ester condensation ii) Friedel Crafts acetylation

i) Claisen ester condensation: In presence of strong bases like Sodium ethoxide, Methyl acetate undergoes condensation forming Aceto acetic ester.
ii) **Friedel Crafts acetylation**: In presence of anhydrous Aluminium chloride acetylation of Benzene takes place with the formation of Acetophenone.
Q.No 63 - Chemistry in Action

1. Explain briefly on (characteristics of) rocket propellants. Or Write a note on Rocket propellants.

1. Rocket motors are used both in space vehicles and in offensive weapons such as missiles. The propulsion system in most space vehicles consists of rocket engines powered by chemical propellants. These also called rocket propellants.

2. Propellants are combustible compounds which on ignition undergo rapid combustion to release large quantities of hot gases. A propellant is a combination of an oxidiser and a fuel.

   Working of a propellant:
   When a propellant is ignited, it burns to produce a large quantity of hot gases. These gases then come out through the nozzle of the rocket motor. The passage of gases through the nozzle of the rocket motor, provides the necessary thrust for the rocket to move forward according to the Newton’s Third law of Motion (to every action, there is an equal and opposite reaction).

   Examples:
   Hydrazine, Liquid hydrogen, Polyurethane, etc.

2. Explain briefly on colour and structure of dyes.

   The relationship between the colour of a substance and its structure was explained by a German scientist Otto Witt through the chromophore and auxochrome theory.

   According to this theory,

1. An organic compound appears coloured due to the presence of certain unsaturated groups (the groups with multiple bonds) in it. Such groups with multiple bonds are called chromophores.

   Examples:

   ![Chemical Structures]

2. The compounds containing the chromophore group is called chromogen. The colour intensity increases with the number of chromophores or the degree of conjugation.

   For example, ethene (CH2 = CH2) is colourless, but the compound CH3 – (CH = CH)6 – CH3 is yellow in colour.

3. The presence of certain groups which are not chromophores themselves, but deepen the colour of the chromogen. Such supporting groups are called auxochromes. Auxochromes may be acidic (phenolic) or basic.

   Examples:

   Some important auxochromes are –OH, –NH2, –NHR, NR2.

   The presence of an auxochrome in the chromogen molecule is essential to make it a dye.

   However, if an auxochrome is present in the meta position to the chromophore, it does not affect the colour.

   For example, in the compound p-hydroxyazobenzene (a bright red dye),
3. Give the characteristics of a dye.
   1. Should have a suitable colour.
   2. Should be able to fix itself or be capable of being fixed to the fabric.
   3. Should be fast to light.
   4. Should be resistant to the action of water, dilute acids and alkalies (all detergents and washing soaps are alkaline in nature).

4. How are Buna-S and Nylon-66 prepared?
   Buna-S is prepared by the polymerization of butadiene and styrene in presence of sodium metal.
   \[ nCH_2=CH\text{-}CH=CH_2 + nCH_2=CH_2 \xrightarrow{Na} \left( -CH_2=CH\text{-}CH=CH_2\text{-}CH_2\text{-}CH=CH_2\text{-} \right)_n \]
   Buna-S

   Nylon-66 is prepared by condensing adipic acid with hexamethylenediamine with the elimination of water molecule.
   \[ nH_2N\left(\text{CH}_2\right)_{6}NH_2 + nHO-C\text{-}(\text{CH}_2)_{4}\text{-}C\text{-}OH \xrightarrow{} \left[ \text{N}\left(\text{CH}_2\right)_{6}\text{-}N\text{-}(\text{CH}_2)_{4}\text{-}C \right]_n \]
   Nylon-66

5. What are chromophores and auxochromes? Give two examples for each.
   Chromophores:
   An organic compound appears coloured due to the presence of certain unsaturated groups (the groups with multiple bonds) in it. Such groups with multiple bonds are called chromophores.
Examples:

Auxochromes:
The presence of certain groups which are not chromophores themselves, but deepen the colour of the chromogen. Such supporting groups are called auxochromes. Auxochromes may be acidic (phenolic) or basic.

Examples:
Some important auxochromes are –OH, –NH₂, –NHR, NR₂.

6. Write a note on anaesthetics.
The drugs which produce loss of sensation are called anaesthetics. They are classified into two types.
1. General anaesthetics are the agent, which bring about loss of all modalities of sensation, particularly pain along with ‘reversible’ loss of consciousness.
2. Local anaesthetics prevent the pain sensation in localised areas without affecting the degree of consciousness.

Examples:
Nitrous oxide, N₂O
Chloroform, CHCl₃
Ether, C₂H₅–O–C₂H₅

7. Write briefly on Buna rubbers.
Buna rubbers are obtained as a result of polymerisation / copolymerization of butadiene with acrylonitrile or styrene. There are two types of Buna rubbers.
1. Buna-S is obtained by the polymerization of butadiene and styrene in presence of sodium metal.

\[
n\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + n\text{CH} = \text{CH}_2 \xrightarrow{\text{Na}} \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\ldots \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\ldots \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\ldots
\]

Properties: Neoprene and Buna-S are extremely resistant towards wear and tear
Uses: for the manufacture of tyres, rubber tubes and other mechanical rubber goods.

2. Buna-N is obtained as a result of copolymerisation of two parts of butadiene with one part of acrylonitrile in the presence of sodium metal.

\[
2\text{CH}_2 = \text{CH} = \text{CH}_2 + \text{CH}_2 = \text{CH} \xrightarrow{\text{Na}} \text{CH}_2 = \text{CH} = \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\ldots \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\ldots 
\]

Buna-N
Properties: Buna-N rubber is hard and extremely resistant to the swelling action of oils (petrol), solvents, heat etc.
Uses: for the manufacture of storage tanks for the solvents.
**10-MARKS**

**Q.No-64(a)-Periodic classification - II**

1. **Explain any three factors which affect the ionisation energy.**

   1. **Size of atom or ion**

      **Ionization energy \( \alpha \ 1 / \text{Size of atom or ion} \)**

      The ionization energy decreases with the increasing size of atom. The larger the size of atom, lesser is the ionization energy.

      This is due to the fact that **electrons are tightly held in smaller atoms whereas in large atoms, electrons are held quite loose**, i.e., lesser energy is required for removal of electrons from larger atoms than the smaller one.

      Hence **ionization energy is lower for larger atoms and higher for smaller atoms.**

   2. **Magnitude of nuclear charge**

      **Ionization energy \( \alpha \ \text{Effective nuclear charge} \)**

      The higher the nuclear charge of protons in the nucleus, the higher is the ionization energy.

      Because of the higher nuclear charge, the **electrons are bound with more force** and hence higher energy will be required for their removal.

   3. **Effect of number of electrons in the inner shells.** (Screening or shielding effect)

      **Ionization energy \( \alpha \ 1 / \text{Shielding effect} \)**

      The attractive force exerted by the nucleus on the most loosely bound electron is at least partially counterbalanced by the repulsive forces exerted by the electrons present in the inner shells. The electron to be removed is thus shielded from the nucleus by the electrons in the inner shell. Thus, the **electron in the valence shell experiences less attraction from the nucleus.** Hence the ionization energy will be low. This is another reason why ionization energy decreases in moving down a group.

   4. **Effect of shape of orbital.** The shape of orbital also influences the ionization potential. As **s-electrons remain closer to the nucleus than p-,d-, and f-electrons of the same valence shell**, the ionization energy decreases in the order given below:

      \( s > p > d > f \)

   5. **Effect of arrangement of electrons.** The **more stable the electronic arrangement, the greater is the ionization energy.** As the noble gases have the stabllest electronic arrangements, they show maximum ionization energy.

2. **Explain how electronegativity values help to find out the percentage of ionic character in polar covalent bond.**

   Pauling estimated the percentage of ionic character in various \( A\delta^-B\delta^+ \) polar covalent bonds from known \( (XA-XB) \) values and has derived the following conclusions:

   1. When \( (XA-XB) = 1.7 \), the amount of ionic character in \( A\delta^-B\delta^+ \) bond is 50% and that of covalent character is also 50%. Thus A-B bond is **50% ionic and 50% covalent.**

   2. When \( (XA-XB) < 1.7 \), the amount of ionic character in \( A\delta^-B\delta^+ \) bond is less than 50% and that of covalent character is more than 50%. Thus \( A\delta^-B\delta^+ \) bond is **predominantly covalent** and hence is represented as A–B.
3. When \((XA–XB) > 1.7\), the amount of ionic character in \(A\delta–B\delta^+\) bond is more than 50% and that of covalent character is less than 50%. Hence \(A\delta–B\delta^+\) bond is predominantly ionic and hence is represented as \(A–B^+\).

3. **Explain Pauling’s method to determine / calculate ionic radii. Or How is ionic radius determined by Pauling’s method?**

Pauling has calculated the radii of the ions on the basis of the observed inter nuclear distances in four crystals namely NaF, KCl, RbBr and CsI. In each ionic crystal the cations and anions are isoelectronic with inert gas configuration.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Cation</th>
<th>Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF crystal</td>
<td>Na⁺</td>
<td>F⁻</td>
</tr>
<tr>
<td>KCl crystal</td>
<td>K⁺</td>
<td>Cl⁻</td>
</tr>
</tbody>
</table>

Further the following two assumptions are made to assign the ionic radii.

1. The cations and anions of an ionic crystal are assumed to be in contact with each other and hence the sum of their radii will be equal to the inter nuclear distance between them.

\[
r(C^+) + r(A^-) = d(C^+–A^-) \tag{1}
\]

Where,
- \(r(C^+)\) - radius of cation, C⁺
- \(r(A^-)\) - radius of anion, A⁻
- \(d(C^+–A^-)\) - internuclear distance between C⁺ and A⁻ ions in C⁺A⁻ ionic crystal

2. For a given noble gas configuration, the radius of an ion is inversely proportional to its effective nuclear charge. i.e.

\[
r(C^+) \propto \frac{1}{Z^*(C^+)} \tag{2}
\]

\[
r(A^-) \propto \frac{1}{Z^*(A^-)} \tag{3}
\]

Where,
- \(Z^*(C^+)\) & \(Z^*(A^-)\) are the effective nuclear charges of cation (C⁺) and anion (A⁻) respectively.

On combining (2) & (3)

\[
r(C^+) / r(A^-) = Z^*(A^-) / Z^*(C^+) \tag{4}
\]

Hence the above two equations (1) & (4) can be used to evaluate the values of \(r(C^+)\) and \(r(A^-)\) provided that the values of \(d(C^+–A^-)\), \(Z^*(C^+)\) and \(Z^*(A^-)\) are known.

4. **Explain the various factors that affect / influence electron affinity.**

1. **Atomic size**

Electron affinity \(\propto \frac{1}{\text{Size of atom}}\)

Smaller the size of an atom, greater is its electron affinity. As the size of atom increases, the effective nuclear charge decreases or the nuclear attraction for adding electron decreases. Consequently, atom will have less tendency to attract additional electron towards itself.

Therefore, **Electron affinity \(\propto \text{Effective nuclear charge}\)**.

In general, electron affinity decreases in going down the group and increases in going from left to right across the period. On moving down the group atomic size increases and on going from left to right in a period atomic size decreases.

2. **Shielding or Screening Effect**
Electron affinity $\alpha$ / Shielding effect

Electronic energy state, lying between nucleus and outermost state hinder the nuclear attraction for incoming electron. Therefore, *greater the number of inner lying state less will be the electron affinity*.  

3. **Electronic Configuration** - The electronic configurations of elements influence their electron affinities to a considerable extent. **2np6 configuration** in their valence shell and there is no possibility for addition of an extra electron. Completely / half filled or stable electronic configuration leads to zero or low electron affinity.

Electron affinities of inert gases are zero. This is because their atoms have stable ns.

5. **How do electronegativity values help to find out the nature of bonding between atoms?**

The concept of electronegativity can be used to predict whether the bond between similar or dissimilar atoms is non-polar covalent bond, polar covalent bond (or) ionic bond.  

1. When $X_A = X_B$, i.e. $X_A - X_B = 0$, then A-B bond is **non polar covalent bond** or simply covalent bond and is represented as $A-B$.
   
   **Example:** H-H bond in H2 molecule is a covalent bond and is represented as H-H bond.  

2. When $X_A$ is slightly greater than $X_B$, i.e. $X_A - X_B$ is small, the A-B bond is **polar covalent bond** and is represented as $A\delta-\delta B$.
   
   **Example:** The O-H bonds in H2O molecule are polar covalent bonds and are represented as Oδ-Hδ+, since XO > XH and XO - XH is small.

3. When $X_A >> X_B$, i.e., $X_A - X_B$ is very large, A-B bond is **more ionic or polar bond** and is represented as $A-\delta B+$, Since $X_A >> X_B$.  

**Example:** Na-Cl bond in NaCl molecule is an ionic bond and is represented as Na+Cl- (Here Cl = A and Na = B).

6. **Write notes on Pauling’s and Mulliken’s Scale of Electronegativity.** Or Explain the Pauling scale for the determination of electronegativity. Give the disadvantage of Pauling scale.

1. **Pauling’s scale** is based on an empirical relation between the energy of a bond and the electronegativities of bonded atoms.

Consider a bond A-B between two dissimilar atoms A and B of a molecule AB. Let the bond energies of A-A, B-B and A-B bonds be represented as $E_{A-A}$, $E_{B-B}$ and $E_{A-B}$ respectively. It may be seen that the bond dissociation energy of A-B is almost higher than the geometric mean of the bond dissociation energies of A-A and B-B bonds i.e.,  

$E_{A-B} > \sqrt{E_{A-A} \times E_{B-B}}$

Their difference ($\Delta$) is related to the difference in the electronegativities of A and B according to the following equation

$$\Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$$

$$\Delta = (X_A - X_B)^2 \text{ (or)}$$

$0.208 \sqrt{\Delta} = X_A - X_B$

Here, $X_A$ and $X_B$ are the electronegativities of A and B respectively. The factor 0.208 arises from the conversion of kcals to electron volt.
Considering arbitrarily the electronegativity of hydrogen to be 2.1, Pauling calculated electronegativities of other elements with the help of this equation.

**Disadvantage of Pauling's scale:**
Bond energies are not known with any degree of accuracy for many solid elements.

2. Mulliken suggested an alternative approach to electronegativity based on ionization energy and electron affinity of an atom. According to this method electronegativity could be regarded as the average of the ionization energy and electron affinity of an atom

Electronegativity = \( \frac{I.E + E.A}{2} \)

Mulliken used ionisation energy and electron affinity values measured in electron volts and values were found to be 2.8 times higher than Pauling values. The values of ionisation energy and electron affinity are measured in kJ mol\(^{-1}\) and 1eV = 96.48 kJ mol\(^{-1}\). Therefore the commonly accepted Pauling values are more nearly obtained by

Electronegativity = \( \frac{I.E + E.A}{2} \times 2.8 \times 96.48 = \frac{I.E + E.A}{540} \)

This method has an ordinary theoretical basis and also has advantage that different values can be obtained for different oxidation states of the same element.

**Disadvantage of Mulliken’s scale:**
Electron affinities with the exception of a few elements are not reliably known

7. **Explain the variation of ionisation energy along the group and period.**

In a period, the value of ionisation energy increases from left to right with breaks where the atoms have somewhat stable configurations. This is due to the reason that the nuclear charge increases whereas atomic radius decreases.

In a group, the ionisation energy decreases from top to bottom. This is due to the effect of the increased atomic radius
Q.No-64(b)-p - Block Elements - II

1. Describe in detail how noble gases are isolated by Dewar's process. Or How are noble gases separated by Dewar's method?

1. Principle:
The mixture of noble gases obtained by the Ramsay - Rayleigh's method is separated into individual constituents by the use of coconut charcoal which adsorbs different gases at different temperatures.

2. Separation of noble gases (Dewar’s method)
The mixture of noble gases is passed into a double-walled bulb containing coconut charcoal and placed in a low temperature bath at 173K. It is allowed to remain in contact with the charcoal for about half an hour.

3. At 173K, only argon, krypton and xenon are adsorbed by the charcoal while helium and neon remain unadsorbed. These are pumped out and collected.

4. at 93K which completely adsorbs neon leaving free helium.

The charcoal at 173K containing argon, krypton and xenon is placed in contact with another charcoal

5. at the temperature of the liquid air (temp.77K) when argon diffuse into the other charcoal.

The temperature of the first charcoal (temp.173K) still containing krypton and xenon is

6. raised to 183K when krypton is set free while xenon remain adsorbed in the charcoal. When it is heated, xenon is recovered.

2. Describe in detail how noble gases are isolated from air by Ramsay - Rayleigh's method.
A mixture of air and oxygen is constantly admitted into a glass globe of about 50 litres capacity. Two platinum electrodes are introduced and a discharge from a transformer of about 6000 - 8000 volts is passed by the action of which nitrogen and oxygen rapidly combine to form oxides of nitrogen. The oxides are dissolved out in a solution of sodium hydroxide continuously circulated through the flask.

\[
\begin{align*}
N_2 + O_2 & \rightarrow 2 \text{ NO} \\
2 \text{ NO} + O_2 & \rightarrow 2\text{NO}_2 \\
2\text{NO}_2 + 2\text{NaOH} & \rightarrow \text{NaNO}_3 + \text{NaNO}_2 + \text{H}_2\text{O}
\end{align*}
\]

Oxygen if any is removed by introducing alkaline pyrogallol in the globe. The supply of air and electric discharge is shut after some time and the remaining mixture of noble gases is pumped out.

Chemical method for isolation of noble gases

3. Discuss the structure of interhalogen compounds of AX and AX3 type.

Type AX. As expected, the compounds of the type AX are linear. Thus CIF, BrF, BrCl, IBr and ICl are all linear in structure.

Electronic structure of Chlorine atom, in the ground state and hybridized state is represented as

Linear structure of the interhalogen compounds of the type AX
Although the spatial arrangement of the four electron pairs \((\text{bp} = 1 \text{ and } \text{lps} = 3)\) around the central chlorine atom is \textit{tetrahedral}, due to the presence of three lone pairs of electrons in three hybrid orbitals, the shape of AX molecule gets distorted and become linear. 

\textbf{Type AX3} Compounds of the type AX3 have \textit{trigonal bipyramidal structure}, Fig. 3.5 for the ClF3 molecule.

Bipyramidal structure arises out of \textit{sp3d} hybridisation involved in the formation of this compound, as illustrated in the Fig.3.6. The three dotted arrows indicate electrons contributed by the three fluorine atoms (without lone pair it is T-shaped).

\textbf{Fig. 3.5 Bi pyramidal structure of ClF3 molecule}

\textbf{Fig. 3.6 sp3d hybridisation involved in the formation of ClF3 molecule}

4. Explain the extraction of lead from its ore. Or \textbf{How is lead extracted from its ore?}

\textbf{Extraction:} Lead is mainly extracted from the sulphide ore \textit{galena}. Galena contains lead sulphide and small quantities of silver.

1. \textbf{Concentration:} Froth floatation process.
2. \textbf{Smelting in a Reverbory furnace:} The concentrated ore is roasted in a reverberatory furnace at a moderate temperature. The temperature of furnace is controlled by regulating the air supply. During roasting, \textit{galena is partly oxidized to lead monoxide and partly to lead sulphate}.

\[2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2\]
\[\text{PbS} + 2\text{O}_2 \rightarrow \text{PbSO}_4\]

More of galena is then added. The temperature is raised and simultaneously the air supply is reduced. Lead sulphide reacts with the two oxidised products giving lead.

\[\text{PbS} + 2\text{PbO} \rightarrow 3\text{Pb} + \text{SO}_2\]
\[\text{PbS} + \text{PbSO}_4 \rightarrow 2\text{Pb} + 2\text{SO}_2\]
Thus in this process roasting and smelting are carried out in the same furnace, at two different temperatures. About 90% of lead is obtained as metal, the rest passes into slag. Lead is recovered from the slag by heating with lime and powdered coke.

**Purification of Lead**
Lead extracted by the above method contains impurities such as silver, copper, tin, bismuth, gold and iron. It is refined by the following processes.

**a. Liquidation**
The impure metal is heated on a sloping hearth. Lead melts and flows down the slope. The infusible impurities remain on the hearth.

**b. Desilverisation**
Silver is removed by either Pattinson’s process or Park’s process.

**c. Electrolytic refining**
- **Anode** – Impure lead
- **Cathode** – Very pure lead
- **Electrolyte** – Lead fluosilicate (PbSiF$_6$) + Hydrofluosilicic Acid (H$_2$SiF$_6$

The metallic impurities which are more electropositive than lead, such as iron and tin, go into the solution while the rest of the impurities are thrown down as anode mud.

5. Explain the following: i) dehydrating property of P$_2$O$_5$ ii) oxidizing power of fluorine.

i) Phosphorus pentoxide extracts water from many inorganic compounds including sulphuric acid, nitric acid and several organic compounds. It is therefore, used as a powerful dehydrating agent.

\[
P_4O_{10} 
\]
\[
H_2SO_4 \rightarrow SO_3 
- H_2O 
P_4O_{10} 
\]
\[
2HNO_3 \rightarrow N_2O_5 
- H_2O 
P_4O_{10} 
\]
\[
RCONH_2 \rightarrow RCN 
- H_2O 
\]

ii) An important feature of the halogen is their oxidizing property which is due to high electron affinity of halogen atoms. The oxidizing power decreases from fluorine to iodine. Fluorine is the strongest oxidising agent. It oxidises other halide ions to halogens in solution or when dry.

\[
F_2 + 2X^- \rightarrow 2F^- + X_2 \quad (X^- = Cl^-, Br^-, I^-) 
\]

Halogen of low atomic number oxidises the halide ion of higher atomic number.

7. How does Fluorine differ from other halogens? Or Write the anomalous nature of fluorine.

1. Fluorine is the most reactive element among halogen. This is due to the minimum value of F–F bond dissociation energy.
2. Fluorine decomposes cold dilute alkalies liberating OF$_2$ and with conc. alkali, O$_2$ is liberated. Under similar conditions, the other halogens will give rise to the hypohalites and halates respectively.
3. It has the **greatest affinity for hydrogen**, forming HF which is associated **due to the hydrogen bonding**. Hydrofluoric acid is a weak acid whereas the other hydrohalic acids are strong acids. 

...... H– F...... H– F..... H– F.

4. It differs markedly from the other halogens in that it can **form two types of salts with metals**. NaF and NaHF₂.

5. The salts of HF differ from the corresponding salts of other hydrogen acids. **AgF is soluble in water** while the other AgX are insoluble.

6. Being strongly electronegative it **can have only a negative oxidation state** while the other halogens can have negative as well as positive oxidation state.

7. **HF attacks glass** while others do not.

8. Fluorine, **because of the absence of d-orbitals in its valence shell does not form any polyhalides**. Thus we have I₃–, Br₃–, Cl₃– ions but no F₃– ion.

**8. How is fluorine isolated from their fluorides by Dennis method?**

In **Dennis' Method** fluorine is prepared by the **electrolysis of fused sodium or potassium hydrogen fluoride (perfectly dry)**. Electrolysis is carried out between graphite electrodes in a V-shaped electrically heated copper tube. The ends of the tube are covered with copper caps into which the graphite electrodes are fixed with bakelite cement. The copper tube is thickly lagged to prevent loss of heat.

\[
\begin{align*}
\text{KHF}_2 & \rightarrow \text{KF} + \text{HF} \\
\text{HF} & \rightarrow \text{H}^+ + \text{F}^- \\
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2 \quad \text{(At cathode)} \\
2\text{F}^- & \rightarrow 2e^- \rightarrow \text{F}_2 \quad \text{(At anode)}
\end{align*}
\]

**Preparation of fluorine**

Fluorine liberated at the anode is passed through the U-tube containing sodium fluoride. This removes the hydrogen fluoride vapours coming with fluorine.

\[
\text{NaF} + \text{HF} \rightarrow \text{NaHF}_2
\]

9. **Illustrate i) tribasic nature of orthophosphoric acid ii) reducing property of Phosphorus acid.**
Orthophosphoric acid is a tribasic acid. It combines with alkalies like NaOH to form three series of salts.

\[
\begin{align*}
H_3PO_4 + NaOH & \rightarrow NaH_2PO_4 + H_2O \\
& \quad \text{Sodium Di hydrogen Phosphate} \\
H_3PO_4 + 2NaOH & \rightarrow Na_2HPO_4 + 2H_2O \\
& \quad \text{Disodium hydrogen Phosphate} \\
H_3PO_4 + 3NaOH & \rightarrow Na_3PO_4 + 3H_2O \\
& \quad \text{Sodium Phosphate}
\end{align*}
\]

Phosphorus acid is a powerful reducing agent because it has P-H bond. It reduces silver nitrate solution into silver.

\[
2AgNO_3 + H_3PO_3 + H_2O \rightarrow 2Ag + H_3PO_4 + 2HNO_3
\]

10. **Mention the uses of silicones.**
   1. Excellent insulators for electric motors and other appliances
   2. Straight chain polymers of 20 to 500 units are used as silicone fluids. These polymers are used in waterproofing textiles, as lubricants and as polish.
   3. Silicone rubbers are mixed with paints to make them damp-resistant.
   4. Silicone resins are used as non-stick coating for pans and are used in paints and varnish.
   5. Silicone oils are used for high temperature oil bath, high vacuum pump etc.

11. **Write any five uses of Fluorine**
   1. Fluorine is used in the manufacture of freons. These non-toxic, non-combustible and volatile liquids are used as refrigerants in refrigerators, deep freezers and air conditioners.
   2. CaF_2_ is used as flux in metallurgy.
   3. NaF is used as a preservative to prevent fermentation and also for preventing dental cavities.
   4. SF_6_ is used as an insulating material in high voltage equipment.
   5. Teflon is used as container to store hydrofluoric acid.
   6. UF_6_ is used in the separation of U-235 from U-238.

12. **Write a short note on Etching on glass**

Industrially, Hydrogen fluoride is obtained by heating fluorspar (CaF_2_) with conc. H_2SO_4_ in a lead vessel.

\[
\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{HF}
\]

HF distils over and the vapours are condensed in water in a lead receiver. Aqueous HF thus obtained is stored in wax bottles. It cannot be stored in glass or silica bottles as it attacks silicates and silica.

\[
\begin{align*}
\text{Na}_2 \text{SiO}_3 + 6\text{HF} & \rightarrow \text{Na}_2\text{SiF}_6 + 3\text{H}_2\text{O} \\
\text{SiO}_2 + 4\text{HF} & \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}
\end{align*}
\]

The action of hydrofluoric acid on silica and silicates is used for etching glass. The glass article is first covered with a film on wax. The design to be etched is now drawn on the waxed surface and is then exposed to the action of hydrofluoric acid. Now the glass can be very soon etched. The wax is finally washed off with turpentine.
Q.No-65(a)-Coordination Compounds

1. Explain the type of hybridisation, magnetic property and geometry for [Ni(CN)4]2– and [Ni(NH3)4]2+ using VB theory. Or [Ni(CN)4]2– is diamagnetic whereas [Ni(NH3)4]2+ is paramagnetic. Explain (using VB theory). Or Apply VB theory to find out the geometry of [Ni(NH3)4]2+ and calculate its magnetic moment.

1) [Ni(NH3)4]2+

Nickel atom
Outer electronic configuration 3d84s2

Number of unpaired electrons = 2
\[ \mu_s = \sqrt{2(2+2)} \]

Paramagnetic moment, \( \mu_s = 2.83 \text{BM} \)
The molecule is paramagnetic.
Since the hybridisation is sp3, the geometry of the molecule is tetrahedral.

2) [Ni(CN)4]2–

The ligand CN- is a powerful ligand. Hence it forces the unpaired electrons to pair up in d orbitals.
Hence this complex ion does not contain unpaired electrons.

Paramagnetic moment, \( \mu_s = 0 \)
The molecule is diamagnetic.

Since the hybridisation is dsp2 hybridization, the geometry of the molecule is square planar.
2. Apply V.B. theory for magnetic properties of $[\text{Fe(CN)}_6]^{4-}$ and $[\text{FeF}_6]^{4-}$ and explain the shape. Or In what way does $[\text{FeF}_6]^{4-}$ differ from $[\text{Fe(CN)}_6]^{4-}$? Or Mention the type of hybridisation, magnetic property and geometry of the following complexes using VB theory. Or Write the application of VB theory on the following complexes: i) $[\text{FeF}_6]^{4-}$ ii) $[\text{Fe(CN)}_6]^{4-}$

$[\text{Fe(CN)}_6]^{4-}$

1) Nickel atom

**Outer electronic configuration** $3d^64s^2$

<table>
<thead>
<tr>
<th>3d</th>
<th>4s</th>
<th>4p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe atom</td>
<td>↑↓ ↑↑ ↑↑ ↑↑</td>
<td></td>
</tr>
<tr>
<td>Fe+2 ion</td>
<td>↑↓ ↑↑ ↑↑ ↑↑</td>
<td></td>
</tr>
</tbody>
</table>

$[\text{Fe(CN)}_6]^{4-}$

<table>
<thead>
<tr>
<th>3d</th>
<th>4s</th>
<th>4p</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CN-CN]</td>
<td>x x x x x x</td>
<td></td>
</tr>
</tbody>
</table>

$d_{2sp^3}$ hybridisation

The ligand CN- is a powerful ligand. Hence it forces the unpaired electrons to pair up in d orbitals. Hence this complex ion does not contain unpaired electrons.

**Paramagnetic moment, $\mu_s = 0$**

The molecule is diamagnetic.

Since the hybridisation is $d_{2sp^3}$, the geometry of the molecule is **Octahedral**.

$[\text{FeF}_6]^{4-}$

Fe atom

**Outer electronic configuration** $3d^64s^2$

<table>
<thead>
<tr>
<th>3d</th>
<th>4s</th>
<th>4p</th>
<th>4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe atom</td>
<td>↑↓ ↑↑ ↑↑ ↑↑</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe +2 ion</td>
<td>↑↓ ↑↑ ↑↑ ↑↑</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$[\text{FeF}_6]^{4-}$

Number of unpaired electrons = 4
Paramagnetic moment, $\mu_s = 4.90 \text{BM}$

The molecule is paramagnetic.

Since the hybridisation is sp$^3$d$^2$, the geometry of the molecule is Octahedral.

Or

$[\text{FeF}_6]^{4–}$ differ from $[\text{Fe(CN)}_6]^{4–}$

S.No. 1. Diagrammatic electronic configuration of the complexes

![Diagram of electronic configurations]

<table>
<thead>
<tr>
<th>S.No.</th>
<th>$[\text{FeF}_6]^{4–}$</th>
<th>$[\text{Fe(CN)}_6]^{4–}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>sp$^3$d$^2$ hybridisation</td>
<td>d$^2$sp$^3$ hybridisation</td>
</tr>
<tr>
<td>3</td>
<td>Number of unpaired electrons, $n = 4$</td>
<td>No unpaired electrons, $n = 0$</td>
</tr>
<tr>
<td>4</td>
<td>Paramagnetic</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>5</td>
<td>Paramagnetic moment, $\mu_s = 4.90 \text{BM}$</td>
<td>Paramagnetic moment, $\mu_s = 0$</td>
</tr>
<tr>
<td>6</td>
<td>$\text{F–}$ is a weak ligand</td>
<td>$\text{CN–}$ is a powerful ligand</td>
</tr>
</tbody>
</table>

3. Explain / Give / Write the postulates of Werner’s theory. Or State the postulates of Werner’s theory on co-ordination compound.

1) Every metal atom has two types of valencies
   i) Primary valency or ionisable valency
   ii) Secondary valency or non ionisable valency

2) The primary valency corresponds to the oxidation state of the metal ion.
   The primary valency of the metal ion is always satisfied by negative ions.

3) Secondary valency corresponds to the coordination number of the metal ion or atom. The secondary valencies may be satisfied by either negative ions or neutral molecules.

4) The molecules or ions that satisfy secondary valencies are called ligands.

5) The ligands which satisfy secondary valencies must project in definite directions in space. So the secondary valencies are directional in nature whereas the primary valencies are non-directional in nature.

6) The ligands have unshared pair of electrons. These unshared pair of electrons are donated to central metal ion or atom in a compound. Such compounds are called coordination compounds.
4. Explain Co-ordination isomerism and ionisation isomerism with suitable examples.

**Coordination isomerism:** In a bimetallic complex, both complex cation and complex anion may be present. In such a case the distribution of ligands between the two coordination spheres can vary, giving rise to isomers called the coordination isomers. This phenomenon is called coordination isomerism.

**Example:**

\[ [\text{Co}^{III}(\text{NH}_3)_6][\text{Cr}^{III}(\text{CN})_6] \] and \[ [\text{Cr}^{III}(\text{NH}_3)_6][\text{Co}^{III}(\text{CN})_6] \]

**Ionisation isomerism:** Coordination compounds having the same molecular formula but forming different ions in solution are called ionisation isomers. This property is known as ionisation isomerism.

**Example:**

\[ [\text{Co(NH}_3)_5\text{Br}]\text{SO}_4 [\text{Co(NH}_3)_5\text{SO}_4]\text{Br} \]

The red-violet isomer yields sulphate ion and the red isomer furnishes bromide ion in solution.

5. For the complexes \( \text{K}_4[\text{Fe(CN)}_6] \), \( [\text{Cu(NH}_3)_4]\text{SO}_4 \) mention a) IUPAC names b) Central metal Ion c) Ligand d) Co-ordination number e) Charge on the complex ion f) Geometry of the complex g) Nature of complex

\( \text{K}_4[\text{Fe(CN)}_6] \)

a) IUPAC names - Potassium hexacyanoferrate (II)

b) Central metal Ion - Fe(II) / Fe\(^{2+}\) / ferrous ion

c) Ligand - CN\(^-\), cyano

d) Co-ordination number - 6

e) Charge on the complex ion - -4

f) Geometry of the complex - Octahedral

g) Nature of complex - Anionic complex

\( [\text{Cu(NH}_3)_4]\text{SO}_4 \)

- Tetraamminecopper (II) sulphate

- Cu(II)

- NH3, ammine

- 4

- Square planar

- Cationic complex

6. How is chlorophyll important in environmental chemistry? Mention its function.

1. Chlorophyll is a magnesium-porphyrin complex. The magnesium is at the centre of the modified porphyrin ring septeon (corrin). The oxidation state of magnesium is +2 (Mg\(^{2+}\)). The modified porphyrin acts as the ligand.

2. There are several kinds of chlorophyll that vary slightly in their molecular structure.

3. In plants, chlorophyll ‘a’ is the pigment directly responsible for the transformation of light energy to chemical energy.

4. Hence in plants, the green pigment chlorophyll helps photosynthesis.

5. The conversion of atmospheric carbon dioxide and atmospheric moisture into carbohydrate and molecular oxygen in the presence of sunlight, by the plant is called as photosynthesis.

6. Chlorophyll acts as a light sensitisier in this important process.

7. \( x\text{CO}_2 + y\text{H}_2\text{O} \rightarrow Cx(\text{H}_2\text{O})y + \text{O}_2 \)
7. **In the coordination complex** \([\text{Co(NH}_3\text{)}_6\text{Cl}_3]\) **mention the following:**
   a) IUPAC name of the complex
   b) Ligand
   c) Central metal ion
   d) Co-ordination number
   e) Nature of complex

8. Photosynthesis requires, in addition to chlorophyll, the help of **four other metal complexes**, a manganese complex, two iron complexes and a copper complex.

9. All oxygenated animals take molecular oxygen through haemoglobin and release CO\(_2\). But chlorophyll helps in the conversion of atmosphere CO\(_2\) into molecular oxygen which acts as a fuel for human cell.
   a) IUPAC name of the complex - Hexaamminecobalt (III) chloride
   b) Ligand - NH\(_3\), ammine
   c) Central metal ion - Cobalt(III)
   d) Co-ordination number - 6
   e) Nature of complex - Cationic complex

8. **Mention the function of haemoglobin in natural process.**

1. Haemoglobin in the red blood cells **carries oxygen from the lungs to the tissues.**
2. It **delivers the oxygen molecule to myoglobin in the tissues.**
3. When the oxygen has been released for cell respiration, haemoglobin **loses its bright red colour and becomes purple.**
4. It then **combines with the waste carbon dioxide produced by the cells.**
5. **Deposits in the lungs so that the gas can be exhaled.**

9. **Explain hydrate and linkage isomerisms with suitable examples.**

**Hydrate isomerism or Solvate isomerism**

The best known examples of this type of isomerism occurs for chromium chloride CrCl\(_3\).6H\(_2\)O” which may contain 4, 5, (or) 6 coordinated water molecules.

1. \([\text{Cr(H}_2\text{O)}_4\text{Cl}_2]\).Cl.2H\(_2\)O - Bright green
2. \([\text{Cr(H}_2\text{O)}_5\text{Cl}]\).Cl.H\(_2\)O - grey-green
3. \([\text{Cr(H}_2\text{O)}_6]\).Cl\(_3\) - Violet

These isomers have very different chemical properties and on reaction with AgNO\(_3\) to test for Cl- ions, would find 1,2, and 3 Cl- ions in solution respectively.

**Linkage isomerism**

Linkage isomerism **occurs with ambidentate ligands.** These ligands are capable of coordinating in more than one way. The best known cases involve the monodentate ligands SCN-/NCS- and NO\(_2\)/ONO-

**Example:**

- \([\text{Co(NH}_3\text{)}_3\text{ONO}]\).Cl\(_2\) the **nitrito** isomer - O attached - red colour
- \([\text{Co(NH}_3\text{)}_3\text{NO}_2]\).Cl\(_2\) the **nitro** isomer - N attached - yellow colour

10. **Explain the following terms:** i) **Neutral ligand** ii) **chelates** iii) **coordination sphere.**

**i) Neutral ligand:** The neutral ligands are named as such without any special name. But water is written as ‘aqua’ : Ammonia is written as ammine. Note that two m’s to distinguish from organic amine
CO-Carbonyl, NO-Nitrosyl, NH$_2$ - CH$_2$ - NH$_2$- ethylenediamine (en), Pyridine C$_5$H$_5$N.

ii) **chelates**: If a ligand is capable of forming more than one bond with the central metal atom (or) ion then the ring structures are produced which are known as metal chelates. Hence the ring forming group is described as **chelating agents (or) polydentate ligands**.

![Diagram of chelation](image)

iii) **coordination sphere**: In a complex compound, it usually, central metal ion and the ligands are enclosed with in square bracket is called as coordination sphere. This represents a single constituent unit. The ionisable species are placed outside the square bracket.

$$[M(L)n](n^-) \text{ (or) } (n^+)$$

$$[\text{Fe(CN)}_6]^{4-}, [\text{Cu(NH}_3)_4]^{2+}$$

These ions do not ionise to give the test for constituent ions

11. **What are the postulates of valence bond theory?**

5. The following **table** gives the coordination number, orbital hybridisation and spatial geometry of the more important geometries.

<table>
<thead>
<tr>
<th>Coordination number</th>
<th>Types of hybridisation</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>sp</td>
<td>linear</td>
</tr>
<tr>
<td>4</td>
<td>sp$^3$</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>4</td>
<td>dsp$^2$</td>
<td>square planar</td>
</tr>
<tr>
<td>6</td>
<td>d$^2$sp$^3$</td>
<td>octahedral</td>
</tr>
<tr>
<td>6</td>
<td>sp$^3$d$^2$</td>
<td>octahedral</td>
</tr>
</tbody>
</table>
12. For the complex K₃[Cr(C₂O₄)₃].3H₂O mention a) Name  b) Central metal ion  c) Ligand  d) Co–ordination number  e) Geometry

a) Name  Potassiumtrioxalatocobaltate(III). trihydrate
b) Central metal ion  Chromium
c) Ligand  Cr₂O₄²⁻ / Oxalato
d) Co–ordination number  6 (3 bidentate ligands present)
e) Geometry  Octahedral

13. Write : a) IUPAC Name  b) Central metal ion  c) Ligand  d) Coordination number  e) Geometry of the complex [Co(en)₃]Cl₃

a) IUPAC Name  Tris(ethylenediamine)cobalt(III) chloride
b) Central metal ion  Co³⁺ / CoIII / Cobalt(III)
c) Ligand  en / ethylenediamine / NH₂ - CH₂ - CH₂ - NH₂
d) Coordination number  6 (3 bidentate ligands present)
e) Geometry of the complex  Octahedral

14. For the complex [Co(NH₃)₃(NO₂)₃] Write the following a) IUPAC Name  b) Central metal ion  c) Ligand  d) Coordination number  e) Geometry

a) IUPAC Name  Triamminetrinitrocobalt(III)
b) Central metal ion  Co³⁺ / CoIII / Cobalt(III)
c) Ligand  NH₃ / ammine & NO₂⁻ / nitro
d) Coordination number  6 (3 + 3 unidentate ligands present)
e) Geometry  Octahedral

15. Mention the the following for the complex [Co(NH₃)₄Cl₂]NO₂ a) IUPAC Name  b) Central metal ion  c) Ligand  d) Charge on the Co–ordination sphere  e) Co–ordination number

a) IUPAC Name  Tetraamminedichlorocobalt(III) nitrite
b) Central metal ion  Co³⁺ / CoIII / Cobalt(III)
c) Ligand  NH₃ / ammine & Cl⁻ / Chloro
d) Charge on the Co–ordination sphere  + 3 / Cationic complex / Positive Charge
e) Co–ordination number  6 (4 + 2 unidentate ligands present)
Q.No-65(b)-Nuclear Chemistry

1. Differentiate between chemical reaction and nuclear reaction. Or Distinguish chemical reactions from nuclear reactions.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Chemical reactions</th>
<th>Nuclear reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Involve some loss, gain or overlap of outer orbital electrons of the reactant atoms.</td>
<td>Involve emission of alpha, beta and gamma particles from the nucleus.</td>
</tr>
<tr>
<td>2</td>
<td>Balanced in terms of mass only</td>
<td>Balanced in terms of both mass and energy.</td>
</tr>
<tr>
<td>3</td>
<td>Energy changes are very less when compared with nuclear reactions.</td>
<td>Energy changes are far exceeding when compared with chemical reactions.</td>
</tr>
<tr>
<td>4</td>
<td>Energy is expressed in kJ / mol.</td>
<td>Energy is expressed in MeV / individual nucleus.</td>
</tr>
<tr>
<td>5</td>
<td>No new element is produced since nucleus is unaffected.</td>
<td>New element / isotope may be produced.</td>
</tr>
</tbody>
</table>

2. Distinguish between nuclear fusion reactions and nuclear fission reactions.
Both, nuclear fusion and nuclear fission reactions lead to the production of new nuclei, there are some basic differences between the two.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Nuclear Fission Reaction</th>
<th>Nuclear Fusion Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Splitting of a heavy nucleus into two or more light nuclei</td>
<td>Combination of two light nuclei to form a heavy nucleus</td>
</tr>
<tr>
<td>2</td>
<td>Fission reactions can be spontaneous.</td>
<td>Fusion reaction can never be spontaneous.</td>
</tr>
<tr>
<td>3</td>
<td>Fission reaction can be started by bombarding one nuclei with high energy on the other nuclei.</td>
<td>Fusion reaction can be started by increasing the temperature of the nuclei to be fused.</td>
</tr>
<tr>
<td>4</td>
<td>Takes place at room temperature</td>
<td>Requires a very high temperature of 108 K</td>
</tr>
<tr>
<td>5</td>
<td>It is a chain reaction</td>
<td>It is not a chain reaction</td>
</tr>
<tr>
<td>6</td>
<td>It is accompanied by emission of neutrons</td>
<td>It is not accompanied by emission of neutrons</td>
</tr>
<tr>
<td>7</td>
<td>Nuclear fission can be sustained and controlled in practical situations.</td>
<td>Nuclear fusion has not been sustained in the laboratory conditions.</td>
</tr>
</tbody>
</table>
3. Explain nuclear fission reaction with an example.
In the fission process, the heavy nucleus absorbs a neutron and forms an unstable compound nucleus. The compound nucleus then breaks up more or less in the middle to give fission product.
Example
A typical example of the fission process in the fission of uranium by neutrons is explained by the following equation.

\[ ^{92}_{235}U + ^{0}_{1}n \rightarrow ^{56}_{141}Ba + 3 ^{0}_{1}n + 200 \text{ MeV} \]

Further, the neutrons released (say three) from the fission of first uranium atoms can hit three other uranium atoms. In this way a chain reaction is set up resulting into the liberation of an enormous amount of energy. In the case of nuclear fission, \(^{92}_{235}U\) formed breaks up in several ways.

\[ ^{56}_{141}Ba + 3 ^{0}_{1}n \rightarrow ^{56}_{140}Ba + ^{36}_{18}Kr \]

\[ ^{92}_{235}U + ^{0}_{1}n \rightarrow ^{92}_{236}U \rightarrow ^{54}_{138}Xe + ^{38}_{19}Sr + 2 ^{0}_{1}n \]

4. Explain nuclear reactions that take place in sun.
It has been estimated that the sun is giving out energy equally in all possible directions at the rate of \(3.7 \times 10^{33}\) ergs/sec. The energy of the sun is supposed to arise from the fusion of hydrogen nuclei into helium nuclei which in going on inside it all the time.

The various fusion reactions taking place in the sun are as follows:

**Proton - proton chain reaction:**

\[ ^{1}_{1}H + ^{1}_{1}H \rightarrow ^{1}_{1}H + ^{1}_{0}e + \text{energy} \]

\[ ^{1}_{1}H + ^{1}_{1}H \rightarrow ^{2}_{1}He + ^{1}_{0}e + \text{energy} \]

The overall reaction, therefore, may be written as:

\[ 4 ^{1}_{1}H \rightarrow 2 ^{2}_{1}He + 2 ^{1}_{0}e + \text{energy} \]

5. Explain Radio carbon dating. Or Write a note on / briefly about radio carbon dating.
Radio carbon dating is based on the fact that \(^{6}_{14}C\), radioactive isotope of carbon is formed in the upper atmosphere by reaction with neutrons (from cosmic rays).

\[ ^{7}_{14}N + ^{0}_{1}n \rightarrow ^{6}_{14}C + ^{1}_{1}H \]

The \(^{14}C\) atoms thus produced are rapidly oxidised to \(^{14}CO_2\) which in turn is incorporated in plants as result of photosynthesis. Animals too consume \(^{14}C\) by eating plants.

On death, organisms cease to take in fresh carbonations. \(^{14}C\)-14 begins to decay.

\[ ^{6}_{14}C \rightarrow ^{7}_{14}N + ^{-1}_{0}e \]

5700 years a fossil (plant or animal) will lose half the amount of Carbon-14 present in its living state.
Therefore by knowing either the amount of C14 or the number of β-particles emitted per minute per gram of carbon at the initial and final stages, the age of carbon material can be determined by the following equation.

\[ t = \frac{2.303 \times t^{1/2}}{0.693} \log \frac{\text{Amount of C}^{14} \text{ in fresh wood}}{\text{Amount of C}^{14} \text{ in dead wood}} \]

Or

\[ t = \frac{2.303}{\lambda} \log \frac{\text{Amount of C}^{14} \text{ in fresh wood}}{\text{Amount of C}^{14} \text{ in dead wood}} \]

**Uses of Radio carbon dating**

1. For correlating facts of historical importance.
2. In understanding the evolution of life and
3. In understanding the rise and fall of civilizations or used to determine the age or period.


The highly destructive hydrogen bomb is also based on the fusion reactions of hydrogen to form helium producing large amount of energy. Hydrogen bomb consists of an arrangement for nuclear fission in the centre surrounded by a mixture of deuterium (1H2) and lithium isotope (3Li6). Fission reaction provides the high temperature necessary to start the fusion.

**Fusion reactions take place in hydrogen bomb.**

i) Fission → Heat + Neutrons

ii) 3Li6 + 0n1 → 1H3 + 2He4 + 4.78 MeV

\[ 1H2 + 1H3 \rightarrow 2He4 + 0n1 + 17.6 \text{ MeV} \]

8. How are radioactive isotopes useful in medicine? Or List the medicinal uses of radioactive isotopes.

Radioactive isotopes which are useful in medicine

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H3</td>
<td>Tritium</td>
</tr>
<tr>
<td>6C11</td>
<td>Carbon - 11</td>
</tr>
<tr>
<td>6C14</td>
<td>Carbon - 14</td>
</tr>
<tr>
<td>53I131</td>
<td>Iodine - 131</td>
</tr>
<tr>
<td>80Hg197</td>
<td>Mercury - 197</td>
</tr>
<tr>
<td>15P32</td>
<td>Phosphorous - 32</td>
</tr>
<tr>
<td>26Fe59</td>
<td>Iron - 59</td>
</tr>
<tr>
<td>27Co60</td>
<td>Cobalt - 60</td>
</tr>
<tr>
<td>11Na24</td>
<td>Sodium - 24</td>
</tr>
<tr>
<td>79Au198</td>
<td>Gold - 198</td>
</tr>
</tbody>
</table>

9. Mention the use of radio isotopes in the field of a) study of hydrolysis of ester, b) mechanism of photosynthesis in plants.

a) Study of hydrolysis of ester
By labelling oxygen, the mechanism of ester hydrolysis can be studied by using water labelled with O18. The hydrolysis of an ester by water enriched with radioactive oxygen is indicated as:

\[
\text{R} - \text{C}^\ast - \text{OR} + \text{HOH} \quad \rightleftharpoons \quad \text{R} - \text{C}^\ast - \text{OH} + \text{R} - \text{OH}
\]

Therefore it is the **acid and not alcohol produced which is radioactive** confirming the above mechanism.

b) **Mechanism of photosynthesis in plants**

A small quantity of Radioactive C\(^\ast\)O\(_2\) containing radioactive oxygen O18 is mixed with ordinary carbondioxide and the process is carried out. It has been found that oxygen gas evolved along with sugar formation is non-radioactive. Therefore **O\(_2\) produced comes from water and not from carbondioxide**. So the correct mechanism is as follows.

\[
6\text{CO}_2 + 6\text{H}_2\text{O} \quad \rightarrow \quad \text{C}_6\text{H}_12\text{O}_6 + 6\text{O}_2
\]
Q.No-66(a)-Solid State - II

1. Explain Bragg's spectrometer method (in / for crystal study / the study of crystals).

   1. Bragg's spectrometer method is one of the important methods for studying crystals using X-rays.
   2. The apparatus consists of a X-ray tube from which a narrow beam of X-rays is allowed to fall on the crystal mounted on a rotating table. The rotating table is provided with scale and vernier, from which the angle of incidence, θ can be measured. An arm which is rotating about the same axis as the crystal table carries an ionisation chamber.
   3. X-ray spectrometer
   4. The rays reflected from the crystal enter into the ionization chamber and ionise the gas present inside.
   5. Due to the ionisation, current is produced which is measured by electrometer.
   6. The current of ionisation is a direct measure of intensity of reflected beam from the crystal. For different angles of incidence, the corresponding ionisation current is measured from the electrometer.
   7. These values are plotted in the form of graph.
   8. For sodium chloride, the maximum reflection or peaks for 100 plane occurred at θ = 5.9°, 11.85° and 18.15°. The sines of these angles are 0.103, 0.205 and 0.312 which are in the ratio 1 : 2 : 3. These peaks represent the first, second and third order reflections.

     The ratio confirms the correctness of Bragg’s equation.

2. Explain Schottky defect and Frenkel defect (in crystals).

   1. Schottky defect is caused if some of the lattice points are unoccupied. The points which are unoccupied are called lattice vacancies.
   2. The number of missing positive and negative ions is the same in this case and thus, the crystal remains neutral.
The existence of two vacancies, one due to a missing Na\(^+\) ion and the other due to a missing Cl\(^-\) ion in a crystal of NaCl is shown in Fig

![Schottky Defects in NaCl Crystal](image)

A Schottky defect appears generally in ionic crystals in which the positive and negative ions do not differ much in size.

A few examples of ionic compounds exhibiting Schottky defect are NaCl, KCl, KBr, CsCl etc.,

2. Frenkel defect arise when an ion occupies an interstitial position between the lattice points.

This defect occurs generally in ionic crystals in which the anion is much larger in size than the cation.

AgBr is an example for this type of defect.

One of the Ag\(^+\) ion occupies a position in the interstitial space rather than its own appropriate site in the lattice is shown in Fig

![Frenkel Defects in AgBr Crystal](image)

The crystal remains neutral since the number of positive ions is the same as the number of negative ions.

A few examples of ionic compounds exhibiting Frenkel defect are AgCl, AgBr, AgI, ZnS etc.,

<table>
<thead>
<tr>
<th>S. No</th>
<th>Schottky defect</th>
<th>Frenkel defect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Caused if some of the lattice points are unoccupied. (lattice vacancies)</td>
<td>Arise when an ion occupies an interstitial position between the lattice points.</td>
</tr>
<tr>
<td></td>
<td>Appears generally in ionic crystals in which the positive and negative ions do not differ much in size.</td>
<td>Occurs generally in ionic crystals in which the anion is much larger in size than the cation.</td>
</tr>
<tr>
<td>---</td>
<td>--------------------------------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>2</td>
<td>Crystal remains neutral since the number of missing positive and negative ions is the same.</td>
<td>Crystal remains neutral since the number of positive ions is the same as the number of negative ions.</td>
</tr>
<tr>
<td>3</td>
<td>Example: NaCl, KCl, KBr, CsCl</td>
<td>Example: AgCl, AgBr, AgI, ZnS</td>
</tr>
</tbody>
</table>

3. **Explain the nature of glass.**
   1. The chief characteristics of a glass are **hardness**, **rigidity** and ability to withstand shearing stresses which are all properties of the solid state.
   2. On the other hand glasses are **optically isotropic** and on heating without any sharp transition passes into a mobile liquid.
   3. At a high temperature glasses undergo phase transition when crystals separate first as they do form super cooled liquid. Therefore, glasses are regarded as **amorphous solids** or **super cooled liquids** as well.
   4. Thus, **glassy** or **vitreous state** is a condition in which certain substance can exist, lying between the solid and liquid states.

4. **What are superconductors? Write their uses.**
   **Super conductors**
   The ability of certain ultra cold **substances to conduct electricity without resistance** is called superconductivity. This superconductivity state is a **state in which a material has virtually zero electrical resistance**. Substances having this property are called super conductors.
   **Uses of superconductors**
   1. It is a basis of **new generation of energy saving power systems**. Super conducting generators are smaller in size and weight when we compare with conventional generators. These generators consume very low energy and so we can save more energy.
   2. **High efficiency ore separating machines** may be built using superconducting magnets.
   3. **Superconducting solenoids** are used in Nuclear Magnetic Resonance Imaging equipment which is a whole body scan equipment.

5. **Write notes on any two point defects in Crystals.**
   If the deviation occurs due to missing atoms, displaced atoms or extra atoms, the imperfection is named as a point defect.
   Such defects arise due to imperfect packing during the original crystallisation or they may arise from thermal vibrations of atoms at elevated temperatures.
   The most common point defects are the Schottky defect and Frenkel defect. Comparatively less common point defects are the **metal excess defect** and the **metal deficiency defect**.
1. Metal excess defects
If a crystal of NaCl is heated in sodium vapour, it acquires a yellow colour. This yellow colour is due to the formation of a non-stoichiometric compound of NaCl in which there is a slight excess of sodium ions. This defect is called the metal excess defect.

2. Metal deficiency defects
In certain cases, one of the positive ions is missing from its lattice site and the extra negative charge is balanced by some nearby metal ion acquiring additional charges instead of original charge. This type of defect is generally found in compounds of transition metals which can exhibit variable valency. FeO and FeS show this type of defects.

6. Write the properties of ionic crystals.
   1. The heats of vapourisation of ionic crystals are high.
   2. The vapour pressure of ionic crystals at ordinary temperature are very low.
   3. The melting and boiling points of ionic crystals are very high.
   4. Ionic crystals are hard and brittle.
   5. Ionic crystals are insulators in the solid state.
   6. Ionic crystals are soluble in water and also in other polar solvents.
   7. Ionic solids are good conductors when dissolved in water.
Q.No-66(b)-Surface Chemistry

1. Explain the intermediate compound formation theory of catalysis. Or Write briefly on intermediate compound formation theory of catalysis with an example.

Intermediate compound formation theory explains the mechanism of homogeneous catalysis. According to this theory, the catalyst first forms an intermediate compound with one of the reactants. The compound is formed with less energy consumption than needed for the actual reaction. The intermediate compound being unstable combines with other reactant to form the desired product and the catalyst is regenerated.

For example, a reaction of the type

\[ C \]

\[ A + B \rightarrow AB \]

which occurs in presence of a catalyst C, may take place as

\[ A + C \rightarrow AC \]

\[ \text{Catalyst} \quad \text{Intermediate compound} \]

\[ AC + B \rightarrow AB + C \]

\[ \text{Product Catalyst} \]

The catalytic oxidation of SO2 to SO3 in the lead chamber process probably takes place as;

\[ 2NO + O_2 \rightarrow 2NO_2 \]

\[ \text{Catalyst} \quad \text{Intermediate compound} \]

\[ NO_2 + SO_2 \rightarrow SO_3 + NO \]

\[ \text{Product Catalyst} \]

2. Give any 5 main differences between physical adsorption and chemical adsorption.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Physical adsorption</th>
<th>Chemical adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>It is due to intermolecular Vander waal’s force.</td>
<td>It is due to chemical bond formation.</td>
</tr>
<tr>
<td>2</td>
<td>Depends on the nature of gas. Easily liquefiable gases are adsorbed readily.</td>
<td>More specific than the physical adsorption.</td>
</tr>
<tr>
<td>3</td>
<td>Heat of adsorption is small.</td>
<td>Heat of adsorption is large.</td>
</tr>
<tr>
<td>4</td>
<td>Reversible.</td>
<td>Irreversible.</td>
</tr>
<tr>
<td>5</td>
<td>If occurs rapidly at low temperature and decreases with increase of temperature.</td>
<td>Increases with increase of temperature.</td>
</tr>
<tr>
<td>6</td>
<td>Increase of pressure increases adsorption.</td>
<td>Change of pressure has no effect.</td>
</tr>
<tr>
<td>7</td>
<td>Forms multimolecular layers on adsorbent surface.</td>
<td>Forms unimolecular layer.</td>
</tr>
</tbody>
</table>

3. How are colloids prepared by chemical methods? Or Write any two chemical methods for the preparation of colloids.

The chemical methods involve chemical reaction in a medium in which the dispersed phase is sparingly soluble. Some of the methods are:
1. **Double decomposition**: An arsenic sulphide sol is prepared by passing a slow stream of hydrogen sulphide gas through a cold solution of arsenious oxide.

   \[ \text{As}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow \text{As}_2\text{S}_3 + 3\text{H}_2\text{O} \]

2. **Oxidation**: A colloidal solution of sulphur is obtained by passing H2S into a solution of sulphur dioxide.

   \[ 2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\text{S} \]

3. **Reduction**: Silver sols and gold sols can be obtained by treating dilute solution of silver nitrate or gold chloride with organic reducing agents like tannic acid or formaldehyde.

   \begin{align*}
   \text{AgNO}_3 + \text{tannic acid} & \rightarrow \text{Ag Sol} \\
   \text{AuCl}_3 + \text{tannic acid} & \rightarrow \text{Au Sol}
   \end{align*}

4. **Hydrolysis**: A colloidal solution of ferric hydroxide is obtained by boiling a dilute solution of ferric chloride.

   \[ \text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{HCl} \]

   Colloidal solutions of the hydroxides of Cr, Al etc can be prepared by hydrolysis of their salts.

4. **How can colloidal solutions be purified by dialysis?**

   Animal membranes (bladder) or those made of parchment paper and cellophane sheet, have very fine pores. These pores permit ions (or small molecules) to pass through but not the large colloidal particles.

   When a sol containing dissolved ions (electrolyte) or molecules is placed in a bag of semi permeable membrane dipping in pure water, the ions diffuse through the membrane. By using a continuous flow of fresh water, the concentration of the electrolyte outside the membrane tends to be zero. Thus diffusion of the ions into pure water remains brisk all the time. In this way, practically all the electrolyte present in the sol can be removed easily.

   The process of removing ions (or molecules) from a sol by diffusion through a permeable membrane is called **Dialysis**. The apparatus used for dialysis is called a **Dialyser**.

5. **What is electro-osmosis? Explain the experiment.**
The movement of the dispersion medium under the influence of applied potential is known as electro-osmosis.

The phenomenon of electro-osmosis can be demonstrated by using a U-tube in which a plug of wet clay (a negative colloid) is fixed. The two limbs of the tube are filled with water to the same level. The platinum electrodes are immersed in water and potential applied across them. It will be observed that water level rises on the cathode side and falls on anode side. This movement of the medium towards the negative electrode shows that the charge on the medium is positive. Similarly, for a positively charged colloid electro-osmosis will take place in the reverse direction.

6. Write any three methods for the preparation of colloids by dispersion methods. Or How are colloids prepared by using i) mechanical dispersion method ii) electro dispersion method?

1. Mechanical dispersion: (Colloidal mill)

The solid along with the liquid is fed into a colloidal mill. The colloidal mill consists of two steel plates nearly touching each other and rotating in opposite directions with high speed. The solid particles are ground down to colloidal size and then dispersed in the liquid.
1. Electrophoretic dispersion method

Colloidal graphite, Cement, Face powder and printing inks are made by this method.

2. Electro-dispersion method: (Bredig’s Arc Method)

An arc is struck between the metal electrodes under the surface of water containing some stabilising agent such as trace of alkali. The water is cooled by immersing the container in a cold bath. The intense heat of the arc vapourises some of the metal which condenses under cold water.

Use:

This method is suitable for the preparation of colloidal solution of metals like gold, silver, platinum etc.

3. Ultra-sonic dispersion:

The sound waves of high frequency are usually called ultra-sonic waves. Ultrasonic waves are passed through the solution containing larger particles. They break down to form colloidal solution.
4. Peptisation:
The dispersion of a precipitated material into colloidal solution by the action of an electrolyte in solution is termed as peptisation. The electrolyte used is called a peptizing agent.

Precipitate + Electrolyte (Peptizing agent) → Colloidal solution (Sol)

Examples:
1. Silver chloride can be converted into a sol by adding hydrochloric acid
2. Ferric hydroxide yields a sol by adding ferric chloride

7. Write briefly about the adsorption theory of catalysis.
This theory explains the mechanism of heterogeneous catalysis. Here, the catalyst functions by adsorption of the reacting molecules on its surface.

In general, there are four steps involved in the heterogeneous catalysis.

Catalyst
A(g) + B(g) → C(g) + D(g)

Step - 1 Adsorption of reactant molecules
The reactant molecules A and B strike the surface of the catalyst. They are held at the surface by weak van der waal’s forces or by partial chemical bonds.

Step - 2 Formation of Activated complex
The particles of the reactants adjacent to one another join to form an intermediate complex (A - B). The activated complex is unstable.

Step - 3 Decomposition of Activated complex
The activated complex breaks to form the products C and D. The separated particles of the products hold to the catalyst surface by partial chemical bonds.

Step - 4 Desorption of Products
The particles of the products are desorbed or released from the surface.

8. Write notes on i) Ultrafiltration and ii) Helmholtz double layer.

i) Ultrafiltration
Sols pass through an ordinary filter paper. Its pores are too large to retain the colloidal particles. However, if the filter paper is impregnated with collodion or a regenerated cellulose such as cellophane or visking, the pore size is much reduced. Such a modified filter paper is called an ultrafilter.
The separation of the sol particles from the liquid medium and electrolytes by filtration through an ultrafilter is called ultrafiltration.
Ultrafiltration is a slow process. Gas pressure (or suction) has to be applied to speed it up. The colloidal particles are left on the ultrafilter in the form of slime. The slime may be stirred into fresh medium to get back the pure sol. By using graded ultrafilters, the technique of
ultrafiltration can be employed to separate sol particles of different sizes.

ii) Charge on Colloidal particles
The important property of colloidal dispersions is that all the suspended particles possess either a positive or negative charge. The mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity. This gives stability to the sol.

Adsorption of ions from dispersion medium gives charge to sol particles which do not settle on account of mutual repulsions.
Helmholtz Double layer
The surface of colloidal particle acquires a positive charge by selective adsorption of a layer of positive ions around it. This layer attracts counter ions from the medium which form a second layer of negative charges. The combination of the two layers of charges around the sol particle is called Helmholtz double layer.


i) Auto catalyst
When one of the products formed during the reaction acts as a catalyst for that reaction. Such type of catalyst is called auto catalyst and the phenomenon is known as auto catalysis.

Example:
In the oxidation of oxalic acid by potassium permanganate, one of the products MnSO4 acts as a auto-catalyst because it increases the speed of the reaction.

\[
\text{COOH} + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O}
\]

ii) Promoters
The activity of a catalyst can be increased by addition of a small quantity of a second material. A substance which, though itself not a catalyst, promotes the activity of a catalyst is called a promoter.

Example:
In the Haber’s process for the synthesis of ammonia, traces of molybdenum increase the activity of finely divided iron which acts as a catalyst.

\[
\text{Fe} + \text{N}_2 + 3\text{H}_2 \xrightarrow{\text{Mo}} 2\text{NH}_3 + \text{Mo}
\]

10. Write the general characteristics of catalytic reactions.
1. The catalyst remains unchanged in mass and in chemical composition at the end of the reaction.
2. Only a small quantity of catalyst is generally needed.
3. A catalyst cannot initiate a reaction. The function of a catalyst is only to alter the speed of the reaction which is already occurring at a particular rate.
4. A catalyst does not alter the position of equilibrium in a reversible reaction.
5. The catalyst is generally specific in its action
**Q.No-67(a) Electrochemistry – I**

1. Derive / Derive an expression for / Explain Ostwald's dilution law

Ostwald’s dilution law relates the dissociation constant of the weak electrolyte with the degree of dissociation and the concentration of the weak electrolyte.

Consider the dissociation equilibrium of CH$_3$COOH which is a weak electrolyte in water.

$$
\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+
$$

$\alpha$ is the degree of dissociation which represents the fraction of total concentration of CH$_3$COOH that exists in the completely ionised state. Hence $(1 - \alpha)$ is the fraction of the total concentration of CH$_3$COOH, that exists in the unionised state. If ‘C’ is the total concentration of CH$_3$COOH initially, then at equilibrium $C$ $\alpha$, $C$ $\alpha$ and $C$ $(1 - \alpha)$ represent the concentration of H$^+$, CH$_3$COO$^-$ and CH$_3$COOH respectively.

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$COOH</th>
<th>CH$_3$COO$^-$</th>
<th>H$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial number of moles</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Number of moles ionised</td>
<td>$\alpha$</td>
<td>$\alpha$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Number of moles remaining at equilibrium</td>
<td>$1 - \alpha$</td>
<td>$\alpha$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Equilibrium concentration</td>
<td>$(1 - \alpha).C$</td>
<td>$\alpha.C$</td>
<td>$\alpha.C$</td>
</tr>
</tbody>
</table>

Then $K_a = C$ $\alpha$ . $C$ $\alpha$ / $(1 - \alpha)$

If $\alpha$ is too small, then $K_a = a^2C$ and $\alpha = \sqrt{K_a / C}$

Also $[\text{H}^+] = [\text{CH}_3\text{COO}^-] = C.\alpha$

$[\text{H}^+] = C \ (K_a / C)^{1/2} = (K_a.C)^{1/2} = \sqrt{K_a . C}$

$K_a = a^2C / 1 - \alpha$ is known as the Ostwald’s dilution law.

For weak bases, $K_b = a^2C / 1 - \alpha$ and $\alpha = \sqrt{K_b / C}$ at $\alpha = $ small values. $K_b$ = dissociation constant for weak base.

**Disadvantage:**

Ostwald’s dilution law fails for strong electrolytes. For strong electrolytes, $\alpha$ tends to 1.0 and therefore $K_a$ increases tremendously.

2. Derive Henderson Equation.

The pH of an acid buffer can be calculated from the dissociation constant, $K_a$ of the weak acid and the concentrations of the acid and the salt used.

The dissociation expression of the weak acid, HA, may be represented as

$$
\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-
$$

and $K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$

or $[\text{H}^+] = K_a . [\text{HA}] / [\text{A}^-]$ ...

(1)
The weak acid is only slightly dissociated and its dissociation is further depressed by the addition of the salt (Na\(^+\) A\(^-\)) which provides A\(^-\) ions (Common ion effect). As a result the equilibrium concentration of the unionised acid is nearly equal to the initial concentration of the acid. The equilibrium concentration [A\(^-\)] is presumed to be equal to the initial concentration of the salt added since it is completely dissociated. Thus we can write the equation (1) as

\[
[H^+] = \text{Ka} \times \frac{[\text{acid}]}{[\text{salt}]}
\] ...

(2)

Where [acid] is the initial concentration of the added acid and [salt] that of the salt used. Taking negative logs of both sides of the equation (2), we have

\[-\log [H^+] = -\log \text{Ka} - \log \frac{[\text{acid}]}{[\text{salt}]}
\]

...(3)

But \(-\log [H^+] = pH\) and \(-\log \text{Ka} = p\text{Ka}\)

Thus from (3) we have

\[\text{pH} = p\text{Ka} - \log \frac{[\text{acid}]}{[\text{salt}]} = p\text{Ka} + \log \frac{[\text{salt}]}{[\text{acid}]}
\]

This relationship is called the Henderson-Hasselbalch equation or simply Henderson equation.

The Henderson-Hasselbalch equation for a basic buffer can be stated as:

\[\text{pOH} = p\text{Kb} + \log \frac{[\text{salt}]}{[\text{base}]}
\]

3. Differentiate between electronic conduction and electrolytic conduction.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Electronic conduction</th>
<th>Electrolytic conduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure metals and their solid solutions such as alloys are called as metallic conductors.</td>
<td>Electrovalent (or) ionic compounds conduct electricity through their ions present in fused state or in dissolved state.</td>
</tr>
<tr>
<td>2</td>
<td>Free and mobile electrons of the metallic atoms or alloys are responsible for electrical conductance.</td>
<td>Ions with positive and negative charges conduct electricity and move towards cathode and anode respectively.</td>
</tr>
<tr>
<td>3</td>
<td>Positive holes in the metals move in the opposite direction to electrons.</td>
<td>Electrolysis occurs when electrical current is passed through electrolytic solutions.</td>
</tr>
<tr>
<td>4</td>
<td>There is no chemical change in the material when electricity is passed.</td>
<td>Chemical change occurs.</td>
</tr>
<tr>
<td>5</td>
<td>There is only flow of electrical energy but there is no transfer of matter.</td>
<td>There is actual transfer of matter since ions move towards respective electrodes.</td>
</tr>
<tr>
<td>6</td>
<td>Conductivity of metal decreases with increase in temperature due to the enhanced thermal vibration of metal atoms disrupting the movement of electrons passing through them.</td>
<td>The conductivity of electrolytes increases with increase in temperature. This is due to increase with ionic mobility.</td>
</tr>
</tbody>
</table>

4. Explain / Write the postulates of Arrhenius theory of electrolytic dissociation.
1. When dissolved in water, neutral electrolyte molecules are split up into two types of charged particles. These particles were called ions and the process was termed ionisation. The positively charged particles were called cations and those having negative charge were called anions.

\[ A^+ + B^- \rightarrow A^+ + B^- \]

2. The ions present in solution constantly reunite to form neutral molecules. Thus there is a state of equilibrium between the undissociated molecules and the ions.

\[ AB \leftrightharpoons A^+ + B^- \]

Applying the Law of Mass Action to the ionic equilibrium we have,

\[ [A^+][B^-] / [AB] = K \]

Where, \( K \) is called the Dissociation constant.

3. The charged ions are free to move through the solution to the oppositely charged electrode. This is called as migration of ions. This movement of the ions constitutes the electric current through electrolytes. This explains the conductivity of electrolytes as well as the phenomenon of electrolysis.

4. The electrical conductivity of an electrolyte solution depends on the number of ions present in solution. Different ions move with different rates.

5. The properties of solution of electrolytes are the properties of ions. The solution of electrolyte as a whole is electrically neutral unless an electric field is applied to the electrodes dipped into it.

Examples: Presence of hydrogen ions (H+) renders the solution acidic while presence of hydroxide ions (OH–) renders the solution basic.

6. There are two types of electrolytes.
   a) Strong electrolytes are those when dissolved in water are completely ionised into ions of positive and negative charges.

Examples: \( \text{Al}_2(\text{SO}_4)_3 \rightarrow 2\text{Al}^3+ + 3\text{SO}_4^{2–} \)
NaCl, KCl, AgNO\(_3\) etc.,

b) Weak electrolytes are those when dissolved in water are partially dissociated into ions and an equilibrium exists between the dissociated ions and the undissociated electrolyte.

Example: \( \text{CH}_3\text{COOH} \leftrightharpoons \text{CH}_3\text{COO}– + \text{H}^+ \).

5. Explain Ostwald’s theory of indicators.
   1. Ostwald’s theory of indicators is based on Arrhenius theory.
   2. The acid-base indicator is either a weak organic acid or a weak organic base.
   3. They are partially ionised in solution.
   4. The ionised and unionised forms have different colours.
   5. The indicator exists predominantly in one of the two forms depending on the nature of the medium and hence there is colour change when the nature of the medium changes.
   6. Phenolphthalein is a weak organic acid and it is partially ionised in solutions.

\[ \text{HPh} \leftrightharpoons \text{H}^+ + \text{Ph}– \]
Unionised form

(Colourless)

In acidic medium, excess H+ ions are present which suppress the dissociation of Hph due to common ion effect. Hence the indicator exists predominantly in unionised form and it is colourless.

In alkaline medium, the OH– ion neutralises H+ ion to form water. Consequently the dissociation of Hph is favoured and the indicator is predominantly in the ionised form and it is pink in colour.

7. Methyl orange is a weak base and its is partially ionised in solutions as

MeOH ⇌ Me+ + OH–

Unionised form

(Yellow)

In basic medium, excess OH– ions are present which suppress the dissociation of MeOH due to common ion effect. Hence the indicator is mostly in unionised form which is yellow.

In acidic medium, the H+ ions combine with OH– ions to form unionized water. Hence the indicator is mostly in ionised form and has pink colour.

6. Explain Quinonoid theory of indicators.

1. The colour change of an acid-base indicator arises as a result of structural change.
2. It is supposed that an indicator exists as an equilibrium mixture of two tautomeric forms namely, benzenoid and quinonoid forms.

benzenoid form

quinonoid form

3. One form exists in acidic solution and the other form in basic solution.
4. At least one of the tautomers is a weak acid or a weak base.
5. The two forms possess two different colours and as the pH of the solution containing the indicator is changed, the solution shows a change of colour.
6. The colour change is due to the fact that one tautomer changes over to the other.
7. For example, phenolphthalein is tautomeric mixture of the two forms.
7. Explain the buffer action of acidic buffer with an example.

Acidic buffer consists of a weak acid together with a salt of the same acid.

Eg., Acetic acid and Sodium acetate (CH₃COOH / CH₃COONa).

The pH of the buffer is governed by the equilibrium

\[ \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ \quad \ldots (1) \]

The buffer solution has a large excess of CH₃COO⁻ ions produced by complete ionisation of sodium acetate,

\[ \text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+ \quad \ldots (2) \]

1. Addition of HCl: When HCl is added to the buffer solution, the increase of H⁺ ions is counteracted by association with the excess of CH₃COO⁻ ions to form unionised CH₃COOH. Thus the added H⁺ ions are neutralised and the pH of the buffer solution remains unchanged. However owing to the increased concentration of CH₃COOH, the equilibrium (1)
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shifts slightly to the right to increase H+ ions. This explains the marginal increase of pH of the buffer solution on addition of HCl.

2. Addition of NaOH: When NaOH is added to the buffer solution, the additional OH– ions combine with H+ to give neutral H2O. Thus pH of the buffer solution is maintained almost constant.

8. What are the evidences in favour of Arrhenius theory of electrolytic dissociation?
   1. The enthalpy of neutralisation of strong acid by strong base is a constant value and is equal to −57.32 kJ. gm. equiv-1 because
      a) Strong acids and strong bases are completely ionised in water and produce H+ and OH– ions respectively along with the counter ions.
      b) The net reaction in the acid-base neutralisation is the formation of water from H+ and OH– ions.
         \[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}; \Delta \text{H}_{\text{ro}} = -57.32 \text{ kJ.mol}^{-1} \]
   2. The colour of certain salts or their solution is due to the ions present.
      For example, copper sulphate is blue due to Cu2+ ions. Nickel salts are green due to Ni2+ ions. Metallic chromates are yellow due to CrO42– ions.
   3. Ostwald’s dilution law, common ion effect and solubility product and other such concepts are based on Arrhenius theory.
   4. Chemical reactions between electrolytes are almost ionic reactions. This is because these are essentially the reaction between oppositely charged ions.
      For example, \[ \text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \downarrow \]
   5. Electrolytic solutions conduct current due to the presence of ions which migrate in the presence of electric field.
   6. Colligative properties depend on the number of particles present in the solution. Electrolytic solution has abnormal colligative properties.
      For example, 0.1 molal solution of NaCl has elevation of boiling point about twice that of 0.1 molal solution of non-electrolyte.

9. Explain the Buffer action of basic buffer with an example
Basic buffer consists of **a weak base and its salt with a strong acid.**

**Eg.,** Ammonium hydroxide and Ammonium chloride (NH$_4$OH + NH$_4$Cl)

The pH of the buffer is governed by the equilibrium

\[
\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \quad \text{... (1)}
\]

The buffer solution has a large excess of NH$_4^+$ ions produced by complete ionisation of Ammonium chloride,

\[
\text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^- \quad \text{... (2)}
\]

**1. Addition of HCl:** When HCl is added to the buffer solution, the increase of H$^+$ ions combine with NH$_4$OH to form NH$_4^+$ and H$_2$O. pH is retained.

**2. Addition of NaOH:** When NaOH is added to the buffer solution, the OH$^-$ ions combine with NH$_4^+$ ions present in the buffer solution to give NH$_4$OH and hence pH is maintained

---

10. **What is ionic product of water? Give its value.**

Water is a weak electrolyte. The dissociation equilibrium of water can be considered as,

\[
2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- 
\]

According to law of mass action,

\[
\text{Keq} = [\text{H}_3\text{O}^+][\text{OH}^-] / [\text{H}_2\text{O}]^2 
\]

Since water as a solvent is always in excess and change in concentration due its dissociation is negligible. Hence water concentration is assumed to be constant.

\[
\therefore \text{Keq} \times [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-] = \text{Kw} 
\]

The constant Kw is called as the ionic product of water and its value is given by the product of concentrations of hydronium (H$_3$O$^+$) and hydroxide (OH$^-$) ions.

At 298 K, Kw = 1 x 10^-14 mol$^2$.dm$^{-6}$.

11. **What are indicators? Give an example.**

An indicator is a substance which indicates the completion of a reaction by sharp colour change at the end point without taking part in the reaction.

The substances which are used to indicate the end point in acid-base reactions are called as acid-base indicators.
Example - Phenolphthalein, Methyl orange.


Molar conductance ‘μC’ is defined as the conductance of a solution containing one mole of the electrolyte dissolved in it.

\[ \mu C = k \times 10^{-3} / M \]

Where, M is the Molarity of the electrolyte solution.

Unit

- mho.m2.mole-1
- ohm-1 m2 mole-1
- Siemen m2 mole-1
Q.No-67(b) Electrochemistry – II

1. Derive Nernst equation (of reversible cell.)

The reaction occurring in a reversible cell is represented by the equation

\[ A + B \rightleftharpoons C + D \]

The decrease in free energy, \(-\Delta G\), accompanying the process is given by

\[-\Delta G = -\Delta G_o - RT \ln J\]

Where,

\(-\Delta G_o\) is the decrease in free energy accompanying the same process when all the reactants and products are in their standard states of unit activity.

\(J\) stands for the reaction quotient of the activities of the products and reactants at any given stage of the reaction.

Substituting the value of \(J\), we have

\[-\Delta G = -\Delta G_o - RT \ln (a_C a_D / a_A a_B)\]

If \(E\) is the E.M.F. of the cell in volts and the cell reaction involves the passage of \(n\) faradays i.e., \(nF\) coulombs, the electrical work done by the cell is in \(nFE\) volt-coulombs or Joules.

Hence free energy decrease of the system, \(-\Delta G\), is given by the expression

\[-\Delta G = nFE\]

\[ nFE = -\Delta G_o - RT \ln (a_C a_D / a_A a_B) \]

\[ = nFEo - RT \ln (a_C a_D / a_A a_B) \]

\[ E = E_o - RT / nF \ln (a_C a_D / a_A a_B) \]

is known as the Nernst equation

Where,

\(E_o\) is the E.M.F. of the cell in which the activity, or as an approximation, the concentration of each reactant and each product of the cell reaction is equal to unity. \(E_o\) is known as the standard E.M.F. of the cell.

Replacing activities by concentrations the Nernst equation may be written as

\[ E = E_o - RT / nF \ln \left[ C[D] / [A][B]\right] \]

Replacing \([C][D] / [A][B]\) as equal to \(K\), the equilibrium constant in the molar concentration units,
E = E₀ – RT / nF ln K.

E = E₀ – 2.303 RT / nF log K

Where,

E₀ = Standard electrode potential

R = Gas constant,

T = Kelvin temperature

n = Number of electrons transferred in the half-reaction

F = Faraday of electricity

K = Equilibrium constant for the half-cell reaction as in equilibrium law.

Substituting the values of R (8.314 J K⁻¹ mol⁻¹), F (96,495 coulombs) and T at 25°C (273 + 25 = 298 K), the quantity 2.303 RT / F comes to be 0.0591.

Thus the Nernst equation can be written in its simplified form as

E = E₀ – 0.0591 / n log K

6. Determine the standard e.m.f of the cell and standard free energy change of the cell reaction. Zn, Zn²⁺ || Ni²⁺, Ni. The standard reduction potentials (E°) of Zn²⁺, Zn and Ni²⁺, Ni half cells are −0.76 V and −0.25 V respectively.

E_{ocell} = E₀R − E₀L

= −0.25 − (−0.76)

= + 0.51 V

E_{ocell} is + ve. ∴ ΔG₀ = − ve.

∴ ΔG₀ = − n F E_{ocell}

n = 2 electrons

∴ ΔG₀ = −2 x 96495 x 0.51

= −98425 Joules

= −98.43 kJ.

The standard hydrogen half-cell or Standard Hydrogen Electrode (SHE) is selected for coupling with the unknown half-cell. It consists of a platinum electrode immersed in a 1 M solution of H\(^+\) ions maintained at 25\(^\circ\)C. Hydrogen gas at one atmosphere enters the glass hood and bubbles over the platinum electrode. The hydrogen gas at the platinum electrode passes into solution, forming H\(^+\) ions and electrons.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So, SHE can be used as a standard for other electrodes.

The half-cell, whose potential is desired, is combined with the hydrogen electrode and the emf of the complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell.

For example, it is desired to determine the emf of the zinc electrode, Zn | Zn\(^2+\). It is connected with the SHE. The complete electrochemical cell may be represented as:

\[
\text{Zn} \mid \text{Zn}^{2+} \mid | \text{H}^+ \mid \text{H}_2 \text{(1 atm)}, \text{Pt}
\]

The emf of the cell has been found to be \(-0.76\) V which is the emf the zinc half-cell. Similarly, the emf of the copper electrode, Cu\(^2+\) | Cu can be determined by pairing it with the SHE when the electrochemical cell can be represented as:

\[
\text{Pt}, \text{H}_2 \text{(1 atm)} \mid \text{H}^+ \mid | \text{Cu}^{2+} \mid \text{Cu}
\]

The emf of this cell has been determined to be \(0.34\) V which is the emf of the copper half-cell.

\[
E_{\text{cell}} = E_{\text{Cu}/\text{Cu}^{2+}} - E_{\text{SHE}}
\]

\[
= 0.34 - \text{Zero}
\]

\[
= 0.34 \text{ V}
\]

The two situations are explained as follows:
When it is placed on the right-hand side of the zinc electrode, the hydrogen electrode reaction is

\[ 2H^+ + 2e^- \rightarrow H_2 \]

The electrons flow to the SHE and it acts as the cathode.

When the SHE is placed on the left hand side, the electrode reaction is

\[ H_2 \rightarrow 2H^+ + 2e^- \]

The electrons flow to the copper electrode and the hydrogen electrode as the anode. Evidently, the SHE can act both as anode and cathode and, therefore can be used to determine the emf of any other half-cell electrode (or single electrode).

8. The e.m.f of the half cell Cu²⁺(aq) / Cu(s) containing 0.01M Cu²⁺ solution is + 0.301 V. Calculate the standard e.m.f of the half cell.

The e.m.f of the half cell, ECu²⁺/Cu = 0.301 V

\[ Cu^{2+} (aq) + 2e^- \rightarrow Cu (s) \]

\[ n = 2 \] electrons

\[ [Cu^{2+}] = 0.01M = 10^{-2} M \]

Standard e.m.f of the half cell, E_{oCu²⁺/Cu} = ?

\[ ECu^{2+}/Cu = E_{oCu^{2+}/Cu} - 0.0591 / 2 \log 1 / [Cu^{2+}] \]

\[ 0.301 = E_{oCu^{2+}/Cu} + 0.0591 / 2 \log [Cu^{2+}] \]

Or

\[ E_{oCu^{2+}/Cu} = 0.301 - 0.0591 / 2 \log [Cu] / [Cu^{2+}] \]

\[ 0.301 = E_{oCu^{2+}/Cu} + 0.0591 / 2 \log 10^{-2} \]

Or

\[ E_{oCu^{2+}/Cu} = 0.301 - 0.0591 / 2 \log 1 / 102 M \]

\[ 0.301 = E_{oCu^{2+}/Cu} + 0.0591/2 x (-2) \]

\[ 0.301 = E_{oCu^{2+}/Cu} - 0.0591 \]

\[ E_{oCu^{2+}/Cu} = 0.301 + 0.0591 \]

\[ = 0.3601 V \]

9. Write an account on Cell terminology.

1. Current is the flow of electrons through a wire or any conductor.

2. Electrode is a metallic rod / bar / strip which conducts electrons into and out of a solution.
3. **Anode** is the electrode at which oxidation occurs. It sends electrons into the outer circuit. It has negative charge and is shown as (−) in cell diagrams.

4. **Cathode** is the electrode at which reduction occurs. It receives electrons from the outer circuit. It has a positive charge and is shown as (+) in the cell diagrams.

5. **Electrolyte** is the salt solution in a cell.

6. **Anode compartment** is the compartment of the cell in which oxidation half-reaction occurs. It contains the anode.

7. **Cathode compartment** is the compartment of the cell in which reduction half-reaction occurs. It contains the cathode.

8. **Half-cell** - Each half of an electrochemical cell, where oxidation occurs and the half where reduction occurs, is called the half cell.

10. **Derive the relation between e.m.f and free energy.** Or **Establish a relation between free energy and e.m.f** Or **Write a brief account on the relation between EMF and free energy.**

    When a cell produces a current, the current can be used to do work – to run a motor, for instance. Thermodynamic principles can be employed to derive a relation between electrical energy and the maximum amount of work, Wmax, obtainable from the cell. The maximum amount of work obtainable from the cell is the product of charge flowing per mole and maximum potential difference, E, through which the charge is transferred.

    \[ W_{\text{max}} = - nFE \]  
    \[ \text{Where,} \]

    \[ n \] is the number of moles of electrons transferred and is equal to the valence of the ion participating in the cell reaction.

    \[ F \] stands for Faraday and is equal to 96,495 coulombs

    \[ E \] is the emf of the cell.

    According to thermodynamics, the maximum work that can be derived from a chemical reaction is equal to the free energy (\( \Delta G \)) for the reaction,

    \[ W_{\text{max}} = \Delta G \]  
    \[ \text{Therefore, from (1) and (2), we can write} \]

    \[ \Delta G = - nFE \]  
    \[ \text{Thus only when } E \text{ has a positive value, } \Delta G \text{ value will be negative and the cell reaction will be spontaneous and the e.m.f. of the cell can be measured.} \]
Here E refers to the Ecell.

Thus, the electrical energy supplied by the cell is \((nFE)\) equal to the free energy decrease \((-\Delta G)\) of the cell reaction occurring in the cell.

11. Describe Daniel cell.

Daniel cell or a galvanic cell is an example of electrochemical cell.

The overall reaction taking place in the cell is the redox reaction given as

\[
\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)
\]

This overall reaction is made of the summation of two half reactions such as oxidation half reaction and reduction half reaction.

The oxidation half reaction occurring at the zinc electrode in contact with the aqueous electrolyte containing Zn\(^{2+}\), accumulates the electrons at the zinc rod.

\[
\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-
\]

The reduction half reaction occurring at the copper electrode in contact with the aqueous electrolyte containing Cu\(^{2+}\) ions receives the electrons from the zinc electrode when connected externally, to produce metallic copper according to the reaction as,

\[
\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}(s)
\]

The decrease in the energy which appears as the heat energy when a zinc rod is directly dipped into the zinc sulphate solution, is converted into electrical energy when the same reaction takes place indirectly in an electrochemical cell.

The Daniel cell is also called as the voltaic cell. However for continuous supply of current for a long period, the two half cells each comprising the metal electrode and its aqueous electrolyte kept in separate containers and can be connected externally as below:
When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form Zn\(^{2+}\) ions. The Cu\(^{2+}\) ions in the cathode half cell pick up electrons and are converted to Cu atoms on the cathode.

12. How is e.m.f of a half cell determined?

The emf of the unknown half-cell \(E_o\) is calculated by constructing a cell with standard half-cell.

\[
E_{measured} = E_R - E_L
\]

If the standard half-cell acts as anode, the equation becomes \(E_R = E_{measured} (\therefore E_L = 0)\)

If standard half-cell acts as cathode \(E_L = -E_{measured} (\therefore E_R = 0)\)

The standard hydrogen half-cell or Standard Hydrogen Electrode (SHE) is selected for coupling with the unknown half-cell.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So, SHE can be used as a standard for other electrodes.

The SHE can act both as anode and cathode and, therefore can be used to determine the emf of any other half-cell electrode (or single electrode).
13. Write IUPAC representation of a cell. Or Write notes on IUPAC convention of representation of a cell. Or Write the IUPAC conventions for writing cell diagram with examples.

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell.

An electrochemical cell consists of two half-cells. Each half-cell is made of a metal electrode in contact with metal ion in solution.

IUPAC recommended the following conventions for writing cell diagram. We will illustrate these with reference to Zinc-Copper cell.

**Cell Diagram**

```
<table>
<thead>
<tr>
<th>anode</th>
<th>cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(s)</td>
<td>Cu(s)</td>
</tr>
<tr>
<td>Zn^2+(aq)</td>
<td>Cu^2+(aq)</td>
</tr>
</tbody>
</table>

-half-cell (oxidation) - half-cell (reduction)

salt bridge
```

1. **A single vertical line ( | )** represents a phase boundary between metal electrode and ion solution (electrolyte).

```
Zn | Zn^2+       Cu^2+ | Cu

Phase Boundary
```

**Anode half-cell**  **Cathode half-cell**

It may be noted that the metal electrode in anode half-cell is on the left, while in cathode half-cell it is on the right of the metal ion.

2. **A double vertical line ( || )** represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing.
3. **Anode half-cell** is written on the left and **cathode half-cell** on the right.

4. In the complete cell diagram, the **two half-cells** are separated by a double vertical line (salt bridge) **in between**. The zinc-copper cell can now be written as

\[
\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \parallel \text{Cu}
\]

Anode half-cell    Cathode half-cell

5. The symbol for an **inert electrode**, like the platinum electrode is often **enclosed in a bracket**. **Example**

\[
\text{Mg} \mid \text{Mg}^{2+} \parallel \text{H}^{+} \parallel \text{H}_2 \text{ (Pt)}
\]

Anode half-cell    Cathode half-cell

6. The **value of emf of a cell (E)** is written on the right of the cell diagram. Thus a zinc-copper cell has emf 1.1 V and is represented as

\[
\text{Zn} \mid \text{ZnSO}_4 \parallel \text{CuSO}_4 \parallel \text{Cu}
\]

\[E = +1.1 \text{ V}\]

**Direction of electron flow**

If the emf acts in the opposite direction through the cell circuit it is denoted as a **negative value**.

\[
\text{Cu} \mid \text{CuSO}_4 \parallel \text{ZnSO}_4 \parallel \text{Zn}
\]

\[E = -1.1 \text{ V}\]

**Direction of electron flow**
The negative sign also indicates that the cell is not feasible in the given direction and the reaction will take place in the reverse direction only. The overall cell reaction for $E = -1.1 \text{ V}$ of the Daniel cell is

$$\text{Cu(s)} + \text{Zn(aq)}^{2+} \xrightleftharpoons{\text{Cu(aq)}^{2+} + \text{Zn(s)}}$$

The reversal of the cell current is accompanied by the reversal of direction of the cell reaction.

14. Write notes on single electrode potential.

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the Single electrode potential. Thus in Daniel cell in which the electrodes are not connected externally, the anode $\text{Zn / Zn}^{2+}$ develops a negative charge and the cathode $\text{Cu / Cu}^{2+}$, a positive charge. The amount of the charge produced on an individual electrode determines its single electrode potential.

The single electrode potential of a half-cell depends on:

a. Concentration of ions in solution

b. Tendency to form ions and

c. Temperature.

**Standard emf of a cell**

The emf generated by an electrochemical cell is given by the symbol $E$. It can be measured with the help of a potentiometer. When the emf of a cell is determined under standard conditions, it is called the standard emf. The standard emf may be defined as the emf of a cell with $1 \text{ M}$ solutions of reactants and products in solution measured at $25^\circ \text{C}$. Standard emf of a cell is represented by the symbol $E_0$. For gases $1 \text{ atm.}$ pressure is a standard condition instead of concentration. For $\text{Zn-Cu}$ voltaic cell, the standard emf, $E_0$ is $1.10 \text{ V}$.

$$\text{Zn | Zn}^{2+}(\text{aq, 1M}) || \text{Cu}^{2+}(\text{aq, 1M}) | \text{Cu}$$

$E_0 = 1.10 \text{ V}$

**Applications of Single electrode potential**

1. **Predicting Cell EMF:**

   The standard emf $E_0$, of a cell is the standard reduction potential of right-hand electrode (cathode) minus the standard reduction potential of the left-hand electrode (anode).

   That is, $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$

   $= \text{Cathode potential} - \text{Anode potential}$

2. **Predicting Feasibility of Reaction:**
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The feasibility of a redox reaction can be predicted with the help of the electrochemical series. The net emf of the cell reaction, $E_{\text{cell}}$, can be calculated from the expression

$$E_{\text{cell}} = E_{\text{o cathode}} - E_{\text{o anode}}$$

In general, if $E_{\text{cell}} = +\text{ve}$, the reaction is feasible. If $E_{\text{cell}} = -\text{ve}$, the reaction is not feasible.

**Q No. 70(C) - PROBLEM**

**CARBONYL COMPOUND**

1. Compound (A) of molecular formula $C_7H_8$ when treated with air in presence of $V_2O_5$ at 773 K gives a compound (B) of molecular formula $C_7H_6O$, which has the smell of bitter almonds. Alkaline $KMnO_4$ oxidises compound (B) to (C) of molecular formula $C_7H_6O_2$. Compound (B) on treatment with $N_2H_4$ and KOH gives back compound (A). Identify (A), (B) & (C) and explain the reactions.

<table>
<thead>
<tr>
<th>ANSWER</th>
<th>(A) Toluene</th>
<th>(B) Benzaldehyde</th>
<th>(C) Benzoic acid</th>
</tr>
</thead>
</table>

2. An organic compound A ($C_7H_8$) on oxidation by air in the presence of $V_2O_5$ at 773 K gives B ($C_7H_6O$), which reduces Tollen’s reagent. B when heated with acetic anhydride and sodium acetate gives C ($C_7H_6O_2$). Identify A, B and C. Write the reactions.

<table>
<thead>
<tr>
<th>ANSWER</th>
<th>(A) Toluene</th>
<th>(B) Benzaldehyde</th>
<th>(C) Cinnamic acid</th>
</tr>
</thead>
</table>

3. An organic compound A ($C_7H_6O$) reduces Tollen's reagent. On treating with an alkali compound A forms B and C. B on treating with soda lime forms benzene and C ($C_7H_6O_2$) is an antiseptic. Identify compounds A, B and C. Explain the reactions.

<table>
<thead>
<tr>
<th>ANSWER</th>
<th>(A) Benzaldehyde</th>
<th>(B) Benzoic acid</th>
<th>(C) Benzyl alcohol</th>
</tr>
</thead>
</table>

4. Compound A with molecular formula $C_7H_6O$ reduces Tollen's reagent and also gives Cannizzaro reaction. A on oxidation gives the compound B with molecular formula $C_7H_6O_2$. Calcium salt of B on dry distillation gives the compound C with molecular formula $C_{13}H_{10}O$. Find A, B and C. Explain the reaction.

<table>
<thead>
<tr>
<th>ANSWER</th>
<th>(A) Benzaldehyde</th>
<th>(B) Benzoic acid</th>
<th>(C) Benzophenone</th>
</tr>
</thead>
</table>

5. An organic compound (A) of molecular formula $C_7H_6O$ is not reduced by Fehling's solution but will undergo Cannizzaro reaction. Compound (A) reacts with Aniline to give compound (B). Compound (A) also reacts with $Cl_2$ in the presence of catalyst to give compound (C). Identify (A), (B) and (C) and explain the reactions.

<table>
<thead>
<tr>
<th>ANSWER</th>
<th>(A) Benzaldehyde</th>
<th>(B) Benzanilide</th>
<th>(C) m-Chloro benzaldehyde</th>
</tr>
</thead>
</table>
6. An aromatic compound (A) with molecular formula \(C_7H_6O\) has the smell of bitter almonds. (A) reacts with \(Cl_2\) in the absence of catalyst to give (B) and in the presence of catalyst compound (A) reacts with chlorine to give (C). Identify (A), (B) and (C). Explain the reactions.

**ANSWER**

<table>
<thead>
<tr>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>Benzoic acid</td>
<td>m-Chloro benzaldehyde</td>
</tr>
</tbody>
</table>

7. An organic compound A \(C_7H_6O\) forms a bisulphate. A when treated with alcoholic KCN forms B \(C_{14}H_{12}O_2\) and A on refluxing with sodium acetate and acetic anhydride forms an acid C \(C_9H_8O_2\). Identify A, B and C. Explain the conversion of A to B and C.

**ANSWER**

<table>
<thead>
<tr>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>Benzoic acid</td>
<td>Cinnamic acid</td>
</tr>
</tbody>
</table>

8. An aromatic aldehyde (A) of molecular formula \(C_7H_6O\) which has the smell of bitter almonds on treatment with \((CH_3CO)_2O\) and \(CH_3COONa\) to give compound (B) which is an aromatic unsaturated acid. (A) also reacts with (A) in the presence of alc. KCN to give dimer (C). Identify (A), (B) and (C). Explain the reactions.

**ANSWER**

<table>
<thead>
<tr>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>Cinnamic acid</td>
<td>Benzoin</td>
</tr>
</tbody>
</table>

9. Compound A \(C_2H_4O\) reduces Tollen’s reagent. A on treatment with zinc amalgam and conc. HCl gives compound B. In presence of conc.\(H_2SO_4\) A forms a cyclic structure C which is used as hypnotic. Identify A, B and C. Explain the reactions.

**ANSWER**

<table>
<thead>
<tr>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>Propane</td>
<td>Paraldehyde</td>
</tr>
</tbody>
</table>

10. Compound (A) with molecular formula \(C_2H_4O\) reduces Tollen’s reagent. (A) on treatment with HCN gives compound (B). Compound (B) on hydrolysis with an acid gives compound (C) with molecular formula \(C_3H_6O_3\). Compound (C) is optically active. Compound (C) on treatment with Fenton’s reagent gives compound (D) with molecular formula \(C_3H_4O_3\). Compounds (C) and (D) give effervescence with NaHCO\(_3\) solution. Identify the compounds (A), (B), (C) and (D) and explain the reactions.

**ANSWER**

<table>
<thead>
<tr>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
<th>(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>Acetaldehyde cyanohydrin</td>
<td>Lactic acid (Optically active)</td>
<td>Pyruvic acid</td>
</tr>
</tbody>
</table>

11. An organic compound A \(C_2H_4O\) with HCN gives B \(C_3H_5ON\). B on hydrolysis gives C \(C_3H_5O_3\) which is an optically active compound. C also undergoes iodoform test. What are A, B and C? Explain the reactions.

**ANSWER**

<table>
<thead>
<tr>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>Acetaldehyde cyanohydrin</td>
<td>Lactic acid (Optically active)</td>
</tr>
</tbody>
</table>

12. Compound A having the molecular formula \(C_2H_4O\) reduces Tollen’s reagent. A on treatment with HCN followed by hydrolysis gives the compound B with molecular formula \(C_3H_6O_3\). Compound B on oxidation by Fenton’s reagent gives the compound C with the molecular formula \(C_3H_4O_3\). Find A, B and C. Explain the reactions.
13. An aromatic compound (A) (C₂H₄O) reduces Tollen's reagent. (A) reacts with HCN and followed by hydrolysis in acid medium gives (B) (C₃H₆O₃) which is optically active. Compound (B) on reaction with Fenton's reagent forms (C) (C₃H₄O₃). This answers iodoform reaction. Identify (A), (B) and (C). Write the reactions involved.

ANSWER

<table>
<thead>
<tr>
<th>(A) Acetaldehyde</th>
<th>(B) Lactic acid</th>
<th>(C) Pyruvic acid</th>
</tr>
</thead>
</table>


ANSWER

<table>
<thead>
<tr>
<th>(A) Acetone</th>
<th>(B) iso-Propyl alcohol</th>
<th>(C) iso-Propyl chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


ANSWER

<table>
<thead>
<tr>
<th>(A) Acetone</th>
<th>(B) Propane</th>
<th>(C) Mesitylene / 1,3,5-Trimethyl benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

17. An organic compound (A) with molecular formula C₃H₆O undergoes iodoform reaction. Two molecules of compound (A) react with dry HCl to give compound (B) (C₆H₁₀). Compound (B) reacts with one more molecule of compound (A) to give compound (C) (C₉H₁₄O). Identify (A), (B), (C) and (D). Explain the reactions.

ANSWER

<table>
<thead>
<tr>
<th>(A) Acetone</th>
<th>(B) Mesityl oxide</th>
<th>(C) Phorone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

18. Compound A (C₃H₆O) does not reduce Tollen's reagent but undergoes haloform reaction. Compound A undergoes dehydration reaction in the presence of dry HCl to give compound B (C₆H₁₀O). Three molecules of compound A undergoes condensation reaction in the presence of conc.H₂SO₄ to give a cyclic hydrocarbon (C). Identify A, B and C. Give the reactions.

ANSWER

<table>
<thead>
<tr>
<th>(A) Acetone</th>
<th>(B) Mesityl oxide</th>
<th>(C) Mesitylene / 1,3,5-Trimethyl benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
19. An organic compound (A) C₂H₃OCl on treatment with Pd and BaSO₄ gives (B) C₂H₄O which answers iodoform test. (B) when treated with conc. H₂SO₄ undergoes polymerization to give (C) a cyclic compound. Identify (A), (B) and (C) and explain the reaction.

<table>
<thead>
<tr>
<th>ANSWER</th>
<th>(A) Acetyl chloride</th>
<th>(B) Acetaldehyde</th>
<th>(C) Paraldehyde</th>
</tr>
</thead>
</table>

20. An organic compound A (C₂H₃N) on reduction with SnCl₂ / HCl gives C₂H₄O which reduces Tollen’s reagent. Compound B on reduction with N₂H₄ / C₂H₅ONa gives C (C₂H₆). Identify the compounds A, B and C. Explain the reactions involved.

<table>
<thead>
<tr>
<th>ANSWER</th>
<th>(A) Methyl cyanide</th>
<th>(B) Acetaldehyde</th>
<th>(C) Ethane</th>
</tr>
</thead>
</table>

21. An organic compound (A) of molecular formula C₃H₆O on treatment with PCl₅ gives compound (B). Compound (B) reacts with KCN to give a compound (C) of molecular formula C₃H₅N which undergoes acid hydrolysis to give compound (D) which on treatment with Soda lime gives a hydrocarbon. Identify (A), (B), (C) and (D) and explain the reactions.

<table>
<thead>
<tr>
<th>ANSWER</th>
<th>(A) Ethyl alcohol</th>
<th>(B) Ethyl chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(C) Ethyl cyanide</td>
<td>(D) Propanoic acid</td>
</tr>
</tbody>
</table>

22. An organic compound A (C₇H₆O₂) reacts with NH₂OH forming a crystalline compound. On warming with NaOH it forms two compounds B and C. ‘B’ is neither soluble in NaOH nor in HCl but can be oxidised to A. The compound ‘C’ on treatment with Conc. HCl forms acid ‘D’ which on treating with soda lime gives ‘phenol’. Identify A to D.

<table>
<thead>
<tr>
<th>ANSWER</th>
<th>(A) o-Hydroxy benzaldehyde / Salicylaldehyde</th>
<th>(B) o-Hydroxy benzyl alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(C) Sodium salicylate</td>
<td>(D) Sodium Benzoate</td>
</tr>
</tbody>
</table>
Q No. 70(D)- PROBLEM ELECTROCHEMISTRY-I

1. What is the pH of a solution containing 0.5 M propionic acid and 0.5 M sodium propionate? The Ka of propionic acid is $1.34 \times 10^{-5}$.

Ka of propionic acid = $1.34 \times 10^{-5}$

$\therefore \text{pKa} = - \log \text{Ka} = - \log (1.34 \times 10^{-5})$

= $5 - \log 1.34$

= $5 - 0.1271$

pKa = $4.8729$

$\text{pH} = \text{pKa} + \log [\text{salt}] / [\text{acid}]$ ... Henderson - Hasselbalch equation

= $4.8729 + \log 0.5 / 0.5$

$\text{pH} = 4.8729$

Or

The dissociation equilibrium of propionic acid will be

$\text{C}_2\text{H}_5\text{COOH} \rightleftharpoons \text{C}_2\text{H}_5\text{COO}^- + \text{H}^+$

$\text{Ka} = [\text{C}_2\text{H}_5\text{COO}^-][\text{H}^+] / [\text{C}_2\text{H}_5\text{COOH}]$

= $0.5 \times [\text{H}^+] / 0.5$

$\text{Ka} = [\text{H}^+]$

$\therefore \text{pH} = - \log [\text{H}^+] = - \log \text{Ka}$

= $- \log (1.34 \times 10^{-5})$

= $5 - \log 1.34$

= $5 - 0.1271$

$\therefore \text{pH} = 4.8729$

2. Find the pH of a buffer solution containing 0.30 mole per litre of CH₃COONa and 0.15 mole per litre of CH₃COOH. Ka for acetic acid is $1.8 \times 10^{-5}$.

Ka = $1.8 \times 10^{-5}$

$p\text{Ka} = - \log \text{Ka}$

$p\text{Ka} = - \log (1.8 \times 10^{-5})$

= $5 - \log 1.8$

= $5 - 0.2553$

$p\text{Ka} = 4.7447$

$\text{pH} = p\text{Ka} + \log [\text{salt}] / [\text{acid}]$ ... Henderson - Hasselbalch equation

= $4.7447 + \log 0.30 / 0.15$

$\text{pH} = 4.7447 + \log 2$

= $4.7447 + 0.3010$

$\text{pH} = 5.0457$

3. Calculate the pH of the buffer solution containing 0.04 M NH₄Cl and 0.02 M NH₄OH. For NH₄OH Kb is $1.8 \times 10^{-5}$.
Kb = 1.8 x 10^-5  

pKb = – log Kb  

pKb = – log (1.8 x 10^-5)  

= 5 – log 1.8  

= 5- 0.2553  

pKa = 4.7447  

pOH = pKb + log[salt] / [base] ... Henderson - Hasselbalch equation  

= 4.7447 + log 0.04 / 0.02  

pOH = 4.7447 + 0.3010 = 5.0457  

pH + pOH = 14.00  

pH = 14.00 – pOH  

pH = 14.00 – 5.0457  

pH = 8.9543  

4. Equivalent conductivity of acetic acid at infinite dilution is 390.7 and for 0.1 M acetic acid the equivalent conductance is 5.2 mho.cm^2.gm.equiv^-1. Calculate degree of dissociation, H+ ion concentration and dissociation constant of the acid.  

Equivalent conductivity of acetic acid at infinite dilution, \[ \lambda_\infty = 390.7 \]  

Equivalent conductance of acetic acid, \[ \lambda_c = 5.2 \text{ mho.cm}^2.\text{gm.equiv}^-1 \]  

Concentration of acetic acid, \[ C = 0.1 \text{ M} \]  

Degree of dissociation, \( \alpha = \frac{\lambda_c}{\lambda_\infty} \)  

= \frac{5.2}{390.7}  

\approx 0.01333  

= 1.33 \times 10^{-2} \text{ = 1.33%}  

CH_3COOH \rightleftharpoons H^+ + CH_3COO^-  

C (1 - \alpha)  

C\alpha  

C\alpha  

∴ H+ ion concentration, \[ [H^+] = C\alpha \]  

= 0.1 \times 0.0133  

= 0.00133  

= 1.33 \times 10^{-2} \text{ M}  

Dissociation constant of acetic acid, \[ K = \frac{\alpha^2C}{1 - \alpha} \]  

= \frac{(0.0133)^2 \times 0.1}{(1 - 0.0133)}  

= 0.000017689 / 0.9867  

= 1.79 \times 10^{-5} \text{ M}  

5. Calculate / Find the pH of a buffer solution containing 0.2 / 0.20 mole per litre CH_3COONa and 0.15 mole per litre CH_3COOH. Ka for acetic acid is 1.8x10^-5.  

Ka = 1.8 \times 10^{-5}  

pKa = – log Ka  

pKa = – log (1.8 x 10^-5)  

= 5 – log 1.8  

= 5- 0.2553
**pKa = 4.7447**

**pH = pKa + log [salt] / [acid]** ... Henderson - Hasselbalch equation

\[ \text{pH} = 4.7447 + \log \frac{0.20}{0.15} \]

\[ \text{pH} = 4.7447 + \log 4 / 3 \]

\[ \text{pH} = 4.7447 + \log 4 - \log 3 \]

\[ \text{pH} = 4.7447 + 0.6021 - 0.4771 \]

\[ \text{pH} = 4.8697 \]

6. An electric current is passed through three cells in series containing respectively solutions of copper sulphate, silver nitrate and potassium iodide. What weights of silver and iodine will be liberated while 1.25 g of copper is being deposited?

\[ \frac{\text{Wt. of Copper}}{\text{Wt. of Iodine}} = \frac{\text{Eqvt. wt. Copper (31.7)}}{\text{Eqvt. wt. of Iodine (127)}} \]

\[ 1.25 / x = 31.7 / 127 \]

\[ \text{Wt. of Iodine, } x = 1.25 \times 127 / 31.7 \]

Hence, \[ \text{Wt. of Iodine, } x = 5.0 \text{ g} \]

Also, \[ \frac{\text{Wt. of Copper}}{\text{Wt. of Silver}} = \frac{\text{Eqvt. wt. of Copper (31.7)}}{\text{Eqvt. wt. of Silver (108)}} \]

\[ 1.25 / y = 31.7 / 108 \]

\[ \text{Wt. of Silver, } y = 108 \times 1.25 / 317 \]

\[ \text{Wt. of Silver, } y = 4.26 \text{ g} \]

Or

31.7 g of Copper (1g eqvt) is liberated by \( = 96,495 \) coulomb

1.25 g of Copper is liberated by \( 96,495 \times 1.25 / 31.7 \) coulomb

Quantity of electricity = 3805 coulombs

96,495 coulomb deposits 127 g of Iodine

\[ \therefore 3805 \text{ coulomb deposits } = 127 \times 3805 / 96,495 \]

\[ = 5.0 \text{ g of Iodine} \]

96,495 coulomb deposits 108 g of Silver

\[ \therefore 3805 \text{ coulomb deposits } = 108 \times 3805 / 96,495 \]

\[ = 4.26 \text{ g of Silver} \]

7. The equivalent conductance of HCl, CH₃COONa and NaCl at infinite dilution are 426.16, 91.0 and 126.45 ohm⁻¹ cm² (gram equivalent)-¹ respectively. Calculate the equivalent conductance \( \lambda_\infty \) of acetic acid.

\[ \lambda_\infty \text{CH}_3\text{COOH} = \lambda_\infty \text{CH}_3\text{COONa} + \lambda_\infty \text{HCl} - \lambda_\infty \text{NaCl} \]

\[ \lambda_\infty \text{CH}_3\text{COOH} = 91.0 + 426.16 - 126.45 = 517.16 - 126.45 \]

\[ \lambda_\infty \text{CH}_3\text{COOH} = 390.71 \]

8. 0.1978 g of copper is deposited by a current of 0.2 ampere in 50 minutes. What is the electrochemical equivalent of copper?

Current, \( I = 0.2 \) ampere

Time, \( t = 50 \text{ minutes} = 50 \times 60 \text{ seconds} \)

Quantity of electricity used, \( Q = I \times t = 0.2 \times 50 \times 60 = 600 \text{ coulombs} \)

Amount of copper deposited by 600 coulombs, \( m = 0.1978 \text{ g} \)

Amount of copper deposited by 1 coulomb, \( Z = 0.1978 / 600 \text{g} = 0.0003296 \text{ g} \)
Electrochemical equivalent of copper, \( Z = \frac{\text{gm}}{\text{I \cdot t}} \)

\[ = 0.0003296 \text{ gC}^{-1} \]
\[ = 3.296 \times 10^{-4} \text{ gC}^{-1} \]
\[ = 3.206 \times 10^{-7} \text{ kgC}^{-1} \]

Or

Electrochemical equivalent of copper, \( Z = \frac{\text{gm}}{\text{I \cdot t}} \)

(or) \( Z = \frac{\text{gm}}{Q} \)

\[ = 0.1978 \text{ g} / 0.2 \text{ amp} \times 50 \times 60 \text{ sec} \]
\[ = 0.1978 \text{ g} / 600 \text{ C} \quad [\because \text{amp \cdot sec = C}] \]
\[ = 0.0003296 = 3.296 \times 10^{-4} \text{ gC}^{-1} \]
\[ = 3.206 \times 10^{-7} \text{ kgC}^{-1} \]

9. Calculate the pH of 0.1 M acetic acid / CH₃COOH solution. Dissociation constant of acetic acid is 1.8 \( \times 10^{-5} \) M.

For weak acids, \([H^+] = \sqrt{K_a \times C}\)

\[ = \sqrt{1.8 \times 10^{-5} \times 0.1} = \sqrt{1.8 \times 10^{-6}} \]
\[ = 1.34 \times 10^{-3} \text{ M} \]

\[ \therefore \text{pH} = - \log [H^+] \]
\[ = - \log (1.34 \times 10^{-3}) \]
\[ = 3 - \log 1.34 \]
\[ = 3 - 0.1271 \]

\[ \therefore \text{pH} = 2.8729 \]

10. 0.04 N solution of a weak acid has a specific conductance \( 4 \times 10^{-4} \text{ mho.cm}^{-1} \). The degree of dissociation of acid at this dilution is 0.05. Calculate the equivalent conductance of weak acid at infinite solution.

Specific conductance, \( \kappa = 4 \times 10^{-4} \text{ mho.cm}^{-1} \)

Equivalent conductance of weak acid, \( \lambda_c = \kappa \cdot 1000 / C \)

\[ = 4 \times 10^{-4} \times 1000 / 0.04 \]
\[ \lambda_c = 10 \text{ mho.cm2.eq-1} \]

Degree of dissociation, \( \alpha = 0.05 \)

\[ \alpha = \frac{\lambda_c}{\lambda_\infty} \]

Equivalent conductance of weak acid at infinite solution, \( \lambda_\infty = \lambda_c / \alpha \)

\[ \lambda_\infty = 10 / 0.05 \]

\[ \therefore \lambda_\infty = 200 \text{ mho.cm2.gm.equiv.-1} \]

11. Ionic conductances at infinite dilution of Al³⁺ and SO₄²⁻ are 189 ohm−1 cm² gm⁻¹ and 160 ohm−1 cm² gm⁻¹. Calculate equivalent and molar conductance of the electrolyte at infinite dilution.

Equivalent conductance of the electrolyte at infinite dilution,

\( \lambda_\infty = 1/n+, \lambda A+ + 1/m-, \lambda B^- \)

Where,

\( \lambda_\infty^+ \) and \( \lambda_\infty^- \) are the cationic and anionic equivalent conductances at infinite dilution.

\( n^+ \) and \( m^- \) correspond the valency of cations and anions.
The electrolyte is Al$_2$(SO$_4$)$_3$

$$\lambda_{\infty} Al_2(SO_4)_3 = \frac{1}{3} \lambda_{\infty} Al^{3+} + \frac{1}{2} \lambda_{\infty} SO^{-}$$

$$\lambda_{\infty} Al_2(SO_4)_3 = \frac{189}{3} + \frac{160}{2} = 63 + 80$$

$$= 143 \text{ mho cm}^2 \text{ gm.equiv}^{-1}$$

Molar conductance of the electrolyte at infinite dilution,

$$\mu_{\infty} = \gamma^{+} \mu_{\infty}^{++} + \gamma^{-} \mu_{\infty}^{-}$$

Where,

$$\mu_{\infty}$$ and $$\mu_{\infty}^{\pm}$$ are the ionic conductances at infinite dilution

$$\gamma^{+} = \text{number of cations and } \gamma^{-} = \text{number of anions}$$

$$\mu_{\infty} Al_2(SO_4)_3 = 2 \mu_{\infty}^{++} + 3 \mu_{\infty}^{-}$$

$$= (2 \times 189) + (3 \times 160) = 378 + 480$$

$$= 858 \text{ mho cm}^2 \text{ mol}^{-1}$$

12. What current strength in amperes will be required to liberate 10 g of iodine from potassium iodide solution in one hour?

127 g of iodine (1 g eqvt) is liberated by = 96,495 coulomb

10 g of iodine is liberated by = (96,495 x 10 / 127) coulomb

Let the current strength be = I

Time (in seconds) = 1 x 60 x 60 = 3600 seconds

The quantity of electricity used, Q = I x Time (in seconds)

Current strength, I = \frac{Q}{t}

$$= 96,495 \text{ coulomb} \times \frac{10}{127} \times 3600 \text{ seconds}$$

$$= 2.11 \text{ coulomb . second}^{-1}$$

or

$$= 2.11 \text{ ampere}$$

13. Calculate the potential of the following cell at 298 K

Zn / Zn$^{2+}$ ($a = 0.1$) $\parallel$ Cu$^{2+}$ ($a = 0.01$) / Cu

$E^{o}_{Zn^{2+}/Zn} = -0.762 \text{ V}$

$E^{o}_{Cu^{2+}/Cu} = +0.337 \text{ V}$

The overall cell reaction is : Zn + Cu$^{2+}$ ($a = 0.01$) $\rightarrow$ Zn$^{2+}$ ($a = 0.1$) + Cu
The cell potential given by Nernst equation

\[ E_{\text{cell}} = E^0_{\text{cell}} \frac{RT}{2F} \ln \frac{a_{Zn}^{2+}}{a_{Zn}^{2+} a_{Cu}^{2+}} \]

\[ = E^0_{\text{cell}} \frac{RT}{2F} \ln \frac{a_{Zn}^{2+}}{a_{Cu}^{2+}} \]

(Since activity of a pure metal is unity)

\[ E^0_{\text{cell}} = 0.337 - (-0.762) = 1.099 \text{ V} \]

\[ E_{\text{cell}} = 1.099 - \frac{0.0591}{2} \log \frac{0.1}{0.01} \]

\[ = 1.099 - \frac{0.0591}{2} \log 10 \]

\[ = 1.099 - 0.02956 \]

\[ = 1.0694 \text{ V} \]