1. **(b)** For a first-order reaction, the half-life ($t_{1/2}$) is given by the formula $t_{1/2} = \frac{0.693}{k}$. Since this equation does not contain the initial concentration $[R]_0$, the half-life is independent of $[R]_0$. This is correctly shown by a horizontal line in graph (b).
2. **(b)** Freezing point depression is a colligative property that depends on the number of solute particles ($i \times M$). $CaCl_2$ dissociates into 3 ions (Ca^{2+} and 2 Cl^-), giving it the highest van 't Hoff factor ($i = 3$). This produces the highest particle concentration (0.3 M), resulting in the lowest freezing point.
3. **(c)** By definition, transition metals must have an incompletely filled d subshell in their ground state or common oxidation states. Mercury (Hg) has a completely filled d-orbital ($3d^{10}$) in both its elemental form and its ionic forms (Hg^{2+}). Thus, it is a d-block element but not a transition metal.
4. **(b)** According to the Arrhenius equation and kinetic molecular theory, the Boltzmann factor represents the fraction of molecules with kinetic energy equal to or greater than the activation energy (E_a). This factor is mathematically written as $e^{-E_d/RT}$.
5. **(d)** During the electrolysis of aqueous $CuCl_2$:
   • At Cathode: Cu^{2+} ions are reduced to copper metal (Cu) because copper has a higher reduction potential than hydrogen.
   • At Anode: Cl^-ions are oxidized to chlorine gas (Cl_2) instead of oxygen because of the thermodynamic overvoltage required to release oxygen gas on a platinum surface.
6. **(c)** Aspirin (acetylsalicylic acid) is synthesized by reacting salicylic acid, chemically known as 2-hydroxybenzoic acid, with acetic anhydride in the presence of an acid catalyst.
7. **(d)** Secondary valency represents the coordination number of the central metal atom. In this complex, cobalt is bonded to $5NH_3$ molecules and $1NO_2^-$ion, giving a total coordination number of 6 .
8. **(d)** Electrophilic substitution of phenol with dilute nitric acid at a low temperature (298 K) yields a mixture of both ortho-nitrophenol and paranitrophenol due to the highly activating nature of the -OH group.
9. **(b)** Enantiomers possess equal but opposite specific rotations; one rotates plane-polarized light to the right (dextrorotatory), while the other rotates it to the left (levorotatory). Their other physical and chemical properties in an achiral environment remain identical.
10. **(c)** In strongly acidic nitrating mixtures, aniline is protonated to form the strongly deactivating and meta-directing anilinium ion ($C_6H_5NH_3^+$). This results in a significant amount of the meta isomer alongside the para and ortho isomers.
11. **(a)** A lower pK_b value corresponds to a stronger base. The presence of two electron-donating methyl ($-CH_3$) groups increases electron density on the nitrogen atom through the inductive effect ($+I$), making $C_6H_5 - N(CH_3)_2$ the strongest base among the options.
12. **(c)** Vitamin E acts as an important antioxidant that protects cell membranes. Its deficiency leads to increased fragility of erythrocytes (red blood cells) and muscular dystrophy.
13. **(a)** • Assertion (A): True. Azeotropes cannot be separated by fractional distillation.
    • Reason (R): True. They share identical compositions in liquid and vapor phases and boil at a constant temperature.
    • Explanation: Since the composition does not change upon boiling, fractional distillation fails to separate them.
    So, Both (A) and (R) are true and (R) is the correct explanation of (A).
14. **(d)** • Assertion (A): False. The -OH group is strongly ortho/para-directing, not metadirecting.
    • Reason (R): True. The $-OH$ group donates electron density into the ring, activating it for electrophilic attack.
15. **(b)** • Assertion (A): True. Actinoids display a wide range of oxidation states (+3 to +7).
    • Reason (R): True. All actinoid elements are unstable and radioactive.
    • Explanation: The true cause of the varied oxidation states is the close energy levels of the 5f, 6d, and 7s orbitals, not radioactivity.
    So, Both (A) and (R) are true, but (R) is not the correct explanation of (A).
16. **(c)**• Assertion (A): True. Glucose pentaacetate fails to react with hydroxylamine (H_2N-OH).
    • Reason (R): False. This absence of reaction confirms the absence of a free -CHO group in the cyclic pentaacetate structure.

17. Deviation from Raoult's Law:

A mixture of phenol and aniline shows a negative deviation from Raoult's law.

Reason:

• Phenol is acidic due to the presence of the phenolic proton, and aniline contains a basic nitrogen atom with a lone pair of electrons. When mixed, strong intermolecular hydrogen bonding forms between the phenolic hydroxyl group ($-OH$) of phenol and the amino group ($-NH_2$) of aniline. These new $A-B$ intermolecular interactions are significantly stronger than the original $A-A$ (phenol-phenol) and $B-B$ (anilineaniline) interactions, lowering the vapor pressure of the solution below the value expected from Raoult's law.

• Effect on Boiling Point:

Because the vapor pressure decreases, the boiling point of the solution increases compared to the boiling points of the individual components. The mixture forms a maximum-boiling azeotrope.

18. Haloarenes are less reactive towards nucleophilic substitution reactions due to the following two primary reasons:

(1) Resonance Effect: The lone pair of electrons on the halogen atom is in conjugation with the π-electrons of the benzene ring. This creates partial double-bond character in the carbon-halogen ($C-X$) bond, making it much stronger and harder to break than a single bond.

(2) Hybridization of Carbon Atom: The carbon atom bonded to the halogen in haloarenes is sp^2 hybridized, whereas it is sp^3 hybridized in haloalkanes. An sp^2 hybridized carbon is more electronegative and holds the electron pair of the $C-X$ bond more tightly, resulting in a shorter, stronger bond that is resistant to substitution.

19. **(A) (i)** $[Ag(NH_3)_2][Ag(CN)_2]$

• IUPAC Name: Diamminesilver(I) dicyanidoargentate(I)

(ii) $K_3[Fe(C_2O_4)_3]$

• IUPAC Name: Potassium trioxalatoferrate(III)

(B) (i) Chemical Test to Distinguish Ionisation Isomers:

• Test for $[Co(NH_3)_5SO_4]Cl$: Dissolve the compound in water and add a few drops of silver nitrate ($AgNO_3$) solution. A white precipitate of silver chloride ($AgCl$) forms, confirming the presence of free chloride ions in the outer sphere. It will not form a precipitate with barium chloride ($BaCl_2$).

• Test for $[Co(NH_3)_5Cl]SO_4$: Dissolve the compound in water and add a few drops of barium chloride ($BaCl_2$) solution. A white precipitate of barium sulfate ($BaSO_4$) forms, confirming the presence of free sulfate ions in the outer sphere. It will not form a precipitate with silver nitrate ($AgNO_3$).

(ii) Chelate Effect:

When a di- or polydentate ligand uses two or more of its donor atoms simultaneously to bind to a single central metal ion, it forms one or more stable ring structures known as chelate rings. The enhanced stability of complexes containing chelate rings over similar complexes containing only monodentate ligands is called the chelate effect.

• Example: The tris(ethane-1,2-diamine)cobalt(III) ion, $[Co(en)_3]^{3+}$, forms three stable five-membered rings and is far more stable than the corresponding hexaamminecobalt(III) ion, $[Co(NH_3)_6]^{3+}$.

20. **(i)** Peptide linkage vs Glycosidic linkage

• Peptide linkage: An amide bond ($-CO-NH-$) formed between the carboxyl group ($-COOH$) of one amino acid and the amino group ($-NH_2$) of another amino acid. It links amino acids together to form proteins.

• Glycosidic linkage: An oxide bond ($-O-$) formed through the elimination of a water molecule between two monosaccharide units. It links sugar units together to form carbohydrates.

(ii) Essential amino acids vs Non-essential amino acids

• Essential amino acids: Amino acids that cannot be synthesized by the human body and must be obtained directly through the diet (e.g., valine, leucine).

• Non-essential amino acids: Amino acids that can be synthesized internally by the body and do not strictly need to be supplied by dietary sources (e.g., glycine, alanine).

21. Since the reaction takes place in one step, it is an elementary reaction. The experimental rate law matches its molecularity:

$Rate_1 = k[A]^2[B]$

When the volume (V) of the reaction vessel is decreased to one third ($\frac{1}{3}V$), the concentration $\left([C] = \frac{n}{V}\right)$ of each reactant increases by a factor of 3 because concentration is inversely proportional to volume.

The new concentrations are $[A]' = 3[A]$ and $[B]' = 3[B]$. Substituting these into the rate law gives:

$Rate_2 = k(3[A])^2(3[B]) = k \cdot 9[A]^2 \cdot 3[B] = 27 \cdot k \mid A]^2[B] = 27 \cdot Rate_1$

• Change in rate: The rate of the reaction will increase by 27 times.

• Change in order: No, there will be no change in the order of the reaction because the underlying chemical mechanism remains the same.

22. First-order decomposition of C_2H_5Cl

$C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$

Given:

$P_0 = 0.30\ atm, P_t = 0.50\ atm, t = 30\ s$

Let x atm be the pressure of C_2H_5Cl decomposed.

Since 1 mole gives 2 moles,

$P_t = P_0 + x$

$0.50 = 0.30 + x$

$x = 0.20\ atm$

Pressure of undecomposed reactant after 30 s :

$P_A = P_0 - x = 0.30 - 0.20 = 0.10\ atm$

For a first-order reaction:

$$k = \frac{2.303}{t}\log\frac{P_0}{P_A}$$

$$k = \frac{2.303}{30}\log\frac{0.30}{0.10}$$

$$= \frac{2.303}{30}\log 3$$

$$= \frac{2.303 \times 0.48}{30}$$

$$k = 3.68 \times 10^{-2} s^{-1}$$

23. (A) (i) Relationship of K_c : At chemical equilibrium, the cell reaction stops and no current flows, which means the cell potential drops to zero ($E_{ccll} = 0$). Consequently, the Nernst equation simplifies to link the equilibrium constant directly to the standard cell potential (E^*_{ccll}), which is a fixed standard constant.

(ii) Hydrogen Liberation: Metal 'A' (with $E^* = -0.24\ V$) will liberate hydrogen gas. Metals with a negative standard reduction potential are stronger reducing agents than hydrogen $\left(E_{H^+/H_2} = 0V\right)$ and can reduce H^+ions from dilute acids.

(iii) Charging Reaction (Lead Storage Battery):

$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$

OR

(B)

• Battery Type: The mercury cell is a primary battery (non-rechargeable).

• Advantage: Its cell potential remains nearly constant (around 1.35 V) throughout its entire operating life because the overall chemical reaction does not involve any ions in solution whose concentrations change.

• Overall Reaction:

$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

24. Step 1: Calculate the Van 't Hoff factor (i)

Benzoic acid dimerizes in CS_2 :

$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$

• Degree of association $(\alpha) = 88\% = 0.88$

• Number of particles undergoing association $(n) = 2$

$$i = 1 - \alpha + \frac{\alpha}{n} = 1 - 0.88 + \frac{0.88}{2} = 0.12 + 0.44 = 0.56$$

Step 2: Calculate the molality (m) of the solution

• Mass of solute $(w_2) = 0.61\ g$

• Molar mass of solute $(M_2) = 122\ g\ mol^{-1}$

• Mass of solvent $(w_1) = 5\ g$

$$m = \frac{w_2 \times 1000}{M_2 \times w_1} = \frac{0.61 \times 1000}{122 \times 5} = \frac{610}{610} = 1\ mol\ kg^{-1}$$

Step 3: Determine the elevation in boiling point (ΔT_b)

$\Delta T_b = i \times K_b \times m$

$\Delta T_b = 0.56 \times 2.3\ K\ kg\ mol^{-1} \times 1\ mol\ kg^{-1} = 1.288\ K(\text{ or } ^\circ C)$

Step 4: Calculate the final boiling point (T_b)

$T_b = T_b^* + \Delta T_b$
$T_b = 46.2\,^\circ C + 1.288^\circ C = 47.488^\circ C$

25. Reactions of D-Glucose

(A) With HI

On prolonged heating with HI in presence of red phosphorus:

$CH_2OH(CHOH)_4CHO \xrightarrow[\text{Red P}]{\text{HI}} CH_3(CH_2)_4CH_3$

D-Glucose → n-Hexane

(B) With Bromine Water

The aldehyde group is oxidized to carboxylic acid:

$CHO(CHOH)_4CH_2OH \xrightarrow{Br_2/H_2O} COOH(CHOH)_4CH_2OH$

Gluconic acid

(C) With Conc. HNO_3

Both terminal groups (CHO and $-CH_2OH$) are oxidized:

$CHO(CHOH)_4CH_2OH \xrightarrow{\text{conc. } HNO_3} COOH(CHOH)_4COOH$

Saccharic acid (Glucaric acid)

26. Give reasons

(A) Carboxylic acids have higher boiling points than alcohols

Carboxylic acids exist as dimers due to strong intermolecular hydrogen bonding.
Hence their boiling points are higher than alcohols of comparable molar mass.

(B) α-Hydrogens of aldehydes and ketones are acidic

Removal of an α-hydrogen forms an enolate ion, which is stabilized by resonance.
Resonance stabilization makes α-hydrogens acidic.

(C) Nucleophilic addition of ammonia and its derivatives does not occur in strongly acidic medium

In strongly acidic medium, ammonia and its derivatives are protonated:

$NH_3 + H^+ \rightarrow NH_4^+$

The protonated species loses nucleophilicity and cannot attack the carbonyl carbon effectively.
Therefore nucleophilic addition is suppressed.

27. **(A)** Reimer-Tiemann Reaction

$C_6H_5OH + CHCl_3 + 3NaOH \rightarrow 0 - HOC_6H_4CHO + 3NaCl + 2H_2O$

Product: Salicylaldehyde

(B) Kolbe's Reaction

$C_6H_5ONa + CO_2 \xrightarrow[6-7\text{ atm}]{400\text{ K}} 0 - HOC_6H_4COONa$

$\xrightarrow{H^+} 0 - HOC_6H_4COOH$

Product: Salicylic acid

(C) Friedel-Crafts Acylation of Anisole

$C_6H_5OCH_3 + CH_3COCl \xrightarrow{AlCl_3}$ o - and p-methoxyacetophenone

Major product: p-Methoxyacetophenone

28. Given: Molecular formula C_4H_9Br

(A) Structures of X and Y

Rate depends only on concentration of X ⇒ SN1 reaction
Thus X is tertiary bromide:
$X = (CH_3)_3CBr$
(2-Bromo-2-methylpropane, tert-butyl bromide)
Y is optically active and rate depends on both substrate and OH^- ⇒ SN2 reaction
Optically active isomer:
$Y = CH_3CHBrCH_2CH_3$
(2-Bromobutane)

(B) X

Reason: X undergoes SN1 reaction through a planar carbocation intermediate. Nucleophile attacks from both sides, giving racemisation.

(C) Y

Reason: Y undergoes SN 2 reaction involving backside attack by OH', producing Walden inversion (inversion of configuration).

29. (A) (i) In an aqueous medium, the basic strength of amines depends on three competing factors: inductive effect $(+I$, solvation (hydration) effect, and steric hindrance.

(1) Solvation Effect: The conjugate acid of methylamine $(CH_3NH_3^+)$has three hydrogen atoms available to form strong hydrogen bonds with water molecules, making it highly stable. The conjugate acid of trimethylamine $((CH_3)_3NH^+)$has only one hydrogen atom for hydrogen bonding, making it much less stable.

(2) Steric Hindrance: The three bulky methyl groups in $(CH_3)_3$ N create steric hindrance, obstructing the attack of water molecules and lowering its stability in water.

Due to the dominant stabilization from solvation and minimal steric hindrance, methylamine $(CH_3 - NH_2)$ acts as a stronger base than trimethylamine $((CH_3)_3$ N) in aqueous solution.

(ii) Structural formulae of Compound A and B :

(1) Formation of A (Hoffmann Bromamide Degradation):

$$CH_3CONH_2 \xrightarrow{NaOBr} \underbrace{CH_3 - NH_2}_{A}$$

• Compound A: Methylamine (Methanamine)

(2) Formation of B (Benzoylation / Schotten-Baumann Reaction):

$$CH_3 - NH_2 + C_6H_5COCl \xrightarrow{Base} \underbrace{C_6H_5 - CONH - CH_3}_{B} + HCl$$

Compound B: N-Methylbenzamide

(B) Identify Compound ' X ' $(C_3H_9$ N) :

• Principle:

• Primary amines react with Hinsberg reagent ($C_6H_5SO_2Cl$) to form a product that is soluble in alkali.

• Secondary amines react to form a product that has no acidic hydrogen on the nitrogen atom, making it insoluble in alkali.

• Conclusion: Since ' X ' gives a product insoluble in alkali, it must be a secondary amine.

• Structure of " X ": For the molecular formula C_3H_9 N, the secondary amine is N Methylethanamine.

$X = CH_3 - NH - CH_2 - CH_3$

OR

(B) This conversion is carried out in two steps:

(1) Diazotization: React aniline with nitrous acid $(NaNO_2 + HCl)$ at $0 - 5°C$ to form Benzene diazonium chloride.

$$C_6H_5NH_2 \xrightarrow[0-5°C]{NaNO_2+HCl} C_6H_5\ N_2^+Cl^-$$

(2) Sandmeyer Reaction: Treat the benzene diazonium chloride with cuprous cyanide (CuCN) dissolved in KCN to obtain benzonitrile.

$$C_6H_5\ N_2^+Cl^- \xrightarrow{CuCN/KCN} \underbrace{C_6H_5CN}_{\text{Benyonitrile}} + N_2$$

(C) (1) Prevents Oxidation and Multi-substitution: The $-NH_2$ group is highly activating. Direct nitration with strong acids $(HNO_3 + H_2SO_4)$ results in extensive oxidation of aniline into tarry matter and multi-substituted products.

(2) Prevents Meta-product Formation: In a strongly acidic nitrating mixture, the $-NH_2$ group gets protonated to form the anilinium ion $(-NH_3^+)$. This ion is strongly deactivating and meta-directing, leading to a significant amount of the undesired meta-nitroaniline.

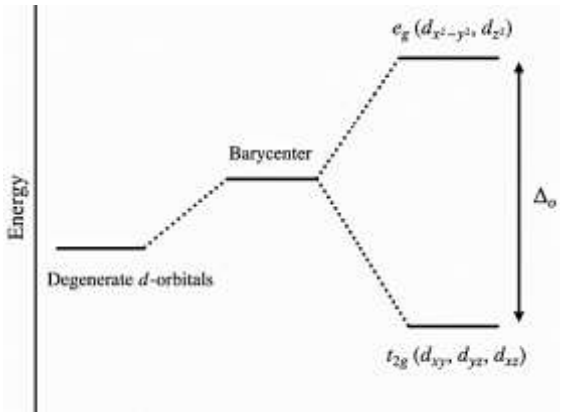
Role of Acetylation:

Acetylation converts $-NH_2$ to the less activating acetamido group $(-NHCOCH_3)$. The lone pair of electrons on the nitrogen is delocalized into the carbonyl group by resonance, which reduces its electron-donating power, protects it from protonation, and ensures controlled mono-nitration predominantly at the para-position.

30. (A) Octahedral Crystal Field Splitting

• Answer: The energies of the $d_{x^2-y^2}$ and d_{z^2} orbitals (collectively called the e_g set) will be raised.

• Reason: In an octahedral complex, six ligands approach the central metal ion directly along the Cartesian axes (x, y and z axes). The lobes of the $d_{x^2} - y^2$ and d_{z^2} orbitals lie directly along these axes, whereas the lobes of the $d_{xy}d_{yz}$, and d_{xz} orbitals (t_{2g} set) lie in between the axes. Consequently, electrons in the e_g orbitals experience greater electrostatic repulsion from the incoming ligands, raising their potential energy relative to the t_{2g} orbitals.



(B) Crystal Field Electronic Configurations

Cobalt (Co. $Z = 27$) has a ground-state configuration of $[Ar]3d^7 4s^2$. In both complexes below, Cobalt is in the +3 oxidation state (Co^{3+}), leaving it with a $3d^6$ configuration.

(i) $[CoF_6]^{3-}$

• Ligand Field: $F^-$is a weak field ligand, meaning the crystal field splitting energy is less than the pairing energy ($\Delta_o < P$).

• Configuration: Electrons remain unpaired as much as possible across both levels.

• Result: $t_{2g}^4 e_g^2$

(ii) $[Co(NH_3)_6]^{3+}$

• Ligand Field: NH_3 is a strong field ligand, meaning the splitting energy is greater than the pairing energy ($\Delta_o > P$).

• Configuration: Electrons preferentially pair up entirely in the lower energy level before occupying the higher level.

• Result: $t_{2g}^6 e_g^0$

(C) Magnetic Properties of Nickel Complexes

Nickel (Ni, $Z = 28$) has a ground-state configuration of $[Ar]3d^8 4s^2$.

• In $[NiCl_4]^{2-}$:

• Nickel is in the +2 oxidation state ($Ni^{2+}: 3d^8 4s^0$).

• $Cl^-$is a weak field ligand and cannot force the electrons to pair up.

• The 3d orbital layout retains two unpaired electrons, making the complex paramagnetic.

• In $[Ni(CO)_4]$:

• Nickel is in the 0 oxidation state ($Ni^0: 3d^8 4s^2$).

• CO is a strong field ligand. It forces the two 4s electrons to shift completely into the 3d orbitals and pair up.

• This rearranges the configuration into a fully filled $3d^{10}$ state. With zero unpaired electrons, the complex is diamagnetic.

OR

(C) Hybridization and Magnetic Behaviour of $[Fe(CN)_6]^{3-}$

• Oxidation State: Iron ($Fc, Z = 26$) has a ground state of $[Ar]3d^6 4s^2$. Here, it is in the +3 oxidation state (Fe^{3+}), yielding a $3d^5$ configuration.

• Ligand Effect: $CN^-$is a strong field ligand that forces internal pairing among the five 3d electrons, packing them into three 3d orbitals ($\uparrow\downarrow, \uparrow\downarrow, \uparrow$).

• Hybridization: This leaves two inner 3d orbitals completely vacant. These combine with the 4s and three 4p orbitals to form d^2sp^3 hybridization (inner orbital octahedral complex).

• Magnetic Behaviour: One unpaired electron remains in the 3d subshell, making the complex paramagnetic.

31. (A) (i) Structures of $X(C_5H_{10}O)$

(I) Does not give Tollens' test but gives positive iodoform test It should be a methyl ketone.

$CH_3COCH_2CH_2CH_3$

Pentan-2-one

(II) Does not give Tollens" test and iodoform test but undergoes Aldol condensation It should be a ketone with α-hydrogen but without CH_3CO - group.

$CH_3CH_2COCH_2CH_3$

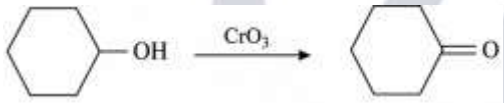
Pentan-3-one

(III) Undergoes Cannizzaro reaction

It must be an aldehyde without α-hydrogen.
$(CH_3)_3CCHO$
2,2-Dimethylpropanal (Pivaldehyde)
(ii) Conversion into benzoic acid
(I) Acetophenone - Benzoic acid
$C_6H_5COCH_3 \xrightarrow{I_2/NaOH} C_6H_5COONa \xrightarrow{H^+} C_6H_5COOH$
(II) Ethylbenzene - Benzoic acid
$C_6H_5CH_2CH_3 \xrightarrow[\Delta]{KMnO_4/OH^-} C_6H_5COOH$

OR

(B) (i) 2,4-Dinitrophenylhydrazone derivative of benzaldehyde
$C_6H_5CHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow C_6H_5CH = NNHC_6H_3(NO_2)_2 + H_2O$
Structure:
$C_6H_5CH = NNH - C_6H_3(NO_2)_2$
(ii) Increasing order of reactivity towards HCN
Di-tert-butyl ketone $<$ Acetone $<$ Acetaldehyde
(iii) Distinguish between benzoic acid and ethyl benzoate
Sodium bicarbonate test
• Benzoic acid gives brisk effervescence of CO_2.
• Ethyl benzoate does not react.
$NaHCO_3$ test
(iv) Reagent to convert ethanenitrile to ethanal
Stephen reduction
$CH_3CN \xrightarrow{SnCl_2/HCl} CH_3CHO$
$SnCl_2/HCl$
(v) Draw the structure of X
The given compound is cyclohexanol.
Oxidation with CrO 3 converts a secondary alcohol into a ketone.
Cyclohexanol $\xrightarrow{CrO_3}$ Cyclohexanone
Structure of X :



Cyclohexanol X (Cyclohexanone)

32. (A) (i) Answers regarding $E^*_{M^{2+}/M}$ values:

(I) Irregular trend: It is due to the irregular variation in sublimation (atomization) energies and sum of the first two ionization enthalpies ($\Delta H_1 + \Delta H_2$) across the transition series.
(II) Exceptionally positive copper value: Copper has a high enthalpy of atomization and a very high ionization enthalpy. The hydration energy released when Cu^{2+} ions form is not high enough to compensate for these large energy requirements.
(III) Highly negative manganese value: Mn^{2+} has a highly stable, half-filled d^5 electronic configuration ($[Ar]3d^5$). This extra stability makes it easier to remove two electrons from Mn metal.
(ii) Ionic equations for $KMnO_4$ reacting with I^-:
• Acidic medium:
$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$
• Alkaline medium:
$2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + IO_3^- + 2OH^-$

OR

(B) (i) Lanthanoid series members:
(I) +4 oxidation state: Cerium (Ce)
(II) +2 oxidation state: Europium (Eu)
(ii) Good catalysts: They provide a large surface area for reactant adsorption and can exhibit variable oxidation states to form stable intermediate complexes.

(iii) Melting points: $Cr(3d^5 4s^1)$ has six unpaired electrons contributing to strong metallic bonding. $Mn(3d^5 4s^2)$ has a highly stable half-filled d-shell where electrons are strongly held by the nucleus, resulting in weaker metallic bonding.

(iv) Acidic $KMnO_4$ standing: It slowly decomposes by oxidizing water, liberating oxygen gas. This is a chemical decomposition/redox reaction.

$4MnO_4^- + 12H^+ \rightarrow 4Mn^{2+} + 5O_2 \uparrow + 6H_2O$

33. (A)(1) Calculate standard cell potential (E^*_{cell}):

$E^*_{cell} = E^*_{cathode} - E^*_{anodec}$

$E^*_{cell} = 0.80\ V - (-2.37\ V) = 3.17\ V$

(2) Calculate cell potential (E_{cell}) using Nernst Equation:

The overall balanced reaction transfers $n = 2$ electrons: $Mg(s) + 2Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s)$

$$E_{ccll} = E^*_{ccll} - \frac{0.0591}{n}\log\frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$E_{ccll} = 3.17 - \frac{0.0591}{2}\log\frac{0.01}{(0.001)^2}$$

$E_{ccll} = 3.17 - 0.02955\log(10^4)$

$E_{ccll} = 3.17 - (0.02955 \times 4) = 3.17 - 0.1182 = 3.052V$

(3) Calculate Gibbs free energy change (ΔG):

$\Delta G = -nFE_{ccll}$

$\Delta G = -2 \times 96500C\ mol^{-1} \times 3.052\ V = -589{,}036\ J\ mol^{-1} \approx -589.04\ kJ\ mol^{-1}$

OR

(B) (1) Find standard cell potential (E^*_{cell}):

$\Delta G^* = -nFE^*_{cell}$ (where $n = 2$)

$-43500 = -2 \times 96500 \times E^*_{cell}$

$$E^*_{cell} = \frac{43500}{193000} = 0.2254\ V$$

(2) Calculate cell potential (E_{cell}):

$$Q = \frac{[H^+]^2 \cdot [Cl^-]^2}{p_{H_2}} = \frac{(0.1)^2 \cdot (0.2)^2}{0.4} = \frac{10^{-2} \times 0.04}{0.4} = 10^{-3}$$

Using the Nernst Equation:

$$E_{ccll} = E^*_{cell} - \frac{0.0591}{2}\log Q$$

$E_{ccll} = 0.2254 - 0.02955\log(10^{-3})$

$E_{ccll} = 0.2254 - (0.02955 \times -3) = 0.2254 + 0.08865 = 0.314\ V$

34. (a) Calculate $\Delta_r G^\circ$

Given:

$E^\circ_{Ag^+/Ag} = 0.80\ V$

$E^\circ_{Zn^{2+}/Zn} = -0.76\ V$

Cell potential:

$E^\circ_{cell} = 0.80 - (-0.76) = 1.56\ V$

Number of electrons transferred:

$n = 2$

Using

$\Delta_r G^0 = -nFE^0_{cell}$

$= -2 \times 96500 \times 1.56$

$= -301080\ J\ mol^{-1}$

$= -301.080\ kJ\ mol^{-1}$

35. (b) Analysis of options:

(a) Molecularity of a reaction is an experimental quantity. → Incorrect. Order of reaction is experimental; molecularity is a theoretical concept.

(b) For complex reactions molecularity has no meaning. → Correct. Molecularity is only defined for elementary steps. For an overall complex mechanism, overall molecularity has no significance.

(c) Molecularity of a reaction can be zero or even a fraction. → Incorrect.

Molecularity is always a positive whole number (1,2,3).

(d) Molecularity more than three is very common in chemical reactions. → Incorrect. Molecularity greater than three is very rare because the probability of more than three molecules colliding simultaneously is negligible.

36. (a) The overall order of a reaction is the sum of the powers of the concentration terms in the rate law equation.

Order $= \frac{1}{2} + 1 = 1.5$

37. (c) Step-by-Step Solution:

• Chromium (Cr) has an atomic number of 24 .

• Expected configuration: $[Ar]3d^4 4s^2$

• Due to extra stability associated with a half-filled d-subshell (d^5), one electron from the 4s orbital shifts to the 3d orbital.

• Actual stable configuration: $[Ar]3d^5 4s^1$

38. (b) (1) Identify ligands and arrange alphabetically:

• NH_3 = ammine

• Cl = chlorido

• Since there are two of each: diamminedichlorido

(2) Determine the oxidation state of Platinum (Pt):

$x + 2(0) + 2(-1) = 0 \Longrightarrow x = +2$

The metal is in a neutral complex, so its name remains platinum followed by its oxidation state in Roman numerals: platinum(II).

3. Combine according to IUPAC rules (no spaces):

• diamminedichloridoplatinum(II)

39. (d) • Definition: A heteroleptic complex contains more than one type of ligand attached to the central metal atom.

Analysis:

(a) $[Co(NH_3)_6]^{3+}$ - Homoleptic (only NH_3 ligands).

(b) $[Cr(NH_3)_6]^{3+}$ - Homoleptic (only NH_3 ligands).

(c) $[Ni(H_2O)_6]^{2+}$ - Homoleptic (only H_2O ligands).

(d) $[Co(NH_3)_4Cl_2]^{+}$- Heteroleptic (contains two different ligands: NH_3 and Cl^-).

40. (b) • Definition: A chiral molecule contains an asymmetric carbon atom (a stereocenter) bonded to four entirely different groups.

Analysis:

(a) Propan-2-ol: $CH_3 - CH(OH) - CH_3$ (Two identical $-CH_3$ groups; achiral).

(b) Butan-2-ol: $CH_3 - CH(OH) - CH_2CH_3$ (The second carbon is attached to $-H, -OH, -CH_3$, and $-CH_2CH_3$. All four groups are different; chiral).

(c) 1-Bromobutane: $CH_3CH_2CH_2CH_2Br$ (No carbon has 4 different groups; achiral).

(d) 2-Bromopropane: $CH_3 - CH(Br) - CH_3$ (Two identical $-CH_3$ groups; achiral).

41. (c) • Boiling point increases with increasing molecular mass (more surface area, stronger Van der Waals forces). Therefore: Propan-1-ol < Butan-1-ol < Pentan-1-ol.

• For isomeric alcohols (same molecular formula), branching increases spherical shape, which decreases surface area and lowers the boiling point. Therefore: Butan-2-ol (branched) < Butan-1-ol (straight chain).

• Combined Order: Propan-1-ol < Butan-2-ol < Butan-1-ol < Pentan-1-ol.

42. (a) • Chemical Equation: Ethanenitrile ($CH_3C \equiv N$) undergoes complete reduction when treated with $LiAlH_4$:

$CH_3 - C \equiv N \xrightarrow{LiAlH_4} CH_3 - CH_2 - NH_2$

• Product: The resulting molecule ($CH_3CH_2NH_2$) is commonly named Ethylamine.

43. (c) • DNA contains the nitrogenous bases Adenine (A), Guanine (G), Cytosine (C), and Thymine (T).

• RNA contains Adenine (A), Guanine (G), Cytosine (C), and Uracil (U) instead of Thymine.

44. (b) Fact: Amino acids link together via an amide linkage ($-CO - NH -$) formed between the carboxyl group of one amino acid molecule and the amino group of another. This specific linkage is called a peptide bond.

45. (d) • Options (a), (b), and (c) are all successfully explained by the open-chain structure of glucose, confirming the presence of a 6 -carbon straight chain, a carbonyl group, and an aldehyde group respectively.

• However, the existence of glucose in two distinct crystalline forms- α and β (anomers)-cannot be explained by an open-chain structure. It requires a cyclic structure (hemiacetal form) resulting from the reaction between the -CHO group and the -OH group at the $C - 5$ carbon.

46. (a) • Assertion (A) is true: The given decomposition reaction of hydrogen iodide ($2HI \longrightarrow H_2 + I_2$) is an elementary bimolecular reaction, making its molecularity equal to 2 .

• Reason (R) is true: By definition, molecularity is the number of reactant molecules that must collide simultaneously to result in a chemical reaction. Here, two molecules of HI collide, perfectly explaining why the molecularity is 2 .

47. (a) • Assertion (A) is true: Zinc (Zn), cadmium (Cd), and mercury (Hg) belong to Group 12 and are classified as d-block elements but are not strictly considered transition elements.

• Reason (R) is true: A transition element is defined as one that has an incompletely filled d-orbital in its ground state or in any of its common oxidation states. Since Zn, Cd, and Hg possess completely filled d^{10} configurations in both their atomic ground states and their +2 oxidation states, they do not fit this definition. The reason directly explains the assertion.

48. (d) Gabriel phthalimide synthesis cannot be used to prepare aromatic primary amines because aryl halides do not undergo nucleophilic substitution ($S_N 2$) with the phthalimide anion due to resonance stabilization (partial double-bond character of the C-X bond) and steric hindrance.

49. (c) Bromine water is a mild oxidizing agent that successfully oxidizes the aldehyde (-CHO) group of open-chain glucose into a carboxylic acid (-COOH) group, forming gluconic acid. Therefore, a carbonyl group is very much present in the open-chain form.

SECTION - B

50. (A) Given:

• Initial concentration $([A]_0) = 0.6 \text{ mol } L^{-1}$

• Final concentration $([A]) = 0.2 \text{ mol } L^{-1}$

• Time $(t) = 5$ minutes

• $\log 3 = 0.48$

Formula for first-order rate constant (k):

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

Calculation:

$$k = \frac{2.303}{5} \log \left(\frac{0.6}{0.2}\right)$$

$$k = \frac{2.303}{5} \log 3$$

$$k = \frac{2.303 \times 0.48}{5} = \frac{1.10544}{5} \approx 0.221 \text{ min}^{-1}$$

(In seconds: $k = \frac{a221}{60} \approx 3.68 \times 10^{-3} s^{-1}$)

OR

(B) Given:

• Rate constant $(k) = 2.54 \times 10^{-3} \text{ s}^{-1}$

• Amount decomposed $= \frac{3}{4}$ th, so remaining reactant $([A]) = 1 - \frac{3}{4} = \frac{1}{4}[A]_0$

• $\log 4 = 0.60$

Formula:

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

Calculation:

$$t = \frac{2.303}{2.54 \times 10^{-3}} \log \left(\frac{[A]_0}{\frac{1}{4}[A]_0}\right)$$

$$t = \frac{2.303}{2.54 \times 10^{-3}} \log 4$$

$$t = \frac{2.303 \times 0.60}{2.54 \times 10^{-3}} = \frac{1.3818}{2.54 \times 10^{-3}} \approx 544 \text{ seconds}$$

51. (A) Define activation energy:

• Activation energy (E_a) is the minimum extra amount of energy required by reactant molecules to cross the energy barrier and convert into products.

(B) Units of rate constant:
(i) Zero-order reaction: $\text{molL}^{-1}\ \text{s}^{-1}$
(ii) Second-order reaction: $\text{Lmol}^{-1}\ \text{s}^{-1}$ (or $\text{mol}^{-1}\ \text{L}\ \text{s}^{-1}$)

52. **(A)** Chromium (Cr): Electronic configuration is $[\text{Ar}]3\text{d}^5 4\text{s}^1$. Removing the solitary electron from the 4s subshell requires less energy.

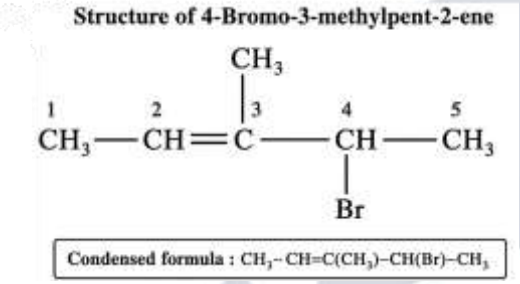
• Zinc (Zn): Electronic configuration is $[\text{Ar}]3\text{d}^{10}4\text{s}^2$. It has a fully filled stable 4s subshell and a significantly higher nuclear charge (higher effective nuclear charge), making it harder to remove an electron.

(B) Mention any one property of the transition elements which makes them good catalysts:
They can exhibit variable oxidation states and possess vacant d-orbitals to form unstable intermediate complexes easily.

53. **(A)** The total number of coordinate covalent bonds formed by the surrounding ligands directly attached to the central metal atom or ion in a coordination complex.

(B) It exhibits Optical Isomerism (dextro and laevo forms) because it is a symmetric tris-chelate complex lacking a plane of symmetry, forming non-superimposable mirror images.

54. **(A)** Structure of 4-Bromo-3-methylpent-2-ene
Parent chain: Pent-2-ene (5 carbons, double bond between C_2 and C_3)
• Methyl group at C_3
• Bromo group at C_4
Structure:



Condensed formula:
$\text{CH}_3 - \text{CH} = \text{C}(\text{CH}_3) - \text{CH}(\text{Br}) - \text{CH}_3$
(B) Chloroethane undergoes nucleophilic substitution (hydrolysis). The chlorine atom is replaced by the hydroxyl group to form ethanol.
$\text{CH}_3\text{CH}_2\text{Cl} + \text{KOH}_{(\text{aq})} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{KCl}$
Product formed: Ethanol (ethyl alcohol).
Reaction type: Nucleophilic substitution reaction (SN2).

55. Molar mass of the solute
Given:
• Mass of solute $= 1.5\ \text{g}$
• Mass of benzene $= 90\ \text{g} = 0.090\ \text{kg}$
• $\text{K}_\text{b} = 2.52\text{K kg mol}^{-1}$
• $\Delta\text{T}_\text{b} = 353.93 - 353.23 = 0.70\ \text{K}$
Using:
$\Delta\text{T}_\text{b} = \text{K}_\text{b}\text{m}$
$\text{m} = \dfrac{0.70}{2.52} = 0.278\ \text{mol kg}^{-1}$
Number of moles of solute:
$\text{n} = \text{m} \times 0.090$
$\text{n} = 0.278 \times 0.090 = 0.0250\ \text{mol}$
Molar mass:
$\text{M} = \dfrac{1.5}{0.0250}$
$\text{M} = 60\ \text{g mol}^{-1}$

56. EMF of the cell
Cell:
$\text{Sn}|\text{Sn}^{2+}(0.001\text{M})||\text{H}^{+}(0.01\text{M})|\text{H}_2(1\ \text{bar})\ |\ \text{Pt}$
Left electrode (Anode)

$Sn^{2+} + 2e^- \rightleftharpoons Sn$

$E_{Sn} = E^\circ - \frac{0.0591}{2}\log\frac{1}{[Sn^{2+}]}$

$= -0.14 - \frac{0.0591}{2}\log\frac{1}{0.001}$

$= -0.14 - 0.08865$

$E_{Sn} = -0.229\ V$

Right electrode (Hydrogen electrode)

$2H^+ + 2e^- \rightleftharpoons H_2$

$E_H = 0 - \frac{0.0591}{2}\log\frac{1}{(0.01)^2}$

$= -0.0591 \times 2$

$E_H = -0.118\ V$

Cell emf

$E_{cell} = E_{cathode} - E_{anode}$

$= (-0.118) - (-0.229)$

$E_{cell} = 0.111\ V$

57. **(A)** Complete and balance the following equations:

(i) Thermal decomposition of potassium permanganate:

$2KMnO_4 \xrightarrow{513\ K} K_2MnO_4 + MnO_2 + O_2$

(ii) Preparation of potassium dichromate:

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

(B) Why is it difficult to separate lanthanoid elements in pure state?

• Due to lanthanoid contraction, the atomic and ionic radii of lanthanoid elements are nearly identical.

• Consequently, they exhibit very similar chemical and physical properties, making separation by standard chemical methods difficult.

58. **(A)** Justify magnetic behavior (Co atomic number = 27)

The electronic configuration of Co is $[Ar]3d^74s^2$. In both complexes, cobalt is in the +3 oxidation state (Co^{3+}), with a $3d^6$ configuration.

• $[Co(NH_3)_6]^{3+}$: NH_3 is a strong-field ligand. It forces the 3d electrons to pair up.

Paired arrangement: $(t_{2g})^6(e_g)^0$

Since there are zero unpaired electrons, it is diamagnetic.

• $[CoF_6]^{3-}$: F^- is a weak-field ligand. It cannot force electron pairing.

Unpaired arrangement: $(t_{2g})^4(e_g)^2$

Since there are four unpaired electrons, it is paramagnetic.

(B) Electronic configuration for d^4 ion if $\Delta_o > P$

• $\Delta_o > P$ means the crystal field splitting energy is greater than the pairing energy.

• This favors a low-spin complex where electrons prefer pairing up in the lower energy orbitals over moving to a higher energy level.

• Therefore, the fourth electron pairs up in the t_{2g} orbital:

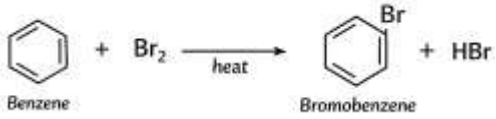
$t_{2g}^4 e_g^0$

59. **(A)** Given reaction:

Cyclohexene $+Br_2$ (heat) $\rightarrow$?

In the presence of heat, bromination occurs at the allylic position (free radical substitution).

Major Product: 3-Bromocyclohexene



(B) A racemic mixture is an equimolar mixture of two enantiomers (d- and I-forms) which rotates planepolarized light equally in opposite directions, resulting in zero net optical rotation.

(C) p-Dichlorobenzene is more symmetrical than the ortho and meta isomers. Due to its symmetrical structure,

molecules pack more efficiently in the crystal lattice, leading to stronger intermolecular forces and hence a higher melting point.

60. **(A)** Rosenmund Reduction

Reduction of acid chloride to aldehyde:

$$RCOCl + H_2 \xrightarrow[BaSO_4]{pd^2} RCHO + HCl$$

(B) Cannizzaro Reaction

Aldehydes without α-hydrogen undergo disproportionation in concentrated alkali:

$$2C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$$

(C) Hell-Volhard-Zelinsky (HVZ) Reaction

α-Halogenation of carboxylic acids:

$$CH_3COOH \xrightarrow[\Delta]{Br_2/P} CH_2BrCOOH$$

61. **(A) (i)** A reducing sugar is a carbohydrate that contains a free aldehyde group or a free ketone group (through tautomerism) and can reduce Tollens' reagent or Fehling's solution.

Examples: Glucose, Maltose.

(ii) (I) Fibrous Proteins and Globular Proteins

Fibrous Proteins	Globular Proteins
Long, thread-like structure	Spherical structure
Insoluble in water	Generally soluble in water
Structural function	Functional/metabolic role
Example: Keratin	Example: Hemoglobin

(II) Nucleotide and Nucleoside

Nucleoside	Nucleotide
Nitrogenous base + Sugar	Nitrogenous base + Sugar + Phosphate
No phosphate group	Contains phosphate group
Example: Adenosine	Example: AMP

OR

(B) Reactions of Glucose

(i) With Hydroxylamine (NH_2OH)

Glucose forms glucose oxime.

$$\text{Glucose} + NH_2OH \rightarrow \text{Glucose oxime} + H_2O$$

(ii) With Acetic Anhydride $(CH_3CO)_2O$

Glucose forms glucose pentaacetate.

$$\text{Glucose} + 5(CH_3CO)_2O \rightarrow \text{Glucose pentaacetate}$$

(iii) With Concentrated HNO_3

Both terminal groups are oxidized to give saccharic acid (glucaric acid).

$$CHO(CHOH)_4CH_2OH \xrightarrow{\text{conc. } HNO_3} HOOC(CHOH)_4COOH$$

Product: Saccharic acid (Glucaric acid).

62. **(A)** Calculation of the mass of $CaCl_2$

(1) Given Data:

• Osmotic pressure $(\pi) = 0.70$ atm

• Van't Hoff factor (i) $= 2.59$
• Volume of water (V) $= 2.46$ L
• Temperature (T) $= 27°C = 27 + 273 = 300$ K
• Gas constant (R) $= 0.082$ L atm K^{-1} mol^{-1}
• Molar mass of $CaCl_2$(M) $= 111$ g mol^{-1}
(2) Formula:
$\pi = i \cdot C \cdot R \cdot T$
$\pi = i \cdot \left(\frac{w}{M \cdot V}\right) \cdot R \cdot T$
Where w is the mass of $CaCl_2$ dissolved.
(3) Calculation:
Rearranging the formula to find the mass (w):
$w = \frac{\pi \cdot M \cdot V}{i \cdot R \cdot T}$
Substitute the values into the equation:
$w = \frac{0.70 \times 111 \times 2.46}{2.59 \times 0.082 \times 300}$
Since $0.082 \times 300 = 24.6$:
$w = \frac{0.70 \times 111 \times 2.46}{2.59 \times 24.6}$
Simplify the terms $\left(\frac{2.46}{24.6} = 0.1\right)$:
$w = \frac{0.70 \times 111 \times 0.1}{2.59}$
$w = \frac{7.77}{2.59} = 3$ g
Answer: The amount of $CaCl_2$ dissolved is 3 g.
(B) Swelling of Raisins
• Phenomenon: Endosmosis (a type of osmosis where water moves into the cell/raisin).

OR

(B) Advantages of Osmotic Pressure Measurement
Osmotic pressure measurement is preferred over other colligative properties (like depression of freezing point or elevation of boiling point) because:
• Room Temperature: Measurements are taken at room temperature, which prevents the denaturation of sensitive biomolecules like proteins.
• Large Magnitude: The pressure values are relatively large and easily measurable even for highly dilute solutions.
• Molarity used: It uses molarity instead of molality, which is easier to prepare experimentally.
(C) Desalination of Sea Water
• Phenomenon: Reverse Osmosis (RO).

63. **(A)** Complete the following equations:
(i) Reduction of Acetamide
• Reaction:
$CH_3CONH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} CH_3CH_2NH_2$
• Explanation: Lithium aluminum hydride ($LiAlH_4$) reduces the carbonyl group ($C = O$) of the amide into a methylene group (CH_2), forming a primary amine (Ethylamine).
(ii) Reduction of 4-Nitrotoluene
• Reaction:
$O_2\ N - C_6H_4 - CH_3 \xrightarrow{Fe+HCl} H_2\ N - C_6H_4 - CH_3$
• Explanation: Iron and hydrochloric acid ($Fc + HCl$) selectively reduce the nitro group ($-NO_2$) attached to the benzene ring into a primary amino group ($-NH_2$). producing 4-methylaniline (p -toluidine).
(B) Hydrogen Bonding: Primary amines (R-NH2) have two hydrogen atoms directly attached to the highly electronegative nitrogen atom. This allows them to form strong intermolecular hydrogen bonds.
• No Hydrogen Atoms: Tertiary amines (R_3 N) have no hydrogen atoms attached to the nitrogen atom, preventing them from forming intermolecular hydrogen bonds with each other.

• Result: More energy is required to break the intermolecular hydrogen bonds in primary amines, resulting in a higher boiling point.

(C) Classify the following amines as primary, secondary or tertiary:

(i) Tertiary (3^*) amine: The nitrogen atom is bonded to three carbon atoms (one from the naphthalene ring and two from the methyl groups).

(ii) Primary (1^*) amine: The nitrogen atom is directly bonded to only one carbon atom (from the naphthalene ring) and carries two hydrogen atoms.

OR

(C) Out of Butan-1-amine and Butan-1-ol, which is more soluble in water?

• Answer: Butan-1-ol is more soluble in water than Butan-1-amine.

• Reasoning: Oxygen is more electronegative than nitrogen ($O = 3.5, N = 3.0$). As a result, the O-H bond in Butan-1-ol is more polar than the N-H bond in Butan-1amine, allowing alcohol molecules to form stronger hydrogen bonds with water molecules.

64. **(A)(i)** How will you convert the following :

(I) Propanone to Propene

(1) Reduction : Reduce propanone to propan−2−ol using sodium borohydride ($NaBH_4$) or lithium aluminum hydride ($LiAlH_4$) .

$$CH_3COCH_3 \xrightarrow{NaBH_4} CH_3CH(OH)CH_3$$

(2) Dehydration : Heat propan−2−ol with concentrated sulfuric acid (H_2SO_4) at 443 K (or heating with Al_2O_3) to undergo dehydration.

$$CH_3CH(OH)CH_3 \xrightarrow{\text{conc. } H_2SO_4, \Delta} CH_3CH = CH_2 + H_2O$$

(II) Benzoic acid to Benzaldehyde

(1) Chlorination : React benzoic acid with thionyl chloride （ $SOCl_2$ ） to form benzoyl chloride.

$$C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl + SO_2 + HCl$$

(2) Rosenmund Reduction : Reduce benzoyl chloride using hydrogen gas over a palladium catalyst supported on barium sulfate （ $Pd/BaSO_4$ ） poisoned with sulfur or quinoline.

$$C_6H_5COCl \xrightarrow{H_2, Pd/BaSO_4} C_6H_5CHO + HCl$$

(III) Benzene to m-Nitroacetophenone

(1) Friedel-Crafts Acylation: React benzene with acetyl chloride (CH_3COCl) in the presence of anhydrous aluminum chloride ($AlCl_3$) to form acetophenone.

$$C_6H_6 + CH_3COCl \xrightarrow{\text{Anhyd. } AlCl_3} C_6H_5COCH_3 + HCl$$

(2) Nitration: Acetophenone contains an acyl group ($-COCH_3$), which is a metadirecting group. Treat acetophenone with a nitrating mixture (concentrated HNO_3 and concentrated H_2SO_4) to obtain m-nitroacetophenone.

$$C_6H_5COCH_3 \xrightarrow{\text{conc. } HNO_3 / \text{ conc. } H_2SO_4} m - NO_2 - C_6H_4 - COCH_3$$

(ii) (I) The nucleophilic addition of HCN depends on steric hindrance (bulkier groups slow it down) and electronic factors (alkyl groups decrease the electrophilicity of the carbonyl carbon).

• Steric hindrance order: Di-tert-butyl ketone > Acetone > Acetaldehyde.

• Increasing order of reactivity:

$$[(CH_3)_3C]_2C = O < (CH_3)_2C = O < CH_3CHO$$

(II) Compounds must have at least one **α**-hydrogen atom to undergo Aldol condensation.

• HCHO (Formaldehyde): No α-hydrogen → Cannot undergo Aldol

• C_6H_5CHO (Benzaldehyde): No α-hydrogen → Cannot undergo Aldol

• CH_3CHO (Acetaldehyde): Has 3α-hydrogens → Can undergo Aldol

• Cyclohexanone: Has 4α-hydrogens → Can undergo Aldol

OR

(B) (i) (I) Acetophenene ($C_6H_5COCH_3$) and Benzophenone ($C_6H_5COC_6H_5$)

• Test: Iodoform Test

• Observation: Acetophenone contains a methyl ketone group ($-COCH_3$). When warmed with iodine (I_2) and sodium hydroxide ($NaOH$), it gives a yellow precipitate of iodoform (CHI_3). Benzophenone does not contain a methyl ketone group and does not give this test.

(II) Propanal (CH_3CH_2CHO) and Propanone (CH_3COCH_3)

• Test: Tollen's Test (or Fehling's Test)
• Observation: Propanal is an aldehyde; it reduces Tollen's reagent to form a shiny silver mirror on the walls of the test tube. Propanone is a ketone and does not react with Tollen's reagent.
(III) Pentan-2-one ($CH_3COCH_2CH_2CH_3$) and Pentan-3-one ($CH_3CH_2COCH_2CH_3$)
• Test: lodoform Test
• Observation: Pentan-2-one contains a methyl ketone unit ($-COCH_3$) and reacts with $I_2/NaOH$ to yield a yellow precipitate of iodoform (CHI_3). Pentan-3-one lacks this structure and produces no precipitate.
(ii) (I) Stronger Acid: Fluoroacetic acid (CH_2FCOOH) is stronger than acetic acid (CH_3 COOH).
• Reason: Fluorine is a highly electronegative atom that exerts a powerful electronwithdrawing inductive effect ($-I$ effect). This stabilizes the carboxylate anion (CH_2FCOO^-) formed after losing a proton by dispersing the negative charge, making it easier to release the H^+ion. In contrast, the methyl group ($-CH_3$) in acetic acid has an electron-donating $(+I)$ effect, which destabilizes the conjugate base.
(II) Boiling points depend heavily on the strength of intermolecular forces:
(1) $CH_3CH_2CH_3$ (Propane): Weak nonpolar van der Waals dispersion forces (Lowest).
(2) CH_3OCH_3 (Dimethyl ether): Weak dipole-dipole interactions.
(3) CH_3CHO (Acetaldehyde): Stronger dipole-dipole attractions due to the highly polar carbonyl group.
(4) CH_3CH_2OH (Ethanol): Intermolecular hydrogen bonding (Highest).
Increasing order of boiling points:
$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

65. (A) (i) Calculation of Molar Conductivity and Degree of Dissociation
• Molar Conductivity (Λ_m) :

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

$$\Lambda_m = \frac{1.06 \times 10^{-2}\ S\ cm^{-1} \times 1000}{0.1\ mol\ L^{-1}} = 106\ S\ cm^2\ mol^{-1}$$

• Limiting Molar Conductivity (Λ_m^*) :

$$\Lambda_m^* = \lambda_{Na^+}^* + \lambda_{Cl}^* = 50.1 + 76.5 = 126.6\ S\ cm^2\ mol^{-1}$$

• Degree of Dissociation (α):

$$\alpha = \frac{\Lambda_m}{\Lambda_m^*} = \frac{106}{126.6} \approx 0.837$$

(ii) (I) Direction of Current Flow
• Electrons flow from the anode to the cathode (Zinc electrode to Silver electrode).
• Therefore, conventional current flows in the opposite direction: from the Silver (Ag) electrode to the Zinc (Zn) electrode.
(II) Difference Between Primary and Secondary Batteries
• Primary Battery: Cell reactions are irreversible; the battery becomes dead after use and cannot be recharged (e.g., Dry cell).
• Secondary Battery: Cell reactions are reversible; the battery can be recharged and reused multiple times (e.g., Lead storage battery).

OR

(B) (i) Calculation of Conductivity and Molar Conductivity
• Cell Constant (G^*) :

$$G^* = \kappa_1 \times R_1 = 1.29 \times 10^{-2}\ S\ cm^{-1} \times 100\Omega = 1.29\ cm^{-1}$$

• Conductivity of 0.01 M Solution (κ_2):

$$\kappa_2 = \frac{G^*}{R_2} = \frac{1.29\ cm^{-1}}{300\Omega} = 4.3 \times 10^{-3}\ S\ cm^{-1}$$

• Molar Conductivity (Λ_{m2}) :

$$\Lambda_{m2} = \frac{\kappa_2 \times 1000}{M_2} = \frac{4.3 \times 10^{-3} \times 1000}{0.01} = 430\ S\ cm^2\ mol^{-1}$$

(ii) (I) Advantages of $H_2 - O_2$ Fuel Cell
• Highly efficient (around 70% efficiency).
• Eco-friendly and pollution-free (produces only water vapor as a byproduct).
(II) Constant Potential of Mercury Cell
• The overall reaction does not involve any ions in solution whose concentration changes over time.

66. (A) Identification of Compounds

• A: Ethanol (CH_3CH_2OH)
• B: Sodium ethoxide (CH_3CH_2ONa)
• C: Iodoform (CHI_3)
• D: Diethyl ether ($CH_3CH_2OCH_2CH_3$)
• E: Ethyl iodide (CH_3CH_2I)
Chemical Reactions Involved
(1) Reaction with Sodium:
$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2ONa + H_2 \uparrow$
(2) Iodoform Reaction:
$CH_3CH_2OH + 4I_2 + 6NaOH \rightarrow CHI_3 \downarrow + HCOONa + 5NaI + 5H_2O$
(3) Dehydration at 413 K :
$2CH_3CH_2OH \xrightarrow{H_2SO_4, 413\ K} CH_3CH_2OCH_2CH_3 + H_2O$
(4) Reaction with excess HI:
$CH_3CH_2OCH_2CH_3 + 2HI \xrightarrow{\Delta} 2CH_3CH_2I + H_2O$

OR

(B) (i) Reagents for Conversions
(I) Phenol to 2,4,6-tribromophenol: Bromine water (Br_2/H_2O).
(II) Propene to propan-1-ol: Diborane followed by alkaline hydrogen peroxide (B_2H_6 then H_2O_2/OH^-).
(III) Butan-2-one to butan-2-ol: Sodium borohydride ($NaBH_4$) or $LiAlH_4$.
(ii) Mechanism of Acid-Catalyzed Hydration of Alkene
• Step 1: Protonation of alkene to form a stable carbocation via electrophilic attack by H_3O^+.
$H_2O + H^+ \rightleftharpoons H_3O^+$
$R - CH = CH_2 + H_3O^+ \rightleftharpoons R - C^+H - CH_3 + H_2O$
• Step 2: Nucleophilic attack of water molecule on the carbocation intermediate.
$R - C^+H - CH_3 + H_2O \rightleftharpoons R - CH(O^+H_2) - CH_3$
• Step 3: Deprotonation by a water molecule to generate the alcohol and regenerate the catalyst.
$R - CH(O^+H_2) - CH_3 + H_2O \rightleftharpoons R - CH(OH) - CH_3 + H_3O^+$

67. (b) • In (B) 4-chlorotoluene, the chlorine atom is directly attached to the benzene ring (aryl halide). The lone pairs on the chlorine atom undergo resonance with the π-electrons of the benzene ring.
• This resonance imparts a partial double bond character to the $C - Cl$ bond, making it extremely strong and difficult to break.
• Therefore, aryl halides are highly unreactive toward nucleophilic substitution compared to alkyl or benzyl halides.

68. (d) • The mechanism of acid-catalyzed dehydration of alcohols involves three main steps:
• Protonation of alcohol to form a protonated alcohol (oxonium ion).
• Loss of a water molecule to form a carbocation intermediate (Slowest / Rate-determining step).
• Deprotonation of the carbocation to form an alkene.
• Because step 2 is the slowest step, the intermediate formed during this ratedetermining step is a carbocation.

69. (a) • First, dissociate the coordination compound into its constituent ions:
$[Co(en)_3]_2(SO_4)_3 \rightarrow 2[Co(en)_3]^{3+} + 3SO_4^{2-}$
• Now, determine the oxidation state of Cobalt (Co) in the complex cation [$Co(en)_3]^{3+}$:
• Let the oxidation state of Co be x.
• 'en' (ethylenediamine) is a neutral ligand, so its charge is 0.
• Set up the equation equal to the net charge of the complex (+3) :
$x + 3(0) = +3$
$x = +3$

70. (c) • Primary valency: Corresponds to the oxidation state of the metal. It is ionizable and always satisfied by negative ions (anions).
• Secondary valency: Corresponds to the coordination number. It is non-ionizable and satisfied by neutral molecules or negative ions.

71. (b) • $(C_2H_5)_2NH$ is a secondary (2*) amine, and $(C_2H_5)_3$ N is a tertiary (3*) amine.
• Hinsberg's reagent ($C_6H_5SO_2Cl$) reacts with 2° amines to form a precipitate that is insoluble in alkali, whereas it does not react with 3° amines at all.

72. (b)• In benzylamine (b), the lone pair of electrons on the nitrogen atom is attached to an sp^3 hybridized carbon $(-CH_2-)$.

• This lone pair is not delocalized into the benzene ring by resonance, making it fully available for donation and significantly more basic than aromatic amines ((a),(c) , and (d)).

73. (b) In an alkaline (basic) medium, the orange dichromate ion $(Cr_2O_7^{2-})$ converts into the yellow chromate ion (CrO_4^{2-}) :

$Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O$

74. (a) • A minimum-boiling azeotrope has a higher vapor pressure than the individual pure components.

• A higher-than-expected vapor pressure is the defining characteristic of a positive deviation from Raoult's Law, indicating weaker intermolecular forces between the different molecules in the mixture.

75. (c) • Understand Molality (m): A 2.0 molal aqueous solution means there are 2.0 moles of solute dissolved in 1 kg(1000 g) of water (solvent).

• Moles of solute $(n_{solute}) = 2.0$ mol

• Find Moles of Solvent (Water):

Molar mass of $H_2O = 18$ g/mol

$n_{water} = \frac{1000\ g}{18\ g/mol} \approx 55.55$ mol

• Calculate Mole Fraction (X_{solute}) :

$X_{solute} = \frac{n_{solute}}{n_{solute} + n_{water}}$

$X_{solutce} = \frac{2.0}{2.0 + 55.55} = \frac{2.0}{57.55} \approx 0.03475$

76. (c,d) In a very dilute aqueous NaCl solution, the concentrations of $Na^+$and Cl^-ions are extremely low, so water molecules primarily undergo electrolysis:

(1) At Cathode (Reduction): Water is reduced instead of Na^+because it has a higher reduction potential.

$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$

• Therefore, H_2 gas is evolved at the cathode (Option d).

(2) At Anode (Oxidation): Due to high dilution, water is oxidized instead of Cl^-ions.

$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$

• Therefore, O_2 gas is evolved at the anode (Option c).

77. (b) • For the chemical reaction: $3\ A \rightarrow 2\ B$

(1) Write the rate of reaction expression using stoichiometric coefficients:

$\text{Rate} = -\frac{1}{3}\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt}$

(2) Rearrange the equation to isolate $+\frac{d|\mathbf{B}|}{dt}$:

$+\frac{d[B]}{dt} = -\frac{2}{3}\frac{d[A]}{dt}$

78. (d)• Sucrose: Hydrolyzes into Glucose + Fructose.

• Galactose: It is a monosaccharide and does not undergo hydrolysis.

• Lactose: Hydrolyzes into Glucose + Galactose.

• Maltose: Hydrolyzes into two units of Glucose only.

79. (b) • Assertion: Separation of Zr and Hf is difficult. → True

• Reason: Zr and Hf lie in the same group. → True

Separation is difficult because they have almost identical atomic radii and chemical properties (due to lanthanoid contraction), not merely because they are in the same group.

80. (d) • Assertion: Phenol is less acidic than 4-methylphenol. → False

A methyl group is electron-releasing (+1 effect), which decreases acidity. Therefore, 4-methylphenol is less acidic than phenol.

• Reason: The presence of an electron-releasing group in phenol makes it less acidic. → True

81. (a) • Assertion: Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis. →True

• Reason: Gabriel phthalimide synthesis is used for the preparation of primary aliphatic amines. → True

The reason correctly explains why aromatic primary amines are not obtained by this method.

82. (b) • Assertion: Order of reaction is applicable to elementary as well as complex reactions. →True
• Reason: Order of a reaction is an experimental quantity. → True
But being an experimental quantity does not explain why it is applicable to both elementary and complex reactions.

83. (A) Most reactive isomer towards S_N1 displacement
• Answer: 2-Bromo-2-methylpropane (tert-butyl bromide).
• Structure: $(CH_3)_3C-Br$
• Reason: It forms a tertiary (3^*) carbocation intermediate, which is highly stable due to inductive and hyperconjugation effects.
(B) Isomer giving 2,5-Dimethylhexane with Na/dry ether
• Answer: 1-Bromo-2-methylpropane (isobutyl bromide).
• Structure: $(CH_3)_2CH-CH_2-Br$
• Reason: The Wurtz reaction symmetrically couples two alkyl groups. Cleaving 2,5dimethylhexane in half yields two isobutyl fractions.

84. Overall Order of the Reaction
• Calculation: Order $= 1+\frac{3}{2}=\frac{5}{2}=2.5$
• Can this reaction be elementary?
= No.
• Reason: Elementary reactions happen in a single step. Their order matches their molecularity, which must be a whole integer because fractions of molecules cannot collide. A fractional order proves it is a complex reaction.

85. Addition of KCl: KCl is a non-volatile solute. It lowers the vapor pressure of water. A higher temperature is needed to boil the solution, causing an elevation in boiling point.
• Addition of Methyl Alcohol: Methyl alcohol is a volatile solute with a lower boiling point than water. It increases the total vapor pressure of the solution, causing it to boil at a lower temperature (depression in boiling point).

86. (A): IUPAC Names
(i) $[PtCl_2(en)_2]_{SO_4}$: Dichloridobis(ethane-1,2-diamine)platinum(IV) sulfate
(ii) $(NH_4)_2[CoF_4]$: Ammonium tetrafluoridocobaltate(II)
OR
(B) Definitions and Examples
(i) Ambidentate ligand: A ligand possessing two different donor atoms that can coordinate to a metal center through only one atom at a time.
• Example: Thiocyanate (SCN^-), which binds via S or N.
(ii) Double salt: An addition compound made of two distinct stable salts that exists only in the solid state and completely breaks down into its individual ions in water.
• Example: Mohr's salt $[FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O]$.

87. (A) Presence of a straight chain
• Explanation: Heating glucose with hydroiodic acid (HI) for a long duration yields n hexane.
• Chemical Reaction:
$C_6H_{12}O_6+14HI\xrightarrow{\Delta}CH_3-CH_2-CH_2-CH_2-CH_2-CH_3+6H_2O+7I_2$
(B) Presence of five -OH groups on different carbons
• Explanation: Reacting glucose with acetic anhydride yields glucose pentaacetate, confirming five -OH groups. Because the molecule is stable, these groups must reside on separate carbons.
• Chemical Reaction:
$C_6H_{12}O_6+5(CH_3CO)_2O\rightarrow$ Glucose pentaacetate $+5CH_3COOH$

88. (1) Identify Given Values
• Half-life period $(T_{1/2})=1.5\times10^{10}$ years
• Final activity (A) $=75\%$ of initial activity $(A_0)\rightarrow A=0.75A_0$
• Given log values: $\log2=0.30,\log3=0.48,\log4=0.60$
(2) Formula
For a first-order radioactive decay process:
Decay constant $(k)=\frac{2.303\log2}{T_{1/2}}$

Time (t) $= \frac{2.303}{k}\log\left(\frac{A_0}{A}\right)$

(3) Step-by-Step Calculation

Substitute k into the time formula:

$t = \frac{T_{1/2}}{\log 2}\log\left(\frac{A_0}{0.75A_0}\right)$

$t = \frac{T_{1/2}}{\log 2}\log\left(\frac{100}{75}\right) = \frac{T_{1/2}}{\log 2}\log\left(\frac{4}{3}\right)$

Using logarithmic properties $\left(\log\frac{a}{b} = \log a - \log b\right)$:

$\log\left(\frac{4}{3}\right) = \log 4 - \log 3 = 0.60 - 0.48 = 0.12$

Substitute the numbers into the equation:

$t = \frac{1.5 \times 10^{10}}{0.30} \times 0.12$

$t = 1.5 \times 10^{10} \times 0.4 = 0.6 \times 10^{10}$ years

$t = 6 \times 10^{9}$ years

89. (1) Kohlrausch's Law Statement

Kohlrausch's law states that at infinite dilution, when the dissociation of an electrolyte is complete, each ion makes a definite contribution toward the molar conductivity of the electrolyte, regardless of the nature of the other ion with which it is associated.

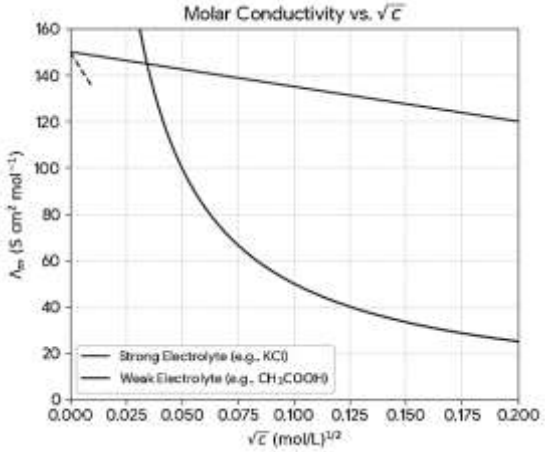
$\Lambda_m^* = v_+\lambda_+^* + v_-\lambda_-^*$

Where $v_+$and $v_-$are the number of cations and anions per formula unit, and λ_+^* and λ_-^* are their limiting molar conductivities.

2. Explanation with Curve

• Strong Electrolytes: Dissociate completely at all concentrations. The molar conductivity (Λ_m) increases slowly with dilution and follows a linear relationship at lower concentrations ($\Lambda_m = \Lambda_m^* - A\sqrt{c}$). Extrapolating the straight line to zero concentration ($\sqrt{c} = 0$) easily gives the limiting molar conductivity (Λ_m^*).

• Weak Electrolytes: Have a very low degree of dissociation at higher concentrations. As dilution increases near zero concentration, the dissociation increases rapidly, causing a sharp, steep rise in Λ_m. The curve becomes parallel to the vertical axis, making direct extrapolation to $c = 0$ impossible.



90. (1) Identify Given Values

• Mass of solute (ethylene glycol, W_B) $= 31$ g

• Molar mass of solute $(M_B) = 62$ g mol^{-1}

• Mass of solvent (water, W_A) $= 600$ g $= 0.6$ kg

• Molal depression constant $(K_f) = 1.86$ K kg mol^{-1}

(2) Formula

$\Delta T_f = K_f \times m$

Molality (m) $= \frac{W_B}{M_B \times W_A(\text{ in kg})}$

(3) Step-by-Step Calculation

Calculate molality (m):

$$m = \frac{31}{62 \times 0.6} = \frac{0.5}{0.6} = 0.833 \text{ mol kg}^{-1}$$

Calculate depression in freezing point (ΔT_f):

$$\Delta T_f = 1.86 \times \frac{0.5}{0.6} = 1.55 \text{ K}$$

Calculate the freezing point of the solution (T_f):

Knowing that the freezing point of pure water (T_f^*) is 273.15 K$(0°C)$:

$T_f = T_f^* - \Delta T_f$

$T_f = 273.15 - 1.55 = 271.60$ K

91. **(A)** Given: Atomic number of Nickel (Ni) = 28.

In both complexes, Nickel is in the +2 oxidation state (Ni^{2+}).

• Electronic configuration of Ni $= [Ar]3d^8 4s^2$

• Electronic configuration of $Ni^{2+} = [Ar]3d^8 4s^0$

(i) Hybridization involved:

• $[NiCl_4]^{2-}$: $Cl^-$is a weak field ligand and cannot pair up the unpaired 3d electrons. The four pairs of electrons from the ligands enter one 4s and three 4p orbitals, resulting in sp^3 hybridization (Tetrahedral geometry).

• $[Ni(CN)_4]^{2-}$: $CN^-$is a strong field ligand and forces the two unpaired electrons in the 3d orbitals to pair up. This leaves one 3d orbital vacant. The four ligand pairs enter one 3d, one 4s, and two 4p orbitals, resulting in dsp^2 hybridization (Square planar geometry).

(ii) Inner vs. Outer orbital complex:

• $[Ni(CN)_4]^{2-}$ utilizes an inner d-orbital (3d) for bonding, making it an inner orbital complex (low-spin).

• $[NiCl_4]^{2-}$ does not utilize inner d-orbitals for hybridization, making it an outer orbital complex (high-spin).

(iii) Magnetic behavior:

• $[NiCl_4]^{2-}$ has two unpaired electrons in its 3d subshell, making it paramagnetic.

• $[Ni(CN)_4]^{2-}$ has all electrons completely paired up, making it diamagnetic.

OR

(B) **(i)** Two important biological coordination compounds:

(1) Hemoglobin: An iron (Fe) complex responsible for oxygen transport in blood.

(2) ChlorophyII: A magnesium (Mg) complex vital for photosynthesis in plants.

(ii) Chelate effect:

When a di- or polydentate ligand binds to a single central metal atom using two or more donor atoms simultaneously, it forms a stable ring structure known as a chelate ring. The enhanced stability of such complexes compared to similar complexes formed with monodentate ligands is called the chelate effect.

• Example: $[Co(en)_3]^{3+}$ is significantly more stable than $[Co(NH_3)_6]^{3+}$ due to the chelating rings formed by the bidentate ethylenediamine (en) ligand.

(iii) In a tetrahedral field, the crystal field splitting energy (Δ_t) is relatively small ($\Delta_t = \frac{4}{9}\Delta_o$). Because this splitting energy is almost always less than the electron pairing energy (P), electrons preferentially occupy higher energy levels singly rather than pairing up, favoring high-spin configurations.

92. Give reasons for the following

(A) Chlorine is electron-withdrawing, yet ortho-, para-directing:

Chlorine exhibits a strong electron-withdrawing inductive effect ($-I$) which deactivates the benzene ring. At the same time, it possesses lone pairs that participate in a resonance effect $(+R)$ with the ring. Resonance donation stabilizes the intermediate carbocation specifically at the ortho and para positions, directing the incoming electrophile to these locations.

(B) Aryl halides cannot be prepared by reacting phenol with halogen acids:

In phenol, the lone pairs of electrons on the oxygen atom enter into resonance with the benzene ring. This gives the carbon-oxygen ($C - OH$) bond a partial double bond character, making it much stronger and shorter than a regular single bond. Consequently, it is highly resistant to cleavage by halogen acids or phosphorus halides under ordinary conditions.

(C) Chloroform is stored in closed dark-colored bottles:

In the presence of sunlight and atmospheric oxygen, chloroform ($CHCl_3$) undergoes slow oxidation to form an extremely poisonous gas called phosgene (carbonyl chloride, $COCl_2$). Storing it in tightly closed, dark-colored bottles blocks light and prevents this decomposition.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl$$

93. Conversions from Benzenediazonium Chloride ($C_6H_5N_2^+Cl^-$)

(A) Chlorobenzene (Sandmeyer Reaction):

$$C_6H_5\ N_2^+Cl^- \xrightarrow{Cu_2Cl_2/HCl} C_6H_5Cl + N_2$$

(B) Benzene:

$$C_6H_5\ N_2^+Cl^- + H_3PO_2 + H_2O \rightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$$

(C) Benzonitrile (Sandmeyer Reaction):

$$C_6H_5\ N_2^+Cl^- \xrightarrow{CuCN/KCN} C_6H_5CN + N_2$$

94. Identification:

(1) Compound (A): The molecular formula $C_3H_5\ N$ indicates a nitrile that reacts with a Grignard reagent to ultimately form a ketone. Thus, (A) is Propanenitrile ($CH_3CH_2\ CN$).

(2) Compound (B): Reaction of propanenitrile with phenylmagnesium bromide followed by hydrolysis produces an aromatic ethyl ketone. Thus, (B) is Propiophenone (1-phenylpropan-1-one, $C_6H_5COCH_2CH_3$).

(i) Verification: It forms an orange-red precipitate with 2,4-DNP, does not give the iodoform test (not a methyl ketone), and reduces neither Tollens' nor Fehling's reagents.

(4) Compound (C): Drastic oxidation of propiophenone cleaves the aliphatic side chain next to the carbonyl group, yielding an aromatic carboxylic acid with the formula $\mathbf{C_7H_6O_2}$. Thus, (C) is Benzoic acid (C_6H_5COOH).

Chemical Reaction Equations:

$$CH_3CH_2C \equiv N + C_6H_5MgBr \xrightarrow{\text{dry ether}} CH_3CH_2C(C_6H_5) = NMgBr$$

$$CH_3CH_2C(C_6H_5) = NMgBr \xrightarrow{H_3O^+} \underset{\text{(B) Propiophenone}}{CH_3CH_2COC_6H_5} + NH_3 + Mg(OH)Br$$

95. **(A)** Basic Building Units

• Proteins: α-amino acids

• Nucleic acids: Nucleotides

Structural Differences Between Fibrous and Globular Proteins

Property	Fibrous Proteins	Globular Proteins
Structure	Linear, elongated thread-like polypeptide chains running parallel.	Polypeptide chains folded into spherical, compact three-dimensional shapes.
Bonds	Stabilized mainly by intermolecular hydrogen and disulfide bonds.	Stabilized by internal hydrogen bonding, disulfide links, and ionic bonds.
Solubility	Insoluble in water.	Soluble in water.

(B) (i) When a nucleotide from DNA containing thymine is completely hydrolyzed, it breaks down into its three constituent chemical units:

(1) Pentose Sugar: β-D-2-deoxyribose

(2) Nitrogenous Base: Thymine

(3) Acidic Group: Phosphoric acid (H_3PO_4)

OR

(ii)• DNA: Contains 2-deoxy-D-ribose sugar (lacks an -OH group at the C-2 position).

• RNA: Contains D-ribose sugar (has a hydroxyl -OH group at the C-2 position).

(C)• Fat-soluble vitamin: Vitamin A (or D, E, K)
• Water-soluble vitamin: Vitamin C (or B-complex vitamins)

96. (A) Reagents for Alcohol Oxidation

(i) Oxidation of a primary alcohol to an aldehyde:
• A mild/controlled oxidizing agent is required to prevent further oxidation to a carboxylic acid.
• Reagent: Pyridinium chlorochromate (PCC) in dichloromethane (CH_2Cl_2), or heating with copper (Cu) at 573 K .

(ii) Oxidation of a primary alcohol to a carboxylic acid:
• A strong oxidizing agent is required to completely oxidize the alcohol.
• Reagent: Acidified potassium permanganate ($KMnO_4$), acidified potassium dichromate ($K_2Cr_2O_7$), or Jones reagent (CrO_3 in H_2SO_4).

(B) Kolbe's Reaction

In Kolbe's reaction, phenol is treated with sodium hydroxide ($NaOH$) to generate a highly reactive phenoxide ion. This ion undergoes electrophilic substitution with carbon dioxide (CO_2) at high temperature and pressure, followed by acidification to produce Salicylic acid (2-hydroxybenzoic acid).

$$\text{Phenol} \xrightarrow{NaOH} \text{Sodium Phenoxide} \xrightarrow[(ii)\ H^+]{(i)\ CO_2} \text{Salicylic acid}$$

Chemical Equation:

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

$$C_6H_5ONa + CO_2 \xrightarrow{410\ K, 4-7\ atm} C_6H_4(OH)COONa \xrightarrow{H^+} C_6H_4(OH)COOH$$

(C) (i) Why Tertiary Alcohols are Resistant to Oxidation

Oxidation of alcohols requires the cleavage of $C-H$ bond from the carbon atom holding the hydroxyl group (α-carbon) to form a carbon-oxygen double bond ($C=O$). Tertiary alcohols do not have any hydrogen atoms attached to the α-carbon.

Because this crucial α-H is missing, they cannot easily undergo oxidation under normal or mild conditions.

OR

(ii) Products of the Reaction with HI

When an unsymmetrical ether contains a tertiary alkyl group (like the tert-butyl group here), the reaction with hydrogen iodide (HI) follows an S_N1 mechanism.

(1) Protonation of the ether occurs.
(2) The $C-O$ bond breaks to yield a highly stable tertiary carbocation, $(CH_3)_3C^+$.
(3) The iodide nucleophile (I^-)attacks the stable carbocation.

Reaction:

$$(CH_3)_3C-O-C_2H_5 + HI \rightarrow (CH_3)_3C-I + C_2H_5OH$$

Products:
• tert-Butyl iodide (2-Iodo-2-methylpropane)
• Ethanol

97. (A) (i) Properties and Reasons

(I) Fe or Cu - higher melting point
• Answer: Fe (Iron)
• Reason: Fe ($3d^64s^2$) has more unpaired d-electrons than $Cu(3d^{10}4s^1)$. More unpaired electrons lead to stronger metallic bonding (d - d orbital overlap).

(II) Ti^{3+} or Sc^{3+} - coloured in aqueous solution
• Answer: Ti^{3+}
• Reason: Ti^{3+} has a $3d^1$ configuration containing an unpaired electron, allowing for $d-d$ electronic transitions by absorbing visible light. Sc^{3+} has a $3d^0$ configuration with no d-electrons available for transition.

(III) Cr or Zn - higher third ionisation enthalpy
• Answer: Zn (Zinc)
• Reason: For Zn , the third electron must be removed from a fully filled, highly stable $3d^{10}$ configuration ($Zn^{2+} = [Ar\beta d^{10}$), which requires exceptionally high energy.

(ii) Ionic Equations for Oxidizing Action of MnO_4^-

(I) With Fe^{2+} ion:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(II) With I^- ion:

$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

OR

(B) (i) Identification and Reactions

• Identification:

• Solid (A): Manganese dioxide (MnO_2) - Black-brown solid

• Compound (B): Potassium manganate (K_2MnO_4) - Dark green compound

• Compound (C): Potassium permanganate ($KMnO_4$) - Dark purple compound

• Chemical Equations involved:

(1) Fusion with KOH in air:

$2MnO_2 + 4KOH + O_2 \rightarrow 2\ K_2MnO_4 + 2H_2O$

(2) Electrolytic oxidation:

$MnO_4^{2-} \xrightarrow{\text{Electrolytic oxidation}} MnO_4^- + e^-$

(ii) Action of Acidic Solution on Compound (B)

• Observation: The green solution turns purple and a brown precipitate settles down.

• Chemical Equation:

$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

• Type of Reaction: This is a disproportionation reaction, where Mn in the +6 oxidation state is simultaneously oxidized to $+7(MnO_4^-)$and reduced to $+4(MnO_2$).

98. (A) (i) (I)

Aldehyde + 1 mole alcohol gives hemiacetal.

$CH_3CHO + CH_3OH \xrightarrow[\text{dry HCl}]{} CH_3CH(OH)OCH_3$

Product: 1-Methoxyethanol (hemiacetal)

(II) Benzaldehyde undergoes Cannizzaro reaction.

$2C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$

Products: Benzyl alcohol and Sodium benzoate

(III) P_2O_5 acts as a dehydrating agent.

$2CH_3COOH \xrightarrow{P_2O_3} (CH_3CO)_2O + H_2O$

Product: Acetic anhydride $(CH_3CO)_2O$

(ii) Simple chemical test to distinguish between Ethanal and Propanal Iodoform Test

• Ethanal gives yellow precipitate of CHI_3 -

• Propanal does not give iodoform test.

(iii) Reagent to transform Allyl alcohol to Propenal

$CH_2 = CHCH_2OH \xrightarrow{MnO_2} CH_2 = CHCHO$

Reagent: MnO_2 (Manganese dioxide)

OR

(B) (i) Structure of Semicarbazone of Acetone

Acetone:

$(CH_3)_2C = O$

Semicarbazone:

$(CH_3)_2C = NNHCONHH_2$

(ii) Because removal of an α-hydrogen forms an enolate ion, which is resonance stabilized.

(iii) Arrange the compounds in increasing order of reactivity towards HCN Reactivity towards nucleophilic addition:

$(CH_3)_2CO < CH_3CHO < HCHO$

Acetone < Ethanal < Formaldehyde

(iv) Etard Reaction

Oxidation of toluene with chromyl chloride gives benzaldehyde.

$C_6H_5CH_3 \xrightarrow{CrO_2Cl_2} C_6H_5CHO$

Product: Benzaldehyde

(v) Product when cyclohexane carbaldehyde reacts with $Zn(Hg)$/ conc. HCl This is Clemmensen reduction.

$C_6H_{11}CHO \xrightarrow[\text{conc. HCl}]{Zn(H_H)} C_6H_{11}CH_3$

Product: Methylcyclohexane

99. (A) (i) Calculation of Electrode Potential

• Given data:

Standard reduction potential $\left(E_{Zn^{2+}/7n}\right) = -0.76$ V
Concentration of Zn^{2+} ions $(|Zn^{2+}|) = 0.01M = 10^{-2}M$
Temperature $= 25°C(298$ K)
Reduction half-reaction:
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ (Number of electrons, $n = 2$)
Using the Nernst Equation:

$$E = E^* - \frac{0.0591}{n}\log\frac{1}{[Zn^{2+}]}$$

$$E = -0.76 - \frac{0.0591}{2}\log\left(\frac{1}{10^{-2}}\right)$$

$$E = -0.76 - 0.02955\log(10^2)$$

$$E = -0.76 - 0.02955 \times 2\log(10)$$

$$E = -0.76 - 0.0591 = -0.8191 \text{ V}$$

(ii) Dry Cell Reactions
• Anode reaction (Oxidation):
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
• Cathode reaction (Reduction):
$2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow 2MnO(OH)(s) + 2NH_3(g)$
• Overall reaction:
$Zn(s) + 2MnO_2(s) + 2NH_4^+(aq) \rightarrow Zn^{2+}(aq) + 2MnO(OH)(s) + 2NH_3(g)$
(iii) Relationship of Equilibrium Constant to E^*_{cell}
• At chemical equilibrium, the forward and reverse cell reactions proceed at equal rates, causing the net cell potential (E_{ccll}) to drop to zero ($E_{ccll} = 0$).
• Because E_{ccll} is dynamic and always zero at equilibrium, it cannot directly measure the equilibrium state. Conversely, the standard cell potential (E^*_{ccll}) represents a constant fixed value under standard conditions, which relates directly to K_c via:

$$E^*_{ccll} = \frac{2.303RT}{nF}\log K_c$$

OR

(B) (i) Molar Conductivity and Degree of Dissociation Calculation
• Given data:
• Concentration $(C) = 0.001$ M
• Conductivity $(\kappa) = 3.905 \times 10^{-5}$ S cm^{-1}
• $\lambda_{CH_3COO} = 40.9$ S cm^2 mol^{-1}
• $\lambda_{H^+} = 349.6$ S cm^2 mol^{-1}
(1) Molar Conductivity (Λ_m) :

$$\Lambda_m = \frac{\kappa \times 1000}{C} = \frac{3.905 \times 10^{-5} \times 1000}{0.001} = 39.05 \text{ S cm}^2 \text{ mol}^{-1}$$

(2) Limiting Molar Conductivity (Λ^*_m) :
$\Lambda^*_m(CH_3COOH) = \lambda^*_{CH_3COO-} + \lambda^*_{H^+}$
$\Lambda^*_m = 40.9 + 349.6 = 390.5$ S cm^2 mol^{-1}
(3) Degree of Dissociation (α):

$$\alpha = \frac{\Lambda_m}{\Lambda^*_m} = \frac{39.05}{390.5} = 0.1$$

• Answer: The molar conductivity is 39.05 S cm^2 mol^{-1} and the degree of dissociation (α) is 0.1.
(ii) Conceptual Reasons
(I) Constant Voltage of Mercury Cell:
The overall reaction in a mercury cell does not involve any ionic species in the solution phase whose concentration could change over time. Because the chemical composition of the electrolyte remains constant during discharge, its voltage remains stable at approximately 1.35 V .
(II) Necessity of a Salt Bridge:
A salt bridge is essential because it completes the electrical circuit by allowing the flow of ions between the half-cells. It also maintains overall electrical neutrality in each compartment, preventing charge accumulation that would otherwise halt the cell's function.

100. **(d)** Oxidation of chloroform by air in the presence of sunlight produces a poisonous gas known as:

$2CHCl_3 + O_2 \xrightarrow{\text{sunlight}} 2COCl_2 + 2HCl$

$COCl_2$ is phosgene gas.

101. **(c)** • Lucas reagent produces cloudiness immediately with:

Lucas reagent ($ZnCl_2 + HCl$) gives:

• Tertiary alcohol → immediate turbidity

• Secondary alcohol - turbidity after a few minutes

• Primary alcohol → no turbidity at room temperature

Among the options:

(a) 2-methyl-1-propanol → Primary

(b) Butan-2-ol - Secondary

(c) 2-methyl-2-propanol - Tertiary (correct)

(d) Butan-1-ol → Primary

102. **(b)**In an octahedral field, ligands approach along the x, y, and z axes. Orbitals directed along these axes experience maximum repulsion:

$d_{x^2}y^2, d_{z^2}$

These form the ϵ_g set and lie at higher energy.

103. **(d)** Calcium-disodium EDTA (Ethylene diamine tetraacetic acid) is a powerful chelating agent that binds to lead ions in the body to form a stable, nontoxic complex that can be safely excreted in urine.

104. **(a)** In the manganate ion (MnO_4^{2-}), manganese is in the +6 oxidation state. The electronic configuration of Mn^{6+} is $[Ar]3d^1$, which contains exactly one unpaired electron, causing paramagnetism.

105. **(d)** In aqueous solutions, the basic strength of ethyl-substituted amines depends on inductive effects, steric hindrance, and hydration energy. The combined effect results in the order: Secondary (2^*) > Tertiary (3^*) > Primary (1^*).

106. **(b)** $\Delta T_b = i \times K_b \times m$

• Since NaCl dissociates completely ($NaCl \rightarrow Na^+ + Cl^-$), the van 't Hoff factor $i = 2$.

$\Delta T_b = 2 \times 0.52 \times 1 = 1.04°C$

• Boiling point $= 100°C + 1.04°C = 101.04°C$.

107. **(c)** According to Le Chatelier's principle, lowering the pressure shifts the equilibrium towards the side with more gas molecules (Liquid → Vapour). Since vaporization is an endothermic process, it absorbs heat from the liquid, causing the temperature to drop.

108. **(a)** The cell notation is given as:

$Mg(s)|Mg^{2+}(1.0M)||Cu^{2+}(1.0M)|Cu(s)$

The overall cell reaction is:

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

According to the Nernst equation at 298 K:

$$E_{ccll} = E^*_{cell} - \frac{0.0591}{2}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

To increase the electromotive force (E_{ccll}), the value of the logarithmic term $\frac{|Mg^{2+}|}{|Cu^{2+}|}$ must be decreased. This can be achieved by:

• Decreasing the concentration of products ($[Mg^{2+}]$)

• Increasing the concentration of reactants ($[Cu^{2+}]$)

Thus, decreasing only the [Mg^{2+}] to 0.1 M will increase the cell potential.

109. **(d)** For a first-order reaction, the rate law expression is:

Rate $= k \cdot [\text{ Reactant }]$

Given:

Rate $= 5.6 \times 10^{-4}$ mol L^{-1} s^{-1}

[Reactant] $= 0.2$ mol L^{-1}

Substitute the values into the formula to find the rate constant (k):

$5.6 \times 10^{-4} = k \cdot (0.2)$

$$k = \frac{5.6 \times 10^{-4}}{0.2} = 2.8 \times 10^{-3}\ s^{-1}$$

110. **(c)** Nucleic acids (such as DNA and RNA) are biopolymers made up of repeating monomeric units called nucleotides. Each nucleotide consists of a pentose sugar, a nitrogenous base, and a phosphate group.

111. **(c)** The reaction of an amide with NaOBr (or $Br_2 + NaOH$) is known as the Hofmann bromamide degradation reaction.

The general equation is:

$R - CONH_2 + Br_2 + 4NaOH \rightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

During this reaction, the carbonyl carbon of the amide is eliminated and lost in the form of a carbonate ion (CO_3^{2-}).

112. **(a)** • Assertion (A): Alcohols act as Bronsted bases as well as Bronsted acids. → True

• Explanation: Alcohols act as acids by donating a proton $(H^+)$from the polar $O - H$ bond, and as bases by accepting a proton using the lone pairs on the oxygen atom.

• Reason (R): It is due to the presence of unshared electron pairs on oxygen atom and presence of polar O - H bond. → True

• Explanation: The lone pairs allow proton acceptance (base), and the polar bond allows proton release (acid). This directly explains the assertion.

So, Both (A) and (R) are true and (R) is the correct explanation of (A).

113. **(c)** • Assertion (A): Diazonium salts of aromatic amines are more stable than those of aliphatic amines. → True

• Explanation: Aromatic diazonium salts are stable at low temperatures $(0 - 5°C)$, while aliphatic diazonium salts decompose instantly.

• Reason (R): Diazonium salts of aliphatic amines undergo resonance. → False

• Explanation: It is aromatic diazonium salts that undergo resonance stabilization with the benzene ring, not aliphatic ones.

114. **(b)**• Assertion (A): For complex reaction, order of reaction is given by the slowest step. → True

• Explanation: The slowest step in a multi-step reaction is the rate-determining step, which determines the overall reaction rate and order.

• Reason (R): Order of reaction is an experimental quantity. → True

• Explanation: Reaction order must be determined experimentally and cannot be deduced solely from a balanced chemical equation. However, this fact does not explain why the slowest step determines the overall rate.

So, Both (A) and (R) are true, but (R) is not the correct explanation of (A).

115. **(a)** • Assertion (A): $E^0_{Sc^{34}/Sc^{24}}$ has low value. → True

• Explanation: This standard reduction potential has a highly negative (low) value, meaning Sc^{3+} is very difficult to reduce to Sc^{2+}.

• Reason (R): Because of the stability of Sc^{3+} ion which has a noble gas configuration. → True

• Explanation: Scandium $(Z = 21)$ has the configuration $[Ar]3d^14s^2$. The Sc^{3+} ion achieves the highly stable argon noble gas configuration ([Ar]), making it strongly resist reduction.

So, Both (A) and (R) are true and (R) is the correct explanation of (A).

116. **(A)** Reaction Order & Example

• Order: Zero-order reactions show a rate that is completely independent of the concentration of the reactants ($Rate = k|A|^0 = k$).

• Example: The decomposition of gaseous ammonia on a hot platinum catalyst surface:

$2NH_3(g) \xrightarrow{Pt,\Delta} N_2(g) + 3H_2(g)$

(B) Condition for a Bimolecular Reaction to behave as First Order

• Condition: A bimolecular reaction becomes kinetically first order (known as a pseudo-first-order reaction) when one of the reactants is present in a large excess compared to the other. Its concentration remains virtually constant during the reaction.

• Example: Acid-catalyzed hydrolysis of ethyl acetate in water, where water is in excess.

117. **(A)** Explanations using Henry's Law

(i) Bends: According to Henry's law, gas solubility increases with pressure. Deepsea divers breathe air at high pressure, increasing dissolved nitrogen in blood. When ascending rapidly, pressure drops, reducing solubility; nitrogen bubbles out of the blood, blocking capillaries and causing painful, dangerous conditions called bends.

(ii) Anoxia: At high altitudes, atmospheric pressure is low, meaning the partial pressure of oxygen is low. By Henry's law, this decreases dissolved oxygen levels in the blood of climbers, causing tissues to lack oxygen, which leads to weakness and impaired thinking (anoxia).

OR

(B) Clearing Snow from Roads

• Mechanism: Sprinkling salt lowers the freezing point of water below $0°C$, preventing water from freezing and causing existing ice/snow to melt at ambient winter temperatures.

• Colligative Property: Depression of freezing point.

118. IUPAC Names

(A) $[Cr(NH_3)_4(ONO)Cl]NO_3$: Tetraamminechloridonitrito-O-chromium(III) nitrate

(B) $Na[Ag(CN)_2]$: Sodium dicyanidoargentate(I)

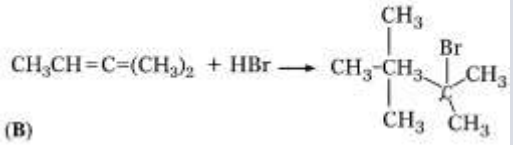
119. Hydrolysis Products

(A) Lactose: β-D-galactose and β-D-glucose.

(B) DNA containing Thymine: β-2-deoxy-D-ribose (sugar), Phosphoric acid (H_3PO_4), and nitrogenous bases (Thymine, Adenine, Guanine, and Cytosine).

120. Structures of Major Products

(A)



(B)

121. Write the structures of A, B and C

(A) Step 1: Aniline $+(CH_3CO)_2O$

Acetylation of aniline gives acetanilide.

$C_6H_5NH_2 \xrightarrow{(CH_3CO)_2O} C_6H_5NHCOCH_3$

A = Acetanilide ($C_6H_5, NHCOCH_3$)

Step 2: Bromination (Br_2/CH_3COOH)

$-NHCOCH_3$ is o,p-directing; para product predominates.

B = p-Bromoacetanilide

$p-BrC_6H_4NHCOCHH_3$

Step 3: Acidic hydrolysis

Removal of acetyl group gives:

$C =$ p-Bromoaniline

$p-BrC_6H_4NH_2$

(B) Starting compound = 2-bromo-4-nitrotoluene

Step 1: Fe/HCl

$-NO_2 \rightarrow -NH_2$

A = 2-bromo-4-methylaniline

Step 2: $NaNO_2 + HCl(273-278\ K)$

Diazotization:

$-NH_2 \rightarrow -N_2^+Cl$

B = 2-bromo-4-methylbenzenediazonium chloride

Step 3: $H_3PO_2 + H_2O$

Diazonium group is replaced by H .

$C =$ o-Bromotoluene (2-bromotoluene)

122. What happens when:

(A) Propanenitrile is treated with phenyl magnesium bromide followed by hydrolysis?

Grignard reagent adds to nitrile to form a ketone after hydrolysis.

$CH_3CH_2CN + C_6H_5MgBr \rightarrow CH_3CH_2COC_6H_5$

Product: Ethyl phenyl ketone (Propiophenone)

$C_6H_5COCH_2CH_3$

(B) p-Fluorotoluene is treated with CrO_3 in acetic anhydride followed by hydrolysis
The methyl side chain is oxidized to an aldehyde.

$$p-FC_6H_4CH_3 \xrightarrow[Ae_2O]{CrO_3} p-FC_6H_4CHO$$

Product: p-Fluorobenzaldehyde (4-fluorobenzaldehyde)
(C) Phthalic acid is treated with NH_3 followed by heating
First forms ammonium phthalate, which on heating gives phthalimide.

$$C_6H_4(COOH)_2 + NH_3 \rightarrow C_6H_4(CO)_2NH + 2H_2O$$

Product: Phthalimide

$$C_6H_4(CO)_2NH$$

123. **(A)** Why direct current (DC) is not used

- Composition changes: DC causes electrolysis, changing the solution's concentration.
- Electrode polarization: Accumulation of decomposition products increases cell resistance and skews results.

(B) Different products of electrolysis

- With Silver Electrodes: Silver is reactive. The silver anode oxidizes to form Ag^+ ions ($Ag \rightarrow Ag^+ + e^-$), while Ag^+reduces at the cathode.
- With Platinum Electrodes: Platinum is inert. Water oxidizes at the anode to release O_2 gas ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$), while Ag^+ions reduce to silver metal at the cathode.

(C) Fixing magnesium blocks to iron pipelines

- Sacrificial protection: Magnesium is more reactive than iron (lower reduction potential).
- Anodic action: Magnesium corrodes preferentially, saving the iron pipe from rusting.

124. **(A)** • Structural Formula: $[Co(NH_3)_6 \mid Cl_3$ (since 3 moles of AgCl precipitate, all $3Cl^-$ are counter-ions).

- IUPAC Name: Hexaamminecobalt(III) chloride
- Valence Bond Theory Analysis:
- Oxidation state of Cobalt is +3 . Electronic configuration of $Co^{3+} = [Ar]3\,d^6$.
- NH_3 is a strong-field ligand and forces pairing of the 3d electrons.
- This creates two vacant inner 3d orbitals.
- Hybridisation: d^2sp^3 (Inner orbital octahedral complex)
- Magnetic Behaviour: Diamagnetic (all electrons are paired; zero unpaired electrons).

OR

(B) **(i)** Geometrical Isomers
(I) $[Cr(C_2O_4)_3]^{3-}$: 0 (Symmetrical bidentate complexes of type [M(AA)3] do not show geometrical isomerism).
(II) $[Co(NH_3)_3Cl_3]$: 2 (fac-facial and mer-meridional isomers).
(ii) Inner vs. Outer Orbital Complex

- $[Co(NH_3)_6]^{3+}$: Co^{3+} has a 3 d^6 configuration. The strong ligand NH_3 pairs up electrons, leaving two inner $3d$ orbitals available for inner-orbital d^2sp^3 hybridization.
- $[Ni(NH_3)_6]^{2+}$: Ni^{2+} has a 3 d^8 configuration $\left(t_{2g}^6 e_g^2\right)$. It cannot provide two vacant inner $3d$ orbitals even with pairing, forcing the use of outer $4d$ orbitals for sp^3 d^2 hybridization.

(iii) Wilkinson's Catalyst

- Formula: $[Rh(PPh_3)_3Cl]$
- Use: Used as a homogeneous catalyst for the hydrogenation of alkenes.

125. Given Data

- Mass of benzoic acid $(W_2) = 61$ g
- Molar mass of benzoic acid $(M_2) = 122$ g mol^{-1}
- Mass of benzene $(W_1) = 500$ g
- Molar mass of benzene $(M_1) = 78$ g mol^{-1}
- Vapour pressure of pure benzene $(P^*) = 66$ torr

(2) Van 't Hoff Factor (i)
Benzoic acid dimerizes completely in benzene:

$$2C_6H_5COOH \rightarrow (C_6H_5COOH)_2$$

$$i = 1 - \alpha + \frac{\alpha}{n} = 1 - 1 + \frac{1}{2} = 0.5$$

(3) Calculation of Moles

- Moles of solute $(n_2) = \frac{61}{122} = 0.5$ mol

• Moles of solvent $(n_1) = \frac{500}{78} = 6.41$ mol

(4) Vapour Pressure Calculation

Using the formula for relative lowering of vapour pressure:

$$\frac{P^* - P}{P} = \frac{i \cdot n_2}{n_1}$$

$$\frac{66 - P}{P} = \frac{0.5 \times 0.5}{6.41} = \frac{0.25}{6.41} = 0.039$$

$$66 - P = 0.039P$$

$$1.039P = 66$$

$$P = \frac{66}{1.039} \approx 63.52\text{torr}$$

126. **(A)** Rule: The overall rate of a chemical reaction is determined by its slowest step (the rate-determining step).

• Slow Step (Step I): $H_2O_2 + I^- \longrightarrow H_2O + IO^-$

• Rate Law: Rate $= k[H_2O_2][\,^-]$

(where k is the rate constant)

(B) Order with respect to H_2O_2 : 1 (exponent of $[H_2O_2]$ in the rate law)

• Order with respect to I^-: 1 (exponent of $[I^-]$in the rate law)

• Overall order: $1 + 1 = 2$

(C) Rule: Molecularity is the number of reacting species colliding simultaneously in an elementary step.

• Step II: $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

• There are two reactant particles (H_2O_2 and IO^-) involved in this step.

• Molecularity: 2 (Bimolecular)

127. **(A)** Reasoning: S_N1 reaction rates depend on the stability of the carbocation intermediate formed. Tertiary $(3°)$ carbocations are the most stable.

• Isomer: 2-Bromo-2-methylpropane (tert-Butyl bromide).

• Structure: $(CH_3)_3C - Br$

(B) Predict the alkene that would be formed by dehydrohalogenation of 1-Bromo-1-methylcyclohexane.

• Reasoning: According to Saytzeff's Rule, dehydrohalogenation preferentially forms the more highly substituted, more stable alkene.

• Major Product: 1 -Methylcyclohexene (the double bond forms inside the ring connected to the methyl group, yielding a trisubstituted alkene).

(C) Although chlorine shows strong-I effect, yet it is ortho- and para-directing in electrophilic aromatic substitution reactions. Why?

• Chlorine has lone pairs of electrons on its atom.

• Through its +R (resonance) effect, it shares these lone pairs with the benzene ring.

• This resonance increases electron density specifically at the ortho and para positions.

• Even though its strong -I (inductive) effect deactivates the ring overall, the +R effect determines the orientation, directing incoming electrophiles to the ortho and para positions.

128. **(A)** Mechanism of Acid Dehydration of Ethanol to Ethene

The dehydration of ethanol (CH_3CH_2OH) to ethene ($CH_2 = CH_2$) in the presence of concentrated sulfuric acid (H_2SO_4) at 443 K proceeds through the following three steps:

Step 1: Protonation of ethanol to form ethyl oxonium ion

The lone pair of electrons on the oxygen atom of ethanol attacks a proton $(H^+)$from the acid.

$$CH_3CH_2 - \ddot{O} - H + H^+ \rightleftharpoons CH_3CH_2 - \overset{+}{\underset{H}{O}} - H$$

Step 2: Formation of carbocation (Rate-determining step)

The $C - O$ bond breaks, releasing a water molecule and forming a stable primary carbocation.

$$CH_3CH_2 - \overset{+}{\underset{H}{O}} - H \xrightarrow{\text{Slow}} CH_3 - \overset{+}{C}H_2 + H_2O$$

Step 3: Elimination of a proton to form ethene

The conjugate base of the acid removes a proton from the β-carbon atom to form the carbon-carbon double bond.

$$H - CH_2 - \overset{+}{C}H_2 \xrightarrow{\text{Fast}} CH_2 = CH_2 + H^+$$

(B) (i) Why are tertiary alcohols resistant to oxidation?

• Absence of α-hydrogen: Oxidation of alcohols requires the breakage of both an O -H bond and $C - H$ bond on the carbon atom holding the hydroxyl group (α^- carbon).

• Structural barrier: Tertiary alcohols do not have a hydrogen atom attached to this α-carbon atom, making regular oxidation into a carbonyl group ($C=O$) impossible under mild or normal conditions.

OR

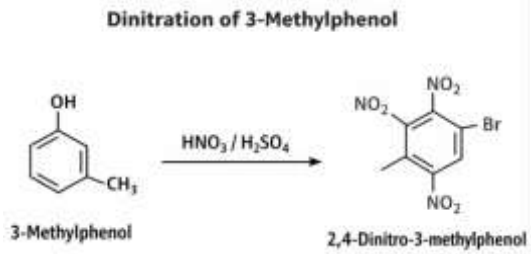
(ii) Structure of the major product from the dinitration of 3methylphenol

In 3-methylphenol (m-cresol), both the -OH group (strongly activating) and the $-CH_3$ group (weakly activating) direct incoming electrophiles to their respective ortho and para positions. The strongly directing -OH group controls the orientation.

Dinitration introduces two nitro ($-NO_2$) groups into the positions that are ortho and para relative to the -OH group. Due to steric hindrance at the position between the two groups, substitution occurs primarily at the 4 and 6 positions.

• Major Product Name: 3 -methyl-4,6-dinitrophenol

• Structure:



(C) Electron-withdrawing effect $(-NO_2)$: The nitro group $(-NO_2)$ acts as a strong electron-withdrawing group through both resonance $(-R)$ and inductive $(-I)$ effects. It decreases electron density on the oxygen atom, making the $O-H$ bond weaker and stabilizing the resulting phenoxide ion.

• Electron-releasing effect $(-OCH_3)$: The methoxy group $(-OCH_3)$ acts as an electron-donating group through resonance $(+R)$. It increases electron density on the oxygen atom, making it harder to release the H^+ion and destabilizing the phenoxide ion.

129. **(A)** **(i)** Presence of a carbonyl group in glucose

The presence of an aldehyde (-CHO) group in glucose is proved by the following reactions:

• Glucose reduces Tollens' reagent to give a silver mirror.

• Glucose reduces Fehling's solution to form red Cu_2O.

• On oxidation with bromine water, glucose forms gluconic acid.

These reactions confirm the presence of a carbonyl (aldehyde) group in glucose.

(ii) Presence of five - OH groups in glucose attached to different carbon atoms Glucose reacts with acetic anhydride to form glucose pentaacetate.

Glucose $+5(CH_3CO)_2O \rightarrow$ Glucose pentaacetate

Formation of pentaacetate shows that glucose contains five hydroxyl (-OH) groups, each attached to a different carbon atom.

(B) Carbohydrates that contain a free aldehydic or ketonic group (or can generate one in solution) and hence reduce Tollens' reagent or Fehling's solution are called reducing sugars.

Examples: Glucose, fructose, lactose, maltose.

(C) **(i)** D indicates that the configuration of glucose is related to D-glyceraldehyde (the -OH group on the penultimate carbon lies on the right in the Fischer projection).

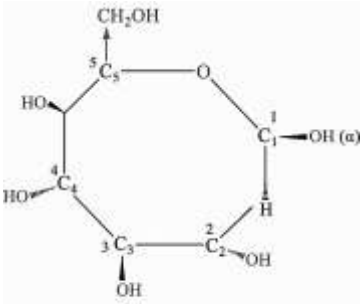
• (+) indicates that glucose is dextrorotatory, i.e., it rotates plane-polarized light to the right (clockwise).

OR

(ii) Six-membered ring structure of α-D(+)-glucose (α-D-glucopyranose)

Haworth projection:

• CH_2OH at $C-5$ is up.



α-D(+)-Glucose
(α-D-Glucopyranose)

130. **(A) (i)** Account for the following:

(I) MnO is basic while Mn_2O_7 is acidic.

• In MnO, Mn is in the +2 oxidation state. Oxides of metals in low oxidation states are generally basic.

• In Mn_2O_7, Mn is in the +7 oxidation state. Oxides of metals in high oxidation states are generally acidic and form acids with water.

$Mn_2O_7 + H_2O \rightarrow 2HMnO_4$

Hence, MnO is basic whereas Mn_2O_7 is acidic.

(II) Iron has higher enthalpy of atomization than copper.

Iron has more unpaired electrons ($3\,d^6 4\,s^2$) than copper ($3\,d^{10} 4\,s^4$), resulting in stronger metallic bonding. Therefore, more energy is required to separate Fe atoms.

Hence,

$\Delta H_{atom}\,(Fe) > \Delta H_{atom}\,(Cu)$

(III) Mn^{3+} is a stronger oxidising agent than Cr^{3+}.

$Mn^{3+} + e^- \rightarrow Mn^{2+}$

Mn^{2+} has a particularly stable $3\,d^3$ (half-filled) configuration. Therefore Mn^{3-} readily gains an electron and acts as a strong oxidising agent.

Cr^{3+} already has the stable $3\,d^3$ configuration and does not readily gain electrons.

Hence Mn^{3+} is a stronger oxidising agent than Cr^{3+}.

(ii) Preparation of potassium dichromate from sodium chromate

Step 1: Conversion of sodium chromate into sodium dichromate

Acidify sodium chromate with dilute sulphuric acid:

$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

Step 2: Conversion of sodium dichromate into potassium dichromate

Treat sodium dichromate with KCl:

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

Potassium dichromate crystallizes because it is less soluble than sodium dichromate.

OR

(B) (i) Reason: Actinoids display a wider variety of oxidation states (up to +7) compared to lanthanoids (which mostly show +3). This happens because the energy gap between the $5f, 6d$, and $7s$ subshells in actinoids is very small, allowing electrons from all three subshells to participate in bonding.

(ii) Reason: The standard electrode potential (E^*) is determined by a combination of three distinct thermodynamic factors: sublimation enthalpy, ionization enthalpy, and hydration enthalpy. The irregular trends in ionization energies and sublimation energies across the $3d$ series prevent the overall electrode potentials from showing a regular trend.

(iii) Identify the following:

(I) Oxoanion of chromium stable in acidic medium: Dichromate ion ($Cr_2O_7^{2-}$)

(II) Lanthanoid element that exhibits +4 oxidation state: Cerium (Ce)

(iv) When potassium permanganate is heated, it decomposes to yield potassium manganate, manganese dioxide, and oxygen gas:

$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$

• Products: Potassium manganate (K_2MnO_4), Manganese dioxide (MnO_2), and Oxygen gas (O_2).

(v) Predict which of the following ions will be coloured in aqueous solution: Cu^+, $Sc^{3+}, Fe^{2+}, Ti^{3+}, Zn^{2+}$

• Rule: lons containing partially filled d-orbitals (d^1 to d^9) exhibit color due to $d-d$ electron transitions. Empty (d^0) or fully filled (d^{10}) subshells are colorless.
• $Cu^+(3d^{10})$: Colorless
• $Sc^{3+}(3d^0)$: Colorless
• $Fc^{2+}(3d^6)$: Coloured (Green)
• $Ti^{3+}(3d^1)$: Coloured (Purple/Violet)
• $Zn^{2+}(3d^{10})$: Colorless

131. **(A) (i)** Conversions

(I) Bromobenzene to 1-phenylethanol

Step 1: React bromobenzene with magnesium (Mg) metal in the presence of dry ether to prepare the Grignard reagent, phenylmagnesium bromide (C_6H_5MgBr).

$$C_6H_5Br + Mg \xrightarrow{\text{Dry ether}} C_6H_5MgBr$$

Step 2: React phenylmagnesium bromide with ethanal (acetaldehyde, CH_3CHO), followed by acidic hydrolysis to obtain 1-phenylethanol.

$$C_6H_5MgBr + CH_3CHO \xrightarrow{H_3O^+} C_6H_5 - CH(OH) - CH_3$$

(II) Benzene to m-nitroacetophenone

Step 1 (Friedel-Crafts Acetylation): React benzene with acetyl chloride (CH_3 COCl) in the presence of anhydrous $AlCl_3$ to form acetophenone.

$$C_6H_6 + CH_3COCl \xrightarrow{\text{Anhydrous } AlCl_3} C_6H_5COCH_3 + HCl$$

Step 2 (Nitration): React acetophenone with a nitrating mixture (concentrated HNO_3 + concentrated H_2SO_4). The $-COCH_3$ group is meta-directing, yielding m -nitroacetophenone.

$$C_6H_5COCH_3 \xrightarrow{\text{Conc. } HNO_3/\text{ Conc. } H_2SO_4} m - NO_2 - C_6H_4 - COCH_3$$

(ii) Identification of Compound

• Identification: The compound is 2-methylbenzaldehyde (o-tolualdehyde, $CH_3 - C_6H_4 - CHO$).
• Reasoning:
• Formation of a 2,4-DNP derivative indicates a carbonyl group.
• Reduction of Tollens' reagent and undergoing the Cannizzaro reaction proves it is an aldehyde with no α-hydrogen atoms.
• Vigorous oxidation converts both the $-CH_3$ and -CHO groups on adjacent positions into carboxylic acid groups, forming benzene-1,2-dicarboxylic acid (phthalic acid).
• Cannizzaro Reaction Products: When treated with concentrated alkali, it undergoes self-oxidation and reduction to yield:
(1) 2-Methylbenzyl alcohol (Reduction product)
(2) Sodium 2-methylbenzoate (Oxidation product, assuming NaOH is used)

$$2CH_3 - C_6H_4 - CHO \xrightarrow{\text{Conc. NaOH}} CH_3 - C_6H_4 - CH_2OH + CH_3 - C_6H_4 - CO$$

(iii) Acid Strength Order

• Increasing Order: $C_6H_5COOH < HCOOH < O_2\ N - CH_2 - COOH < CF_3 - COOH$
• Reason: The strong electron-withdrawing $-I$ effect of $-CF_3$ makes CF_3COOH the strongest acid, followed by the highly electron-withdrawing nitro group in $O_2\ N - CH_2 - COOH$. Formic acid (HCOOH) is stronger than benzoic acid (C_6H_5 COOH) because the phenyl ring reduces acidity via electron donation through resonance.

OR

(B) (i) Reaction Products of Benzaldehyde

(I) With 2,4-Dinitrophenylhydrazine: Forms a crystalline orange-red precipitate called Benzaldehyde 2,4-dinitrophenylhydrazone.

$$C_6H_5CHO + H_2\ N - NH - C_6H_3(NO_2)_2 \rightarrow C_6H_5CH = N - NH - C_6H_3(NO_2)_2 +$$

(II) With Acetophenone in dilute NaOH and heat (Crossed Aldol Condensation): Forms an α,β-unsaturated ketone known as Chalcone (1,3-diphenylprop-2-en-1one).

$$C_6H_5CHO + CH_3CO - C_6H_5 \xrightarrow[\Delta]{\text{Dil. NaOH}} C_6H_5 - CH = CH - CO - C_6H_5 + H_2$$

(ii) Give Reasons

(I) Benzoic acid does not undergo Friedel-Crafts reaction: The carboxylic acid group (-COOH) is strongly electron-withdrawing, which severely deactivates the benzene ring toward electrophilic attack. Furthermore, the Lewis acid catalyst ($AlCl_3$) complexes with the oxygen of the carboxyl group, further lowering its reactivity.

(II) Carboxylic acids have higher boiling points than alcohols of comparable mass: Carboxylic acid molecules form stronger and more extensive extensive intermolecular hydrogen bonds, existing as stable cyclic dimers even in the vapor phase.

(iii) Chemical Test to Distinguish Propanal and Propanone

• Tollens' Test:

Propanal (aldehyde) reacts with Tollens' reagent (ammoniacal silver nitrate) to form a bright, shiny silver mirror on the inner walls of the test tube.

Propanone (ketone) does not react with Tollens' reagent.

• Iodoform Test:

Propanone contains a methyl ketone group (CH_3CO -) and reacts with $I_2/NaOH$ to yield a yellow precipitate of iodoform (CHI_3).

Propanal does not give this test.

132. **(A) (i)** Calculate E^*_{cell} for the reaction at equilibrium

• Given:

Equilibrium constant $(K_c) = 10^{15}$

Number of electrons transferred $(n) = 2$ (since $Cu \rightarrow Cu^{2+} + 2e^-$)

Formula:

At equilibrium, cell potential $(E_{ccll}) = 0$.

$$E^*_{ccll} = \frac{0.059}{n} \log K_c$$

• Calculation:

$$E^*_{ccll} = \frac{0.059}{2} \log(10^{15})$$

$$E^*_{ccll} = 0.0295 \times 15 \log(10) = 0.0295 \times 15 \times 1$$

$$E^*_{cell} = 0.4425\ V$$

(ii) Reactions of Lead Storage Battery (when in use/discharging)

• Anode Reaction:

$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

• Cathode Reaction:

$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

• Overall Cell Reaction:

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

(iii) Electricity required for oxidation of 1 mol of FeO to Fe_2O_3

• Oxidation half-reaction:

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

Converting 1 mol of Fe^{2+} to Fe^{3+} involves the transfer of 1 mol of electrons ($n = 1$).

• Calculation:

Quantity of electricity (Q) $= n \times F$

$Q = 1 \times 96500C = 96500C$

OR

(B) (i) Calculate the degree of dissociation (α) of acetic acid

• Given:

Concentration $(C) = 0.0024M$

Conductivity $(\kappa) = 7.2 \times 10^{-5}\ S\ cm^{-1}$

Limiting molar conductivity $(\Lambda^*_m) = 390.5\ S\ cm^2\ mol^{-1}$

Step 1: Calculate Molar Conductivity (Λ_m)

$$\Lambda_m = \frac{\kappa \times 1000}{C}$$

$$\Lambda_m = \frac{7.2 \times 10^{-5} \times 1000}{0.0024} = \frac{0.072}{0.0024} = 30\ S\ cm^2\ mol^{-1}$$

Step 2: Calculate Degree of Dissociation (a)

$$\alpha = \frac{\Lambda_m}{\Lambda^*_m}$$

$$\alpha = \frac{30}{390.5} \approx 0.0768$$

(ii) Calculate the cell potential for the half-cell reaction

• Given:

$E^*_{Ag^+/Ag} = +0.80\ V$

$[Ag^+] = 0.01M = 10^{-2}M$

Number of electrons $(n) = 1$

Formula (Nernst Equation):

$$E = E^* - \frac{0.059}{n}\log\frac{1}{[Ag^+]}$$

• Calculation:

$$E = 0.80 - \frac{0.059}{1}\log\frac{1}{10^{-2}}$$

$$E = 0.80 - 0.059\log(10^2)$$

$$E = 0.80 - 0.059 \times 2 = 0.80 - 0.118$$

$$E = 0.682\ V$$

(iii) Electrolytes used

(I) Dry cell: A moist paste of Ammonium chloride (NH_4Cl) and Zinc chloride ($ZnCl_2$).

(II) Fuel cell $(H_2 - O_2)$: Concentrated aqueous Potassium hydroxide (KOH) solution.

133. **(b)** Conversion:

$R_2C = O \rightarrow R_2CH_2$

• This is achieved by Wolff-Kishner reduction (or Clemmensen reduction).

134. **(c)** • Reagents used in Hofmann Bromamide Degradation

Hofmann bromamide reaction:

$RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

Required reagents are:

(I) Amide $RCONH_2$

(II) NaOH

(III) Br_2

• $CHCl_3$ is used in the carbylamine reaction, not Hofmann degradation.

135. **(d)** The carbylamine reaction (also known as Hoffmann's carbylamine test) occurs when a primary amine is heated with chloroform ($CHCl_3$) and ethanolic potassium hydroxide (KOH). The product is an alkyl isocyanide (carbylamine), which is easily detected by its characteristically foul odor.

136. **(d)** Unlike lanthanoids, the energy differences between the 5f, 6d, and 7s orbitals in actinoids are extremely small. This allows electrons from all three subshells to participate in bond formation, leading to a wider variety of oxidation states.

137. **(a)** This is the Finkelstein reaction, a classic nucleophilic substitution (S_N2) mechanism used for halogen exchange. Alkyl chlorides react with sodium iodide (NaI) in dry acetone to yield alkyl iodides. NaCl precipitates out because it is insoluble in acetone, driving the reaction forward.

138. **(c)** Hinsberg's reagent is benzenesulfonyl chloride. It is used in chemistry labs to distinguish between primary, secondary, and tertiary amines.

139. **(b)**• Calculation:

For a first-order reaction, the relationship between the rate constant (k) and halflife ($t_{1/2}$) is given by:

$$k = \frac{0.693}{t_{1/2}}$$

Substitute the given value ($t_{1/2} = 1386\ s$):

$$k = \frac{0.693}{1386} = 0.0005 = 5.0 \times 10^{-4}\ s^{-1}$$

140. **(d)** A chelating ligand must be didentate or polydentate. The oxalate ion ($C_2O_4^{2-}$) binds to a central metal ion through two oxygen donor atoms simultaneously, forming a stable 5 -membered ring. Ammonia, water, and nitrite (NO_2^-) are monodentate ligands.

141. **(a)** Lucas reagent $(HCl + ZnCl_2)$ reacts with alcohols at different rates to form insoluble alkyl chlorides (turbidity). Tertiary alcohols react immediately, secondary alcohols react within 5 minutes, and primary alcohols do not produce turbidity at room temperature.

142. **(a)** • Aniline ($C_6H_5NH_2$) is the least basic because its lone pair is delocalized into the benzene ring via resonance.
• Ammonia (NH_3) is stronger than aniline as its lone pair is localized.
• Benzylamine ($C_6H_5CH_2NH_2$) is stronger than ammonia due to the aliphatic nature of the carbon attached to nitrogen.
• Aliphatic amines are the most basic due to the electron-donating inductive effect (+I) of alkyl groups. In aqueous solution, secondary ethylamine $(C_2H_5)_2$ NH is more basic than primary ethylamine $C_2H_5NH_2$.

143. **(d)** Glucose and fructose are monosaccharides. Maltose is a disaccharide. Cellulose is a long-chain carbohydrate polymer (polysaccharide) consisting of numerous glucose units linked together.

144. **(a)** The linear, specific sequence of amino acids linked together by peptide bonds forms the primary structure of a protein. Secondary, tertiary, and quaternary structures describe the subsequent folding and spatial arrangements.

145. **(a)** • Assertion (A): D(+)- Glucose is dextrorotatory in nature. (True)
• Reason (R): (+) represents dextrorotatory nature and D represents the configuration. (True)
The (+) symbol explicitly denotes that the compound rotates plane-polarized light to the right (dextrorotatory). The letter 'D' denotes the stereochemical configuration relative to D-glyceraldehyde. Since the reason correctly explains the notation used in the assertion, (R) is the correct explanation of (A).

146. **(b)** • Assertion (A): Highest oxidation state of Mn is +7 in first series of transition elements. (True)
• Reason (R): Transition metals exhibit variable oxidation states. (True)
Manganese (Mn) has the maximum number of valence electrons ($3d^5 4s^2$) in the 3d series, allowing it to reach a +7 oxidation state. While it is true that transition metals show variable oxidation states, this general statement does not specifically explain why Manganese achieves the highest state. Therefore, (R) is not the correct explanation of (A).

147. **(a)** • Assertion (A): p-nitrophenol is more acidic than phenol. (True)
• Reason (R): Nitro group is an electron-withdrawing group, it stabilises phenoxide ion by dispersal of negative charge. (True)
• Explanation:
The nitro group ($-NO_2$) at the para position exerts strong electron-withdrawing inductive ($-I$) and resonance ($-R$) effects. This stabilizes the conjugate base (p nitrophenoxide ion) by delocalizing its negative charge, making it easier to lose a proton. Thus, (R) is the correct explanation of (A).

148. **(c)** • Assertion (A): All aliphatic aldehydes give a positive Fehling's test. (True)
• Reason (R): Aliphatic aldehydes are reduced by Fehling's reagent. (False)
Aliphatic aldehydes reduce Fehling's solution to form a red precipitate of Cu_2O. During this reaction, the aldehydes themselves undergo oxidation to form carboxylate ions, while the Fehling's reagent is reduced. Therefore, Assertion (A) is true, but Reason (R) is false.

149. **(A)** (1) Identify given values:
• Molality of solution $(m) = 1.00$ molal
• Boiling point of solution $(T_b) = 100.18°C$
• Boiling point of pure water $(T_b^+) = 100.00°C$
• Molal elevation constant $(K_b) = 0.512\ K\ kg\ mol^{-1}$
(2) Calculate elevation in boiling point (ΔT_b):
$\Delta T_b = T_b - T_b^* = 100.18°C - 100.00°C = 0.18°C = 0.18\ K$
(3) Calculate van't Hoff factor (i):
$\Delta T_b = i \cdot K_b \cdot m$
$$i = \frac{\Delta T_b}{K_b \cdot m} = \frac{0.18}{0.512 \times 1.00} \approx 0.352$$

OR

(B) • Henry's Law: At a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of the liquid or solution. Mathematically, $p = K_H \cdot x$ (where p is partial pressure, K_H is Henry's constant, and x is the mole fraction of the gas).
• Calculation:
• Given: $p = 760$ mm Hg. $K_H = 1.25 \times 10^6$ mmHg
• Formula: $x = \frac{p}{K_H}$

$$x = \frac{760}{1.25 \times 10^6} = 6.08 \times 10^{-4}$$

150. **(A)** Hydrogen-Oxygen Fuel Cell ($H_2 - O_2$ fuel cell).

(B) Limiting Molar Conductivity (Λ_m^*) : The molar conductivity of a solution when the concentration of the electrolyte approaches zero (i.e., at infinite dilution).

151. **(A)** Completed Equation:

$$C_6H_5 - N_2^+Cl^- + H - C_6H_4 - OH \xrightarrow{OH^-} C_6H_5 - N = N - C_6H_4 - OH + Cl^- + H_2O$$

(Product name: p-hydroxyazobenzene, an orange dye)

(B) Conversion:

• Step 1: Reduction

Reduce nitromethane to methylamine using Sn/HCl or Fe/HCl :

$$CH_3NO_2 + 6[H] \xrightarrow{Sn/HCl} CH_3NH_2 + 2H_2O$$

• Step 2: Carbylamine Reaction

Heat methylamine with chloroform and alcoholic KOH to get methyl isocyanide:

$$CH_3NH_2 + CHCl_3 + 3KOH(\text{ alc. }) \xrightarrow{\Delta} CH_3NC + 3KCl + 3H_2O$$

152. **(A)** Glucose (α-D-glucose) and Fructose (β-D-fructosc).

(B) Essential Amino Acids: Amino acids that cannot be synthesized inside the human body and must be supplied through the diet (e.g., Valine, Leucine).

153. **(A)** Vitamin A and Vitamin D (or Vitamin E/K).

(B) On reaction with acetic anhydride ($(CH_3CO)_2O$), glucose undergoes acetylation to form glucose pentaacetate. The formation of a penta-acetyl derivative confirms the presence of five $-OH$ groups. Since glucose is a stable molecule, these five groups must be attached to five different carbon atoms.

154. EMF of the Cell at 298 K

Cell:

$Cr(s)|Cr^{3+}(0.1M)|Fe^{2+}(0.01M)|Fe(s)$

Given:

$E^\circ_{Cr^{3+}/Cr} = -0.74\ V$

$E^\circ_{Fe^{2+}/Fe} = -0.44\ V$

Step 1: Identify Anode and Cathode

More positive reduction potential acts as cathode.

$E^0_{Fe^{2+}/Fe} > E^0_{Cr^{3+}/Cr}$

Therefore,

• Anode: $Cr \rightarrow Cr^{3+} + 3e^-$

• Cathode: $Fe^{2+} + 2e^- \rightarrow Fe$

Step 2: Standard EMF

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= (-0.44) - (-0.74)$

$E^\circ_{ecll} = 0.30\ V$

Step 3: Balanced Reaction

$2Cr + 3Fe^{2+} \rightarrow 2Cr^{3+} + 3Fe$

$n = 6$

Step 4: Reaction Quotient

$$Q = \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

$$Q = \frac{(0.1)^2}{(0.01)^3}$$

$Q = 10^4$

Step 5: Nernst Equation

$$E = E^\circ - \frac{0.0591}{n}\log Q$$

$$E = 0.30 - \frac{0.0591}{6}\log(10^4)$$

$$E = 0.30 - \frac{0.0591}{6} \times 4$$
$$E = 0.30 - 0.0394$$
$$E_{cell} \approx 0.26\ V$$

155. **(A)** Order of a Reaction

The sum of the powers of the concentration terms in the experimentally determined rate law is called the order of the reaction.

Example:

$$\text{Rate} = k[A]^m[B]^n$$

Order $= m + n$.

(B) Given:

$$\text{Rate} = k[A][B]^2$$

(i) Effect of Doubling Concentration of B

Let initial rate be r.

When B is doubled:

$$r' = k[A](2B)^2$$
$$r' = 4k[A]B^2$$
$$r' = 4r$$

So, the rate becomes 4 times.

(ii) Overall Order when A is Present in Large Excess

Since [A] is nearly constant,

$$k[A] = k'$$

Therefore,

$$\text{Rate} = k'[B]^2$$

The reaction behaves as a pseudo-second-order reaction.

Overall order $= 2$

156. Formula:

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Given:

$T_1 = 298\ K$

$T_2 = 308\ K$

Rate doubles: $\frac{k_2}{k_1} = 2$

$\log 2 = 0.30$

$R = 8.314\ J\ mol^{-1}\ K^{-1}$

Calculation:

$$\log(2) = \frac{E_a}{2.303 \times 8.314}\left(\frac{308 - 298}{298 \times 308}\right)$$
$$0.30 = \frac{E_a}{19.147}\left(\frac{10}{91784}\right)$$
$$E_a = \frac{0.30 \times 19.147 \times 91784}{10}$$
$$E_a = 52721.4\ J/mol \approx 52.72\ kJ/mol$$

157. **(A)** IUPAC Name: Potassium trioxalatochromate(III)

(B) Difference:

• Homoleptic complex: The metal atom is bound to only one type of ligand. (e.g., I $Co(NH_3)_6H^{3+}$)

• Heteroleptic complex: The metal atom is bound to more than one type of ligand. (e.g., $[Co(NH_3)_4Cl_2|^+$)

(C) Isomerism: Geometrical isomerism (It forms cis and trans isomers).

158. **(A)** Structural Formula: Since 2 moles of AgCl precipitate, 2 chloride ions reside outside the coordination sphere.

$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

(B) Properties of $[Fe(H_2O)_6]^{3+}$:

• Oxidation state: +3

• Hybridisation: sp^3d^2 (Since H_2O is a weak-field ligand, no pairing of d electrons occurs).

(C) Color Reason: Ni^{2+} has a $3d^8$ configuration with two unpaired electrons. The absorption of visible light triggers $d-d$ transitions, emitting a complementary color.

159. **(A)** Acetophenone to Benzoic acid:

Treat with sodium hypoiodite ($I_2 + NaOH$) via the haloform reaction, followed by acidification.

$$C_6H_5COCH_3 \xrightarrow{I_2/NaOH} C_6H_5COONa \xrightarrow{H^+} C_6H_5COOH$$

(B) Acetonitrile to Acetone:

React with Grignard reagent (CH_3MgBr) followed by acid hydrolysis.

$$CH_3CN \xrightarrow{CH_3MgBr} CH_3C(=NMgBr)CH_3 \xrightarrow{H_3O^+} CH_3COCH_3$$

(C) Benzoic acid to Benzene:

Heat with soda lime ($NaOH + CaO$) to undergo decarboxylation.

$$C_6H_5COOH \xrightarrow{NaOH+CaO,\Delta} C_6H_6 + Na_2CO_3$$

160. **(A) (i)** Increasing order of acidic strengths

Compounds are:

(1) $CH_3CH(CH_3)COOH$ (2-methylpropanoic acid)

(2) $CH_3CH(Br)CH_2COOH$ (β-bromobutyric acid)

(3) $CH_3CH_2CH(Br)COOH$ (α-bromobutyric acid)

Facts:

• Alkyl groups show +1 effect and decrease acidity.

• Halogens show -1 effect and increase acidity.

• The-I effect decreases with distance from $-COOH$.

Hence,

$CH_3CH(CH_3)COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

(ii) Why is CH_3CHO more reactive than acetone towards HCN ?

HCN adds through nucleophilic addition to the carbonyl group.

Reasons:

(1) In acetone, two CH_3 groups exert a +1 effect, decreasing the positive charge on the carbonyl carbon.

(2) Acetone has greater steric hindrance than acetaldehyde.

Therefore, the carbonyl carbon of acetaldehyde is more electrophilic.

CH_3CHO is more reactive than acetone towards HCN .

(iii) Complete the reaction

Given:

$$CH_3CHO + NH_2NH_2 \xrightarrow{H^+}$$

Aldehyde reacts with hydrazine to form a hydrazone.

$$CH_3CHO + NH_2NH_2 \rightarrow CH_3CH = NNH_2 + H_2O$$

(Product: Acetaldehyde hydrazone)

OR

(B) Given:

• Molecular formula: C_8H_8O

• Forms 2,4-DNP derivative ⇒ contains carbonyl group.

• Reduces Tollens' reagent ⇒ aldehyde.

• Undergoes Cannizzaro reaction ⇒ aldehyde without α-hydrogen.

• On oxidation gives benzene-1,2-dicarboxylic acid (phthalic acid).

Therefore the compound is:

• o-Methylbenzaldehyde (2-methylbenzaldehyde)

$C_6H_4(CH_3)CHO$

• Reaction with 2,4-DNP

$$C_6H_4(CH_3)CHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow C_6H_4(CH_3)CH = NNHCC_6H_3(NO_2)_2 + H_2O$$

(2,4-dinitrophenylhydrazone formed)

• Cannizzaro Reaction

$$2C_6H_4(CH_3)CHO + NaOH \rightarrow C_6H_4(CH_3)CH_2OH + C_6H_4(CH_3)COONa$$

i.e., one molecule is reduced to o-methylbenzyl alcohol and the other is oxidized to sodium o-toluate.

161. **(A) (i)** Anisole $+CH_3Cl/$ Anhyd. $AlCl_3, CS_2$

This is Friedel-Crafts alkylation.

OCH_3 group is ortho-para directing.

Products:
o-Methylanisole + p-Methylanisole
(Major product: p-methylanisole)
(ii) Anisole + Conc. HNO_3/H_2SO_4
This is nitration of anisole.
OCH_3 is ortho-para directing.
Products:
o-Nitroanisole + p-Nitroanisole
(Major product: p-nitroanisole)
(B) (i)
Preparation of tert-butyl ethyl ether by Williamson synthesis
Williamson synthesis:
$RONa + R'X \rightarrow ROR'$
For tert-butyl ethyl ether $(CH_3)_3C - O - C_2H_5$,
the alkyl halide must be primary.
Therefore:
• Sodium alkoxide: Sodium tert-butoxide $(CH_3)_3CONa$
• Alkyl halide: Ethyl bromide (or ethyl iodide)
$(CH_3)_3CONa + C_2H_5Br \rightarrow (CH_3)_3COC_2H_5 + NaBr$
Alkyl halide: Ethyl bromide
Sodium alkoxide: Sodium tert-butoxide

OR

(ii) Reaction:
$C_6H_5OCH_3 + HI \rightarrow C_6H_5OH + CH_3I$
In anisole, the aryl-O bond has partial double-bond character due to resonance and is very strong.
Therefore cleavage occurs at the alkyl-O bond rather than the aryl-O bond.
Hence products are:
$C_6H_5OH + CH_3I$
and not methanol and iodobenzene.
(C) The two alkyl groups attached to oxygen repel each other.
This steric/electronic repulsion increases the bond angle slightly above 109.5°.
$C - O - C$ angle $\approx 111°$
Thus the bond angle in ethers is slightly greater than the tetrahedral angle.

162. **(A) (i)** Electrolysis of aqueous $CuCl_2$ using platinum electrodes
Cathode (reduction):
$Cu^{2+} + 2e^- \rightarrow Cu(s)$
Copper is deposited at the cathode.
Anode (oxidation):
$2Cl \rightarrow Cl_2(g) + 2e$
Chlorine gas is liberated at the anode.
Products:
Cathode: Cu , Anode: Cl_2
(ii) Electrolysis of concentrated H_2SO_4 using platinum electrodes
Cathode:
$2H^+ + 2e^- \rightarrow H_2(g)$
Anode:
$2H_2O \rightarrow O_2(g) + 4H^+ + 4e$
Products:
Cathode: H_2, Anode: O_2
(B) (i)
Charge required for reduction of 1 mol$Ag^+$to Ag
Reaction:
$Ag^+ + e^- \rightarrow Ag$
1 mol of Ag^+requires 1 mol of electrons.
Charge required:
$Q = 1F$

$Q = 96500C$
(approximately $9.65 \times 10^4 C$)

OR

(ii) Faraday's Second Law of Electrolysis
Statement:
When the same quantity of electricity is passed through different electrolytes, the masses of substances liberated or deposited are proportional to their equivalent masses.

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}$$

where E_1 and E_2 are equivalent masses.

(C) Given anodic reactions:

$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^- \; E^\circ = 1.36\ V$

$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \; E^\circ = 1.23\ V$

The reaction requiring lower oxidation potential occurs more readily.
Since

$1.23\ V < 1.36\ V$

water oxidation is thermodynamically easier.
Therefore,

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$

is the feasible anodic reaction.
Reason:
It has the lower electrode potential and hence requires less energy for oxidation.

163. **(A) (i)** Freezing Point of Solution
Given:

- Mass of $MgBr_2 = 10.5\ g$
- Molar mass of $MgBr_2 = 184\ g\ mol^{-1}$
- Mass of water $= 250\ g = 0.250\ kg$
- $K_f = 1.86\ K\ kg\ mol^{-1}$

Step 1: Calculate molality

$$\text{Moles of } MgBr_2 = \frac{10.5}{184} = 0.0571$$

$$m = \frac{0.0571}{0.250} = 0.2284\ mol\ kg^{-1}$$

Step 2: van't Hoff factor

$MgBr_2 \rightarrow Mg^{2+} + 2Br$

$i = 3$

Step 3: Depression in freezing point

$\Delta T_f = iK_f m$
$= 3 \times 1.86 \times 0.2284$
$= 1.27\ K$

Step 4: Freezing point of solution

$T_f = 0 - 1.27$
$T_f = -1.27°C$

(ii) Two Differences between Ideal and Non-Ideal Solutions

Ideal Solution	Non-Ideal Solution
Obeys Raoult's law at all concentrations.	Does not obey Raoult's law.
$\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$.	$\Delta H_{mix} \neq 0$ and / or $\Delta V_{mix} \neq 0$.

OR

(B) (i) Osmotic Pressure
Given:

• Mass of $K_2SO_4 = 0.025$ g
• Molar mass $= 174\ g\ mol^{-1}$
• Volume $= 2L$
• $T = 27°C = 300$ K
• $R = 0.082 L atm K^{-1} mol^{-1}$
Step 1: Moles
$$n = \frac{0.025}{174} = 1.437 \times 10^{-4}\ mol$$
Step 2: Molarity
$$M = \frac{1.437 \times 10^{-4}}{2} = 7.18 \times 10^{-3}\ mol\ L^{-1}$$
Step 3: van't Hoff factor
$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$
$i = 3$
Step 4: Osmotic Pressure
$\pi = iMRT$
$= 3(7.18 \times 10^{-5})(0.082)(300)$
$\pi \approx 5.3 \times 10^{-3}$ atm
(ii) Acetone + Chloroform
Acetone and chloroform form strong intermolecular hydrogen bonding:
$(CH_3)_2CO \cdots H - CCl_3$
Hence they show negative deviation from Raoult's law.
Solutions showing negative deviation form a:
Maximum boiling azeotrope
because the intermolecular attraction is stronger than in the pure liquids.

164. **(A) (i) (I)** Reason: Transition metals have valence electrons in both $(n-1)d$ and ns orbitals.
• The energy difference between these orbitals is very small.
• Consequently, electrons from both shells can participate in chemical bonding.
(II) Mn^{2+} is more paramagnetic.
• Reason:
• Electronic configuration of $Ti^{2+} = [Ar]3d^2$ (contains 2 unpaired electrons).
• Electronic configuration of $Mn^{2+} = [Ar]3d^5$ (contains 5 unpaired electrons).
• Paramagnetism increases with an increasing number of unpaired electrons.
(III) Mn^{3+} is the strongest oxidizing agent.
• Reason:
• Mn^{3+} has a $3d^4$ electronic configuration.
• Gaining one electron converts it into $Mn^{2+}(3d^5)$.
• This $3d^5$ state is highly stable due to its exactly half-filled d-subshell.
• This strong tendency to gain electrons makes Mn^{3+} a powerful oxidizing agent.
(ii) (I) $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$
(II) $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

OR

(B) (i) Definition: The steady, gradual decrease in the atomic and ionic radii of lanthanoid elements with increasing atomic number.
• Cause: This happens due to the poor shielding effect of inner 4f electrons against the increasing nuclear charge.
(ii) Reason: Transition metals have incompletely filled d-orbitals.
• Incoming ligands split these d-orbitals into different energy levels.
• Electrons absorb specific wavelengths of visible light to jump between these levels ($d-d$ transition).
• The unabsorbed, transmitted light gives the compound its complementary color.
(iii) Reason:
• Mn^{2+} has a stable, half-filled d^5 configuration.
• Zn^{2+} has a stable, completely filled d^{10} configuration.
• The exceptional stability of these configurations makes the formation of their +2 ions highly favorable.
(iv) The +2 oxidation state (Cu^{2+}) is the most stable state in aqueous solutions.
• Reason: Cu^{2+} has a highly negative hydration enthalpy.

• This strong release of energy more than compensates for the high second ionization energy required to remove the second electron.

(v) Reason: The most stable and common oxidation state for lanthanoids is +3 .

• Ce^{4+} strongly prefers to gain an electron to reduce itself to the stable Ce^{3+} state.

• This tendency to readily accept electrons makes it an effective oxidizing agent.

165. **(A) (i) (I)** Reactivity towards S_N1 reaction

2-Bromo-2-methylbutane is more reactive.

• Reason: S_N1 reactions proceed via carbocation formation. 2-Bromo-2methylbutane is a tertiary (3°) alkyl halide that forms a highly stable tertiary carbocation, whereas 1 -bromopentane is a primary (1*) alkyl halide that forms an unstable primary carbocation.

(II) Type of halide

The given compound is a Vinylic halide.

• Reason: The halogen atom (chlorine) is directly attached to an sp^2-hybridized carbon atom of a carbon-carbon double bond ($\mathbf{C = C}$).

(III) Storage of chloroform

Chloroform ($CHCl_3$) is slowly oxidized by air in the presence of sunlight to form an extremely poisonous gas called phosgene (carbonyl chloride).

$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2$ (Phosgene) $+ 2HCl$

Storing it in dark-colored bottles cuts off light exposure to prevent this hazardous oxidation.

(ii) Definitions

(I) Ambident Nucleophiles: Nucleophiles that possess two or more nucleophilic center donor atoms but can attack through only one center at any given time during a reaction (e.g., CN^- or NO_2^-).

(II) Racemic mixture: An equimolar mixture containing equal amounts of a pair of enantiomers (dextrorotatory and laevorotatory isomers). It is optically inactive due to external compensation.

OR

(B) (i) (I) Most reactive isomer of C_4H_9Br

2-Bromo-2-methylpropane (tert-butyl bromide) is the most reactive isomer towards S_N1 because it forms the most stable tertiary (3°) carbocation.

(II) Dehydrohalogenation product

The major alkene formed is 1-methylcyclohexene.

• Reason: According to Saytzeff's rule, elimination occurs to yield the more highly substituted, thermodynamically more stable endocyclic alkene.

(III) Directive influence of Chlorine

Chlorine withdraws electrons via its strong inductive effect (-I effect), deactivating the ring overall. However, it donates its lone pair of electrons to the ring through resonance (+R effect), which selectively increases electron density at the ortho and para positions, directing incoming electrophiles there.

(ii) Major Products

(I) Fittig Reaction:

$2C_6H_5Cl \xrightarrow{\text{Na/ dry Ether}} C_6H_5 - C_6H_5$ (Diphenyl / Biphenyl) $+ 2NaCl$

(II) Free Radical Bromination:

Heating with Br_2 results in side-chain substitution at the most stable benzylic position (the tertiary benzylic carbon).

• Major Product: $O_2\ N - C_6H_4 - C(Br)(CH_3)_2$ (1-bromo-1-methylethyl-4nitrobenzene)

166. **(b)**• Reasoning:

• Proteins degrade at higher temperatures.

• Their solutions are very dilute.

• Other colligative properties show tiny changes.

• Osmotic pressure provides measurable values at room temperature.

167. **(c)** • Reasoning:

• Dissociation increases the number of particles.

• Formula: $i = 1 + (n - 1)\alpha$.

• Here, $n = 2$ particles formed.

• Therefore, i must be greater than 1 .

168. **(a)** • Reasoning:

• Lower reduction potential means stronger reducing power.
• Standard values: $B(-1.18\ V) < C(-0.25\ V) < A(+0.34\ V)$.
• Order of reducing power is $B > C > A$.

169. **(b)** • Reasoning:
• Rate equation: Rate $\propto$ [Concentration]^n.
• Doubling concentration doubles the rate: $2 = 2^n$.
• This confirms the reaction order $n = 1$.

170. **(a)** • Reasoning:
• Transition metals have partially filled d-orbitals.
• Mercury (Hg) has a completely filled d-subshell ($5d^{10}$).
• It maintains this in its elemental and ionic states.

171. **(d)**• Reasoning:
• Secondary valency equals the coordination number.
• Ethylenediamine (en) is a bidentate ligand.
• Each en forms two coordinate bonds.
• Total bonds for three en ligands $= 3 \times 2 = 6$.

172. **(c)** Vitamin B_{12} (cyanocobalamin) is a coordination complex containing a central cobalt ion in the +3 oxidation state.

173. **(a)** Chloroform ($CHCl_3$) slowly oxidizes in air and sunlight to form carbonyl chloride ($COCl_2$), commonly called phosgene gas.

174. **(d)** Propan-2-ol is a secondary alcohol. Oxidation of secondary alcohols with CrO_3 yields ketones.

175. **(b)** Excess alkyl halide leads to exhaustive alkylation of ammonia. This produces a quaternary ammonium salt as the major product.

176. **(c)** This is the Hoffmann bromamide degradation reaction. Acetamide (CH_3CONH_2) undergoes degradation to form a primary amine with one less carbon atom.

177. **(a)** Fructose is a ketohexose. Ring closure occurs at the ketone group located at the second carbon ($C-2$).

178. **(a)** Transition Metals and Melting Points
• Assertion (A): True. Transition metals generally possess strong interatomic metallic bonding, which results in high melting points.
• Reason (R): True. Transition metals have incompletely filled d-orbitals, providing unpaired electrons that participate significantly in metallic and covalent bonding. This stronger bonding directly explains their high melting points (unlike Zn, Cd, and Hg, which have completely filled d-orbitals and lower melting points).
So, Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

179. **(c)** Temperature and Rate of Reaction
• Assertion (A): True. Increasing the temperature increases the kinetic energy of the molecules, leading to a faster rate of reaction.
• Reason (R): False. With an increase in temperature, the number of effective collisions increases, not decreases, because a larger fraction of molecules cross the activation energy barrier.

180. **(d)** Acidity of p-Nitrophenol vs Phenol
• Assertion (A): False. p-nitrophenol is more acidic than phenol, not less, because the nitro group exerts a power ful electron-withdrawing effect.
• Reason (R): True. The nitro group ($-NO_2$) is a strong electron-withdrawing group that effectively disperses the negative charge and stabilizes the phenoxide ion.

181. **(a)** Boiling Points of Amines
• Assertion (A): True. Propylamine (a primary amine) has a significantly higher boiling point than trimethylamine (a tertiary amine) of the same molecular formula.
• Reason (R): True. Propylamine contains $-NH_2$ groups capable of forming strong intermolecular hydrogen bonds, whereas trimethylamine has no hydrogen atoms attached to nitrogen and cannot form intermolecular hydrogen bonds. This directly accounts for the difference in boiling points.
So, Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

182. Raoult's Law (Volatile Components)
For a solution of volatile liquids, the partial vapor pressure (p_i) of each component in the solution is directly proportional to its mole fraction (x_i) present in the solution:

$p_i = p_i^* \cdot x_i$
(where p_f^* is the vapor pressure of the pure component)
Characteristics of an Ideal Solution
(1) No enthalpy change on mixing: $\Delta H_{mixing} = 0$
(2) No volume change on mixing: $\Delta V_{mixing} = 0$

183.

Property	Order of a Reaction	Molecularity of a Reaction
Determination	It is an experimentally determined quantity.	It is a theoretical concept.
Values	Can be a whole number, zero, or a fraction.	Always a positive whole number (never zero or fractional).

184. **(A)** Ambidentate ligand: A unidentate ligand containing two different donor atoms that can coordinate to a central metal atom through either of the atoms (e.g., NO_2^- or SCN^-).
(B) Crystal field splitting energy (CFSE): The energy difference between the split sets of **d**-orbitals (t_{2g} and e_g) when surrounded by ligands in a coordination complex.

185. **(A)** n-butyl chloride with alcoholic KOH: It undergoes β-elimination (dehydrohalogenation) to form but-1-ene.
$CH_3CH_2CH_2CH_2Cl + KOH(\text{ alc. }) \rightarrow CH_3CH_2CH = CH_2 + KCl + H_2O$
(B) Chlorobenzene with CH_3Cl / anhydrous $AlCl_3$: It undergoes Friedel-Crafts alkylation to give a mixture of o-chlorotoluene and p-chlorotoluene (major product).
$C_6H_5Cl + CH_3Cl \xrightarrow{\text{anh. } AlCl_3} o - Cl - C_6H_4 - CH_3 + p - Cl - C_6H_4 - CH_3$

186. **(A)** Essential amino acids: Amino acids that cannot be synthesized by the human body and must be supplied through food intake (e.g., valine, leucine).
• Amphoteric behaviour: In aqueous solution, the -COOH group loses a proton and the $-NH_2$ group gains a proton to form a dipolar ion called a zwitterion ($^+H_3N - CH(R) - COO^-$). Since it contains both positive and negative charges, it reacts with both acids and bases.

OR

(B) (i) Peptide linkage: A covalent amide linkage $(-CO - NH-)$ formed between the carboxyl group of one amino acid and the amino group of another amino acid.
(ii) Nucleotide: A chemical unit composed of a nitrogenous base, a pentose sugar, and a phosphoric acid group, which forms the building blocks of nucleic acids like DNA and RNA.

187. Given Data
• Mass percent of KI $= 20\%$
• Density of solution $(d) = 1.2\ g\ mL^{-1}$
• Molar mass of KI$(M_B) = 166\ g\ mol^{-1}$
Assume total mass of solution $= 100\ g$
• Mass of solute $(KI, w_B) = 20\ g$
• Mass of solvent $(H_2O, w_A) = 100 - 20 = 80\ g = 0.08\ kg$
(2) Calculation of Moles of Solute

$$\text{Moles of KI } (n_B) = \frac{\text{Mass}}{\text{Molar Mass}} = \frac{20\ g}{166\ g\ mol^{-1}} \approx 0.1205\ mol$$

(3) Calculation of Molality (m)

$$m = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} = \frac{0.1205\ \text{mol}}{0.08\ \text{kg}} = 1.51\ \text{m}$$

(4) Calculation of Molarity (M)

$$\text{Volume of solution (V)} = \frac{\text{Mass of solution}}{\text{Density}} = \frac{100\ \text{g}}{1.2\ \text{g mL}^{-1}} = 83.33\ \text{mL} = 0.08333\ \text{L}$$

$$M = \frac{\text{Moles of solute}}{\text{Volume of solution in L}} = \frac{0.1205\ \text{mol}}{0.08333\ \text{L}} = 1.45\text{M}$$

188. Conductivity (x): The conductance of a solution of 1 cm length and having a cross-section area of 1 cm^2 (i.e., the conductance of 1 cm^3 or 1 mL of the electrolytic solution).

• Molar Conductivity (Λ_m) : The conducting power of all the ions produced by dissolving one mole of an electrolyte in a given volume (V) of the solution. It is related to conductivity by $\Lambda_m = \frac{\pi \times 1000}{M}$.

• Reason for decrease with concentration: Conductivity depends on the number of current-carrying ions per unit volume. Upon dilution (decrease in concentration), the total number of ions per unit volume decreases, which leads to a decrease in conductivity.

189. Given:

• Time for 50% completion $(t_{1/2}) = 20$ minutes

• $\log 4 = 0.6$

Formula for First-Order Kinetics:

$$k = \frac{2.303}{t}\log\left(\frac{[A]_0}{[A]_t}\right)$$

(1) Find the rate constant (k):

$$k = \frac{2.303}{t_{1/2}}\log(2) = \frac{2.303 \times 0.301}{20} \approx \frac{0.693}{20}\ \text{min}^{-1}$$

(2) Calculate time for 75% completion ($t_{75\%}$):

For 75% completion, the remaining reactant $[A]_f = 100 - 75 = 25\%$.

$$t_{75\%} = \frac{2.303}{k}\log\left(\frac{100}{25}\right) = \frac{2.303}{k}\log(4)$$

Substitute the value of k into the equation:

$$t_{75\%} = \frac{2.303}{\frac{2.303 \times 0.301}{20}} \times \log(4) = \frac{20}{0.301} \times 0.6 = 20 \times 2 = 40\ \text{minutes}$$

190. **(A) (i)** In tetrahedral fields, the crystal field splitting energy (Δ_t) is relatively small ($\Delta_t = \frac{4}{9}\Delta_o$). This splitting energy is always lower than the electron pairing energy (P). Consequently, electrons prefer to occupy higher-energy orbitals rather than pairing up, ensuring that only high-spin complexes are formed.

(ii) $[Co(en)_3]^{3+}$ contains a bidentate chelating ligand (ethane-1,2-diamine or "en"), which forms stable rings with the central cobalt ion. This stabilization via ring formation is known as the chelate effect, making it significantly more stable than [$Co(NH_3)_6]^{3+}$, which contains only unidentate ligands.

(iii) In a tetrahedral complex, all four coordination positions are perfectly adjacent and equidistant to one another. Since every position is equivalent relative to every other position, changing the arrangement of unidentate ligands does not create different spatial/geometric orientations.

OR

(B) (i) Hybridisation and Magnetic Behaviour:

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

• Ni^{2+} has a 3 d^8 configuration.

• $CN^-$is a strong field ligand that forces the pairing of 3d electrons, leaving one empty 3d orbital.

• Hybridisation: dsp2 (Square planar geometry)

• Magnetic Behaviour: Diamagnetic (zero unpaired electrons)

(II) $[FeF_6]^{3-}$:

• Fe^{3+} has a 3 d^5 configuration.

• $F^-$is a weak field ligand and cannot force electron pairing.

• Hybridisation: sp^3 d^2 (Outer orbital octahedral geometry)

• Magnetic Behaviour: Paramagnetic (5 unpaired electrons)

(ii) Type of Isomerism:

• They exhibit linkage isomerism because the ambidentate ligand NO_2^- can coordinate either via the nitrogen atom ($-NO_2$) or via the oxygen atom (-ONO).

191. Differences between S_N1 and S_N2 Reactions:

Feature	S_N1 Reaction	S_N2 Reaction
Kinetics	Unimolecular (First-order kinetics)	Bimolecular (Second-order kinetics)
Mechanism	Occurs in two steps via a carbocation intermediate	Occurs in a single concerted step via a transition state
Stereochemistry	Leads to racemisation	Leads to complete inversion of configuration (Walden inversion)

Reactivity Comparison:

2,4,6-trinitrochlorobenzene is vastly more reactive towards nucleophilic substitution than chlorobenzene.

• Reason: The presence of three strongly electron-withdrawing nitro ($-NO_2$) groups at the ortho and para positions drastically decreases the electron density on the benzene ring and stabilizes the anionic intermediate formed during the nucleophilic attack. Chlorobenzene lack these groups and resists nucleophilic attack due to partial double-bond character of the $C-C1$ bond and resonance stabilization.

192. **(A)** Carbylamine reaction: When a primary aliphatic or aromatic amine is heated with chloroform ($CHCl_3$) and ethanolic potassium hydroxide (KOH), it produces foul-smelling isocyanides (carbylamines).

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$$

(B) Hoffmann's bromamide degradation reaction: An amide is treated with bromine (Br_2) in an aqueous or ethanolic solution of sodium hydroxide (NaOH) to yield a primary amine containing one less carbon atom than the starting amide.

$$R-CONH_2 + Br_2 + 4NaOH \rightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

(C) Diazotisation reaction: An aromatic primary amine (like aniline) reacts with nitrous acid (prepared in situ from $NaNO_2$ and HCl) at low ice-cold temperatures ($0-5°C$) to form a diazonium salt.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0-5°C} C_6H_5\ N_2^+Cl^- + NaCl + 2H_2O$$

193. **(A)** Propanone to Propan-2-ol: Reduce the ketone using lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$).

$$CH_3COCH_3 \xrightarrow{NaBH_4} CH_3CH(OH)CH_3$$

(B) Ethanal to Ethane: Use Clemmensen reduction by heating ethanal with zinc amalgam (Zn/Hg) and concentrated hydrochloric acid (HCl).

$$CH_3CHO \xrightarrow{Zn-Hg/\text{ conc. HCl}} CH_3CH_3$$

(C) Sodium benzoate to Benzene: Heat sodium benzoate with soda-lime (NaOH +CaO) to cause decarboxylation.

$$C_6H_5COONa + NaOH \xrightarrow{CaO,\Delta} C_6H_6 + Na_2CO_3$$

194. **(A) (i)** Major Products

(I) Reimer-Tiemann reaction: Salicylaldehyde (2-Hydroxybenzaldehyde)

(II) Kolbe's reaction: Salicylic acid (2-Hydroxybenzoic acid)

(ii) Method for Aspirin Formation

• Method: Acetylation (or esterification using acetic anhydride/acetyl chloride)

(B) (i) Why Phenol Undergoes Electrophilic Substitution Easily

• Resonance effect: The lone pairs on the oxygen atom of the $-OH$ group are delocalized into the benzene ring.

• Electron density: This increases the electron density on the ring, especially at the ortho and para positions.

• Activation: The highly electron-rich ring attracts electrophiles much faster than benzene.

OR

(ii) Why Phenol is More Acidic than Alcohol

• Phenoxide stability: Phenol loses a proton $(H^+)$to form a phenoxide ion, which is highly stabilized by resonance.

• Alkoxide instability: Alcohols form alkoxide ions where the negative charge is localized on oxygen and further destabilized by the electron-donating alkyl group ($+I$ effect).

(C) Order of Increasing Boiling Points

• Trend: Boiling point increases with molecular mass due to larger van der Waals forces, and decreases with branching due to reduced surface area.

• Order: Ethanol < Propan-1-ol < Butan-2-ol < Butan-1-ol

195. **(A)** two differences between Amylose and Amylopectin

Amylose	Amylopectin
Long unbranched chain of α-glucose units.	Branched chain of a-glucose units.
Contains only $\alpha(1 \rightarrow 4)$ glycosidic linkages.	Contains $\alpha(1-4)$ and $\alpha(1-6)$ glycosidic linkages.
Soluble in water.	Insoluble in water.

(B) (i) Monosaccharides:

• Glucose

• Fructose

Disaccharides:

• Lactose

• Maltose

OR

(ii) Polysaccharides are carbohydrates that yield a large number of monosaccharide units on hydrolysis.

Example: Starch, Cellulose, Glycogen.

(C) Two monosaccharide units are joined by a glycosidic linkage (glycosidic bond).

• Glycosidic linkage

196. **(A) (i)** Oxidation of propanal is easier than propanone.

• Presence of C-H bond: Propanal (CH_3CH_2CHO) has a hydrogen atom attached directly to its carbonyl carbon ($C-H$ bond), which is easily oxidized to a carboxylic acid without breaking any carbon-carbon bonds.

• Absence of C-H bond: Propanone (CH_3COCH_3) lacks this directly attached hydrogen atom; its oxidation requires breaking a strong carbon-carbon ($C-C$) bond, which can only happen under drastic conditions.

(ii) There are two $-NH_2$ groups in semicarbazide. However, only one $-NH_2$ group is involved in the formation of semicarbazones.

• Resonance stabilization: Semicarbazide is represented as $H_2\ N-NH-CO$ $-NH_2$. The lone pair of electrons on the $-NH_2$ group attached directly to the carbonyl group ($C=O$) is involved in resonance.

• Nucleophilic availability: This resonance significantly decreases electron density on that nitrogen atom. The other terminal $-NH_2$ group (the hydrazine end) is not involved in resonance, leaving its lone pair fully available to act as a nucleophile.

(iii) HCHO does not undergo aldol condensation reaction.

• Lack of α-hydrogens: Aldol condensation reactions strictly require the presence of at least one α-hydrogen atom.

• Structure: Formaldehyde (HCHO) does not possess an α-carbon, meaning it completely lacks α-hydrogen atoms.

(iv) Boiling points of carboxylic acids are higher than those of alcohols of comparable molecular masses.

• Extensive hydrogen bonding: Carboxylic acid molecules are held together by stronger and more extensive intermolecular hydrogen bonds than alcohols.
• Dimer formation: They form stable cyclic dimers through two hydrogen bonds per pair of molecules, which persist even in the vapor phase.
(v) Aldehydes are more reactive towards nucleophilic addition reactions than ketones.
• Steric hindrance: Ketones have two relatively bulky alkyl groups attached to the carbonyl carbon, which obstructs the approach of an incoming nucleophile. Aldehydes have only one alkyl group, causing less steric hindrance.
• Electronic effect: Alkyl groups are electron-donating (+I effect). The presence of two alkyl groups in ketones reduces the positive charge density on the carbonyl carbon more effectively than the single group in aldehydes, making it less electrophilic.

OR

(B) (i) (I) Benzoyl chloride undergoes Rosenmund reduction:
• Product: Benzaldehyde (C_6H_5CHO)
(II) Ethanal is treated with CH_3MgBr, followed by hydrolysis:
• Product: Propan-2-ol (or Isopropyl alcohol, $CH_3CH(OH)CH_3$)
(III) Benzaldehyde undergoes Cannizzaro's reaction:
• Products: Benzyl alcohol ($C_6H_5CH_2OH$) and Sodium benzoate (C_6H_5COONa)
(ii) (I) Propanal and Propanone:
• Test: Tollens' Test
• Procedure: Warm each compound with Tollens" reagent (ammoniacal silver nitrate solution).
• Observation: Propanal forms a shining silver mirror on the inner walls of the test tube. Propanone shows no reaction.
(II) Phenol and Benzoic acid:
• Test: Sodium Bicarbonate ($NaHCO_3$) Test
• Procedure: Add a solution of sodium bicarbonate ($NaHCO_3$) to both samples.
• Observation: Benzoic acid reacts vigorously to produce brisk effervescence due to the evolution of CO_2 gas. Phenol does not react or produce effervescence.

197. **(A) (i)** Nernst Equation and EMF Calculation
(1) Standard Cell Potential (E_{cell}^{*}):
$E^*_{ccll} = E^*_{cathode} - E^*_{anode}$
$E^*_{cell} = E^*_{Cu^{2+}/Cu^-} - E^*_{Mg^{2+}/Mg}$
$E^*_{ccill} = 0.34\ V - (-2.36\ V) = +2.70\ V$
(2) Cell Reaction and Electrons (n):
• Anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
• Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
• Net Reaction: $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$
The total number of moles of electrons transferred is $n = 2$.
(3) Nernst Equation:

$$E_{ccll} = E^*_{ccll} - \frac{0.0591}{n}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

(3) Calculation:

$$E_{ccll} = 2.70 - \frac{0.0591}{2}\log\frac{0.001}{0.0001}$$

$E_{cell} = 2.70 - 0.02955\log(10)$
$E_{ccll} = 2.70 - 0.02955 \times 1 = 2.67\ V$
(ii) Fuel Cell Definition & Advantages
• Definition: A galvanic cell that directly converts the chemical energy produced during the combustion of fuels (like H_2, CH_4, or CH_3OH) into electrical energy.
• Advantages:
(1) High Efficiency: They operate with an efficiency of around $70 - 80\%$, which is significantly higher than conventional thermal power plants.
(2) Eco-Friendly: They do not cause environmental pollution since the primary byproduct (e.g., water in a hydrogen-oxygen fuel cell) is completely nontoxic.

OR

(B) (i) Calculation of $\Delta_r G^*$ and $\log K_C$

Given reaction: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$

Here, number of electrons transferred is $n = 2$.

(1) Gibbs Free Energy Change ($\Delta_r G^*$):

$\Delta_r G^* = -nFE^*_{cell}$

$\Delta_r G^* = -2 \times 96500 C\ mol^{-1} \times 0.24\ V$

$\Delta_r G^* = -46320\ J\ mol^{-1} = -46.32\ kJ\ mol^{-1}$

(2) Equilibrium Constant ($\log K_C$) :

$$E^*_{cell} = \frac{0.0591}{n} \log K_C$$

$$0.24 = \frac{0.0591}{2} \log K_C$$

$$\log K_C = \frac{0.24 \times 2}{0.0591} = \frac{0.48}{0.0591} \approx 8.12$$

(ii) Statement of Laws

(I) Faraday's First Law of Electrolysis:

The mass (m) of any substance deposited or liberated at any electrode during electrolysis is directly proportional to the quantity of electricity (Q) passed through the electrolyte ($m \propto Q \Longrightarrow m = Z \cdot I \cdot t$).

(II) Kohlrausch's Law of Independent Migration of Ions:

The limiting molar conductivity (Λ^*_m) of an electrolyte can be represented as the sum of the individual contributions of its anions and cations ($\Lambda^*_m = \nu_+\lambda^*_+ + \nu_-\lambda^*_-$).

198. **(A) (i)** Transition Elements

• Definition: Transition elements are elements that have incompletely filled d subshells in their ground state or in any of their stable oxidation states.

• Characteristics :

• They exhibit multiple variable oxidation states.

• They form colored ions due to $d - d$ electronic transitions.

• They form a large variety of complex compounds.

• They exhibit paramagnetic properties due to the presence of unpaired electrons.

(ii) Preparation of $KMnO_4$ from Pyrolusite Ore (MnO_2)

The industrial preparation occurs in two steps:

(1) Conversion of MnO_2 to Potassium Manganate (K_2MnO_4):

Pyrolusite ore is fused with potassium hydroxide (KOH) in the presence of atmospheric oxygen or an oxidizing agent like KNO_3 to form a dark green mass of potassium manganate.

$2MnO_2 + 4KOH + O_2 \rightarrow 2\ K_2MnO_4 + 2H_2O$

(2) Oxidation of K_2MnO_4 to Potassium Permanganate ($KMnO_4$) :

The green potassium manganate is corverted to purple potassium permanganate either chemically using chlorine/ozone or via electrolytic oxidation.

$2\ K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$

OR

(B) (i) Lanthanoid Contraction

• Definition: Lanthanoid contraction is the steady and gradual decrease in the atomic and ionic radii of the lanthanoid elements with the increase in atomic number from Lanthanum ($Z = 57$) to Lutetium ($Z = 71$). This is caused by the poor shielding effect of the 4f electrons.

• Consequences :

• Similarity in sizes of 4d and 5d elements: Elements of the second and third transition series (e.g., Zirconium and Hafnium) possess nearly identical atomic radii, making their separation difficult.

• Basic strength variation: The basic strength of lanthanoid hydroxides decreases regularly from $La(OH)_3$ (most basic) to $Lu(OH)_3$ (least basic).

• Difficulty in separation: Due to nearly identical chemical properties arising from identical sizes, separating pure lanthanoid elements from mixtures is highly challenging.

(ii) Explanations

(I) Positive value of $E_{Cu^{2+}/Cu}(+0.34\ V)$:

Copper has a positive electrode potential because its high enthalpy of atomization and high ionization energies are not fully compensated by its relatively low hydration enthalpy.

(II) Wide range of oxidation states in Actinoids:

Actinoids display a wide range of oxidation states because the energy difference between the 5f, 6d, and 7s orbitals is exceptionally small, allowing electrons from all three subshells to participate in bonding.