1. (i) $CH_3CH_2CN \xrightarrow[\text{Partial hydrolysis}]{H^+ \text{ or } OH^-} CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2$

Ethyl cyanide → Propionamide

Propionamide $\xrightarrow{Br_2/NaOH}$ Ethylamine

Ethylamine $\xrightarrow[-N_2, -H_2O]{HONO}$ Ethanol

Ethanol $\xrightarrow{\text{Oxidation } K_2Cr_2O_7/H_2SO_4}$ Ethanoic acid

(ii) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Oxidation}]{K_2Cr_2O_7/H_2SO_4} CH_3CH_2CH_2COOH$

Butan-1-ol → Butanoic acid

(iii) Benzoic acid $\xrightarrow{Br_2/FeBr_3}$ 3-Bromobenzoic acid

2. At anode : $Sn^{2+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2e^-] \times 5$

At cathode : $MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}] \times 2$

Net cell reaction :

$2MnO^-_{4(aq)} + 5Sn^{2+}_{(aq)} + 16H^+_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5Sn^{4+}_{(aq)} + 8H_2O_{(l)}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.51\ V - 0.15\ V = 1.36\ V$

Since, cell potential is positive therefore the reaction is product favoured.

3. (i) $C_6H_5NH_2 < (CH_3)_2NH < CH_3NH_2$

1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

(ii) 1° amines have two, 2° amines have one while 3° amines have no hydrogen linked to nitrogen. The degree of association due to hydrogen bonding and hence the boiling point increase as $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2$

4. (i) $FeCl_3 + NaOH \longrightarrow \underset{\text{Negatively charged sol}}{Fe_2O_3 \cdot xH_2O \vdots OH^-}$

(ii) (a) Animal hides are colloidal in nature. When a hide, which has positively charged particles is soaked in tannin, containing negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather.

(b) Lyophilic sol is more stable than lyophobic sol because it is highly hydrated in the solution.

OR

(i) Scattering of light by the colloidal particles takes place and the path of light becomes visible (Tyndall effect).

(ii) The positively charged colloidal particles of ferric hydroxide sol get coagulated by the oppositely charged Cl^- ions provided by KCl.

(iii) On passing electric current through a sol, colloidal particles start moving towards oppositely charged electrodes where they lose their charge and get coagulated (electrophoresis).

5. (i) $[Pt(NH_3)_2Cl(NO_2)]$:

Diamminechloridonitrito-N-platinum(II)

It is square planar and diamagnetic.

(ii) $[Co(NH_3)_4Cl_2]Cl$:

Tetraamminedichloridocobalt (III) chloride

It is octahedral and diamagnetic.

(iii) $Ni(CO)_4$: Tetracarbonylnickel(0)

It is tetrahedral and diamagnetic.

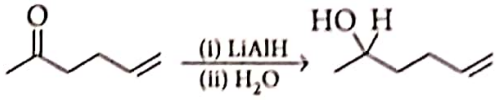
6. (i)

$HCHO + H_3\overset{\alpha}{C}CHO \xrightarrow{NaOH} HOCH_2 - CH_2CHO \xrightarrow{\Delta}$

$CH_2=CH-CH=O \xleftarrow{HCN} CH_2=CH-CHO$ (A)

$CH_2=CH-\underset{CN}{\underset{|}{CH}}-OH \xrightarrow{H_3O^+} CH_2=CH-\underset{COOH}{\underset{|}{CH}}-OH$ (B)

(ii) $LiAlH_4$ reduces $>C=O \longrightarrow >CHOH$ group without affecting the double bond.



7. (a) During electrolysis of aqueous $CuCl_2$ following reactions take place

$CuCl_2 \longrightarrow Cu^{2+} + 2Cl^-$

At cathode $Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$

At anode two reactions are possible

$2Cl^- \longrightarrow Cl_{2(g)} + 2e^-;\ E^\circ = 1.36\ V$

$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-;\ E^\circ = 1.23\ V$

At anode the reaction with lower value of E° should take place and thus water should get oxidised to give

O_2. But on account of overpotential of oxygen, chlorine is produced at anode.

(b) By using Kohlrausch's law, we can easily calculate the limiting molar conductivity of weak electrolyte.

e.g., $\Lambda^\circ_{mCH_3COOH} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$

$= [\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+}] + [\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}] - [\lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}]$

$= \Lambda^\circ_{m(CH3COONa)} + \Lambda^\circ_{m(HCl)} - \Lambda^\circ_{m(NaCl)}$

OR

$\kappa = 1.29 \times 10^{-2}$ ohm^{-1} cm^{-1}

$\kappa = \frac{1}{R} \times$ Cell constant

$\Rightarrow$ Cell constant $= \kappa \times R$

$= 1.29\ \Omega^{-1}\ m^{-1} \times 85\ \Omega = 109.65\ m^{-1}$

For second solution,

$\kappa = \frac{1}{R} \times$ Cell constant $= \frac{1}{96\ \Omega} \times 109.65\ m^{-1}$

$= 1.142\ \Omega^{-1}m^{-1}$

$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.142\ \Omega^{-1}m^{-1} \times 1000\ cm^3}{0.052\ mol}$

$\Lambda_m = \frac{1.142\ \Omega^{-1}cm^{-1} \times 10^{-2} \times 1000\ cm^3}{0.052\ mol}$

$= 219.61\ S\ cm^2\ mol^{-1}$

8. The given compound does not reduce Tollens' reagent, so it is not an aldehyde but the formation of addition compound with sodium hydrogen sulphite indicates it to be a carbonyl compound. Since this compound gives positive iodoform test, so it should contain $-\overset{O}{\overset{\|}{C}}-CH_3$ group.

On the basis of this information, two possible structures are written as under :

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$ (I) and $CH_3-\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$ (II)

On oxidation, this compound gives ethanoic and propanoic acids which confirm its structure to be I.

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3 \xrightarrow[\text{Vigorous oxidation}]{[O]} CH_3COOH + CH_3CH_2COOH$

OR

(i) The overall acid strength increases in the order.

4-Methoxybenzoic acid < benzoic acid < 3,4-dinitrobenzoic acid.

(ii) We know that + *I*-effect decreases while –*I*-effect increases the acid strength of carboxylic acids. The overall acid strength increases in the order :

$(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$.

9. (i) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

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

Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

(ii) E° values for the Cr^{3+}/Cr^{2+} and Mn^{3+}/Mn^{2+} couples are

$Cr^{3+}_{(aq)} + e^- \longrightarrow Cr^{2+}_{(aq)}$; $E^\circ = -0.41$ V

$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)}$; $E^\circ = +1.551$ V

These E° values indicate that Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising agent.

(iii) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

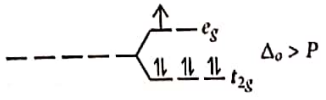
10. (a) $CH_3NH_2 + C_6H_5COCl \longrightarrow CH_2NH-\overset{O}{\overset{\|}{C}}-C_6H_5$

N-Methylbenzamide

(b) Stronger the base, lower will be its pK_b value. Hence increasing order of pK_b values is:

$(C_2H_5)_2NH < C_2H_5NH_2 < NH_3 < C_6H_5NH_2$

11. (i) In presence of strong field ligand, Co(II) has electronic configuration $t^6_{2g}e^1_g$



It can easily lose one electron present in e_g orbital to give stable t^6_{2g} configuration. This is why Co^{2+} is easily oxidised to Co^{3+} in the presence of strong field ligand.

(ii) Coordination number and oxidation state of Pt in the complex $[Pt(en)_2Cl_2]$ are 6 and +2 because *en* is a bidentate and neutral ligand.

OR

(i) Hexaamminechromium(III)hexacyanidocobaltate(III).

(ii) $[Co(en)_2Cl(NH_3)]^{2+}$

Amminechloridobis(ethane-1,2-diamine)cobalt(III) ion

In presence of strong NH_3 and *en* ligand, Co^{3+} $(3d^6)$ forms low spin complex. Hence, complex is diamagnetic.

(b) $[Ni(C_2O_4)_2(H_2O)_2]^{2-}$:

Diaquadioxalatonickelate(II) ion

In the presence of weak H_2O and *ox* ligand, Ni(II) forms high spin complex (sp^3d^2 hybridisation). It is paramagnetic.

12. (a) For a first order reaction :

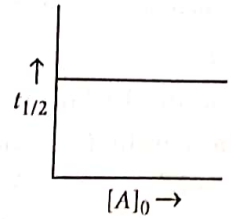
$$t_{1/2} = \frac{0.693}{k}, \; k = 3.01 \times 10^{-3}\ s^{-1}$$

$$\therefore \quad t_{1/2} = \frac{0.693}{3.01 \times 10^{-3}} = 230.3\ s$$

(b) Half life ($t_{1/2}$) of a first order reaction is given as :

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{7.0 \times 10^{-4}} = 990\ s$$

(c) For a first order reactions, $t_{1/2} = k[A]_0^0 = k$. Thus $t_{1/2}$ is independent of initial concentration. Hence plot of $t_{1/2}$ *vs* $[A]_0$ will be a horizontal line.



(d) Yes, for a first order reaction $t_{1/2} = \frac{0.693}{k}$ therefore $t_{1/2}$ depends upon k and hence depends on temperature because rate constant k is a function of temperature.

OR

Let the concentrations of the reactant after 10 min and 20 min be C_1 and C_2 respectively.

$\therefore$ Rate after 10 min $= k.C_1$

$= 0.04 \times 60\ mol\ L^{-1}min^{-1}$

and rate after 20 min $= k.C_2$

$= 0.03 \times 60\ mol\ L^{-1}min^{-1}$

$$\therefore \quad \frac{C_1}{C_2} = \frac{4}{3}$$

Let the reaction starts after 10 minutes.

$$k = \frac{2.303}{10} \log \frac{C_1}{C_2} = \frac{2.303}{10} \log \frac{4}{3} = 0.02878$$

$$\therefore \quad t_{1/2} = \frac{0.6932}{k} = \frac{0.6932}{0.02878} = 24.086\ min$$

☺☺☺