

SOLUTIONS

1. (a) Zero order reaction

(b) $t_{1/2}$ doubles since for zero order reaction, $t_{1/2} \propto$ initial concentration.

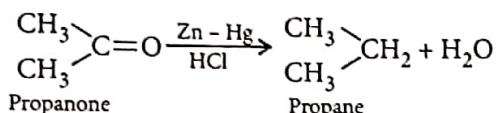
(c) $\text{mol L}^{-1} \text{s}^{-1}$

For a zero order reaction

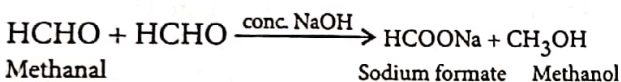
$[R] = -kt + [R]_0$ hence plot of $[R]$, (conc. of A) vs t is a straight line with slope = $-k$.

$$\frac{dx}{dt} = k[A]^0 = \frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1} \text{s}^{-1}$$

2. (a) **Clemmensen reduction**: The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid.



(b) **Cannizzaro reaction**: Aldehydes which do not contain α -H atom undergo disproportionation when heated with concentrated alkali.



3. (a) $\text{Cd}|\text{Cd}^{2+}||\text{Ag}^+|\text{Ag}$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = (0.80) - (-0.40) = 1.20 \text{ V}$$

(b) $\text{Pt}, \text{I}^{-}_{(\text{aq})}|\text{I}_{2(\text{s})}||\text{Cl}_{2(\text{g})}|\text{Cl}^{-}_{(\text{aq})}, \text{Pt}$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = (1.36) - (0.54) = 0.82 \text{ V}$$

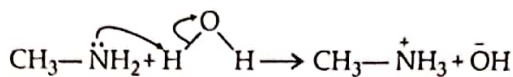
4. (a) Methylamine gives carbylamine test, i.e., on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethylamine does not give this test.

(b) Aniline being an aromatic primary amine on treatment with HNO_2 [$\text{NaNO}_2 + \text{HCl}$ (dil.)] at 273–278 K followed by treatment with an alkaline solution of β -naphthol gives an orange coloured azo dye. Ethylamine does not give this test.

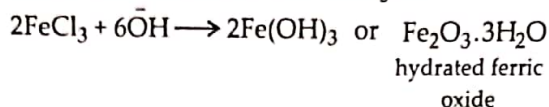
(c) Tertiary amines do not react with benzene sulphonyl chloride while secondary amines react and give a product insoluble in alkali.

OR

(a) The formation of hydrated ferric oxide may be understood by taking into consideration the basic strength of CH_3NH_2 . In presence of CH_3NH_2 , water hydrolyses as

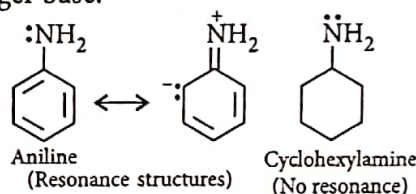


These OH^- ions react with FeCl_3 as:



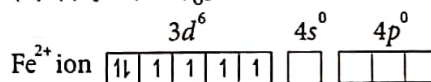
(b) Gabriel phthalimide reaction gives pure primary amines without any contamination of secondary and tertiary amines. Therefore, it is preferred for synthesising primary amines.

(c) Aniline is weaker base than cyclohexylamine because of resonance. Due to electromeric effect, the lone pair on nitrogen is attracted by benzene ring. Hence, donor tendency of $-\ddot{\text{N}}\text{H}_2$ group decreases. There is no resonance in cyclohexylamine. Electron repelling nature of cyclohexyl group further increases the donor property of NH_2 group. So, cyclohexylamine is a stronger base.



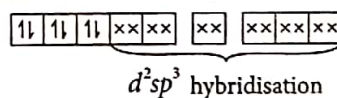
5. (a) Amminebromidochloridonitrito-N-platinate(II)

(b) (i) $[\text{Fe}(\text{CN})_6]^{4-}$ ion:



Fe^{2+} ion hybridised (under the influence of strong field ligand).

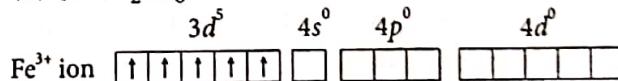
$[\text{Fe}(\text{CN})_6]^{4-}$ ion formation:



Six pairs of electrons from six CN^- ions

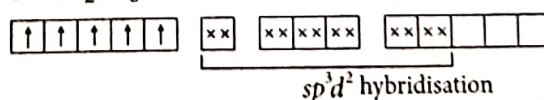
Since the complex ion does not contain any unpaired electron, so it is diamagnetic.

(ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion:



Fe^{3+} ion is hybridised (under the influence of weak field ligand)

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion formation:

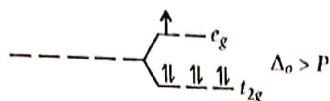


Six electron pairs from six H_2O ligands

As the complex ion contains five unpaired electrons, it is highly paramagnetic in nature.

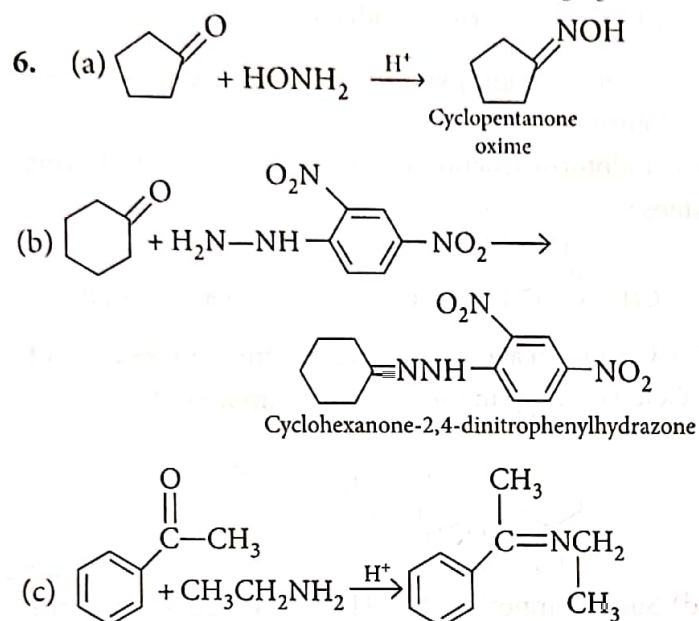
OR

(a) In presence of strong field ligand Co(II) has electronic configuration $t_{2g}^6 e_g^1$



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

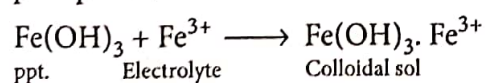
(b) For d^4 ion, if $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$.



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

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

(c) On treating a precipitate of iron (III) oxide with a small amount of FeCl_3 solution, a reddish brown coloured colloidal solution is formed. In this case, Fe^{3+} ions from ferric chloride are adsorbed by $\text{Fe}(\text{OH})_3$ precipitate.



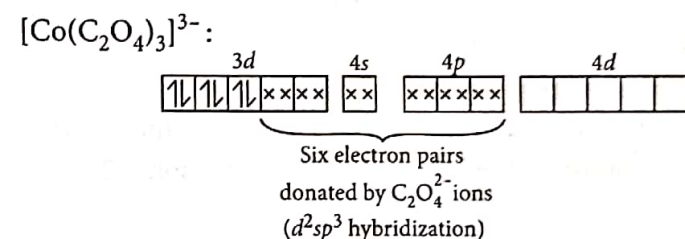
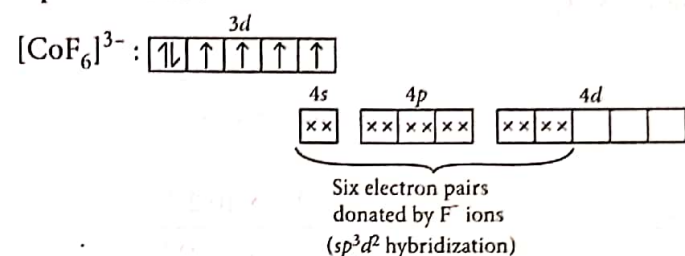
8. (a) The metals of $4d$ and $5d$ -series have more frequent metal bonding in their compounds than the $3d$ -metals because $4d$ and $5d$ -orbitals are more exposed in space than the $3d$ -orbitals. So the valence

electrons are less tightly held and form metal-metal bonding more frequently.

(b) Mn^{3+} is less stable and changes to Mn^{2+} which is more stable due to half-filled d -orbital configuration. That is why, Mn^{3+} undergoes disproportionation reaction.

(c) Since, transition elements contain partially filled d -subshells, therefore, electrons in these subshells go from lower d -subshells to higher d -subshells. This is called $d-d$ transition. This transition takes place by absorbing energy from the visible light. The mixture of the wavelength which is not absorbed is transmitted out. This accounts for the colour of transition elements..

9. Formation of $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ can be represented as :



(a) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ is diamagnetic as all the electrons are paired.

(b) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ is more stable as $\text{C}_2\text{O}_4^{2-}$ is a chelating ligand and forms chelate rings.

(c) $[\text{CoF}_6]^{3-}$ is outer orbital complex as it undergoes sp^3d^2 hybridization using the outer $4d$ -orbital.

OR

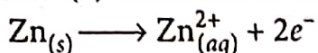
(a) Nickel forms octahedral complexes mainly in +2 oxidation state which has $3d^8$ configuration. In presence of strong field ligand also, it has two unpaired electrons in e_g orbital.

Hence, it does not form low spin octahedral complexes.

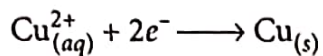
(b) CO is stronger ligand than NH_3 because CO has vacant molecular orbitals with which it can form π -bond with metal through back donation.

(c) Ethane-1,2-diamine is stronger ligand than H_2O . When H_2O molecule is replaced by ethane-1,2-diamine (*en*) the crystal field splitting energy (Δ_o) increases. Complex absorbs light of higher frequency for $d-d$ transition. This is why colour of complex changes from green to violet.

10. (a) Oxidation half reaction :



Reduction half reaction :



(b) $E_{\text{cell}}^{\circ} = 0.34 - (-0.76) = 1.10 \text{ V}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\Rightarrow E_{\text{cell}} = 1.10 - \frac{0.0591}{2} \log \frac{2}{0.5}$$

$$= 1.10 - \frac{0.0591}{2} \log \frac{2}{0.5}$$

$$= 1.10 - \frac{0.059}{2} \times 0.6021$$

$$= 1.10 - 0.0177 = 1.0823 \text{ V}$$

11. (a) Let the rate law for the given reaction be

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

Then, $\frac{r_{\text{II}}}{r_{\text{I}}} = \frac{2.4 \times 10^{-1}}{6.0 \times 10^{-2}} = \frac{k(0.4)^x \times (0.1)^y}{k(0.2)^x \times (0.1)^y}$

$$4 = 2^x \Rightarrow x = 2$$

Again, $\frac{r_{\text{III}}}{r_{\text{I}}} = \frac{1.2 \times 10^{-1}}{6.0 \times 10^{-2}} = \frac{k(0.2)^x \times (0.2)^y}{k(0.2)^x \times (0.1)^y}$

$$\text{or, } 2 = 2^y \Rightarrow y = 1$$

Hence, the rate law = $k[\text{A}]^2[\text{B}]^1$

(b) If half life is independent of the initial concentration, then the order of the reaction is 2.

OR

Radioactive disintegration follows first order kinetics.

Hence,

$$\text{Decay constant of } ^{90}\text{Sr}, (\lambda) = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} \\ = 2.466 \times 10^{-2} \text{ yr}^{-1}$$

To calculate the amount left after 10 years,

Given, $[R_0] = 1 \mu\text{g}$, $t = 10 \text{ years}$,

$$\lambda = 2.466 \times 10^{-2} \text{ yr}^{-1}, [R] = ?$$

$$\text{Using formula, } \lambda = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

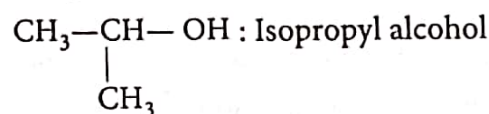
$$\text{or } 2.466 \times 10^{-2} = \frac{2.303}{10} \log \frac{1}{[R]}$$

$$\text{or, } \log [R] = -0.1071$$

$$\text{or, } [R] = \text{Antilog}(-0.1071) = 0.7814 \mu\text{g}$$

12. (a) Iodoform test is given by the organic

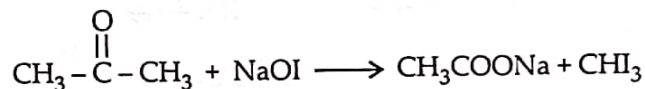
compounds having $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$ or $\text{CH}_3-\overset{\text{OH}}{\text{CH}}-$ group.



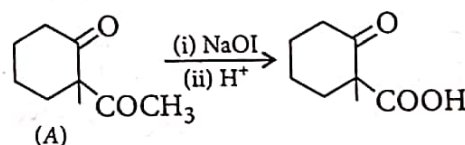
$\text{CH}_3\text{CH}_2\text{CHO} : \text{Propionaldehyde}$

Therefore, isopropyl alcohol will give positive iodoform test.

(b) Iodoform reaction of acetone occurs in following steps :



(c) Given reagents indicate the presence of $-\text{COCH}_3$ group in the starting compound A.



(d) Since compound A ($\text{C}_3\text{H}_6\text{O}$) undergoes iodoform test, it must be CH_3COCH_3 i.e., propan-2-one.

OR

