

LIBERTY PAPER SET

STD. 12 : Chemistry

Full Solution

Time : 3 Hours

ASSIGNMENT PAPER 8

Part A

1. (D) 2. (B) 3. (B) 4. (C) 5. (C) 6. (D) 7. (D) 8. (C) 9. (D) 10. (B) 11. (B) 12. (C) 13. (A) 14. (B)
15. (C) 16. (C) 17. (B) 18. (C) 19. (D) 20. (A) 21. (B) 22. (C) 23. (D) 24. (D) 25. (A) 26. (C)
27. (D) 28. (A) 29. (B) 30. (D) 31. (C) 32. (A) 33. (B) 34. (A) 35. (B) 36. (C) 37. (D) 38. (C)
39. (C) 40. (D) 41. (C) 42. (C) 43. (B) 44. (B) 45. (A) 46. (A) 47. (C) 48. (A) 49. (B) 50. (C)



➤ Write the answer of the following questions : (Each carries 2 Mark)

1.

➤ Integrated rate equation for first order reaction,

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

➤ $[R]_0 = 5\text{g}$ and $[R] = 3\text{g}$, $k = 1.15 \times 10^{-3} \text{ s}^{-1}$

➤ Substituting above values in equation $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

$$t = \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3}$$

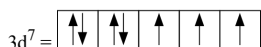
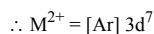
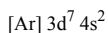
[Note : Here, it is not necessary to convert unit of concentration in mol/L. Because both $[R]_0$ and $[R]$ are in ratio of each other]

$$t = \frac{2.303}{1.15 \times 10^{-3}} \times 0.2219$$

$$t = 444.3 \text{ s}$$

2.

➤ $Z = 27$



i.e., 3 unpaired electrons

$$\therefore n = 3$$

$$(\infty) = \sqrt{n(n+2)}$$

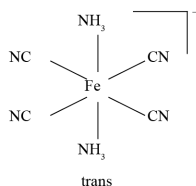
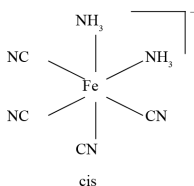
$$= \sqrt{3(3+2)}$$

$$= \sqrt{15}$$

$$= 3.87 \text{ B.M.}$$

3.

➤ Solution :



4.

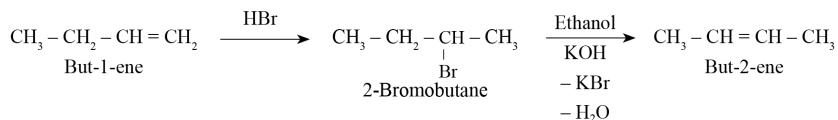
- (i) It involves a number of assumptions.
 (ii) It does not give quantitative interpretation of magnetic data.
 (iii) It does not explain the colour exhibited by coordination compounds.
 (iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.

(v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.

(vi) It does not distinguish between weak and strong ligands.

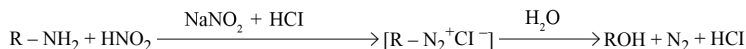
5.

➔ (viii) But-1-ene to but-2-ene :



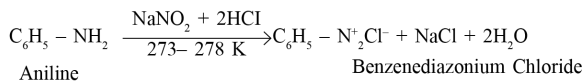
6.

➔ (i) Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts, which are unstable and quantitatively liberate nitrogen gas along with alcohols. Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.



➔ (ii) Aromatic amines react with nitrous acid at low temperatures to form diazonium salts.

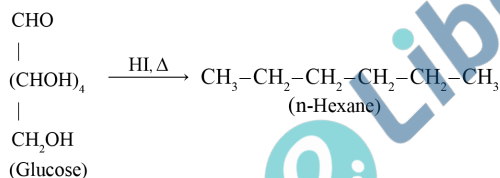
➔ A very important class of compounds used for synthesis of a variety of aromatic compounds.



7.

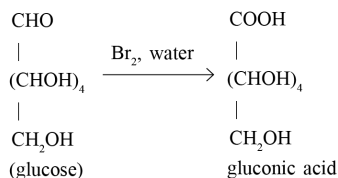
➔ (i) Reactions with HI :

➔ When D-glucose is heated with HI for long time, n-Hexane is formed, it shows all 6-carbon atoms are linked in linear chain.



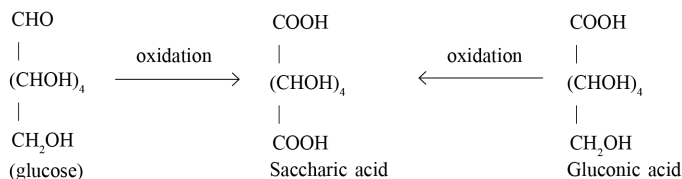
➔ (ii) Reactions with Br₂ water :

➔ Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with mild oxidising agent like Br₂ water. This indicates that the carbonyl group is present as an aldehyde group.



➔ (iii) Reactions with HNO₃ :

➔ On oxidation with HNO₃ glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (-OH) group in glucose.

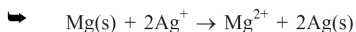


8.

➔ Monosaccharide compounds : Ribose, 2-deoxyribose, galactose, and fructose.

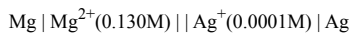
➔ Disaccharide compounds : Maltose and lactose

9.



➔ In above reaction Mg is oxidise and Ag^+ ion reduce

➔ The cell can be written as



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

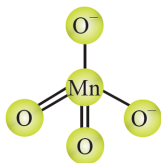
$$= 3.17 - \frac{0.059}{2} \log (0.0001)^2$$

$$= 3.17 - 0.21$$

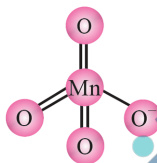
$$= 2.96 \text{ V}$$

10.

➔ The manganate and permanganate ions are tetrahedral.



Tetrahedral
manganate
(green) ion



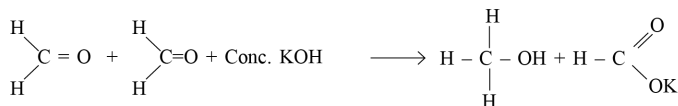
Tetrahedral
permanganate
(purple) ion

➔ The green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic.

➔ The π -bonding takes place by overlap of p orbitals of oxygen with d orbitals of manganese.

11.

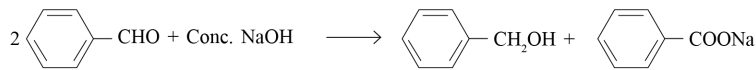
➔ Cannizzaro reaction : "Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt."



Formaldehyde

Methanol

Potassium formate



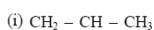
Benzaldehyde

Benzyl alcohol

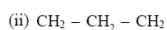
Sodium benzoate

12.

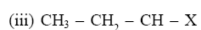
➔



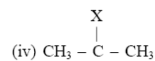
1, 2-dihalopropane



1, 3-dihalopropane



1, 1-dihalopropane



2, 2-dihalopropane

Section B

➤ Write the answer of the following questions : (Each carries 3 Mark)

13.

➤ millimoles of $N_2 = (?)$

$$P_{N_2} = 0.987 \text{ bar}$$

$$K_H = 76.48 \text{ kbar}$$

$$= 76480 \text{ bar}$$

➤ According to Henry's Law

$$P_{N_2} = K_H \cdot X_{N_2}$$

$$\therefore X_{N_2} = \frac{P_{N_2}}{K_H}$$

$$= \frac{0.987}{76480}$$

$$\therefore X_{N_2} = 0.0000129$$

➤ Moles of Water = $\frac{1000}{18} = 55.55$

$$\therefore X_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{H_2O}}$$

$$(n_{N_2} \ll n_{H_2O})$$

$$\therefore X_{N_2} = \frac{n_{N_2}}{n_{H_2O}}$$

$$n_{N_2} = X_{N_2} \cdot n_{H_2O}$$

$$= (0.0000129) \cdot (55.55)$$

$$= 0.000716$$

$$= 0.716 \times 10^{-3} \text{ Mol}$$

$$n_{N_2} = 0.716 \text{ Millimol}$$

14.

➤ For first order reaction,

$$t_{99\%} = \frac{2.303}{k} \log \frac{100}{1} \dots \dots (1)$$

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{10} \dots \dots (2)$$

➤ Taking ratio of equation (1) and (2)

$$\frac{t_{99}}{t_{90}} = \frac{\frac{2.303}{k} \log \frac{100}{1}}{\frac{2.303}{k} \log \frac{100}{10}}$$

$$\therefore \frac{t_{99}}{t_{90}} = \frac{\log 100}{\log 10}$$

$$\therefore \frac{t_{99}}{t_{90}} = \frac{\log 10^2}{\log 10}$$

$$\therefore \frac{t_{99}}{t_{90}} = \frac{2 \log 10}{\log 10}$$

$$\therefore \frac{t_{99}}{t_{90}} = 2$$

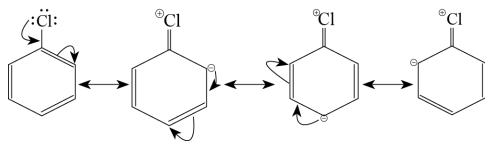
$$\therefore t_{99\%} = 2 \times t_{90\%}$$



15.

➔ Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons :

➔ (i) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with π -electrons of the ring and the following resonating structures are possible :

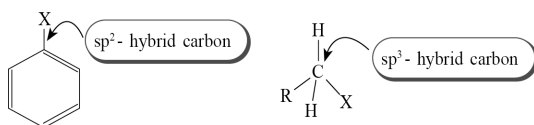


➔ C-Cl bond acquires a partial double bond character due to resonance.

➔ As a result, the bond cleavage in haloarene is more difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

➔ (ii) Difference in hybridization of carbon atom in C-X bond :

➔ In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2 hybridised.



➔ The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C-X bond more tightly than sp^3 hybridised carbon in haloalkane with less s-character.

➔ Thus, C-Cl bond length in haloalkane is 177 pm while in haloarenes is 169 pm.

➔ Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

➔ (iii) Instability of phenyl cation :

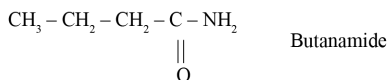
➔ In case of haloarenes, the phenyl cation formed as a result of self-ionization will not be stabilised by resonance and therefore, SN^1 mechanism is ruled out.

➔ (iv) Repulsion :

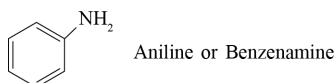
➔ Because of the possible repulsion, it is less likely for the electron rich in nucleophile to approach electron rich arenes.

16.

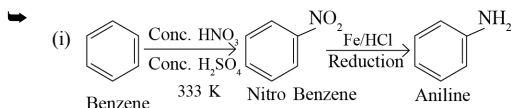
➔ (i) Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms structure and IUPAC name of the starting amide with four carbon atoms are given below :

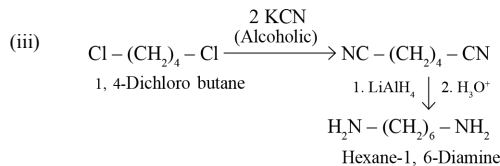
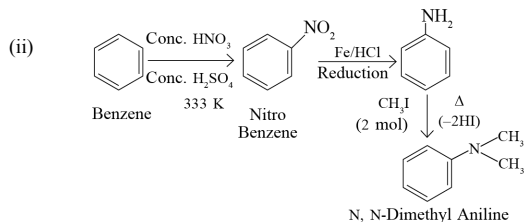


(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amide formed from benzamide is aromatic primary amine containing six carbon atoms.



17.

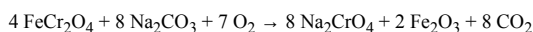




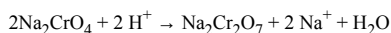
18.

➔ Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore (FeCr_2O_4) with sodium or potassium carbonate in free access of air.

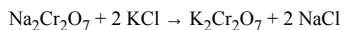
➔ The reaction with sodium carbonate occurs as follows



➔ The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ can be crystallised.

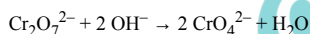
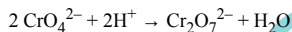


➔ Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.



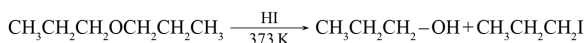
➔ Orange crystals of potassium dichromate crystallise out.

➔ The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution.



19.

➔ (i) 1-propoxypropane :

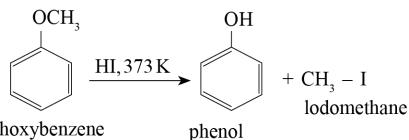


1-propoxypropane

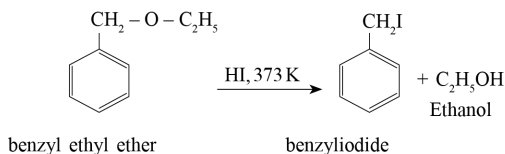
propan-1-ol

1-iodopropane

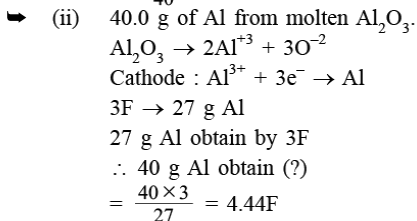
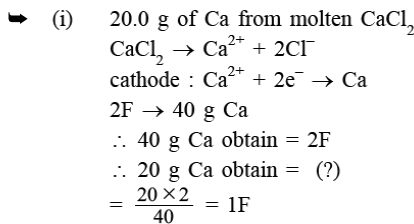
➔ (ii) methoxybenzene :



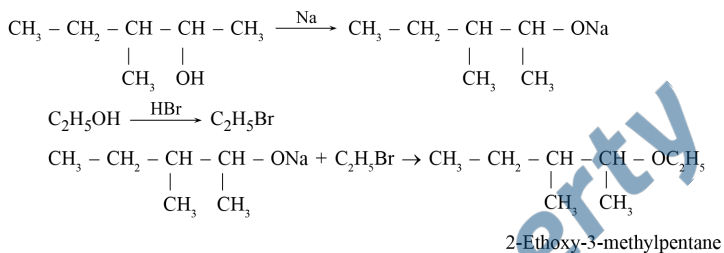
➔ (iii) benzyl ethyl ether :



20.



21.

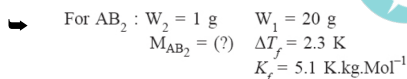


Section C

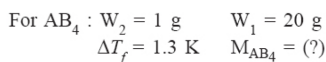
➤ Write the answer of the following questions : (Each carries 4 Mark)

22.

➔
$$M_2 = K_f \cdot \frac{W_2 \times 1000}{\Delta T_f \times W_1}$$



$$M_{\text{AB}_2} = \frac{5.1 \times 1 \times 1000}{2.3 \times 20} = 110.87 \text{ g.Mol}^{-1}$$



$$M_{\text{AB}_4} = \frac{5.1 \times 1 \times 1000}{1.3 \times 20}$$

$$= 196.15 \text{ g.Mol}^{-1}$$

$$\text{A} + 2\text{B} = 110.87$$

$$\text{A} + 4\text{B} = 196.15$$

$$\begin{array}{r} - \\ - \\ - \\ \hline - 2\text{B} = - 85.28 \end{array}$$

$$\therefore \text{B} = 42.64 \text{ u}$$

➔ putting value of B in eq.

$$\text{A} + 2\text{B} = 110.87$$

$$\text{A} + 2(42.64) = 110.87$$

$$\text{A} + 85.28 = 110.87$$

$$\text{A} = 25.59 \text{ u}$$

23.

➔ The cell constant is given by the equation :

$$\text{cell constant (G}^*) = \text{conductivity} \times \text{resistance}$$

$$= 1.29 \text{ S/m} \times 100 \text{ } \Omega = 129 \text{ m}^{-1} = 1.29 \text{ cm}^{-1}$$

$$\text{conductivity of } 0.02 \text{ mol L}^{-1} \text{ KCl solution} = \text{cell constant/resistance}$$

$$= \frac{G^*}{R} = \frac{129 \text{ m}^{-1}}{520 \text{ } \Omega} = 0.248 \text{ S m}^{-1}$$

$$\text{Concentration} = 0.02 \text{ mol L}^{-1}$$

$$= 1000 \times 0.02 \text{ mol m}^{-3}$$

$$= 20 \text{ mol m}^{-3}$$

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c}$$

$$= \frac{248 \times 10^{-3} \text{ S m}^{-1}}{20 \text{ mol m}^{-3}}$$

$$= 124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$\text{Alternatively, } \kappa = \frac{1.29 \text{ cm}^{-1}}{520 \text{ } \Omega} = 0.248 \times 10^{-2} \text{ S cm}^{-1}$$

$$\text{and } \Lambda_m = \kappa \times 1000 \text{ cm}^3 \text{ L}^{-1} \text{ molarity}^{-1}$$

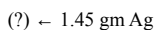
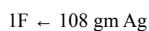
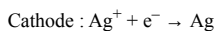
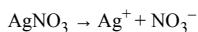
$$= \frac{0.248 \times 10^{-2} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.02 \text{ mol L}^{-1}}$$

$$= 124 \text{ S cm}^2 \text{ mol}^{-1}$$

24.

➔ $I = 1.5 \text{ A}$, $W_{\text{Ag}} = 1.45 \text{ gm}$,

$t = (?)$, $W_{\text{Cu}} = (?)$, $W_{\text{Ni}} = (?)$

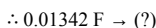
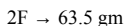


$$F = \frac{1.45}{108} = 0.01342 \text{ F}$$

➔ $\frac{I \times t}{96500} = F$

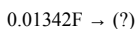
$$\therefore t = \frac{0.01342 \times 96500}{1.5} \text{ t} = 863.35 \text{ sec}$$

➔ For Copper : $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$



$$W_{\text{Cu}} = \frac{0.01342 \times 63.5}{2} = 0.426 \text{ gm copper}$$

➔ For Nickel : $\text{Ni}^{+2} + 2\text{e}^- \rightarrow \text{Ni}$



$$W_{\text{Ni}} = \frac{0.01342 \times 58.7}{2} = 0.3938 \text{ gm Nickel}$$












25.

➔ One of the most distinctive properties of transition metal complexes is their wide range of colours.

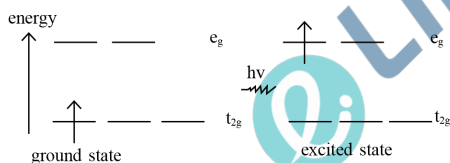
➔ This means that some of the visible spectrum is being removed from white light as it passes through the sample, so the light that emerges is no longer white.

- The colour of the complex is complementary to that which is absorbed.
- The complementary colour is the colour generated from the wavelength left over; if green light is absorbed by the complex, it appears red.

Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities

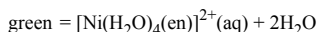
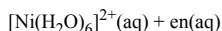
| Coordination entity | Wavelength of light absorbed (nm) | Colour of light absorbed | | Colour of coordination entity | |
|---|-----------------------------------|--------------------------|---|-------------------------------|--|
| $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ | 535 | Yellow |  | Violet |  |
| $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ | 500 | Blue Green |  | Red |  |
| $[\text{Co}(\text{NH}_3)_6]^{3+}$ | 475 | Blue |  | Yellow Orange |  |
| $[\text{Co}(\text{CN})_6]^{3-}$ | 310 | Ultraviolet | Not in visible region | Pale Yellow |  |
| $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ | 600 | Red |  | Blue |  |
| $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ | 498 | Blue Green |  | Violet |  |

- The colour in the coordination compounds can be readily explained in terms of the crystal field theory.
- Consider, for example, the complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, which is violet in colour.
- This is an octahedral complex where the single electron (Ti^{3+} is a $3d^1$ system) in the metal d orbital is in the t_{2g} level in the ground state of the complex.
- The next higher state available for the electron is the empty e_g level. If light corresponding to the energy of blue-green region is absorbed by the complex, it would excite the electron from t_{2g} level to the e_g level ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$).
- Consequently, the complex appears violet in colour.

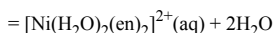
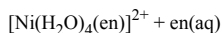


Transition of an electron in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

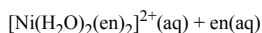
- The crystal field theory attributes the colour of the coordination compounds to d-d transition of the electron.
- It is important to note that in the absence of ligand, crystal field splitting does not occur and hence, the substance is colourless.
- For example, removal of water from $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ on heating renders it colourless.
- Similarly, anhydrous CuSO_4 is white, but $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue in colour.
- The influence of the ligand on the colour of a complex may be illustrated by considering the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex, which forms when nickel(II) chloride is dissolved in water.
- If the didentate ligand, ethane-1,2-diamine(en) is progressively added in the molar ratios en:Ni, 1:1, 2:1, 3:1, the following series of reactions and their associated colour changes occur :

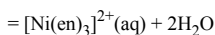


pale blue

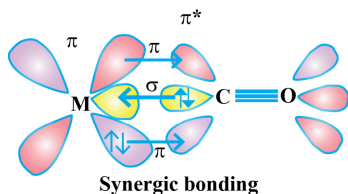
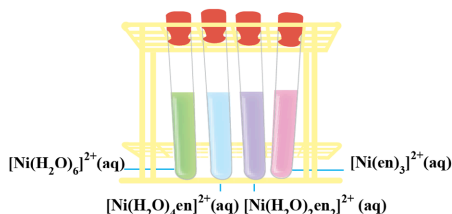


blue/purple





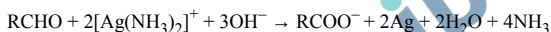
violet



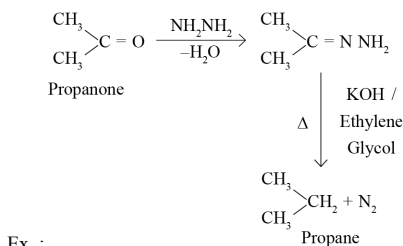
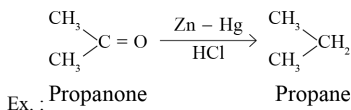
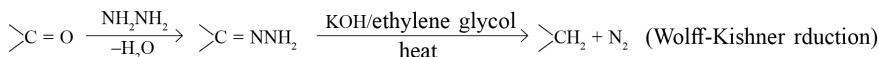
- The metal-carbon bond in metal carbonyls possess both σ and π character.
- The M-C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal.
- The M-C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide.
- The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

26.

- Tollens' test : On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.

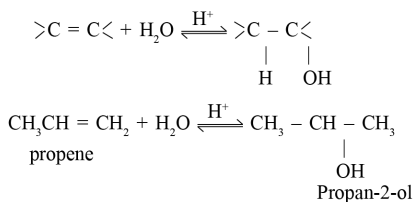


- Reduction to hydrocarbons: The carbonyl group of aldehydes and ketones is reduced to CH_2 group when treated with zinc amalgam and concentrated hydrochloric acid [Clemmensen reduction] or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (Wolff-Kishner reduction).



27.

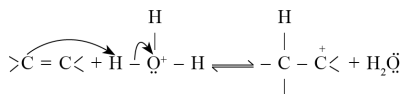
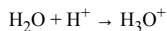
- By acid catalysed hydration : Alkenes react with water in the presence of acid as catalyst to form reaction takes place in accordance with Markovnikov's rule.



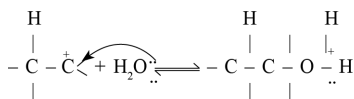
➔ Mechanism :

➔ The mechanism of the reaction involves the following three steps :

➔ Step - 1 : Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



➔ Step - 2 : Nucleophilic attack of water on carbocation.



➔ Step - 3 : Deprotonation to form an alcohol.

