

# LIBERTY PAPER SET

STD. 12 : Chemistry

Full Solution

Time : 3 Hours

ASSIGNMENT PAPER 3

Part A

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



Part B

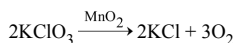
Section A

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

1.

"A catalyst is a substance which increase the rate of a reaction without itself undergoing any permanent chemical change."

For example,  $\text{MnO}_2$  catalyses the following reaction so as to increase its rate considerably.



The word catalyst should not be used when the added substance reduces the rate of reaction. The substance is then called inhibitor.

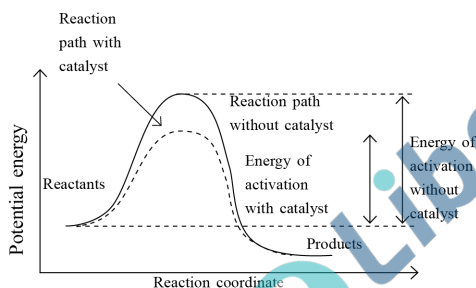
The action of catalyst can be explained by intermediate complex theory.

According to this theory, a catalyst participates in a chemical reaction by forming temporary bond with the reactants resulting in an intermediate complex.

It is believed that the catalyst provides an alternate path or reaction mechanism by reducing the activation energy between reactants and products hence lowering the potential energy barrier as shown in figure.

It is clear from Arrhenius equation that lower the value of activation energy faster will be the rate of reaction.

This has transitory existence and decomposes to yield products and the catalyst.



Characteristics of catalyst :

A small amount of catalyst can catalyses a large amount of reactants.

A catalyst does not alter Gibbs energy of a reaction.

It catalyses the spontaneous reaction but does not catalyze the non-spontaneous reactions.

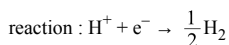
It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as backward reaction to the same extent so that the equilibrium state remains same but is reached earlier.

2.

pH = 10

$$-\log [\text{H}^+] = 10$$

$$\therefore [\text{H}^+] = 10^{-10}$$



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log \frac{1}{[\text{H}^+]}$$

$$= 0.0 - \frac{0.059}{1} \log \frac{1}{10^{-10}}$$

$$= -0.059 \log 10^{10}$$

$$= -0.59 \text{ V}$$

3.

➤ "The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte."

➤ Thus, if  $\lambda_{\text{Na}^+}^0$  and  $\lambda_{\text{Cl}^-}^0$  are limiting molar conductivity of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation :

$$\Lambda_{\text{m}(\text{NaCl})}^0 = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0$$

➤ In general, if an electrolyte on dissociation gives  $v_+$  cations and  $v_-$  anions then its limiting molar conductivity is given by :

$$E_{\text{m}}^0 = v_+ \lambda_+^0 + v_- \lambda_-^0$$

➤ Here,  $\lambda_+^0$  and  $\lambda_-^0$  are the limiting molar conductivities of the cation and anion respectively.

➤ If  $\lambda_{\text{m}^+}^0$  for  $\text{Na}^+ = 50.1 \text{ S cm}^2 \text{ mol}^{-1}$

$$\lambda_{\text{m}^-}^0 \text{ for } \text{Cl}^- = 76.3 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_{\text{m}(\text{NaCl})}^0 = \lambda_{\text{m}(\text{Na}^+)}^0 + \lambda_{\text{m}(\text{Cl}^-)}^0$$

$$= 50.1 + 76.3$$

$$= 126.4 \text{ S} \cdot \text{cm}^2 \text{ mol}^{-1}$$

4.

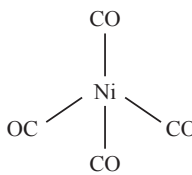
➤ "A complex of transition metal with carbon monoxide (Carbonyl ligand) are known as metal carbonyls."

➤ Example :  $[\text{Ni}(\text{CO})_4]$  Tetrahedral

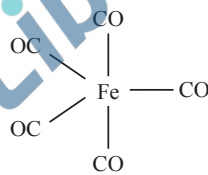
$[\text{Fe}(\text{CO})_5]$  Trigonal bipyramidal

$[\text{Cr}(\text{CO})_6]$  Octahedral

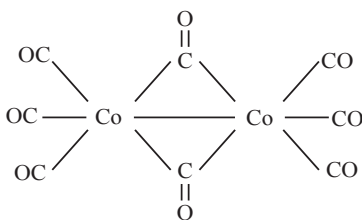
➤ Decacarbonyldimanganese(O) is made up of two square pyramidal  $\text{Mn}(\text{CO})_5$  units joined by a Mn – Mn bond. Octacarbonyldicobalt(O) has a Co – Co bond bridged by two CO groups.



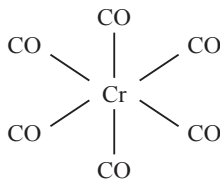
$[\text{Ni}(\text{CO})_4]$   
Tetrahedral



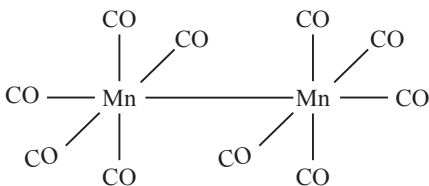
$[\text{Fe}(\text{CO})_5]$  Trigonal  
Bipyramidal



$[\text{Co}_2(\text{CO})_8]$

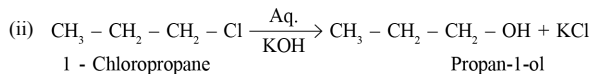
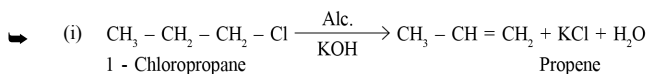


$[\text{Cr}(\text{CO})_6]$   
Octahedral



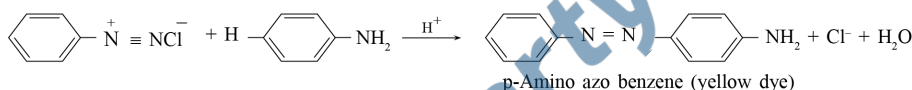
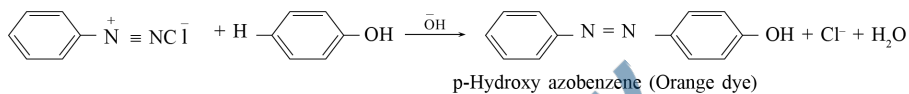
$[\text{Mn}_2(\text{CO})_{10}]$

5.



6.

- ➔ The azo products obtained have an extended conjugate system having both the aromatic rings joined through the  $-\text{N}=\text{N}-$  bond.
- ➔ These compounds are often coloured and are used as dyes.
- ➔ Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-Hydroxyazo benzene.
- ➔ This type of reaction is known as coupling reaction. Similarly, the reaction of diazonium salt with aniline yields p-Aminoazobenzene. This is an example of electrophilic substitution reaction.



7.

➔ Structural difference

DNA	RNA
(i) The sugar moiety in DNA molecules is $\beta$ -D-2-deoxyribose	(i) The sugar moiety in RNA molecules is $\beta$ -D-ribose.
(ii) DNA contains cytosine and thymine as a pyrimidine base where as guanine and adenine as a purine base.	(ii) RNA contains cytosine and uracil as a pyrimidine base where as guanine and adenine as a purine base.
(iii) The helical structure of DNA is double stranded.	(iii) The helical structure of RNA is single stranded.
(iv) DNA molecule is too large. It's molecular mass is $6 \times 10^6 - 16 \times 10^6$ u.	(iv) RNA molecule is quite smaller. It's molecular mass is 20000-40000 u.

➔ Functional differences

DNA	RNA
(i) DNA molecules are capable of self-replication.	(i) RNA molecules are not capable of self-replication.
(ii) DNA is responsible for the transmission of genetic characters.	(ii) RNA is responsible for the synthesis of protein compounds.

8.

- "Protein found in a biological system with a unique 3-D structure and biological activity is called a native protein."
- When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed.
- Due to this globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.
- During denaturation 2° and 3° structures are destroyed but 1° structure remains intact.
- The coagulation of egg white on boiling is a common example of denaturation. Another example is curdling of milk is caused due to the formation of lactic acid by the bacteria present in milk.

9.

➤  $TiCl_3$

- The oxidation number of Titanium in  $TiCl_3$  is +3, so, the electronic configuration is :  $3d^1 3d^1 3d^1$ . It has an unpaired electron which makes it paramagnetic, because paramagnetic property is passed by molecules with unpaired electrons.

➤  $TiCl_4$

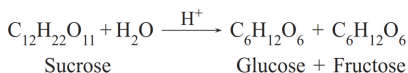
- The Oxidation amount of titanium is +4, which moves all the electrons from the electrons,  $TiCl_4$  is diamagnetic.
- $TiCl_4$  has induced fields that are in opposite directions to cancel each other out.
- Since, One unpaired electron is present in  $TiCl_3$ , it is paramagnetic, whereas in  $TiCl_4$ , all electrons are paired, so it becomes diamagnetic.  $TiCl_4$  has an induced magnetic field which is in opposite directions to each other thus canceling its effect.

10.

- Glucose occurs freely in nature as well as in the combined form. It is present in sweet fruits and honey. Ripe grapes also contain glucose in large amounts. It is prepared as follows :

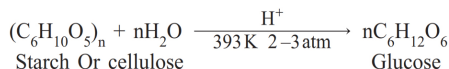
➤ 1. From sucrose (cane sugar) :

- If sucrose is boiled with dilute HCl or  $H_2SO_4$  in alcoholic solution, glucose and fructose are obtained in equal amounts.



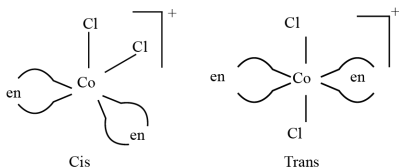
➤ 2. From starch :

- Commercial glucose is obtained by hydrolysis of starch by boiling it with dilute  $H_2SO_4$  at 393 K under pressure.

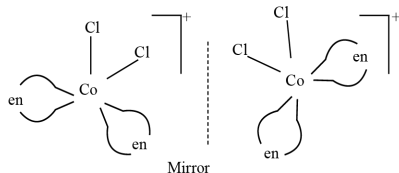


11.

➤ (i)  $[CoCl_2(en)_2]^+$  Geometrical isomerism



Optical isomerism : Since only cis isomer is optically active, it shows optical isomerism.



12.

“An alloy is a solid solution of two or more elements in a metallic matrix. It can either be a partial solid solution or a complete solid solution.”

Alloys are usually found to possess different physical properties than those of the component elements.

An important alloy of lanthanoids is Mischmetal. It contains lanthanoids (94-95%), iron (5%), and traces of S, C, Si, Ca, and Al.

Uses :

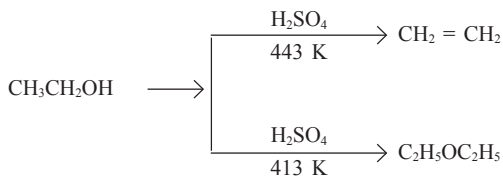
- Mischmetal is used in cigarettes and gas lighters.
- It is used in flame throwing tanks.
- It is used in tracer bullets and shells.

### Section B

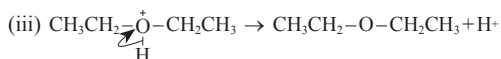
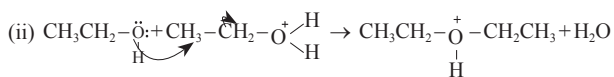
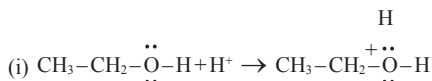
Write the answer of the following questions : (Each carries 3 Mark)

13.

Alcohols undergo dehydration in the presence of protic acids ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ). The formation of the reaction product, alkene or ether depends on the reaction conditions. For example, ethanol is dehydrated to ethene in the presence of sulphuric acid at 443 K. At 413 K, ethoxyethane is the main product.



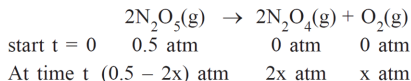
The formation of ether is a nucleophilic bimolecular reaction ( $\text{S}_{\text{N}}2$ ) involving the attack of alcohol molecule on a protonated alcohol, as indicated below :



Acidic dehydration of alcohols, to give an alkene is also associated with substitution reaction to give an ether.

14.

Let the pressure of  $N_2O_5(g)$  decrease by  $2x$  atm. As two moles of  $N_2O_5$  decompose to give two moles of  $N_2O_4(g)$  and one mole of  $O_2(g)$ , the pressure of  $N_2O_4(g)$  increases by  $2x$  atm and that of  $O_2(g)$  increase by  $x$  atm.



$$P_t = P_{N_2O_5} + P_{N_2O_4} + P_{O_2}$$

$$= (0.5 - 2x) + 2x + x = 0.5 + x$$

$$x = p_t - 0.5$$

$$P_{N_2O_5} = 0.5 - 2x$$

$$= 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$$

$$\text{At } t = 100 \text{ s; } p_t = 0.512 \text{ atm}$$

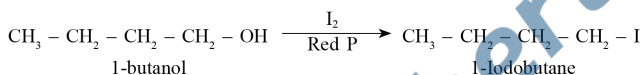
$$P_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476 \text{ atm}$$

$$k = \frac{2.303}{t} \log \frac{P_i}{P_A} = \frac{2.303}{100s} \log \frac{0.5}{0.476}$$

$$= \frac{2.303}{100s} \times 0.0216 = 4.98 \times 10^{-4} \text{ s}^{-1}$$

15.

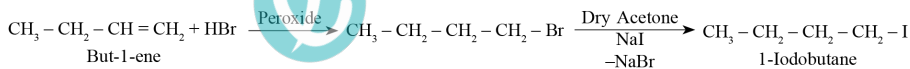
(i) 1-Iodobutane from 1-butanol



(ii) 1-Iodobutane from 1-chlorobutane



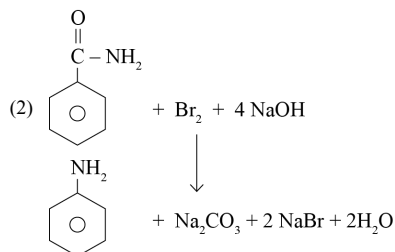
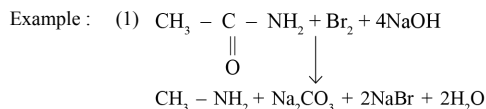
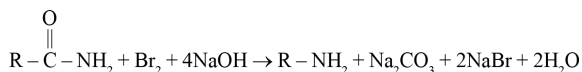
(iii) 1-Iodobutane from but-1-ene



16.

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom.

The amine so formed contains one carbon less than that present in the amide.

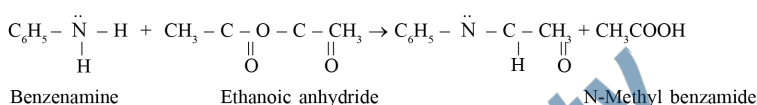
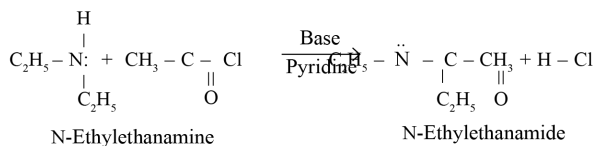
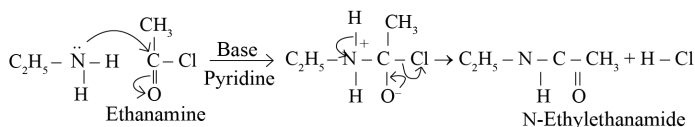


17.

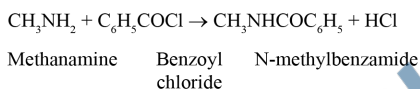
➤ "Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation."

➤ This reaction is the replacement of hydrogen atom of  $\text{-NH}_2$  and  $>\text{N-H}$  of group by the acyl group.

➤ The reaction is carried out in the presence of a base stronger than the amine like pyridine, which removes the formed HCl and shifts the equilibrium to the right hand side.



➤ Amines also react with benzoyl chloride ( $\text{C}_6\text{H}_5\text{COCl}$ ) this reaction is known as benzylation.



18.

➤ (i) Because transition elements have more unpaired electrons, they have stronger interatomic interactions and hence stronger bonding. so....

➤ (ii) In  $\text{Cr}^{2+}$  to  $\text{Cr}^{3+}$   $d^4 \rightarrow d^3$  occurs and in  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$   $d^6 \rightarrow d^5$  occurs. In aq. medium  $d^3$  is more stable than  $d^5$ .

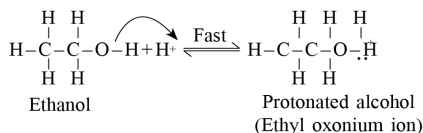
➤ (iii) In 2nd ionisation enthalpy of  $\text{Cu}^{2+}$  is removed from  $3d^{10}$  and in Zn from  $4s^1$ .  $3d^{10}$  is more stable configuration than  $4s^1$ .

19.

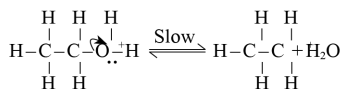
➤ The mechanism of dehydration of ethanol involves the following steps :

➤ Mechanism :

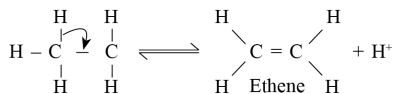
➤ Step 1 : Formation of protonated alcohol



➤ Step 2 : Formation of carbocation : It is the slowest step and hence, the rate determining step of the reaction.



➤ Step 3 : Formation of ethene by elimination of a proton.

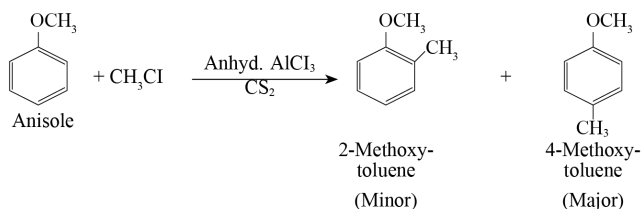


➤ The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

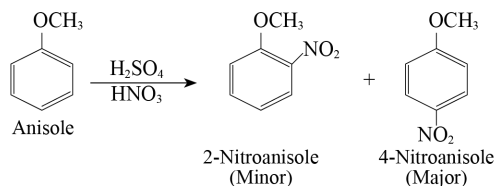


20.

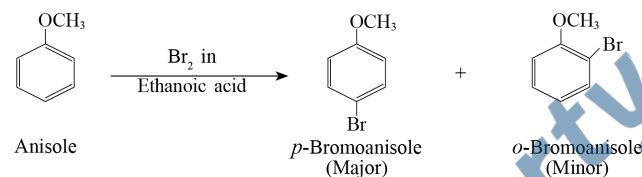
➔ (i) Friedel-Crafts reaction – alkylation of anisole :



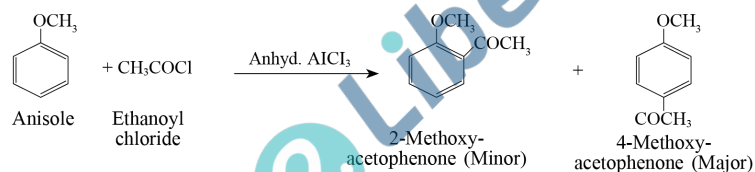
➔ (ii) Nitration of anisole :



➔ (iii) Bromination of anisole in ethanoic acid medium:



➔ (iv) Friedel-Crafts acetylation of anisole :



21.

➔ “When the concentration of solution approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol  $\Lambda_m^0$ ”

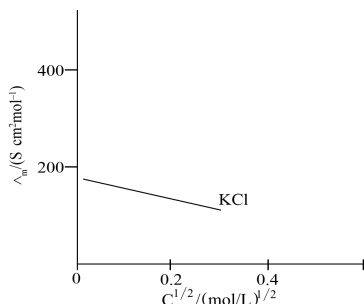
➔ Electrolytes which is completely ionize is known as strong electrolyte.

e.g. KCl, NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub> etc.

➔ For strong electrolytes,  $\Lambda_m$  increases slowly with dilution and can be represented by the equation :

$$\Lambda_m = \Lambda_m^0 - Ac^{\frac{1}{2}}$$

➔ It can be seen that if we plot  $\Lambda_m$  against  $c^{\frac{1}{2}}$ , we obtain a straight line with intercept equal to  $\Lambda_m^0$  and slope equal to  $-A$ .

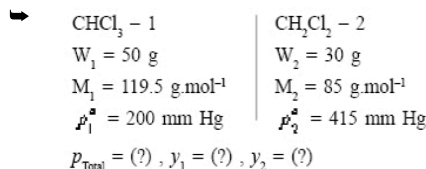


- The value of the constant A for a given solvent and temperature depends on the type of electrolyte.
- Thus, NaCl, CaCl<sub>2</sub>, MgSO<sub>4</sub> are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for 'A'

### Section C

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

22.



(i) Moles of CHCl<sub>3</sub>(n<sub>1</sub>) =  $\frac{W_1}{M_1} = \frac{50}{119.5} = 0.418 \text{ mol}$

Moles of CH<sub>2</sub>Cl<sub>2</sub>(n<sub>2</sub>) =  $\frac{W_2}{M_2} = \frac{30}{85} = 0.35 \text{ mol}$

Total Moles = 0.418 + 0.35 = 0.768 mol

➤ Mole-Fraction of CHCl<sub>3</sub>(X<sub>1</sub>) =  $\frac{n_1}{\text{Total Moles}}$   
 $= \frac{0.418}{0.768} = 0.544$

➤ Mole-Fraction of CH<sub>2</sub>Cl<sub>2</sub> (X<sub>2</sub>) :

$$X_1 + X_2 = 1$$

$$\therefore X_2 = 1 - X_1$$

$$= 1 - 0.544$$

$$\therefore X_2 = 0.456$$

$$P_{\text{Total}} = P_1^0 + X_2(P_2^0 - P_1^0)$$

$$= 200 + 0.456(415 - 200)$$

$$= 200 + 0.456(215)$$

$$= 200 + 98.04$$

$$P_{\text{Total}} = 298.04 \text{ mm Hg}$$

<p>(ii) <math>P_1 = y_1 \cdot P_{\text{Total}}</math>  <math>\therefore y_1 = \frac{P_1^0 \cdot X_1}{P_{\text{Total}}}</math>  <math>\therefore y_1 = \frac{(200) \cdot (0.544)}{298.04}</math>  <math>\therefore y_1 = \frac{108.8}{298.04}</math>  <math>\therefore y_1 = 0.365</math></p>	<p><math>P_2 = y_2 \cdot P_{\text{Total}}</math>  <math>\therefore y_2 = \frac{P_2^0 \cdot X_2}{P_{\text{Total}}}</math>  <math>\therefore y_2 = \frac{(415) \cdot (0.456)}{298.04}</math>  <math>\therefore y_2 = \frac{189.24}{298.04}</math>  <math>\therefore y_2 = 0.634</math></p>
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23.

$$\rightarrow W_2 = 10 \text{ g}, W_1 = 250 \text{ g}$$

$$M_2 = 4(\text{C}) + 7(\text{H}) + \text{Cl} + 2(\text{O}) \quad K_a = 1.4 \times 10^{-3}$$

$$= 4(12) + 7(1) + 35.5 + 2(16)$$

$$= 122.5 \text{ g.Mol}^{-1} \quad K_f = 1.86 \text{ K.kg.Mol}^{-1}$$

$$\Delta T_f = (?)$$

(Molality)

$$C = \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{10 \times 1000}{122.5 \times 250}$$

$$= 0.3265 \text{ Mol/L}$$

$$K_a = \frac{\alpha^2 \cdot C}{1 - \alpha}$$

$$1.4 \times 10^{-3} = \alpha^2 \cdot (0.3265)$$

$$4.287 \times 10^{-3} = \alpha^2$$

$$0.4287 \times 10^{-2} = \alpha^2$$

$$\alpha = 0.6547 \times 10^{-1}$$

$$\alpha = 0.06547$$

$$\alpha = \frac{i-1}{n-1}$$

$$0.06547 = \frac{i-1}{2-1}$$

$$i = 1.06547$$

→ So, depression in the freezing point is

$$\Delta T_f = i \cdot K_f \cdot m$$

$$= (1.06547)(1.86)(0.3265)$$

$$= 0.647 \text{ K}$$

24.

$$\rightarrow \Lambda_m^0(\text{HAc}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{Ac}^-}^0 = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 + \lambda_{\text{Ac}^-}^0 + \lambda_{\text{Na}^+}^0 - \lambda_{\text{Cl}^-}^0 - \lambda_{\text{Na}^+}^0$$

$$= \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{NaAc}) - \Lambda_m^0(\text{NaCl})$$

$$= (425.9 + 91.0 - 126.4) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\rightarrow C = 0.00241 \text{ M}$$

$$k = 7.896 \times 10^{-5} \text{ S cm}^{-1}$$

calculation of molar conductivity ( $\Lambda_m$ )

$$\Lambda_m = \frac{k \text{ S.cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}}{c \text{ mol L}}$$

$$= \frac{7.896 \times 10^{-5} \times 1000}{0.00241}$$

$$= 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

Calculation of dissociation constant

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{32.76}{390.5} \quad \alpha = 8.4 \times 10^{-2}$$

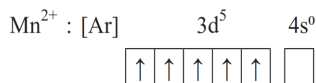
$$k_a = \frac{\alpha^2 \cdot c}{1 - \alpha} = \frac{(8.4 \times 10^{-2})^2 \times 0.00241}{1 - 0.084}$$

$$k_a = 1.85 \times 10^{-5} \text{ mol L}^{-1}$$

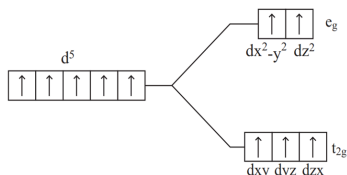
25.

➤ Mn is in the +2 oxidation state in  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

➤ Electronic configuration of  $\text{Mn}^{2+}$



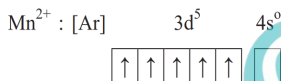
➤ The Crystal field is octahedral. Water is weak field ligand. ( $\Delta_0 < p$ )



➤ Therefore, the arrangement of the electrons in  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  is  $t_{2g}^3 e_g^2$ .

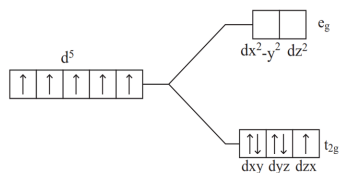
➤ Mn is in the +2 oxidation state in  $[\text{Mn}(\text{CN})_6]^{4-}$

➤ Electronic configuration of  $\text{Mn}^{2+}$



➤ The Crystal field is octahedral. Cyanide is a strong field ligand.

➤ ( $\Delta^0 > P$ )



➤ Therefore, the arrangement of the electrons in  $[\text{Mn}(\text{CN})_6]^{4-}$  is  $t_{2g}^5 e_g^0$ .

➤ Hence, hexaquo manganese (II) ion has five unpaired electrons, while hexacyano ion has only one unpaired electron.

26.

➤ The compound having molecular formula  $\text{C}_9\text{H}_{10}\text{O}$  forms 2, 4-DNP derivative and reduces Tollen's reagent.

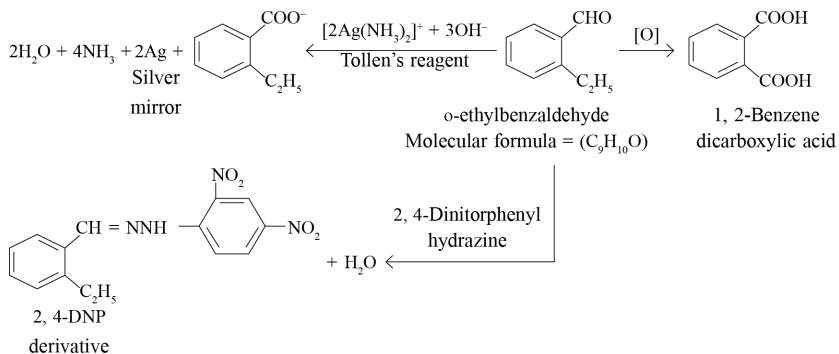
➤ Therefore, the given compound must be an aldehyde.

➤ Again, the compound gives 1, 2 benzene dicarboxylic acids and undergoes Cannizzaro reaction followed by oxidation.

➤ Therefore, the  $-\text{CHO}$  group is directly attached to a benzene ring and this benzaldehyde is ortho-substituted.

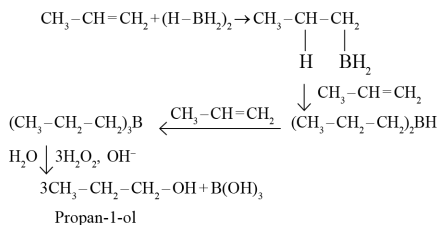
➤ Hence, the compound is found to be 2-ethylbenzaldehyde.

➤ The given reactions can be explained by the following equations.



27.

➤ By hydroboration-oxidation : Diborane ( $\text{BH}_3$ )<sub>2</sub>, reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



➤ The addition of borane to the double bond takes place in such a manner that the boron atom gets attached to the  $\text{sp}^2$  carbon carrying greater number of hydrogen atoms. The alcohol so formed looks as if it a way opposite to the Markovnikov's rule. In this reaction, alcohol is obtained in excellent yield.

