

# SAMPLE QUESTION PAPER

## BLUE PRINT

Time Allowed : 3 hours

Maximum Marks : 70

S. No.	Chapter	Passage based/ MCQs/A & R (1 mark)	SA-I (2 marks)	SA-II (3 marks)	LA (5 marks)	Total
1.	The Solid State	1(1)	–	1(3)	–	12(23)
2.	Solutions	1(1)	1(2)	–	1(5)	
3.	Electrochemistry	1(1)	–	1(3)	–	
4.	Chemical Kinetics	2(2)	1(2)	–	–	
5.	Surface Chemistry	1(1)	1(2)	–	–	
6.	The <i>p</i> -Block Elements	2(2)	1(2)	–	–	8(19)
7.	The <i>d</i> - and <i>f</i> -Block Elements	1(1)	1(2)	–	1(5)	
8.	Coordination Compounds	1(4)	–	1(3)	–	
9.	Haloalkanes and Haloarenes	1(4)	1(2)	–	–	13(28)
10.	Alcohols, Phenols and Ethers	1(1)	–	1(3)	–	
11.	Aldehydes, Ketones and Carboxylic Acids	2(2)	1(2)	–	1(5)	
12.	Amines	1(1)	1(2)	1(3)	–	
13.	Biomolecules	1(1)	1(2)	–	–	
	<b>Total</b>	<b>16(22)</b>	<b>9(18)</b>	<b>5(15)</b>	<b>3(15)</b>	<b>33(70)</b>



## CHEMISTRY

Time allowed : 3 hours

Maximum marks : 70

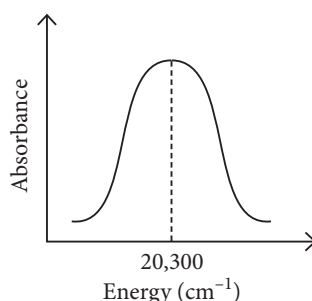
**General Instructions : Read the following instructions carefully.**

- (a) There are 33 questions in this question paper. All questions are compulsory.
- (b) Section A : Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
- (c) Section B : Q. No. 17 to 25 are short answer questions and carry 2 marks each.
- (d) Section C : Q. No. 26 to 30 are short answer questions and carry 3 marks each.
- (e) Section D : Q. No. 31 to 33 are long answer questions carrying 5 marks each.
- (f) There is no overall choice. However, internal choices have been provided.
- (g) Use of calculators and log tables is not permitted.

## SECTION - A (OBJECTIVE TYPE)

## 1. Read the passage given below and answer the following questions:

The extent to which the set of  $d$ -orbitals is split in the electrostatic field produced by the ligands depends upon several factors. Two of the most important factors are the nature of the ligands and the nature of the metal ion. In order to see this effect, consider the complex ion  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ . The  $\text{Ti}^{3+}$  ion has a single electron in the  $3d$ -orbital, and we refer to it as  $d^1$  ion. In the octahedral field generated by six  $\text{H}_2\text{O}$  molecules, the single electron will reside in one of the three degenerate  $t_{2g}$  orbitals. Under spectral excitation, the electron is promoted to an  $e_g$  orbital giving rise to an absorption spectrum consisting of a single peak that can be represented as shown :



The maximum absorption in the spectrum for  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  occurs at  $20,300 \text{ cm}^{-1}$  which is equal to  $243 \text{ kJ mol}^{-1}$ . This gives the value of  $\Delta_o$  directly, but only in case of simple  $d^1$  ions. Other complexes containing the  $\text{Ti}^{3+}$  ion (e.g.,  $[\text{Ti}(\text{NH}_3)_6]^{3+}$ ,  $[\text{TiF}_6]^{3-}$ , etc.) could also be prepared and spectra obtained for these complexes. If this was done, it would be observed that the absorption maximum occurs at a different energy for each complex. Because the maximum corresponds to the splitting of  $d$ -orbitals, the ligands could be ranked in terms of their ability to cause the splitting of orbital energies. Such a ranking is known as the spectrochemical series and for several common ligands the following order of decreasing energy is observed,  $\text{CN}^- > \text{NO}_2^- > \text{en} > \text{NH}_3 > \text{H}_2\text{O} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^-$ . In general, the splitting in tetrahedral fields is only about half as large as that in octahedral fields.



The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) Which of the following ligands is a strong field ligand?  
 (a) CO (b)  $\text{H}_2\text{O}$  (c)  $\text{Br}^-$  (d)  $\text{OH}^-$
- (ii) Which of the following ligands has lowest  $\Delta_o$  value?  
 (a)  $\text{CN}^-$  (b) CO (c)  $\text{F}^-$  (d)  $\text{NH}_3$

OR

The visible spectra of salts of the following complexes are measured in aqueous solution for which complex would the spectrum contain absorption with highest  $E_{\text{max}}$  values?

- (a)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  (b)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  (c)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (d)  $[\text{Co}(\text{CN})_6]^{3-}$
- (iii) Which of the following statements is incorrect for complex  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ?  
 (a)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is violet in colour.  
 (b)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is an octahedral complex.  
 (c) Excitation of electron in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  occurs as,  $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$   
 (d) The colour of the complex  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  arises due to  $d-d$  and  $f-f$  transition of the electron.
- (iv) Which of the following order is correct in spectrochemical series of ligands?  
 (a)  $\text{Cl}^- < \text{F}^- < \text{NO}_2^- < \text{CN}^-$  (b)  $\text{CN}^- < \text{Cl}^- > \text{NO}_2^- < \text{F}^-$   
 (c)  $\text{F}^- > \text{Cl}^- > \text{NO}_2^- < \text{CN}^-$  (d)  $\text{F}^- < \text{Cl}^- < \text{NO}_2^- < \text{CN}^-$

2. Read the passage given below and answer the following questions :

A nucleophilic substitution reaction that occurs by an  $\text{S}_{\text{N}}1$  mechanism proceeds in two steps. In the first step, the bond between the carbon atom and the leaving group breaks to produce a carbocation and most commonly, an anionic leaving group. In the second step, the carbocation reacts with the nucleophile to form the substitution product. The formation of a carbocation is the slow or rate determining step.

The rate of  $\text{S}_{\text{N}}1$  reactions decrease in the order  $3^\circ > 2^\circ > 1^\circ$ , which is the reverse order observed in  $\text{S}_{\text{N}}2$  reactions. In contrast to  $\text{S}_{\text{N}}2$  reactions at stereogenic centers, which occur with inversion of configuration, an  $\text{S}_{\text{N}}1$  reaction gives a racemic mixture of enantiomers that has no optical rotation.

In these questions (Q.No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices :

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.  
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.  
 (c) Assertion is correct statement but reason is wrong statement.  
 (d) Assertion is wrong statement but reason is correct statement.
- (i) **Assertion :** Rate of ethanolysis of  $1^\circ$  halide by  $\text{S}_{\text{N}}2$  mechanism is fast.  
**Reason :** Carbocation is stabilised by resonance.
- (ii) **Assertion :**  $\text{S}_{\text{N}}2$  reactions do not proceed with retention of configuration.  
**Reason :**  $\text{S}_{\text{N}}2$  reactions proceed in single step.

OR

**Assertion :** In an optically active alkyl halide nucleophilic substitution reaction gives a mixture of enantiomers.

**Reason :** Reaction occurs by  $\text{S}_{\text{N}}1$  mechanism.

- (iii) **Assertion :**  $1^\circ$  allylic halides shows higher reactivity in  $\text{S}_{\text{N}}1$  reactions than other  $1^\circ$  alkyl halides.  
**Reason :** Intermediate carbocation is stabilised by resonance.
- (iv) **Assertion :**  $\text{S}_{\text{N}}1$  reaction is carried out in the presence of polar protic solvent.  
**Reason :** A polar protic solvent decreases the stability of carbocation due to solvation.



Following questions (Q. No. 3 - 11) are multiple choice questions carrying 1 mark each :

3. An organic compound of molecular formula  $C_3H_6O$  did not give a silver mirror with Tollens' reagent but give an oxime with hydroxylamine. It may be  
 (a)  $CH_2=CH-CH_2-OH$  (b)  $CH_3COCH_3$   
 (c)  $CH_3CH_2CHO$  (d)  $CH_2=CH-OCH_3$
4. Reactivity of transition elements decreases almost regularly from Sc to Cu because of  
 (a) lanthanoid contraction (b) regular increase in ionisation enthalpy  
 (c) regular decrease in ionisation enthalpy (d) increase in number of oxidation states.

OR

Which pair of compounds shows similar colour?

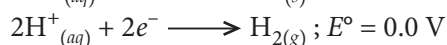
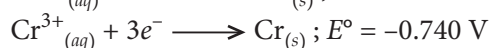
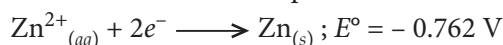
- (a)  $Sm^{3+}$ ,  $Dy^{3+}$  (b)  $La^{3+}$ ,  $Pr^{3+}$  (c)  $Pr^{3+}$ ,  $Pm^{3+}$  (d)  $Sm^{3+}$ ,  $Eu^{3+}$
5. The decreasing order of osmotic pressures of 10 g glucose ( $P_1$ ), 10 g urea ( $P_2$ ) and 10 g sucrose ( $P_3$ ) at 273 K when dissolved in 250 mL of water separately is  
 (a)  $P_1 > P_2 > P_3$  (b)  $P_2 > P_3 > P_1$  (c)  $P_2 > P_1 > P_3$  (d)  $P_3 > P_2 > P_1$
6. The ionic radii of  $Rb^+$  and  $I^-$  are 1.46 Å and 2.16 Å respectively. The most possible type of structure exhibited by it, is  
 (a) CsCl type (b) NaCl type (c) ZnS type (d)  $CaF_2$  type.

OR

In a compound, atoms of element Y form *ccp* lattice and those of element X occupy  $2/3^{rd}$  of tetrahedral voids. The formula of the compound will be

- (a)  $X_3Y_4$  (b)  $X_4Y_3$  (c)  $X_2Y_3$  (d)  $X_2Y$
7. In the synthesis of ammonia from nitrogen and hydrogen gases, if  $6 \times 10^{-2}$  mole of hydrogen disappears in 10 minutes, the number of moles of ammonia formed in 0.3 minutes is  
 (a)  $1.8 \times 10^{-2}$  (b)  $1.2 \times 10^{-3}$  (c)  $4 \times 10^{-2}$  (d)  $3.6 \times 10^{-2}$
8. Hydrogen fluoride is liquid unlike other hydrogen halides because  
 (a) fluorine atom is smaller in size (b) HF is the weakest acid  
 (c) fluorine is highly reactive (d) HF molecules form intermolecular H-bonds.

9. The standard reduction potential at 298 K for the following half cell reactions are given below :



Which is the strongest reducing agent?

- (a)  $Zn_{(s)}$  (b)  $Cr_{(s)}$  (c)  $H_{2(g)}$  (d)  $Fe^{2+}_{(aq)}$

OR

A 0.05 M KOH solution offered a resistance of 31.6 ohm in a conductivity cell of cell constant  $0.367 \text{ cm}^{-1}$  at 298 K. What is the equivalent conductance of KOH solution?

- (a)  $0.2322 \text{ S cm}^2 \text{ eq}^{-1}$  (b)  $2.322 \text{ S cm}^2 \text{ eq}^{-1}$   
 (c)  $23.22 \text{ S cm}^2 \text{ eq}^{-1}$  (d)  $232.28 \text{ S cm}^2 \text{ eq}^{-1}$



10. On oxidation with a mild oxidising agent like  $\text{Br}_2/\text{H}_2\text{O}$ , the glucose is oxidised to  
 (a) saccharic acid (b) glucaric acid  
 (c) gluconic acid (d) valeric acid.
11. Which of the following is not a characteristic of alcohol?  
 (a) The  $-\text{OH}$  group in alcohols is involved in intermolecular hydrogen bonding.  
 (b) Their boiling points rise fairly uniformly with rising molecular weight.  
 (c) Lower members are insoluble in water and organic solvents but the solubility regularly increases with molecular mass.  
 (d) Lower members have a pleasant smell and, higher members are colourless and tasteless.

OR

1-Propanol in the presence of  $\text{HBF}_4$  reacts with diazomethane to give

- (a) di-*n*-propyl ether (b) dimethyl ether  
 (c) 1-methoxypropane (d) 2-methoxypropane.

In the following questions (Q. No. 12-16), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices :

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.  
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.  
 (c) Assertion is correct statement but reason is wrong statement.  
 (d) Assertion is wrong statement but reason is correct statement.
12. **Assertion :** Carboxylic acids do not undergo Friedel — Crafts reaction.  
**Reason :** Carboxyl group is *meta*-directing group.
13. **Assertion :** Fluorine combines with sulphur to form  $\text{SF}_6$  but no other halogen forms hexahalide with sulphur.  
**Reason :** The reactivity of halogens increases as the atomic number increases.
14. **Assertion :** The reaction,  

$$\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$$

Cane sugar
Glucose
Fructose

 is a first order reaction.  
**Reason :** Change in concentration of  $\text{H}_2\text{O}$  is negligible.
15. **Assertion :** Hofmann degradation of benzamide gives aniline.  
**Reason :** Hofmann bromamide degradation reaction can be used for descending amine series.
16. **Assertion :** In physical adsorption, enthalpy of adsorption is very low.  
**Reason :** In physical adsorption, attraction between gas molecules and solid surface is due to weak van der Waals' forces.

OR

**Assertion :** In the coagulation of a negative sol the flocculating power is in the order :  $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$ .

**Reason :** Greater the valence of the flocculating ion added, greater is its power to cause precipitation.

## SECTION - B

The following questions Q.No. 17-25 are short answer type and carry 2 marks each.

17. The freezing point of pure nitrobenzene is 278.8 K. When 2.5 g of unknown substance is dissolved in 100 g of nitrobenzene, the freezing point of solution is found to be 276.8 K. If the freezing point depression constant for nitrobenzene is  $8 \text{ K kg mol}^{-1}$ , what is the molar mass of unknown substance?



OR

A solution of glucose ( $C_6H_{12}O_6$ ) in water is labelled as 10% by weight. What would be the molality of the solution? (Molar mass of glucose =  $180 \text{ g mol}^{-1}$ )

18. (a) Amino acids show amphoteric behaviour. Why?  
(b) Write one difference between  $\alpha$ -helix and  $\beta$ -pleated structures of proteins.
19. Which halogen will produce  $O_2$  and  $O_3$  as passed through water and why?

OR

Account for the following :

- (i)  $H_2S$  has lower boiling point than  $H_2O$ .  
(ii) Reducing character decreases from  $SO_2$  to  $TeO_2$ .
20. Account for the following :
- (i) The  $pK_b$  of aniline is more than that of methylamine.  
(ii) Gabriel phthalimide synthesis is the preferred method for synthesizing primary amines.
21. (i) In the transition series, starting from lanthanum ( $_{57}La$ ), the next element hafnium ( $_{72}Hf$ ) has an atomic number of 72. Why do we observe this jump in atomic number?  
(ii)  $Ce(IV)$  is a good analytical reagent. Why?
22. Explain why :
- (i) Alkyl halides, though polar, are immiscible with water.  
(ii) Tertiary halides are least reactive towards  $S_N2$  reactions.
23. The decomposition of  $Cl_2O_7$  at 400 K in the gas phase to  $Cl_2$  and  $O_2$  is a first order reaction.  
(i) After 55 seconds at 400 K the pressure of  $Cl_2O_7$  falls from 0.062 to 0.044 atm. Calculate the rate constant.  
(ii) Calculate the pressure of  $Cl_2O_7$  after 100 seconds of decomposition at this temperature.
24. Two moles of organic compound 'A' on treatment with a strong base gives two compounds 'B' and 'C'. Compound 'B' on dehydrogenation with Cu gives 'A' while acidification of 'C' yields carboxylic acid 'D' with molecular formula of  $CH_2O_2$ . Identify the compounds A, B, C and D and write all chemical reactions involved.

OR

- (a) Give reason why aldehydes are more reactive than ketones towards nucleophilic reagents.  
(b) Why pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compounds ?
25. Explain the following:
- (i) Physisorption is multi-layered, while chemisorption is mono-layered.  
(ii) True solution does not show Tyndall effect.

## SECTION - C

Q.No. 26-30 are short answer type II carrying 3 marks each :

26. (a) Propanamine and *N,N*-dimethylmethanamine contain the same number of carbon atoms, even though propanamine has higher boiling point than *N,N*-dimethylmethanamine. Why?  
(b) Illustrate the following reactions giving suitable example in each case :  
(i) Ammonolysis  
(ii) Acetylation of amines



27. (a) Why phenol undergoes electrophilic substitution more easily than benzene?  
 (b) Give a separate chemical test to distinguish between the following pairs of compounds :  
 (i) Ethanol and phenol (ii) 2-Pentanol and 3-pentanol

OR

Account for the following :

- (i) Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method.  
 (ii) Phenylmethyl ether reacts with HI to give phenol and methyl iodide and not iodobenzene and methyl alcohol. Why?  
 (iii) Boiling point of ethanol is higher in comparison to methoxymethane. Give reasons.
- 28 (i) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a *fcc* structure. (Atomic mass of Al = 27 g mol<sup>-1</sup>)  
 (ii) If a compound forms *hcp* structure then what is the total number of voids in 0.5 mol of it? Also find out how many of these are tetrahedral voids.
29. Out of [CoF<sub>6</sub>]<sup>3-</sup> and [Co(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup>, which one complex is  
 (i) diamagnetic (ii) more stable  
 (iii) outer orbital complex and (iv) low spin complex ?  
 (Atomic no. of Co = 27)
30. (i) Calculate the equilibrium constant for the reaction,  
 $\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$   
 (Given  $E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.44 \text{ V}$  and  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 \text{ V}$ )  
 (ii) Calculate the emf of half cells given below :  
 (a) Pt, H<sub>2</sub>|HCl  
 2 atm, H<sup>+</sup> = 0.02 ;  $E^\circ_{\text{OP}} = 0 \text{ V}$   
 (b) Pt, Cl<sub>2</sub>|HCl  
 10 atm, Cl<sup>-</sup> = 0.1 ;  $E^\circ_{\text{OP}} = -1.36 \text{ V}$

OR

- (i) Calculate the molar conductivity for NH<sub>4</sub>OH. Given that molar conductivity for Ba(OH)<sub>2</sub>, BaCl<sub>2</sub> and NH<sub>4</sub>Cl are 523.28, 280.0 and 129.8 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> respectively.  
 (ii) The conductivity of a 0.12 N solution of an electrolyte of the type A<sup>+</sup>B<sup>-</sup> is 0.024 S cm<sup>-1</sup>. Calculate its  
 (a) equivalent conductivity (b) molar conductivity.

## SECTION - D

Question No. 31 to 33 are long answer type carrying 5 Marks each.

31. (a) Name the oxo-metal anion of one of the transition metals in which the metal exhibits the oxidation state equal to the group number.  
 (b) Account for the following :  
 (i) Scandium (Z = 21) is regarded as a transition element but zinc (Z = 30) is not.  
 (ii)  $E^\circ(M^{2+}/M)$  value for copper is +ve.  
 (c) Why do transition elements show variable oxidation states? In 3d series (Sc to Zn), which element shows the maximum number of oxidation states and why?

OR

How would you account for the following :

- (i) Among VO<sub>2</sub><sup>+</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and MnO<sub>4</sub><sup>-</sup>, MnO<sub>4</sub><sup>-</sup> is the strongest oxidising agent.  
 (ii) The third ionization enthalpy of manganese (Z = 25) is exceptionally high.





- (iii)  $\text{Cr}^{2+}$  is a stronger reducing agent than  $\text{Fe}^{2+}$ .  
 (iv)  $\text{Mn}^{2+}$  compounds are more stable than  $\text{Fe}^{2+}$  compounds towards oxidation to their +3 state.  
 (v)  $\text{Cr}^{2+}$  is reducing agent and  $\text{Mn}^{3+}$  oxidising agent while both have  $d^4$  configuration.
32. (a) An organic compound (A) which has characteristic odour, on treatment with NaOH forms two compounds (B) and (C). Compound (B) has the molecular formula  $\text{C}_7\text{H}_8\text{O}$  which on oxidation with  $\text{CrO}_3$  gives back compound (A). Compound (C) is the sodium salt of the acid. Compound (C) when heated with soda lime yields an aromatic hydrocarbon (D). Deduce the structures of (A), (B), (C) and (D). Write chemical equations for all reactions taking place.
- (b) Account for the following :
- Aromatic carboxylic acids do not undergo Friedel–Crafts reaction.
  - $\text{p}K_a$  value of 4-nitrobenzoic acid is lower than that of benzoic acid.

OR

- (a) Write the structures of compounds A, B and C in each of the following reactions :
- (i)  $\text{C}_6\text{H}_5\text{Br} \xrightarrow{\text{Mg/dry ether}} \text{A} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) CO}_2(\text{g})} \text{B} \xrightarrow{\text{PCl}_5} \text{C}$
- (ii)  $\text{CH}_3\text{CN} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) SnCl}_2/\text{HCl}} \text{A} \xrightarrow{\text{dil. NaOH}} \text{B} \xrightarrow{\Delta} \text{C}$
- (b) A ketone A ( $\text{C}_4\text{H}_8\text{O}$ ), which undergoes a haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives a compound C which forms monozonide D. D on hydrolysis in presence of zinc dust gives only acetaldehyde E. Identify A, B, C, D and E. Write the reactions involved.
33. (a) Boiling point of water at 750 mm Hg is  $99.63^\circ\text{C}$ . How much sucrose is to be added to 500 g of water so that it boils at  $100^\circ\text{C}$ ? (Molal elevation constant for water is  $0.52 \text{ K kg mol}^{-1}$ .)
- (b) The freezing point of a solution containing  $50 \text{ cm}^3$  of ethylene glycol in 50 g water is found to be  $-34^\circ\text{C}$ . Assuming ideal behaviour, calculate the density of ethylene glycol. ( $K_f$  for  $\text{H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$ )

OR

- (a) Define the term, 'osmosis'. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions?
- (b) (i) What happens when red blood corpuscles (RBC) are placed in
- 0.5% NaCl solution
  - 1% NaCl solution?
- (ii) Heptane and octane form ideal solution. At 373 K, the vapour pressure of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35.0 g of octane?







**12. (b) :** Carboxylic acids do not undergo Friedel-Crafts reaction because the  $-\text{COOH}$  group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.

**13. (c) :** The reactivity of halogens decreases as the atomic number increases.

**14. (a) :** Such reactions are called pseudo first order reactions.

**15. (a) :** In this reaction the amine so formed contains one carbon less than that present in the amide.

**16. (a) :** Physical adsorption is an exothermic process but its enthalpy of adsorption is quite low ( $20 - 40 \text{ kJ mol}^{-1}$ ). This is because the attraction between gas molecules and solid surface is only due to weak van der Waals' forces.

OR

(a) This is known as Hardy-Schulze rule.

**17.** Given,  $w_1 = 2.5 \text{ g}$

$\Delta T_f = 278.8 - 276.8 = 2 \text{ K}$

$w_2 = 100 \text{ g}$ ,  $K_f = 8 \text{ K kg mol}^{-1}$

$$\Rightarrow \Delta T_f = K_f \times \frac{w_1}{M_1} \times \frac{1000}{w_2}$$

$$\Rightarrow 2 = 8 \times \frac{2.5}{M_1} \times \frac{1000}{100}$$

$$\Rightarrow M_1 = 4 \times 2.5 \times 10 \Rightarrow M_1 = 10 \times 10$$

$$\therefore M_1 = 100 \text{ g mol}^{-1}$$

OR

Mass of solution =  $100 \text{ g}$

Mass of solute =  $10 \text{ g}$

Mass of solvent =  $100 - 10 = 90 \text{ g}$

$$= \frac{90}{1000} \text{ kg} = 0.09 \text{ kg}$$

$$\text{Number of moles of solute, } n = \frac{10}{180} = 0.055 \text{ mol}$$

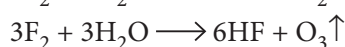
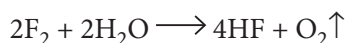
$$\text{Molality } (m) = \frac{0.055 \text{ mol}}{0.09 \text{ kg}} = 0.61 \text{ m}$$

**18. (a) :** As amino acids have both acidic (carboxy group) and basic (amino group) in the same molecule, they react with both acids and bases. Hence, they show amphoteric behaviour.

(b) In  $\alpha$ -helix structure, intramolecular H-bonding takes place whereas in  $\beta$ -pleated structure, intermolecular H-bonding takes place.

**19.**  $\text{F}_2$  is highly reactive and has greater affinity for hydrogen. Therefore, it decomposes water at low temperature and even in dark liberating oxygen and ozone.

Chemistry



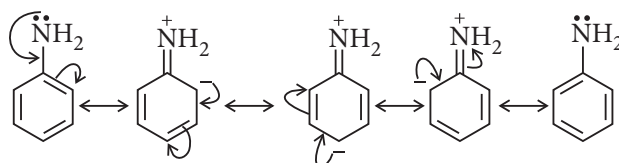
OR

(i)	$\text{H}_2\text{O}$	$\text{H}_2\text{S}$
Boiling point	$373 \text{ K}$	$> 213 \text{ K}$

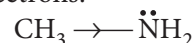
The abnormally high boiling point of  $\text{H}_2\text{O}$  is due to strong intermolecular H-bonding. Since, all other elements have much lower electronegativity than oxygen, they do not undergo H-bonding.

(ii) The +6 oxidation state of S is more stable than +4 therefore,  $\text{SO}_2$  acts as a reducing agent. Further, since the stability of +6 oxidation state decreases from S to Te therefore, the reducing character of the dioxides decreases while their oxidising character increases. Thus,  $\text{TeO}_2$  acts as an oxidising agent.

**20. (i)** In case of aniline, the lone pair of electrons on the N-atom is delocalized with the  $\pi$ -electrons of the benzene ring, making the lone pair of electrons on nitrogen less available for protonation.



On the other hand, in methylamine the electron-releasing methyl group increases the electron density around nitrogen, thereby increasing the availability of the lone pair of electrons.



Therefore, aniline is a weaker base than methylamine and hence, its  $\text{p}K_b$  value is higher than that of methylamine.

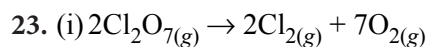
(ii) Gabriel phthalimide synthesis is the only method used to make primary amines because it is not possible to alkylate potassium phthalimide with either  $(\text{CH}_3)_2\text{CH} - \text{X}$  or  $(\text{CH}_3)_3\text{C} - \text{X}$ .

**21. (i)** This is because after  $_{57}\text{La}$ , filling of  $4f$ -orbital starts which is completed at atomic number 71. These 14 elements therefore, belong to  $f$ -block and are placed separately at the bottom of the periodic table.

(ii) The  $E^\circ$  value for  $\text{Ce}^{4+}/\text{Ce}^{3+}$  is  $1.74 \text{ V}$  which suggests that it can oxidise water however, the reaction rate is very slow and hence,  $\text{Ce(IV)}$  is a good analytical reagent.

**22. (i)** Only those compounds which can form hydrogen bonds with water are miscible with it. Alkyl halides, though polar due to the presence of electronegative halogen atom, are immiscible since they cannot form hydrogen bonds.

(ii) Tertiary halides are least reactive toward  $S_N2$  reactions because bulky groups hinder the approach of nucleophile.



For 1<sup>st</sup> order reaction,

$$k = \frac{2.303}{t} \log \left( \frac{P_0}{P} \right) = \frac{2.303}{55} \log \left( \frac{0.062}{0.044} \right) = 6.2 \times 10^{-3} \text{ s}^{-1}$$

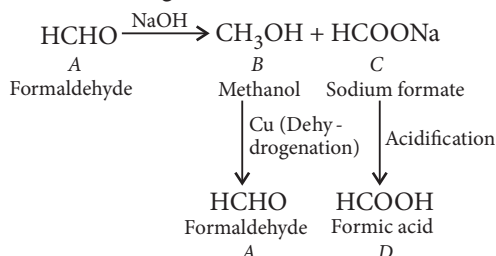
(ii)  $k = \frac{2.303}{t} \log \left( \frac{P_0}{P} \right)$

Here  $k = 6.2 \times 10^{-3} \text{ s}^{-1}$ ,  $t = 100 \text{ s}$ ,  $P_0 = 0.062 \text{ atm}$

$$\therefore 6.2 \times 10^{-3} = \frac{2.303}{100} \log \left( \frac{0.062}{P} \right)$$

$$\text{or } \log \frac{0.062}{P} = \frac{6.2 \times 10^{-3} \times 100}{2.303} \Rightarrow P = 0.033 \text{ atm}$$

24. Since the molecular formula of  $D$  is  $\text{CH}_2\text{O}_2$ , thus,  $D$  is  $\text{HCOOH}$  (formic acid).  $D$  is obtained by the acidification of  $C$ , so,  $C$  is sodium formate ( $\text{HCOONa}$ ). Thus,  $A$  must be formaldehyde (as it undergoes Cannizzaro reaction with a strong base).



Thus,  $A = \text{Formaldehyde (HCHO)}$

$B = \text{Methanol (CH}_3\text{OH)}$

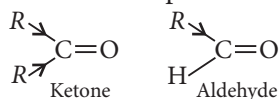
$C = \text{Sodium formate (HCOONa)}$

$D = \text{Formic acid (HCOOH)}$

OR

(a) Ketones are less reactive than aldehydes towards nucleophilic addition reactions because :

The two electron releasing alkyl groups decrease the magnitude of positive charge on carbonyl carbon and make it less susceptible to nucleophilic attack.



The two bulkier alkyl groups hinder the approach of the nucleophile to the carbonyl carbon. This is called steric factor.

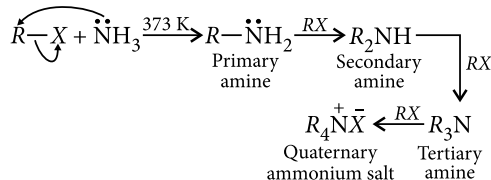
(b) In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic medium,  $\text{OH}^-$  will attack carbonyl group. Therefore, pH of a reaction should be carefully controlled.

25. (i) Physical adsorption occurs due to inter-molecular attractive forces between the adsorbate and adsorbent. If the size of the adsorbent pores is close to the size of adsorbate molecules, multilayer adsorption takes place, i.e., adsorption takes place until all the pores are filled with adsorbate molecules, whereas in chemisorption chemical bonds are formed between adsorbate and adsorbent molecules. Therefore, it is monolayered.

(ii) Tyndall effect is not observed in true solution as the diameter of dispersed particles is much smaller as compared to wavelength of the light used.

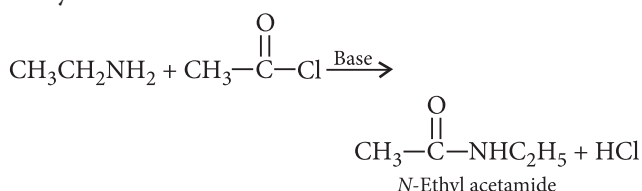
26. (a) Primary amines ( $\text{R-NH}_2$ ) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines ( $\text{R}_3\text{N}$ ). So, primary amines boil at a higher temperature than tertiary amines.

(b) (i) **Ammonolysis** : Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary, tertiary amines and quaternary ammonium salt.



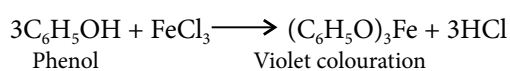
(ii) **Acetylation of amines** : The process of introducing

an acetyl group ( $\text{CH}_3-\text{C}(=\text{O})-$ ) into a molecule is called acetylation.

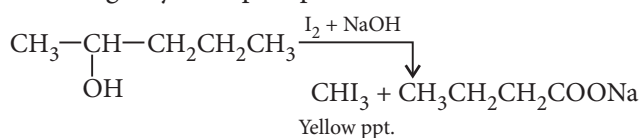


27. (a) Phenol undergoes electrophilic substitution reaction more easily than benzene due to strong activating effect of  $-\text{OH}$  group attached to benzene ring.

(b) (i) Phenol gives a violet colouration with  $\text{FeCl}_3$  solution while ethanol does not.

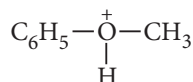


(ii) On adding  $\text{I}_2$  and  $\text{NaOH}$ , 2-pentanol will give yellow precipitate of iodoform whereas 3-pentanol will not give yellow precipitate.



OR

- (i) Acid dehydration of 2° and 3° alcohols give alkenes rather than ethers, due to steric hindrance, as elimination completes over substitution and as a consequence, alkenes are easily formed. The method is suitable for the preparation of ethers giving primary alkyl groups only.
- (ii) Protonation of anisole (phenylmethyl ether) gives methyl phenyl oxonium ion.



In this ion, the stronger bond is O—C<sub>6</sub>H<sub>5</sub>. Therefore, attack by I<sup>−</sup> ion exclusively breaks the weaker O—CH<sub>3</sub> bond forming methyl iodide and phenol. The phenol formed does not react further to give aryl halides.

(iii) Ethanol has higher boiling point because of strong intermolecular hydrogen bonding whereas in methoxymethane, molecules are held by dipole-dipole interaction.

28. (i) As 27 g of Al will contain  $6.023 \times 10^{23}$  atoms

∴ 8.1 g Al will contain

$$= \frac{6.023 \times 10^{23}}{27} \times 8.1 \text{ atoms} = 1.8069 \times 10^{23} \text{ atoms}$$

In fcc, 4 atoms are present in one unit cell

∴  $1.8069 \times 10^{23}$  atoms will be present in

$$\frac{1.8069 \times 10^{23}}{4} = 4.517 \times 10^{22} \text{ unit cells}$$

(ii) Number of atoms in 0.5 mol hcp lattice

$$= 0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$$

∴ Number of octahedral voids = Number of atoms

$$= 3.011 \times 10^{23}$$

Number of tetrahedral voids = 2 × Number of atoms

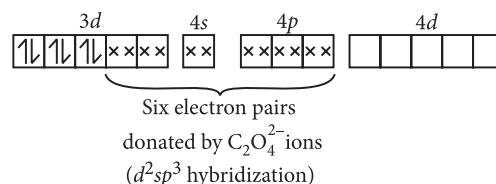
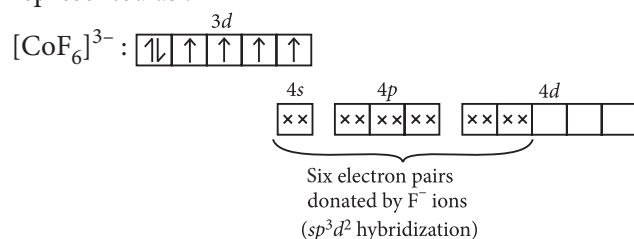
$$= 2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$$

Total number of voids = Number of octahedral voids

+ Number of tetrahedral voids

$$= 3.011 \times 10^{23} + 6.022 \times 10^{23} = 9.033 \times 10^{23} \text{ voids}$$

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



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

(ii)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  is more stable as C<sub>2</sub>O<sub>4</sub><sup>2−</sup> is a chelating ligand and forms chelate rings.

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

(iv)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  is low spin complex due to absence of any unpaired electron.

30. (i)  $E_{\text{cell}}^{\circ} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 1.44 - 0.68 = 0.76 \text{ V}$

$$E_{\text{cell}}^{\circ} = \frac{0.059}{1} \log K_C \quad [n=1]$$

$$\therefore 0.76 = 0.059 \log K_C \quad \text{or} \quad \log K_C = \frac{0.76}{0.059} = 12.8814$$

$$\text{or} \quad K_C = 7.6 \times 10^{12}$$



$$\therefore E_{\text{OP}} = E_{\text{OP}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}}$$

$$= 0 - \frac{0.059}{2} \log \frac{[0.02]^2}{2}$$

$$E_{\text{OP}(\text{H}_2/\text{H}^+)} = +0.109 \text{ V}$$



$$\therefore E_{\text{OP}} = E_{\text{OP}}^{\circ} - \frac{0.059}{2} \log_{10} \frac{P_{\text{Cl}_2}}{[\text{Cl}^-]^2}$$

$$= -1.36 - \frac{0.059}{2} \log \frac{10}{[0.1]^2}$$

$$\therefore E_{\text{OP}(\text{Cl}^-/\text{Cl}_2)} = -1.4485 \text{ V}$$

OR

(i) Given,  $\Lambda_{\text{Ba}(\text{OH})_2}^{\circ} = \lambda_{\text{Ba}^{2+}}^{\circ} + 2\lambda_{\text{OH}^-}^{\circ} = 523.28 \quad \dots(i)$

$\Lambda_{\text{BaCl}_2}^{\circ} = \lambda_{\text{Ba}^{2+}}^{\circ} + 2\lambda_{\text{Cl}^-}^{\circ} = 280.00 \quad \dots(ii)$

$\Lambda_{\text{NH}_4\text{Cl}}^{\circ} = \lambda_{\text{NH}_4^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ} = 129.80 \quad \dots(iii)$

we have to calculate,  $\Lambda_{\text{NH}_4\text{OH}}^{\circ} = \lambda_{\text{NH}_4^+}^{\circ} + \lambda_{\text{OH}^-}^{\circ} = ?$

Multiply eqn. (iii) by 2 and then subtract it from eqn. (ii).

$$\lambda_{\text{Ba}^{2+}}^{\circ} + 2\lambda_{\text{Cl}^-}^{\circ} - 2\lambda_{\text{NH}_4^+}^{\circ} - 2\lambda_{\text{Cl}^-}^{\circ} =$$

$$\lambda_{\text{Ba}^{2+}}^{\circ} - 2\lambda_{\text{NH}_4^+}^{\circ} = 280 - 2 \times 129.80 = 20.4 \quad \dots(iv)$$

Now subtract eqn. (iv) from eqn. (i)

$$\lambda_{\text{Ba}^{2+}}^{\circ} + 2\lambda_{\text{OH}^-}^{\circ} - \lambda_{\text{Ba}^{2+}}^{\circ} + 2\lambda_{\text{NH}_4^+}^{\circ}$$

$$2\lambda_{\text{NH}_4^+}^{\circ} + 2\lambda_{\text{OH}^-}^{\circ} = 523.28 - 20.4 = 502.88$$

$$\therefore \Lambda_{\text{NH}_4\text{OH}}^{\circ} = \frac{502.88}{2} = 251.44 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$



(ii) Normality of a solution is given by the number of equivalent per  $\text{dm}^3$  (or per litre) of the solution. Therefore, concentration of the given solution =  $0.12 \text{ equiv/dm}^3$  conductivity of the solution,  $(\kappa) = 0.024 \text{ S cm}^{-1}$

Then,

(a) The equivalent conductivity is given by,

$$\Lambda_{eq} = \frac{1000\kappa}{C_{eq}} = \frac{1000 \times 0.024}{0.12} \text{ S cm}^2 \text{ equiv}^{-1}$$

$$= 200 \text{ S cm}^2 \text{ equiv}^{-1}$$

(b) The given electrolyte is of the type  $A^+B^-$ . This means that each cation (or anion) carries a charge equivalent to the charge carried by one electron. So,  $Z = 1$ .

$$\text{Then, } \Lambda_m = 1 \times \Lambda_{eq} = 1 \times 200 \text{ S cm}^2 \text{ mol}^{-1} \\ = 200 \text{ S cm}^2 \text{ mol}^{-1}$$

**31.** (a) Oxoanion of chromium in which it shows +6 oxidation state equal to its group number is  $\text{Cr}_2\text{O}_7^{2-}$  (dichromate ion).

(b) (i) Scandium ( $Z = 21$ ), atom has incompletely filled  $d$ -orbitals ( $3d^1$ ) in its ground state, so it is regarded as transition element. On the other hand, zinc ( $Z = 30$ ) atom has completely filled  $d$ -orbitals ( $3d^{10}$ ) in its ground state as well as most common oxidation state of +2.

(ii) Electrode potential ( $E^\circ$ ) value is the sum of three factors :

- Enthalpy of atomisation ;  $\Delta_a H$  for  $\text{Cu}_{(s)} \rightarrow \text{Cu}_{(g)}$
- Ionisation enthalpy ;  $\Delta_i H$  for  $\text{Cu}_{(g)} \rightarrow \text{Cu}_{(g)}^{2+}$
- Hydration enthalpy ;  $\Delta_{hyd} H$  for  $\text{Cu}_{(g)}^{2+} \rightarrow \text{Cu}_{(aq)}^{2+}$

In case of copper the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration. Therefore,  $E^\circ_{M^{2+}/M}$  for Cu is positive.

(c) Transition elements can use their  $ns$  and  $(n-1)d$  orbital electrons for bond formation. Therefore, they show variable oxidation states.

For example, Sc has  $ns^2(n-1)d^1$  electronic configuration. If it utilizes two electrons from its  $ns$  subshell then its oxidation state = +2. When it utilizes both the electrons from its  $ns$  and  $(n-1)d$  subshell then its oxidation state = +3.

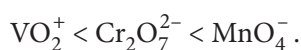
Among the  $3d$  series manganese (Mn) exhibits the largest number of oxidation states from +2 to +7 because it has maximum number of unpaired electrons.

$$\text{Mn} - [\text{Ar}] 3d^5 4s^2$$

OR

(i) The ions in which the central metal atom is present in the highest oxidation state will have the highest oxidising power. In  $\text{VO}_2^+$ , vanadium is present in the +5 oxidation state, while in  $\text{Cr}_2\text{O}_7^{2-}$  ion, Cr is present in the +6 oxidation state. Similarly, in  $\text{MnO}_4^-$ , Mn is present in the +7 oxidation state. Thus, as the oxidation

state of the central atom increases, the oxidising power of oxoanions increases in the order :



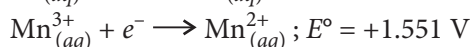
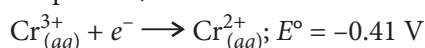
(ii) Third ionization enthalpy of Mn is very high because the third electron has to be removed from the stable half-filled  $3d$ -orbitals [ $\text{Mn}^{2+} (Z = 25) = 3d^5$ ].

(iii)  $\text{Cr}^{2+}$  is a stronger reducing agent than  $\text{Fe}^{2+}$ .

$E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}}$  is negative ( $-0.41 \text{ V}$ ) whereas  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$  is positive ( $+0.77 \text{ V}$ ). Thus,  $\text{Cr}^{2+}$  is easily oxidized to  $\text{Cr}^{3+}$  but  $\text{Fe}^{2+}$  cannot be easily oxidized to  $\text{Fe}^{3+}$ . Hence,  $\text{Cr}^{2+}$  is stronger reducing agent than  $\text{Fe}^{2+}$ .

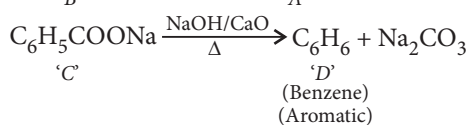
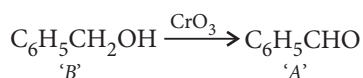
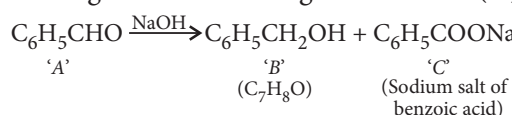
(iv) Electronic configuration of  $\text{Mn}^{2+}$  is  $3d^5$  which is half filled and hence stable. Therefore, third ionization enthalpy is very high, i.e.,  $3^{rd}$  electron cannot be lost easily. In case of  $\text{Fe}^{2+}$ , electronic configuration is  $3d^6$ . Hence, it can lose one electron easily to give the stable configuration  $3d^5$ .

(v) (i)  $E^\circ$  values for the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  and  $\text{Mn}^{3+}/\text{Mn}^{2+}$  couples are,



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

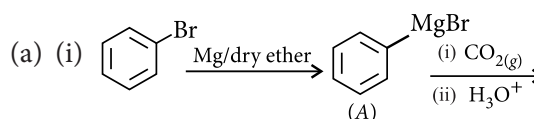
**32.** (a) Benzaldehyde has a characteristic odour. Reaction of 'A' with NaOH appears to be Cannizzaro reaction which gives 'B' (benzyl alcohol) and 'C' (sodium salt of benzoic acid). Oxidation of alcohols gives aldehydes. Sodium salt of benzoic acid on heating with soda lime gives benzene (D).



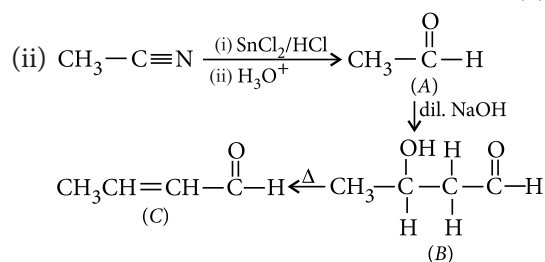
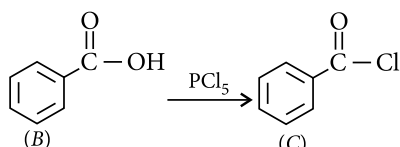
(b) (i) Due to presence of electron withdrawing group ( $-\text{COOH}$ ) in aromatic carboxylic acids, they do not undergo Friedel-Crafts reaction.

(ii) Due to presence of strong electron withdrawing group ( $-\text{NO}_2$ ), 4-nitrobenzoic acid is more acidic than benzoic acid and therefore,  $\text{p}K_a$  value is lower.

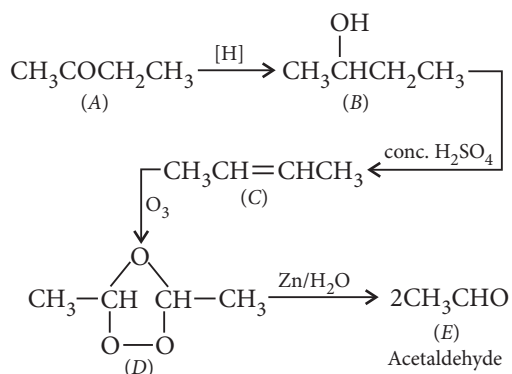
OR



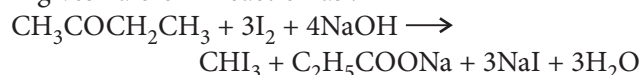




(b) Chemical reactions occur as,



A gives haloform reaction as :



33. (a) Elevation in boiling point ( $\Delta T_b$ )  
 $= 100 - 99.63 = 0.37^\circ\text{C}$

Mass of solvent (water),  $w_1 = 500 \text{ g}$

Mass of solute,  $w_2 = ?$

Molar mass of solvent,  $M_1 = 18 \text{ g mol}^{-1}$

Molar mass of solute, ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ),  $M_2 = 342 \text{ g mol}^{-1}$

Applying the formula,  $\Delta T_b = K_b \times \frac{w_2 \times 1000}{M_2 \times w_1}$

$$\text{or, } w_2 = \frac{M_2 \times w_1 \times \Delta T_b}{1000 \times K_b} = \frac{342 \times 500 \times 0.37}{1000 \times 0.52} = 122 \text{ g}$$

(b) Given:  $V_{\text{ethylene glycol}} = 50 \text{ cm}^3$ ,  $W = 50 \text{ g}$   
 $K_f = 1.86 \text{ K kg mol}^{-1}$ ,  $m = 62 \text{ g/mol}$  (ethylene glycol)  
 $\Delta T_f = 34^\circ\text{C}$ ,  $w = 50 \times d \text{ g}$  (ethylene glycol)

$$\text{We know, } \Delta T_f = \frac{1000 \times K_f \times w}{m \times W}$$

$$\text{Substituting values, } 34 = \frac{1000 \times 1.86 \times 50 \times d}{62 \times 50}$$

$$\therefore d = 1.133 \text{ g/cm}^3$$

OR

(a) The net spontaneous flow of the solvent molecules from the solvent to the solution or from a less concentrated solution to more concentrated solution through a semi-permeable membrane is called osmosis.

The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and its magnitude is large even for very dilute solution.

(b) (i) (a) The cells will swell or even burst due to haemolysis because 0.5% NaCl solution is hypotonic *w.r.t.* salt concentration in blood plasma.

(b) The cells will shrink due to plasmolysis, because 1% solution of NaCl is hypertonic *w.r.t.* salt concentration in blood plasma.

(ii) Molar mass of heptane ( $\text{C}_7\text{H}_{16}$ ) =  $100 \text{ g mol}^{-1}$

Molar mass of octane ( $\text{C}_8\text{H}_{18}$ ) =  $114 \text{ g mol}^{-1}$

$$\text{Number of moles of heptane} = \frac{26.0 \text{ g}}{100 \text{ g mol}^{-1}} = 0.26 \text{ mol}$$

$$\text{Number of moles of octane} = \frac{35.0 \text{ g}}{114 \text{ g mol}^{-1}} = 0.31 \text{ mol}$$

$$x(\text{heptane}) = \frac{0.26}{0.26 + 0.31} = 0.456$$

$$x(\text{octane}) = 1 - 0.456 = 0.544$$

$$p(\text{heptane}) = 0.456 \times 105.2 \text{ kPa} = 47.97 \text{ kPa}$$

$$p(\text{octane}) = 0.544 \times 46.8 \text{ kPa} = 25.46 \text{ kPa}$$

$$P_{\text{Total}} = 47.97 + 25.46 = 73.43 \text{ kPa}$$

