Subject Code : **043**

SQP-5

CHEMISTRY

Time Allowed : 3 Hours *Maximum Marks : 70*

General Instructions :

Read the following instructions carefully.

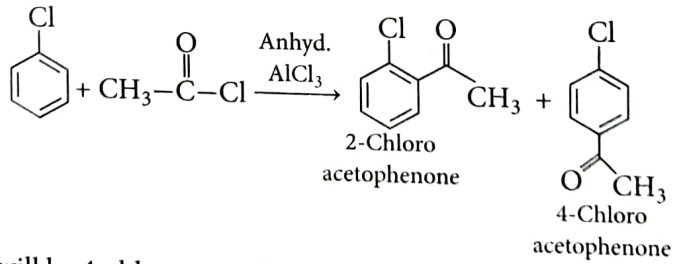
(a) There are 33 questions in this question paper with internal choice.
(b) SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
(c) SECTION B consists of 5 short answer questions carrying 2 marks each.
(d) SECTION C consists of 7 short answer questions carrying 3 marks each.
(e) SECTION D consists of 2 case-based questions carrying 4 marks each.
(f) SECTION E consists of 3 long answer questions carrying 5 marks each.
(g) All questions are compulsory.
(h) Use of log tables and calculators is not allowed.

SECTION A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. The decreasing order of boiling points of the following alcohols is
   (a) 3-methylbutan-2-ol > 2-methylbutan-2-ol > pentan-1-ol
   (b) pentan-1-ol > 3-methylbutan-2-ol > 2-methylbutan-2-ol
   (c) 2-methylbutan-2-ol > 3-methylbutan-2-ol > pentan-1-ol
   (d) 2-methylbutan-2-ol > pentan-1-ol > 3-methylbutan-2-ol.

2. In the reaction,



2-Chloro acetophenone

4-Chloro acetophenone

   (a) the major product will be 4-chloroacetophenone
   (b) the major product will be 2-chloroacetophenone
   (c) both 2-chloroacetophenone and 4-chloroacetophenone are formed in equal amount
   (d) product formed is not correct.

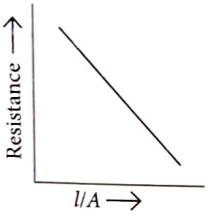
3. Which of the following ions are colourless?

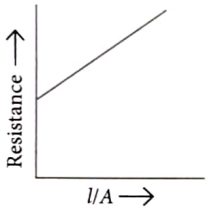
   Ti^{3+}, Sc^{3+}, Ag^{+}, Cd^{2+}, Cu^{2+}

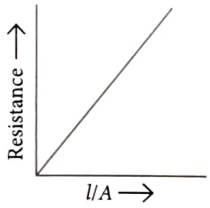
   I II III IV V

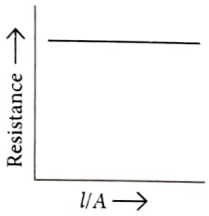
   (a) I and V only
   (b) II, III and IV only
   (c) I, III and V only
   (d) I and IV only

4. Variation of resistance *vs* l/A gives graph of the type.

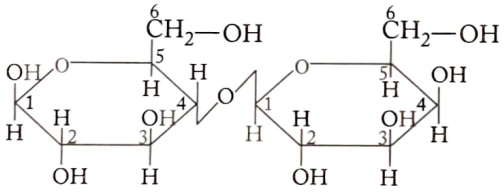
(a) 

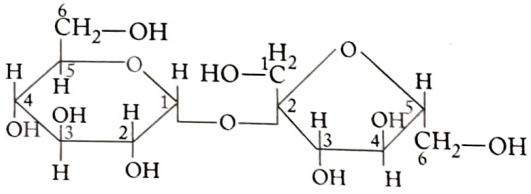
(b) 

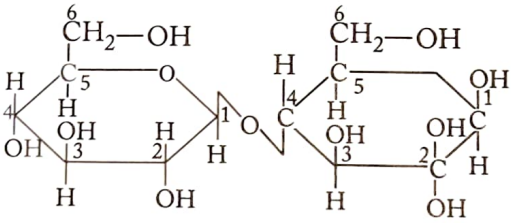
(c) 

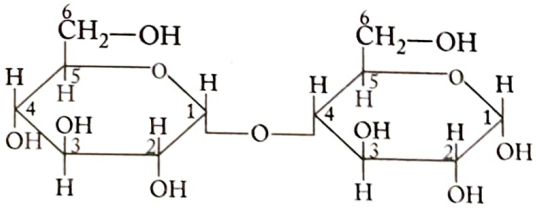
(d) 

5. Which of the following is the correct structure of maltose?

(a) 

(b) 

(c) 

(d) 

6. Which of the following gives Hell–Volhard–Zelinsky (HVZ) reaction?

(a) CH_3CHO (b) HCHO

(c) CH_3COOH (d) CH_3COCH_3

7. Consider the following reaction :

$2A + B + C \longrightarrow$ Products

How will the rate of reaction change when the concentration of *A* is doubled and that of *B* is tripled while *C* is taken in excess?

(a) The rate reduces to 8 times of its original value.

(b) The rate reduces to 12 times of its original value.

(c) The rate increases by 8 times of its original value.

(d) The rate increases by 12 times of its original value.

8. Among the following, which one is paramagnetic and has tetrahedral geometry?

(a) $[Ni(CN)_4]^{2-}$ (b) $[NiCl_4]^{2-}$

(c) $[Ni(CO)_4]$ (d) $[CoCl_2(en)_2]^+$

9. Product *B* in the reaction,

$$C_2H_5Br \xrightarrow[\text{Dry ether}]{Mg} A \xrightarrow{H_2O} B$$

(a) propane (b) ethyl iodide

(c) ethane (d) ethyl methyl ether.

10. Cu^+ ion is not stable in aqueous solution because

(a) $Cu^{2+}_{(aq)}$ is less stable than $Cu^{+}_{(aq)}$

(b) $Cu^{2+}_{(aq)}$ can form interstitial compounds in aqueous solution

(c) the equilibrium constant for
$Cu^{+}_{(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + Cu$ is very high

(d) the equilibrium constant for
$Cu^{+}_{(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + Cu$ is very low.

11. Which of the following alcohols reacts most readily with Lucas reagent?

(a) $CH_3CH_2CH_2OH$

(b) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

(c) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$

(d) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

12. $-NH_2$ group in aniline is

(a) *m*-directing and deactivating

(b) *o*, *p*-directing and deactivating

(c) *o*, *p*-directing and activating

(d) *m*-directing and activating.

13. **Assertion (A) :** Order of a reaction with respect to any reactant or product can be zero, positive, negative and fractional.
Reason (A) : Rate of a reaction cannot decrease with increase in concentration of a reactant or product.
Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A.

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

14. **Assertion (A) :** First nine aliphatic monocarboxylic acids are colourless liquids at room temperature.
Reason (R) : Carboxylic acids with more than five carbon atoms are highly soluble in water.
Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A.

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

15. **Assertion (A) :** α-Amino acids exist as dipolar ions or zwitter ions.
Reason (R) : α-Amino acids are the building blocks of proteins.
Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A.

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

16. **Assertion (A) :** $[Fe(CN)_6]^{3-}$ has d^2sp^3 type hybridisation.
Reason (R) : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A.

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

SECTION B

This section contains 5 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

17. Illustrate the following reactions giving suitable example in each case :

(i) Ammonolysis

(ii) Acetylation of amines

18. Give reasons **(any 2)** :
    (i) Racemic mixture is optically inactive.
    (ii) The presence of nitro group ($-NO_2$) at *o/p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.
    (iii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

19. What is meant by pyranose structure of glucose? Explain.

20. (a) Write the IUPAC name of $[PtCl(NH_2CH_3)(NH_3)_2]Cl$.
    (b) Using IUPAC norms write the formula for potassium tetrahydroxidozincate(II).

OR

Indicate the types of isomerism exhibited by the following complexes:
(i) $[Co(en)_3]Cl_3$ (*en* = ethylene diamine) (ii) $[Pt(NH_3)_2Cl_2]$

21. Explain how and why will the rate for a given reaction be affected when
    (a) a catalyst is added
    (b) the temperature at which the reaction was taking place is decreased?

SECTION C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

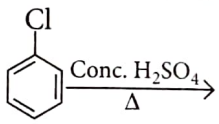
22. Assign reason for each of the following :
    (i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.
    (ii) E° for Mn^{3+}/Mn^{2+} couple is more positive than for Fe^{3+}/Fe^{2+}.
    (iii) The transition elements form interstitial compounds.

23. A reaction is second order in *A* and first order in *B*.
    (i) Write the differential rate equation.
    (ii) How is the rate affected on increasing the concentration of *A* three times?
    (iii) How is the rate affected when the concentration of both *A* and *B* are doubled?

24. Answer the following questions :
    (a) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.
    (b) Write the structures of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH.
    (c) Which would undergo S_N2 reaction faster in the following pair and why?
    CH_3-CH_2-Br and CH_3-CH_2-I

OR

(a) A chloro derivative (*A*) on treatment with zinc-copper couple gives a hydrocarbon with five carbon atoms. When (*A*) is dissolved in ether and treated with sodium then 2, 2, 5, 5 -tetramethylhexane is obtained. What is the original compound (*A*)?
(b) Write the major product of the following reaction :



(c) Out of 2-bromopentane, 2-bromo-2-methylbutane, and 1-bromopentane, which compound is most reactive towards elimination reaction and why?

25. Chromium metal is electroplated using an acidic solution containing CrO_3 according to the following equation :

$CrO_{3(aq)} + 6H^+ + 6e^- \longrightarrow Cr_{(s)} + 3H_2O$

Calculate how many grams of chromium will be electroplated by 24,000 coulombs. How long will it take to electroplate 1.5 g chromium using 12.5 A current?

[Atomic mass of Cr = 52 g mol^{-1}, 1 F = 96500 C mol^{-1}]

26. Give the structures of products *A*, *B* and *C* in the following reactions :

(i) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0\,°C]{HNO_2} C$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOH + Br_2} B \xrightarrow{CHCl_3 + Alc.\ NaOH} C$

27. (a) Some ethylene glycol, $HOCH_2CH_2OH$, is added to your car's cooling system along with 5 kg of water. If the freezing point of water-glycol solution is –15.0 °C, what is the boiling point of the solution? (K_b = 0.52 K kg mol^{-1} and K_f = 1.86 K kg mol^{-1} for water)

(b) What would be the value of van't Hoff factor for a dilute solution of K_2SO_4 in water?

28. (a) Amino acids show amphoteric behaviour. Why?

(b) Write one difference between α-helix and β-pleated structures of proteins.

SECTION D

The following questions are case-based questions. Each question has an internal choice and carries 4 (2+1+1) marks each. Read the passage carefully and answer the questions that follow.

29. The reactions of phenol with metals and sodium hydroxide indicate its acidic nature. The hydroxyl group, in phenol is directly attached to the sp^2 hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule causes the oxygen atom of —OH group to be positive. The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. Phenol also reacts with carboxylic acids, acid chlorides and acid anhydrides to form esters.

Answer the following questions :

(a) How do you convert the following :

(i) Phenol to anisole (ii) Phenol to 2-hydroxybenzoic acid

(b) Phenols are stronger acids than alcohols, why?

OR

Draw resonance structures of phenol and phenoxide ion.

(c) What is aspirin? How is aspirin prepared?

30. Colligative properties depend on the number of solute particles irrespective on their nature, they are, relative lowering in vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure. Abnormal molecular weights and colligative properties are observed in some cases where the experimental and theoretical values differ considerably. Due to dissociation of solute in water (solvent) the number of particles in the solution increases, resulting in increase in experimental values, since

$$\text{Colligative property} \propto \frac{1}{\text{Molecular weight}}$$

Experimental molecular weight < Normal molecular weight.

Answer the following questions :

(a) Write two advantages of osmotic pressure method over boiling point elevation method for determining molecular masses.

(b) The boiling point of solution when 4 g of $MgSO_4$ (M = 120 g mol^{-1}) was dissolved in 100 g of water, assuming $MgSO_4$ undergoes complete ionization, is
(K_b for water = 0.52 K kg mol^{-1})
(i) 100.34°C (ii) 98.25°C (iii) 120.34°C (iv) 89.22°C

(c) If 1 g of solute (molar mass = 50 g mol^{-1}) is dissolved in 50 g of solvent and the elevation in boiling point is 1 K. The molal boiling constant of the solvent is
(i) 2 (ii) 3 (iii) 2.5 (iv) 5

OR

Which of the following statements is not correct?
(i) Osmotic pressure (π) of a solution is given by the relation $\pi = MRT$ where M is the molarity of the solution.
(ii) The correct order of osmotic pressure for 0.2 M aqueous solution of each solute is $CaCl_2 > NaCl > CH_3COOH >$ glucose.
(iii) Two solutions of sucrose of same molality prepared in different solvents will have same elevation in boiling point.
(iv) Relative lowering in vapour pressure of a solution containing non-volatile solute is directly proportional to mole fraction of solute is Raoult's law.

SECTION E

The following questions are long answer types and carry 5 marks each. All questions have an internal choice.

31. Answer the following questions :
(a) Write the names of the following complexes using IUPAC norms :
(i) $Na_3[AlF_6]$ (ii) $[CoCl(en)_2(ONO)]Cl$
(b) What is crystal field splitting?
(c) Explain the difference between a weak field ligand and a strong field ligand.
(d) Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons.
(e) Zr and Hf have almost similar atomic radii. Give reason.

OR

(a) The magnetic moment of a complex ion, $[Cr(CN)_6]^{3-}$ is found to be 3.87 B.M. Calculate the number of unpaired electrons present in it.
(b) Arrange the following complexes in order of decreasing electrical conductivity:
$[Cr(NH_3)_3Br_3]$, $[Cr(NH_3)_5Br]Br_2$, $[Cr(NH_3)_6]Br_3$, $[Cr(NH_3)_4Br_2]Br$
(c) Amongst $[Fe(C_2O_4)_3]^{3-}$ and $[Fe(NH_3)_6]^{3+}$, which is more stable and why?
(d) Write the number of unpaired electrons in Cr^{3+}. (Atomic number of Cr = 24)
(e) Complete the reaction mentioning all the products formed:
$Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow$

32. (a) Accidently chewing of a stray fragment of aluminium foil can cause a sharp tooth pain if the aluminium comes in contact with an amalgam filling. An electric current passes from the aluminium to the filling (of cavity), which is sensed by a nerve in the tooth.
Based on the above information, answer the following questions.
(i) How does electric current pass?
(ii) Write balanced equations taking place at anode, cathode and overall.
(iii) Write the Nernst equation in a form that applies at body temperature (37 °C).
(iv) Calculate E_{cell} at 37 °C, $[Al^{3+}] = 1.0 \times 10^{-9}$ M,
p_{O_2} = 0.20 atm in a saliva that has a pH of 7.0.
E°_{cell} = 2.89 V

(b) On the basis of E° values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl. Give reason.

OR

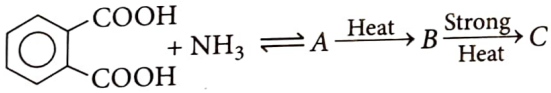
(a) A steady current of 2 amperes was passed through two electrolytic cells *X* and *Y* connected in series containing electrolytes $FeSO_4$ and $ZnSO_4$ until 2.8 g of Fe is deposited at the cathode of cell *X*. How long did the current flow? Calculate the mass of Zn deposited at the cathode of cell *Y*.
(Molar mass : Fe = 56 g mol^{-1}, Zn = 65.3 g mol^{-1}, 1 F = 96500 C mol^{-1})

(b) Why does silver nitrate solution becomes bluish when copper rod is placed in it?

33. (a) Give a chemical test to distinguish between the following :
(i) Benzoic acid and ethyl benzoate
(ii) Benzophenone and acetophenone

(b) Complete the following reaction :

(c) Identify *A*, *B* and *C* in the following sequence:



OR

(a) Give a chemical test to distinguish between ethanal and ethanoic acid.

(b) Why is the α-hydrogen of aldehydes and ketones acidic in nature?

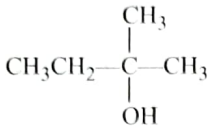
(c) An organic compound '*A*' with molecular formula $C_4H_8O_2$ undergoes acid hydrolysis to form two compounds '*B*' and '*C*'. Oxidation of *C* with acidified potassium permanganate also produces '*B*'. Sodium salt of '*B*' on heating with soda lime gives methane.
(i) Identify '*A*', '*B*' and '*C*'.
(ii) Out of '*B*' and '*C*', which will have higher boiling point? Give reason.

SQP 5 SOLUTIONS

1. **(b)** : $CH_3CH_2CH_2CH_2CH_2OH$ > $CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{3}{|}}{CH}}-\underset{\underset{OH}{|}}{\overset{\overset{2}{|}}{CH}}-CH_3$ >

Pentan-1-ol

3-Methylbutan-2-ol



2-Methylbutan-2-ol

Boiling point is in the order 1° > 2° > 3°.

2. **(a)** : In Friedel-Crafts acylation, the major product is 4-chloroacetophenone. The *ortho* isomer, 2-chloroacetophenone is the minor product due to steric hinderance.

3. **(b)** : Ti^{3+} and Cu^{2+} are coloured. Sc^{3+} is colourless due to empty *d*-orbitals. Ag^+ and Cd^{2+} are colourless due to completely filled *d*-orbitals.

4. **(c)** : We know that the electrical resistance of electrolytic solutions is directly proportional to its length (l) and inversely proportional to its area of cross-section (A) *i.e.*,

$$R \propto \frac{l}{A} \Rightarrow R = \rho\frac{l}{A} \qquad [\because\ l/A = \text{cell constant}]$$

Comparing with $y = mx + c$

The graph of R *vs* (l/A) will be a straight line starting from the origin with slope ρ.

5. **(d)**

6. **(c)** : Carboxylic acids having α-H atom undergo Hell-Volhard-Zelinsky reaction.

7. **(d)** : $2A + B + C \longrightarrow$ Products

$r_1 = k\,[A]^2\,[B]$

$\because$ C is taken in excess, rate does not depend upon C.

$r_2 = k\,[2A]^2\,[3B] \Rightarrow r_2 = 12k\,[A]^2\,[B]$

$$\frac{r_2}{r_1} = \frac{12k[A]^2[B]}{k[A]^2[B]} \Rightarrow r_2 = 12r_1$$

8. **(b)** : $[Ni(CN)_4]^{2-} \rightarrow dsp^2$ hybridisation (square planar complex) $\rightarrow$ No unpaired electrons (diamagnetic)

$[NiCl_4]^{2-} \rightarrow sp^3$ hybridisation (tetrahedral)$\rightarrow$ 2 unpaired electrons (paramagnetic)

$[Ni(CO)_4] \rightarrow sp^3$ hybridisation (tetrahedral)$\rightarrow$ No unpaired electrons (diamagnetic)

$[CoCl_2(en)_2]^+ \rightarrow d^2sp^3$ hybridisation (octahedral)$\rightarrow$ No unpaired electrons (diamagnetic)

9. **(c)** :

$$C_2H_5Br \xrightarrow[\text{Dry ether}]{Mg} \underset{(A)}{C_2H_5MgBr} \xrightarrow{H_2O} \underset{(B)}{C_2H_6} + Mg(BrOH)$$

10. **(c)** : In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

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

Cu^{2+} in aqueous solution is more stable than Cu^+ ion.

Therefore, equilibrium constant for $Cu^+_{(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + Cu$ is very high.

11. **(c)** : The rate of reaction of alcohols with Lucas reagent is 3° > 2° > 1°.

Tertiary alcohols immediately react to give turbidity, secondary alcohols give turbidity after some time and primary alcohols do not give turbidity until heated.

12. **(c)**

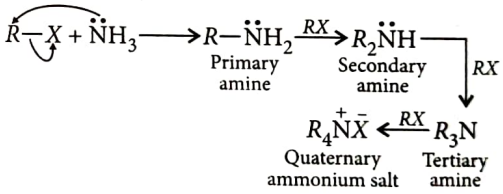
13. **(c)** : Rate of a reaction increases with increase in concentration of products and also depends on the order of reaction.

14. **(c)** : Carboxylic acids ($RCOOH$) dissolves in water due to hydrogen bonding between H-atom of –COOH group and O-atom of water. As alkyl portion ($-R$) is non-polar and lyophobic, solubility decreases as $-R$ gets larger (over five carbon atoms).

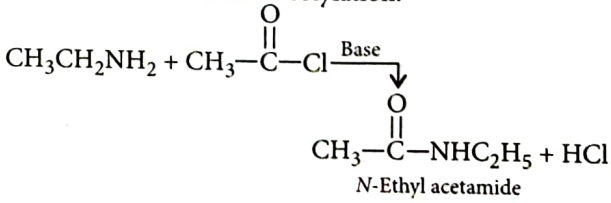
15. **(b)**

16. **(c)** : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to one unpaired electron.

17. (i) Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary, tertiary amines and quaternary ammonium salt. This process of cleavage of the C—X bond by ammonia molecule is known as ammonolysis.



(ii) The process of introducing an acetyl group ($CH_3-\overset{\overset{O}{\|}}{C}-$) into a molecule is called acetylation.



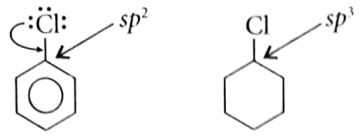
18. (i) Racemic mixture contains equal amount of *d*- and *l*-forms, hence rotation due to one enantiomer is cancelled by another.

(ii) The presence of nitro group at *o*- and *p*-positions withdraws electrons from the benzene ring and thus, facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is further stabilised by resonance.

(iii) There are two reasons :

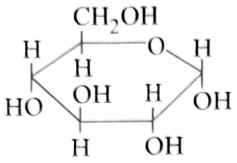
(a) In case of chlorobenzene, the carbon atom to which chlorine is attached is sp^2-hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3-hybridised. So, the net dipole moment is lower in chlorobenzene.

(b) In chlorobenzene C—Cl bond has some double bond character so its bond length is smaller. Hence, dipole moment is smaller than cyclohexyl chloride which has a longer C—Cl single bond.



Chlorobenzene Cyclohexyl chloride

19. The six membered cyclic structure of glucose is called pyranose structure (α- or β -), in analogy with heterocyclic compound pyran.



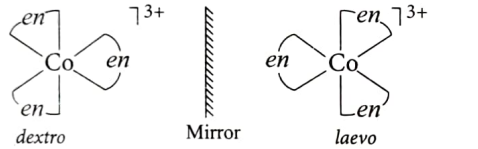
α-*D*-(+)-Glucopyranose

20. (a) : Diamminechlorido(methylamine)platinum(II) chloride.

(b) $K_2[Zn(OH)_4]$

OR

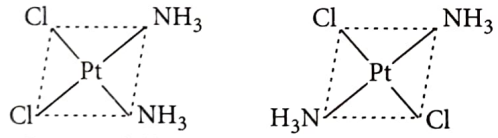
(i) Optical isomerism :



dextro *laevo*

Tris(ethane-1, 2-diamine) cobalt(III) ion *Tris*(ethane-1, 2-diamine) cobalt(III) ion

(ii)



cis-Diamminedichlorido platinum(II) *trans*-Diamminedichlorido platinum(II)

21. (a) The rate of reaction will increase. The catalyst decreases the activation energy of the reaction therefore the reaction becomes faster.

(b) The rate of reaction will decrease. At lower temperatures, the kinetic energy of molecules decrease thereby, the collisions decrease resulting in lowering of rate of reaction.

22. (i) Manganese can form $p\pi$ - $d\pi$ bond with oxygen by utilising 2*p*-orbital of oxygen and 3*d*-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi$ - $d\pi$ bond thus, it can show a maximum of +4 oxidation state.

(ii) Mn^{3+} has a d^4-configuration, so it has greater tendency to accept one electron to acquire stable d^5 configuration. On the other hand, Fe^{3+} has a d^5 configuration which is more stable than the d^6 configuration of Fe^{2+}. As a result, reduction of Fe^{3+} to Fe^{2+} is not favoured. Since, E° values reflect the reduction tendency therefore, E° value for Mn^{3+}/Mn^{2+} couple is more positive than Fe^{3+}/Fe^{2+}.

(iii) The transition elements form a number of interstitial compounds in which atoms of elements such as H, C and N occupy the voids in their lattices. The products obtained in this way are hard and rigid. For example, steel and cast iron become hard due to the formation of an interstitial compound with carbon.

23. Since the reaction is second order in *A* and first order in *B*.

(i) Differential rate equation is

Rate = $k[A]^2[B]$

(ii) The new concentration of $A = [3A]$

$\therefore$ New rate = $k[3A]^2[B] = 9k[A]^2[B]$

$\therefore$ New rate = 9 times of the original rate

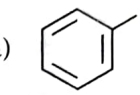
(iii) New concentration of $A = [2A]$

New concentration of $B = [2B]$

$\therefore$ New rate = $k[2A]^2[2B] = 8k[A]^2[B]$

$\therefore$ New rate = 8 times of the original rate.

24. (a)



Chlorobenzene

$+ 2Na + Cl—CH_3$

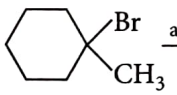
Methyl chloride

Dry ether

$CH_3 + 2NaCl$

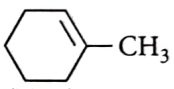
Toluene

(b)



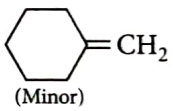
1-Bromo-1-methylcyclohexane

alc. KOH



(Major)

+

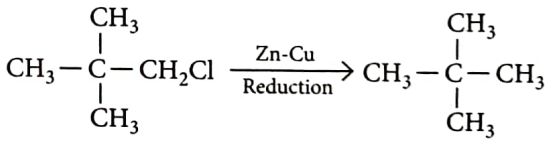


(Minor)

(c) Since, I^- is a better leaving group than Br^-, thus, CH_3CH_2I undergoes S_N2 reaction faster than CH_3CH_2Br.

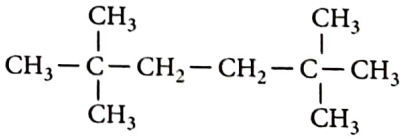
OR

(a)



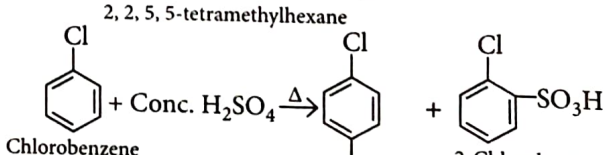
(*A*)

Na, ether
(Wurtz reaction)



2, 2, 5, 5-tetramethylhexane

(b)



Chlorobenzene

4-Chlorobenzene-sulphonic acid (Major)

2-Chlorobenzene sulphonic acid (Minor)

(c) 2-Bromo-2-methylbutane will give fastest elimination reaction because it is a *tert*-halide and *tert*-halides prefer elimination reaction.

25. Charge = 24,000 coulombs

According to the reaction,

$Cr^{6+} + 6e^- \rightarrow Cr_{(s)}$

We require 6F or 6×96500 C to deposit 1 mol or 52 g of Cr.

For 24,000 C, the mass of Cr deposited

$$= \frac{52 \times 24{,}000}{6 \times 96500} = 2.15 \text{ g}$$

According to Faraday's first law of electrolysis,

$$\frac{w_1}{w_2} = \frac{Q_1}{Q_2} \quad \text{or} \quad \frac{2.15}{1.5} = \frac{24{,}000}{12.5 \times t}$$

$$t = \frac{24{,}000 \times 1.5}{12.5 \times 2.15} = 1340 \text{ s}$$

26. (i) $CH_3CH_2Br \xrightarrow{KCN} \underset{(A)}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2CH_2NH_2} \xrightarrow[273\text{ K}]{HNO_2} \underset{(C)}{CH_3CH_2CH_2OH}$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{Br_2 + NaOH} \underset{(B)}{CH_3NH_2} \xrightarrow{CHCl_3 + NaOH} \underset{(C)}{CH_3NC}$

27. (a) $T_f = -15$ °C, $K_f = 1.86$ K kg mol^{-1},

$K_b = 0.52$ K kg mol^{-1}

$\Delta T_f = T_f^\circ - T_f = 0 - (-15\text{ °C}) = 15$ °C or 15 K

$\Delta T_f = K_f \times m$ ....(i)

$\Delta T_b = K_b \times m$ ....(ii)

From eq. (i) and (ii),

$$\frac{\Delta T_f}{\Delta T_b} = \frac{K_f}{K_b}$$

$$\frac{15}{\Delta T_b} = \frac{1.86}{0.52}$$

$\Delta T_b = 4.19$ K or 4.19 °C

$\Delta T_b = T_b - T_b^\circ$

$T_b = \Delta T_b + 100$ °C (T_b° (water) = 100 °C)

$T_b = 4.19$ °C + 100 °C

= 104.19 °C

(b) In dilute solution K_2SO_4 ionises as

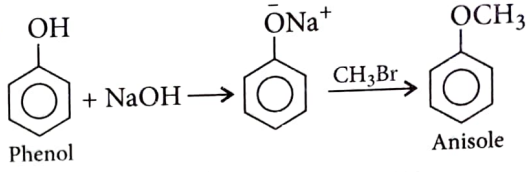
$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$

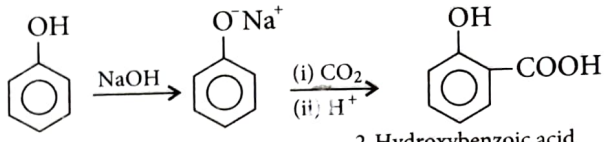
$$\text{van't Hoff factor} = \frac{\text{Number of particles after dissociation}}{\text{Number of particles before dissociation}}$$

$$\therefore \quad i = \frac{3}{1} = 3$$

28. (a) As amino acids have both acidic (carboxyl group) and basic groups (amino group) in the same molecule, they react with both acids and bases. Hence, they show amphoteric behaviour.

(b) In α-helix structure, intramolecular H-bonding takes place whereas in β-pleated structure, intermolecular H-bonding takes place.

29. (a) (i) 

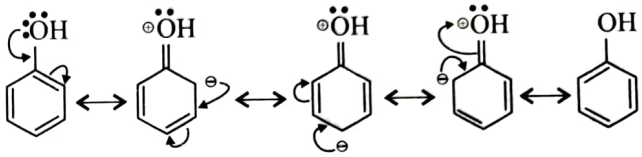
(ii) 

2-Hydroxybenzoic acid

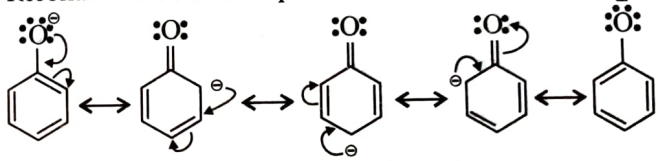
(b) In alcohols, –OH group is attached to electron releasing alkyl group which decreases polarity of O–H bond while in phenols –OH group is attached to electron withdrawing phenyl group which increases polarity of O – H bond.

OR

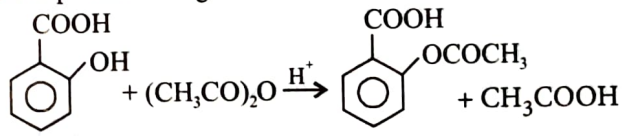
Resonance structures of phenol :



Resonance structures of phenoxide ion :



(c) Aspirin is acetyl salicylic acid which is an analgesic used in pain relieving.



Salicylic acid — Acetyl salicylic acid (Aspirin)

30. (a) (i) Osmotic pressure method gives large value for even small amount of solute.

(ii) This experiment is performed at normal temperature, hence no heating or cooling is required.

(b) **(i) :** $W_2 = 4$ g, $M_2 = 120$ g mol^{-1}

$W_1 = 100$ g, $K_b = 0.52$ K kg mol^{-1}

For complete dissociation, $i = 2$

Using formula, $\Delta T_b = iK_bm$

$$\text{or} \quad \Delta T_b = \frac{i \times K_b \times W_2 \times 1000}{M_2 \times W_1} = 2 \times 0.52 \times \frac{4 \times 1000}{120 \times 100} = 0.34 \text{ K}$$

$$\therefore \quad T_b = T_b^\circ + \Delta T_b = 100 + 0.34 = 100.34 \text{ °C}$$

(c) **(iii) :** $\Delta T_b = K_b \times m$

$$\text{or} \quad K_b = \frac{\Delta T_b}{m} = \frac{1}{\frac{1}{50} \times \frac{1000}{50}} = \frac{5}{2} = 2.5$$

OR

(iii) : With different solvents, the colligative properties change.

31. (a) (i) Sodium hexafluoridoaluminate(III)

(ii) Chlorido*bis*(ethane-1, 2-diamine) nitrito-O-cobalt(III) chloride

(b) In a free transition metal ion, all the five *d*-orbitals are degenerate but when it is involved in a complex formation, the degeneracy is split. This is called crystal field splitting.

(c) The ligands with small value of CFSE (Δ_o) are called weak field ligands whereas those with large value of CFSE are called strong field ligands.

(d) Chemistry of actinoids is more complicated than lanthanoids because

(i) actinoids show greater number of oxidation states due to the comparable energies of 5*f*, 6*d* and 7*s* orbitals.

(ii) most of the actinoids are radioactive and the study of their chemistry in the laboratory is difficult.

(e) Due to lanthanoid contraction the elements of 4*d* and 5*d*-series have similar atomic radii, *e.g.*, Zr = 160 pm and Hf = 159 pm.

OR

(a) The oxidation state of Cr in the complex ion is +3 *i.e.* d^3

Magnetic moment, μ = 3.87 B.M. corresponds to the number of unpaired electrons, $n = 3$.

Since, magnetic moment $\mu = \sqrt{n(n+2)}$

(b) $[Cr(NH_3)_6]Br_3 > [Cr(NH_3)_5Br]Br_2 > [Cr(NH_3)_4Br_2]Br > [Cr(NH_3)_3Br_3]$

This is because number of ions produced from these complexes are 4, 3, 2 and 0 respectively. As the number of ions increases, electrical conductivity increases.

(c) $[Fe(C_2O_4)_3]^{3-}$ is more stable than $[Fe(NH_3)_6]^{3+}$ due to chelate effect, as it forms rings.

(d) At. no. of Cr is 24.

Electronic configuration : [Ar] $3d^5 4s^1$

Cr^{3+} : [Ar]$3d^3$

No. of unpaired $e^- = 3$

(e) $Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 3S$

32. (a) (i) There is formation of tiny galvanic cell. The amalgam filling an alloy of Ag, Sn and Hg acts as cathode, the aluminium behaves as anode and saliva serves as electrolyte. When the aluminium and the filling come in contact, electric current passes from aluminium to the filling.

(ii) Anode : $4Al_{(s)} \rightarrow 4Al^{3+}_{(aq)} + 12e^-$

Cathode : $3O_{2(g)} + 12H^+_{(aq)} + 12e^- \rightarrow 6H_2O_{(l)}$

Overall : $4Al_{(s)} + 3O_{2(g)} + 12H^+_{(aq)} \rightarrow 4Al^{3+}_{(aq)} + 6H_2O_{(l)}$

(iii) $E = E^\circ - \dfrac{2.303\,RT}{nF} \log \dfrac{[Al^{3+}]^4}{p^3_{O_2}[H^+]^{12}}$

T = 310 K, R = 8.3143 J mol^{-1} K^{-1}

n = 12, F = 96500 C

(iv) $E = 2.89 - \dfrac{2.303 \times 8.3143 \times 310}{12 \times 96500} \log \dfrac{(1\times10^{-9})^4}{(0.2)^3(1\times10^{-7})^{12}}$

= 2.89 – 0.26 = 2.63 V

(b) The reaction at anode with lower value of E° is preferred *i.e.*, O_2 gas should be liberated but on account of overpotential of oxygen reaction at anode, preferred reaction is

$$Cl^-_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^-$$

i.e., Cl_2 gas is liberated at anode in the electrolysis of aqueous NaCl.

OR

(a) According to Faraday's first law of electrolysis,

mass of substance deposited $\propto$ quantity of electricity passed

$$\Rightarrow W = ZQ = \frac{E}{F} \times Q \Rightarrow 2.8 = \frac{28}{96500} \times Q$$

$$\Rightarrow Q = \frac{2.8 \times 96500}{28} = 9650\ C$$

Now $Q = It \Rightarrow t = \dfrac{Q}{I} = \dfrac{9650}{2} = 4825$ s

According to Faraday's second law of electrolysis,

$$\frac{\text{Mass of Fe deposited}}{\text{Mass of Zn deposited}} = \frac{\text{Eq. wt. of Fe}}{\text{Eq. wt. of Zn}}$$

$$\Rightarrow \frac{2.8}{\text{Mass of Zn deposited}} = \frac{28}{32.65}$$

$$\Rightarrow \text{Mass of Zn deposited} = \frac{2.8}{28} \times 32.65 = 3.265\ g$$

(b) Copper ($E^\circ_{Cu^{2+}/Cu}$ = 0.34 V)is more electropositive than silver ($E^\circ_{Ag^+/Ag}$ = 0.8 V). Therefore, copper is able to displace silver from silver nitrate solution. The dissolution of copper in the solution as Cu^{2+} ions make it bluish.

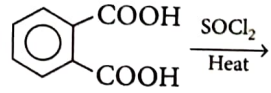
33. (a) (i) $C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2\uparrow$ (Effervescence)

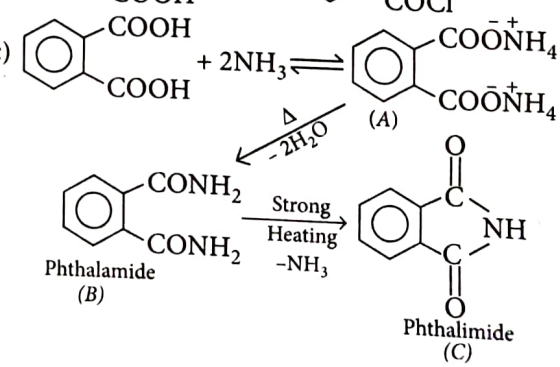
$C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow$ No reaction

(ii) Acetophenone with I_2/NaOH gives yellow precipitate of iodoform but benzophenone does not.

$C_6H_5COCH_3 + 3I_2 + 4NaOH \longrightarrow C_6H_5COONa + CHI_3\downarrow + 3NaI + 3H_2O$ (Yellow ppt.)

$C_6H_5COC_6H_5 + I_2 + NaOH \longrightarrow$ No reaction

(b) 

(c) 

OR

(a) Sodium bicarbonate test can be used to distinguish between ethanal and ethanoic acid as a brisk effervescence of CO_2 gas is observed when ethanoic acid reacts with $NaHCO_3$, whereas ethanal does not react with $NaHCO_3$.

$$CH_3COOH_{(l)} + NaHCO_{3(s)} \rightarrow CH_3COONa_{(aq)} + CO_{2(g)}\uparrow + H_2O_{(l)}$$

(b) The α-hydrogens of aldehydes and ketones are acidic in nature due to the presence of carbonyl group that has a strong electron withdrawing effect. Another reason is the resonance stabilisation of the anion formed after the removal of α-hydrogen.

(c) The given organic compound '*A*' with molecular formula, $C_4H_8O_2$ is an ester that undergoes acid hydrolysis to give carboxylic acid and alcohol.

$$\underset{\text{Ethyl acetate}\ \text{'}A\text{'}}{CH_3COOC_2H_5} + H_2O \xrightarrow[\text{Hydrolysis}]{aq.H_2SO_4} \underset{\text{'}B\text{'}}{CH_3COOH} + \underset{\text{'}C\text{'}}{C_2H_5OH}$$

$$\underset{\text{Ethanol}\ (C)}{C_2H_5OH} \xrightarrow[\text{alkaline } KMnO_4]{\text{acidified } K_2Cr_2O_7} \underset{\text{Ethanoic acid}\ (B)}{CH_3COOH}$$

Now, sodium salt of '*B*' is sodium acetate (CH_3COONa) which reacts with soda lime to give methane as shown:

$$CH_3COONa + NaOH \xrightarrow[633\ K,\ \Delta]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

(i) *A* is $CH_3COOC_2H_5$.
B is CH_3COOH.
C is C_2H_5OH.

(ii) Out of '*B*' and '*C*', *i.e.*, ethanoic acid and **ethanol, the former has a higher boiling point. Due to the formation of a dimer, the van der Waals force in carboxylic acid increases, causing an increase in the boiling point. The dimer is formed due to the presence of H-bonding between carbonyl oxygen and acidic hydrogen.**

☺☺☺