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(4)	–	1(3)	–	**11(23)**
2.	Solutions	1(1)	1(2)	–	–	
3.	Electrochemistry	1(1)	–	–	1(5)	
4.	Chemical Kinetics	2(2)	1(2)	–	–	
5.	Surface Chemistry	1(1)	1(2)	–	–	
6.	The *p*-Block Elements	2(2)	1(2)	–	1(5)	**9(19)**
7.	The *d*- and *f*-Block Elements	1(1)	1(2)	1(3)	–	
8.	Coordination Compounds	1(1)	–	1(3)	–	
9.	Haloalkanes and Haloarenes	1(1)	1(2)	1(3)	–	**13(28)**
10.	Alcohols, Phenols and Ethers	1(1)	1(2)	1(3)	–	
11.	Aldehydes, Ketones and Carboxylic Acids	2(2)	–	–	1(5)	
12.	Amines	1(4)	1(2)	–	–	
13.	Biomolecules	1(1)	1(2)	–	–	
	Total	**16(22)**	**9(18)**	**5(15)**	**3(15)**	**33(70)**

Subject Code : **043**

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)

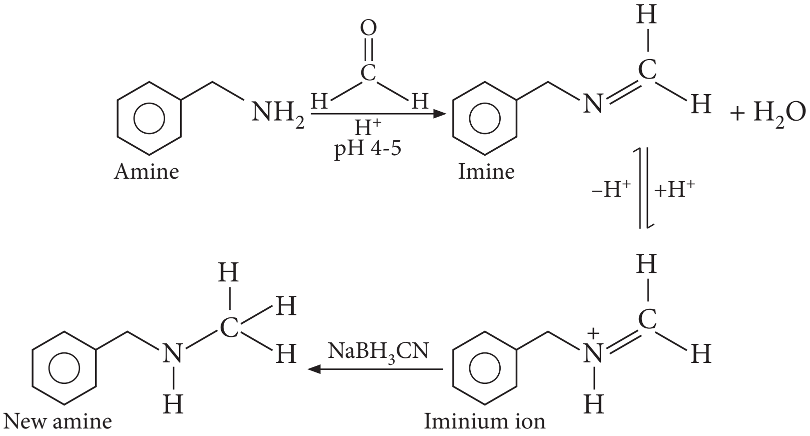
1. **Read the passage given below and answer the following questions:**

Reductive amination is a form of amination that involves the conversion of a carbonyl group to an amine via an intermediate imine. The carbonyl group is most commonly an aldehyde or a ketone. The amine reactant must have at least one α-hydrogen.

Step 1 : Formation of an imine.

Step 2 : Under acidic conditions that imine is protonated to give its conjugate acid, an iminium ion.

Step 3 : In the presence of reducing agent like $NaBH_3CN$ the imine is reduced to give a new amine.

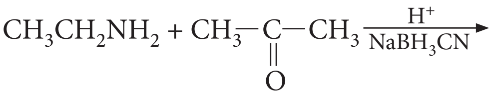


The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following compounds do not undergo reductive amination?

(a) $HCHO + CH_3NH_2$ (b) $CH_3CHO + CH_3CH_2NH_2$

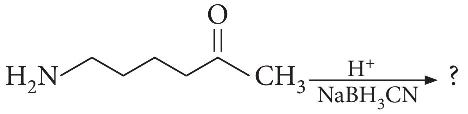
(c) $CH_3COCH_3 + CH_3NHCH_3$ (d) $CH_3COCH_3 + (CH_3)_3N$

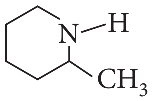
(ii) 

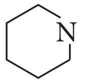
$CH_3CH_2NH_2 + CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[NaBH_3CN]{H^+}$ (*X*). Identify the incorrect statement about (*X*).

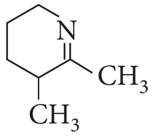
(a) It is a 3° amine.
(b) On reaction with $NaNO_2$ and HCl it gives a primary alcohol.
(c) On reaction with benzene sulphonyl chloride it gives sulphonamide which is soluble in KOH.
(d) All of these.

(iii) What will be the product in the following reaction?



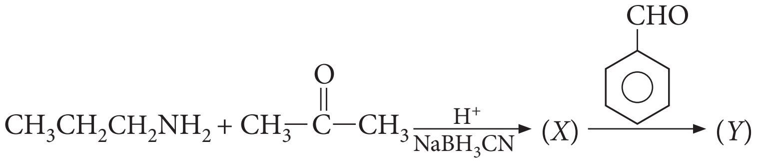
(a) 

(b) 

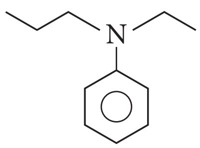
(c) 

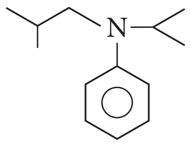
(d) None of these.

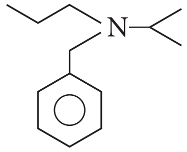
(iv) Identify the product (*Y*) in the following sequence of reactions:

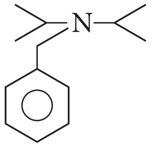


$CH_3CH_2CH_2NH_2 + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[NaBH_3CN]{H^+} (X) \longrightarrow (Y)$

(a) 

(b) 

(c) 

(d) 

OR

On reaction with ammonia in acidic medium in presence of sodiumcyanoborohydride, acetone gives an organic compound (*A*). (*A*) on warming with $CHCl_3$ and caustic soda gives (*B*) which on reduction gives (*C*). (*C*) is

(a) isopropyl methyl amine
(b) ethyl amine
(c) *N*, *N*-dimethylmethanamine
(d) *N*-methylethanamine.

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

In ionic crystals, the positive and negative ions are held together with coulombic forces. A crystal structure is determined by the ratio of ionic radii of its components. In ionic crystals, each ion is surrounded by definite number of the oppositely charged ions. The number of the nearest neighbour is the coordination number of the central ion. This number depends upon the radii of ions and radius ratio of two ions. The ratio of the radii of the positive and negative ions is called the limiting radius ratio.

For a specific structure, we can calculate the limiting radius ratio, which is minimum allowable value for the ratio of ionic radii (r^+/r^-) for the structure to be stable. On the basis of limiting radius ratio, we can say about coordination number and shape of the ionic crystal.

Limiting radius ratio	Coordination no.	Shape	Examples
0-0.155	2	Linear	–
0.155-0.225	3	Trigonal planar	B_2O_3
0.225-0.414	4	Tetrahedral	ZnS, CuCl
0.414-0.732	6	Octahedral	NaCl, MgO
0.732-1.000	8	Body-centred cubic	CsCl, TlBr

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 :** In rock salt structure, the sodium ions occupy octahedral voids.
Reason : The radius ratio r^+/r^- in case of NaCl lies between 0.225 to 0.414.

(ii) **Assertion :** In CsCl crystal, the coordination number of Cs^+ ion is 8.
Reason : Cl^- ions in CsCl adopt *bcc* type of packing.

(iii) **Assertion :** In NaCl crystal, each Na^+ ion is touching 6 Cl^- ions but these Cl^- ions do not touch each other.
Reason : The radius ratio of r_{Na^+}/r_{Cl^-} is greater than 0.414, required for exact fiting.

(iv) **Assertion :** In sodium crystal, the coordination number of Na^+ ion is six.
Reason : Sodium atom is smaller in size than chlorine atom.

OR

Assertion : The number of nearest neighbour is the coordination number of central ions.
Reason : Greater is the radius ratio, greater is the coordination number.

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

3. Find the value of λ°_{eq} for potash alum.

Given : $\lambda^\circ_{m(K^+)} = 73.5\,\Omega^{-1}\,cm^2\,mol^{-1}$, $\lambda^\circ_{m(Al^{3+})} = 189\,\Omega^{-1}\,cm^2\,mol^{-1}$, $\lambda^\circ_{m(SO_4^{2-})} = 160\,\Omega^{-1}\,cm^2\,mol^{-1}$

(a) $145.6\ \Omega^{-1}\ cm^2\ eq^{-1}$
(b) $1165\ \Omega^{-1}\ cm^2\ eq^{-1}$
(c) $532\ \Omega^{-1}\ cm^2\ eq^{-1}$
(d) $195.5\ \Omega^{-1}\ cm^2\ eq^{-1}$

OR

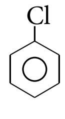
For the cell prepared from electrodes *A* and *B*;
Electrode *A* : $Cr_2O_7^{2-} \mid Cr^{3+}$, $E^\circ_{Red} = 1.33$ V and
Electrode *B* : $Fe^{3+} \mid Fe^{2+}$, $E^\circ_{Red} = 0.77$ V
Which of the following statements is correct?

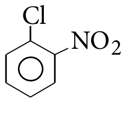
(a) The electrons will flow from *B* to *A* when connections are made.
(b) The emf of the cell will be – 0.56 V.
(c) *A* will be negative electrode.
(d) *B* will be positive electrode.

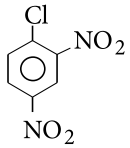
4. Which of the following pairs of ions have same paramagnetic moment ?

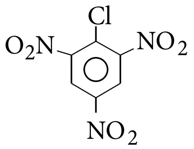
(a) Mn^{2+}, Cu^{2+}
(b) Cu^{2+}, Ti^{3+}
(c) Ti^{4+}, Cu^{2+}
(d) Ti^{3+}, Ni^{2+}

5. Which of the following aryl halides is the most reactive towards nucleophilic substitution?

(a) 

(b) 

(c) 

(d) 

OR

The number of isomeric halopropanes produced, when propane gets halogenated is

(a) 1
(b) 2
(c) 4
(d) 3

6. Identify A and B in following reaction : $H_2SO_4 + 2HI \rightarrow A + B + H_2O$.
(a) I_2, SO_3 (b) I_2, S (c) IO_3^-, SO_3 (d) I_2, SO_2

7. For the non-stoichiometric reaction, $2A + B \rightarrow C + D$, the following kinetic data was obtained in three separate experiments, all at 298 K.

	Initial concentration of A	**Initial concentration of B**	**Initial rate of formation of C (in mol L^{-1} s^{-1})**
I.	0.1 M	0.1 M	1.2×10^{-3}
II.	0.1 M	0.2 M	1.2×10^{-3}
III.	0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is
(a) $\frac{dC}{dt} = k[A]$ (b) $\frac{dC}{dt} = k[A][B]$ (c) $\frac{dC}{dt} = k[A]^2[B]$ (d) $\frac{dC}{dt} = k[A][B]^2$

8. RNA is different from DNA because RNA contains
(a) ribose sugar and thymine (b) ribose sugar and uracil
(c) deoxyribose sugar and thymine (d) deoxyribose sugar and uracil.

OR

Regarding osazone formation of glucose with three molecules of phenylhydrazine which is the correct statement?
(a) All the three molecules react in similar manner.
(b) Two molecules react in similar manner whereas the third reacts in different way.
(c) All the three molecules react in different way.
(d) Only two react in same manner but the third molecules remains unreacted.

9. The carboxylic acid which does not undergo Hell Volhard Zelinsky reaction is
(a) CH_3COOH (b) $(CH_3)_2CHCOOH$
(c) $CH_3CH_2CH_2CH_2COOH$ (d) $(CH_3)_3CCOOH$

10. A 0.01 M complex of $CoCl_3$ and NH_3 (molar ratio = 1 : 4) is found to have effective molarity of 0.02 M (evaluated from colligative property). What is the formula of the complex?
(a) $[Co(NH_3)_4Cl_2]Cl$ (b) $[Co(NH_3)_3Cl_3]$ (c) $[Co(NH_3)_4]Cl_3$ (d) $[Co(NH_3)_5Cl]Cl_2$

OR

In the complex ion ML_6^{n+}, M^{n+} has five d-electrons and L is a weak field ligand. According to crystal field theory, the magnetic properties of the complex ion correspond to how many unpaired electrons?
(a) 0 (b) 5 (c) 2 (d) 3

11. Which of the following are the starting materials for the synthesis of *tert*-butyl alcohol?
(a) $CH_3MgI + CH_3COCH_3$ (b) $CH_3MgI + CH_3CHOHCH_3$
(c) $CH_3CH_2MgBr + CH_3COCH_3$ (d) $CH_3CH_2MgBr + CH_3CHO$

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 :** Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.
Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

13. **Assertion :** The order of a reaction can be fractional but molecularity can never be fractional.
Reason : Order of a reaction does not depend upon the stoichiometric coefficients of the balanced equation.

14. **Assertion :** Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.

Reason : The reaction between nitrogen and oxygen requires high temperature.

15. **Assertion :** Acetone-aniline solution shows negative deviations.

Reason : H-bonding between acetone and aniline is stronger than that between acetone-acetone and aniline-aniline.

OR

Assertion : Azeotropic mixtures are formed only by non-ideal solutions and they may have boiling points either greater than both the components or lesser than both the components.

Reason : The composition of the vapour phase is same as that of the liquid phase of an azeotropic mixture.

16. **Assertion :** For arsenic sulphide sol, $BaCl_2$ has higher coagulation value than NaCl.

Reason : Higher the valency of the oppositely charge ion of the electrolyte added, higher is the coagulating power of the electrolyte.

SECTION - B

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

17. (i) Complete the following reaction : $XeF_6 + KF \longrightarrow$

(ii) Draw the structure of XeF_4 and predict its shape.

18. Give reasons for the following :

(i) $E^\circ_{M^{2+}/M}$ values are not regular for first row transition metals (3*d*-series).

(ii) Although 'F' is more electronegative than 'O', the highest fluoride of Mn is MnF_4, whereas the highest oxide is Mn_2O_7.

OR

Mention the direct consequence of the following factors on the chemical behaviour of the transition elements:

(i) They have incompletely filled *d*-orbitals in the ground state or in one of the oxidised states of their atoms.

(ii) They contribute more valence electrons per atom in the formation of metallic bonds.

19. Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing

(a) 1.2% sodium chloride solution?

(b) 0.4% sodium chloride solution?

20. (i) Of the two bromoderivatives, $C_6H_5CH(CH_3)Br$ and $(C_6H_5)_2CHBr$, which one is more reactive towards S_N1 substitution reaction and why?

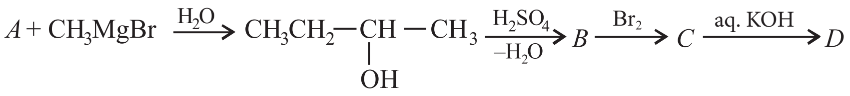
(ii) Give a chemical test to distinguish between C_2H_5Br and C_6H_5Br.

21. Rate constant, *k* for a first order reaction has been found to be $2.54 \times 10^{-3}\ sec^{-1}$. Calculate its 3/4th life. (log 4 = 0.6020)

OR

A first order reaction has $k = 1.5 \times 10^{-6}$ per second at 240°C. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed to products?

22. Write the structural formulae of *A*, *B*, *C* and *D* in the following sequence of reactions.



$$A + CH_3MgBr \xrightarrow{H_2O} CH_3CH_2\!-\!\underset{\displaystyle OH}{\underset{|}{CH}}\!-\!CH_3 \xrightarrow[-H_2O]{H_2SO_4} B \xrightarrow{Br_2} C \xrightarrow{aq.\ KOH} D$$

23. For the coagulation of 100 mL of arsenious sulphide sol, 5 mL of 1 M NaCl is required. What is the flocculation value of NaCl?

24. (a) If one strand of a DNA has the sequences – ATGCTTCA – what is the sequence of the bases in the complementary strand?

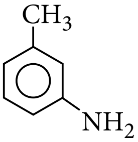
(b) What anticodon sequences of *t*RNAs are coded for by the *m*RNA with the following base sequence?
CUU – AUG – GCU – UGG – CCC – UAA

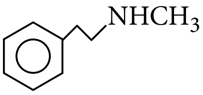
25. (i) Write short note on carbylamine reaction.

(ii) How will you convert ethanoic acid into methanamine?

OR

(a) Give the IUPAC names of the following compounds :

(i) 

(ii) 

(b) Arrange the following in the increasing order of their boiling points : $C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$

SECTION - C

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

26. By X-ray diffraction methods, the unit length of NaCl is observed to be 0.5627 nm. The density of NaCl is found to be 2.164 g cm^{-3}. What type of defect exists in the crystal? Calculate the percentage of Na^+ and Cl^- ions missing.

27. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory :
(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$

OR

(i) Co^{2+} is easily oxidised to Co^{3+} in presence of a strong field ligand. Give reason.

(ii) On the basis of crystal field theory, write the electronic configuration of d^4 ion if $\Delta_o < P$.

28. Give reasons for the following :

(i) Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.

(ii) (±)-2-butanol is optically inactive.

(iii) $C—X$ bond length in halobenzene is smaller than $C—X$ bond length in $CH_3—X$.

29. How are the following conversions carried out?

(i) Benzyl chloride to Benzyl alcohol

(ii) Ethyl magnesium chloride to Propan-1-ol

(iii) Propene to Propan-2-ol

OR

(a) How is toluene obtained from phenol?

(b) When *tert*-butanol and *n*-butanol are separately treated with a few drops of dil. $KMnO_4$ in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate?

30. (i) Out of Cu_2Cl_2 and $CuCl_2$, which is more stable and why?

(ii) What are different oxidation states exhibited by lanthanoids?

SECTION - D

Q. No. 31-33 are long answer type carrying 5 marks each.

31. (i) Find the solubility product of Ag_2CrO_4 in water at 298 K if the e.m.f. of the cell $Ag|Ag^+$ (saturated Ag_2CrO_4 soln.)$||Ag^+$ (0.1 M)$|Ag$ is 0.164 V at 298 K.

(ii) Define molar conductivity of a substance and describe how for weak and strong electrolytes, molar conductivity changes with concentration of solute. How is such change explained?

OR

(i) Calculate the standard cell potential of a galvanic cell in which the following reaction takes place :

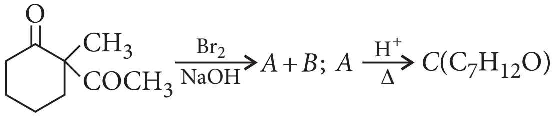
$2Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Cd_{(s)}$

Calculate $\Delta_r G^\circ$ and equilibrium constant, K of the above reaction at 25°C.

[Given : $E^\circ_{Cr^{3+}/Cr} = -0.74$ V, $E^\circ_{Cd^{2+}/Cd} = -0.40$ V, $F = 96{,}500$ C mol^{-1}]

(ii) The specific conductance of a saturated solution of AgCl at 298 K is found to be 1.386×10^{-6} S cm^{-1}. Calculate its solubility in g L^{-1}. ($\lambda^\circ_{Ag^+} = 62.0$ S $cm^2 mol^{-1}$ and $\lambda^\circ_{Cl^-} = 76.3$ S cm^2 mol^{-1})

32. (i) Identify A, B and C and give their structures.



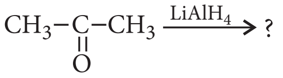
(ii) Write the equations involved in the following reactions :

(a) Stephen reaction (b) Etard reaction

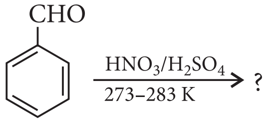
OR

(i) An organic compound (A) having molecular formula, C_2H_4O reduces Tollens' reagent. Two moles of (A) react with $Al(OC_2H_5)_3$ to yield $C_4H_8O_2$ (B) which reacts with NH_3 to give C_2H_6O (C) and C_2H_5NO (D). Identify A, B, C and D.

(ii) Write the main product in the following equations :

(a) 

$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} ?$

(b) 

33. (i) An amorphous solid 'A' burns in air to form a gas 'B' which turns lime water milky. The gas is also produced as a by-product during roasting of sulphide ore. This gas decolourises acidified aqueous $KMnO_4$ solution and reduces Fe^{3+} to Fe^{2+}. Identify the solid 'A' and the gas 'B' and write the reactions involved.

(ii) H_2S acts only as a reducing agent but SO_2 acts as a reducing as well as oxidising agent. Why?

OR

(i) Draw the structure of

(a) H_2SO_3 (b) H_2SO_4 (c) $H_2S_2O_7$

(ii) Account for the following :

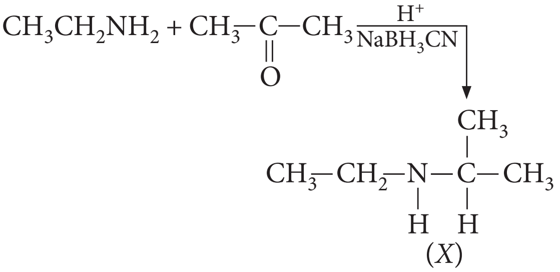
(a) H_2S has lower boiling point than H_2O.

(b) Reducing character decreases from SO_2 to TeO_2.

SOLUTIONS

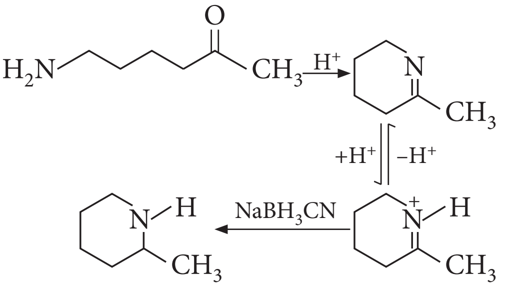
1. (i) (d) : For reductive amination, the reactant amine must have at least one hydrogen at atom attached to N, 3° amines do not react.

(ii) (d) :



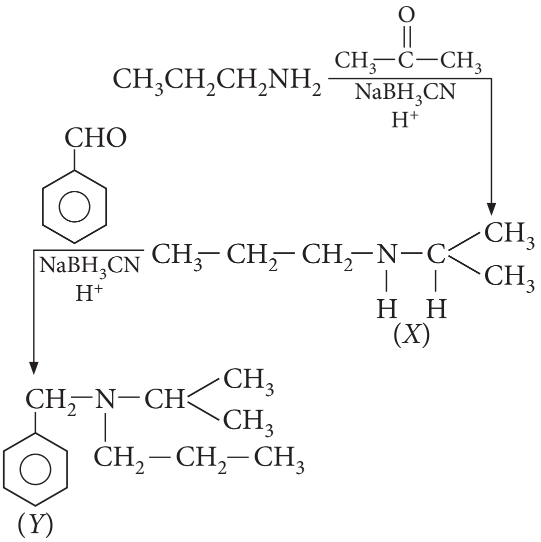
It is a 2° amine. Secondary amines react with $NaNO_2$ and HCl to give *N*-nitrosomine as oily yellow compound. Secondary amines react with benzene sulphonyl chloride to give *N*, *N*-dialkyl benzene sulphonamide which is insoluble in KOH.

(iii) (a) :



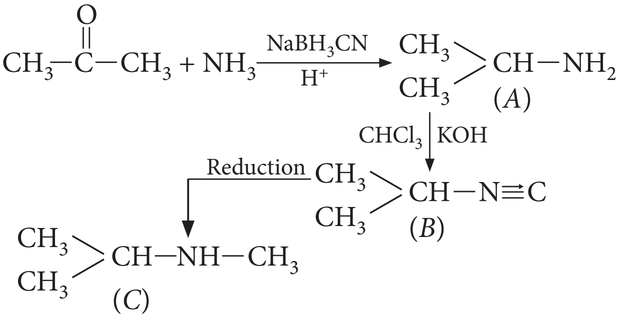
It is an example of intramolecular reductive amination.

(iv) (c) :



OR

(a) :



Isopropylmethylamine

2. (i) (c) : In rock salt structure, the sodium ions occupy octahedral voids. For octahedral voids, r^+/r^- is 0.414-0.732.

(ii) (a)

(iii) (a)

(iv) (b) : Each Na^+ ion is surrounded by six Cl^- ion.

OR

(b)

3. (a) : $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \rightarrow 2K^+_{(aq)} + 2Al^{3+}_{(aq)} + 4SO^{2-}_{4(aq)}$

$$\overset{\circ}{\Lambda}_{m(\text{Potash alum})} = 2\overset{\circ}{\lambda}_{m(K^+)} + 2\overset{\circ}{\lambda}_{m(Al^{3+})} + 4\overset{\circ}{\lambda}_{m(SO_4^{2-})}$$

$= 2 \times 73.5 + 2 \times 189 + 4 \times 160 = 1165\ \Omega^{-1}\ cm^2\ mol^{-1}$

Valency factor for potash alum = 8 (total positive charge)

$$\overset{\circ}{\Lambda}_{eq(\text{Potash alum})} = \frac{\overset{\circ}{\Lambda}_{m\ (\text{Potash alum})}}{8} = \frac{1165}{8}$$

$$= 145.6\ \Omega^{-1}\ cm^2\ eq^{-1}$$

OR

(a) : In an electrochemical cell the one which is having higher reduction potential acts as anode and the one with lower reduction potential acts as cathode.

Here, *A* : $Cr_2O_7^{2-}/Cr^{3+}$ acts anode and *B* : Fe^{3+}/Fe^{2+} acts as cathode.

So, the electrons will flow from cathode to anode *i.e.*, from *B* to *A*.

We know that, $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= 1.33 - 0.77 = 0.56$ V

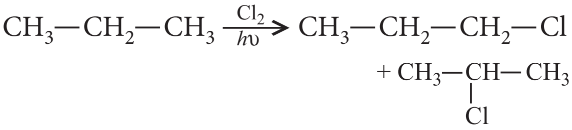
As, *A* is cathode and hence is a positive electrode.

4. (b) : Cu^{2+} and Ti^{3+}, both have one unpaired electron.

5. **(d) :** When in aryl halides, the electron withdrawing groups are attached at *ortho* and *para* positions to the chlorine atom then the removal of chlorine atom as Cl^- ion becomes easy therefore 2, 4, 6-trinitro chlorobenzene is the most reactive among given aryl halides.

OR

(b) :



$$CH_3-CH_2-CH_3 \xrightarrow[h\nu]{Cl_2} CH_3-CH_2-CH_2-Cl + CH_3-\underset{Cl}{CH}-CH_3$$

6. **(d) :** $H_2SO_4 + 2HI \rightarrow I_2 + SO_2 + 2H_2O$

7. **(a) :** $\dfrac{dC}{dt} = k[A]^a[B]^b$

$1.2 \times 10^{-3} = k(0.1)^a(0.1)^b$ ...(i)

$1.2 \times 10^{-3} = k(0.1)^a(0.2)^b$ ...(ii)

$2.4 \times 10^{-3} = k(0.2)^a(0.1)^b$ ...(iii)

Divide eq. (i) by eq. (ii), we get

$1 = (2)^b \quad \therefore \quad (2)^0 = (2)^b \quad \therefore \quad b = 0$

Divide eq. (i) by eq. (iii), we get, $(2) = (2)^a$

$a = 1$

Thus, order w.r.t. $A = 1$ and w.r.t. $B = 0$

$$\therefore \quad \frac{dC}{dt} = k[A][B]^0 = k[A]$$

8. **(b)**

OR

(b) : In osazone formation first phenylhydrazine molecule forms hydrazone at C – 1; second phenyl-hydrazine molecule oxidises the —CHOH group to carbonyl and third phenylhydrazine molecule forms hydrazone with C – 2.

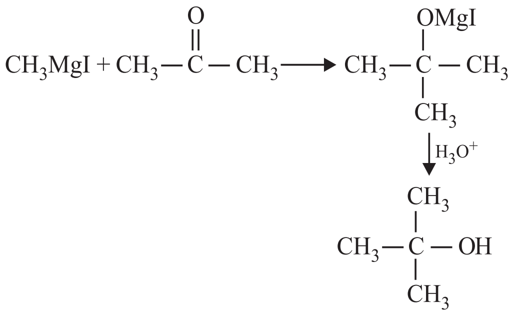
9. **(d) :** The acid does not contain α-hydrogen atom.

10. **(a) :** $$\underset{0.01\ M}{[Co(NH_3)_4Cl_2]Cl} \longrightarrow \underbrace{\underset{0.01\ M}{[Co(NH_3)_4Cl_2]^+} + \underset{0.01\ M}{Cl^-}}_{0.02\ M}$$

OR

(b)

11. **(a) :**



$$CH_3MgI + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{OMgI}{C}}-CH_3 \xrightarrow{H_3O^+} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

(*tert*-butyl alcohol)

12. **(c) :** Aromatic aldehydes and formaldehyde do not contain α-hydrogen and thus undergo Cannizzaro reaction. Formaldehyde is more reactive than aromatic aldehydes.

13. **(a)**

14. **(a) :** Dinitrogen and dioxygen combine to form nitric oxide when the mixture is heated to 2273–3273 K in an electric arc.

15. **(a)**

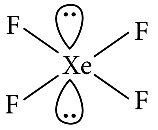
OR

(b) : Non-ideal solutions with positive deviation *i.e.*, having more vapour pressure than expected, boil at lower temperature while those with negative deviation boil at higher temperature than those of the components.

16. **(d) :** For negatively charged As_2S_3 sol, $BaCl_2$ has lower coagulation value (or higher coagulating power) than NaCl.

17. (i) $XeF_6 + KF \longrightarrow K^+[XeF_7]^-$

(ii)



XeF_4

Shape : Square planar

18. (i) The $E^\circ_{M^{2+}/M}$ values are not regular which can be explained from the irregular variation of ionisation enthalpies (*i.e.*, $IE_1 + IE_2$) and the sublimation enthalpies.

(ii) Manganese can form *p*π-*d*π 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*π - *d*π bond thus, it can show a maximum of +4 oxidation state.

OR

(i) Vacant *d*-orbitals can accept lone pair of electrons donated by other groups (ligands), consequently transition elements form a large number of complex compounds. Paramagnetism and colour of compound is also due to incompletely filled *d*-orbital.

(ii) Due to the large number of valence electrons per atom, the metallic bonds in transition elements are quite strong. Due to the presence of strong metallic bonds the transition metals are hard, possess high densities and high enthalpies of atomisation.

19. (a) 1.2% sodium chloride solution is hypertonic with respect to 0.9% sodium chloride solution or blood cells thus, on placing blood cells in this solution exosmosis takes place that results in shrinking of cells.

(b) 0.4% sodium chloride solution is hypotonic with respect to 0.9% sodium chloride solution or blood cells thus, on placing blood cells in this solution endosmosis takes place that results in swelling of cells.

20. (i) Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and$(C_6H_5)_2CHBr$, the $(C_6H_5)_2CHBr$ is more reactive than $C_6H_5CH(CH_3)Br$ towards S_N1 reaction because its carbocation is resonance stabilised by two phenyl groups.
(ii) C_2H_5Br reacts with $AgNO_3$ to give yellow precipitate of AgBr while C_6H_5Br will not.

21. The integrated rate equation for first order reaction is

$$k=\frac{2.303}{t}\log\frac{a}{a-x}\Rightarrow k=\frac{2.303}{t}\log\frac{a}{a-\frac{3}{4}a}$$

$$\Rightarrow\quad k=\frac{2.303}{t}\log\frac{a}{0.25a}$$

$$t_{3/4}=\frac{2.303}{2.54\times10^{-3}\ \text{sec}^{-1}}\times\log\frac{1}{0.25}=546\ \text{s}$$

Therefore, the 3/4th life of the reaction is 546 seconds.

OR

For the first order reaction: $k=\frac{2.303}{t}\log\frac{[A]_0}{[A]}$

Let the initial concentration is 1 mol litre^{-1} and x moles of the reactants have changed to products so that $[A]_0 = 1$ and $[A] = 1 - x$

$k = 1.5 \times 10^{-6}$, t = 10 hrs = 10 × 60 × 60 = 36000 s

Substituting the values,

$$1.5\times10^{-6}=\frac{2.303}{36000}\log\frac{1}{1-x}$$

$$\text{or}\quad \log\frac{1}{1-x}=\frac{1.5\times10^{-6}\times36000}{2.303}$$

$$\text{or}\quad \log\frac{1}{1-x}=0.0234$$

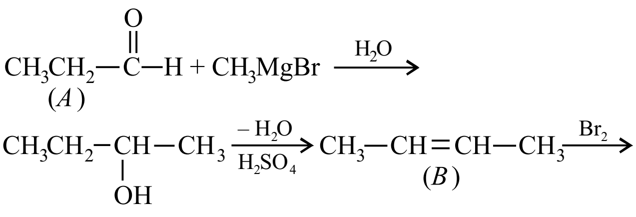
Taking antilogarithm, $\frac{1}{1-x}=1.055$

$$1.055-1.055\,x=1$$

$$\text{or}\quad x=\frac{1.055-1}{1.055}=0.052$$

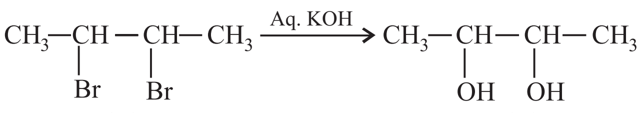
Thus, 5.2% of the initial concentration has changed to products.

22. The given reaction will be as :



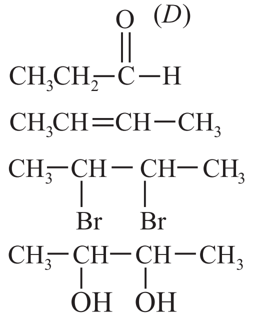
$$\underset{(A)}{CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H}+CH_3MgBr\xrightarrow{H_2O}$$

$$CH_3CH_2-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3\xrightarrow[H_2SO_4]{-H_2O}\underset{(B)}{CH_3-CH=CH-CH_3}\xrightarrow{Br_2}$$



$$\underset{(C)}{CH_3-\underset{\underset{\displaystyle Br}{|}}{CH}-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3}\xrightarrow{\text{Aq. KOH}}\underset{(D)}{CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3}$$

Structural formula of



A : $CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

B : $CH_3CH=CH-CH_3$

C : $CH_3-\underset{\underset{\displaystyle Br}{|}}{CH}-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3$

D : $CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$

23. 5 mL of 1 M NaCl contains NaCl

$$=\frac{1}{1000}\times5\ \text{moles}=5\ \text{millimoles}$$

Thus, 100 mL of As_2S_3 sol require NaCl for complete coagulation = 5 millimoles

∴ 1 L, *i.e.*, 1000 mL of the sol require NaCl for complete coagulation = 50 millimoles

∴ By definition, flocculation value of NaCl = 50

24. (a) We know that in DNA molecule, adenine (A) always pairs with thymine (T) and cytosine (C) always pairs with guanine (G). Thus

Sequence of bases in one strand : A T G C T T C A

∴ Sequence of bases in the complementary strand : T A C G A A G T

(b) Codon sequences in *m*RNA :

CUU – AUG – GCU – UGG – CCC – UAA

Since anticodon sequence of *t*RNA are complementary to the codon sequences on *m*RNA.

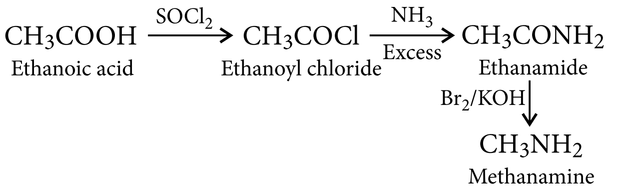
∴ Anticodon sequence of *t*RNAs :

GAA – UAC – CGA – ACC – GGG – AUU

25. (i) Carbylamine reactions : Aliphatic and aromatic primary amines on heating with chloroform and alcoholic potassium hydroxide form isocyanides or carbyl amines which are foul smelling substances. Secondary and tertiary amines do not show this reaction.

$$R\text{—}NH_2+CHCl_3+3KOH\xrightarrow{\text{Heat}}\underset{\substack{\text{Carbylamine}\\\text{(foul smell)}}}{R\text{—}NC}+3KCl+3H_2O$$

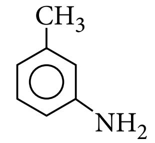
(ii) Ethanoic acid into methanamine :



$$\underset{\text{Ethanoic acid}}{CH_3COOH}\xrightarrow{SOCl_2}\underset{\text{Ethanoyl chloride}}{CH_3COCl}\xrightarrow[\text{Excess}]{NH_3}\underset{\text{Ethanamide}}{CH_3CONH_2}\xrightarrow{Br_2/KOH}\underset{\text{Methanamine}}{CH_3NH_2}$$

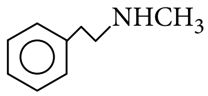
OR

(a) (i)



m-Toluidine or
3-Methylbenzenamine

(ii)



N-methyl-2-phenylethanamine

(b) Increasing order of boiling points :

$(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$

Tertiary amine does not have hydrogen to form hydrogen bonding and hydrogen bonding in alcohol is stronger than that of primary amines because oxygen is more electronegative than nitrogen.

26. Calculated density, $\rho = \dfrac{Z \times M}{a^3 \times N_0}$

$$= \frac{4 \times 58.5 \text{ g mol}^{-1}}{(0.5627 \times 10^{-7} \text{ cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$= 2.1809 \text{ g cm}^{-3}$

Observed density = 2.164 g cm^{-3}

As observed density is less than theoretically calculated value, this means that some Na^+ and Cl^- ions are missing from their lattice sites, *i.e.*, there is Schottky defect.

Actual formula units of NaCl per unit cell can be calculated as follows :

$$Z = \frac{a^3 \times \rho \times N_0}{M}$$

$$= \frac{(0.5627 \times 10^{-7} \text{ cm})^3 \times (2.164 \text{ g cm}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})}{58.5 \text{ g mol}^{-1}}$$

$= 3.968$

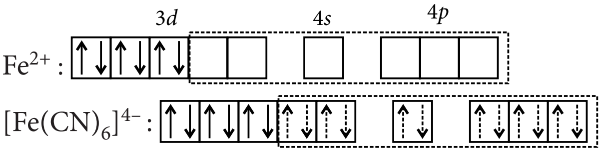
∴ Formula units missing per unit cell $= 4 - 3.968$
$= 0.032$

∴ % of Na^+ and Cl^- ions missing $= \dfrac{0.032}{4} \times 100 = 0.8\%$

27. (i) $[Fe(CN)_6]^{4-}$: Fe(26) : [Ar] $3d^6 4s^2$,

Fe^{2+} : [Ar] $3d^6 4s^0$

CN^- ion causes pairing of electrons because it is a strong field ligand.



d^2sp^3 hybridisation

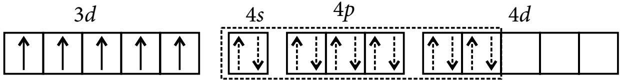
It has octahedral shape and is diamagnetic in nature due to absence of unpaired electrons.

(ii) $[FeF_6]^{3-}$: Fe(26) : [Ar] $3d^6 4s^2$,

Fe^{3+} : [Ar] $3d^5 4s^0$

F^- being a weak field ligand, does not cause pairing of electrons.

$[FeF_6]^{3-}$

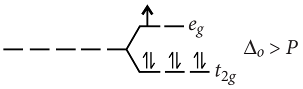


sp^3d^2 hybridisation, octahedral shape

It is paramgnetic in nature.

OR

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



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

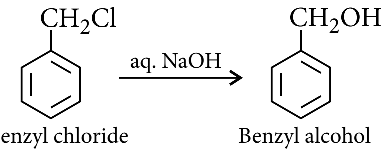
(ii) For d^4 ion, if $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\ e_g^1$.

28. (i) Iodide is a better leaving group because of its larger size than bromide, therefore, ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.

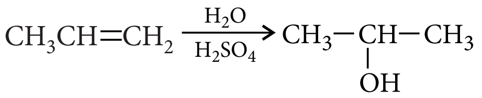
(ii) (±) –2-butanol is a racemic mixture. It is a mixture which contains two enantiomers in equal proportion and thus, have zero optical rotation due to internal compensation. Therefore, it is optically inactive.

(iii) In halobenzenes (like chlorobenzene), the lone pair of electrons on halogen atom is delocalised on the benzene ring. As a result, C—*X* bond (C—Cl bond in case of chlorobenzene) acquires some double bond character while in $CH_3—X$, C—*X* bond is a pure single bond. Therefore, C—*X* bond in halobenzene is shorter than that in $CH_3—X$.

29. (i)



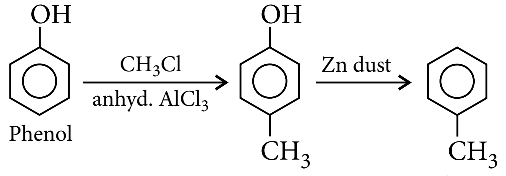
(ii) $\underset{\text{Ethyl magnesium chloride}}{CH_3-CH_2MgCl} + H-\overset{\overset{\Large O}{||}}{C}-H \xrightarrow{\text{Dry ether}} CH_3-CH_2-CH_2-OMgCl \xrightarrow{H_3O^+} \underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-OH}$

(iii) 

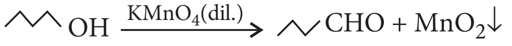
$$CH_3CH{=}CH_2 \xrightarrow[H_2SO_4]{H_2O} CH_3{-}\underset{\underset{OH}{|}}{C}H{-}CH_3$$

Propan-2-ol

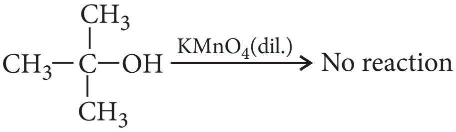
OR

(a) 

Phenol (Major) Toluene

(b) 

n-Butanol Brown precipitate



$$CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH \xrightarrow{KMnO_4(dil.)} \text{No reaction}$$

tert-Butanol

This is because 3° alcohols do not undergo oxidation reaction, under this condition.

30. (i) $CuCl_2$ is more stable than Cu_2Cl_2. Cu^{2+} is more stable than Cu^+ due to the higher negative $\Delta_{hyd}H°$ value of $Cu^{2+}_{(aq)}$ than $Cu^+_{(aq)}$.

(ii) Lanthanum and all the lanthanoids predominantly show +3 oxidation state. However, some of the lanthanoids also show +2 and +4 oxidation states due to attainment of stable empty ($4f^0$), half-filled ($4f^7$) and fully filled ($4f^{14}$) sub shell.

e.g. $Ce^{4+} : 4f^0$, $Eu^{2+} : 4f^7$

$Tb^{4+} : 4f^7$, $Yb^{2+} : 4f^{14}$

31. (i) The cell is $Ag|Ag^+(c_1)||Ag^+(0.1\ M)|Ag$

$$E_{cell} = \frac{0.0591}{n}\log\frac{c_2}{c_1} \qquad \text{(for concentration cell)}$$

$$0.164 = \frac{0.0591}{1}\log\frac{0.1}{c_1} \text{ or } \log\frac{0.1}{c_1} = 2.7750$$

or $0.1/c_1 = 5.957 \times 10^2$ or $c_1 = 1.679 \times 10^{-4}$

i.e., $[Ag^+]$ in saturated Ag_2CrO_4 solution $= 1.679 \times 10^{-4}$ M

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

$[Ag^+] = 1.679 \times 10^{-4}$ M,

$$[CrO_4^{2-}] = \frac{[Ag^+]}{2} = \frac{1.679\times10^{-4}}{2}\text{M}$$

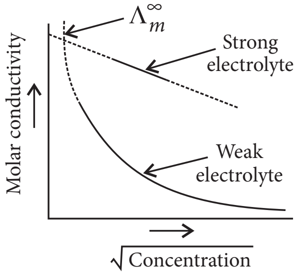
$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$= (1.679\times10^{-4})^2 \times \left(\frac{1.679\times10^{-4}}{2}\right) = 2.37\times10^{-12}$$

(ii) Molar conductivity : It is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.

Strong electrolyte : The molar conductivity of strong electrolyte decreases slightly with the increase in concentration. There are strong forces of attraction between the ions of opposite charges due to which the conducting ability of the ions is less in concentrated solutions. With dilution the ions are far apart, interionic attractions become weaker and conductance increases.

Weak electrolyte : When the concentration of weak electrolyte becomes very low, its degree of ionisation rises sharply. There is sharp increase in the number of ions in the solution. Hence the molar conductivity of a weak electrolyte rises steeply at low concentration.



OR

(i) $T = 273 + 25°C = 298$ K and $n = 6$

$E°_{cell} = E°_{cathode} - E°_{anode} = -0.40\ V - (-0.74)\ V = 0.34\ V$

$\Delta_r G° = -nFE°_{cell} = -6 \times 96500 \times 0.34 = -196860\ J\ mol^{-1}$

Again $\Delta_r G° = -2.303\ RT \log K$

$\Rightarrow \quad -196860 = -2.303 \times 8.314 \times 298 \times \log K$

$\Rightarrow \quad \log K = 34.5014$

$\therefore \quad K = \text{antilog } 34.5014 = 3.172 \times 10^{34}$

(ii) $\Lambda°_{m(AgCl)} = \lambda°_{(Ag^+)} + \lambda°_{(Cl^-)} = 62.0 + 76.3$

$= 138.3\ S\ cm^2\ mol^{-1}$

$\kappa = 1.386 \times 10^{-6}\ S\ cm^{-1}$

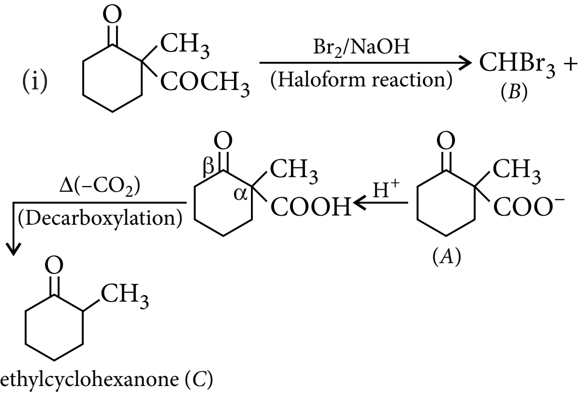
$$\Lambda°_m = \frac{\kappa\times1000}{M} = \frac{\kappa\times1000}{\text{Solubility}}$$

$$\text{Solubility} = \frac{\kappa\times1000}{\Lambda°_m} = \frac{1.386\times10^{-6}\times1000}{138.3}$$

$= 1.0 \times 10^{-5}\ mol\ L^{-1}$

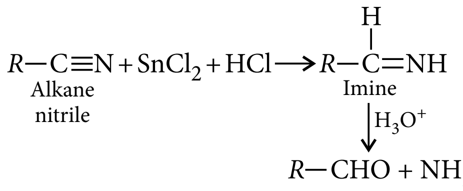
$= 1.0 \times 10^{-5} \times 143.5\ g\ L^{-1}$

$= 1.435 \times 10^{-3}\ g\ L^{-1}$

32. (i) 

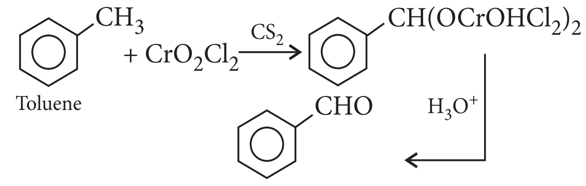
2-Methylcyclohexanone (*C*)
M.F. = $C_7H_{12}O$

(ii) (a)



$$\underset{\text{Alkane nitrile}}{R{-}C{\equiv}N} + SnCl_2 + HCl \longrightarrow \underset{\text{Imine}}{R{-}\overset{\overset{H}{|}}{C}{=}NH} \xrightarrow{H_3O^+} R{-}CHO + NH_3$$

(b)



Toluene

Benzaldehyde

OR

(i) Since compound (*A*) with M.F. C_2H_4O reduces Tollens' reagent, it must be an aldehyde, *i.e.*, acetaldehyde (CH_3CHO).

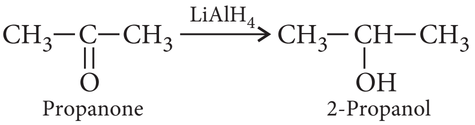
$$\underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \rightarrow CH_3COO^- + 2Ag\downarrow + 4NH_3 + 2H_2O$$

In presence of $Al(OC_2H_5)_3$, aldehydes undergo Tischenko reaction to give esters. Thus, when two moles of acetaldehyde (CH_3CHO) react in presence of $Al(OC_2H_5)_3$, ethyl acetate (*B*) with M.F. $C_4H_8O_2$ is produced.

$$\underset{\text{Acetaldehyde }(A)}{2CH_3CHO} \xrightarrow[\text{(Tischenko reaction)}]{Al(OC_2H_5)_3} \underset{\text{Ethyl acetate }(B)}{CH_3COOCH_2CH_3}$$

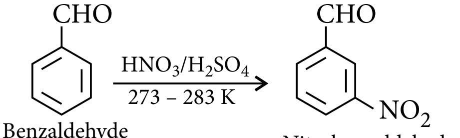
$$\underset{\text{Ethyl acetate }(B)}{CH_3COOCH_2CH_3} \xrightarrow{NH_3} \underset{\text{Ethyl alcohol }(C)}{CH_3CH_2OH} + \underset{\text{Acetamide }(D)}{CH_3CONH_2}$$

(ii) (a)



$$\underset{\text{Propanone}}{CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3} \xrightarrow{LiAlH_4} \underset{\text{2-Propanol}}{CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_3}$$

(b)



Benzaldehyde

m-Nitrobenzaldehyde

33. (i) '*A*' is S_8 and '*B*' gas formed is SO_2.

In air, $\underset{(A)}{S_8} + 8O_2 \xrightarrow{\Delta} \underset{(B)}{8SO_2}$

$$SO_2 + \underset{\text{Lime water}}{Ca(OH)_2} \rightarrow \underset{\text{Milky}}{CaSO_3\downarrow} + H_2O$$

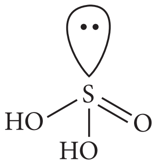
$$\underset{\text{Violet}}{2MnO_4^-} + 5SO_2 + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + \underset{\text{Colourless}}{2Mn^{2+}}$$

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

(ii) Sulphur shows oxidation states – 2, + 2, + 4, + 6. The oxidation number of S in H_2S is – 2 while in SO_2 is + 4. In H_2S, it can only increase oxidation number by losing electrons and hence, acts as a reducing agent. On the other hand, in SO_2, it can increase or decrease its oxidation number by losing or gaining electrons. So, it acts both as reducing as well as oxidising agent.

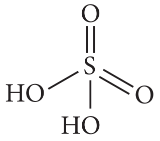
OR

(i) (a)



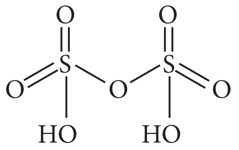
Sulphurous acid (H_2SO_3)

(b)



Sulphuric acid (H_2SO_4)

(c)



Pyrosulphuric acid (oleum) ($H_2S_2O_7$)

(ii) (a)

	H_2O		H_2S
Boiling point :	373 K	>	213 K

The abnormally high boiling point of H_2O is due to strong intermolecular H-bonding. Since, all other elements of group-16 have much lower electronegativity than oxygen, they do not form H-bonding. However, since the atomic size increases regularly from O to Te, therefore, van der Waal's forces increase with increase in molecular size and hence the boiling point increases gradually from H_2S to H_2Te.

(b) The +6 oxidation state of S is more stable than +4 therefore, 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, TeO_2 acts as an oxidising agent.

☺☺☺