



Name	:	_____
Date of Exam.	:	_____
Duration	:	<b>3 hours</b>
Max. Marks	:	<b>80</b>
Study Centre	:	_____

# Chemistry

## INSTRUCTIONS TO TEST TAKERS

- a) There are 35 questions in this question paper with internal choice.
- b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.
- c) SECTION B consists of 7 very short answer questions carrying 2 marks each.
- d) SECTION C consists of 5 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



## Chemistry

## 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.

Q1. The boiling point of an azeotropic mixture of water and ethanol is less than that of water and ethanol. The mixture shows

- (a) No deviation from Raoult's Law.
- (b) Positive deviation from Raoult's Law.
- (c) Negative deviation from Raoult's Law.
- (d) That the solution is unsaturated.

Q2. Which has the lowest boiling point at 1 atm pressure?

- (a) 0.1 M KCl
- (b) 0.1 M Urea
- (c) 0.1 M  $\text{CaCl}_2$
- (d) 0.1 M  $\text{AlCl}_3$

Q3. Standard solution of  $\text{KNO}_3$  is used to make a salt bridge because

- (a) Velocity of  $\text{K}^+$  is greater than that of  $\text{NO}_3^-$
- (b) Velocity of  $\text{NO}_3^-$  is greater than that of  $\text{K}^+$ .
- (c) Velocity of both  $\text{K}^+$  and  $\text{NO}_3^-$  are nearly same
- (d)  $\text{KNO}_3$  is highly soluble in water.

Q4. Galvanised iron sheets are coated with:

- (a) Carbon
- (b) Copper
- (c) Zinc
- (d) Nickel

Q5. In chemical equation  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  the equilibrium constant  $K_p$  depends on:

- (a) Total pressure
- (b) Catalyst used
- (c) Amount of  $\text{H}_2$  and  $\text{I}_2$
- (d) Temperature

Q6. A reaction in which reactants (R) are converted into products (P) follows second order kinetics. If concentration of R is increased by four times, what will be the increase in the rate of formation of P?

- (a) 9 times
- (b) 4 times
- (c) 16 times
- (d) 8 times

Q7. In which of the following pairs, both the ions are coloured in aqueous solutions?

- (a)  $\text{Sc}^{3+}$ , Ti
- (b)  $\text{Sc}^{3+}$ ,  $\text{Co}^{2+}$
- (c)  $\text{Ni}^{2+}$ ,  $\text{Cu}^+$
- (d)  $\text{Ni}^{2+}$ ,  $\text{Ti}^{3+}$

[Atomic no of Sc = 21, Ti = 22, Ni = 28, Co = 27, Cu = 29]

Q8. The number of moles of  $\text{KMnO}_4$  that will be needed to react with one mole of  $\text{SO}_3^{2-}$  in acidic solution are:

- (a) 1



- (b) 3/5
- (c) 4/5
- (d) 2/5

Q9. Which of the following is the coordination entity in  $K_2[Zn(OH)_4]$ ?

- (a)  $K^+$
- (b)  $Zn^{2+}$
- (c)  $OH^-$
- (d)  $[Zn(OH)_4]^{2-}$

Q10. When chlorine is passed through propene at  $400^\circ C$ , which of the following is formed?

- (a) PVC
- (b) Allyl chloride
- (c) Propyl chloride
- (d) 1,2-Di-chloroethane

Q11. Two possible stereo-structures of  $CH_3CHOHCOOH$ , which are optically active are called:

- (a) Atropisomers
- (b) Enantiomers
- (c) Mesomers
- (d) Diastereomers

Q12. The heating of phenyl methyl ether with HI produces:

- (a) Iodobenzene
- (b) Phenol
- (c) Benzene
- (d) Ethyl chloride

Q13. Among the following sets of reactants which one produces anisole?

- (a)  $CH_3CHO$ ;  $RMgX$
- (b)  $C_6H_5OH$ ;  $NaOH$ ,  $CH_3I$
- (c)  $C_6H_5OH$ , neutral  $FeCl_3$
- (d)  $C_6H_5-CH_3$ ;  $CH_3COCl$ ;  $AlCl_3$

Q14. Compound which is used for separation of acetone and acetophenone:

- a) Sodium bisulphate
- b) Grignard reagent
- c) Sodium sulphate
- d) Ammonium chloride

Q15. The polar nature of carbonyl group in aldehydes and ketones is due to:

- a) Very less electronegative difference
- b) Very large electronegative difference
- c) Presence of hydrogen bonding
- d) Presence of  $sp$  hybridised characters in carbonyl compound

Q16. The amine formed from an amide by means of bromine and alkali has how many number of carbon atoms?

- a) Same number of C atoms as that of amide
- b) One less C atom than that of amide
- c) One more C atom than that of amide
- d) Two more C atoms than that of amide



Q17. Ethylamine can be prepared by the action of bromine and caustic potash on which compound?

- a) Acetamide
- b) Propionamide
- c) Formamide
- d) Methyl cyanide

Q18. On oxidation with a mild oxidising agent like  $\text{Br}_2/\text{H}_2\text{O}$ , the glucose is oxidized to:

- (a) Saccharic acid
- (b) Glucaric acid
- (c) Gluconic acid
- (d) Valeric acid

### Section B

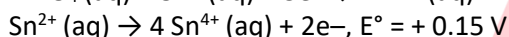
This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

Q19. Explain why on the addition of 1 mol of NaCl to 1 litre of water, the boiling point of water increases, while the addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point.

OR

Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction. Give two reasons for the same.

Q20. Two half-cell reactions of an electrochemical cell are given below:



Construct the redox equation from the two half-cell reactions and predict if this reaction favours formation of reactants or product shown in the equation.

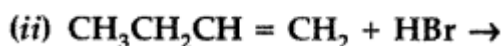
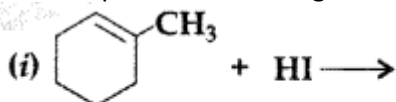
Q21. A reaction is of second order with respect to a reactant. How will the rate of reaction be affected if the concentration of this reactant is

- (i) Doubled,
- (ii) Reduced to half?

Q22. Why is the third ionization energy of Manganese (Mn) so high?

Q23. Give an example of linkage isomerism.

Q24. Complete the following reaction equations:



Q25. Ortho-nitrophenol is more acidic than Ortho-methoxyphenol. Why?

OR

Why are  $E^\circ$  values for Mn, Ni and Zn more negative than expected?

### Section C



This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each.

Q26. Explain why transition metals form colored compounds.

Q27. (i) A hydrocarbon  $C_5H_{12}$  gives only one mono-chlorination product. Identify the hydrocarbon.  
(ii) Give a chemical test to distinguish between  $C_2H_5Br$  and  $C_6H_5Br$ .

Q28. (i) Out of 2-chloroethanol and ethanol which is more acidic and why?  
(ii) Out of o-nitrophenol and p-nitrophenol, which is more volatile? Explain.

Q29. Describe how the following conversions are carried out:

- (i) Toluene to benzoic acid
- (iii) Ethylcyanide to ethanoic acid
- (ii) Bromobenzene to benzoic acid

OR

- (a) Predict the product of the reaction of aniline with bromine in a nonpolar solvent such as  $CS_2$ .
- (b) Why are low spin tetrahedral complexes not formed?

Q30. (a) A primary amine,  $RNH_2$  can be reacted with  $CH_3-X$  to get secondary amine,  $R-NHCH_3$  but the only disadvantage is that  $3^0$  amine and quaternary ammonium salts are also obtained as side products. Can you suggest a method where  $RNH_2$  forms only  $2^0$  amine?

(b) Give the chemical tests to distinguish between the following pairs of compounds:

- (i) Methylamine and Dimethylamine
- (ii) Aniline and N-methylaniline

OR

Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?

### Section D

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

Q31. A compound (X) containing C, H and O is unreactive towards sodium. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (Y) by reaction with red phosphorous and iodine. The compound (Z) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60.

(i) The IUPAC name of the acid formed is:

- (a) Methanoic acid
- (b) Ethanoic acid
- (c) Propanoic acid
- (d) Butanoic acid

(ii) Compound (Y) is

- (a) Ethyl iodide
- (b) Methyl iodide
- (c) Propyl iodide
- (d) Mixture of (a) and (b)

OR



Compound (Z) is

- (a) Methanol
- (b) Ethanol
- (c) Propanol
- (d) Butanol

(iii) Compound (X) on treatment with excess of  $\text{Cl}_2$  in presence of light gives

- (a)  $\alpha$ -chlorodiethyl ether
- (b)  $\alpha, \alpha'$ -dichlorodiethyl ether
- (c) perchlorodiethyl ether
- (d) None of these

Q32. Nucleophilic substitution reactions are of two types; substitution nucleophilic bimolecular ( $\text{S}_{\text{N}}2$ ) and substitution nucleophilic unimolecular ( $\text{S}_{\text{N}}1$ ) depending on molecules taking part in determining the rate of reaction. Reactivity of alkyl halide towards  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  reactions depends on various factors such as steric hindrance, stability of intermediate or transition state and polarity of solvent.  $\text{S}_{\text{N}}2$  reaction mechanism is favoured mostly by primary alkyl halide or transition state and polarity of solvent,  $\text{S}_{\text{N}}2$  reaction mechanism is favoured mostly by primary alkyl halide then secondary and then tertiary. This order is reversed in case of  $\text{S}_{\text{N}}1$  reactions.

(i) Which of the following is most reactive towards nucleophilic substitution reaction?

- (a)  $\text{C}_6\text{H}_5\text{Cl}$
- (b)  $\text{CH}_2=\text{CHCl}$
- (c)  $\text{ClCH}_2\text{CH}=\text{CH}_2$
- (d)  $\text{CH}_3\text{CH}=\text{CHCl}$

(ii) Which of the compounds will react faster in  $\text{S}_{\text{N}}1$  reaction with the "OH" ion?

$\text{CH}_3-\text{CH}_2-\text{Cl}$  or  $\text{C}_6\text{H}_5-\text{CH}_2-\text{Cl}$

(iii) Tertiary alkyl halides are practically inert to substitution by  $\text{S}_{\text{N}}2$  mechanism because of

- (a) Insolubility
- (b) Instability
- (c) Inductive effect
- (d) Steric hindrance

OR

Which of the following is the correct order of decreasing  $\text{S}_{\text{N}}2$  reactivity?

- (a)  $\text{RCH}_2\text{X} > \text{R}_2\text{CHX} > \text{R}_3\text{CX}$
- (b)  $\text{R}_3\text{CX} > \text{R}_2\text{CHX} > \text{RCH}_2\text{X}$
- (c)  $\text{R}_2\text{CHX} > \text{R}_3\text{CX} > \text{RCH}_2\text{X}$
- (d)  $\text{RCH}_2\text{X} > \text{R}_3\text{CX} > \text{R}_2\text{CHX}$

### Section E

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

Q33. (a) Explain what is meant by

- (i) A peptide linkage,
- (ii) A glycosidic linkage.
- (b) What are essential and non-essential amino acids? Give two examples of each.
- (c) What is metabolism? Mention the role of enzymes in metabolism?

OR

- (a) How do you explain the presence of an aldehydic group in a glucose molecule?



- (b) Coagulation of egg white on boiling is an example of the denaturation of protein. Explain it in terms of structural changes.
- (c) Which moieties of nucleosides are involved in the formation of phosphodiester linkages present in dinucleotides? What does the word diester in the name of linkage indicate? Which acid is involved in the formation of this linkage?

Q34. On the basis of Lanthanoid contraction, explain the following

- (i) Nature of bonding in  $\text{Lu}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$
- (ii) Trends in the stability of oxo salts of lanthanides from La to Lu.
- (iii) Stability of the complexes of lanthanides.
- (iv) Radii of 4d and 5d block elements
- (v) Trends in acidic character of lanthanide oxides.

OR

- (a)  $\text{CoSO}_4 \cdot 5\text{NH}_3$  exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with  $\text{AgNO}_3$  to give white precipitate, but does not react with  $\text{BaCl}_2$ . Isomer 'B' gives white precipitate with  $\text{BaCl}_2$  but does not react with  $\text{AgNO}_3$ . Answer the following questions.

- (i) Identify 'A' and 'B' and write their structural formulas.
- (ii) Name the type of isomerism involved.
- (iii) Give the IUPAC name of 'A' and 'B'.

- (b) The molar conductivities at infinite dilution for sodium acetate, hydrochloric acid and sodium chloride are 91.0, 425.9 and 126.4  $\text{S cm}^2 \text{mol}^{-1}$  respectively at 298 K. Calculate the molar conductivity of acetic acid at infinite dilution.

Q35. (a) Using Raoult's law, explain how the total vapour pressure over the solution is related to the mole fraction of components in the following solutions.

- (i)  $\text{CHCl}_3$  (l) and  $\text{CH}_2\text{Cl}_2$  (l) (ii)  $\text{NaCl}$  (s) and  $\text{H}_2\text{O}$  (l)

- (b) For a certain reaction a large fraction of molecules has energy more than the threshold energy, yet the rate of reaction is very slow. Why?

## Solutions

### Section A

Ans1. (b)

Sol. The mixture shows positive deviations from Raoult's law.

Positive deviations from Raoult's law are noticed when

- (i) Exp. value of vapour pressure of mixture is more than calculated value.
- (ii) Exp. value of b.pt. of mixture is less than calculated value.
- (iii)  $\Delta_{\text{mixing}} = +ve$
- (iv)  $\Delta V_{\text{mixing}} = +ve$

Ans2. (b)

Sol. as the concentration of all the three compounds are the same, the boiling point will be compared by using the Van't Hoff factor.

The Van't Hoff factor for the compounds will be as below

KCl : 2

Urea : 1

$\text{AlCl}_3$  : 4

So the lowest Van't Hoff factor is of urea and therefore it will have the lowest boiling point.



Ans3. (c)

Sol. For a good salt bridge, the velocities of ions should be same. If the velocities are not same, then the ions would not be able to neutralize the charge equally in both half cells. Consequently, an opposite force would be developed that restricts the flow of current. For  $\text{KNO}_3$ , the velocities of  $\text{K}^+$  and  $\text{NO}_3^-$  are nearly same. Therefore, it is used to make salt bridges.

Ans4. (c)

Sol. Galvanization is the process of applying a protective zinc coating to steel or iron in order to prevent it from rusting.

Ans5. (d)

Sol. For the reaction,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , the number of moles of gaseous reactants is equal to the number of moles of gaseous products. The equilibrium constant  $K_p$  is independent of (A) Total pressure

(B) Catalyst

(C) The amounts of  $\text{H}_2$  and  $\text{I}_2$  present

However, it changes with Temperature

Ans6. (c)

Sol.  $\text{R} \rightarrow \text{P}$

For a second order reaction,  $\text{rate} = k[\text{R}]^2$

If conc. of R is increased by four times,  $\text{rate} = k[4\text{R}]^2$

Hence, the rate of formation of P increases by 16 times.

Ans7. (d)

Explanation:

(d)  $\text{Ni}^{2+}$ ,  $\text{Ti}^{3+}$  are coloured due to presence of unpaired electrons.

Ans8. (d)

Explanation:

(d)  $2\text{MnO}_4^- + 5\text{SO}_3^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 8\text{H}_2\text{O}$

5 moles of  $\text{SO}_3^{2-}$  needs 2 moles of  $\text{KMnO}_4$

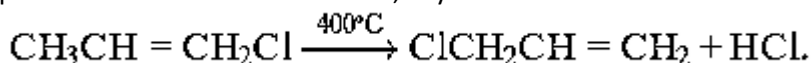
1 mole of  $\text{SO}_3^{2-}$  needs  $2/5$  moles of  $\text{KMnO}_4$

Ans9. (d)

Explanation: A coordination entity consists of a central metal atom bonded to a fixed number of atoms/molecules. Here,  $\text{K}^+$  is the counter ion, OH is the molecule bonded to the central atom which is Zn.

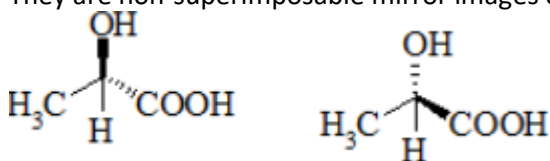
Ans10. (b)

Sol. When chlorine gas is reacted with propene at high temperature ( $400^\circ\text{C}$ ), then substitution takes place in place of addition reaction. Hence, allyl chloride is formed.



Ans11. (b)

Sol. Two possible stereo-structures of  $\text{CH}_3\text{CHOHCOOH}$ , which are optically active, are called enantiomers. They are non-superimposable mirror images of each other and are shown in the image.

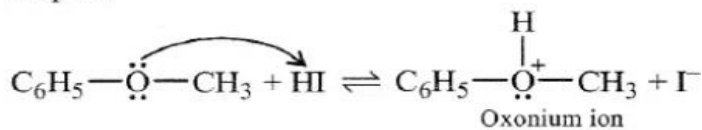


Ans12. (b)

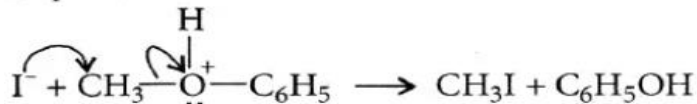


Sol. The heating of phenyl-methyl ether with HI produces phenol.

Step I :

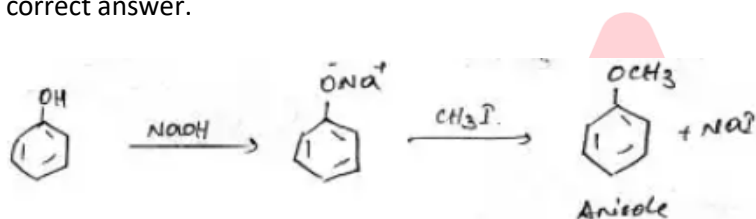


Step II :



Ans13. (b)

Sol. The above reaction is the preparation of Anisole phenol+NaOH+CH<sub>3</sub>I gives anisole. C<sub>6</sub>H<sub>5</sub>OH, NaOH, CH<sub>3</sub>I is the correct answer.



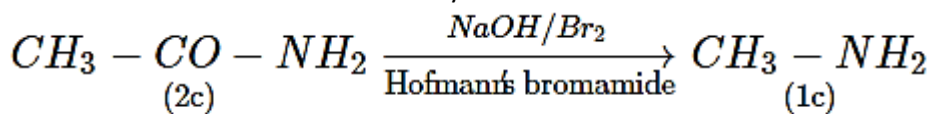
Ans14.(a)

Sol. Sodium bisulphite is used for separation of acetone and acetophenone. Acetophenone (an aromatic ketone) does not react with sodium bisulphite whereas acetone (an aliphatic ketone) reacts with sodium bisulphite to form a solid adduct which can be filtered. Then, it can be decomposed by acid or base to regenerate acetone.

Ans15. (b)

Ans16.(b)

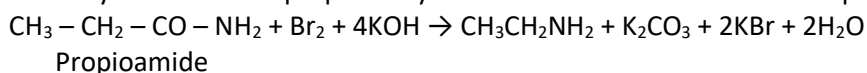
Sol. The amine formed from an amide by means of bromine and alkali has one less C atom than that of amide



e.

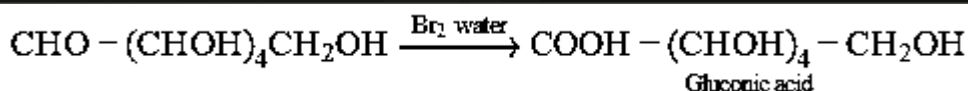
Ans17. (b)

Sol. Ethylamine can be prepared by the action of bromine and caustic potash on propioamide.



Ans18. (c)

Sol. On oxidation with a mild oxidising agent like Br<sub>2</sub>/H<sub>2</sub>O, the glucose is oxidised to six carbon carboxylic acid (gluconic acid). This indicates that the carbonyl group is present as an aldehydic group.



### Section B

Ans19. Sodium chloride (NaCl) is a non-volatile solute. When added to water taken in a beaker, the solute occupies some surface area. As a result, the vapour pressure decreases and the boiling point of the solution increases. On the other hand, methyl alcohol is more volatile than water. The addition of methyl alcohol to water increases the total vapour pressure of the solution. The boiling point of the solution decreases.

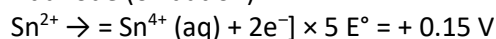
OR

The reasons are:

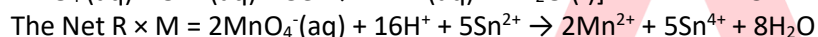
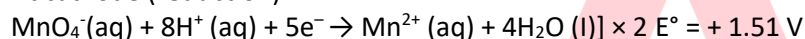
- (i) Due to resonance/diagrammatic representation, C – Cl bond acquires a partial double bond character. As a result, the C – Cl bond in chlorobenzene is shorter and hence stronger. Thus, cleavage of C – Cl bond in benzene becomes difficult which makes it less reactive towards nucleophilic substitution.
- (ii) Due to repulsion between nucleophile and electron rich arenes.

Ans20. The reactions can be represented at anode and at cathode in the following ways :

At anode (oxidation) :



At cathode (reduction) :



$$\text{Now } E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= 1.51 - 0.15 = + 1.36 \text{ V}$$

∴ Positive value of  $E^\circ_{\text{cell}}$  favours formation of product.

Ans21. Since Rate =  $K[A]^2$

For second order reaction Let  $[A] = a$  then Rate =  $Ka^2$

(i) If  $[A] = 2a$  then Rate =  $K(2a)^2 = 4Ka^2$

∴ Rate of reaction becomes 4 times

(ii) If  $[A] = a/2$  then Rate =  $K(a/2)^2 = Ka^2/4$

∴ Rate of reaction will be  $1/4^{\text{th}}$ .

Ans22. The electronic configuration of Mn (at no = 25) is  $[\text{Ar}] 4s^2 3d^5$ . Losing two electrons makes it  $\text{Mn}^{2+}$  and due to that the d-orbital becomes half-filled and stable. Now removing another electron will require a lot of energy, which is why its third ionization energy is so high.

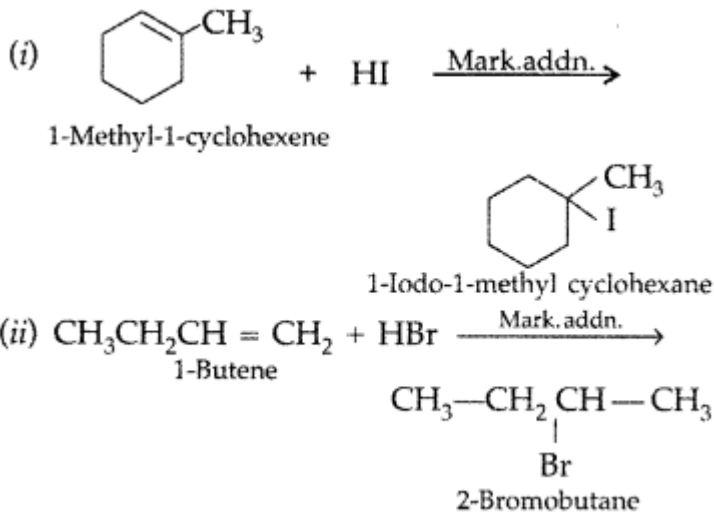
Ans23. When two or more atom in an ambidentate ligand is linked with a central metal ion to form two types of complexes, then the formed isomers are known as linkage isomers and the phenomenon called linkage isomerism.

Examples:  $[\text{Cr}(\text{H}_2\text{O})_5(\text{NCS})]^{2+}$  Pentaquathiocyanate chromium (III) ion,  $[\text{Cr}(\text{H}_2\text{O})_5(\text{NCS})]^{2+}$

Pentaquaisothiocyanate chromium (III) ion.

Ans24.





Ans25. The methoxy group is the electron-donating group while  $\text{NO}_2$  is the electron-withdrawing group in nature, hence the release of  $\text{H}^+$  is easier from O-nitrophenol while it is difficult from methoxy phenol.

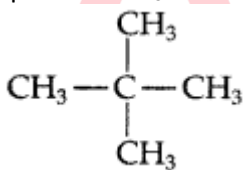
OR

The metals will quickly lose their electrons and get oxidised. A negative E value means that the oxidised species is more stable than the reduced species. Here,  $\text{Mn}^{2+}$  ( $3d^5$ ) and  $\text{Zn}^{2+}$  ( $3d^{10}$ ) have half-filled and fully filled d orbitals, giving them stability and, therefore, prefer to stay that way and not get reduced.  $\text{Ni}^{2+}$  ( $3d^8$ ) has very high negative hydration enthalpy, balanced by first and second ionisation enthalpy.

### Section C

Ans26. Transition metals are visible in color both in solid and aqueous mediums. They form colored compounds due to d-d transition. Transition elements possess an incomplete d-subshell leading to the delocalization of electrons from one energy level to another in the same d subshell is feasible. The energy required to excite electrons is related to the energy levels of the various spectrums of visible light. When light falls on a transition element, it absorbs the energy of a certain color causing the delocalization of electrons, while the rest of it is emitted back resulting in the compound being colored.

Ans27. (i) Since there is only one monochloroderivative, the compound contains 12 equivalent hydrogen in four equivalent  $\text{CH}_3$ . The compound is 2, 2-dimethyl propane



(ii) Both are heated with aqueous NaOH.  $\text{C}_2\text{H}_5\text{Br}$  gives ethanol and NaBr, which on reacting with  $\text{AgNO}_3$ , gives yellow precipitate of AgBr.

$\text{C}_6\text{H}_5\text{Br}$  does not respond to this test.

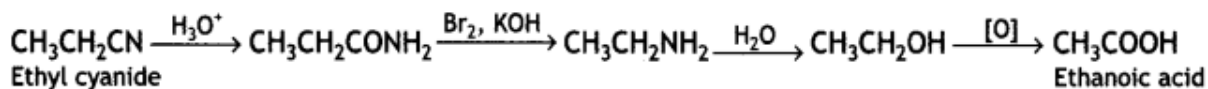
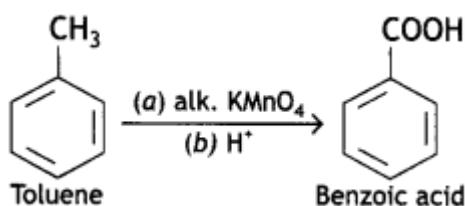
Ans28. (i) The acidity of 2-chloroethanol is higher than that of ethanol. The Cl atom have electron-withdrawing nature so it will withdraw the electron density from the O-H bond thus making the O-H bond weak. As a result, the O-H bond of 2-chloroethanol weakens compared to the O-H bond of ethanol. As a result, 2-chloroethanol is acidic in comparison to ethanol.

$\text{Cl} < \text{CH}_2 < \text{CH}_2 < \text{O} < \text{H} > \text{CH}_3 > \text{CH}_2 > \text{O} > \text{H}$

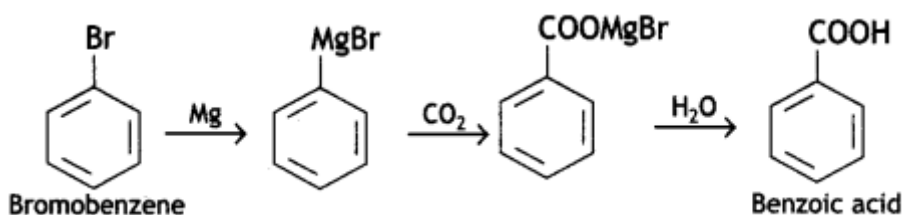
Stronger acid due to the -I effect of Cl.

(ii) o-nitrophenol is more volatile than p-nitrophenol due to the presence of intramolecular hydrogen bonding. In para nitrophenol intermolecular hydrogen bonding is present. This intermolecular hydrogen bonding causes the association of molecules.

Ans29. (i)



(ii)

(iii)  
OR

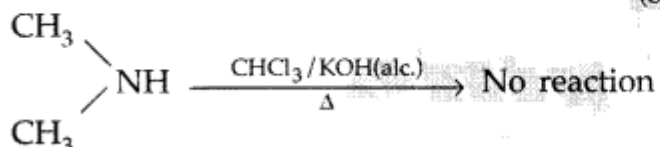
- (a) The products formed in the reaction of aniline with bromine in a nonpolar solvent such as CS<sub>2</sub> are 4-Bromoaniline and 2-Bromoaniline, where 4-Bromoaniline is the major product. In a nonpolar solvent medium, the activating effect of the –NH<sub>2</sub> group of aniline is reduced because of resonance, and thus, mono-substitution occurs only at ortho- and para-positions.
- (b) In a tetrahedral complex, the d-orbital is split too small as compared to octahedral. For the same metal and same ligand  $\Delta_t = 4/9\Delta_o$ .

Hence, the orbital energies are not enough to force pairing. As a result, low spin configurations are rarely observed in tetrahedral complexes.

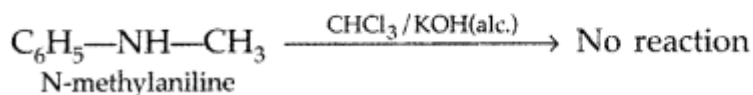
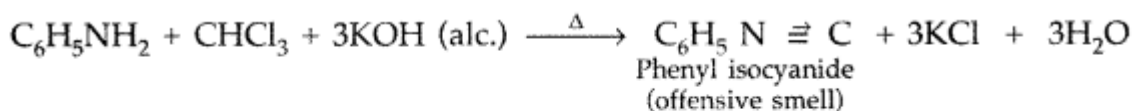
Ans30. (a) Carbylamine reaction is shown by 1° amine only, which replaces two hydrogen atoms attached to the nitrogen atom of the NH<sub>2</sub> group with one carbon atom. The isocyanide will give a secondary amine with one methyl group on catalytic reduction.

(b) (i) Methylamine and dimethylamine can be distinguished by the carbylamine test.

Carbylamine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.



(ii) Aniline and N-methylaniline can be distinguished using the Carbylamine test. Primary amines, on heating with chloroform and ethanolic potassium hydroxide, form foul-smelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamine test. However, N-methylaniline, being a secondary amine does not.



OR

Elementary reactions proceed in a single step while complex reactions generally take place in many steps. In multiple step reactions, each step has its own molecularity and the molecularity of these steps are not added up. Therefore, complex reactions have no molecularity. On the other hand, in a complex reaction the order as determined for the slowest step, also called rate determining step, represents the order for the entire reaction. Hence, we may conclude that molecularity is applicable only to the single step reactions whereas order applies to both elementary and complex reactions.

### Section D

Ans31.

(i) (b)

(ii) (a)

OR

(b)

(iii) (c)

**X**  $\xrightarrow{\text{Sodium}}$  **No reaction**  
(contains C,H and O) So it can't have acid or alcohol

$\xrightarrow{\text{Br}_2}$  **No reaction**

$\xrightarrow{\text{Schiff reagent}}$  **No reaction**

So it can't be aldehyde and ketone, it can be only ether

Further **x**  $\xrightarrow{-\text{HI}}$  **only 1 product** so it must be symmetrical ether

**Y**  $\xrightarrow{\text{Hodrolysis}}$  **Z**  $\xrightarrow{\text{I}_2/\text{P}_4(\text{red})}$  **Y**

$\downarrow$   
**KMnO<sub>4</sub>**  
**Oxidation**  
**Carboxylic acid., (Eq.wt =60) It has -COOH group**  
**Wt of -COOH group =12+16 x 2+1 =45 g**

So it can have only CH<sub>3</sub> unit attached to -COOH group, So acid is CH<sub>3</sub> - COOH.

So **Z** will be CH<sub>3</sub> - CH<sub>2</sub> - OH

**Y** will be CH<sub>3</sub> - CH<sub>2</sub> - I

**X** will be CH<sub>3</sub> - CH<sub>2</sub> - O - CH<sub>2</sub> - CH<sub>3</sub> } **Ans**

**C<sub>2</sub>H<sub>5</sub> - O - C<sub>2</sub>H<sub>5</sub> + 2HI  $\longrightarrow$  2C<sub>2</sub>H<sub>5</sub>I + H<sub>2</sub>O**

Ans32. (i) (c) Allylic chlorides are most reactive.

(ii) In the rate-determining phase of the S<sub>N</sub>1 reaction, a carbocation intermediate is initially generated. The benzyl carbocation is resonance stabilised in benzyl chloride.

In the case of ethyl chloride or chloroethane, however, the  $\text{CH}_3\text{CH}_2^+$  carbocation can only have a hyper-conjugation effect. It is less stable in comparison. As a result, in the  $\text{S}_{\text{N}}1$  reaction, benzyl chloride reacts faster with the  $\text{OH}^-$  ion than ethyl chloride.

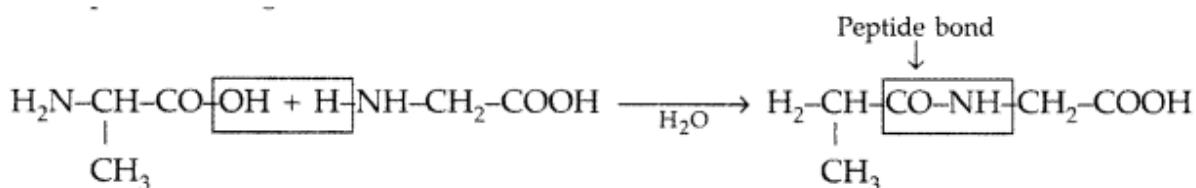
(iii) d

OR

(a) Larger the number of alkyl groups at alpha-carbon atom, more is the steric hindrance and hence lesser the reactivity towards  $\text{S}_{\text{N}}2$  mechanism.

### Section E

Ans33. (a) (i) **Peptide linkage:** A peptide linkage is an amide linkage formed between  $-\text{COOH}$  group of one  $\alpha$ -amino acid and  $\text{NH}_2$  group of the other  $\alpha$ -amino acid by loss of a molecule of water.



(ii) **Glycosidic linkage:** The two monosaccharide units are joined together through an ether or oxide linkage formed by loss of a molecule of water. Such a linkage between two monosaccharide units through oxygen atom is called glycosidic linkage.

(b) **Non-essential amino acids:** The amino acids which can be synthesized in the body, are known as non-essential amino acids.

Example: Glycine, Alanine etc.

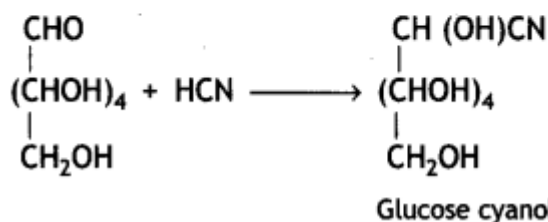
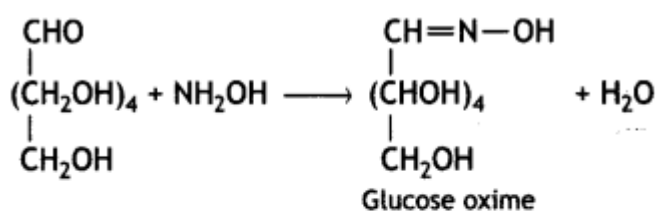
**Essential amino acids:** The amino acids which cannot be synthesized in the body and must be obtained through diet are known as essential amino acids.

Example: Valine, Leucine etc.

(c) Metabolism is described as the chemical reactions in the cells which turn food into energy. Enzymes are responsible for directing metabolic pathways. Catalysts are enzymes. Enzymes are organic catalysts that are highly specialised and are created by living cells. Biochemical pathways are the sequences of reactions that occur in cells. Enzymes direct metabolic pathways in the desired direction. They have an active site. The substrate binds to the active site of the enzyme, resulting in the formation of an enzyme-substrate complex.

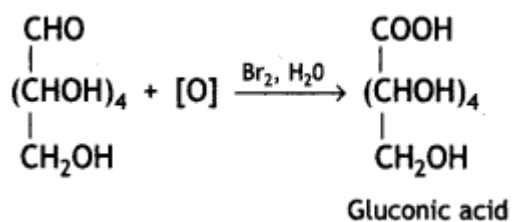
OR

(a) Glucose reacts with hydroxylamine to form a monoxime and adds one molecule of hydrogen cyanide to give cyanohydrin.



Therefore, it contains a carbonyl group which can be an aldehyde or a ketone. On mild oxidation with bromine water, glucose gives gluconic acid which is a carboxylic acid-containing six carbon atoms.





This indicates that the carbonyl group present in glucose is an aldehydic group.

- (b) When the egg white is boiled, the soluble globular protein albumin is converted into insoluble fibrous protein. During this denaturation, (i) biological activity is lost and (ii) secondary and tertiary structures of albumin protein are destroyed while the primary structure (representing the sequence of amino acids) remains intact.
- (c) Phosphoric acid is involved in the formation of phosphodiester linkage. The word 'diester' in this linkage indicates that two -OH groups of phosphoric acid are involved in forming two ester linkages. In the formation of dinucleotides, the 3-OH group of the pentose sugar of one nucleotide unit and the 5-OH group of the pentose sugar of the other nucleotide unit are involved in generating the phosphodiester linkage.

Ans34. (i) Due to lanthanide contraction, size reduces. With the size reduction, the covalent character increases. Therefore,  $\text{Lu}_2\text{O}_3$  is more covalent than  $\text{La}_2\text{O}_3$ .

(ii) Oxosalts contain oxygen as an anion. As the size of the cation reduces from La to Lu, according to Fajan's rules, the polarising power of the cation will increase, and it will distort the cloud of oxygen (anion) significantly. Thus the bond weakens, and the stability also reduces.

(iii) As the size of the central atom reduces, the stability of the complex increases. A small metal ion with a greater charge attracts the ligands better.

(iv) In 5d block elements, the effective nuclear charge increases due to poor shielding off orbitals, thereby reducing the size. This is called lanthanide contraction. So, the radii of 4d and 5d block elements end up being very similar.

(v) From La to Lu, the acidic character increases. As the size reduces from La to Lu, the ability to lose electrons (Lewis base character) reduces, so the acidity increases.

OR

(i) As isomer A reacts with  $\text{AgNO}_3$  to give a white precipitate, Cl must be present in the ionisation sphere.

As it does not react with  $\text{BaCl}_2$ ,  $\text{SO}_4^{2-}$  must be present in the coordination sphere.

Therefore the formula of A =  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$  (coordination no. of Co = 6)

As reactions are reversed for isomer B, formula B =  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$

(ii) The type of isomerism involved is Ionisation isomerism

(iii) The IUPAC name of

A = Pentaamminesulphatocobalt (III) chloride ,

B = Pentaamminechloridocobalt (III) sulphate.

(b) Molar conductivity at infinite dilution for acetic acid can be calculated as:

$$\Lambda^\circ(\text{CH}_3\text{COOH}) = \lambda^\circ\text{H}^+ + \lambda^\circ\text{CH}_3\text{COO}^-$$

$$= \lambda^\circ\text{CH}_3\text{COO}^- + \lambda^\circ\text{Na}^+ + \lambda^\circ\text{H}^+ + \lambda^\circ\text{Cl}^- - \lambda^\circ\text{Na}^+ - \lambda^\circ\text{Cl}^-$$

$$\Lambda^\circ(\text{CH}_3\text{COOH}^+) = \Lambda^\circ(\text{CH}_3\text{COONa}) + \Lambda^\circ(\text{H}^+\text{Cl}) - \Lambda^\circ(\text{NaCl})$$

$$\Lambda^\circ(\text{CH}_3\text{COONa}) = 91.0 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ(\text{H}^+\text{Cl}) = 425.9 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ(\text{NaCl}) = 126.4 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\therefore \Lambda^\circ(\text{CH}_3\text{COOH}^+) = 91.0 + 425.9 - 126.4 = 390.5 \text{ S cm}^2 \text{ mol}^{-1}.$$

Ans35. (a) (i) In this case,  $\text{CH}_3\text{Cl}$  (l) and  $\text{CH}_2\text{Cl}_2$  (l) both the components are volatile liquids.

According to Raoult's law,



$$P_A = P_A^0 \chi_A ; P_B = P_B^0 \chi_B$$

$$P = P_A + P_B$$

$$P = P_A^0 \chi_A + P_B^0 \chi_B = P_A^0 \chi_A + P_B^0 (1 - \chi_A)$$

Here, A and B are volatile components

$P_A$  and  $P_B$  are the partial pressures while P is the total vapour pressure.

$\chi_A$  and  $\chi_B$  are the mole fractions of the components in the binary solution.

(ii) In this case, NaCl (s) is non-volatile and Raoult's law is applicable only to water which is of volatile nature

According to Raoult's law,

$$P = P_A^0 \chi_A$$

Here the total vapour pressure of the solution is dependent on the mole fraction of solvent only.

(b) The reaction rate generally depends on two factors: orientation factor and energy factor. Apart from possessing energy equal to threshold energy. The reacting species must be properly oriented at the time of collision. In the reaction under observation, the orientation effect is not proper. Therefore, effective collisions are not much as expected. The reaction is therefore, a slow reaction.

