

Reduced Syllabus Chemistry

Class XII

(2020-21) (Theory)

Time : 3 Hours

70 Marks

Unit No.	Title	No. of Periods	Marks
Unit I	Solid State	8	23
Unit II	Solutions	8	
Unit III	Electrochemistry	7	
Unit IV	Chemical Kinetics	5	
Unit V	Surface Chemistry	5	
Unit VII	p -Block Elements	7	19
Unit VIII	d -and f -Block Elements	7	
Unit IX	Coordination Compounds	8	
Unit X	Haloalkanes and Haloarenes	9	28
Unit XI	Alcohols, Phenols and Ethers	9	
Unit XII	Aldehydes, Ketones and Carboxylic Acids	10	
Unit XIII	Amines	7	
Unit XIV	Biomolecules	8	
Total		98	70

Unit I: Solid State

8 Periods

Classification of solids based on different binding forces: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea). Unit cell in two dimensional and three dimensional lattices, calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell, point defects.

Unit II: Solutions

8 Periods

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, Raoult's law, colligative properties - relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties.

Unit III: Electrochemistry

7 Periods

Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis.

Unit IV: Chemical Kinetics

5 Periods

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions).

Unit V: Surface Chemistry

5 Periods

Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, colloidal state: distinction between true solutions, colloids and suspension; lyophilic, lyophobic, multi-molecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation.



Unit VII : p-Block Elements

7 Periods

Group -15 Elements : General introduction, electronic configuration, occurrence, oxidation states, trends in physical and chemical properties; Nitrogen preparation properties and uses; compounds of Nitrogen: preparation and properties of Ammonia and Nitric Acid.

Group 16 Elements : General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties, dioxygen: preparation, properties and uses, classification of Oxides, Ozone, Sulphur -allotropic forms; compounds of Sulphur: preparation properties and uses of Sulphur-dioxide, Sulphuric Acid: properties and uses; Oxoacids of Sulphur (Structures only).

Group 17 Elements : General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties; compounds of halogens, Preparation, properties and uses of Chlorine and Hydrochloric acid, interhalogen compounds, Oxoacids of halogens (structures only).

Group 18 Elements: General introduction, electronic configuration, occurrence, trends in physical and chemical properties, uses.

Unit VIII :d and f Block Elements

7 Periods

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation.

Lanthanoids - Electronic configuration, oxidation states and lanthanoid contraction and its consequences.

Unit IX : Coordination Compounds

8 Periods

Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT.

Unit X : Haloalkanes and Haloarenes.

9 Periods

Haloalkanes : Nomenclature, nature of C–X bond, physical and chemical properties, optical rotation mechanism of substitution reactions.

Haloarenes : Nature of C–X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only).

Unit XI : Alcohols, Phenols and Ethers

9 Periods

Alcohols : Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration.

Phenols : Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols.

Ethers : Nomenclature, methods of preparation, physical and chemical properties, uses.

Unit XII : Aldehydes, Ketones and Carboxylic Acids

10 Periods

Aldehydes and Ketones : Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses.

Carboxylic Acids : Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

Unit XIII : Amines

7 Periods

Amines : Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

Unit XIV : Biomolecules

8 Periods

Carbohydrates - Classification (aldoses and ketoses), monosaccharides (glucose and fructose), D-L configuration

Proteins -Elementary idea of - amino acids, peptide bond, polypeptides, proteins, structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only), denaturation of proteins.

Nucleic Acids : DNA and RNA.



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C.B.S.E. SAMPLE QUESTION PAPER–2021 (SOLVED)

(Issued by CBSE)

CHEMISTRY – THEORY (043)

M.M. : 70

Time : 3 Hours

General Instructions. Read the following instructions carefully.

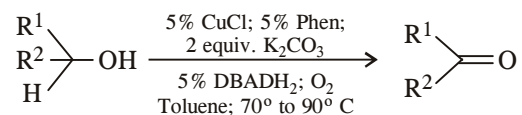
- There are 33 questions in this question paper. All questions are compulsory.
- Section A : Q. Nos. 1 and 2 are case-based questions having four MCQs or Reason Assertion type based on given passage each carrying 1 mark.
- Section A : Questions 3 to 16 are MCQs and Reason/Assertion type questions carrying 1 mark each.
- Section B : Q. Nos. 17 to 25 are short answer questions and carry 2 marks each.
- Section C : Q. Nos. 26 to 30 are short answer questions and carry 3 marks each.
- Section D : Q. Nos. 31 to 33 are long answer questions carrying 5 marks each.
- There is no overall choice. However, internal choices have been provided
- Use of calculators and log tables is not permitted.

SECTION – A (Objective Type)

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

(1 × 4 = 4)

An efficient, aerobic catalytic system for the transformation of alcohols into carbonyl compounds under mild conditions, copper-based catalyst has been discovered. This copper-based catalytic system utilizes oxygen or air as the ultimate, stoichiometric oxidant, producing water as the only by-product.



A wide range of primary, secondary, allylic and benzylic alcohols can be smoothly oxidised to the corresponding aldehydes or ketones in good to excellent yields. Air can be conveniently used instead of oxygen without affecting the efficiency of the process. However, the use of air requires slightly longer reaction times.

This process is not only economically viable and applicable to large-scale reactions, but it is also environment friendly.

The following questions are multiple choice questions, choose the most appropriate answer :

- The copper based catalyst mentioned in the study above, can be used to convert :
 - propanol to propanoic acid
 - propanone to propanoic acid
 - propanone to propan-2-ol
 - propan-2-ol to propanone.
- The carbonyl compound formed when ethanol gets oxidised using this copper-based catalyst can also be obtained by ozonolysis of :
 - But-1-ene
 - But-2-ene
 - Ethene
 - Pent-1-ene

Or

Which of the following is a secondary allylic alcohol ?

- But-3-en-2-ol
 - But-2-en-2-ol
 - Prop-2-enol
 - Butan-2-ol
- Benzyl alcohol on treatment with this copper-based catalyst gives a compound 'A' which on reaction with KOH gives compounds 'B' and 'C'. Compound 'B' on oxidation with KMnO_4 gives compound 'C'. Compounds 'A', 'B' and 'C' respectively are :
 - Benzaldehyde, Benzyl alcohol, potassium salt of benzoic acid
 - Benzaldehyde, potassium salt of Benzoic acid, benzyl alcohol
 - Benzaldehyde, Benzoic acid, Benzyl alcohol
 - Benzoic acid, Benzyl alcohol, Benzaldehyde.
 - An organic compound 'X' with molecular formula $\text{C}_3\text{H}_8\text{O}$ on reaction with this copper based catalyst gives compound 'Y' which reduces Tollen's reagent. 'X' on reaction with sodium metal gives 'Z'. What is the product of reaction of 'Z' with 2-chloro-2-methylpropane ?
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{OC}(\text{CH}_3)_3$

- (b) $\text{CH}_3\text{CH}_2\text{OC}(\text{CH}_3)_3$
 (c) $\text{CH}_2=\text{C}(\text{CH}_3)_2$
 (d) $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$.

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

(1 × 4 = 4)

The amount of moisture that leather adsorbs or loses is determined by temperature, relative humidity, degree of porosity, and the size of the pores. Moisture has great practical significance because its amount affects the durability of leather, and in articles such as shoes, gloves, and other garments, the comfort of the wearer. High moisture content accelerates deterioration and promotes mildew action. On the other hand, a minimum amount of moisture is required to keep leather properly lubricated and thus prevent cracking.

The study indicates that adsorption of moisture by leather is a multi-molecular process and is accompanied by low enthalpies of adsorption. Further at 75-percent relative humidity the extent of adsorption is a function of surface area alone. Untanned hide and chrome-tanned leathers have the largest surface areas. The leathers tanned with the vegetable tanning materials have smaller surface areas since they are composed of less hide substance and the capillaries are reduced to smaller diameters, in some cases probably completely filled by tanning materials. This process of tanning occurs due to mutual coagulation of positively charged hide with negatively charged tanning material. The result of the study indicated that untanned hide and chrome-tanned leather adsorb the most water vapour.

In these questions [Q.Nos. (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** : Vegetable tanned leather cannot adsorb a large amount of moisture.
Reason : Porous materials have higher surface area.
- (ii) **Assertion** : Animal hide soaked in tannin results in hardening of leather.
Reason : Tanning occurs due to mutual coagulation.
- (iii) **Assertion** : Adsorption of moisture by leather is physisorption.
Reason : It is a multimolecular process and is accompanied by low enthalpies of adsorption.
- (iv) **Assertion** : The vegetable tanning materials have smaller surface areas.
Reason : The capillaries present in leather are reduced to smaller diameters.

Or

- Assertion** : Leather adsorbs different amount of moisture.
Reason : Some moisture is necessary to prevent cracking of leather.

Following questions (Nos. 3-11) are multiple choice questions carrying 1 mark each :

3. Which of the following options will be the limiting molar conductivity of CH_3COOH if the limiting molar conductivity of CH_3COONa is $91.0 \text{ S cm}^2 \text{ mol}^{-1}$? Limiting molar conductivities for individual ions are given in the following table.

S.No.	Ions	Limiting molar conductivity ($\text{S cm}^2 \text{ mol}^{-1}$)
1.	H^+	349.6
2.	Na^+	50.1
3.	K^+	73.5
4.	OH^-	199.1

- (a) $350 \text{ S cm}^2 \text{ mol}^{-1}$
 (b) $375.3 \text{ S cm}^2 \text{ mol}^{-1}$
 (c) $390.5 \text{ S cm}^2 \text{ mol}^{-1}$
 (d) $340.4 \text{ S cm}^2 \text{ mol}^{-1}$.
4. Curdling of milk is an example of :
 (a) breaking of peptide linkage
 (b) hydrolysis of lactose
 (c) breaking of protein into amino acids
 (d) denaturation of protein.

Or

Dissacharides that are reducing in nature are :

- (a) sucrose and lactose
 (b) sucrose and maltose
 (c) lactose and maltose
 (d) sucrose, lactose and maltose
5. When 1 mole of benzene is mixed with 1 mole of toluene, the vapour will contain :
 (Given : vapour pressure of benzene = 12.8 kPa and vapour pressure of toluene = 3.85 kPa).

- (a) equal amount of benzene and toluene as it forms an ideal solution
 (b) unequal amount of benzene and toluene as it forms a non ideal solution
 (c) higher percentage of benzene
 (d) higher percentage of toluene.
6. Which of the following is the reason for zinc not exhibiting variable oxidation state ?
 (a) inert pair effect (b) completely filled 3d-subshell
 (c) completely filled 4s-subshell (d) common ion effect.

Or

Which of the following is a diamagnetic ion : (Atomic numbers of Sc, V, Mn and Cu are 21, 23, 25 and 29 respectively)

- (a) V^{2+} (b) Sc^{3+}
 (c) Cu^{2+} (d) Mn^{3+} .
7. Propanamide on reaction with bromine in aqueous NaOH gives :
 (a) Propanamine (b) Ethanamine
 (c) N-Methylethanamine (d) Propanenitrile

Or

IUPAC name of product formed by reaction of methylamine with two moles of ethyl chloride

- (a) N, N-Dimethylethanamine (b) N, N-Diethylmethanamine
 (c) N-Methyl ethanamine (d) N-Ethyl-N-methylethanamine

8. Ambidentate ligands NO_2^+ and SCN^- are :
 (a) unidentate (b) didentate
 (c) polydentate (d) has variable denticity.

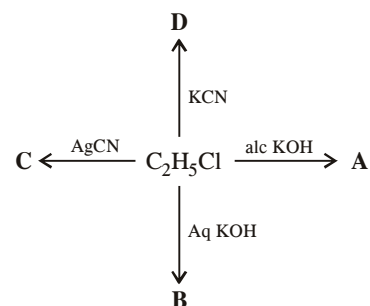
Or

The formula of the coordination compound tetraammineaquachloridocobalt(III) chloride is

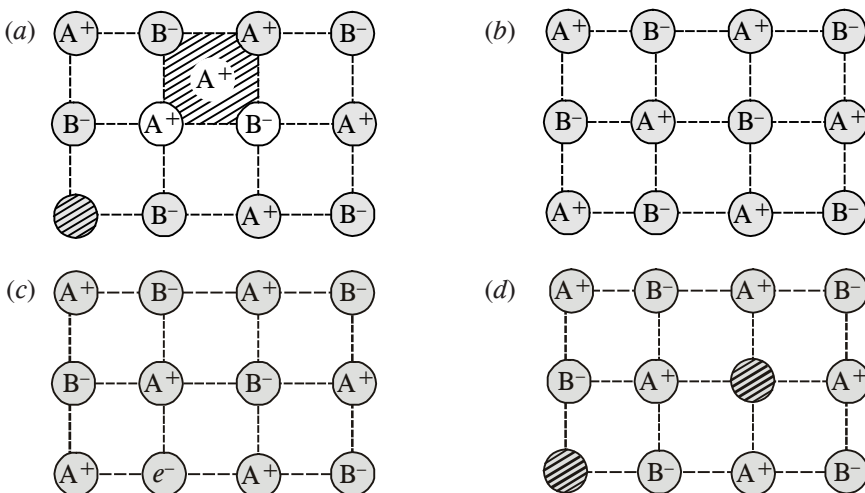
- (a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (b) $[Co(NH_3)_4(H_2O)Cl]Cl_3$
 (c) $[Co(NH_3)_2(H_2O)Cl]Cl_2$ (d) $[Co(NH_3)_4(H_2O)Cl]Cl$.
9. Which set of ions exhibit specific colours ? (Atomic number of Sc = 21, Ti = 22, V = 23, Mn = 25, Fe = 26, Ni = 28, Cu = 29 and Zn = 30)
 (a) Sc^{3+} , Ti^{4+} , Mn^{3+} (b) Sc^{3+} , Zn^{2+} , Ni^{2+}
 (c) V^{3+} , V^{2+} , Fe^{3+} (d) Ti^{3+} , Ti^{4+} , Ni^{2+} .

10. Identify A, B, C and D :

- (a) A = C_2H_4 , B = C_2H_5OH , C = C_2H_5NC , D = C_2H_5CN
 (b) A = C_2H_5OH , B = C_2H_4 , C = C_2H_5CN , D = C_2H_5NC
 (c) A = C_2H_4 , B = C_2H_5OH , C = C_2H_5CN , D = C_2H_5NC
 (d) A = C_2H_5OH , B = C_2H_4 , C = C_2H_5NC , D = C_2H_5CN .



11. The crystal showing Frenkel defect is :



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** : The two strands are complementary to each other.
Reason : The hydrogen bonds are formed between specific pairs of bases.
13. **Assertion** : Ozone is thermodynamically stable with respect to oxygen.
Reason : Decomposition of ozone into oxygen results in the liberation of heat.
14. **Assertion** : Aquatic species are more comfortable in cold waters rather than in warm waters.
Reason : Different gases have different K_H values at the same temperature.

Or

- Assertion** : Nitric acid and water form maximum boiling azeotrope.
Reason : Azeotropes are binary mixtures having the same composition in liquid and vapour phase.
15. **Assertion** : Carboxylic acids are more acidic than phenols.
Reason : Phenols are ortho and para directing.
16. **Assertion** : Methoxyethene reacts with HI to give ethanol and iodomethane.
Reason : Reaction of ether with HI follows S_N2 mechanism.

SECTION – B

The following questions, Q.Nos. 17–25 are short answer type I and carry 2 marks each.

17. Which the help of resonating structures explain the effect of presence of nitro group at ortho position in chlorobenzene.

Or

Carry out the following conversions in not more than 2 steps :

- (i) Aniline to chlorobenzene
 (ii) 2-Bromopropane to 1-bromopropane.

18. A glucose solution which boils at 101.04°C at 1 atm. What will be relative lowering of vapour pressure of an aqueous solution of urea which is equimolar to given glucose solution ? (Given : K_b for water is $0.52\text{ K kg mol}^{-1}$).

19. (i) Write the electronic configuration of iron ion in the following complex ion and predict its magnetic behaviour :



- (ii) Write the IUPAC name of the coordination complex : $[\text{CoCl}_2(\text{en})_2]\text{NO}_3$.

Or

- (i) Predict the geometry of $[\text{Ni}(\text{CN})_4]^{2-}$.
 (ii) Calculate the spin only magnetic moment of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion.

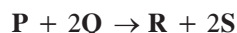
20. For a reaction the rate law expression is represented as follows :

$$\text{Rate} = k[\text{A}][\text{B}]^{1/2}$$

- (i) Interpret whether the reaction is elementary or complex. Give reason to support your answer.
 (ii) Write the units of rate constant for this reaction if concentration of **A** and **B** is expressed in moles/L.

Or

The following results have been obtained during the kinetic studies of the reaction :



Exp.	Initial P(mol/L)	Initial Q(mol/L)	Init. Rate of Formation of R (M min^{-1})
1.	0.10	0.10	3.0×10^{-4}
2.	0.30	0.30	9.0×10^{-4}
3.	0.10	0.30	3.0×10^{-4}
4.	0.20	0.40	6.0×10^{-4}

Determine the rate law expression for the reaction.

21. The C-14 content of an ancient piece of wood was found to have three tenths of that in living trees. How old is that piece of wood ? ($\log 3 = 0.4771$, $\log 7 = 0.8540$, Half-life of C-14 = 5730 years).

22. When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place :



Give a mechanism for this reaction.

23. Give the formula and describe the structure of a noble gas species which is isostructural with IF_6^- .

24. The following haloalkanes are hydrolysed in presence of *aq* KOH.

- (i) 1-Chlorobutane (ii) 2-Chloro-2-methylpropane.

Which of the above is most likely to give (a) an inverted product (b) a racemic mixture ? Justify your answer.

25. Atoms of element P form *ccp* lattice those of the element Q occupy $1/3$ rd of tetrahedral voids and all octahedral voids. What is the formula of the compound formed by the elements P and Q ?

SECTION – C

Q. Nos. 26-30 are Short Answer Type II carrying 3 mark each.

26. Give reasons for the following :

- (i) Transition elements act as catalysts
- (ii) It is difficult to obtain oxidation state greater than two for copper
- (iii) CrO is basic but Cr_2O_3 is amphoteric.

Or

Observed and calculated values for the standard electrode potentials of elements from Ti to Zn in the first transition series are depicted in Fig. 1.

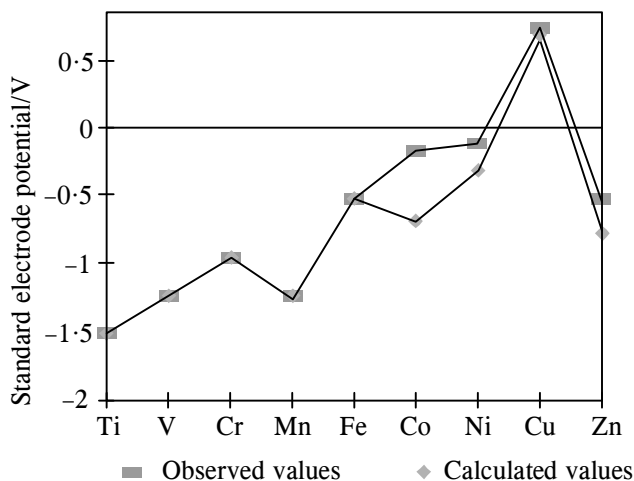


Fig. 1

Explain the following observations :

- (i) The general trend towards less negative E° values across the series
- (ii) The unique behaviour of copper
- (iii) More negative E° values of Mn and Zn.

27. Arrange the following in increasing order of property specified :

- (i) Aniline, ethanamine, N-ethylethanamine (solubility in water)
- (ii) Ethanoic acid, ethanamine, ethanol (boiling point)
- (iii) Methanamine, N, N dimethylmethanamine and N-methylmethanamine (basic strength in aqueous phase).

Or

- (i) Give a chemical test to distinguish between N-methylethanamine and N, N-dimethyl ethanamine.
- (ii) Write the reaction for catalytic reduction of nitrobenzene followed by reaction of product so formed with bromine water.
- (iii) Out of butan-1-ol and butan-1-amine, which will be more soluble in water and why ?

28. A metal crystallizes into two cubic system-face centred cubic (*fcc*) and body centred cubic (*bcc*) whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio densities of *fcc* and *bcc*.
29. Three amino acids are given below :
 Alanine : $\text{CH}_3\text{CH}(\text{COCH})(\text{NH}_2)$, Aspartic acid : $\text{HOOC}-\text{CH}_2\text{CH}(\text{COOH})(\text{NH}_2)$ and
 Lysine : $\text{H}_2\text{N}-(\text{CH}_2)_4-\text{CH}(\text{COOH})(\text{NH}_2)$.
 (i) Make two tripeptides using these amino acids and mark the peptide linkage in both cases.
 (ii) Represent alanine in the zwitter ionic form.
30. (i) Arrange the following in decreasing order of bond dissociation enthalpy
 $\text{F}_2, \text{Cl}_2, \text{Br}_2, \text{I}_2$.
 (ii) Bi does not form *pπ-pπ* bonds. Give reason for the observation.
 (iii) Electron gain enthalpy of oxygen is less negative than sulphur. Justify.

SECTION – D

Q. Nos. 31 to 33 are long answer type carrying 5 marks each.

31. (i) Answer the following questions : (2+3)
 (a) Write the balanced chemical reaction for reaction of Cu with dilute HNO_3 .
 (b) Draw the shape of ClF_3 .
 (ii) 'X' has a boiling point of 4.2 K, lowest for any known substance. It is used as a diluent for oxygen in modern diving apparatus. Identify the gas 'X'. Which property of this gas makes it usable as diluent ? Why is the boiling point of the gas 'X' so low ?

Or

- (i) Answer the following questions : (2+3)
 (a) Arrange the following in the increasing order of thermal stability :
 $\text{H}_2\text{O}, \text{H}_2\text{S}, \text{H}_2\text{Se}, \text{H}_2\text{Te}$
 (b) Give the formula of the brown ring formed at the interface during the ring test for nitrate.
 (ii) A greenish yellow gas 'A' with pungent and suffocating odour, is a powerful bleaching agent. 'A' on treatment with dry slaked lime it gives bleaching power. Identify 'A' and explain the reason for its bleaching action. Write the balanced chemical equation for the reaction of 'A' with hot concentrated NaOH.
32. An organic compound 'A' C_8H_6 on treatment with dilute H_2SO_4 containing mercuric sulphate gives compound 'B'. This compound 'B' can also be obtained from a reaction of benzene with acetyl chloride in presence of anhy. AlCl_3 . 'B' on treatment with I_2 in aq. KOH gives 'C' and a yellow compound 'D'. Identify A, B, C and D. Give the chemical reactions involved. (5)

Or

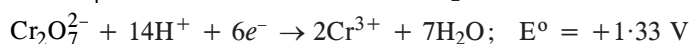
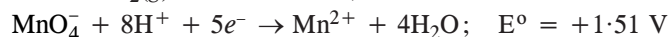
- (i) Write the reaction for cross aldol condensation of acetone and ethanal.
 (ii) How will you carry out the following conversions :
 (a) Benzyl alcohol to phenyl ethanoic acid
 (b) Propanone to propene
 (c) Benzene to *m*-Nitroacetophenone.
33. (i) State Kohlrausch law. (1 + 4)
 (ii) Calculate the emf of the following cell at 298 K :



(Given $E^\circ(\text{Al}^{3+}/\text{Al}) = -1.66 \text{ V}$, $E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$, $\log 0.15 = -0.8239$, $\log 0.025 = -1.6020$)

Or

- (i) On the basis of E° values identify which amongst the following is the strongest oxidising agent



- (ii) The following Fig. 2, represents variation of (Λ_m) vs \sqrt{C} for an electrolyte. Here Λ_m is the molar conductivity and C is the concentration of the electrolyte.

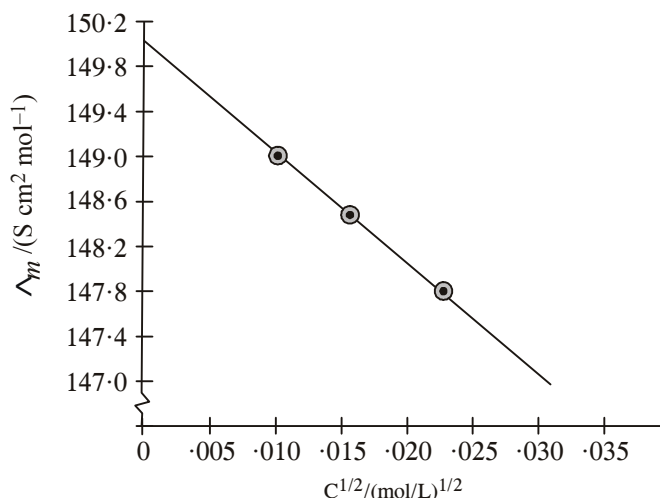


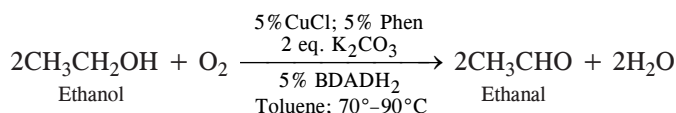
Fig. 2

- (a) Define molar conductivity.
 (b) Identify the nature of electrolyte on the basis of the above plot. Justify your answer.
 (c) Determine the value of Λ_m° for the electrolyte.
 (d) Show how to calculate the value of A for the electrolyte using the above graph.

SOLUTION

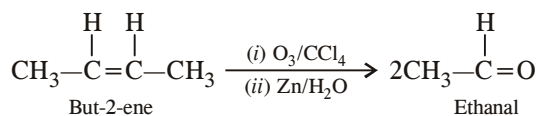
1. (i) (d) **Explanation :** Propan-2-ol is a 2° alcohol. The given copper based catalyst will oxidise it to corresponding ketone *i.e.*, propanone.

(ii) (b) **Explanation :**



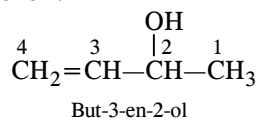
Phen : Phenanthroline

DBADH₂ : Di-terbutyl azo dicarboxylate (Di-terbutyl hydrazine-1, 2-dicarboxylate)

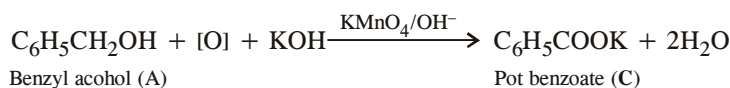
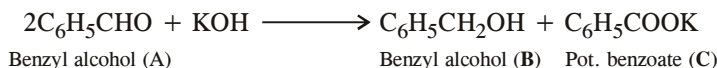


Or

(a) **Explanation :** Formula of *sec*-allylic alcohol :



- (iii) (a) **Explanation :** $2\text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{O}_2 \xrightarrow{\text{Cu-based catalyst}} 2\text{C}_6\text{H}_5\text{CHO} + 2\text{H}_2\text{O}$
 Benzyl alcohol Benzaldehyde (A)



A : Benzaldehyde

B : Benzyl alcohol

C : Pot. benzoate (potassium salt of benzoic acid)

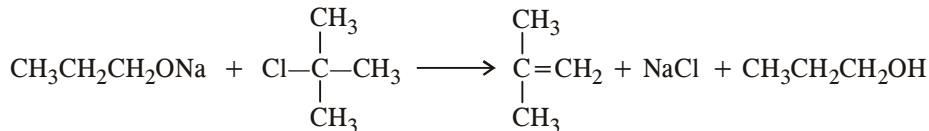
- (iv) (c) **Explanation :** X(C₃H₈O) can be propyl alcohol or isopropyl alcohol. Oxidation of X with air and copper based catalyst gives Y. As Y reduces Tollen's reagent, it is an aldehyde, therefore X is a 1° alcohol, i.e., propyl alcohol (CH₃CH₂CH₂OH).



Propyl alcohol (X)

Sod propanoixde (Z)

As 2-chloro-2-methylpropane is a 3° alkyl halide, its reaction with Z leads to elimination reaction.



2-Chloro-2-methyl propane

2. (i) (b) **Correct explanation :** Vegetable tanned leather has smaller surface area due to blockage of capillaries by tanning materials.
- (ii) (a) Reason is the correct explanation of assertion.
- (iii) (a) Reason is the correct explanation of assertion.
- (iv) (a) Reason in the correct explanation of assertion.
- (iv) (b) **Correct explanation :** The amount of water adsorbed by leather depends upon the nature of tanning.

3. (c) **Explanation :**

$$\begin{aligned}\Lambda_m^\circ(\text{CH}_3\text{COOH}) &= \Lambda_m^\circ(\text{CH}_3\text{COONa}) + \Lambda_m^\circ(\text{H}^+) - \Lambda_m^\circ(\text{Na}^+) \\ &= (91 + 349.6 - 50.1) \text{ S cm}^2 \text{ mol}^{-1} \\ &= (440.6 - 50.1) \text{ S cm}^2 \text{ mol}^{-1} \\ &= \mathbf{390.5 \text{ S cm}^2 \text{ mol}^{-1}}.\end{aligned}$$

4. (d) **Explanation :** Curdling of milk is an example of denaturation of protein.

Or

(c) **Explanation :** Sucrose is a non-reducing sugar.

5. (c) **Explanation :**

$$\begin{aligned}n_T &= 1 \text{ mol}, n_B = 1 \text{ mol} \\ x_T &= \frac{n_T}{n_T + n_B} = \frac{1}{1 + 1} = \frac{1}{2} = 0.5 \\ x_B &= 1 - 0.5 = 0.5 \\ p_T &= p_T^\circ \times x_T = 3.85 \text{ kPa} \times 0.5 \\ &= 1.925 \text{ kPa} \\ p_B &= p_B^\circ \times x_B = 12.8 \text{ kPa} \times 0.5 \\ &= 6.4 \text{ kPa}\end{aligned}$$

Mole fraction of toluene in vapour,

$$\begin{aligned}y_T &= \frac{p_T}{p_T + p_B} = \frac{1.925}{1.925 + 6.4} = \frac{1.925}{8.325} \\ &= \mathbf{0.23}\end{aligned}$$

Mole fraction of benzene in vapour phase is,

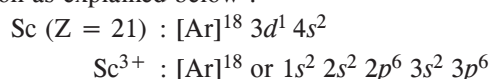
$$y_B = 1 - y_T = 1 - 0.23 = \mathbf{0.77}$$

As mole fraction of benzene in vapour phase is more, the vapour will have a higher percentage of benzene.

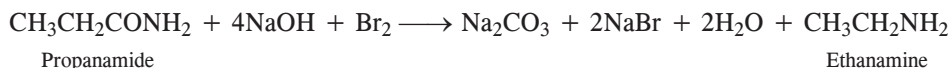
6. (b) **Explanation :** Zinc (Z = 30) does not show variable oxidation state because it has completely filled 3d-sub shell.

Or

- (b) **Explanation :** An ion is diamagnetic if it has no unpaired electron. Out of the given four choices, Sc³⁺ has no unpaired electron as explained below :

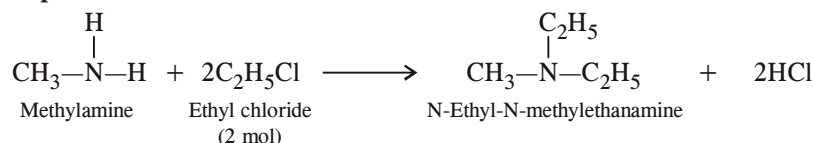


7. (b) **Explanation :** Hoffmann bromamide reaction



Or

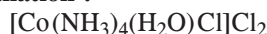
- (d) **Explanation :**



8. (a) **Explanation :** Ambidentate ligand has two or more donor atoms, but only one atom can donate a pair of electrons at a time. As such ambidentate ligand is unidentate.

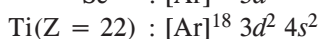
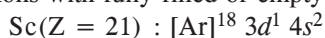
Or

- (a) **Explanation :**

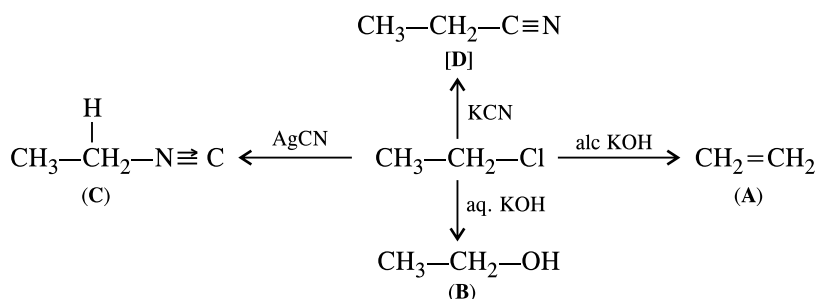


tetraammineaquachloridocobalt(III) chloride

9. (c) **Explanation :** Ions with fully filled or empty $(n-1)d$ -subshell are colourless.



10. (a) **Explanation :**



11. (a) **Explanation :** Frenkel defect involves dislocation of the smaller ions (generally cation) from its lattice sites to some interstitial site.

12. (a) Reason is the correct explanation of the assertion.

13. (d) **Correct assertion :** Ozone is thermodynamically unstable with respect to oxygen.

14. (b) **Correct explanation :** Dissolution of O_2 in water increases with decrease in temperature.

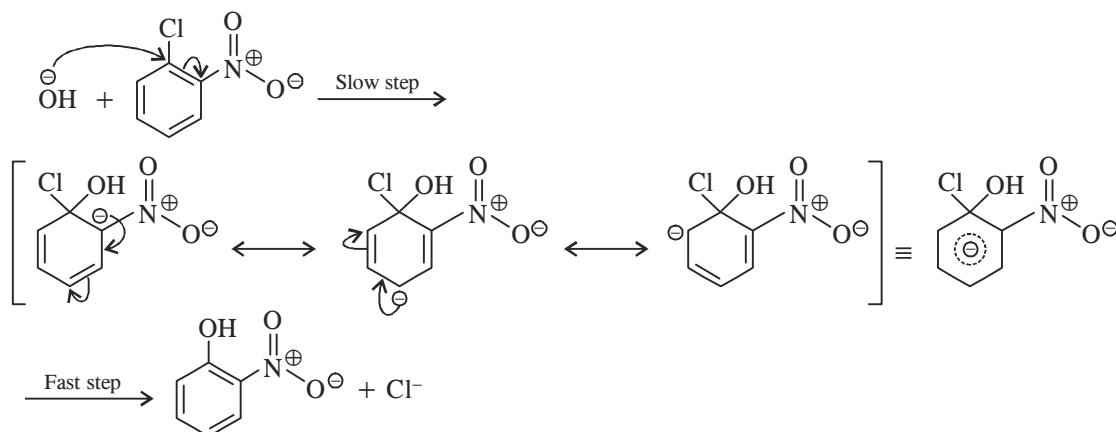
Or

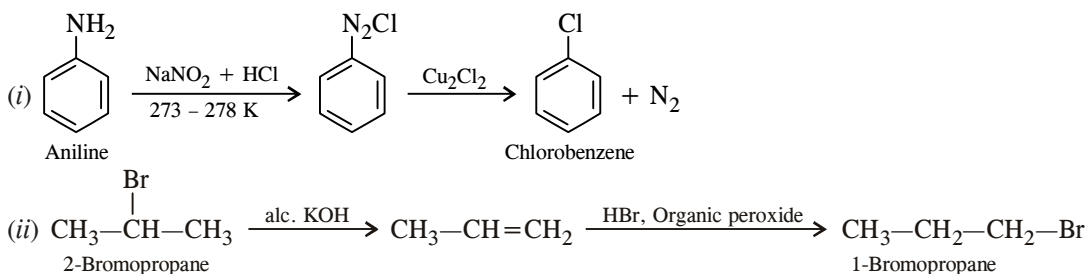
- (b) **Correct explanation :** A mixture of nitric acid and water shows negative deviation from ideal behaviour.

15. (b) **Correct explanation :** Resonance stabilisation of carboxylate ion is more than that of phenoxide ion.

16. (a) Reason is the correct explanation of the assertion.

17. Nitro group at ortho position withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene.





18.

$$\Delta T_b = T_b - T_b^\circ = (10.04 - 100)^\circ \text{C} = 1.04^\circ \text{C} = 1.04 \text{ K}$$

$$K_b (\text{water}) = 0.52 \text{ K kg mol}^{-1}$$

$$\Delta T_b = K_b \times m$$

$$m = \frac{\Delta T_b}{K_b} = \frac{1.04 \text{ K}}{0.52 \text{ K kg mol}^{-1}} = 2 \text{ mol kg}^{-1},$$

Hence, the solution contains 2 mol of solute (glucose) in 1 kg (1000 g) of water. Given urea solution has same molality as the glucose solution. Hence

$$\text{No. of moles of urea, } n_2 = 2$$

$$\text{No. of moles of water, } n_1 = \frac{1000 \text{ g}}{18 \text{ g mol}^{-1}} = 55.55 \text{ mol}$$

$$\text{Mole fraction of urea, } x_2 = \frac{n_2}{n_1 + n_2} = \frac{2}{2 + 55.55} = \frac{2}{57.55} = 0.034.$$

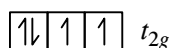
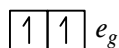
$$\text{Relative lowering of V.P.} = x_2 = 0.034.$$

19. (i) O.S. of iron in the complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} = +2$

$$\text{Fe} (Z = 26) : [\text{Ar}]^{18} 3d^6 4s^2$$

$$\text{Fe}^{2+} : [\text{Ar}]^{18} 3d^6$$

Water is a strong field ligand. Hence, electronic configuration of iron in the complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is $t_{2g}^4 e_g^2$.



Due to the presence of 4 unpaired electrons, the complex is paramagnetic.

(ii) $[\text{CoCl}_2(\text{en})_2]\text{NO}_3$

IUPAC name : dichloridobis(ethane-1, 2-diamine)cobalt(III) nitrate

Or

(i) O.S. of nickel in the complex $[\text{Ni}(\text{CN})_4]^{2-} = +2$

$$\text{Ni} (Z = 28) : [\text{Ar}]^{18} 3d^8 4s^2$$

$$\text{Ni}^{2+} : [\text{Ar}]^{18} 3d^8$$

CN^- is a strong field ligand. As such, pairing of electrons will take place in $3d$ -subshell. Hybridisation is dsp^2 and the shape of the complex is square planar.

(ii) O.S. of copper in the complex $[\text{Cu}(\text{NH}_3)_4]^{2+} = +2$

$$\text{Cu} (Z = 29) : [\text{Ar}]^{18} 3d^{10} 4s^1$$

$$\text{Cu}^+ : [\text{Ar}]^{18} 3d^9$$

No. of unpaired electrons, $n = 1$

$$\mu_{\text{spin only}} = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.732 \text{ BM}$$

20.

$$\text{Rate} = k[\text{A}][\text{B}]^{1/2}$$

$$\text{Order of the reaction} = 1 + \frac{1}{2} = 1.5$$

As the order of the reaction is a fraction, it is a **complex reaction**.

$$k = \frac{\text{Rate}}{(\text{conc.})^{3/2}}$$

$$\text{Units of } k = \frac{\text{mol L}^{-1} \text{ s}^{-1}}{(\text{mol L}^{-1})^{3/2}} = \text{mol}^{-1/2} \text{ L}^{1/2} \text{ s}^{-1}.$$

Or

Let the rate law expression is ;

$$\text{Rate} = k[\text{P}]^a [\text{Q}]^b$$

From Experiment No. 1

$$3.0 \times 10^{-4} = k(0.10)^a (0.10)^b \quad \dots(i)$$

From Experiment No. 2

$$9.0 \times 10^{-4} = k(0.30)^a (0.30)^b \quad \dots(ii)$$

From Experiment No. 3

$$3.0 \times 10^{-4} = k(0.10)^a (0.30)^b \quad \dots(iii)$$

From Experiment No. 4

$$6.0 \times 10^{-4} = k(0.20)^a (0.40)^b \quad \dots(iv)$$

Dividing Eqn. No. (ii) by Eqn. No. (iii),

$$\frac{9.0 \times 10^{-4}}{3.0 \times 10^{-4}} = \frac{k(0.30)^a (0.30)^b}{k(0.10)^a (0.30)^b}$$

$$3 = 3^a \Rightarrow a = 1$$

Dividing Eqn. No. (iv) by Eqn. No. (i),

$$\frac{6.0 \times 10^{-4}}{3.0 \times 10^{-4}} = \frac{k(0.20)^a (0.40)^b}{k(0.10)^a (0.10)^b}$$

$$2 = 2^a 4^b$$

But $a = 1 \Rightarrow b = 0$

Hence, rate law expression is :

$$\text{Rate} = k[\text{P}].$$

21.

$$t_{1/2} = 5730 \text{ years}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} \text{ year}^{-1} = 1.21 \times 10^{-4} \text{ year}^{-1}$$

(Radioactive decay follows 1st order kinetics)

$$[\text{R}]_0 = 1(\text{say}); [\text{R}] = \frac{3}{10}$$

$$t = \frac{2.303}{k} \log \frac{[\text{R}]_0}{[\text{R}]}$$

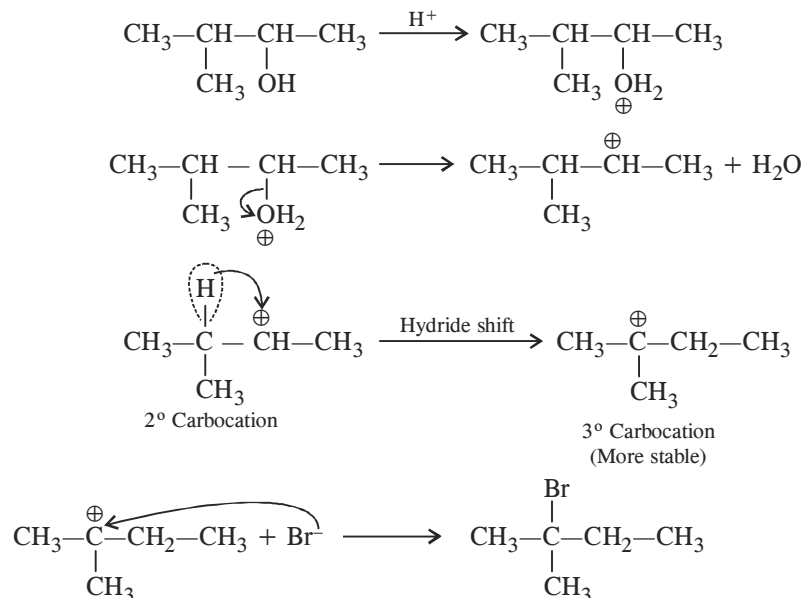
$$t = \frac{2.303}{1.21 \times 10^{-4} \text{ year}^{-1}} \log \frac{1}{3/10}$$

$$= \frac{2.303}{1.21 \times 10^{-4} \text{ year}^{-1}} \log \frac{10}{3} = \frac{2.303}{1.21 \times 10^{-4}} (\log 10 - \log 3) \text{ year}$$

$$= \frac{2.303(1 - 0.4771)}{1.21 \times 10^{-4}} \text{ year} = \frac{2.303 \times 0.5229 \times 10^4}{1.21} \text{ year}$$

$$= 0.99524 \times 10^4 \text{ year} = \mathbf{9952.4 \text{ year.}}$$

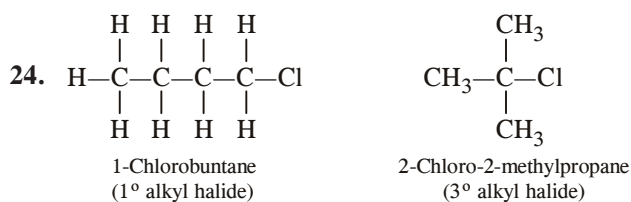
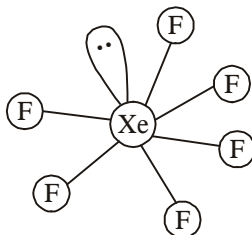
22. Mechanism of the reaction



23. IF_6^- has six bond pairs and one lone pair. Noble gas species isoelectronic with IF_6^- is XeF_6 .

Structure of XeF_6

In XeF_6 , the central Xe atom has 8 valence electrons. It forms 6 bonds with six F-atoms and has one lone pair. According to VSEPR theory, presence of 6 *b.p.* and 1 *l.p.* results in distorted octahedral geometry as shown below :



(a) Alkyl halides with aq KOH give alcohols. It is a nucleophilic substitution reaction. In this reaction 1° alkyl halide undergo $\text{S}_{\text{N}}2$ reaction giving inverted product. Thus 1-chlorobutane will give inverted product.

(b) In nucleophilic substitution reaction 3° alkyl halide undergoes $\text{S}_{\text{N}}1$ reaction, giving a racemic mixture. Hence 2-chloro-2-methylpropane will give a racemic mixture.

25. Let number of atoms of element P in *ccp* lattice = n

$$\begin{aligned}
 \therefore \quad \text{Octahedral voids} &= n \\
 \text{Tetrahedral voids} &= 2n
 \end{aligned}$$

$$\begin{aligned}
 \text{Number of atoms of element Q} &= \text{No. of octahedral voids} + \frac{1}{3} \times \text{No. of tetrahedral voids} \\
 &= n + \frac{2n}{3} = \frac{5n}{3}
 \end{aligned}$$

$$\therefore \text{Formula of compound is } \text{P}_n \text{Q}_{\frac{5n}{3}} \text{ or } \text{P}_3\text{Q}_5$$

26. (i) Transition elements and their compounds act as good catalysts due to the following two reasons :
- Ability of transition elements to show variable oxidation states.
 - Due to the presence of incomplete d -subshell in transition elements, they can form unstable intermediates. These intermediates give reaction path of lower activation energy and therefore increase the rate of the reaction.
- (ii) It is due to high value of third ionisation enthalpy.
- (iii) In CrO , O.S. of Cr is +2 and in Cr_2O_3 , O.S. of Cr is +3. As the O.S. of metal in its oxide increases, the basic character of oxide decreases, while its acidic nature increases. Thus CrO is basic while Cr_2O_3 is amphoteric (*i.e.*, it shows both acidic as well as basic characters).

Or

- The general trend towards less negative E° values across the series is due to the general increase in the sum of first and second ionisation enthalpies.
 - In $3d$ -series, copper has +ve E° value. It is due to high energy of transformation of $\text{Cu}(s)$ to $\text{Cu}^{2+}(g)$, which is not balanced by its hydration enthalpy.
 - The stability of the half filled d -subshell in Mn^{2+} and completely filled d^{10} configuration in Zn^{2+} are related to their more negative E° values.
27. (i) Increasing order of solubility in water :



(Aromatic amines are less soluble than aliphatic amines and solubility of aliphatic amines follows the order $3^\circ < 2^\circ < 1^\circ$ due to H-bonding with water molecules)

- (ii) Increasing order of boiling points :



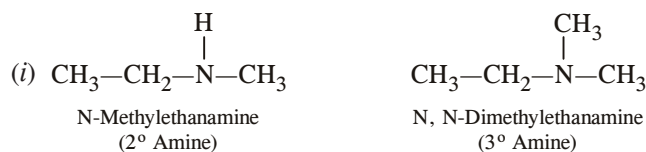
(Acids have higher boiling points than corresponding alcohols due to dimer formation. H-bonding is stronger in alcohols than amines).

- (iii) Increasing basic character in aqueous solution :

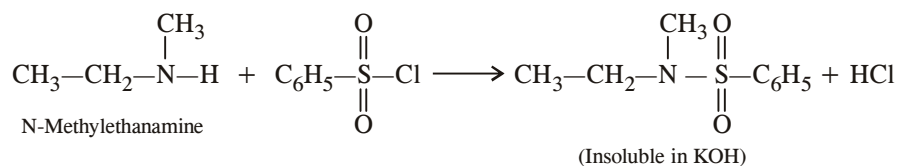


(In aqueous solution, 2° amine is most basic).

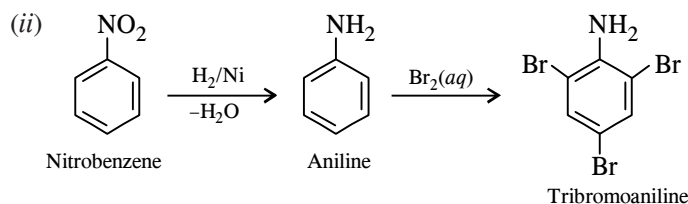
Or



A 2° amine reacts with benzene sulphonyl chloride as follows. The product formed is insoluble in KOH.



A 3° amine cannot react with benzene sulphonyl chloride. Thus out of these two amines only N-methylethanamine will react with benzene sulphonyl chloride to give a product insoluble in KOH.



- (iii) Butan-1-ol is more soluble in water. Alcohol forms stronger H-bonds with water than amines. It is due to higher electronegativity and smaller size of O in alcohol than N in amine.

28. Density,
$$d = \frac{z \times M}{N_A \times a^3}$$

where

z = No. of atoms per unit cell

M = Molar mass (g mol^{-1})

$$N_A = \text{Avogadro's Number } (6.022 \times 10^{23} \text{ mol}^{-1})$$

a = Edge length of cube (cm)

For *f.c.c.* structure

$$z = 4$$

$$a = 3.5 \text{ \AA} = 3.5 \times 10^{-8} \text{ cm}$$

\therefore

$$d = \frac{4 \times M}{N_A \times (3.5 \times 10^{-8})^3}$$

For *b.c.c.* structure

$$z = 2$$

$$a = 3.0 \text{ \AA} = 3.0 \times 10^{-8} \text{ cm}$$

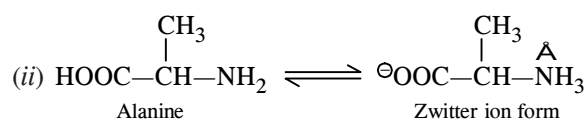
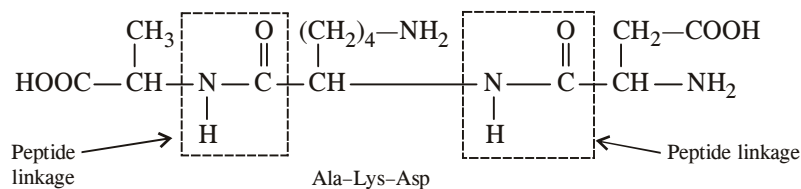
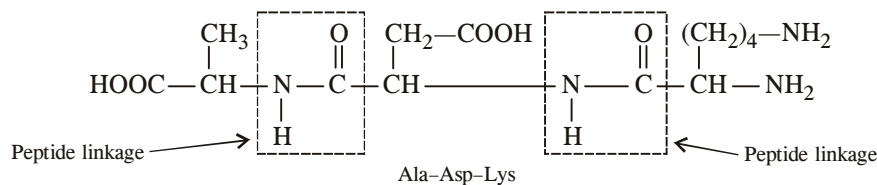
\therefore

$$d = \frac{2 \times M}{N_A \times (3.0 \times 10^{-8})^3}$$

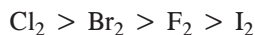
$$\frac{d}{d'} = \frac{4 \times (3.0 \times 10^{-8})^3}{2 \times (3.5 \times 10^{-8})^3} = \frac{4 \times 3 \times 3 \times 3}{2 \times 3.5 \times 3.5 \times 3.5}$$

$$= \frac{1.26}{1.00} \text{ (approx.)}$$

29. (i) There are 3 different amino acids. Hence, total number of tripeptides with different amino acids = 6
Out of these 6, two tripeptides can be;



30. (i) Decreasing order of bond dissociation enthalpy :



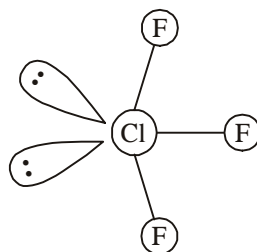
Bond dissociation enthalpy of F_2 is exceptionally low. It is due to strong repulsions between lone pairs on two F-atoms which are very near to each other.

(ii) Bismuth (Bi) does not form $p\pi-p\pi$ bonds as its atomic orbitals are large and diffuse. As such effective overlapping is not possible.

(iii) Due to small size of O, strong interelectronic repulsions take place in the relatively compact $2p$ -subshell and thus incoming electron is less firmly held by the nucleus.

31. (i) (a)
- $$\begin{array}{l} 2\text{HNO}_3(\text{dil}) \longrightarrow \text{H}_2\text{O} + 2\text{NO} + 3[\text{O}] \\ \text{Cu} + 2\text{HNO}_3 + [\text{O}] \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{O} \times 3 \\ \hline 3\text{Cu} + 8\text{HNO}_3(\text{dil}) \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O} \end{array}$$

(b) ClF_3 molecule has 3 bond pairs and 2 lone pairs. As such it is a T-shaped molecule as shown below :



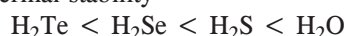
(ii) Gas X is helium.

Helium is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Helium is a monoatomic gas with just 2 electrons. As such the interatomic forces are very weak London dispersion forces, resulting in extremely low boiling point.

Or

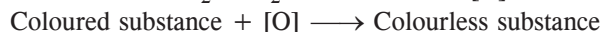
(i) (a) Increasing order of thermal stability



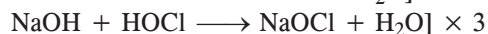
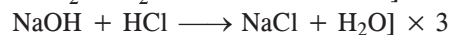
(b) Formula for brown ring in ring test for nitrate : $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$.

(ii) Gas A is chlorine (Cl_2).

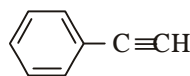
Cl_2 acts as a strong bleaching agent due to its oxidising nature. It bleaches coloured organic substance due to oxidation.



Reaction of Cl_2 with hot conc. NaOH

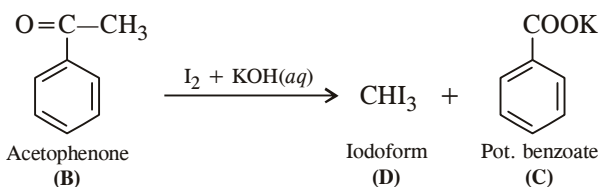
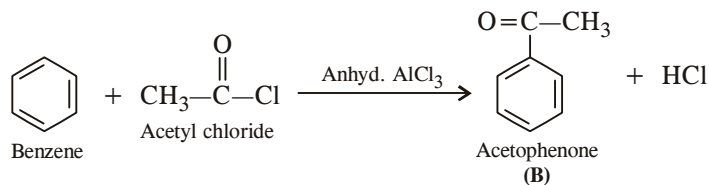
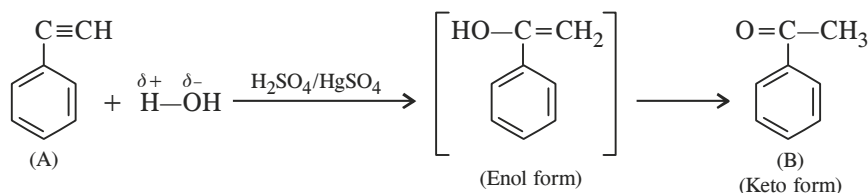


32. As A reacts with dil H_2SO_4 in the presence of HgSO_4 , A is an alkyne. Its molecular formula (C_8H_6) indicates that it has the following structure.



(A)

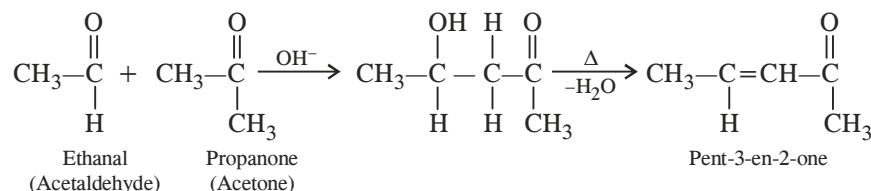
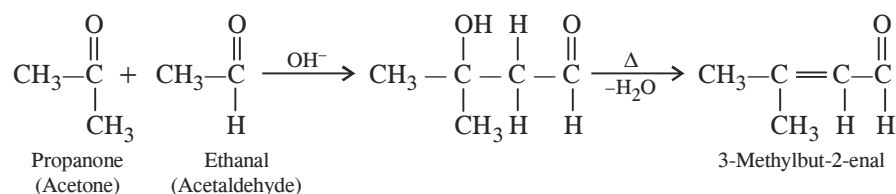
Reaction of A with dil $\text{H}_2\text{SO}_4/\text{HgSO}_4$ is;



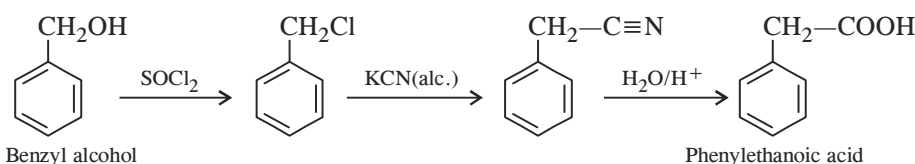
Iodoform forms a yellow ppt.

OR

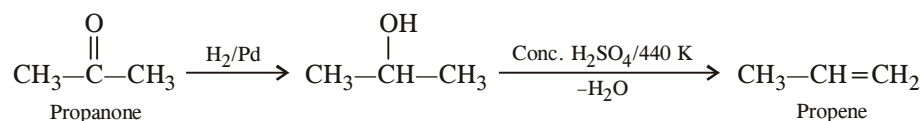
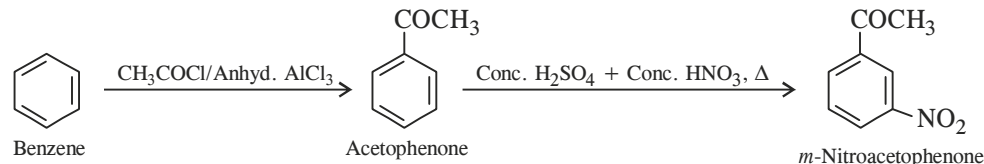
(i) Two different cross-aldol products are possible as shown below :



(ii) (a) Benzyl alcohol to phenylethanoic acid



(b) Propanone to propene

(c) Benzene to *m*-nitroacetophenone33. (i) **Kohlrausch Law** : At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated.If molar conductivity at infinite dilution of cation is λ_+^0 and that of anion is λ_-^0 , then according to Kohlrausch law ;

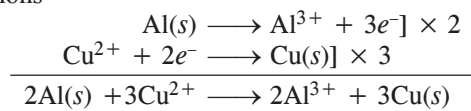
$$\lambda_m^0 = x\lambda_+^0 + y\lambda_-^0$$

where x and y are number of cations and anions per formula unit of the electrolyte.

(ii) Cell representation is ;



Half cell reactions

Here n (no. of electrons) = 6

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Al}^{3+}/\text{Al}}^{\circ} \\ &= [0.34 - (-1.66)] \text{ V} \\ &= 2.00 \text{ V} \end{aligned}$$

Nernst equation for the cell at 298 K is

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.059 \text{ V}}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3} \\ &= 2.00 \text{ V} - \frac{0.059 \text{ V}}{6} \log \frac{(0.15)^2}{(0.025)^3} \end{aligned}$$

$$\begin{aligned}
 &= 2.00 \text{ V} - \frac{0.059}{6} \text{ V} [\log (0.15)^2 - \log(0.025)^3] \\
 &= 2.00 \text{ V} - \frac{0.059 \text{ V}}{6} [2 \log 0.15 - 3 \log 0.025] \\
 &= 2.00 \text{ V} - \frac{0.059 \text{ V}}{6} [2 \times (-0.8239) - 3 \times (-1.6020)] \\
 &= 2.00 \text{ V} - \frac{0.059 \text{ V}}{6} [4.806 - 1.6478] \\
 &= \left(2.00 - \frac{0.059 \times 3.1582}{6} \right) \text{ V} \\
 &= (2.00 - 0.031) \text{ V} = \mathbf{1.9689 \text{ V}}.
 \end{aligned}$$

Or

(i) Higher the reduction potential, easier to reduce and hence strongest oxidising agent. Thus, the strongest oxidising agent out of the three given choices : MnO_4^-

(ii) (a) **Molar conductivity** : It is defined as the conductance of a solution containing 1 gram mole of the electrolyte placed between two plates kept 1 cm apart.

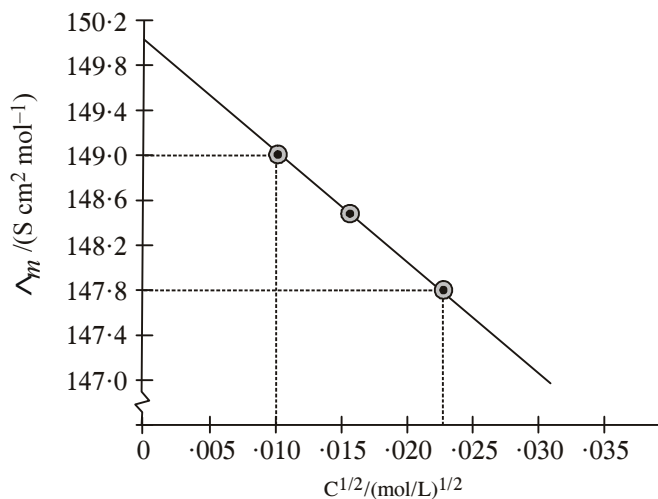
(b) **Nature of electrolyte** : Strong electrolyte.

Reason : For strong electrolyte molar conductivity increases linearly with dilution.

(c) $\Lambda_m^\circ =$ Intercept on y-axis
 $= 150 \text{ S cm}^2 \text{ mol}^{-1}$

(d) $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$

$$A = - \text{Slope of the graph} = - \frac{y_2 - y_1}{x_2 - x_1}$$



$$\begin{aligned}
 A &= - \text{slope} = - \frac{y_2 - y_1}{x_2 - x_1} \\
 &= - \frac{(149.0 - 147.8) \text{ S cm}^2 \text{ mol}^{-1}}{(0.010 - 0.022) (\text{mol L}^{-1})^{1/2}} \\
 &= - \frac{1.2}{(-0.012)} \text{ S cm}^2 \text{ mol}^{-1} / (\text{mol L}^{-1})^{1/2} \\
 &= \mathbf{100 \text{ S cm}^2 \text{ mol}^{-1} / (\text{mol L}^{-1})^{1/2}}.
 \end{aligned}$$

SAMPLE QUESTION PAPERS (SOLVED)

Chemistry (Theory)–XII

Time Allowed : 3 hours

Maximum Marks : 70

General Instructions : Read the following instructions carefully.

- There are 33 questions in this question paper. All questions are compulsory.
- Section A** : Q. No. 1 to 2 are case-based questions having four MCQs or Reason Assertion type based on given passage each carrying 1 mark.
- Section A** : Question 3 to 16 are MCQs and Reason Assertion type questions carrying 1 mark each.
- Section B** : Q. No. 17 to 25 are short answer questions and carry 2 marks each.
- Section C** : Q. No. 26 to 30 are short answer questions and carry 3 marks each.
- Section D** : Q. No. 31 to 33 are long answer questions carrying 5 marks each.
- There is no overall choice. However, internal choices have been provided.
- Use of calculators and log tables is not permitted.

Sample Question Paper – 1

SECTION – A (Objective Type)

1. Read the passage given below and answer the questions (i) to (iv) that follow :

Adsorption is a surface phenomenon and it differs from absorption which occurs throughout the body of the substance which absorbs. In physisorption, the attractive forces are mainly van der Waals' forces while in chemisorption actual bonding occurs between the particles of adsorbent and adsorbate. Generally, easily liquefying gases are adsorbed more easily on the surface of a solid as compared to the gases which are liquefied with difficulty. Adsorption increases with the increase in pressure and decreases as the temperature is increased.

Choose the most appropriate answer.

- Which of the following gas will be most easily adsorbed ?
(a) H_2 (b) CH_4
(c) CO (d) NH_3 .
- Adsorption of gases on the solid surface is exothermic because during adsorption,
(a) enthalpy increases (b) entropy decreases
(c) entropy increases (d) free energy increases.
- When SO_2 is adsorbed on charcoal, the SO_2 is called :
(a) Adsorbent (b) Adsorbate
(c) Adsorber (d) Absorber.
- In physical adsorption, the forces associated are
(a) ionic bonds (b) covalent bonds
(c) van der Waals' (d) hydrogen bond.

OR

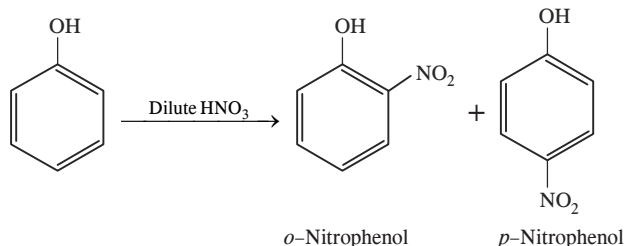
In chemical adsorption, which is not true ?

- It is irreversible
- Increases with increase in temperature.
- Highly specific in nature
- Enthalpy of adsorption is low.

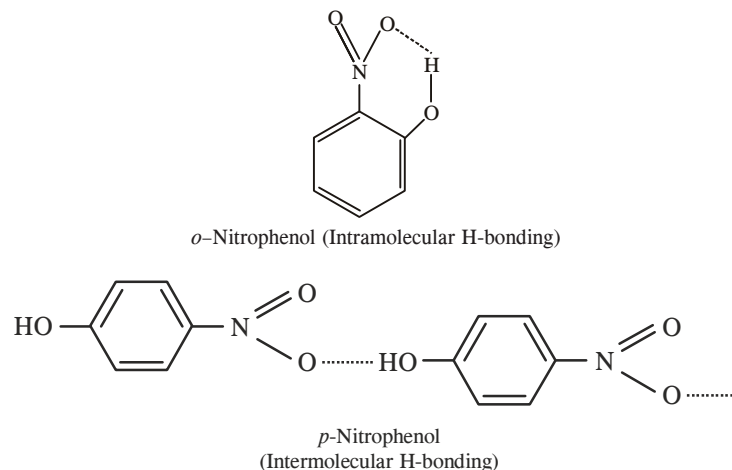
$4 \times 1 = 4$

2. Read the following passage and answer the questions (i) to (iv) that follow :

With dilute nitric acid at low temperature (298 K), phenol yields a mixture of *ortho* and *para* nitrophenols.



The *ortho* and *para* isomers can be separated by steam distillation. *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



With concentrated nitric acid, phenol is converted to 2, 4, 6-trinitrophenol (Picric acid). The yield of the reaction is poor.

The question given below consist of Assertion and Reason. Use the following key to select the correct answer.

- (a) If the both assertion and reason are correct and reason is correct explanation for assertion.
 (b) If both assertion and reason are correct but reason is not correct explanation for assertion.
 (c) If assertion is correct but reason is incorrect.
 (d) If assertion is wrong but reason is correct.
- (i) **Assertion** : Phenol gives *o*- and *p*-nitrophenols on nitration with conc. HNO_3 and conc. H_2SO_4 mixture.
Reason : The $-\text{OH}$ group in phenol is *o*- and *p*-directing.
- (ii) **Assertion** : *o*-Nitrophenol is less soluble in water than *m*- and *p*-isomers.
Reason : The *m*- and *p*-nitrophenols exist as associated molecules.
- (iii) **Assertion** : Out of *o*- and *p*-nitrophenols, *o*-nitrophenol has lesser boiling point.
Reason : It is due to the presence of intramolecular H-bonding in *o*-nitrophenol.
- (iv) **Assertion** : A mixture of *o*- and *p*-nitrophenols can be separated by steam distillation.
Reason : Boiling point of *p*-nitrophenol is less than that of *o*-nitrophenol.

OR

Assertion : A mixture of *o*-nitrophenol and water can be separated by using separating funnel.

Reason : *o*-Nitrophenol is immiscible with water.

$4 \times 1 = 4$

Multiple Choice Questions (Q. No. 3 to Q. No. 11)

• Select the correct answer

3. The unit of specific conductance is :
 (a) ohm (b) $\text{ohm}^{-1} \text{cm}^{-1}$
 (c) $\text{ohm}^{-1} \text{cm}$ (d) ohm^2 .
4. Hot concentrated H_2SO_4 acts as a moderately strong oxidising agent. It oxidises both metals and non-metals. Which of the following elements is oxidised by hot conc. H_2SO_4 into two gaseous products ?
 (a) Cu (b) S
 (c) C (d) Zn

OR

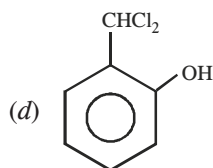
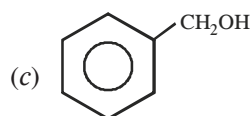
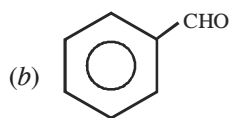
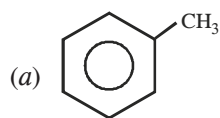
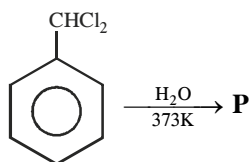
Which of the following is most basic ?

- (a) BiH_3 (b) NH_3
 (c) PH_3 (d) AsH_3 .
5. Which of the following compounds is not coloured ?
 (a) FeCl_3 (b) CrCl_3
 (c) TiCl_3 (d) HgI_2 .

6. How many ions are given by $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$ complex in water ?
 (a) 4 (b) 2
 (c) 6 (d) 3.
7. In the given alkyl halides which one has the minimum boiling point ?
 (a) $\text{C}_2\text{H}_5\text{F}$ (b) $\text{C}_2\text{H}_5\text{I}$
 (c) $\text{C}_2\text{H}_5\text{Cl}$ (d) $\text{C}_2\text{H}_5\text{Br}$.

OR

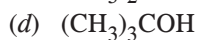
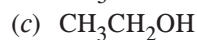
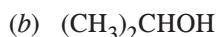
In following reaction, product P is;



8. Which of the following is most basic in aqueous solution ?
 (a) CH_3NH_2 (b) $(\text{CH}_3)_2\text{NH}$
 (c) $(\text{CH}_3)_3\text{N}$ (d) $\text{C}_6\text{H}_5\text{NH}_2$.
9. Which of the following is not present in DNA ?
 (a) Adenine (b) Guanine
 (c) Thymine (d) Uracil.
10. $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[443\text{K}]{\text{H}_2\text{SO}_4} \text{X}$; what is X ?
 (a) $\text{CH}_2=\text{CH}_2$ (b) $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
 (c) $\text{CH}_3 - \text{OCH}_2\text{CH}_3$ (d) $\text{CH}_3\text{CH}_2\text{HSO}_4$.

OR

Which is weakest acid in the following ?



11. $2\text{HCHO} + \text{conc. NaOH} \longrightarrow \text{CH}_3\text{OH} + \text{HCOONa}$ is
 (a) Cross aldol condensation (b) Aldol condensation
 (c) Cannizzaro reaction (d) Rosenmund reaction.

OR

The acid that does not contain carboxylic acid group is

**Assertion-Reason Type Questions (Q. No. 12 to Q. No. 16)**

- The questions given below consists of Assertion and Reason. Use the following key to select the correct answer.
- (a) If both assertion and reason are correct statements and reason is the correct explanation of the assertion.
- (b) If both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.
- (c) If assertion is correct, but reason is wrong.
- (d) If assertion is wrong, but reason is correct.

12. **Assertion:** Copper is less reactive than hydrogen.
Reason : $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ}$ is negative.
13. **Assertion :** The presence of a large number of Schottky defects lowers the density of NaCl crystal.
Reason : In NaCl, there are approximately 10^6 Schottky pairs per cm^3 at room temperature.
14. **Assertion:** Molarity of a solution changes with temperature.
Reason : The volume of solution changes with change in temperature.
15. **Assertion:** Order of a reaction can be zero or fractional.
Reason : We cannot determine order of a reaction from its balanced chemical equation.
16. **Assertion:** The two strands in double strand helix structure of DNA are complementary to each other.
Reason : Disulphide bonds are formed between specific pairs of bases.

OR

- Assertion:** Glucose reacts with hydroxylamine to form an oxime and also adds a molecule of hydrogen cyanide to give cynohydrin.
Reason : The carbonyl group present in open chain structure of glucose is an aldehyde group.

SECTION – B

The following questions (Q.No. 17–25) are short answer type I and carry 2 marks each.

17. State Raoult's law for solutions of volatile liquid components. Taking a suitable example, explain the meaning of positive deviation from Raoult's law. 2

OR

Define the term 'osmotic pressure'. Describe how the molecular mass of a substance can be determined on the basis of osmotic pressure measurement. 2

18. In the first transition series,
 (i) Name the element showing maximum number of oxidation states
 (ii) Name the element which shows only +3 oxidation state
19. Complete the following reaction equations :
 (i) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{KI} \longrightarrow \dots\dots$
 (ii) $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array} + \text{Br}_2 \xrightarrow{\text{CCl}_4} \dots\dots$ 2
20. (i) Arrange the following in increasing order of basic strength in water :
 $\text{C}_6\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$ and NH_3 .
 (ii) Arrange the following in increasing order of basic strength in gas phase :
 $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$ and CH_3NH_2 . 2
21. Write one chemical reaction each to illustrate the following : 2
 (i) Hoffmann's bromamide reaction
 (ii) Gabriel phthalimide synthesis
22. Explain, why ortho-nitrophenol is more acidic than ortho-methoxyphenol ? 2
23. Convert (i) Propene to propan-1-ol. (ii) Phenol to benzoquinone. 2
24. A solution containing 16 g of a substance in 200 g of diethyl ether boils at 36.86°C , whereas pure ether boils at 35.60°C . Determine the molecular mass of the solute. (for ether $K_b = 2.02 \text{ K kg mol}^{-1}$) 2

OR

Calculate the temperature at which a solution containing 54 g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, in 250 g of water will freeze. [K_f for water = $1.86 \text{ K kg mol}^{-1}$ and Freezing point of water = 273.15 K] 3

25. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500Ω . What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$? 2

OR

Zinc rod is dipped in 0.01 M solution of zinc sulphate when temperature is 298 K. Calculate the electrode potential of zinc. [Given $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$, $\log 10 = 1$]

2

SECTION – C

26. Copper crystallises with face centred cubic unit cell. If the radius of copper atom is 127.8 pm, calculate the density of copper metal. (Atomic mass of Cu = 63.55 u and avogadro's number $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)

3

OR

Iron has a body centred cubic unit cell with the cell dimension of 286.65 pm. Density of iron is 7.87 g cm^{-3} . Use this information to calculate Avogadro's number. (Atomic mass of Fe = 56.0 u)

3

27. Answer the following :

(i) Which neutral molecule would be isoelectronic with ClO^- ?

(ii) Which form of sulphur show paramagnetic behaviour ?

(iii) Noble gases have very low boiling points. Why ?

3

28. How would you account for the following situations ?

(i) The transition metals generally form coloured compounds.

(ii) $E_{\text{M}^{2+}/\text{M}}^{\circ}$ values are not regular for first row transition elements (3d-series).

(iii) With $3d^4$ configuration, Cr^{2+} acts as a reducing agent but Mn^{3+} acts as an oxidising agent, (Atomic numbers, Cr = 24, Mn = 25).

3

29. (a) What is the basis of formation of the spectro-chemical series ?

1

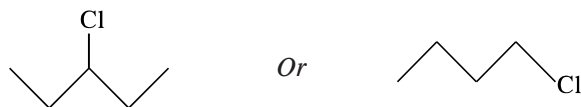
(b) Give IUPAC names of the following complexes.



2

30. (i) Why are haloalkanes more reactive towards nucleophilic substitution reactions than haloarenes ?

(ii) Which one of the following two substances undergoes $\text{S}_{\text{N}}1$ reaction faster and why ?



- (iii) Write the structure of 1-bromo-4-sec-butyl-2-methylbenzene.

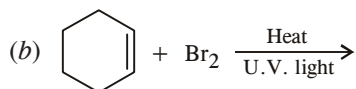
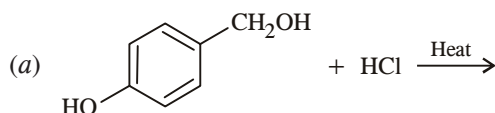
3

OR

(i) Why is sulphuric acid not used during the reaction of alcohols with KI ?

1

(ii) Draw the structures of major monohalo products in each of the following reactions :



2

SECTION – D

The following questions Q.No. 31-33 are long answer type questions.

31. (a) Derive the general expression for half-life of a first order reaction.

(b) The decomposition of NH_3 on platinum surface is a zero order reaction. What would be the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$?

2,3

OR

- (a) List the factors that determine the rate of a chemical reaction.
- (b) The half-life for decay of radioactive ^{14}C is 5730 years. An archaeological artefact containing wood had only 80% of the ^{14}C activity as found in a living tree. Calculate the age of the artefact. 2, 3
32. (a) Assign reasons for the following :
- (i) The negative value of electron gain enthalpy of fluorine is less than that of chlorine.
- (ii) SF_6 is much less reactive than SF_4 .
- (iii) Of all the noble gases, only xenon is known to form well-established chemical compounds.
- (b) Write the balanced chemical equation for the reaction of Cl_2 with hot and conc. NaOH . Is this reaction disproportionation reaction ? Explain why ? 3, 2

OR

- (a) (i) Give reasons for the following :
- Where R is alkyl group, $\text{R}_3\text{P}=\text{O}$ exists but $\text{R}_3\text{N}=\text{O}$ does not.
- (ii) At room temperature N_2 is much less reactive.
- (b) Draw the structures of the following :
- (i) XeOF_4 (ii) $\text{S}_8(s)$ (iii) $\text{ClF}_3(g)$ 2, 3
33. (a) Giving a chemical equation for each, illustrate the following processes :
- (i) Cannizzaro reaction
- (ii) Acetylation
- (iii) Decarboxylation
- (b) State chemical tests to distinguish between the following pairs of compounds :
- (i) Propanal and Propanone
- (ii) Phenol and Benzoic acid 3, 2

OR

- (a) An organic compound A contains 69.77% carbon, 11.63% hydrogen and the rest is oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition product with sodium hydrogensulphite and gives positive iodoform test. On vigorous oxidation, it gives ethanoic and propanoic acids. Write the possible structure of the compound A.
- (b) Write the chemical tests to distinguish between the following pairs of compounds :
- (i) Acetophenone and Benzophenone
- (ii) Ethanal and Propanal 3, 2

SOLUTION

1. (i) (d) **Explanation :** Ammonia (NH_3) can easily be liquefied due to extensive intermolecular H-bonding.
- (ii) (b) **Explanation :** Adsorption of gases on solid surface is exothermic because during adsorption, entropy decreases.
- (iii) (b) **Explanation :** The substance being adsorbed is called adsorbate.
- (iv) (c) **Explanation :** In physical adsorption, the forces of attraction between adsorbent and adsorbate are van der Waals' forces.

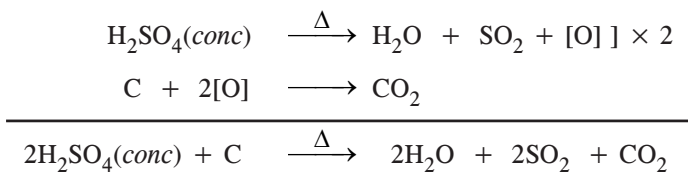
OR

- (d) **Explanation :** In chemical adsorption, enthalpy of adsorption is more.
2. (i) (d) **Correct assertion :** Phenol gives *o*- and *p*-nitrophenol on nitration with dilute HNO_3 at low temperature (298 K).
- (ii) (c) **Correct reason :** Intramolecular H-bonding in *o*-nitrophenol makes it less soluble in water as compared to *m*- and *p*-nitrophenols.
- (iii) (a) Reason is the correct explanation for assertion.
- (iv) (c) **Correct reason :** Boiling point of *o*-nitrophenol is less than *p*-nitrophenol.

OR

(a) Reason is the correct explanation for assertion.

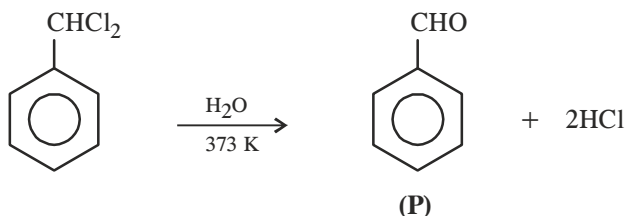
3. (b) **Explanation** : Unit of specific conductance is $\text{ohm}^{-1} \text{cm}^{-1}$.
4. (c) **Explanation** : Hot conc. H_2SO_4 oxidises carbon to CO_2 and in the process it itself is reduced to SO_2 . Both CO_2 and SO_2 are gases at room temperature.



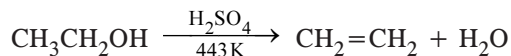
OR

- (b) **Explanation** : Out of all the hydrides of Group 15, NH_3 is most basic. It is due to small atomic size of N-atom.
5. (d) **Explanation** : HgI_2 is white. It is due to $5d^{10}$ configuration of Hg^{2+} ion with no unpaired electron.
6. (d) **Explanation** : $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2 (\text{aq}) \longrightarrow [\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} (\text{aq}) + 2 \text{Cl}^- (\text{aq})$
7. (a) **Explanation** : Out of all the given alkyl halides, fluoride has the lowest boiling point. It is due to lowest molecular mass.

OR

(b) **Explanation** :

8. (b) **Explanation** : Alkyl amines are more basic than aryl amines. Out of 1° , 2° and 3° alkyl amines, 2° alkyl amine is most basic in aqueous solution.
9. (d) **Explanation** : Uracil is not present in DNA.
10. (a) **Explanation** :



OR

- (d) **Explanation** : Acidic nature of 1° , 2° and 3° alcohols is in the order $3^\circ < 2^\circ < 1^\circ$.
11. (c) **Explanation** : It is an example of Cannizzaro reaction.

OR

(c) **Explanation** : Picric acid is 2, 4, 6-trinitrophenol. It does not have a carboxylic acid group.

12. (c) **Correct reason** : $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ is positive. 1
13. (b) **Correct explanation** : The density of NaCl crystal get lowered because a large number of ions (cations and anions) are missing from their lattice sites. 1
14. (a) Reason is the correct explanation for the assertion. 1
15. (c) **Correct reason** : The sum of powers of the concentration terms of the reactants in the rate law expression is called the order of the reaction. 1
16. (c) **Correct reason** : Hydrogen bonds are formed between specific pairs of bases. 1

OR

(a) Reason is the correct explanation for the assertion. 1

17. **Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.** 1

When the solute-solvent interaction is weaker than those between the solute-solute and solvent-solvent molecules, then solution shows positive deviation from Raoult's law because the partial pressure of each component is greater.

For example, a mixture of ethanol and acetone or carbon disulphide and acetone behave in this manner. 1/2, 1/2

OR

The extra pressure applied on the solution side that just stops the flow of solvent to solution through semipermeable membrane is called osmotic pressure of the solution. 1

If π is the osmotic pressure of a solution containing n_2 moles of non-volatile, non-electrolyte solute in V L of solution at T K.

$$\pi = \frac{n_2}{V} RT$$

where R = 0.0821 L atm K⁻¹ mol⁻¹

$$\pi = \frac{W_2}{M_2} \frac{RT}{V}$$

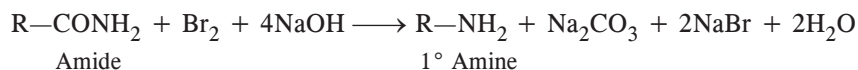
where W_2 is the mass of the solute and M_2 is its molar mass.

$$M_2 = \frac{W_2 RT}{\pi V}$$

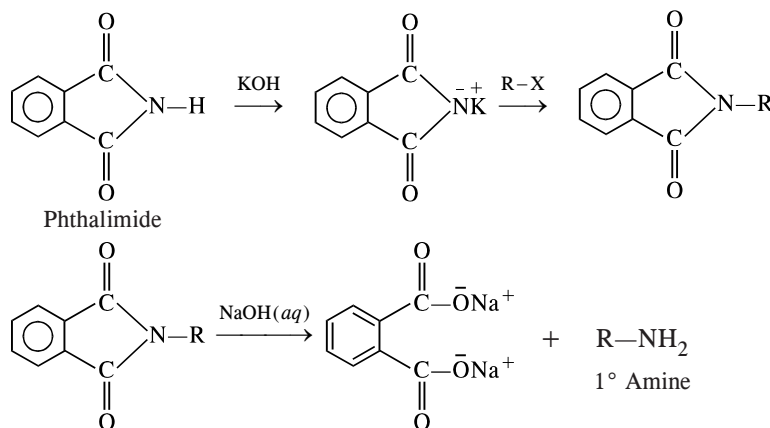
Thus, knowing the quantities W_2 , T, π and V, we can calculate the molar mass, M_2 of the

solute.

18. (i) In first transition series, manganese (Z = 25) shows maximum number of oxidation states. It shows +2, +3, +4, +5, +6 and +7 oxidation states. 1
 (ii) In first transition series Scandium (Sc) shows only +3 oxidation state. 1
19. (i) $C_6H_5N_2^+Cl^- + KI \longrightarrow C_6H_5I + KCl + N_2$ 1
 (ii) $CH_2=CH_2 + Br_2 \longrightarrow CH_2(Br)-CH_2(Br)$ 1
20. (i) $C_6H_5NH_2 < NH_3 < (C_2H_5)_3N < (C_2H_5)_2NH$ in water 1
 (ii) $CH_3NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$ in gas phase. 1
21. (i) **Hoffmann Bromamide reaction :** 1



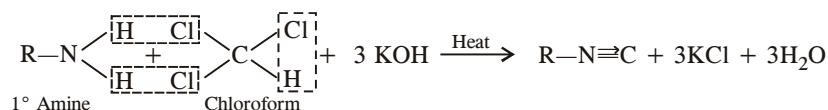
(ii) **Gabriel Phthalimide synthesis :**



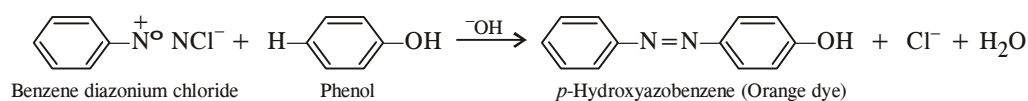
N-Alkylphthalimide

OR

(i) **Carbylamine reaction :**



(ii) **Coupling reaction :**

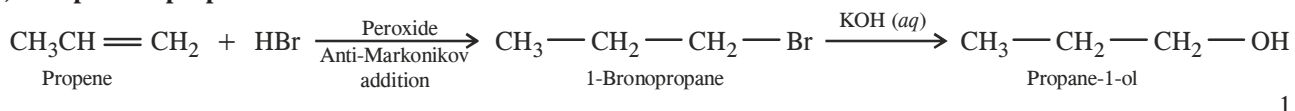


22. *o*-Nitrophenol is more acidic than *o*-methoxyphenol.

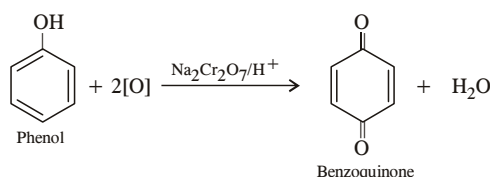


Electrons withdrawing groups like $-\text{NO}_2$ decreases the electron density on O-atom of phenolic group, especially when present at *o* or *p*-position *w.r.t.* $-\text{OH}$ group. This increases the acidic nature. On the other hand, electron donating groups like $-\text{OCH}_3$ increases the electron density on O-atom of phenolic group, especially when present at *o* or *p*-position *w.r.t.* $-\text{OH}$ group. This decreases the acidic nature. 2

23. (i) Propene to propan-1-ol



(ii) Phenol of benzoquinone



24. $\Delta T_b = (36.86 - 35.60)^\circ\text{C} = 1.26^\circ\text{C} = 1.26 \text{ K}$ 1/2

$$\text{No. of moles of solute} = \frac{16 \text{ g}}{M}$$

where M is molar mass of the solute

$$\text{Molality of solution, } m = \left[\frac{16 \text{ g}}{M} \right] \times \left[\frac{1000}{200 \text{ kg}} \right]$$

$$\Delta T_b = K_b m$$

$$1.26 \text{ K} = (2.02 \text{ K kg mol}^{-1}) \times \left(\frac{16 \text{ g}}{M} \right) \times \left(\frac{1000}{200 \text{ kg}} \right)$$

$$M = 128.25 \text{ g mol}^{-1}$$

OR

$$\Delta T_f = K_f m$$

$$\text{No. of moles of glucose} = \frac{54 \text{ g}}{180 \text{ g mol}^{-1}} = \frac{54}{180} \text{ mol}$$

$$\text{Molality of glucose solution, } m = \left(\frac{54}{180} \text{ mol} \right) \times \left(\frac{1000}{250 \text{ kg}} \right) = 1.20 \text{ mol kg}^{-1}$$

$$\Delta T_f = K_f m = (1.86 \text{ K kg mol}^{-1}) \times (1.20 \text{ mol kg}^{-1}) = 2.23 \text{ K}$$

Temperature at which solution freezes

$$T_f = T_f^\circ - \Delta T_f = (273.15 - 2.23) \text{ K} = 270.92 \text{ K}$$

25. $R = \rho(l/A)$

(Writing the correct formula carries one mark) 1

Cell constant, $l/A = R/\rho = R \cdot \kappa$

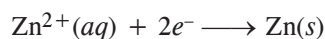
Here $R = 1500 \Omega$ and

$$\kappa = 0.146 \times 10^{-3} \text{ S cm}^{-1} = 1.46 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$$

$$\therefore \text{Cell constant} = (1500 \Omega) \times (1.46 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}) = 0.219 \text{ cm}^{-1}$$

(Deduct $\frac{1}{2}$ mark if proper units are not given in the answer).

OR



Here $n = 2$

$$E_{\text{Zn}^{2+}/\text{Zn}} = E_{\text{Zn}^{2+}/\text{Zn}}^\circ - \frac{0.059}{2} \log \frac{1}{[\text{Zn}^{2+}]}$$

1

$$\begin{aligned}
 &= -0.76 - \frac{0.059}{2} \log \frac{1}{10^{-2}} && 1 \\
 &= -0.76 - \frac{0.059}{2} \log 10^2 \\
 &= -0.76 - \frac{0.059}{2} \times 2 \log 10 \\
 &= (-0.76 - 0.059)V = -0.819 \text{ V} && 1
 \end{aligned}$$

(Deduct half mark if correct units are not given)

26. $z = 4$ (f.c.c.) ; $r = 127.8$ pm
 $a = 2\sqrt{2}r = 2 \times 1.414 \times 127.8$ pm = 361.42 pm
 $M = 63.55$ g mol⁻¹ ; $N_A = 6.02 \times 10^{23}$ mol⁻¹

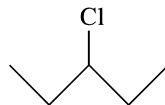
$$\begin{aligned}
 \text{Density, } \rho &= \frac{z \times M}{N_A \times a^3 \times 10^{-30}} = \frac{4 \times (63.55 \text{ g mol}^{-1})}{(6.02 \times 10^{23} \text{ mol}^{-1}) \times (361.42)^3 \times 10^{-30} \text{ cm}^3} \\
 &= \frac{4 \times 63.55}{6.02 \times (3.6)^3 \times 10^{-30+23+6}} \text{ g cm}^{-3} = \frac{40 \times 63.55}{6.02 \times (3.6)^3} \text{ g cm}^{-3} = \frac{40 \times 63.55}{6.02 \times (46.66)^3} \text{ g cm}^{-3} \\
 &= \mathbf{9.05 \text{ g cm}^{-3}}
 \end{aligned}$$

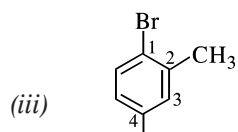
OR

$$z = 2$$
 (b.c.c.) ; $r = 286.65$ pm ; $M = 56$ g mol⁻¹ ; $\rho = 7.87$ g cm⁻³

$$\begin{aligned}
 N_A &= \frac{z \times M}{\rho \times a^3 \times 10^{-30}} = \frac{2 \times (56 \text{ g mol}^{-1})}{(7.87 \text{ g cm}^{-3}) \times (286.65)^3 \times 10^{-30} \text{ cm}^3} \\
 &= \frac{2 \times 56 \times 10^{24}}{7.87 \times (2.87)^3} \text{ mol}^{-1} = \frac{20 \times 56 \times 10^{23}}{7.87 \times 23.64} \text{ mol}^{-1} = \mathbf{6.02 \times 10^{23} \text{ mol}^{-1}}
 \end{aligned}$$

27. (i) CIF (or any other)
(ii) In vapour state, sulphur exists as S₂ molecule, like O₂ it has two unpaired electrons in π*-orbitals (antibonding orbitals).
(iii) Noble gases have weak inter-atomic dispersion forces and as such they liquefy at very low temperatures.
28. (i) Transition metal ions contain unpaired electrons and are excited to higher energy levels called *d-d* transition. This leads to absorption in visible region.
(ii) It is mainly due to the fact that variation in enthalpy of atomisation and enthalpy of hydration of M²⁺ ions is not regular across the 3*d*-series.
(iii) Cr²⁺ is reducing as its configuration changes from *d*⁴ to *d*³ the latter having half filled *t*_{2g} level whereas Mn³⁺ to Mn²⁺ results in half filled *d*⁵ configuration.
29. (a) Ligands are arranged in the increasing order of field strength based on absorption of light of complexes with different ligands (extent of splitting).
(i) K₂[Zn(OH)₄]
potassium tetrahydroxidozincate(II)
(ii) K₃[Al(C₂O₄)₃]
potassium trioxalatoaluminate(III)
30. (i) Aryl halides are less reactive towards nucleophilic reagents because of any of the following reasons.
(a) Resonance effect stabilisation.
(b) *sp*²-hybridization in haloarenes and *sp*³ in haloalkanes.
(c) Instability of phenyl cation
(d) Possible repulsion between electron rich nucleophile and electron rich arenes. 1

- (ii)  undergoes S_N1 reaction faster. It is because of the greater stability of secondary carbocation than primary carbocation. 1



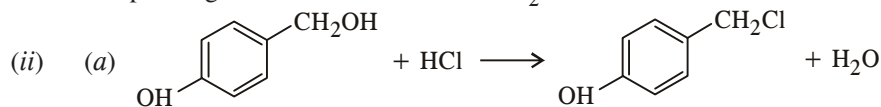
CH₃—CH—CH₂—CH₃
1-Bromo-4-sec-butyl-2-methylbenzene

1

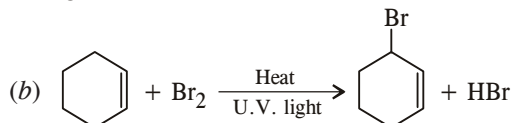
OR

- (i) H₂SO₄ cannot be used along with KI in the conversion of alcohol to an alkyl iodide as it converts KI to corresponding HI and then oxidises it to I₂.

1



1



1

31. (a) **Half life of a first order reaction :**

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad \dots(i) \quad 1/2$$

at $t = t_{1/2}$; $[R] = \frac{[R]_0}{2}$ 1/2

Equation (i) becomes

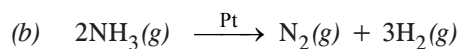
$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]_0/2}$$

or $t_{1/2} = \frac{2.303}{k} \log 2$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

$$t_{1/2} = \frac{0.693}{k}$$

1



$$\text{Rate} = -\frac{d[\text{NH}_3]}{dt} = k[\text{NH}_3]^0 = k$$

$$= 2.5 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1}$$

1

$$-\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = +\frac{d[\text{N}_2]}{dt} = +\frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$\text{Rate of production of N}_2 = \frac{d[\text{N}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$= \frac{1}{2} \times (2.5 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1}) = 1.25 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1}$$

1

$$\text{Rate of production of hydrogen} = \frac{d[\text{H}_2]}{dt} = -\frac{3}{2} \frac{d[\text{NH}_3]}{dt}$$

$$= \frac{3}{2} \times (2.5 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1}) = 3.75 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1}$$

1

OR

- (a) Factors affecting rate of chemical reaction are as follows :

(i) Concentration of reactants

(ii) Temperature

(iii) Presence of catalyst

(iv) Surface area

(v) Activation energy

(vi) Radiation (any four)

2

(b) $k = \frac{0.693}{t_{1/2}}$

1/2

$$k = \frac{0.693}{5730 \text{ y}} = 1.21 \times 10^{-4} \text{ y}^{-1} \quad 1/2$$

$$[R]_0 = 100 \text{ (say)}, [R] = 80$$

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} \quad 1/2$$

$$t = \frac{2.303}{1.21 \times 10^{-4} \text{ y}^{-1}} \log \frac{100}{80} = \frac{2.303}{1.21 \times 10^{-4} \text{ y}^{-1}} \log 1.25 \quad 1/2$$

$$t = \frac{2.303 \times 0.0969 \text{ y}}{1.21 \times 10^{-4}} = \mathbf{1845 \text{ years}} \quad 1$$

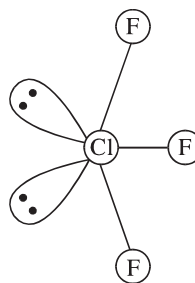
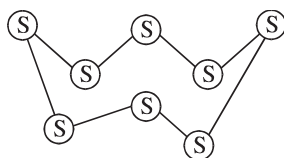
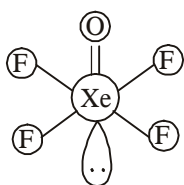
32. (a) (i) It is due to stronger interelectronic repulsions in relatively compact $2p$ -subshell of F. 1
(ii) The much less reactivity of SF_6 can be explained on the basis of its exceptional stability, which is due to steric reasons. 1
(iii) Because of comparatively lower ionisation enthalpy of Xe (comparable to that of O_2) as compared to those of other noble gases. 1
- (b) $\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{HCl} + \text{HOCl}] \times 3$
 $\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O}] \times 3$
 $\text{NaOH} + \text{HOCl} \longrightarrow \text{NaOCl} + \text{H}_2\text{O}] \times 3$
 $3\text{NaOCl} \longrightarrow \text{NaClO}_3 + 2 \text{NaCl}$



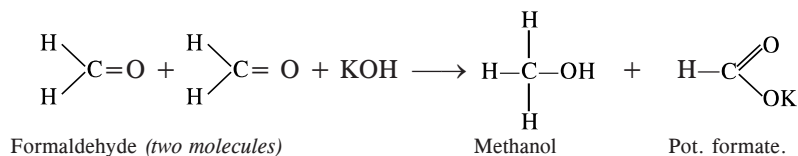
Yes. It is a disproportionation reaction. Here O.S. of Cl simultaneously increases from 0 (in Cl_2) to + 5 (in NaClO_3) and decreases from 0 (in Cl_2) to -1 (in NaCl). 2

OR

- (a) (i) Nitrogen does not have vacant d -orbitals in its valence shell. Therefore, it cannot extend its covalency to five and $d\pi - p\pi$ bonding is not possible. As a result, the molecules of $\text{R}_3\text{N}=\text{O}$ does not exist. However, phosphorus and rest of the members of the Group 15 have vacant d -orbitals in the valence shell which can be involved in $d\pi - p\pi$ bonding. Under the circumstances $\text{R}_3\text{P}=\text{O}$ molecule can exist.
(ii) Very low reactivity of N_2 at room temperature is due to the high bond enthalpy of $\text{N} \equiv \text{N}$ bond.
- (b) **Structures of XeOF_4 , $\text{S}_8(\text{s})$ and $\text{ClF}_3(\text{g})$**

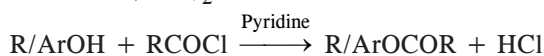
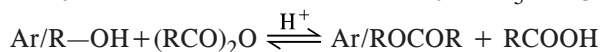


33. (a) (i) **Cannizzaro Reaction** : Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction reaction on treatment with concentrated alkali. $1 \times 3 = 3$

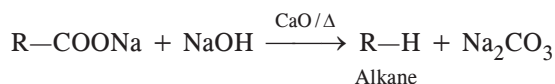


(or any other suitable reaction)

- (ii) **Acetylation** : The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as acetylation.



- (iii) **Decarboxylation** : Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime ($\text{NaOH} + \text{CaO}$).
The reaction is known as decarboxylation.



(Note : Award full marks for correct chemical equation ; award ½ mark if only statement is written) 1

- (b) (i) **Propanal and propanone** : Propanone gives yellow ppt of iodoform (CHI_3) on heating with NaOH/I_2 while propanal does not give this test. 1

Propanal gives Tollen's test/or Fehling's test while propanone does not give any of these tests.

(Any one test)

- (ii) **Phenol and benzoic acid** : 1 Add neutral FeCl_3 to both of them. Phenol gives violet colour.

2. Benzoic acid gives effervescence with $\text{NaHCO}_3(\text{aq})$ while phenol does not react with $\text{NaHCO}_3(\text{aq})$.

(Any one test)

OR

Element	Percentage/Atomic mass	Molar ratio
C	$69.77/12 = 5.81$	$5.71/1.16 = 5$
H	$11.63/1 = 11.63$	$11.63/1.16 = 10$
O	$18.60/16 = 1.16$	$1.16/1.16 = 1$

1

Empirical formula : $\text{C}_5\text{H}_{10}\text{O}$

Empirical formula mass = $60 + 10 + 16 = 86$

Molecular mass = 86 (given)

$$n = \frac{\text{Mol. mass}}{\text{E. F. mass}} = \frac{86}{86} = 1$$

∴ Molecular formula = $(\text{E.F.})_n = \text{C}_5\text{H}_{10}\text{O}$

It is a ketone as it gives ethanoic and propanoic acids on oxidation. Hence the compound is $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$

- (b) (i) **Acetophenone and Benzophenone** : Heat both of them with NaOH/I_2 . Only acetophenone forms yellow ppt. of iodoform.
- (ii) **Ethanal and Propanal** : Heat both of them with NaOH/I_2 . Only ethanal forms yellow ppt. of iodoform.

Sample Question Paper – 2

Time Allowed : 3 Hours

Maximum Marks : 70

General instructions : Same as in Sample Paper 1.

Section – A (Objective Type)

Passage Based Questions (Q. No. 1 to Q. No. 2)

• Read the following passage and answer the questions that follow.

1. Adsorption arises due to the fact that the surface particles of the adsorbent are not in the same environment as the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides, and hence they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface. The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.

Another important factor featuring adsorption is the heat of adsorption. During adsorption, there is always a decrease in residual forces of the surface, *i.e.*, there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably and exothermic process. In other words, ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to decrease in the entropy of the gas after adsorption *i.e.*, ΔS is negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative. *i.e.*, there is a decrease in Gibbs energy. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as $-T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes ΔG negative. As the adsorption proceeds, ΔH becomes less and less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. At this state equilibrium is attained.

Choose the most appropriate answer.

- (i) At a given temperature and pressure, the extent of adsorption,
- decreases with decrease in surface area of adsorbent.
 - increases with decrease in surface area of adsorbent.
 - decreases with increase in surface area of adsorbent.
 - None of these.
- (ii) Adsorption is an
- | | |
|--|--|
| (a) exothermic process and sign of ΔH is +ve. | (b) exothermic process and sign of ΔH is -ve. |
| (c) endothermic process and sign of ΔH is -ve. | (d) endothermic process and sign of ΔH is +ve. |
- (iii) During adsorption,
- | | |
|---|---|
| (a) randomness increases and ΔS is +ve. | (b) randomness increases and ΔS is -ve |
| (c) randomness decreases and ΔS is +ve. | (d) randomness decreases and ΔS is -ve. |
- (iv) As adsorption is a spontaneous process,
- | | |
|-------------------------------|------------------------------|
| (a) ΔG is always zero | (b) ΔG is always +ve |
| (c) ΔG is always -ve. | (d) None of these. |

OR

During adsorption at constant temperature and pressure, at equilibrium

- | | |
|--------------------|--------------------|
| (a) $\Delta G = 0$ | (b) $\Delta H = 0$ |
| (c) $\Delta S = 0$ | (d) All of these. |

2. Read the following passage and answer the questions that follow :

Aldehydes and ketones undergo nucleophilic addition reactions. Some examples of nucleophilic addition reactions are addition of HCN, NaHSO₃, Grignard reagents, alcohols, ammonia and ammonia derivatives.

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon more than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively than in former.

In general, aromatic aldehydes and ketones are less reactive than aliphatic aldehydes and ketones. For example, propanal is more reactive than benzaldehyde in nucleophilic addition reactions. This is because the carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of carbonyl group is reduced in benzaldehyde due to resonance.

The questions given below consist of Assertion and Reason. Use the following key to select the correct answer.

- (a) If both assertion and reason are correct and reason is correct explanation for assertion.
 (b) If both assertion and reason are correct but reason is not correct explanation for assertion.
 (c) If assertion is correct but reason is incorrect.
 (d) If assertion is wrong but reason is correct.
- (i) **Assertion :** Carbonyl compounds take part in nucleophilic addition reactions.
Reason : These reactions are initiated by nucleophilic attack at the electron deficient carbon atom.
- (ii) **Assertion :** The addition of ammonia derivatives to carbonyl compounds is carried in weakly acidic medium.
Reason : In weakly acidic medium attacking nucleophile is also protonated.
- (iii) **Assertion :** Benzaldehyde is less reactive towards nucleophilic addition than acetaldehyde.
Reason : In benzaldehyde polarity of the carbonyl group is reduced due to resonance.
- (iv) **Assertion :** Propanone is more reactive towards nucleophilic addition than propanal.
Reason : It is due to more steric hinderance in propanone.

OR

Assertion : Acetone is less reactive than acetaldehyde in nucleophilic addition reaction.

Reason : In acetone, polarity of carbonyl group is reduced due to resonance.

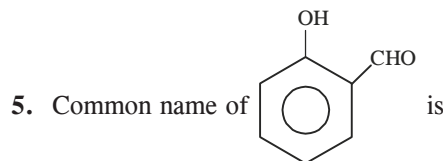
3. Reaction of ethylamine with chloroform in alcoholic KOH gives
- (a) C_2H_5CN (b) C_2H_5NC
 (c) CH_3CN (d) CH_3NC .
4. If value of K_b is large, then value of pK_b will be
- (a) more (b) less
 (c) same (d) None of these.

OR



X is :

- (a) C_2H_5OH (b) C_2H_5NHOH
 (c) C_2H_6 (d) $C_2H_5NO_2$.



- (a) Vanillin (b) Benzaldehyde
 (c) Salicylaldehyde (d) Salicylic Acid.

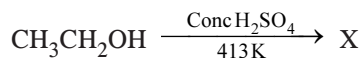
OR

The solution used to preserve biological specimens in

- (a) Tollen's Reagent (b) Formalin
 (c) Vanillin (d) Acetone.
6. Which one is the complementary base of adenine in one strand to that in other strand of DNA ?
- (a) Guanine (b) Cytocine
 (c) Thymine (d) Uracil.

7. Which amino acids are essential building units of proteins ?
 (a) α -amino acids (b) β -amino acids
 (c) γ -amino acids (d) None of these.
8. α -D(+) glucose and β -D(+) glucose are
 (a) enantiomers (b) geometrical isomers
 (c) epimers (d) anomers.
9. In the following which is the strongest acid ?
 (a) CH_3OH (b) $\text{CH}_3\text{CH}_2\text{OH}$
 (c) $(\text{CH}_3)_2\text{CHOH}$ (d) $(\text{CH}_3)_3\text{COH}$

OR



X will be

- (a) $\text{CH}_2=\text{CH}_2$ (b) $\text{C}_2\text{H}_5\text{HSO}_4$
 (c) $(\text{C}_2\text{H}_5)_2\text{O}$ (d) $(\text{C}_2\text{H}_5)_2\text{SO}_4$
10. On adding AgNO_3 solution in 1 mol of $\text{PdCl}_2 \cdot 4\text{NH}_3$, two moles of AgCl are formed the secondary valence of Pd in the complex will be
 (a) 0 (b) 2
 (c) 4 (d) 1.

OR

Oxidation state of Pt in $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ is

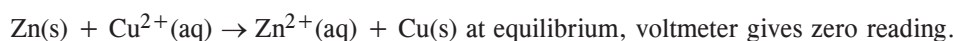
- (a) +1 (b) +2
 (c) +3 (d) +4.
11. The oxidation number of cobalt in $\text{K}[\text{Co}(\text{CO})_4]$ is
 (a) +1 (b) -1
 (c) +3 (d) -3.

Assertion-Reason Type Questions (Q. No. 12 to Q. No. 16)

- The questions given below consists of Assertion and Reason. Use the following key to select the correct answer.

- (a) Both assertion and reason are correct statements and reason is the correct explanation of the assertion.
 (b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.
 (c) Assertion is correct, but reason is wrong.
 (d) Assertion is wrong, but reason is correct.
12. **Assertion.** Conductivity of all electrolytes decreases on dilution.
Reason. On dilution number of ions per unit volume decreases.
13. **Assertion.** Colloidal solution show colligative properties.
Reason. Colloidal particles are larger in size than 1000 nm.
14. **Assertion.** When NaCl is added to water, a depression in freezing point is observed.
Reason. The lowering of vapour pressure of a solution causes depression in the freezing point.
15. **Assertion.** In Daniell cell, if concentration of Cu^{2+} and Zn^{2+} ions are doubled, the emf of the cell does not change.
Reason. If the concentration of the ions in contact with the metal is doubled, the electrode potential will also be doubled.

OR

Assertion. For a cell reaction :**Reason.** At the equilibrium, there is no change in the concentration of Cu^{2+} and Zn^{2+} ions.

16. **Assertion.** $\text{C}_2\text{H}_5\text{OH}$ is a weaker base than phenol but a stronger nucleophile than phenol
Reason. In phenol, the lone pair of electrons on oxygen is withdrawn towards the ring due to resonance.

SECTION – B

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

17. Treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain 2
18. Explain as to how the two complexes of nickel, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$, have different structures but do not differ in their magnetic behaviour. (At. no. of Ni = 28) 2
19. State Henry's law correlating the pressure of a gas and its solubility in a solvent and mention two applications for the law. 2
20. A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its half life period.

OR

The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact contained wood that has only 80% of the ^{14}C found in living tree. Estimate the age of the sample. 2

21. What is meant by the 'rate constant, k of a reaction? If the concentration be expressed in mol L^{-1} units and time in seconds, what would be the units for rate constant, k
- (i) for a zero order reaction and 2
- (ii) for a first order reaction? 2
22. Heptane and octane form ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 k Pa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35.0 g of octane?

OR

An antifreeze solution is prepared from 222.6 g of ethylene glycol, $\text{C}_2\text{H}_4(\text{OH})_2$ and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1} , then what shall be the molarity of the solution?

23. Differentiate between lyophilic and lyophobic sols giving one example 2
24. (i) Explain why fluorine forms only one oxo-acid (HOF). 2
- (ii) Give the formula and describe the structure of a noble gas species which is isostructural with ICl_4^- .
25. An element has a body centred cubic (bcc) structure with a cell edge of 288 pm. The density of element is 7.2 g/cm^3 . How many atoms are present in 208 g of the element?

OR

An element with molar mass $2.7 \times 10^{-2} \text{ kg mol}^{-1}$ forms a cubic unit cell with edge length 405 pm. If its density is $2.7 \times 10^3 \text{ kg m}^{-3}$, what is the nature of cubic unit cell?

SECTION – C

The following questions (Q.No. 26-31) are short answer Type II and carry 3 Marks each.

26. Account for the following observations : 3
- (i) pK_b for aniline is more than that for methylamine.
- (ii) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.
- (iii) Aniline does not undergo Friedel-Craft's reaction. 3

OR

(a) Identify X and Y in the following :



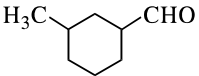
- (b) Amino group is *o*, *p*-directing for aromatic electrophilic substitution reactions. Why does aniline on nitration gives *m*-nitroaniline in significant amount? 1
27. (a) Explain why phenols are more acidic than alcohols. 1
- (b) Predict the products of the following reactions :
- (i) $(\text{CH}_3)_3\text{C}-\text{O}-\text{C}_2\text{H}_5 + \text{HI} \longrightarrow$ 2
- (ii) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3 + \text{HI} \longrightarrow$

OR

How are the following conversions carried out ?

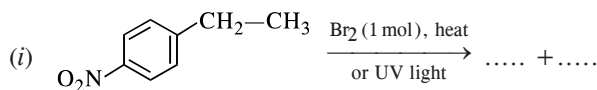
- (i) Ethyl magnesium chloride \longrightarrow Propan-1-ol
 (ii) Methyl magnesium bromide \longrightarrow 2-Methylpropan-2-ol
 (iii) Benzyl chloride \longrightarrow Benzyl alcohol

3 \times 1 = 3

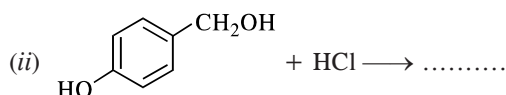
28. (a) Give IUPAC name of : 

1

(b) Complete the following chemical equations :



1



1

29. Write chemical equations for the following processes :

3

- (i) Sulphur is heated with conc. H_2SO_4 .
 (ii) XeF_6 is completely hydrolysed.
 (iii) PtF_6 and xenon are mixed together.

30. Write IUPAC names of the following co-ordination compounds

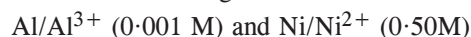
- (i) $[\text{Pt}(\text{en})_3(\text{NO}_3)_2]$
 (ii) $\text{K}_2[\text{PdCl}_4]$
 (iii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$

SECTION - D

Following questions (Q.No. 31-33) are long answer type and carry 5 marks each.

31. Conductivity of 0.00241 M acetic acid solution is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity in this solution. If Λ_m^0 for acetic acid be $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what would be its dissociation constant ?

OR

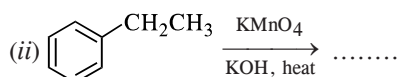
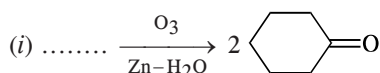
(a) A voltaic cell is set up at 25°C with the following half cells :

Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

$$E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V} \text{ and } E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66 \text{ V}$$

(b) Calculate the maximum work that can be obtained from this cell under standard conditions.

32. (a) Complete the following reaction statements by giving the missing starting material, reagent or product as required :



(b) Describe the following reactions :

- (i) Cannizzaro reaction
 (ii) Cross-aldol condensation

3, 2

OR

- (a) How would you account for the following ?
- Aldehydes are more reactive than ketones towards nucleophiles.
 - The boiling points of aldehydes and ketones are lower than that of the corresponding acids.
 - The aldehydes and ketones undergo a number of addition reactions.
- (b) Give chemical tests to distinguish between :
- Acetaldehyde and benzaldehyde
 - Propanone and propanol
33. Assign reasons for the following :
- The enthalpies of atomisation of transition elements are high. 1
 - The transition metals and many of their compounds act as good catalyst. 1
 - Why is the highest oxidation state of a transition metal exhibited in its oxide or fluoride only. 1
 - The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} . 1
 - Scandium ($Z = 21$) does not exhibit variable oxidation states and yet it is regarded as a transition element.

OR

- (a) What may be the possible oxidation states of the transition metals with the following d -electronic configurations in the ground state of their atoms : $3d^34s^2$, $3d^54s^2$ and $3d^64s^2$. 3
Indicate relative stability of oxidation states in each case.
- (b) Explain giving reasons :
- Transition metals and many of the compounds show paramagnetic behaviour. 1
 - The transition metals generally form coloured compounds. $3 \times 1 = 3$

SOLUTION

- (a) **Explanation :** Extent of adsorption decreases with decrease in surface area.
 - (b) **Explanation :** Adsorption is an exothermic process and ΔH is $-ve$.
 - (d) **Explanation :** During adsorption, randomness decreases and ΔS is $-ve$.
 - (c) **Explanation :** Adsorption is a spontaneous process and as such ΔG is always $-ve$.

OR

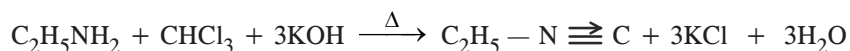
(d) **Explanation :** During adsorption, at equilibrium, $\Delta G = 0$, $\Delta H = 0$ and $\Delta S = 0$.

- (a) Reason is the correct explanation for assertion.
 - (c) **Correct reason :** Attacking nucleophile is not protonated in weakly acidic medium.
 - (a) Reason is the correct explanation for assertion.
 - (d) **Correct assertion :** Propanone is less reactive towards nucleophilic addition than propanal.

OR

(c) **Correct reason :** In acetone, the presence of two methyl groups increases steric hinderance.

3. (b) **Explanation :**



4. (b) **Explanation :**

$$pK_b = \log \frac{1}{K_b}$$

Hence, more K_b implies less pK_b

5. (c) **Explanation :** Common name of o -hydroxybenzaldehyde is salicylaldehyde.

OR

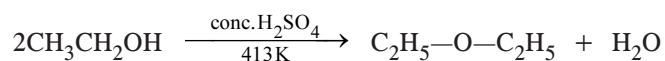
(b) **Explanation :** Formalin (an aqueous solution of formaldehyde) is used to preserve biological specimens.

- (c) **Explanation :** In DNA, complementary base of adenine is thymine.
- (a) **Explanation :** α -Amino acids form the basic building units of proteins.
- (d) **Explanation :** α -D(+)-glucose and β -D(+)-glucose are anomers.

9. (a) **Explanation :** Acidic strength of alcohols follows the order $1^\circ > 2^\circ > 3^\circ$. Further methanol is more acidic than ethanol.

OR

- (c) **Explanation :**



10. (c) **Explanation :** As one mole of the complex gives two moles of AgCl, the complex contains two ionisable Cl^- ions and has the structure :



Thus, secondary valency of Pd in the complex is four.

OR

- (b) **Explanation :** Let O.S. of Pt = x

O.S. of Cl^- = -1 and C_2H_4 = 0

$$\therefore x + 0 + 3(-1) = -1$$

$$\text{or } x = +2$$

11. (b) **Explanation :** Let O.S. of Co = x , O.S. of K^+ = $+1$ and O.S. of CO = 0

$$\therefore +1 + x + 4 \times 0 = 0$$

$$\therefore x = -1$$

12. (a) Reason is the correct explanation for assertion. 1
 13. (c) **Correct explanation.** Colloidal particles share their kinetic energy with the particles of the dispersion medium. 1
 14. (a) Reason is the correct explanation for assertion. 1
 15. (b) **Correct reason :** The effect of concentration on electrode potential is guided by Nernst equation. On doubling the

concentration, *emf* will remain unchanged since $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$ will remain same.

OR

- (a) Reason is the correct explanation for assertion.

16. (d) **Correct assertion :** $\text{C}_2\text{H}_5\text{OH}$ is a stronger base than phenol and also a stronger nucleophile than phenol.
 17. In aqueous KOH, nucleophile is OH^- . It can easily attack alkyl chloride ($\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$) to give an alcohol (*substitution*). In case of alcoholic KOH, nucleophile is bulkier $^- \text{OR}$ ions. It will prefer to act as a base and abstract a proton rather than approach a tetravalent carbon due to steric reasons and vice-versa. Thus, the main product of the reaction in this case will be an alkene. 2

18. $[\text{Ni}(\text{CN})_4]^{2-}$: dsp^2 -hybridization

Structure : Square planar

Diamagnetic in nature as its $3d$ -orbitals contain paired electrons. (Or diagram) $\frac{1}{2} + \frac{1}{2}$

$[\text{Ni}(\text{CO})_4]$: sp^3 -hybridization

Structure : Tetrahedral

Diamagnetic in nature as its $3d$ -orbitals contain paired electrons. (Or diagram) $\frac{1}{2} + \frac{1}{2}$

19. **Henry's Law :** Henry's law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution. 1

Applications of Henry's Law :

- (i) To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
 (ii) Scuba divers must cope with high concentrations of dissolved nitrogen when breathing air at high pressure underwater. To avoid this air is diluted with He.
 (iii) At high altitudes the partial pressure of oxygen is less than that at the ground level. Low blood oxygen causes anoxia.

20.
$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$[A]_0 = 100 \text{ (say)} ; [A] = 100 - 30 = 70, t = 40 \text{ min}$$

$$k = \frac{2.303}{40 \text{ min}} \log \frac{100}{70} = \frac{2.303 \times 0.155}{40 \text{ min}} = 0.00892 \text{ min}^{-1}$$

1/2

$$t_{1/2} = \frac{0.693}{k} \quad 1/2$$

$$t_{1/2} = \frac{0.693}{0.00892 \text{ min}^{-1}} = 77.7 \text{ min} \quad 1/2$$

OR

Radioactive decay follows first order kinetics.

$$\text{Decay constant, } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} \text{ yr}^{-1}$$

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} = \frac{2.303}{(0.693/5730 \text{ yr}^{-1})} \log \frac{100}{80}$$

$$= \frac{2.303 \times 5730}{0.693} \times 0.0969 \text{ yr} = 1845 \text{ years}$$

21. Rate constant 'k' of a reaction is defined as the rate of reaction when the concentration of the reactant(s) is unity or Rate constant is the proportionality factor in the rate law.

For an *n*th order reaction

$$k = \frac{\text{rate}}{(\text{conc.})^n}$$

$$\text{units of } k = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})^n} = \text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$$

(i) Units for 'k' for a zero order (*n* = 0) reaction = mol L⁻¹s⁻¹ 1/2

(ii) Units for 'k' for a first order (*n* = 1) reaction = s⁻¹ 1/2

22. Molar mass of heptane (C₇H₁₆) = 100 g mol⁻¹; Molar mass of octane (C₈H₁₈) = 114 g mol⁻¹

V.P. of heptane at 373 K, *p*_A[°] = 105.2 k Pa

V.P. of octane at 373 K, *p*_B[°] = 46.8 k Pa

$$\text{No. of moles of heptane, } n_A = \frac{26.0 \text{ g}}{100 \text{ g mol}^{-1}} = 0.26 \text{ mol}$$

$$\text{No. of moles of octane, } n_B = \frac{35.0 \text{ g}}{114 \text{ g mol}^{-1}} = 0.31 \text{ mol}$$

$$\text{Mole fraction of heptane, } x_A = \frac{n_A}{n_A + n_B}$$

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

$$\text{Mole fraction of octane, } x_B = 1 - x_A = 1 - 0.456 = 0.544$$

$$p_A = p_A^\circ x_A = 105.2 \text{ k Pa} \times 0.456$$

$$= 47.97 \text{ k Pa}$$

$$p_B = p_B^\circ x_B = 46.8 \text{ k Pa} \times 0.544$$

$$= 25.45 \text{ k Pa}$$

$$p_s = p_A + p_B = (47.97 + 25.45) \text{ k Pa}$$

$$= 73.42 \text{ k Pa}$$

OR

Mass of the solute, C₂H₄(OH)₂ = 222.6 g

Molar mass of C₂H₄(OH)₂ = 62 g mol⁻¹

$$\therefore \text{Moles of the solute} = \frac{222.6 \text{ g}}{62 \text{ g mol}^{-1}} = 3.59 \text{ mol}$$

$$\text{Mass of the solvent} = 200 \text{ g} = 0.200 \text{ kg}$$

$$\begin{aligned}\text{Molality} &= \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}} = \frac{3.59 \text{ mol}}{0.200 \text{ kg}} \\ &= \mathbf{17.95 \text{ mol kg}^{-1}}\end{aligned}$$

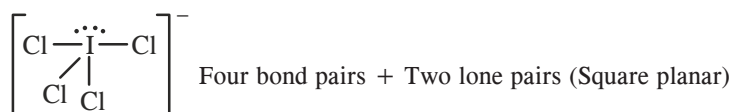
$$\text{Total mass of the solution} = 422.6 \text{ g}$$

$$\begin{aligned}\text{Volume of the solution} &= \frac{\text{Mass}}{\text{Density}} = \frac{422.6 \text{ g}}{1.072 \text{ g mL}^{-1}} \\ &= 394.2 \text{ mL} = 0.3942 \text{ L}\end{aligned}$$

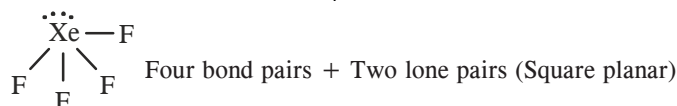
$$\begin{aligned}\text{Molarity} &= \frac{\text{Moles of solute}}{\text{Volume of solution (L)}} = \frac{3.59 \text{ mol}}{0.3942 \text{ L}} \\ &= \mathbf{9.1 \text{ mol L}^{-1}}\end{aligned}$$

23. **Lyophobic sol** : The sol in which there is no affinity between the dispersion medium and dispersed phase is called a lyophobic sol. For example, a sol of sulphur in water is a lyophobic sol.
24. (i) Fluorine cannot show higher oxidation states like +3, +5, +7 which other halogens show *e.g.*, chlorine shows O.S. of +3 in HOClO, +5 in HOClO₂, +7 in HOClO₃ 1

(ii) Structure of ICl₄⁻



XeF₄ is isostructural with ICl₄⁻.



25.

$$\begin{aligned}a &= 288 \text{ pm} = 288 \times 10^{-10} \text{ cm} = 2.88 \times 10^{-8} \text{ cm} \\ z &= 2 \text{ (for } b.c.c. \text{ lattice), } d = 7.2 \text{ g cm}^{-3}\end{aligned}$$

Mass of the sample, $m = 208 \text{ g}$

If n is the number of atoms in the sample of mass $m \text{ g}$, then density,

$$d = \frac{z \times m}{a^3 \times n} \quad \text{(Modified formula)}$$

Number of atoms,

$$n = \frac{z \times m}{a^3 \times d}$$

$$\begin{aligned}&= \frac{2 \times 208 \text{ g}}{(2.88 \times 10^{-8} \text{ cm})^3 \times (7.2 \text{ g cm}^{-3})} \\ &= \frac{416 \times 10^{24}}{2389 \times 7.2} = \mathbf{2.42 \times 10^{24}}\end{aligned}$$

OR

$$\begin{aligned}a &= 405 \text{ pm} = 405 \times 10^{-12} \text{ m} = 4.05 \times 10^{-10} \text{ m} \\ M &= 2.7 \times 10^{-2} \text{ kg mol}^{-1}, N_A = 6.022 \times 10^{23} \text{ mol}^{-1}\end{aligned}$$

$$d = \frac{z \times M}{a^3 \times N_A}$$

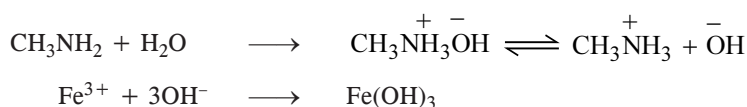
$$z = \frac{d \times a^3 \times N_A}{M}$$

$$\begin{aligned}&= \frac{(2.7 \times 10^3 \text{ kg m}^{-3}) \times (4.05 \times 10^{-10} \text{ m})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}{2.7 \times 10^3 \text{ kg mol}^{-1}} \\ &= 3.99 \approx 4 \text{ (nearest whole number)}\end{aligned}$$

Thus, there are 4 atoms of the element per unit cell. Therefore, element forms *f.c.c.* (or *c.c.p.*) lattice *i.e.*, cubic unit cell is face centred.

26. (i) It is because in aniline the —NH_2 group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. (or any other suitable reason)

(ii) Methylamine in water gives OH^- ions which react with FeCl_3 to give precipitate of ferric hydroxide/or

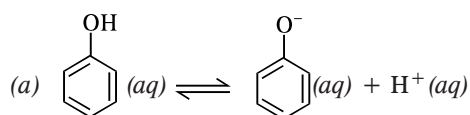


(iii) Aniline does not undergo Friedel-Crafts reaction due to salt formation with aluminium chloride- a Lewis acid. $1 \times 3 = 3$

OR

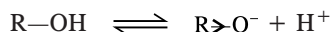


(b) Aniline gets protonated and is converted to anilinium ion which is *m*-directing. 1



27.

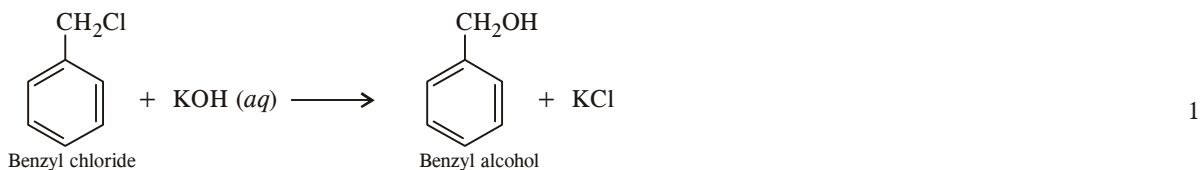
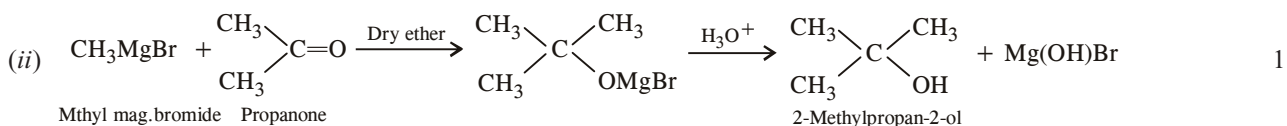
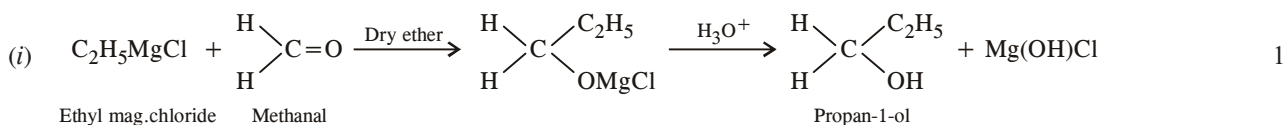
Both phenol and phenoxide ion are resonance stabilised, but phenoxide ion is better resonance stabilised than phenol. It is due to charge separation in the resonance structures of phenol. This shifts the equilibrium in the forward direction, making phenol fairly acidic.



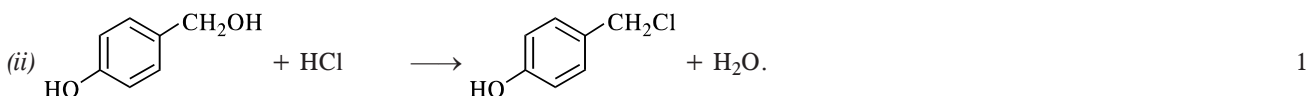
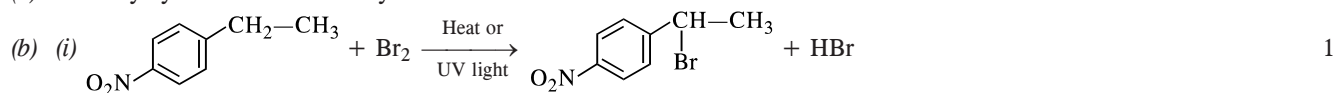
The alkoxide ion formed in alcohols is destabilised due to the +I effect of R-group. This reduces the acidic character of alcohols. 1

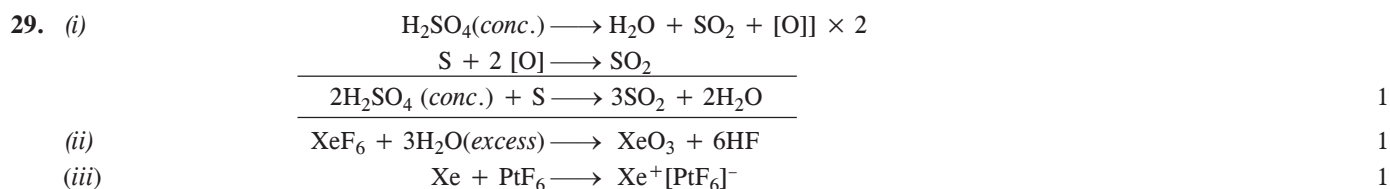
- (b) (i) $(\text{CH}_3)_3\text{C—O—C}_2\text{H}_5 + \text{HI} \longrightarrow (\text{CH}_3)_3\text{CI} + \text{C}_2\text{H}_5\text{OH}$ 1
- (ii) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—O—CH}_3 + \text{HI} \longrightarrow \text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH} + \text{CH}_3\text{I}$ 1

OR



28. (a) 3-Methylcyclohexanecarbaldehyde 1





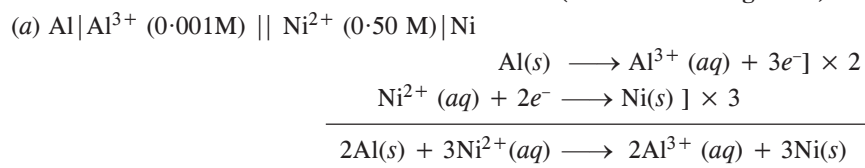
30. (i) $[\text{Pt}(\text{en})_3](\text{NO}_3)_2$
tris(ethane -1, 2-diamine)platinum(II)nitrate
- (ii) $\text{K}_3 [\text{PdCl}_4]$
potassium tetrachloridopalladate(II)
- (iii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$
diamminechlorido(methanamine)platinum(II) chloride

31.
$$\Lambda_m = \frac{\kappa \times (1000 \text{ cm}^3 \text{ L}^{-1})}{C}$$
 1

$$= \frac{(7.896 \times 10^{-5} \text{ S cm}^{-1}) \times (1000 \text{ cm}^3 \text{ L}^{-1})}{0.00241 \text{ mol L}^{-1}} = 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{32.76 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.084$$
 1
$$K = \frac{C^2 \alpha^2}{C(1-\alpha)} = C\alpha^2$$
 1
$$K = 0.00241 \times (0.084)^2$$

$$K = 1.7 \times 10^{-5} \text{ or } 1.865 \times 10^{-5} \text{ (if } 1-\alpha \text{ is not neglected)}$$
 1



$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3}$$

$$= \left[E^\circ_{\text{Ni}^{2+}/\text{Ni}} - E^\circ_{\text{Al}^{3+}/\text{Al}} \right] - \frac{0.059}{6} \log \frac{[10^{-3}]^2}{[5 \times 10^{-1}]^3}$$

$$= [-0.25 \text{ V} - (-1.66 \text{ V})] - \frac{0.059}{6} \text{ V} \log \frac{1}{125 \times 10^3}$$

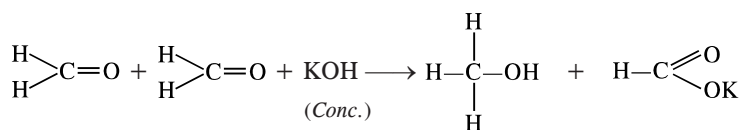
$$= [1.66 - 0.25] \text{ V} - \frac{0.059 \text{ V}}{6} [\log 1 - \log 1.25 \times 10^5]$$

$$= 1.41 \text{ V} + \frac{0.059}{6} \times 5.0969 \text{ V} = (1.41 + 0.05) \text{ V} = 1.46 \text{ V}$$

- (b) Maximum work, $\Delta G^\circ = nE^\circ F$
Hence $n = 6$, $E^\circ = 1.41 \text{ V}$ and $F = 96500 \text{ C mol}^{-1}$
 $\therefore \Delta G = -6 \times 1.41 \times 96500 \text{ J}$
 $= -816390 \text{ J} = -816.39 \text{ kJ}$



- (b) (i) **Cannizzaro reaction** : Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction reaction on treatment with concentrated alkali. 1



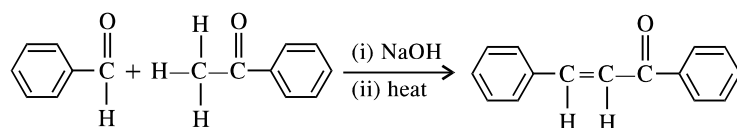
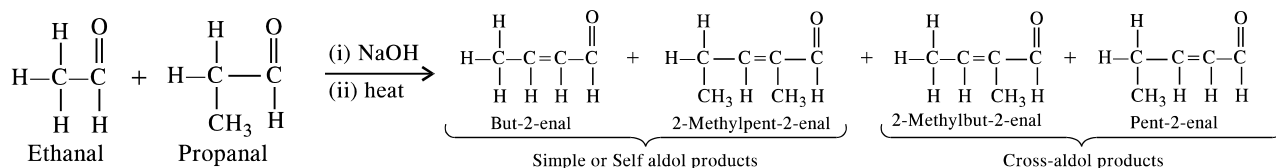
Formaldehyde (Two molecules)

Methanol

Potassium formate

(or any other suitable reaction)

- (ii) **Cross-aldol condensation** : When aldol condensation is carried out between two different aldehydes and/or ketones, it is called cross aldol condensation. 1



Benzaldehyde

Acetophenone

(or any other suitable reaction)

(Note : Award full marks for correct chemical equation ; award ½ mark if only statement is written)

OR

- (a) (i) Because two alkyl groups in ketones reduce the positive charge on carbon atoms of the carbonyl group more effectively than in aldehydes. 1

OR

Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.

(ii) Because of the absence of hydrogen bonding in aldehydes and ketones.

(iii) Because of the presence of the sp^2 -hybridised orbitals (or π -bond) of carbonyl carbon. 1 × 3 = 3

- (b) (i) **Acetaldehyde and benzaldehyde** : Acetaldehyde gives yellow ppt. of iodoform (CHI_3) on heating with NaOH/I_2 whereas benzaldehyde does not give this test. (or any other suitable test)

(ii) **Propanone and propanol** : Propanone gives yellow ppt. of iodoform (CHI_3) on heating with NaOH/I_2 whereas propanol does not give this test. 1 + 1

OR

Propanol gives brisk effervescence on adding a piece of sodium metal whereas propanone does not give this test. 1 + 1

(or any other suitable test)

33. (i) Because of larger number of unpaired electrons in their atoms they have stronger interatomic interactions and hence stronger bonding between atoms resulting in higher enthalpies of atomisation.

(ii) Because of their ability to adopt multiple oxidation states and to form complexes.

(iii) Due to small size and high electronegativity oxygen or fluorine can oxidise the metal to its highest oxidation state.

(iv) Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this.

(v) Because of the presence of incomplete d -subshell ($3d^1 4s^2$). 1 × 5 = 5

OR

- (a) $3d^3 4s^2$ (Vanadium) : Oxidation states +2, +3, +4, +5

Stable oxidation states : +4 as VO^{2+} , +5 as VO^{3+} ;

$3d^5 4s^2$ (Manganese) : Oxidation states +2, +3, +4, +5, +6, +7

Stable oxidation states : +2 as Mn^{2+} , +7 as MnO_4^- ;

$3d^6 4s^2$ (Iron) : Oxidation states + 2, + 3

Stable oxidation state : +3 as Fe^{3+} . 1 × 3 = 3

- (b) (i) Transition metals and many of their compounds are generally paramagnetic in nature. This is due to the presence of partly filled d -subshell which has unpaired electrons. More the number of unpaired d -electrons, more is the paramagnetic character. 1

(ii) In the presence of ligands, compounds of transition elements are generally coloured. It is due to the presence of partly filled d -subshell. In the presence of ligands, d -subshell of valence shell splits into two sets of orbitals with slightly different energies. Electronic transitions ($d-d$ transitions) between these two levels takes place with the absorption in the visible region. The colour of the compound is the complementary colour of the light absorbed, which depends upon the difference in energies of these two sets of orbitals. 1

Sample Question Paper—3

Chemistry (Theory)–XII

Time Allowed : 3 Hours

Maximum Marks : 70

General Instructions : Same as in Sample Paper-1

Section – A (Objective Type)

SECTION – A

Passage Based Questions (Q. No. 1 to Q. No. 5)

1. Read the following and answer the questions (i) to (iv) that follows :

The substitution reaction of alkyl halide mainly occurs by S_N1 or S_N2 mechanism. Whatever mechanism alkyl halides follow for the substitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of S_N1 reactions is governed by the stability of carbocation whereas for S_N2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.

(i) A primary alkyl halide would prefer to undergo

(a) S_N1 reaction

(b) S_N2 reaction

(c) α -Elimination

(d) Racemisation

(ii) Which of the following alkyl halides will undergo S_N1 reaction most readily ?

(a) $(CH_3)_3C-F$

(b) $(CH_3)_3C-Cl$

(c) $(CH_3)_3C-Br$

(d) $(CH_3)_3C-I$

(iii) Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows

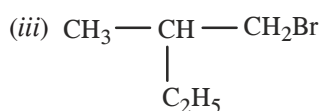
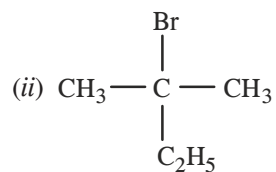
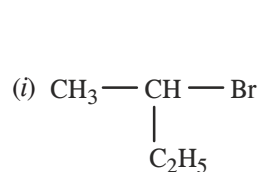
(a) S_N1 mechanism

(b) S_N2 mechanism

(c) Any of the above two depending upon the temperature of reaction

(d) Saytzeff rule

(iv) Which of the following compounds will give racemic mixture on nucleophilic substitution of OH^- ion ?



(a) (i)

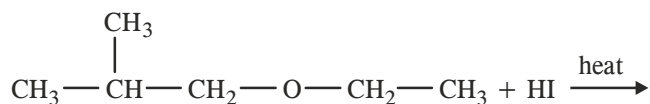
(b) (i), (ii), (iii)

(c) (ii), (iii)

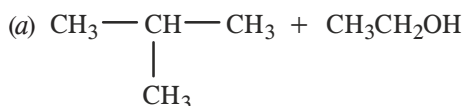
(d) (i), (iii)

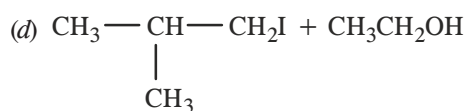
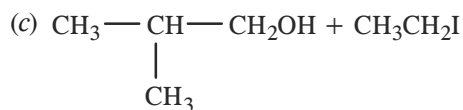
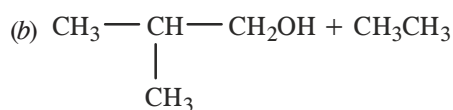
OR

In the reaction :



Which of the following compounds will be formed ?





2. Read the passage given below and answer the questions (i) to (iv) that follows :

Surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. The molecular species or substance, which concentrates or accumulates at the surface is termed adsorbate and the material on the surface of which the adsorption takes place is called adsorbent.

Adsorption is essentially a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents. For example.

- If a gas like CO , Cl_2 , NH_3 or SO_2 is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal *i.e.*, gases are adsorbed at the surface.
- Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.
- The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

It is clear from the above examples that solid surfaces can hold the gas or liquid molecules by virtue of adsorption. The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.

The questions given below consist of Assertion and Reason. Use the following key to select the correct answer.

- If both assertion and reason are correct and reason is correct explanation for assertion.
- If both assertion and reason are correct but reason is not correct explanation for assertion.
- If assertion is correct but reason is incorrect.
- If assertion is wrong but reason is correct.
 - Assertion :** Finely divided solids are good adsorbents
Reason : It is due to their large surface area.
 - Assertion :** When raw sugar solution is passed over beds of animal charcoal, sugar is adsorbed by the animal charcoal.
Reason : Animal charcoal is a good adsorbent due to large surface area.
 - Assertion :** When powdered charcoal is added to a cylinder containing ammonia, the pressure in the cylinder decreases.
Reason : Powdered charcoal adsorbs ammonia.
 - Assertion :** Air becomes dry in the presence of silica gel.
Reason : Silica gel adsorbs moisture from the air

OR

Assertion : When powdered charcoal is added to a cylinder containing SO_2 , the pressure in the cylinder decreases.

Reason : Powdered charcoal adsorbs O_2 .

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

3. When one mole of $\text{CoCl}_3 \cdot 5\text{NH}_3$ was treated with excess of silver nitrate solution, 2 mol of AgCl was precipitated. The formula of the compound is :

- $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}$
- $[\text{Co}(\text{NH}_3)_3\text{Cl}]\text{Cl}_2$
- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2](\text{NH}_3)\text{Cl}$
- $[\text{Co}(\text{NH}_3)\text{Cl}_3](\text{NH}_3)_2$

4. The absorption maxima of several octahedral complex ions are as follows :

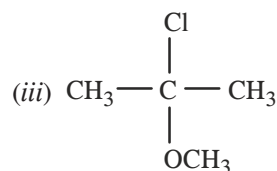
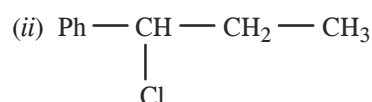
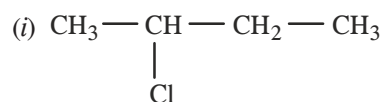
S.No.	Compound	λ_{\max} (nm)
1.	$[\text{Co}(\text{NH}_3)_6]^{3+}$	475
2.	$[\text{Co}(\text{CN})_6]^{3-}$	310
3.	$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	490

The correct order of Δ_o for the ions is :

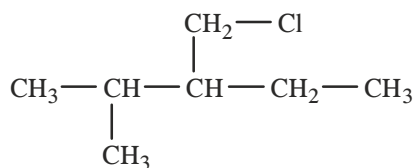
- (a) $[\text{Co}(\text{H}_2\text{O})_6]^{3+} < [\text{Co}(\text{CN})_6]^{3-} < [\text{Co}(\text{NH}_3)_6]^{3+}$
 (b) $[\text{Co}(\text{CN})_6]^{3-} < [\text{Co}(\text{NH}_3)_6]^{3+} < [\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 (c) $[\text{Co}(\text{H}_2\text{O})_6]^{3+} < [\text{Co}(\text{NH}_3)_6]^{3+} < [\text{Co}(\text{CN})_6]^{3-}$
 (d) $[\text{Co}(\text{NH}_3)_6]^{3+} < [\text{Co}(\text{CN})_6]^{3-} < [\text{Co}(\text{H}_2\text{O})_6]^{3+}$
5. Magnetic moment 2.83 BM is given by which of the following ions ?

[At. nos. Ti = 22, Cr = 24, Mn = 25, Ni = 28].

- (a) Mn^{2+} (b) Cr^{3+}
 (c) Ni^{2+} (d) Ti^{3+}
6. The correct order of reactivity in $\text{S}_{\text{N}}1$ reaction for the following compounds is



- (a) (i) > (ii) > (iii) > (iv)
 (b) (ii) > (i) > (iii) > (iv)
 (c) (iii) > (ii) > (i) > (iv)
 (d) (iv) > (iii) > (ii) > (i)
7. IUPAC name of the following compound is ,



- (a) 1-Chloro-2-isopropylbutane (b) 3-Chloromethyl-2-methylpentane
 (c) 3-Chloromethyl-4-methylpentane (d) 1-Chloro-2 (1-methylethyl)butane
8. Nucleic acids are the polymers of
 (a) Nucleosides (b) Nucleotides
 (c) Bases (d) Sugars
9. Which of the following statements is **not** true about glucose ?
 (a) It is an aldohexose. (b) On heating with HI, it forms *n*-hexane.
 (c) It is present in furanose form. (d) It does not give 2, 4-DNP test.
10. Each polypeptide in a protein has amino acids linked with each other in a specific sequence. This sequence of amino acids is said to be.
 (a) primary structure of proteins (b) secondary structure of proteins
 (c) tertiary structure of proteins (d) quaternary structure of proteins

11. Which of the following is more basic than aniline ?

- (a) Benzylamine (b) Diphenylamine
(c) Triphenylamine (d) *p*-Nitroaniline

For question numbers 12 to 16, two statements are given – one labelled Assertion (A) and the other labelled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below :

- (a) Both assertion (A) and reason (R) are correct statements, and reason (R) is the correct explanation of the Assertion (A).
(b) Both assertion (A) and reason (R) are correct statements, but reason (R) is *not* the correct explanation of the assertion (A).
(c) Assertion (A) is correct, but reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but reason (R) is correct statement.

12. **Assertion :** The molecularity of the reaction $\text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr}$ appears to be 2.

Reason : Two molecules of the reactants are involved in the given elementary reaction.

13. **Assertion :** F-F bond in F_2 molecule is weak.

Reason : F atom is small in size.

14. **Assertion :** Nitration of benzoic acid gives meta nitrobenzoic acid.

Reason : Carboxyl group deactivates the ortho and para positions in the ring.

15. **Assertion :** Carboxylic acids do not give characteristic reactions of carbonyl group.

Reason : The carbonyl group is sterically hindered in carboxylic acid.

16. **Assertion :** Nitration of chlorobenzene leads to the formation of 1-chloro-4-nitrobenzene as the major product.

Reason : $-\text{NO}_2$ group is an *o*, *p*-directing group.

SECTION – B

17. Write short notes on

- (i) Finkelstein reaction (ii) Sandmeyer reduction

OR

Write short notes on

- (i) Reimer – Tiemann reaction (ii) Rosenmund's reduction.

2

18. For a 5% solution of urea (Molar mass = 60 g/mol), calculate the osmotic pressure at 300 K. [$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$]

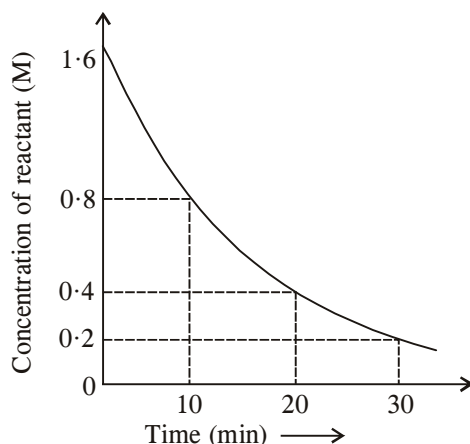
OR

Visha took two aqueous solutions — one containing 7.5 g of urea (Molar mass = 60 g/mol) and the other containing 42.75 g of substance **Z** in 100 g of water, respectively. It was observed that both the solutions froze at the same temperature. Calculate the molar mass of **Z**.

2

19. Analyse the given graph, drawn between concentration of reactant vs. time.

$1 \times 2 = 2$



(a) Predict the order of reaction.

(b) Theoretically, can the concentration of the reactant reduce to zero after infinite time ? Explain.

20. Draw the shape of the following molecules :

$1 \times 2 = 2$

(a) XeOF_4

(b) BrF_3

21. Give the formulae of the following compounds :

- (a) potassium tetrahydroxidozincate(II)
 (b) hexaammineplatinum(IV) chloride

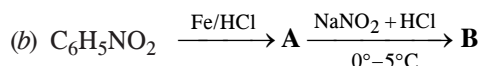
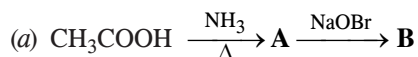
22. What happens when

- (a) Propanone is treated with methyl magnesium iodide and then hydrolysed,
 (b) Benzene is treated with CH_3COCl in presence of anhydrous AlCl_3 ?

$1 \times 2 = 2$

23. The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain. 2

24. Give the structures of **A** and **B** in the following sequence of reactions :



$\frac{1}{2} \times 4 = 2$

OR

How will you distinguish between the following pairs of compounds :

$1 \times 2 = 2$

- (i) Aniline and Ethanamine
 (ii) Aniline and N-methylaniline

25. Give the plausible explanation for the following :

$1 \times 2 = 2$

- (a) Glucose doesn't give 2, 4-DNP test.
 (b) The two strands in DNA are not identical but are complementary.

SECTION - C

26. Account for the following :

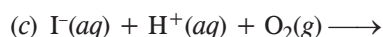
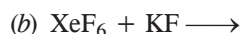
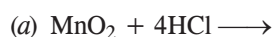
$1 \times 2 = 2$

- (a) Sulphurous acid is a reducing agent.
 (b) Fluorine forms only one oxoacid.
 (c) Boiling point of noble gases increases from He to Rn.

$1 \times 3 = 3$

OR

Complete the following chemical reactions :



$1 \times 3 = 3$

27. (a) What happens when white phosphorus is heated with conc. NaOH solution in an inert atmosphere of CO_2 .

(b) Why does NH_3 act as a Lewis base.

(c) Though nitrogen exhibits +5 oxidation state, it does not form pentahalides.

$1 \times 3 = 3$

28. An element having bcc geometry has atomic mass 50. Calculate the density if unit cell edge length is 290 pm. 3

OR

Analysis shows that nickel oxide has the formula $\text{Ni}_{0.98}\text{O}$. What fraction of nickel exist as Ni^{2+} and Ni^{3+} ions ? 3

29. How will the rate of the reaction be affected when

- (a) Surface area of the reactant is reduced,
 (b) Catalyst is added in a reversible reaction, and
 (c) Temperature of the reaction is increased ?

$1 \times 3 = 3$

30. Calculate the mass of ascorbic acid (Molar mass = 176 g mol^{-1}) to be dissolved in 75 g of acetic acid, to lower its freezing point by 15°C . ($K_f = 3.9 \text{ K kg mol}^{-1}$) 3

SECTION – D

31. (a) Calculate ΔG° for the reaction
- $$\text{Zn}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s). \quad 3$$
- Given : E° for $\text{Zn}^{2+}/\text{Zn} = -0.76 \text{ V}$ and E° for $\text{Cu}^{2+}/\text{Cu} = +0.34 \text{ V}$, $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $F = 96500 \text{ C mol}^{-1}$.
- (b) Why does the *e.m.f.* of a galvanic cell decrease on drawing current from it ? When does it falls to zero ? 2
- OR**
- (a) Out of the following pairs, predict with reason which pair will allow greater conduction of electricity : 1 × 3 = 3
- (i) Silver wire at 30°C or silver wire at 60°C.
- (ii) 0.1 M CH_3COOH solution or 1 M CH_3COOH solution.
- (iii) KCl solution at 20°C or KCl solution at 50°C.
- (b) Give two points of differences between galvanic and electrolytic cells. 2
32. (a) Account for the following : 1 × 3 = 3
- (i) Copper(I) compounds are white whereas copper(II) compounds are coloured.
- (ii) The transition metals and their many compounds act as good catalyst. Explain why.
- (iii) Zn, Cd, Hg are considered as *d*-block elements but not as transition elements.
- (b) Calculate the spin-only moment of Co^{2+} ($Z = 27$) by writing the electronic configuration of Co and Co^{2+} . 2
- OR**
- (a) What is lanthanoid contraction ? What are its causes and its consequences ? 3
- (b) Give reason and select one atom/ion which will exhibit asked property :
- (i) Sc^{3+} or Cr^{3+} (Exhibit diamagnetic behaviour)
- (ii) Cr or Cu (Higher melting and boiling point) 2
33. (a) Out of *t*-butyl alcohol and *n*-butanol, which one will undergo acid catalyzed dehydration faster and why ? 2
- (b) Carry out the following conversions : 1 × 3 = 3
- (i) Phenol to Salicylaldehyde
- (ii) *t*-Butyl chloride to *t*-Butyl ethyl ether
- (iii) Propene to 1-Propanol
- OR**
- (a) Give the mechanism for the formation of ethanol from ethene. 2
- (b) Predict the reagent for carrying out the following conversions : 1 × 3 = 3
- (i) Phenol to benzoquinone
- (ii) Anisole to *p*-bromoanisole
- (iii) Phenol to 2, 4, 6-tribromophenol

SOLUTION

- (i) (b) **Explanation :** A 1° alkyl halide prefers to undergo $\text{S}_{\text{N}}2$ reaction.
- (ii) (d) **Explanation :** All are 3° alkyl halides but cleavage of C–I bond is the easiest.
- (iii) (a) **Explanation :** This 1° alkyl halide is expected to take part in $\text{S}_{\text{N}}2$ reaction. However, it actually participates in $\text{S}_{\text{N}}1$ reaction since $\text{C}_6\text{H}_5\overset{+}{\text{C}}\text{H}_2$ carbocation is resonance stabilised.
- (iv) (a) Structure (ii) is achiral. Structure (iii) is chiral but Br atom is not attached to chiral centre. Structure (i) is chiral and Br-atom is attached to chiral centre. It is a 2° alkyl halide. By $\text{S}_{\text{N}}1$ mechanism it will give a racemic mixture.

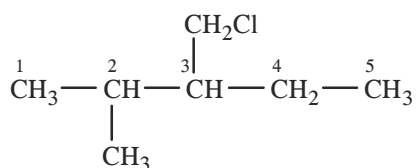
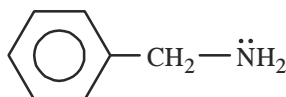
OR

- (c) **Explanation :** Iodide ion (I^-) will get attached to smaller alkyl group to minimise steric hinderance.
2. (i) (a) Reason is the correct explanation for assertion
- (ii) (d) **Correct assertion :** When raw sugar solution is passed over beds of animal charcoal, the colouring substances are adsorbed by the charcoal.
- (iii) (c) **Correct reason :** Powdered charcoal adsorbs ammonia.
- (iv) (a) Reason is the correct explanation for assertion.

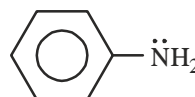
OR

(b) **Correct explanation :** Powdered charcoal adsorbs SO_2 .3. (b) **Explanation :** $[\text{Co}(\text{NH}_3)]\text{Cl}_2(\text{aq}) \rightarrow [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$ 4. (c) **Explanation :** $\Delta_o \propto \frac{1}{\lambda_{\text{max}}}$ Hence the correct order of Δ_{o_m} for the ions is,5. (c) **Explanation :** $\mu = \sqrt{n(n+2)}$ Here $\mu = 2.83$ (given)

$$\therefore 2.83 = \sqrt{n(n+2)}$$

The solution for this equation is $n = 2$ (nearest whole number) with $3d^8$ -configuration, number of unpaired electrons in Ni^{2+} ion is two.6. (c) **Explanation :** This order of reactivity in $\text{S}_{\text{N}}1$ reactions is directly proportional to the relative stabilities of carbocations which is tertiary > secondary > primary \therefore The correct order of reactivity is :7. (b) **Explanation :****IUPAC name :** 3-Chloromethyl-2-methylpentane.8. (b) **Explanation :** Nucleic acids are the polymers of nucleotides9. (c) **Explanation :** Glucose is not present in the furanose form10. (a) **Explanation :** The sequence of amino acids in protein is called its primary structure.11. (a) **Explanation :** Benzylamine is more basic than aniline. This is because benzene ring does not exert any conjugation effect in benzylamine. In all other amines the effect operates.

Benzylamine

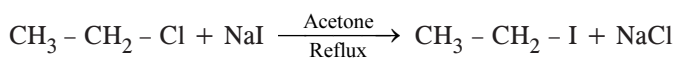


Aniline

12. (a) Reason is the correct explanation for assertion.

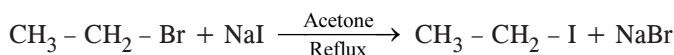
13. (b) **Correct explanation :** It is due to strong inter-electronic repulsions between the lone pairs of electrons on the two fluorine atoms.

14. (a) Reason is the correct explanation for assertion.

15. (c) **Correct reason :** It is due to the absence of positive charge on the carbon atoms of $-\text{COOH}$ group in its resonating structure.16. (c) **Correct reason :** Chloro group is *o*-, *p*-directing and ortho position is sterically hindered to some extent.17. (i) **Finkelstein reaction.** An alkyl iodide may be prepared by treating an alkyl chloride or bromide with sodium iodide in acetone. The chlorine or bromine atom of the alkyl halide is replaced by iodine atom in the reaction.

Chloroethane

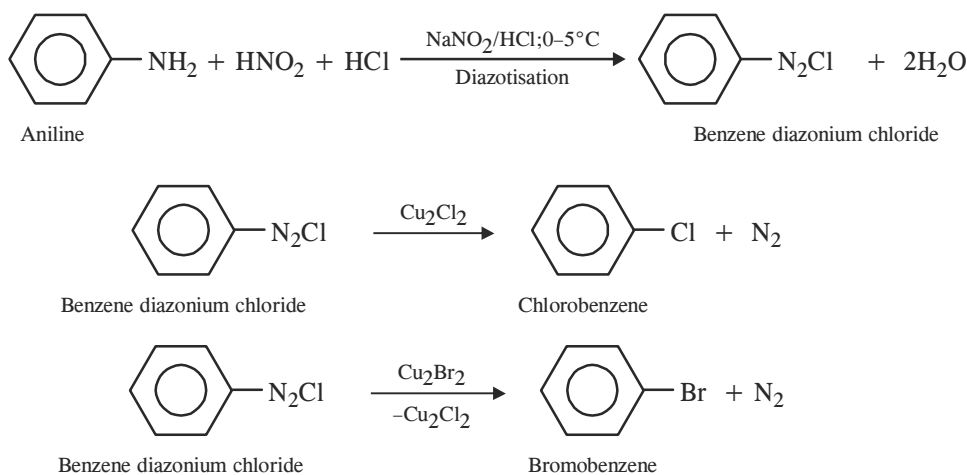
Iodoethane



Bromoethane

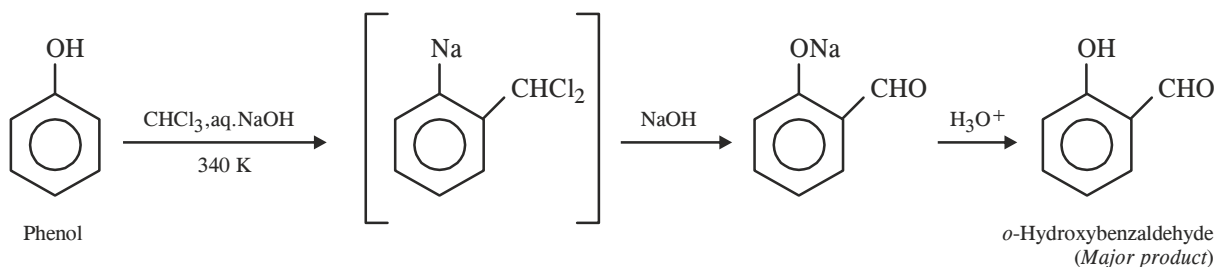
Iodoethane

(iii) **Sandmeyer Reaction.** Introduction of chlorine or bromine into benzene ring by treating the diazonium salt solution with cuprous chloride (or cuprous bromide) to get chlorobenzene (or bromobenzene) is called Sandmeyer's reaction.

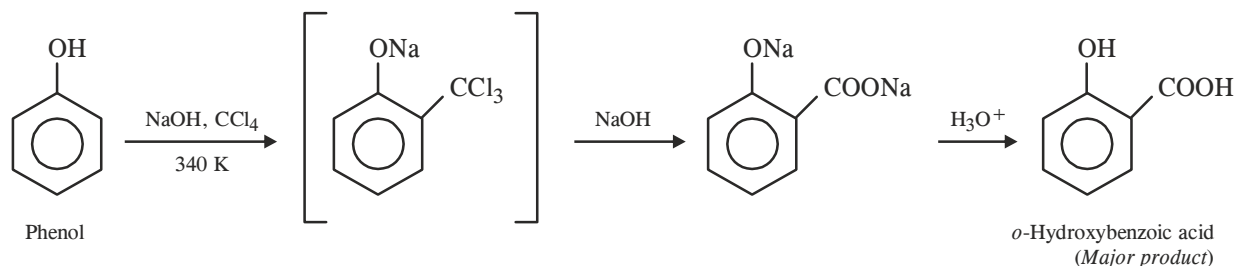


OR

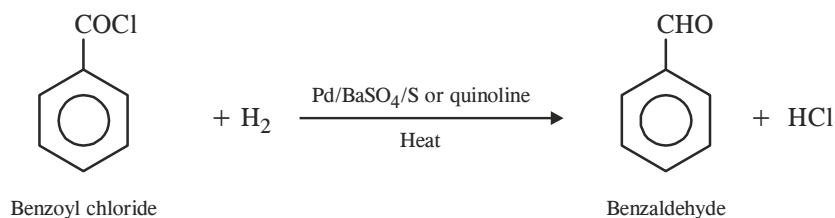
(i) **Reimer Tiemann Reaction.** Treatment of phenol with chloroform in the presence of aqueous alkali at 340 K results in the formation of *o*-hydroxybenzaldehyde (salicylaldehyde) and *p*-hydroxybenzaldehyde, the ortho isomer being the major product.



If carbon tetrachloride is used in place of chloroform, *o*-hydroxybenzoic acid (salicylic acid) is obtained as the major product.



(ii) **Rosenmund's Reduction :** This reaction involves the heating of an acid chloride with H_2 in the presence of Pd deposited over BaSO_4 poisoned with S or quinoline.



This method can be used to make both aliphatic and aromatic aldehydes.

18. $w_B = 5 \text{ g}$, $M_B = 60 \text{ g mol}^{-1}$, $T = 300 \text{ K}$, $V = 100 \text{ mL} = 0.1 \text{ L}$ (Take density of solution as 1 g mL^{-1}),
 $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$, $\pi = ?$

$$\pi = \frac{n}{V}RT = \frac{w_B}{M_B} \times \frac{RT}{V}$$

$$= \frac{5 \text{ g}}{60 \text{ g mol}^{-1}} \times \frac{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times 300 \text{ K}}{0.1 \text{ L}} = 20.5 \text{ atm}$$

OR

For solution of urea

$$w_{\text{urea}} = 7.5 \text{ g}, M_{\text{urea}} = 60 \text{ g mol}^{-1}, w_A = 100 \text{ g} = 0.1 \text{ kg}$$

For solution of Z

$$w_z = 42.75 \text{ g}, M_z = ?, w_A = 100 \text{ g} = 0.1 \text{ kg}$$

$$K_f \times \frac{w_{\text{urea}}}{M_{\text{urea}}} \times \frac{1}{W_A(\text{kg})} = K_f \times \frac{w_z}{M_z} \times \frac{1}{w_A(\text{kg})}$$

$$\frac{7.5 \text{ g}}{60 \text{ g mol}^{-1}} \times \frac{1}{0.1 \text{ kg}} = \frac{42.75 \text{ g}}{M_z} \times \frac{1}{0.1 \text{ kg}}$$

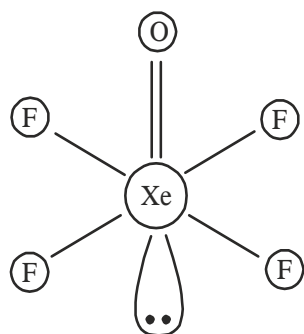
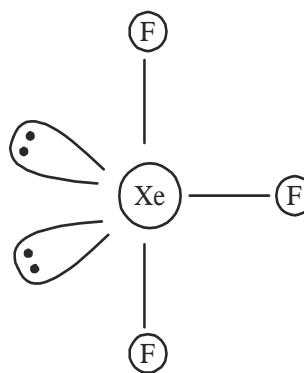
$$M_z = \frac{42.75 \text{ g}}{7.5 \text{ g}} \times 60 \text{ g mol}^{-1} = 342 \text{ g mol}^{-1}$$

19. (a) In first 10 min. concentration of reactant reduces from 1.6 M to 0.8 M *i.e.*, it becomes half. In next 10 min. concentration of reactant reduces from 0.8 M to 0.4 M *i.e.*, it becomes half. In next 10 min. concentration of reactant reduces from 0.4 M to 0.2 M *i.e.*, it becomes half. Thus half life period is independent of initial concentration. Hence it is a first order reaction.
 (b) Theoretically, for a first order reaction, the concentration of reactant will never reduce to zero even after infinite time.

OR

Due to exponential relation, the curve never touches the x -axis and hence concentration of reactant will never become zero.

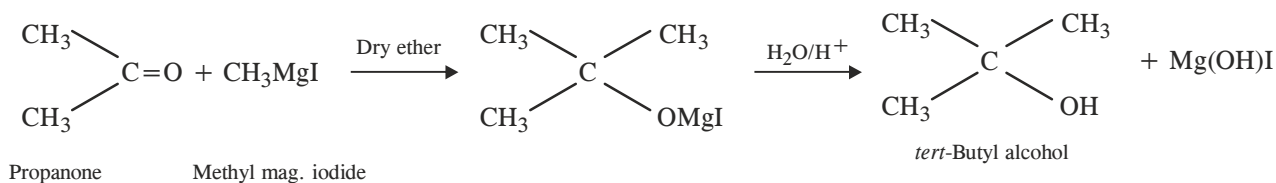
20. (a)

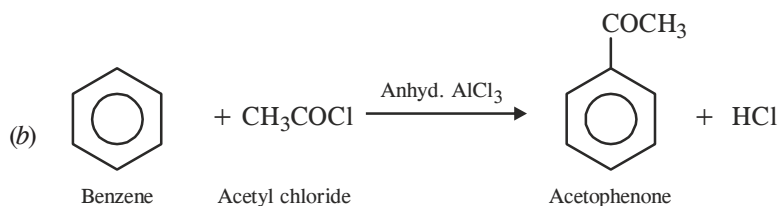
XeOF₄BrF₃

21. (a) $\text{K}_2[\text{Zn}(\text{OH})_4]$
 potassium tetrahydroxidozincate(II)

- (b) $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$
 hexaammineplatinum(IV) chloride

22. (a)



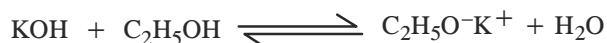


23. KOH when dissolved in water provides K^+ and OH^- ions.

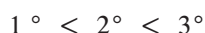


These OH^- ions act as strong nucleophiles leading to nucleophilic substitution (S_N^1 or S_N^2).

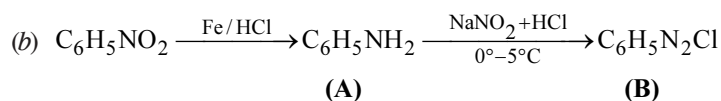
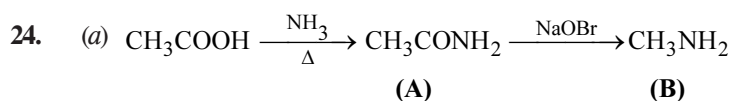
KOH when dissolved in alcohol (say ethanol) gives ethoxide ions and K^+ ions.



The bulkier nucleophile (alkoxide ion) in this case will prefer to act as a base and abstract a proton rather than approach a tetravalent carbon atom (steric reasons). However, the exact nature of products formed also depends upon the nature of alkyl halide used. The ease of elimination follows the order :



Therefore, in case of a 3° alkyl halide, alkene is the major product even with *aq.* KOH. However in case of 1° alkyl halides almost pure alcohols (with *aq.* KOH) and almost pure alkenes (with *alc.* KOH) can be obtained.



OR

(i) Add ice cold ($NaNO_2 + HCl$) followed by phenol to both the compounds. Only aniline forms a orange dye.

(ii) Add $CHCl_3$ and KOH (*alc.*) to both the compounds and heat. Only aniline gives foul smelling isocyanide.

25. (a) In glucose the $-CHO$ group is not free as it is involved in the formation of hemiacetal in the cyclic structure. Hence glucose does not give 2, 4-DNP test (a test for carbonyl group).

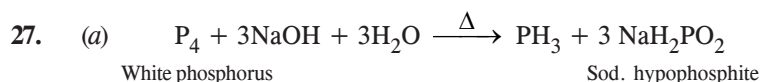
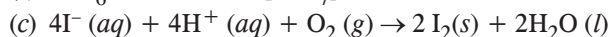
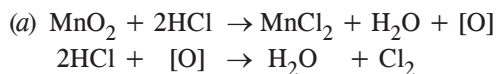
(b) This is because, the hydrogen bonds are formed between specific pairs of bases ($A = T$ and $C \equiv G$)

26. (a) In sulphurous acid (H_2SO_3) O.S. of sulphur is $+4$. Because sulphur readily gets oxidised itself to more stable $+6$ oxidation state, hence H_2SO_3 acts as a reducing agent.

(b) Because of absence of *d*-orbitals in fluorine, it forms and one oxo acid (HOF).

(c) As the number of electrons increases from He to Rn the magnitude of London dispersion forces also increases down the group. It results in increase in boiling point from He to Rn.

OR



(b) It is due to the presence of lone pair of electrons on nitrogen atom in ammonia.

(c) Due to the absence of *d*-orbitals in its valence shell, nitrogen cannot expand its covalency beyond four.

28. $a = 290 \text{ pm} = 290 \times 10^{-10} \text{ cm} = 2.9 \times 10^{-8} \text{ cm}$

$M = 50 \text{ g mol}^{-1}$, $z = 2$ (for *bcc* unit cell), $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

$$\begin{aligned} \text{Density, } d &= \frac{z \times M}{a^3 \times N_A} = \frac{2 \times (50 \text{ g mol}^{-1})}{(2.9 \times 10^{-8} \text{ cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})} \\ &= \frac{100}{(2.9)^3 \times 10^{-24+23} \times 6.022} \text{ g/cm}^3 = \frac{1000}{(2.9)^3 \times 6.022} \text{ g/cm}^3 \\ &= \frac{1000}{24.389 \times 6.022} \text{ g/cm}^3 = \frac{1000}{16.87} \text{ g/cm}^3 = \mathbf{6.8 \text{ g/cm}^3} \end{aligned}$$

OR

In the given nickel oxide 98 Ni atoms are associated with 100 O-atoms. Out of 98 Ni atoms, suppose Ni present as $\text{Ni}^{2+} = x$. Then Ni present as $\text{Ni}^{3+} = 98 - x$.

Total charge on $x \text{ Ni}^{2+}$ and $(98 - x) \text{ Ni}^{3+}$ should be equal to charge on 100 O^{2-} ions. Hence,

$$\begin{aligned} x \times 2 + (98 - x) \times 3 &= 100 \times 2 \\ 2x + 294 - 3x &= 200 \quad \text{or } x = 94 \end{aligned}$$

$$\therefore \text{Fraction of Ni present as } \text{Ni}^{2+} = \frac{94}{98} \times 100 = \mathbf{96\%}$$

$$\text{Fraction of Ni present as } \text{Ni}^{3+} = \frac{4}{98} \times 100 = \mathbf{4\%}$$

29. (a) On reducing surface area of reactant, the rate of the reaction decreases.
 (b) On adding a positive catalyst to a reversible reaction, the time taken to reach equilibrium is reduced. It is due to increase in the rate of both forward and backward reactions. However, there will not be any change in the position of equilibrium.
 (c) On increasing the temperature, the rate of a chemical reaction also increases.

30. $w_B = ?$ $M_B = 176 \text{ g mol}^{-1}$, $w_A = 75 \text{ g} = 0.075 \text{ kg}$,

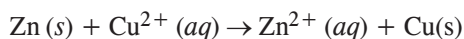
$$K_f = 3.9 \text{ K kg mol}^{-1}, \Delta T_f = 15^\circ\text{C} = 15 \text{ K}$$

$$\Delta T_f = K_f \times \frac{w_B}{M_B} \times \frac{1}{w_A (\text{kg})}$$

$$w_B = \frac{\Delta T_f \times M_B \times w_A (\text{kg})}{K_f}$$

$$= \frac{15 \text{ K} \times (176 \text{ g mol}^{-1}) \times (0.075 \text{ kg})}{3.9 \text{ K kg mol}^{-1}} = \mathbf{5.08 \text{ g}}$$

31. (a) For the reaction



$$n = 2$$

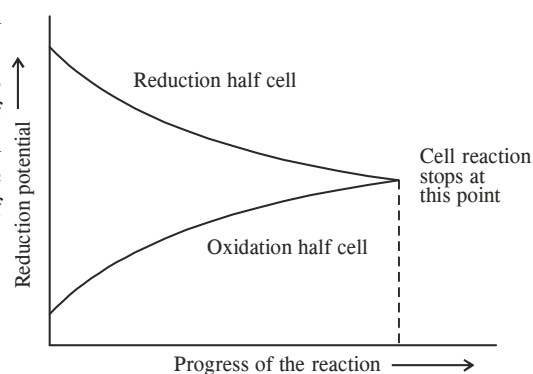
Cell representation is, $\text{Zn} \mid \text{Zn}^{2+} (1 \text{ mol}) \parallel \text{Cu}^{2+} (1 \text{ mol}) \mid \text{Cu}$

$$\begin{aligned} \therefore E^\circ_{\text{cell}} &= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} \\ &= +0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V} \\ F &= 96500 \text{ C mol}^{-1}, \Delta G^\circ = ? \\ \Delta G^\circ &= -nE^\circ F \\ &= -2 \times (1.10 \text{ V}) \times (96500 \text{ C mol}^{-1}) \\ &= -212300 \text{ J mol}^{-1} = \mathbf{-212.3 \text{ kJ mol}^{-1}} \end{aligned}$$

- (b) In a galvanic cell, electrons flow from the electrode at a lower reduction potential (*i.e.*, anode) to an electrode at a higher reduction potential (*i.e.*, cathode). When the current is drawn from a cell, the concentration of cations in the oxidation half cell (*i.e.*, anode) increases while the concentration of cations in the reduction half cell (*i.e.*, cathode) decreases. As the reduction potential is directly proportional to the concentration of ions in solution, the reduction potential of anode start increasing, whereas reduction potential of cathode start decreasing. As *e.m.f.* of cell is given by the expression,

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

e.m.f. of the cell gradually decreases with time. Ultimately a stage is reached when the E_{cathode} and E_{anode} becomes equal and cell stops working.



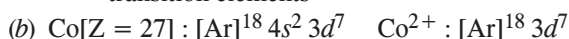
- (a) (i) Silver wire at 30°C because as temperature decreases, resistance decreases so conductance increases.
 (ii) 0.1 M CH_3COOH , because on dilution degree of ionisation increases and hence conduction (molar conductivity) increases.
 (iii) KCl solution at 50°C, because at high temperature mobility of ions increases and hence conductance increases.

S.No.	Galvanic cell	Electrolytic cell
1.	The redox reaction is spontaneous.	The redox reaction is non-spontaneous.
2.	Electricity is produced	Electricity is consumed.
3.	Anode is -ve and cathode is +ve.	Anode is +ve and cathode is -ve.
4.	The electrodes are generally of different materials	The electrodes may be of same of different material.
5.	Two different electrolytes are used.	One electrolyte is used.

32. (a) (i) Cu^+ ($3d^{10}$) compounds are white because of absence of unpaired electrons while Cu^{2+} ($3d^9$) compounds are coloured due to the presence of unpaired electron.
 (ii) Many transition metals and their compounds are found to act as catalyst. Because of the presence of the incomplete *d*-subshell, they can form unstable intermediate products with the reactants. These intermediates give reaction path of lower activation energy and therefore increase the rate of reaction.

For example :

- (i) Finally divided nickel, platinum and palladium are used as a catalyst in hydrogenation.
 (ii) V_2O_5 is used for the oxidation of SO_2 to SO_3 in the Contact process for the manufacture of H_2SO_4 .
 (iii) Iron and molybdenum are used as catalyst in the manufacture of ammonia from N_2 and H_2 in Haber's process.
 (iii) Zn, Cd and Hg are considered as *d*-block elements because their last electron enters the *d*-subshell of penultimate shell. As these elements and none of their oxidation states have partly filled *d*-subshell, they are not considered as transition elements



Hence number of unpaired electrons, $n = 3$

$$\begin{aligned} \therefore \mu_{\text{spin only}} &= \sqrt{n(n+2)} \\ &= \sqrt{2(3+2)} = \sqrt{10} = 3.92 \text{ B.M.} \end{aligned}$$

OR

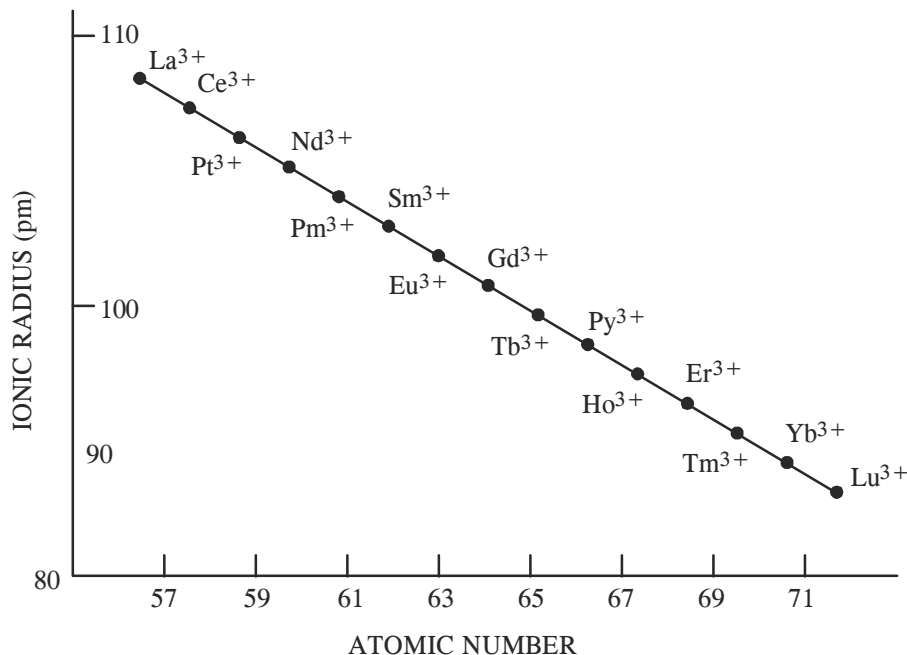
- (a) **Lanthanoid contraction.** In lanthanoids there is a regular decrease in the size of atoms and ions with increasing atomic number. Lanthanoid contraction may be defined as *the steady decrease in the size of lanthanoid ions (Ln^{3+}) with the increase in atomic number*. Due to lanthanoid contraction ionic radii decrease from Ce^{3+} (111 pm) to Lu^{3+} (93 pm).

Cause of Lanthanoid contraction. As we move through the lanthanoid series, 4*f*-electrons are being added one at each step. The mutual shielding effect of 4*f*-electrons is very little. This is due to the shape of *f*-orbitals, as they are much diffused. The nuclear charge however, increases by one at each step. Hence, the inward pull experienced by the 4*f*-electrons increases. The causes a

reduction in the size of entire $4f^n$ subshell. The sum of successive reductions give the total lanthanoid contraction. The decrease in atomic size is not so regular, it is more in case of first six elements. However, the decrease in ionic size of tripositive ion M^{3+} with atomic number is quite regular along the series.

Consequences of lanthanoid contraction.

- Lanthanoid contraction is an important factor in allowing the separation of lanthanoids from one another as they resemble each other chemically. The separation is done by ion exchange methods.

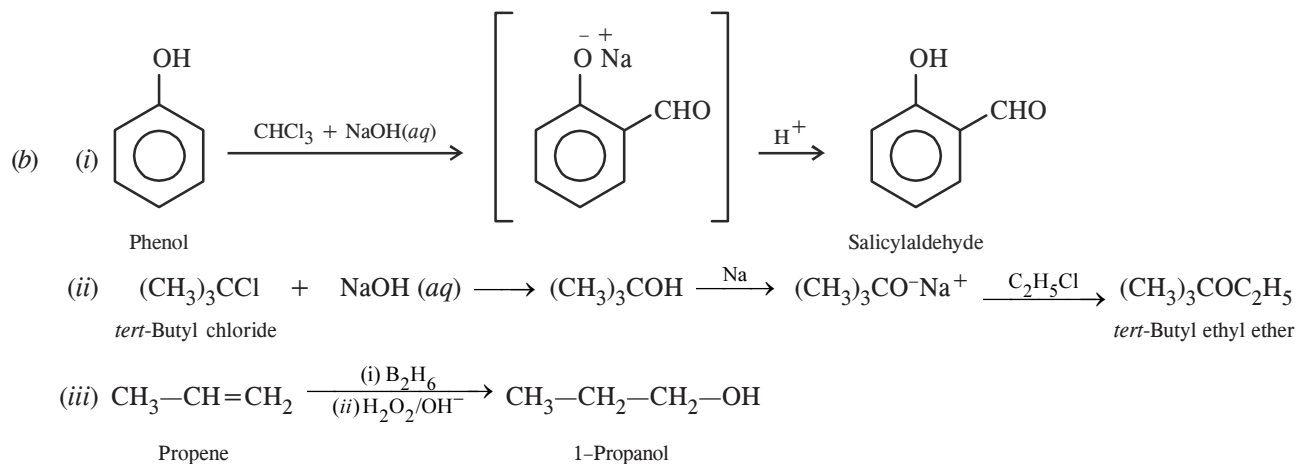


- Due to lanthanoid contraction, elements of $4d$ and $5d$ -series have similar atomic radii *e.g.*, Zr = 145 pm and Hf = 144 pm. Thus Zr and Hf have almost identical physical and chemical properties.
- Due to lanthanoid contraction basic strength of oxides and hydroxide decreases along the series.
- There is a small but steady increase in the standard reduction potential (E°) for the process ;

$$M^{3+} (aq) + 3e^- \longrightarrow M(s)$$
- Due to lanthanoid contraction elements of the second and third transition series resembles each other more closely than to the elements of 1st and 2nd transition series.
 - Out of Sc^{3+} ($3d^0$) and Cr^{3+} ($3d^3$), Sc^{3+} is diamagnetic. It is due to the absence of any unpaired d -electron.
 - Out of Cr ($4s^1 3d^5$) or Cu ($4s^1 3d^{10}$), Cr has higher melting and boiling points. It is due to the presence of large number of unpaired d -electrons in Cr which result in strong interatomic bonding.

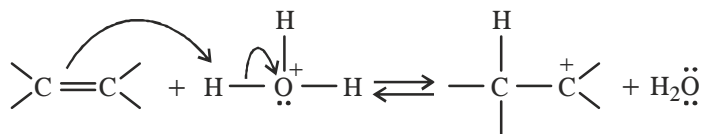
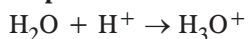
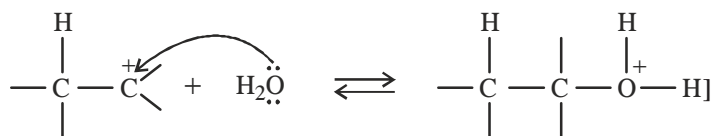
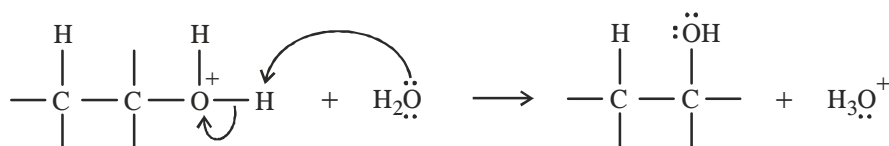
33. (a) *tert*-Butyl alcohol

Reason : Acid catalysed dehydration of alcohol involves the formation of a carbocation as an intermediate and 3° carbocation is more stable than a 1° carbocation.

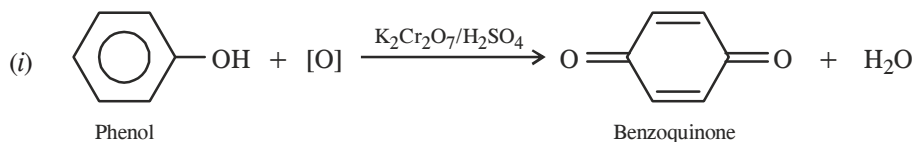
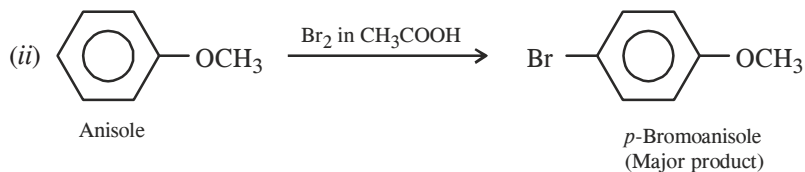
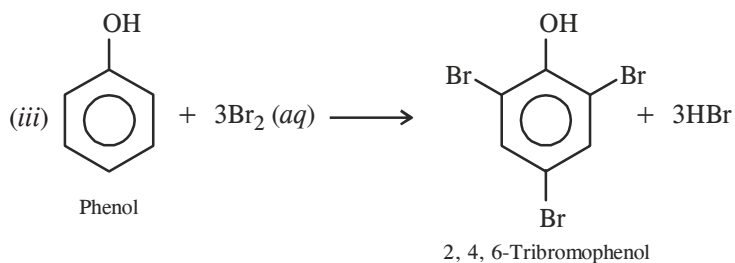


OR

(a) It involves following three steps

Step 1. Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .**Step 2.** Nucleophilic attack of water on carbocation.**Step 3.** Deprotonation to form an alcohol.

(b)

**Reagent used :** $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ **Reagent used :** Br_2 in ethanoic acid (CH_3COOH)**Reagent used :** Bromine water or $\text{Br}_2(\text{aq})$

Sample Question Paper—4

Chemistry (Theory)–XII

Time Allowed : 3 Hours

Maximum Marks : 70

General Instructions : Same as in Sample Paper-1

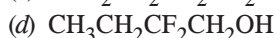
SECTION – A (Objective Type)

1. Read the following and answer the questions (i) to (iv) that follows :

Both alcohols and phenols contain a hydroxyl group, but phenols are more acidic than alcohols. The reason being that the phenoxide ion left after the removal of a proton is resonance stabilized while alkoxide is not. However, both are weaker acids than carbonic acid and hence do not decompose aqueous NaHCO_3 solution evolving CO_2 . The presence of electron-donating groups in the benzene ring decrease the acid strength while the presence of electron withdrawing groups in the benzene ring increase the acid strength of phenols. The relative strength of *o*, *m* and *p* substituted phenols however, depends upon a combination of inductive and resonance effects of the substituent.

Alcohols are very weak acids even weaker than water. Because of the +1 effect of the alkyl groups, the acid strength of alcohols decreases in the order : 1° alcohol > 2° alcohol > 3° alcohol.

(i) Which of the following is the strongest acid ?



(ii) The acidic strength decreases in the order

(a) *p*-Nitrophenol > *m*-Nitrophenol > *o*-Nitrophenol

(b) *p*-Nitrophenol > *o*-Nitrophenol > *m*-Nitrophenol

(c) *m*-Nitrophenol > *o*-Nitrophenol > *p*-Nitrophenol

(d) *o*-Nitrophenol > *m*-Nitrophenol > *p*-Nitrophenol

(iii) Which of the following is the strongest acid ?

(a) Phenol

(b) 2-Nitrophenol

(c) 2, 4-Dinitrophenol

(d) 2, 4, 6- Trinitrophenol

OR

The acidic strength decreases in the order

(a) *o*-Chlorophenol > *m*-Chlorophenol > *p*-Chlorophenol

(b) *o*-Chlorophenol > *p*-Chlorophenol > *m*-Chlorophenol

(c) *p*-Chlorophenol > *o*-Chlorophenol > *m*-Chlorophenol

(d) *p*-Chlorophenol > *m*-Chlorophenol > *o*-Chlorophenol

(iv) Which of the following is the strongest acid ?

(a) Phenol

(b) *o*-Cresol

(c) *m*-Cresol

(d) *p*-Cresol.

2. Read the following and answer the questions (i) to (iv) that follows :

There are certain substances which behave as normal strong electrolytes at low concentration but at higher concentration they behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called associated colloids and the aggregated particles are called **micelles**. Soaps and detergents are the examples of associated colloids. The formation of micelles takes place above certain concentration called critical micellization concentration (CMC) and a characteristic temperature called Kraft temperature.

The questions given below consist of Assertion and Reason. Use the following keys to select the correct answer.

(a) If both assertion and reason are correct and reason is correct explanation for assertion.

(b) If both assertion and reason are correct but reason is not correct explanation for assertion.

(c) If assertion is correct but reason is incorrect.

(d) If assertion is wrong but reason is correct.

(i) **Assertion** : A mixture of a synthetic detergent in water above a certain concentration and temperature behaves as a colloidal sol.

Reason : Synthetic detergents are associated colloids.

(ii) **Assertion :** A gold sol in water when sufficiently diluted can easily pass through an ultrafilter paper.

Reason : A gold sol in a multimolecular colloid.

(iii) **Assertion :** A colloidal solution of soap in water, when sufficiently diluted can easily pass through ultrafilter paper.

Reason : Soap is an example of multimolecular colloid.

(iv) **Assertion :** A colloidal solution of a detergent when sufficiently diluted becomes a true solution.

Reason : On dilution the micelles present break upto give ions with size less than 1 nm.

OR

Assertion : A mixture of soap in water above a certain concentration and temperature behaves as a colloidal solution.

Reason : Soap is generally a sodium or potassium salt of a fatty acid.

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

3. Out of the following, the strongest base in aqueous solution is ;

- (a) Methylamine (b) Dimethylamine
(c) Trimethylamine (d) Aniline

OR

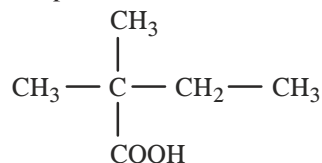
Iodoform test is **not** given by

- (a) Ethanol (b) Ethanal
(c) Pentan-2-one (d) Pentan-3-one

4. Out of the following transition elements, the maximum number of oxidation states are shown by

- (a) Sc (Z = 21) (b) Cr (Z = 24)
(c) Mn (Z = 25) (d) Fe (Z = 26)

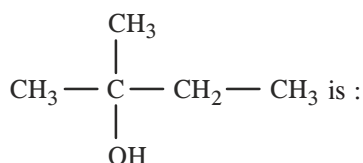
5. What is the correct IUPAC name of the given compound ?



- (a) 2, 2-Dimethylbutanoic acid (b) 2-Carboxy1-2-methylbutane
(c) 2-Ethyl-2-methylpropanoic acid (d) 3-Methylbutanecarboxylic acid

OR

The correct IUPAC name of



- (a) *tert*-Butyl alcohol (b) 2, 2-Dimethylpropan-1-ol
(c) 2-Methylbutan-2-ol (d) 3-Methylbutane-3-ol

6. The **incorrect** statement about interstitial compounds is :

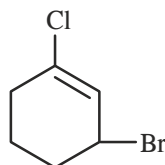
- (a) They are chemically reactive. (b) They are very hard
(c) They retain metallic conductivity (d) They have high melting point.

OR

Total number of unpaired electrons present in Co^{3+} (Atomic number = 27) is

- (a) 4 (b) 7
(c) 6 (d) 3

7. The IUPAC name of the compound shown below is :



(a) 2-Bromo-6-Chlorocyclohex-1-ene

(b) 6-Bromo-2-Chlorocyclohex-1-ene

(c) 3-Bromo-1-chlorocyclohex-1-ene

(d) 1-Bromo-3-Chlorocyclohex-1-ene

8. Among the following the correct order of acidity is :

(a) $\text{HClO}_2 < \text{HClO} < \text{HClO}_3 < \text{HClO}_4$ (b) $\text{HClO}_4 < \text{HClO}_2 < \text{HClO} < \text{HClO}_3$ (c) $\text{HClO}_3 < \text{HClO}_4 < \text{HClO}_2 < \text{HClO}$ (d) $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$

OR

Least volatile hydrogen halide is ;

(a) HF

(b) HCl

(c) HBr

(d) HI

9. Which of the following compounds will give butanone on oxidation with alkaline KMnO_4 solution ?

(a) Butan-1-ol

(b) Butan-2-ol

(c) Both of these

(d) None of these

10. Which of the following is most acidic ?

(a) Benzyl alcohol

(b) Cyclohexanol

(c) Phenol

(d) *m*-Chlorophenol11. The oxidation number of chromium in $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ is

(a) +2

(b) +3

(c) +4

(d) +5

For question numbers 12 to 16, two statements are given – one labelled Assertion (A) and the other labelled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below :

(a) Both assertion (A) and reason (R) are correct statements, and reason (R) is the correct explanation of the Assertion (A).

(b) Both assertion (A) and reason (R) are correct statements, but reason (R) is *not* the correct explanation of the assertion (A).

(c) Assertion (A) is correct, but reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but reason (R) is correct statement.

12. Assertion (A) : Boiling points of alkyl halides decrease in the order



Reason (R) : van der Waals forces decrease with increase in the size of halogen atom.

13. Assertion (A) : Low spin tetrahedral complexes are rarely observed.

Reason (R) : The orbital splitting energies are not sufficiently large to force pairing.

14. Assertion (A) : Albumin is a globular protein.

Reason (R) : Polypeptide chain coils around to give a straight chain.

15. Assertion (A) : *o*-Nitrophenol is a weaker acid than *p*-nitrophenol.Reason (R) : Intramolecular hydrogen bonding makes *ortho* isomer weaker than *para* isomer.

16. Assertion (A) : Carbylamine reaction is applicable only to primary aliphatic amines.

Reason (R) : In carbylamine reaction, the $-\text{NH}_2$ group is converted into $-\text{N} \equiv \text{C}$ group.

OR

Assertion (A) : $\text{C}_2\text{H}_5\text{OH}$ is a weaker base than phenol but a stronger nucleophile than phenol.

Reason (R) : In phenol, the lone pair of electrons on oxygen is withdrawn towards the ring due to resonance.

SECTION - B

17. Write short notes on

(i) Connizzaro's reaction (ii) Wolf-Kishner reduction


OR

Write short notes on

(i) Clemmenson reduction (ii) HVZ reaction

18. Give reasons for the following :

1 × 2 = 2

(a) Bond angle  in alcohol is slightly less than the tetrahedral angle.

(b) C—OH bond length in CH_3OH is slightly more than the C—OH bond length in phenol.

19. Explain why
 (i) Transition metals forms a large number of alloys.
 (ii) Transition metals have a tendency to form complexes.
20. What are the conditions and consequences of Schottky defect ?

OR

Write short note on F-centres.

2

21. A reaction is first order w.r.t. reactant A as well as w.r.t. reactant B. Give the rate law. Also give one point of difference between average rate and instantaneous rate. 2
22. For an electrochemical cell

$$\text{Mg}(s) + 2\text{Ag}^+(aq) \longrightarrow 2\text{Ag}(s) + \text{Mg}^{2+}(aq),$$
 give the cell representation. Also write the Nernst equation for the above cell at 25°C. 2
23. Sodium crystallizes in a bcc unit cell. Calculate the approximate no. of unit cells in 9.2 grams of sodium. (Atomic mass of Na = 23 u).
24. Why haloarenes are less reactive than haloalkanes towards nucleophilic substitution reactions.

OR

Haloalkanes react with KCN (alc) to give alkyl cyanide as main product while with AgCN(alc) they form isocyanides as the main product. Why ?

25. Account for the following : 1 × 3 = 3
 (a) Aniline is a weaker base compared to ethanamine.
 (b) Aniline does not undergo Friedel-Crafts reaction.

SECTION – C

26. Justify and arrange the following compounds of each set in increasing order of reactivity towards the asked displacement :

$$1\frac{1}{2} \times 2 = 3$$

- (a) 1-Bromobutane, 2-Bromobutane, 2-Bromo-2-methylpropane (S_N1 reaction)
 (b) 1-Bromobutane, 2-Bromobutane, 2-Bromo-2-methylpropane (S_N2 reaction)
27. (a) Give the IUPAC name and electronic configuration of central metal atom in terms of t_{2g} and e_g of $K_4[Mn(CN)_6]$.
 (b) What is meant by 'Chelate effect' ? Give an example. 2 + 1 = 3

OR

Write the hybridisation and magnetic characters of the following complexes :

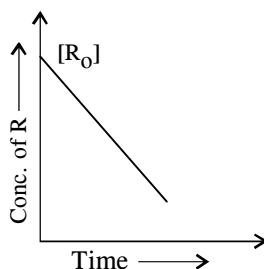
- (i) $[\text{Fe}(\text{CN})_6]^{4-}$ (ii) $[\text{CoF}_6]^{3-}$
 (iii) $[\text{Ni}(\text{CO})_4]$

[Atomic number : Fe = 26, Co = 27, Ni = 28]

28. (a) What are transition elements ? Would you classify Zn, Cd and Hg as transition elements ? Give reasons for your answer. 1
 (b) What is meant by 'disproportionation' ? Give two examples of disproportionation reactions in aqueous solution. 2
29. Conductivity of 2×10^{-3} M methanoic acid is 8×10^{-5} S cm^{-1} . Calculate its molar conductivity and degree of dissociation if Λ_m° for methanoic acid is 404 S $\text{cm}^2 \text{mol}^{-1}$. 3
30. An antifreeze solution is prepared by dissolving 31 g of ethylene glycol (Molar mass = 62 g mol^{-1}) in 600 g of water. Calculate the freezing point of the solution. (K_f for water = 1.86 K kg mol^{-1}) 3

SECTION – D

31. (a) Visha plotted a graph between concentration of R and time for a reaction $R \longrightarrow P$. On the basis of this graph, answer the following questions : 1 × 3 = 3



- (i) Predict the order of reaction.
 (ii) What does the slope of the line indicate ?
 (iii) What are the units of rate constant ?
- (b) A first order reaction takes 25 minutes for 25% decomposition. Calculate $t_{1/2}$. 2
 [Given : $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$]

OR

- (a) The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the initial concentration of the reactant to its $\frac{1}{16}$ th value ? 3
- (b) Write four factors that affect the rate of a chemical reaction. 2
32. (a) Write an equation for the thermal decomposition of ammonium dichromate in solid state. 1
 (b) SCl_6 is not known, but SF_6 is known. Why ? 1
 (c) Why electron gain enthalpies of noble gases are large positive. 1
 (d) Give the molecular shapes of the following 2
 (i) XeO_2F_2 (ii) BrF_5 .

OR

- (a) Give reasons for the following observations :
 (i) Halogens are strong oxidising agents.
 (ii) Noble gases have very low boiling points.
 (iii) O and Cl have nearly same electronegativity, yet oxygen forms H-bond while Cl doesn't.
- (b) Complete and balance the following chemical equations : 1 × 2 = 2
 (i) $\text{NaOH} + \text{Cl}_2 \longrightarrow$
 (cold + dil.)
 (ii) $\text{I}^-(aq) + \text{H}_2\text{O}(l) + \text{O}_3(g) \longrightarrow$
33. (a) An organic compound 'A' having molecular formula $\text{C}_5\text{H}_{10}\text{O}$ gives negative Tollen's test, forms *n*-pentane on Clemmenson reduction but doesn't give iodoform test. Identify 'A' and give all the reactions involved. 1 + 1 = 2
 (b) Carry out the following conversions : 1 × 2 = 2
 (i) Propanoic acid to 2-Bromopropanoic acid
 (ii) Benzoyl chloride to benzaldehyde

- (c) How will you distinguish between benzaldehyde and acetaldehyde ? 1

OR

- (a) Complete the following sequence of reactions :

$$\text{CH}_3\text{COCH}_3 \xrightarrow{\text{Ba(OH)}_2} \text{(A)} \xrightarrow[-\text{H}_2\text{O}]{\Delta} \text{(B)} \xrightarrow{\text{NaOH/I}_2} \text{(C)} + \text{(D)}$$
 $\frac{1}{2} \times 4 = 2$
 (i) Identify (A) to (D).
 (ii) Give the IUPAC name of (A). 1
- (b) How can you distinguish between : 2
 (i) Ethanol and Propanone, and
 (ii) Benzoic acid and Phenol ?

SOLUTION

1. (i) (d) **Explanation :** -I effect of F-atom stabilises the alkoxide ion.
 (ii) (b) **Explanation :** -R effect of $-\text{NO}_2$ group stabilises the phenoxide ion. *o*-Nitrophenol is slightly less acidic than *p*-nitrophenol. It is due to intramolecular H-bonding in *o*-nitrophenol.
 (iii) (d) **Explanation :** Presence of three electrons withdrawing $-\text{NO}_2$ groups at *o*- and *p*-positions make 2,4, 6-trinitrophenol (picric acid) a strong acid.

OR

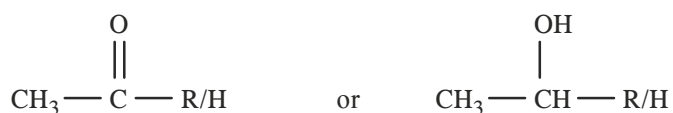
- (a) **Explanation :** Chlorine with its – I effect stabilises the phenoxide ion. The stabilising –I effect of chlorine decreases with the distance from oxygen.
- (iv) (a) **Explanation :** Presence of electron donating methyl group in cresols destabilises the phenoxide ion. As such cresols are less acidic than phenol.
2. (i) (a) Reason is correct explanation of assertion
 (ii) (d) **Correct assertion :** A gold sol in water, even when sufficiently diluted cannot pass through an ultrafilter paper.
 (iii) (c) **Correct reason :** Soap is an example of associated colloid.
 (iv) (a) Reason is correct explanation for assertion.

OR

- (b) **Correct explanation :** Soap is an example of associated colloid.
3. (b) **Explanation :** Aromatic amines are weaker than aliphatic amines. In aqueous solution 2° amine is most basic.

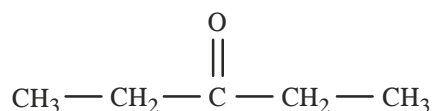
OR

- (d) **Explanation :** Iodoform test is given by compounds having the structures :



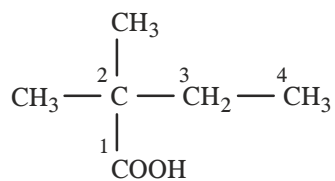
Hence pentan-3-one does not give iodoform test

Explanation :



Pentan-3-one.

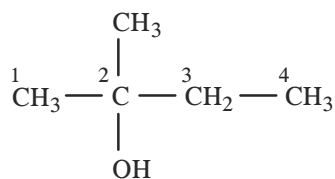
4. (c) **Explanation :** In 3d-series, Mn (Z = 25) shows maximum number of oxidation states.
5. (a) **Explanation :**



2, 2-Dimethylbutanoic acid

OR

- (c) **Explanation :**

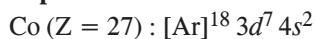


2-Methylbutan-2-ol

6. (a) **Explanation :** Interstitial compounds are chemically inert.

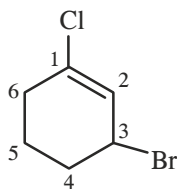
OR

- (a) **Explanation :**



Hence number of unpaired electrons = 4

(c) **Explanation :**



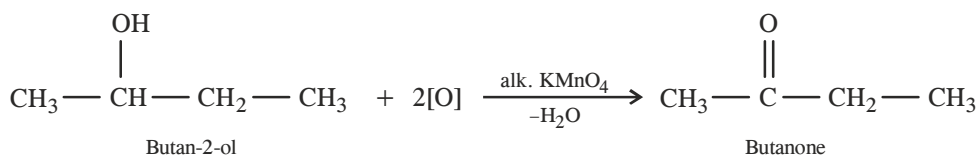
3-Bromo-1-chlorocyclohex-1-ene.

8. (d) **Explanation :** More the number of resonating structures of the conjugate base, more is the acidic strength.

OR

(a) **Explanation :** Due to H-bonding, H-F has highest boiling point *i.e.*, it is least volatile.

9. (b) **Explanation :**



10. (d) **Explanation :** Phenols are more acidic than alcohols. Presence of electron withdrawing group (like chloro) increases the acidic strength.

11. (b) **Explanation :**

Let O.N. of Cr = x

O.N. of $\text{NH}_3 = 0$ and O.N. of $\text{Cl}^- = -1$

$\therefore x + 4 \times 0 + 2(-1) = +1$

$\therefore x = +3$

12. (c) **Correct reason :** van der Waals forces increase with increase in the size of halogen atom.

13. (a) Reason is the correct explanation for assertion.

14. (c) **Correct reason :** Polypeptide chain coils around to give it a globular shape.

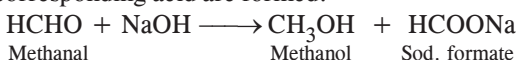
15. (a) Reason is the correct explanation for assertion.

16. (d) **Correct assertion :** Carbylamine reaction or test is applicable to all primary amines both aliphatic and aromatic.

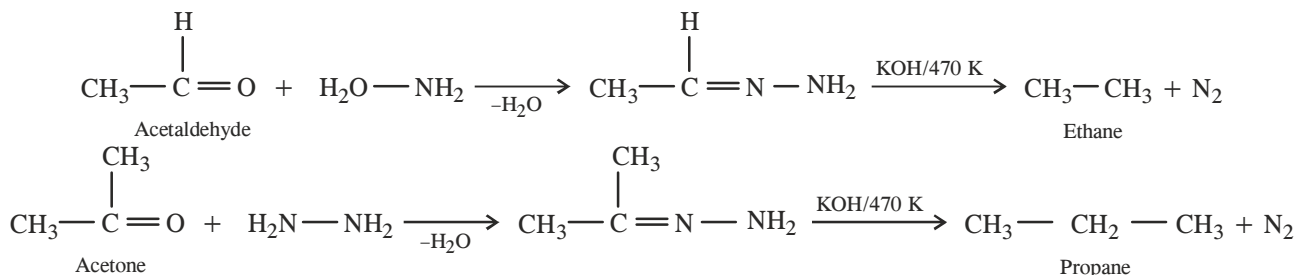
OR

(d) **Correct assertion :** $\text{C}_2\text{H}_5\text{OH}$ is a stronger base than phenol and also a stronger nucleophile than phenol.

17. (i) **Cannizzaro's reaction.** When formaldehyde or benzaldehyde (aldehydes containing no α -H atom) is treated with NaOH, then alcohol and sodium salt of the corresponding acid are formed.

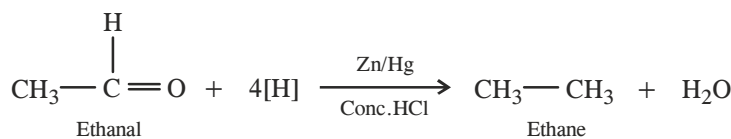


(ii) **Wolf-Kishner reduction.** In this reduction aldehydes or ketones are reduced to hydrocarbons with hydrazine ($\text{H}_2\text{N}-\text{NH}_2$) and KOH.

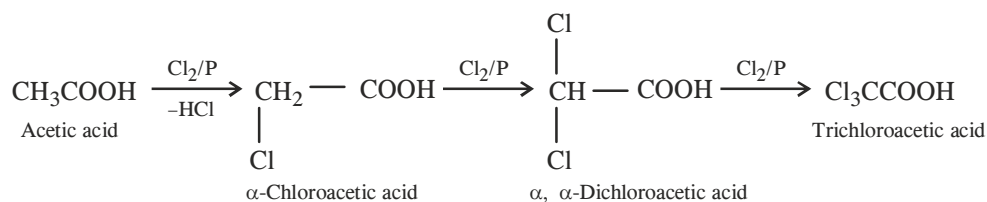


OR

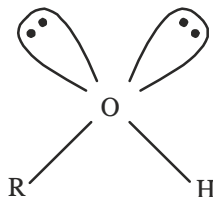
(i) **Clemmenson reduction.** It involves the reduction of aldehydes and ketones to the corresponding hydrocarbons with amalgamated zinc (Zn/Hg) and conc. HCl.



- (ii) **Hell-Volhard Zelinsky reaction.** Carboxylic acids (having α -hydrogen) on heating with chlorine or bromine in the presence of small amount of red phosphorus undergo substitution at α -carbon atom to form α -haloacids.



18. (a) In alcohols, the oxygen atom is sp^3 -hybridised with two lone pairs of electrons on it. Due to greater repulsion between two lone pairs of electrons, the C—O—H bond angle is less than the tetrahedral angle of $109^\circ 28'$.



- (b) The C—OH bond in CH_3OH is a pure single bond while the C—OH bond in $\text{C}_6\text{H}_5\text{OH}$ has some double bond character due to resonance. Hence the C—OH bond length in methanol is slightly more than the C—OH bond length in phenol.
19. (i) The tendency of transition metals to form alloys can be explained on the basis of their atomic sizes. The atomic size of transition metals are very similar and hence in the crystal lattice, atoms of one metal can readily be replaced with atoms of another transition metals. This result in the formation of alloys.
- (ii) Transition metals form a large number of complexes due to the following reasons :
- (a) The presence of vacant $(n - 1)$ d -orbitals, which can accept one or more electron pairs from ligands.
- (b) High charge density of transition metal cations.

For example, $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Fe}(\text{CN})_6]^{4-}$

20. **Schottky Defect** : In a crystalline solid of type $\text{A}^+ \text{B}^-$ this type of defect is created when equal number of positive ions and negative ions are missing from their respective positions. Since the number of missing positive ions is equal to the number of missing negative ions the crystal as a whole is electrically neutral. This defect is more common in ionic compounds with high coordination number and where the ions (positive and negative) are of similar size. For example, NaCl, KCl, CsCl and KBr.

Consequences of Schottky defect

- (i) As ions are missing from their lattice sites, presence of large number of Schottky defect lowers the density of the crystal.
- (ii) Ionic conductivity and diffusion in solid state in stoichiometric solids is due to the presence of lattice vacancies.

OR

F-centres. The anionic sites occupied by unpaired electrons and responsible for the colour of the crystal are called **F-centres**.

For example, When crystals of NaCl are heated in an atmosphere of sodium vapour, the Na atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to form NaCl. This happens with the loss of electron by Na atoms to form Na^+ ions. The released electron



diffuse into the crystal and occupy anionic sites. As a result the crystal now has excess of sodium. The anionic sites occupied by unpaired electrons are called F-centres. They impart yellow colour to the crystals of NaCl. The colour is due to the excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of Li in LiCl crystals makes it pink and excess of K in KCl crystals makes it violet.

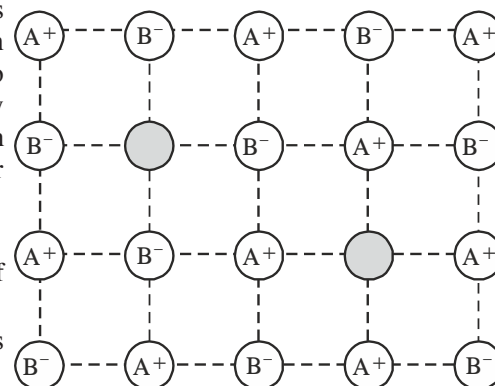


Fig. Schottky defect

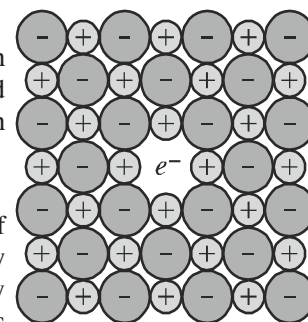


Fig. An F-centre in a crystal

21. The reaction is first order *w.r.t.* **A** as well as *w.r.t.* **B**. Hence rate law is ;

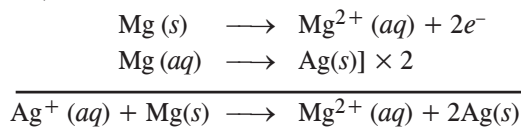
$$\text{Rate} = k [\text{A}] [\text{B}]$$

Difference between average and instantaneous rates of a reaction :

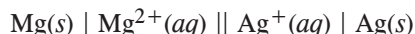
Average rate of a reaction : Rate of reaction for a particular period of time or interval of time.

Instantaneous rate of a reaction. Rate of reaction at a particular instant of time.

22. The cell reactions involved are ;



Hence cell representation is ;



Here n (Numbers of electrons transferred) = 2

Hence Nernst equation is ;

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q_c$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 RT}{2F} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, F = 96500 \text{ C mol}^{-1},$$

$$T = 25^{\circ}\text{C} = (25 + 273) \text{ K} = 298 \text{ K}$$

Substituting these values ;

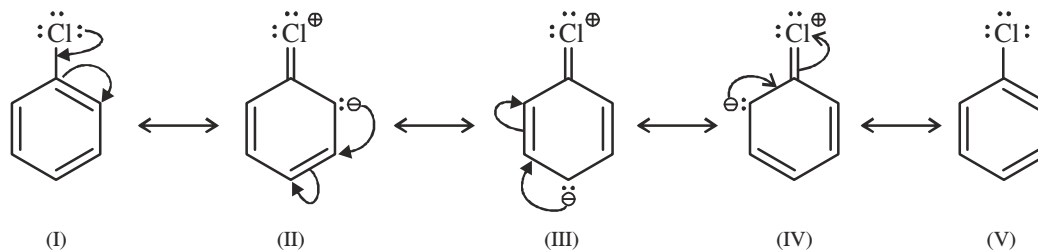
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059 \text{ V}}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

23. Mass of one unit cell = $z \times \frac{M}{N_A} = \frac{2(\text{for } b.c.c. \text{ lattice}) \times 23 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 7.66 \times 10^{-23} \text{ g}$

Number of unit cells in 9.2 g = $\frac{9.2 \text{ g}}{7.66 \times 10^{-23} \text{ g}} = 1.20 \times 10^{23}$

24. The lesser reactivity of haloarenes (say chlorobenzene) than haloalkanes (say chloromethane) in nucleophilic substitution reactions can be explained as follows :

- (i) **Resonance effect :** Haloarenes are resonance stabilised. For example, chlorobenzene is a resonance hybrid of various contributing structures (I) to (V) as shown below :

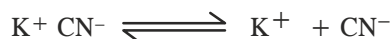


As a result of resonance, in structure (II) to (IV), C—Cl bond acquires some double bond character. On the other hand, no such resonance occurs in alkyl halides. Therefore, C—Cl bond in aryl halides is stronger than carbon—halogen bond in haloalkanes and hence can not be easily broken, so chlorobenzene is less reactive.

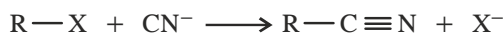
- (ii) **Hybridisation of carbon bearing the halogen atom.** In haloalkanes, the carbon atom attached to the halogen atom (C—X) is sp^3 -hybridised whereas in haloarenes, the carbon atom attached to the halogen atom is sp^2 -hybridised. Now sp^2 -hybrid orbital of carbon is slightly smaller in size than the sp^3 -hybrid orbital. Therefore, the carbon—halogen bond in haloarenes is shorter and stronger than the carbon—halogen bond in haloalkanes. This also justifies the low reactivity of haloarenes.

OR

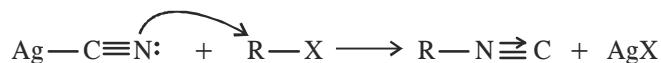
KCN is an ionic solid which ionises in polar solvents like ethanol to give CN^- ions.



Attack of CN^- on alkyl halides gives alkyl cyanide as main product.

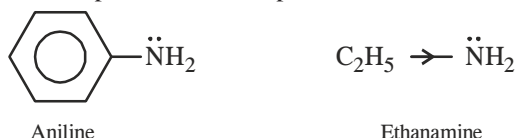


On the other hand, AgCN is a covalent solid in which $\text{Ag}-\text{CN}$ bond has a large covalent character. As such, it does not give CN^- ions to act as nucleophiles. Here $\text{Ag}-\text{C}\equiv\ddot{\text{N}}$ itself act as a nucleophile with the lone pair of electrons on nitrogen acting as electrohilic centre.



As such the main product obtained in this case is an isocyanide.

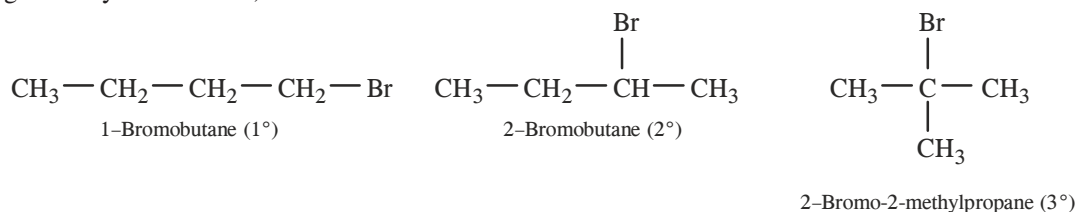
25. (a) Basic character of amines is due to the presence of lone pair of electrons on nitrogen atom.



In aniline the lone pair of electrons on nitrogen atom is in conjugation with the benzene ring. This reduces the availability of lone pair of electrons thus reducing its basic character. On the other hand, the +I effect of ethyl group in ethanamine increases the availability of electron pair on nitrogen atom thus increasing its basic character.

- (b) Aniline is a Lewis base while anhydrous AlCl_3 (which is used as a catalyst in Friedel Crafts reaction) is a Lewis acid. This results in a salt formation between the two and as such Friedel Crafts reaction is not possible in aniline.

26. The three given alkyl halides are ;



- (i) In $\text{S}_{\text{N}}1$ reactions, more stable the carbocation formed, more is the reactivity. The stability of carbocation is in the order $3^\circ > 2^\circ > 1^\circ$

Hence, the order of reactivity of given alkyl halides is ;



- (ii) In $\text{S}_{\text{N}}2$ reactions, more the steric hindrance on the C-atom attached to halogen, lesser is the reactivity. Hence the order of reactivity of given alkyl halides is ;



27. (a) $\text{K}_4[\text{Mn}(\text{CN})_6]$

IUPAL name : potassium hexacyanidomanganate(II)

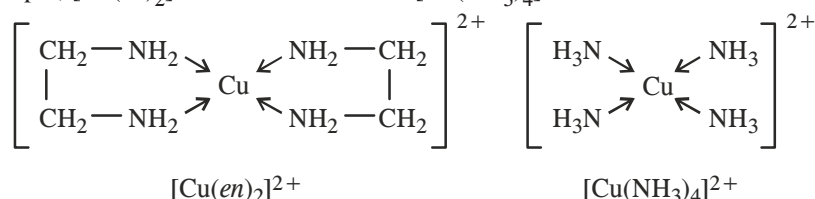
$\text{Mn}(Z = 25) : [\text{Ar}]^{18} 4s^2 3d^5$

$\text{Mn}^{2+} : [\text{Ar}]^{18} 3d^5$

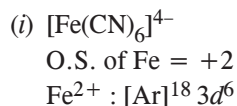
Here, CN^- is a strong field ligand. It will pair up the five $3d$ -electrons in three orbitals with lower energy of t_{2g} set. Thus electronic configuration of Mn in the presence of six CN^- ions is ;



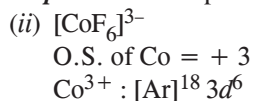
- (b) **Chelate effect :** Increased stability of the complex due to the presence of chelating (didentate or polydentate) ligands is called chelate effect. For example, $[\text{Cu}(\text{en})_2]^{2+}$ is more stable than $[\text{Cu}(\text{NH}_3)_4]^{2+}$



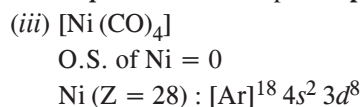
OR



In the presence of six CN^- ligands (CN^- is a strong field ligand) the six $3d$ -electrons pair up in three $3d$ -orbitals. Thus hybridisation is d^2sp^3 and the complex is **diamagnetic** as there is no unpaired electron in the complex.



In the presence of six F^- ligands (F^- is a weak field ligand) the electrons in the $3d$ -subshell do not pair up. As such hybridisation is sp^3d^2 and the complex is **paramagnetic** as it has four unpaired electrons.

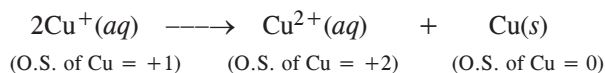


In the presence of four CO ligands (CO is a strong field ligand) the eight $3d$ -electrons pair up in four $3d$ -orbitals. Thus hybridisation is dsp^2 and the complex is **diamagnetic** as there is no unpaired electron in the complex.

28. (a) According to definition, *the transition elements are those which have partly filled d-orbitals in their elementary form or in their commonly occurring oxidation state*. Since Zn, Cd and Hg do not have partly filled d -orbitals in their elementary states or most common oxidation states, these are not classified as transition elements.
- (b) *When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation.*

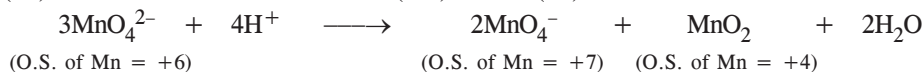
Examples :

- (i) Copper(I) ion is not stable in aqueous solutions. This is because Cu(I) becomes unstable relative to Cu(II) and Cu(0) in aqueous solution.



The E^0 value for this reaction is favourable. This is because the $\Delta_{\text{hyd}}H^\circ$ of $\text{Cu}^{2+}(aq)$ is much more negative than Cu^+ , which more than compensates for the second ionisation enthalpy of copper.

- (ii) Manganese(VI) becomes unstable relative to Mn(VII) and Mn(IV) in acidic solution.



29. $\kappa = 8 \times 10^{-5} \text{ S cm}^{-1}$, $C = 2 \times 10^{-3} \text{ mol L}^{-1}$

$$\lambda_m = ?$$

$$\lambda_m = \frac{\kappa \times 1000 \text{ cm}^3 \text{ L}^{-1}}{C}$$

$$= \frac{(8 \times 10^{-5} \text{ S cm}^{-1}) \times (1000 \text{ cm}^3 \text{ L}^{-1})}{(2 \times 10^{-3} \text{ mol L}^{-1})}$$

$$= 40 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\lambda_m}{\lambda_m^\circ} = \frac{40 \text{ S cm}^2 \text{ mol}^{-1}}{404 \text{ S cm}^2 \text{ mol}^{-1}} = 0.099$$

30.

$$W_B = 31 \text{ g} \quad W_A = 600 \text{ g} = 0.6 \text{ kg}$$

$$M_B = 62 \text{ g mol}^{-1}, K_f = 1.86 \text{ K kg mol}^{-1}, \Delta T_f = ?$$

$$\Delta T_f = K_f \times \frac{W_B}{M_B} \times \frac{1}{W_A(\text{kg})}$$

$$= \frac{(1.86 \text{ K kg mol}^{-1}) \times (31 \text{ g})}{(62 \text{ g mol}^{-1}) \times (0.6 \text{ kg})} = 1.55 \text{ K}$$

$$\begin{aligned}
 T_f^\circ &= 273 \cdot 15 \text{ K}, T_f = ? \\
 \Delta T_f &= T_f^\circ - T_f \\
 T_f &= T_f^\circ - \Delta T_f = (273 \cdot 15 - 15 - 1 \cdot 55) \text{ K} \\
 &= \mathbf{271 \cdot 6 \text{ K}}
 \end{aligned}$$

31. (a) (i) As graph between conc. of R vs. time is a straight line, it is a **zero order** reaction.

(ii) For a zero order reaction, rate of reaction

$$-\frac{d[\text{R}]}{dt} = k$$

or $-d[\text{R}] = k dt$

Integrating, $-\int d[\text{R}] = k \int dt$

$$-[\text{R}] = kt + c$$

when $t = 0, [\text{R}] = [\text{R}]_0$

$\therefore -[\text{R}]_0 = c$

substituting $-[\text{R}] = 0 - kt - [\text{R}]_0$

$$[\text{R}] = -kt + [\text{R}]_0$$

Thus graph of $[\text{R}]$ (along y-axis) and t (along x-axis) is a straight line with

$$\text{slope} = -k$$

(iii) For a zero order reaction,

$$\text{Rate} = k$$

\therefore units of k = units of rate of reaction

$$= \mathbf{\text{mol L}^{-1} \text{s}^{-1}}$$

(b) $[\text{R}]_0 = 100$ (say) $\therefore [\text{R}] = 100 - 25 = 75$

$$t = 25 \text{ min}, k = ?$$

For a first order reaction,

$$k = \frac{2 \cdot 303}{t} \log \frac{[\text{R}]_0}{[\text{R}]} = \frac{2 \cdot 303}{25 \text{ min}} \log \frac{100}{75}$$

$$= \frac{2 \cdot 303}{25 \text{ min}} \log \frac{4}{3} = \frac{2 \cdot 303}{25 \text{ min}} [\log 4 - \log 3]$$

$$= \frac{2 \cdot 303}{25 \text{ min}} (0 \cdot 6021 - 0 \cdot 4771)$$

$$= \frac{2 \cdot 303 \times 0 \cdot 01250}{25} \text{ min}^{-1} = 0 \cdot 0115 \text{ min}^{-1}$$

$$\therefore t_{1/2} = \frac{0 \cdot 693}{k} = \frac{0 \cdot 693}{0 \cdot 0115 \text{ min}^{-1}} = \mathbf{60 \cdot 26 \text{ min}}$$

OR

(a) $k = 60 \text{ s}^{-1}$, $[\text{R}]_0 = 1$ (say), $[\text{R}] = \frac{1}{16}$, $t = ?$

For a first order reaction,

$$t = \frac{2 \cdot 303}{k} \log \frac{[\text{R}]_0}{[\text{R}]}$$

$$= \frac{2 \cdot 303}{60 \text{ s}^{-1}} \log \frac{1}{1/16}$$

$$\begin{aligned}
 &= \frac{2.303}{60\text{s}^{-1}} \log 16 = \frac{2.303}{60\text{s}^{-1}} \log 2^4 \\
 &= \frac{2.303 \times 4 \log 2}{60} \text{ s} \\
 &= \frac{2.303 \times 4 \times 0.3010}{60} \text{ s} = \mathbf{0.046 \text{ s}}
 \end{aligned}$$

(b) Four factors that affect the rate of a chemical reaction are ;

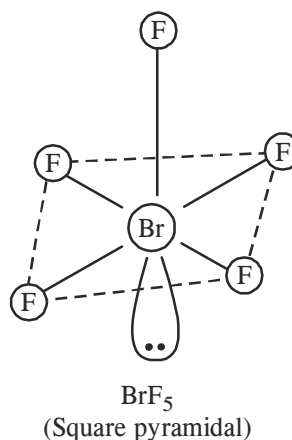
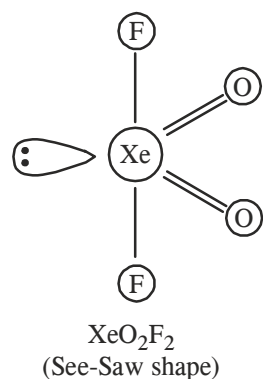
(i) Temperature (ii) Concentration of reactants (iii) Pressure (iv) Presence of light in case of photochemical reactions (v) Surface area or physical state of solid reactant.



(b) Fluorine is a much stronger oxidising agent than chlorine, therefore, it can easily oxidise sulphur to its maximum oxidation state of +6 and hence forms SF_6 . Chlorine, on the other hand, being a weaker oxidising agent can oxidise sulphur only to its +4 oxidation state and hence can form SO_2 but not SO_3 .

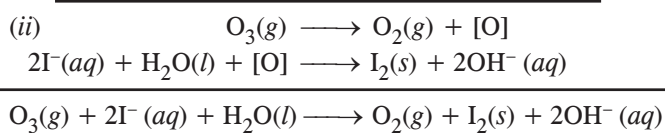
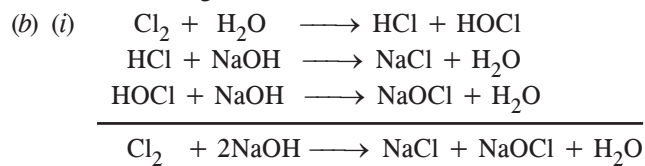
(c) The members of the noble gas family have $ns^2 np^6$ configuration. As such noble gases have no tendency to accept electrons and thus have large positive electron gain enthalpies *i.e.*, large amount of energy is needed to add an electron to an atom of the noble gas.

(i) (d)

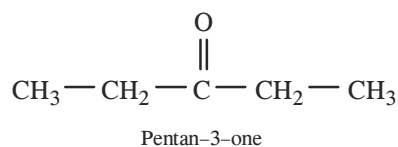


OR

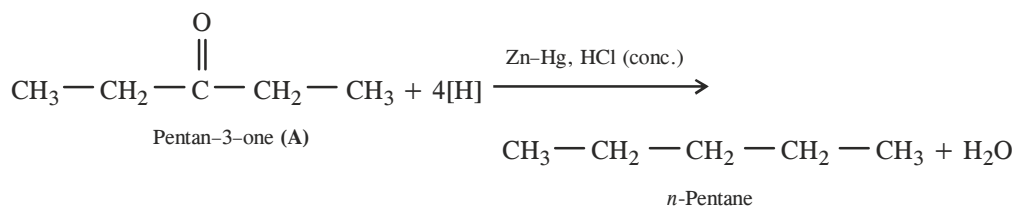
- (a) (i) Halogens are strong oxidising agents because they can readily accept one electron to attain nearest noble gas configuration.
(ii) Noble gases have very low boiling points because the intermolecular forces of attraction are very weak London dispersion forces.
(iii) Two factors needed for an element to form H-bonding are high electronegativity and small atomic size. As atomic size of Cl is much larger than O, O form H-bond while Cl cannot form H-bond.



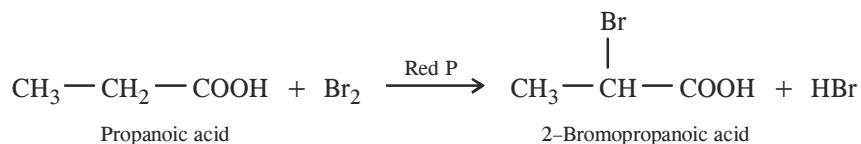
33. (a) As compound **A** gives negative Tollen's test and on Clemmenson reduction gives *n*-pentane, compound **A** is a ketone. As **A** does not give iodoform test, it is not a methyl ketone. Hence **A** is ;



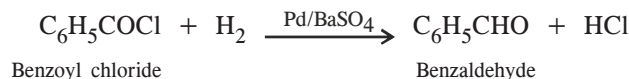
Clemmenson reduction of **A** ;



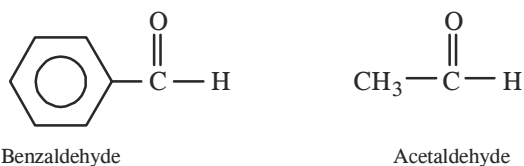
- (b) (i) Propanoic acid to 2-Bromopropanoic acid



- (ii) Benzoyl chloride to Benzaldehyde

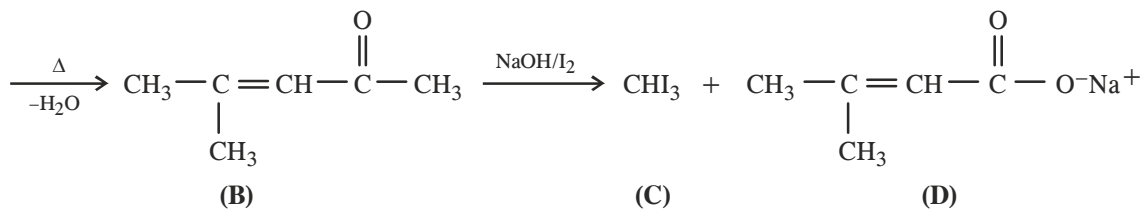
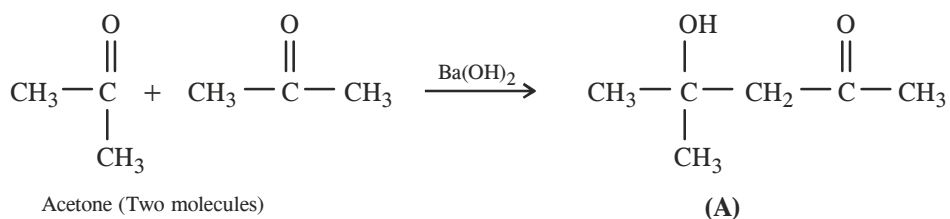


(c)

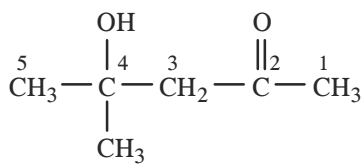


Out of these two aldehydes only acetaldehyde will give a yellow ppt. of iodoform (CHI_3) on heating with $\text{I}_2 + \text{NaOH}$ (Iodoform test).

OR

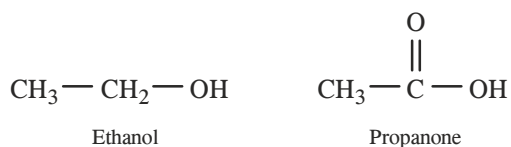


IUPAC name of A



4-Methyl-4-hydroxypentan-2-one

(b) (i)



Out of these two compounds only propanone gives an orange ppt. with 2, 4-dinitrophenylhydrazine.

(ii)



Out of these two compounds only an aqueous solution of benzoic acid gives brisk effervescence with NaHCO_3 .

Sample Question Paper—5

Chemistry (Theory)–XII

Time Allowed : 3 hours

Maximum Marks : 70

General Instructions : Same as in Sample Paper - 1

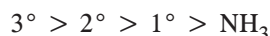
SECTION - A (Objective Type)

1. Read the following and answer the questions (i) to (iv) that follows :

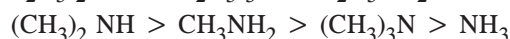
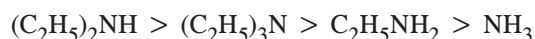
1 × 4 = 4

In **alkylamines**, a combination of electron releasing, steric and H-bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. Alkyl amines are found to be stronger bases than ammonia. In **aromatic amines**, electron releasing and withdrawing groups, respectively increase and decrease their basic character. **Aniline** is a weaker base than ammonia.

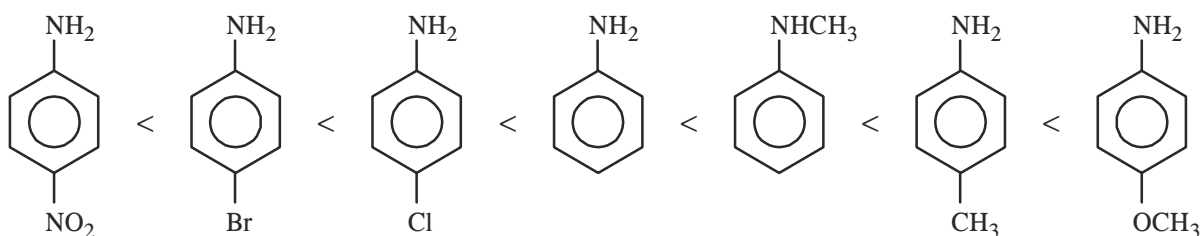
Basic character of amines in non-aqueous solutions or in vapour state :



Basic character of aliphatic amines (methyl and ethyl) in aqueous solutions :



Basic character of aromatic amines :



o-Substituted amines are usually weaker bases than aniline irrespective of nature of substituent (*i.e.*, electron withdrawing or releasing group) due to *ortho* effect, which is due to steric hindrance.

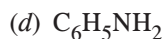


This is because phenyl group is electron withdrawing in nature due to $-\text{R}$ effect.

(i) Which is most basic in aqueous medium ?



(ii) Among the compounds $\text{C}_3\text{H}_7\text{NH}_2$, NH_3 , CH_3NH_2 , $\text{C}_2\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NH}_2$, the least basic is :



(iii) The order of basicity of

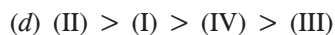
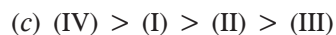
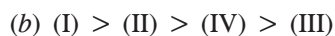
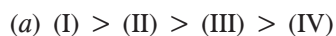
(I) *p*-Methylaniline

(II) *m*-Methylaniline

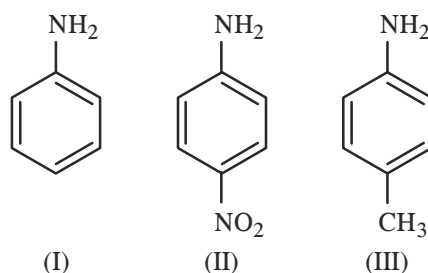
(III) Aniline

(IV) *o*-Methylaniline

is :



(iv) The correct increasing order of basic strength for the following compounds is :



(a) II < III < I

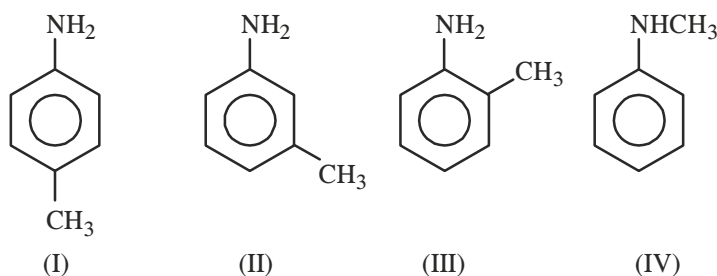
(c) III < II < I

(b) III < I < II

(d) II < I < III.

OR

Which is least basic ?



(a) (I) (b) (II) (c) (III) (d) (IV).

2. Read the following and answer the questions (i) to (iv) that follows :

Colloidal particles always carry an electric charge which may be either positive or negative. For example, when AgNO_3 solution is added to KI solution, a negatively charged colloidal sol is obtained. The presence of equal and similar charges on colloidal particles provide stability to the colloidal sol and if, somehow, charge is removed, coagulation of sol occurs. Lyophobic sols are readily coagulated as compared to lyophilic sols.

The questions given below consist of Assertion and Reason. Use the following keys to select the correct answer.

(a) If both assertion and reason are correct and reason is correct explanation for assertion.

(b) If both assertion and reason are correct but reason is not correct explanation for assertion.

(c) If assertion is correct but reason is incorrect.

(d) If assertion is wrong but reason is correct.

(i) **Assertion** : When an aqueous solution of AgNO_3 is added to a solution of KI in water, a negatively charged colloidal solution is obtained.

Reason : It is due to the adsorption of negatively charged NO_3^- ions by the colloidal particles.

(ii) **Assertion** : When an aqueous solution of KI is added to a solution of AgNO_3 in water a positively charged sol is obtained.

Reason : It is due to the adsorption of positively charged Ag^+ ions by the colloidal particles.

(iii) **Assertion** : Lyophobic sols are readily coagulated.

Reason : This is because dispersed phase is insoluble in the dispersion medium.

(iv) **Assertion** : Lyophilic sols are not readily coagulated.

Reason : In lyophilic sols colloidal particles are highly solvated.

OR

Assertion : When an aqueous solution of ferric chloride is added to a solution of sodium hydroxide in water, a negatively charged colloidal sol of hydrated ferric oxide is obtained.

Reason : It is due to the adsorption of negatively charged oxide ions by the colloidal particles.

Following questions (Q.No. 3 to Q.No. 11) are multiple choice questions carrying 1 mark.

3. The number of unpaired electrons in Fe^{2+} are :
- (a) 2 (b) 4
(c) 6 (d) 3.
4. The magnetic nature of elements depend on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.
- (a) $3d^7$ (b) $3d^5$
(c) $3d^8$ (d) $3d^2$.
5. Electronic configuration of a transition element X in + 3 oxidation state is $[\text{Ar}]3d^5$. What is its atomic number ?
- (a) 25 (b) 26
(c) 27 (d) 24.

OR

With respect to aqueous solutions of copper salts, which of the following is correct ?

- (a) Cu(II) is more stable (b) Cu(II) is less stable
(c) Cu(I) and Cu(II) are equally stable (d) Cu(I) and Cu(II) are equally unstable.
6. The species having tetrahedral shape is :
- (a) $[\text{PdCl}_4]^{2-}$ (b) $[\text{Ni}(\text{CN})_4]^{2-}$
(c) $[\text{Pb}(\text{CN})_4]^{2-}$ (d) $[\text{NiCl}_4]^{2-}$

OR

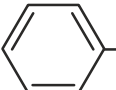
Which of the following forms with an excess of CN^- ions, a complex having co-ordination number two ?

- (a) Cu^+ (b) Ag^+
(c) Ni^{2+} (d) Fe^{2+} .
7. Shape of XeOF_4 is :
- (a) octahedral (b) square pyramidal
(c) pyramidal (d) T-shaped
8. Among trihalide of nitrogen, which one is least basic ?
- (a) NF_3 (b) NCl_3
(c) NBr_3 (d) NI_3 .
9. What is maximum no. of hydrogen bonds in which a water molecule may participate is :
- (a) 1 (b) 2
(c) 3 (d) 4

OR

Which of the following element has maximum electron gain enthalpy (negative) ?

- (a) F (b) Cl
(c) Br (d) I.

10.  $\text{CH}_2\text{—NH}_2$ on heating with CHCl_3 and alcoholic KOH gives foul smell of

- (a)  CH_2OH (b)  CH_2NC
(c)  CH_2CN (d)  CH_2Cl

11. 50 mL of an aqueous solution of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ (Molar mass : 180 g/mol) contains 6.02×10^{22} molecules. The concentration of the solution will be
- (a) 0.1 M (b) 0.2 M
(c) 1.0 M (d) 2.0 M

OR

If the standard electrode potential of an electrode is greater than zero, then we can infer that its

- (a) reduced form is more stable compared to hydrogen gas
- (b) oxidised form is more stable compared to hydrogen gas
- (c) reduced and oxidised forms are equally stable
- (d) reduced form is less stable than the hydrogen gas

For question numbers 12 to 16 two statements are given — one labelled Assertion (A) and the other labelled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below : $1 \times 5 = 5$

- (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
 - (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is *not* the correct explanation of the Assertion (A).
 - (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
 - (d) Assertion (A) is incorrect, but Reason (R) is correct statement.
12. **Assertion (A)** : Conductivity of an electrolyte decreases with decrease in concentration.
Reason (R) : Number of ions per unit volume increase on dilution.
13. **Assertion (A)** : The C—O—H bond angle in alcohols is slightly less than the tetrahedral angle.
Reason (R) : This is due to the repulsive interaction between the two lone pairs of electron on oxygen.
14. **Assertion (A)** : $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ complex is less stable than $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$ complex.
Reason (R) : $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ complex shows chelate effect.
15. **Assertion (A)** : Osmotic pressure is a colligative property.
Reason (R) : Osmotic pressure is directly proportional to molarity.
16. **Assertion (A)** : Reactivity of ketones is more than aldehydes.
Reason (R) : The carbonyl carbon of ketones is less electrophilic as compared to aldehydes.

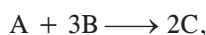
OR

Assertion (A) : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason (R) : Aromatic aldehydes are almost as reactive as formaldehyde.

SECTION - B

17. In the given reaction



the rate of formation of C is $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

Calculate the average

- (i) rate of reaction, and
 - (ii) rate of disappearance of B. 2
18. Illustrate how copper metal can give different products on reaction with HNO_3 .

OR

- (i) The HNH angle value is higher than HPH, H as H and H sh H angles. Why ?
 - (ii) Explain why NH_3 is basic while BiH_3 is only feebly basic. 2
19. Write two differences between Lyophilic colloids and Lyophobic colloids. 2

OR

Define the following terms with a suitable example of each : 2

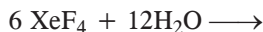
- (i) Associated colloids
 - (ii) Multimolecular colloids
20. (a) Write the IUPAC name and hybridisation of the complex $[\text{CoF}_6]^{3-}$.
(Given : Atomic number of Co = 27)
- (b) $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic, though both are tetrahedral. Why ? 2
21. Differentiate between globular and fibrous proteins. 2

22. Write short notes on the following :
 (i) Finkelstein reaction (ii) Hunsdiecker reaction.

OR

Write short notes on the following :
 (i) Etard reaction (ii) Gatterman-Koch reaction

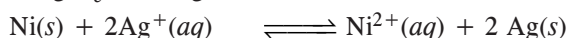
23. Write the products of the following reaction :



Is this reaction a disproportionation reaction? Give reasons in support of your answer.

2

24. Calculate the $\log K_c$ for the given reaction at 298 K :



Given :

$$E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}, E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}, 1 \text{ F} = 96500 \text{ C mol}^{-1}$$

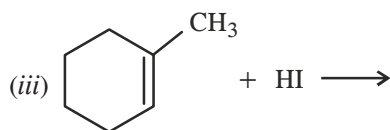
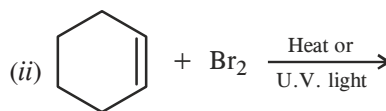
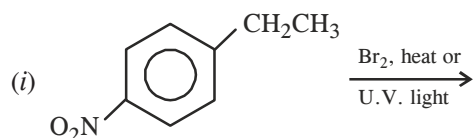
25. A first order reaction is 40% complete in 80 minutes. In what time will the reaction be 90% completed ?
 [Given : $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$, $\log 5 = 0.6990$, $\log 6 = 0.7782$]

SECTION – C

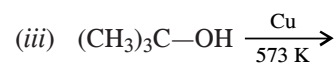
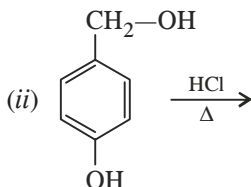
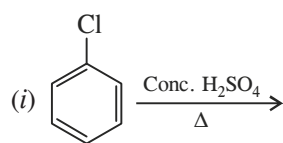
26. An organic compound (A) with molecular formula $\text{C}_8\text{H}_8\text{O}$ gives positive DNP and iodoform tests. It does not reduce Tollen's or Fehling's reagents and does not decolourise bromine water also. On oxidation with chromic acid (H_2CrO_4), it gives a carboxylic acid (B), with molecular formula $\text{C}_7\text{H}_6\text{O}_2$. Deduce the structures of 'A' and 'B'.

OR

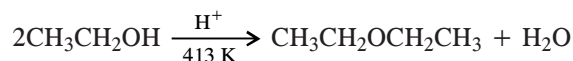
Draw the structure of monohalo products in each of the following reactions :



27. Write the major product(s) of the following reactions :



28. (a) Write the mechanism of the following reaction :



- (b) Write the preparation of phenol from cumene.

2+1=3

OR

How can you convert the following :

3

- (i) Sodium phenoxide to *o*-hydroxybenzoic acid
 (ii) Acetone to propene
 (iii) Phenol to chlorobenzene

29. Write the products formed when $(\text{CH}_3)_3\text{C}-\text{CHO}$ reacts with the following reagents :

3

- (i) CH_3COCH_3 in the presence of dilute NaOH
 (ii) HCN
 (iii) Conc. NaOH

30. X-ray diffraction studies show that copper crystallises in an *fcc* unit cell with cell edge of 3.608×10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.96 g/cm^3 , calculate the atomic mass of copper. 3

SECTION - D

31. (a) Give reasons : 3
 (i) Helium does not form compounds like Xenon.
 (ii) HClO_4 is a stronger acid than HOCl .
 (iii) Sulphur is a polyatomic solid whereas oxygen is a diatomic gas.
 (b) Write one reaction as an example of each, to show that conc. H_2SO_4 acts as
 (i) an oxidising agent, and (ii) a dehydrating agent. 2

OR

- (a) Account for the following :
 (i) Hydration enthalpy of F^- ion is more than Cl^- ion. 1
 (ii) SO_2 is a reducing agent, whereas TeO_2 is an oxidising agent in Group-16 oxides. 1
 (b) Write the reaction of F_2 with water. Why does I_2 not react with water ? 1+1
 (c) Draw the structure of XeF_2 . 1
 32. (a) Give reasons : 3
 (i) Although $-\text{NH}_2$ group is *o/p* directing in electrophilic substitution reactions, yet aniline, on nitration gives good yield of *m*-nitroaniline.
 (ii) $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in an aqueous solution.
 (iii) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines.
 (b) Distinguish between the following : 2
 (i) $\text{CH}_3\text{CH}_2\text{NH}_2$ and $(\text{CH}_3\text{CH}_2)_2\text{NH}$
 (ii) Aniline and CH_3NH_2

OR

- (a) Write the structures of A and B in the following reactions :
 (i) $\text{CH}_3\text{COOH} \xrightarrow[\Delta]{\text{NH}_3} \text{A} \xrightarrow{\text{NaOBr}} \text{B}$ 1
 (ii) $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[\Delta]{\text{N}_2\text{SO}_4} \text{A} \xrightarrow{453-473 \text{ K}} \text{B}$
 (b) Write the chemical reaction of methylamine with benzoyl chloride and write the IUPAC name of the product obtained. 1+1
 (c) Arrange the following in the increasing order of their pK_b values : 1
 $\text{C}_6\text{H}_5\text{NH}_2, \text{NH}_3, \text{C}_2\text{H}_5\text{NH}_2, \text{C}_2\text{H}_5\text{NH}_2, (\text{C}_2\text{H}_5)_2\text{NH}$
 33. (a) Calculate the (i) molality (ii) molarity and (iii) mole fraction of KI if density of 20% (mass/mass) of aqueous KI solution is 1.202 g mL^{-1} . 3
 (b) State Henry's law. Why is air diluted with helium in the tanks used by scuba divers ? 1+1

OR

- (a) A solution of glucose in water is labelled as 10 percent w/w. What would be the molality and mole fraction of each component in the solution ? If the density of the solution is 1.2 g mL^{-1} , then what shall be the molarity of the solution ? 3
 (b) Why a mixture of acetone and chloroform shows a negative deviation from Raoult's law ? 1
 (c) Why osmotic pressure method is preferred for finding molecular mass of macro molecules ? 1

SOLUTION

SECTION - A

1. (i) (d) Aromatic amines are less basic than aliphatic amines. In aqueous solution aliphatic 2° amine is more basic than 1° amine.
 (ii) (d) Aromatic amines are less basic than aliphatic amines.
 (iii) (a) Due to *ortho* effect *o*-methylaniline is less basic than aniline.

- (iv) (d) $-\text{NO}_2$ group with $-\text{R}$ effect will decrease the basic character while $-\text{CH}_3$ group with $+\text{I}$ effect will increase the basic character.

OR

- (c) *o*-Methylaniline or *o*-toluidine will be least basic due to ortho effect.
2. (i) (c) **Correct reason** : It is due to the adsorption of negatively charged I^- ions by the colloidal particles.
- (ii) (a) Reason is the correct explanation for assertion.
- (iii) (c) **Correct reason** : The colloidal particles of lyophobic sols are not solvated.
- (iv) (a) Reason is the correct explanation for assertion.

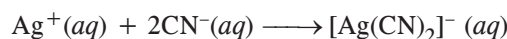
OR

- (c) **Correct reason** : It is due to the adsorption of negatively charged hydroxide ions by the colloidal particles of hydrated ferric oxide.
3. (b) **Explanation** : Fe^{2+} with $3d^6$ configuration has four unpaired electrons.
4. (b) **Explanation** : Element with $3d^5$ configuration will have maximum number (*i.e.*, five) unpaired electrons.
5. (b) **Explanation** : $\text{X}^{3+} = [\text{Ar}]^{18} 3d^5$. Hence atomic number of element X = $18 + 5 + 3 = 26$

OR

- (a) **Explanation** : Cu(II) is more stable than Cu(I) in aqueous solutions because hydration enthalpy of Cu^{2+} ion is very high.
6. (d) **Explanation** : Ni^{2+} with $3d^8$ configuration will form a tetrahedral complex only with a weak field ligand *e.g.*, Cl^- . Pd^{2+} with $4d^8$ configuration forms a square planar complex with N^- (a strong field ligand). It is mainly due to more diffused shape of $4d$ -orbitals.

OR

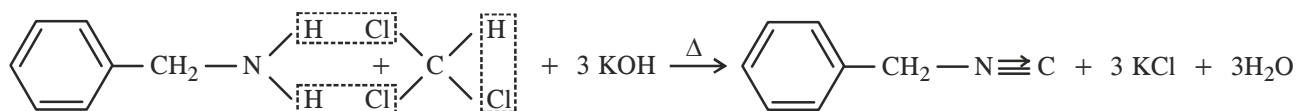


7. (b) **Explanation** : Shape of XeOF_4 is square pyramidal.
8. (a) **Explanation** : Out of all the trihalides of nitrogen NF_3 is least basic. It is due to high electronegativity of fluorine.
9. (d) **Explanation** : One molecule of water can form 4 H-bonds, two with O-atom and one H-bond with each of the two H-atoms.

OR

- (b) **Explanation** : Out of all the halogens, chlorine has the maximum negative electron gain enthalpy.

10. (b) **Explanation** :



11. (d) **Explanation** : No. of moles of solute = $\frac{6.02 \times 10^{22}}{6.02 \times 10^{23}} = 0.1 \text{ mol}$

$$\text{Volume of solution} = 50 \text{ mL} = 0.05 \text{ L}$$

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Vol. of solution (L)}}$$

$$= \frac{0.1 \text{ mol}}{0.05 \text{ L}} = 2 \text{ mol L}^{-1} = 2 \text{ M}$$

OR

- (a) **Explanation** : If the standard electrode potential of an electrode is greater than zero *i.e.*, positive this means that its reduced form is more stable compared to hydrogen gas.
12. (c) **Correct reason** : Number of ions per unit volume decrease with dilution.
13. (a) Reason is the correct explanation for the assertion.
14. (d) **Correct assertion** : $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ complex is more stable than $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$ complex.
15. (a) Reason is the correct explanation for the assertion.
16. (d) **Correct assertion** : Reactivity of ketones of less than aldehydes.

OR

(c) **Correct reason** : Aromatic aldehydes and formaldehyde do not have α -hydrogen atom.

SECTION - B

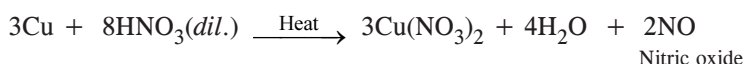
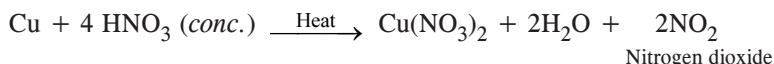


$$\text{Average rate of reaction} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{3} \frac{\Delta[B]}{\Delta t} = \frac{1}{2} \frac{\Delta[C]}{\Delta t}$$

$$\frac{\Delta[C]}{\Delta t} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \text{ (given)}$$

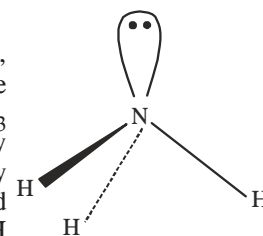
$$\therefore \text{Average rate of reaction} = \frac{1}{2} \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = 1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\begin{aligned} \text{Average rate of disappearance of B} &= -\frac{\Delta[B]}{\Delta t} = \frac{3}{2} \frac{\Delta[C]}{\Delta t} \\ &= \frac{3}{2} \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

18. On heating with dil. HNO_3 , copper gives copper nitrate and nitric oxide.With conc. HNO_3 , instead of NO, NO_2 is evolved.

OR

(i) In NH_3 the nitrogen atom is sp^3 -hybridised. Three of the four sp^3 -orbitals form three N—H, σ -bonds while the fourth contains the lone pair of electrons as shown in the Fig. Since the lone pair-bond pair repulsions are stronger than the bond pair-bond pair repulsions, therefore, in NH_3 the bond angle decreases from 109.5° to 107.8° . As we move from N to Sb, the electronegativity of the central atom goes on decreasing and hence the bond pairs of electrons lie away and away from the central atom. In other words, bond pair-bond pair repulsion is maximum in NH_3 and minimum in SbH_3 . Consequently, HNH bond angle is maximum (107.8°), followed by HPH with bond angle (93.6°), HAsH with bond angle of 91.8° while HSbH bond angle (91.3°) is the minimum.

Fig. Structure of NH_3

(ii) Both N in NH_3 and Bi in BiH_3 have a lone pair of electrons on the central atom and hence should behave as *Lewis bases*. But NH_3 is much more basic than BiH_3 . This can be explained on the basis of electron density on the central atom. Since the atomic size of N (70 pm) is much smaller than that of Bi (148 pm), therefore, electron density on the N-atom is much more than that on Bi-atom. Consequently, the tendency of N in NH_3 to donate its pair of electrons is much higher than that of Bi in BiH_3 . Thus, NH_3 is much more basic than BiH_3 .

19. S.No.	Lyophilic Colloids	Lyophobic Colloids
1.	Ease of preparation. Form easily by mere shaking or warming of dispersed phase and dispersion medium. No stabilizer if needed.	Difficult to prepare. They are formed only by special methods. Needs the addition of a stabilizer.
2.	Nature of particles. Particles are solvent loving and are in the form of single molecules.	Particles are solvent hating and are in the form of aggregates of large number of associated molecules.
3.	Viscosity. Higher than that of dispersion medium.	About the same as that of dispersion medium.
4.	Stability. Very stable.	Poor stability.
5.	Action of electrolytes. Coagulation possible only by adding a large quantity of electrolyte.	Coagulation possible even with a very small amount of electrolyte.
6.	Surface tension. Less than that of dispersion medium.	Same as that of dispersion medium.
7.	Nature of coagulation. The coagulation is reversible	The coagulation is irreversible.

OR

(i) **Associated colloids (Micelles).** They behave as normal strong electrolytes at low concentration but show colloidal properties at higher concentrations *i.e.*, these get associated to give micelles *e.g.*, soap. Formation of micelle takes place above a certain concentration called critical miceller concentration (CMC) and above a particular temperature called Kraft temperature (T_k). When the solution has less concentration than CMC, it behaves as normal electrolyte as the micelle become unstable on dilution.

(ii) **Multimolecular colloids.** These colloidal solution consists of aggregates of atoms or small molecules with diameter less than 10^3 pm. The colloidal particles are held by weak van der Waal forces *e.g.*, colloidal sol of sulphur, gold, silver etc.

20. (a) $[\text{CoF}_6]^{3-}$

IUPAC Name : hexafluoridocobaltate(IV) ion.

Co ($Z = 27$) : $[\text{Ar}]^{18} 4s^2 3d^7$

Co^{3+} : $[\text{Ar}]^{18} 3d^6$

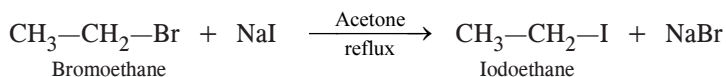
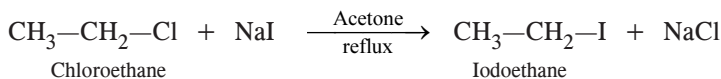
Fluoride ion is a weak field ligand. Hence no pairing. Thus hybridisation is sp^3d^2 .

(b) In $[\text{Ni}(\text{CO})_4]$, Ni is in zero oxidation state whereas in $[\text{NiCl}_4]^{2-}$, it is in +2 oxidation state. In the presence of CO ligand, the unpaired *d*-electrons of Ni pair up but Cl^- being a weak ligand is unable to pair up the unpaired electrons.

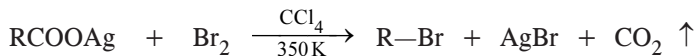
21.

S.No.	Globular protein	Fibrous protein
1.	These proteins consist of molecules which are extensively folded into compact units approaching almost spherical shapes.	These proteins consist of linear thread like molecules which lie side by side.
2.	Hydrogen bonding and van der Waal's interaction exist between different parts of polypeptide chain.	There is formation of extensive hydrogen bonding between neighbouring chains.
3.	They are soluble in water.	They are insoluble in water.
4.	They function as enzymes, regulate metabolic processes and act as antibodies.	They serve as the chief structural material of animal tissues.

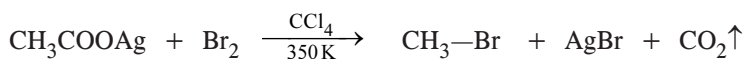
22. (i) **Finkelstein reaction.** An alkyl iodide may be prepared by treating an alkyl chloride or bromide with sodium iodide in acetone. The chlorine or bromine atom of the alkyl halide is replaced iodine atom in the reaction.



(ii) **Hunsdiecker reaction.** This reaction consists of the decomposition of silver salt of a carboxylic acid by chlorine or bromine in carbon tetrachloride solution to form an alkyl or aryl halide with one carbon atom less than the original acid.



Silver salt of
carboxylic acid

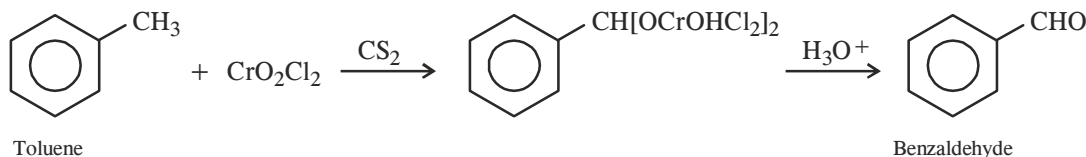


Silver acetate

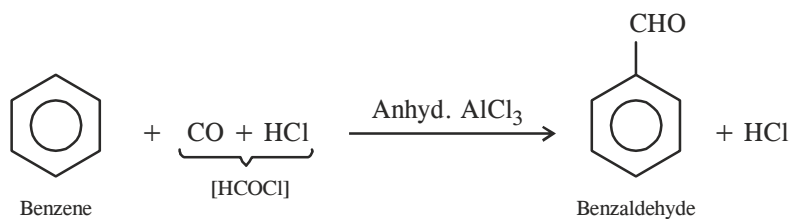
Methyl bromide

OR

(i) **Etard reaction :** It involves oxidation of toluene with chromyl chloride $[\text{CrO}_2\text{Cl}_2]$. Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives benzaldehyde.



- (ii) **Gatterman Koch reacton** : When benzene or its derivative is treated with CO and HCl(g) in the presence of anhydrous AlCl₃ or Cu₂Cl₂ it gives benzaldehyde or substituted benzaldehyde.



Yes. It is a disproportionation reaction because O.S. of Xe in XeF₄ is +4 which decreases to zero in Xe (reduction) and simultaneously increases to six in XeO₃ (oxidation).

24. Cell representation is :



Here $n = 2$, $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$, $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Ni}^{2+}/\text{Ni}} = [+0.80 - (-0.25)] \text{ V} \\ &= [+0.80 + 0.25] \text{ V} = 1.05 \text{ V} \end{aligned}$$

At 298 K

$$\begin{aligned} E^\circ_{\text{cell}} &= \frac{0.059}{n} \log K_c \\ \log K_c &= \frac{n \times E^\circ_{\text{cell}}}{0.059} \\ &= \frac{2 \times 1.05}{0.059} = 35.59 \end{aligned}$$

25. When 40% complete :

$[\text{R}]_0 = 100$ (say), $[\text{R}] = 100 - 40 = 60$, $t = 80$ min.

For a first order reaction

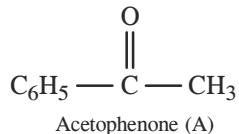
$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]} \\ &= \frac{2.303}{80 \text{ min}} \log \frac{100}{60} = \frac{2.303}{80 \text{ min}} \log \frac{5}{3} \\ &= \frac{2.303}{80 \text{ min}} [\log 5 - \log 3] = \frac{2.303}{80 \text{ min}} [0.6990 - 0.4771] \\ &= \frac{2.303}{80 \text{ min}} \times 0.2219 = 6.4 \times 10^{-3} \text{ min}^{-1} \end{aligned}$$

For 90% completion

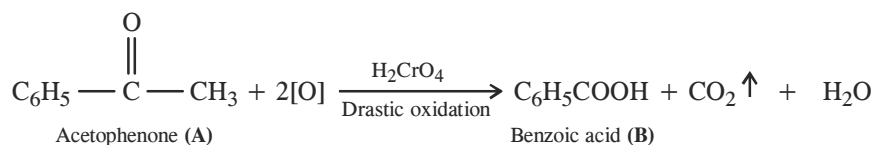
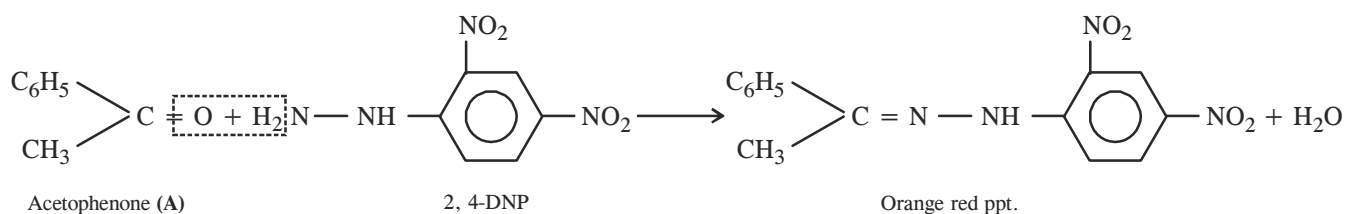
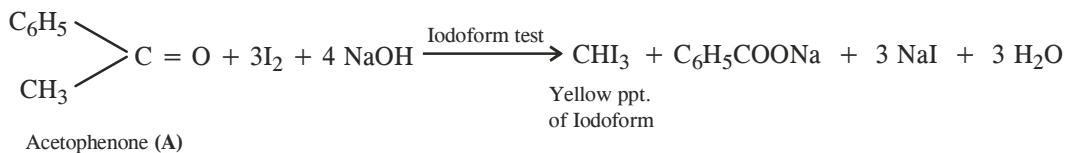
$$\begin{aligned} [\text{R}]_0 &= 100 \text{ (say)}, [\text{R}] = 100 - 90 = 10, k = 6.4 \times 10^{-3} \text{ min}^{-1} \\ t &= \frac{2.303}{k} \log \frac{[\text{R}]_0}{[\text{R}]} \\ &= \frac{2.303}{6.4 \times 10^{-3} \text{ min}^{-1}} \log \frac{100}{10} = \frac{2.303}{6.4 \times 10^{-3} \text{ min}^{-1}} \log 10 \\ &= \frac{2.303}{6.4 \times 10^{-3}} \text{ min} = 360 \text{ min (approx)} \end{aligned}$$

26. (i) Compounds A (C_8H_8O) gives positive DNP and iodoform test. This indicates that it contains CH_3-CO- group.
(ii) It does not reduce Tollen's or Fehling's reagent. It shows that it is not an aldehyde.
(iii) It does not decolourise Br_2 water. This indicates that it behaves as a saturated compound.
(iv) On oxidation with chromic acid it is oxidised to carboxylic acid **B** ($C_7H_6O_2$). It is possible only if **B** is benzoic acid, C_6H_5COOH .

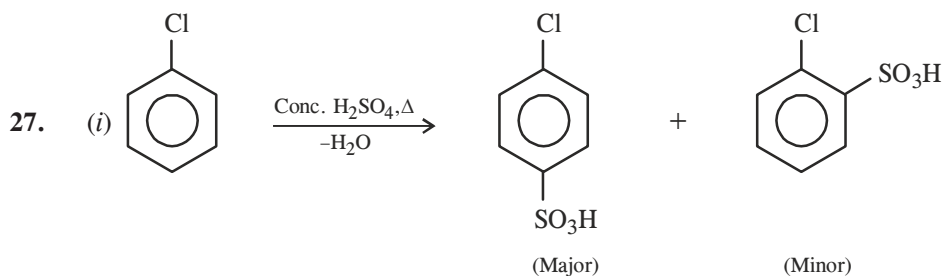
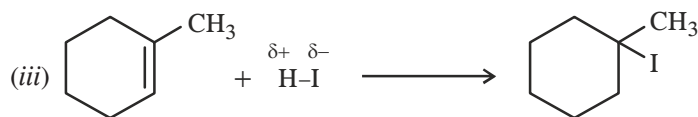
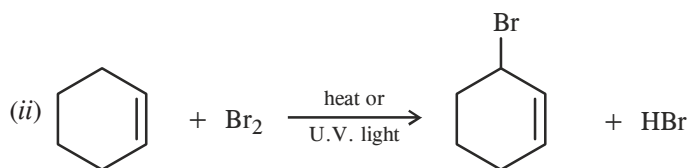
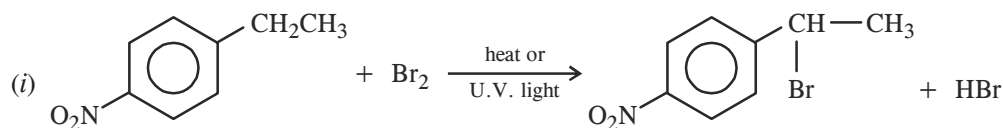
This indicates that **A** is acetophenone with the following structure :

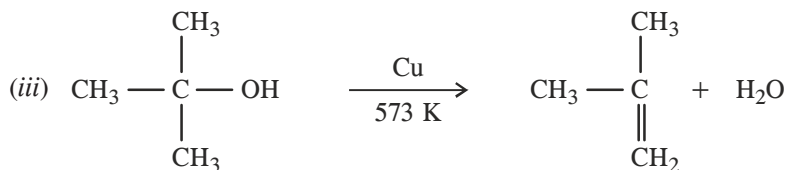
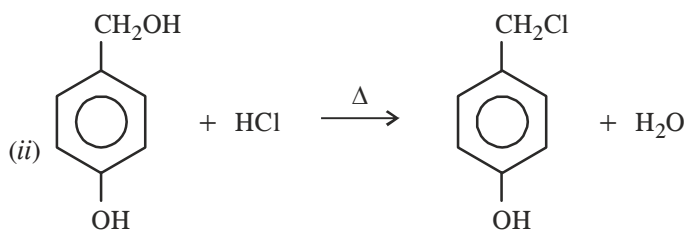


The sequence of reactions can be written as follows :

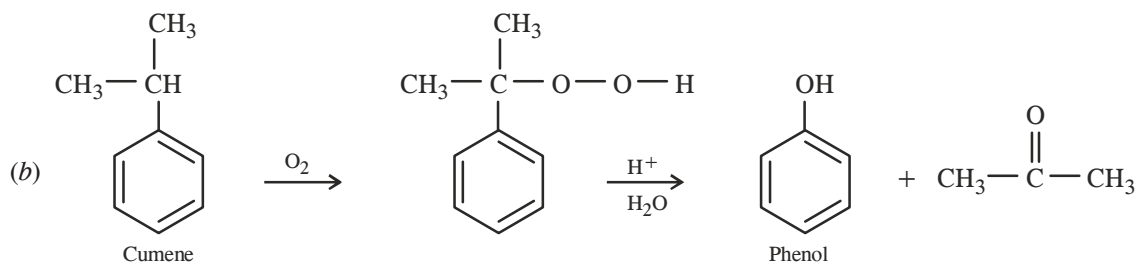
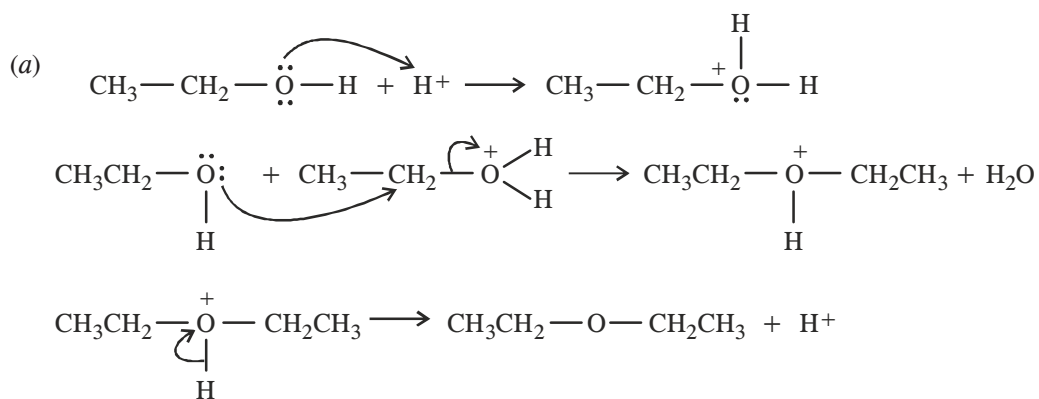


OR

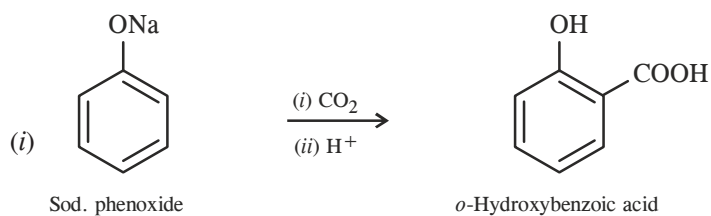


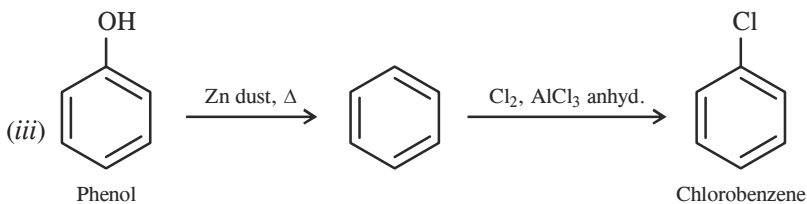


28.

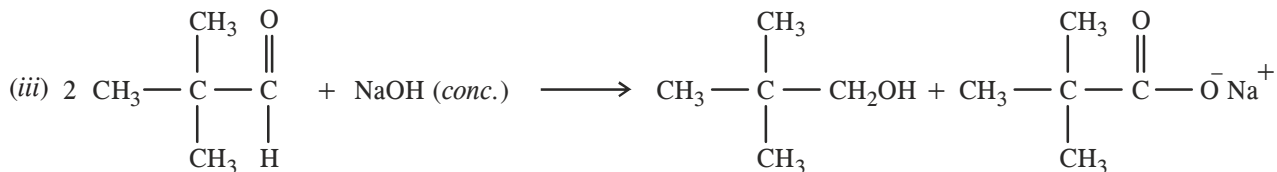
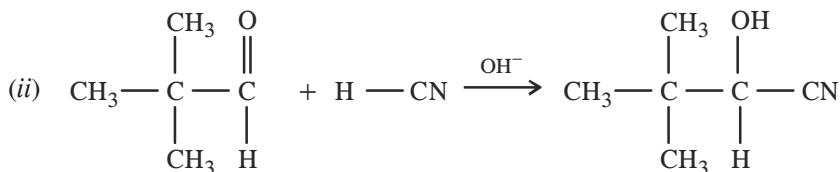
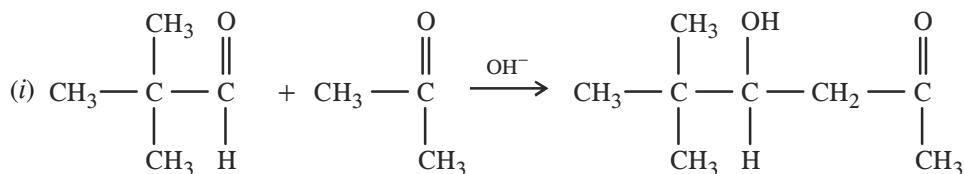


OR





29.



30. $z = 4$ (f.c.c. lattice), $a = 3.608 \times 10^{-8}$ cm, $d = 8.96$ g/cm³, $N_A = 6.022 \times 10^{23}$ mol⁻¹, $M = ?$

$$d = \frac{z \times M}{a^3 \times N_A} \quad \text{or} \quad M = \frac{d \times a^3 \times N_A}{z}$$

$$M = \frac{(8.96 \text{ g cm}^{-3}) \times (3.608 \times 10^{-8} \text{ cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}{4} = 63.1 \text{ g mol}^{-1}$$

\therefore Atomic mass of copper = 63.1 u

31. (a)(i) Helium does not form compounds like xenon because ionisation enthalpy of helium is very high.



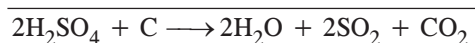
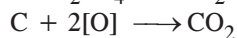
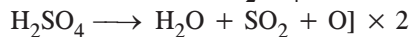
Due to resonance, $^-\text{O}-\text{ClO}_3$ ion is more stable than $^-\text{O}-\text{Cl}$, hence HClO_4 is a stronger acid than HOCl .

(iii) It is due to the following two reasons :

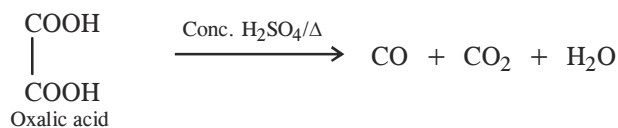
(a) Oxygen can form $p\pi-p\pi$ multiple bond more effectively than sulphur.

(b) The $\text{—}\ddot{\text{O}}\text{—}\ddot{\text{O}}\text{—}$ bond is weaker than $\text{—}\ddot{\text{S}}\text{—}\ddot{\text{S}}\text{—}$ bond

(b) (i) **Conc. H_2SO_4 as an oxidising agent** : Hot conc. H_2SO_4 oxidises carbon to carbon dioxide.

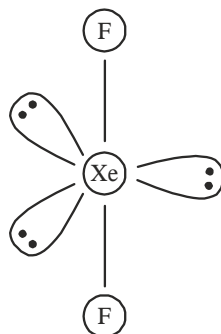


(ii) **conc. H_2SO_4 as a dehydrating agent**. Hot conc. H_2SO_4 dehydrates oxalic acid to a mixture of carbon monoxide and carbon dioxide.

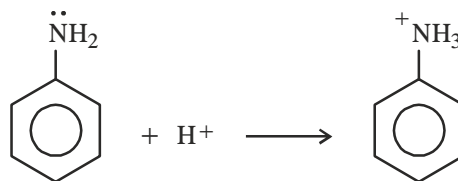


OR

- (a) (i) Hydration enthalpy of F^- ion is more than Cl^- ion because F^- ion is smaller than Cl^- ion.
(ii) SO_2 is a reducing agent while TeO_2 is an oxidising agent because sulphur is more stable in +6 oxidation state while tellurium is more stable in +4 oxidation state (*inert pair effect*).
- (b) $2F_2 + 2H_2O \longrightarrow 4HF + O_2$
 I_2 can not react with water because I_2 is a weak oxidising agent.
- (c) Structure of XeF_2



32. (a) (i) Nitration of aniline is done with nitrating mixture (conc. HNO_3 + conc. CH_2SO_4). The H^+ ions from these acids protonate the $-NH_2$ group of aniline to form anilinium ion.

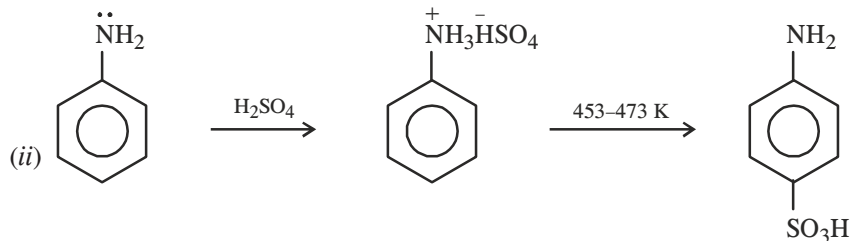
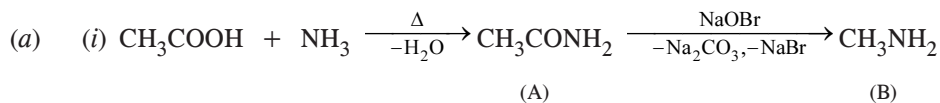


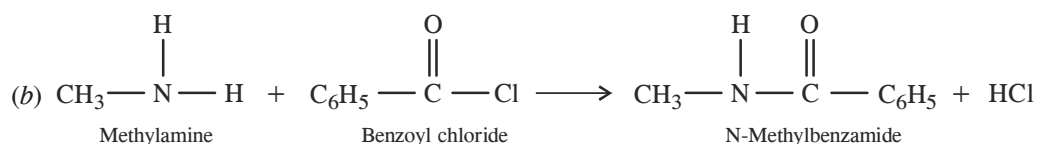
+

The $-NH_3^+$ group is deactivating and *m*-directing in nature due to its electron withdrawing effect.

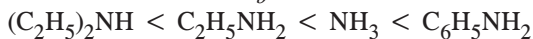
- (ii) A 2° alkylamine is more basic than a 3° alkylamine in aqueous medium. This is due to the combined effect of solvation (H-bonding with water molecules) and electron donating effect of alkyl groups.
- (iii) Ammonolysis of alkyl halides give a mixture of 1° , 2° and 3° amines along with quaternary ammonium salts. Thus this method is not suitable to prepare pure 1° amines.
- (b) (i) On heating with chloroform ($CHCl_3$) and KOH (alc.), $CH_3CH_2NH_2$ gives a foul smelling isocyanide while $(CH_3CH_2)_2NH$ does not. This is because $CH_3CH_2NH_2$ is a 1° amine while $(CH_3CH_2)_2NH$ is a 2° amine.
- (ii) On adding ice cold solution of benzene diazonium chloride to aniline in an acidic medium, a yellow coloured dye is obtained. On the other hand, in case of CH_3NH_2 no such dye formation takes place.

OR





(c) Increasing order of pK_b (or decreasing order of basic character)



33. (a) 20% (mass/mass) aqueous KI solution means that 20 g of KI is dissolved in 100 g of solution.

$$\text{Mass of KI} = 20$$

$$\therefore \text{Mass of solvent (water)} = 100 - 20 = 80 \text{ g} = 0.080 \text{ kg}$$

(i) **Calculation of molality**

$$\text{Molar mass of KI} = 39 + 127 = 166 \text{ g mol}^{-1}$$

$$\therefore \text{Mol of KI} = \frac{20 \text{ g}}{166 \text{ g mol}^{-1}} = 0.120 \text{ mol.}$$

$$\text{Molality of solution} = \frac{\text{No. of mol of KI}}{\text{Mass of solvent in kg}} = \frac{0.120 \text{ mol}}{0.080 \text{ kg}} = \mathbf{1.5 \text{ mol kg}^{-1}}$$

(iii) **Calculation of molarity**

$$\text{Density of solution} = 1.202 \text{ g mL}^{-1}$$

$$\therefore \text{Volume of solution} = \frac{100 \text{ g}}{1.202 \text{ g mL}^{-1}} = 83.2 \text{ mL} = 0.0832 \text{ L}$$

$$\text{Molarity of solution} = \frac{\text{Mol of solute}}{\text{Volume of solution in L}} = \frac{0.120 \text{ mol}}{0.0832 \text{ L}} = \mathbf{1.44 \text{ M.}}$$

(iii) **Calculation of mole fraction of KI**

$$\text{No. of moles of KI} = \frac{\text{Mass of H}_2\text{O}}{\text{Molar mass of H}_2\text{O}} = \frac{80 \text{ g}}{18 \text{ g mol}^{-1}} = \mathbf{4.44 \text{ mol}}$$

$$\begin{aligned}
 \text{Mole fraction of KI} &= \frac{\text{No. of mol of KI}}{\text{No. of mol of KI} + \text{No. of mol of H}_2\text{O}} \\
 &= \frac{0.120 \text{ mol}}{(0.120 + 4.44) \text{ mol}} = \frac{0.120}{4.560} = \mathbf{0.0263.}
 \end{aligned}$$

(b) **Henry's Law** : The partial pressure of a gas in vapour phase is directly proportional to the mole fraction of the gas in the solution.

When air diluted with helium is used by scuba divers it prevents a very painful condition called 'Bends'.

OR

(a) A 10% (w/w) glucose solution means 10 g of glucose in 100 g of solution.

$$\therefore \text{Mass of glucose} = 10 \text{ g}$$

$$\text{Molar mass of glucose, C}_6\text{H}_{12}\text{O}_6 = 180 \text{ g mol}^{-1}$$

$$\text{No. of moles of glucose, } n_B = \frac{\text{Mass}}{\text{Molar mass}} = \frac{10 \text{ g}}{180 \text{ g mol}^{-1}} = 0.0555 \text{ mol}$$

$$\text{Mass of water} = (100 - 10) \text{ g} = 90 \text{ g} = \frac{90}{1000} \text{ kg} = 0.09 \text{ kg}$$

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}} = \frac{0.0555}{0.09 \text{ kg}} = 0.617 \text{ mol kg}^{-1} = \mathbf{0.617 \text{ m}}$$

$$\text{No. of moles of water, } n_A = \frac{90 \text{ g}}{18 \text{ g mol}^{-1}} = 5 \text{ mol}$$

(Molar mass of water, $\text{H}_2\text{O} = 18 \text{ g mol}^{-1}$)

$$\text{Mole fraction of glucose, } x_B = \frac{n_B}{n_A + n_B} = \frac{0.0555}{5 + 0.0555} = \mathbf{0.01}$$

$$\text{Mole fraction of water, } x_A = 1 - x_B = 1 - 0.01 = \mathbf{0.99}$$

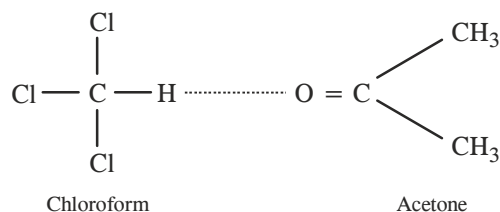
Mass of solution = 100 g

Density of solution = 1.2 g mL^{-1}

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{100 \text{ g}}{1.2 \text{ g mL}^{-1}} = 83.33 \text{ mL} = 0.08333 \text{ L}$$

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (L)}} = \frac{0.0555 \text{ mol}}{0.08333 \text{ L}} = 0.67 \text{ mol L}^{-1} = \mathbf{0.67 \text{ M}}$$

- (b) Both chloroform and acetone cannot take part in hydrogen bonding when present alone. But when chloroform and acetone are mixed, the hydrogen bonding takes place between the two as explained below :



Due to hydrogen bonding escaping tendencies of both the liquids become less and as such the mixture shows a negative deviation from Raoult's law.

- (c) As the molecular masses of macro-molecules are of the order of 10^6 a.m.u., the molality of the solution taken is very low. For such solutions, other methods like elevation in boiling point, depression in freezing point etc., cannot be used because changes measured in these properties are very small and thus cannot be accurately measured. On the other hand, osmotic pressure for such solutions can be easily measured due to its much larger magnitude.