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CLASS
12

CBSE CHAMPION

11 yrs. 2017-07 SOLVED PAPERS

CHAPTERWISE-TOPICWISE

11 YEARS TOPICWISE GRAPHICAL ANALYSIS

- Comprehensive Theory
- Delhi, All India, Foreign & Compartment Papers
- Answers as per CBSE Marking Scheme
- 10 Practice Papers and Latest CBSE Sample Paper

CHEMISTRY

CBSE CHAMPION

11 yrs. 2017-07 SOLVED PAPERS

CHAPTERWISE-TOPICWISE

CHEMISTRY

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PREFACE

We feel pleased and delighted in presenting the book “CBSE Chapterwise-Topicwise Chemistry”. Special efforts have been put to produce this book in order to equip students with practice material including previous 11 years’ CBSE Board Examination questions. It will give them comprehensive knowledge of subject according to the latest syllabus and pattern of CBSE Board Examination. The book will be helpful in imparting students a clear and vivid understanding of the subject.

Salient features

Comprehensive and Lucid Theory : Well explained theory with important formulae, flowcharts and tables for quick recap.

Topicwise Graphical Analysis : Graphical analysis of previous 11 years’ CBSE Board papers’ questions (VSA, SA I, SA II, VBQ, LA) provided to let students figure out which chapter and which topic is to be revised hard and how much is the weightage of that topic.

Topicwise-Chapterwise Questions and Answers : Theory is followed by topicwise-chapterwise questions pulled from previous 11 years’ CBSE-DELHI, ALL INDIA, FOREIGN and COMPARTMENT papers. Answers are given according to the CBSE marking scheme.

Strictly Based on NCERT Pattern : In the previous years’ CBSE papers SA I, SA II or LA type questions are generally framed by clubbing together questions from different topics and chapters. These questions are segregated strictly according to NCERT topics. *e.g.*, (*1/3, Delhi 2016*), this question of 1 mark was asked in SA II type category, (*1/5, AI 2015*), this question of 1 mark was asked in LA type category, (*1/2, Foreign 2016*), this question of 1 mark was asked in SA I type category.

Topicwise questions are arranged in descending chronological (2017-2007) order so, that latest years’ questions come first in practice and revision.

Key Concepts Highlight : Key concepts have been highlighted for their reinforcement.

Value Based Questions : Separate section for Value based questions has been added.

Latest Solved CBSE Sample Paper : Solved CBSE sample paper is included with the marking scheme.

Practice Papers as per CBSE Blue Print : 10 Practice Papers strictly based on design and blue print issued by CBSE Board are also incorporated.

We are sure that the value addition done in this book will prove helpful to students in achieving success in board examinations. Every possible effort has been made to make this book error free. Useful suggestions by our readers for the rectification and improvement of the book content would be gracefully acknowledged and incorporated in further editions.

Readers are welcome to send their suggestions at **editor@mtg.in.**

All The Best
MTG Editorial Board

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	Total	**160**	**70**

Unit I : Solid State [10 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, electrical and magnetic properties. Band theory of metals, conductors, semiconductors and insulators and *n* and *p* type semiconductors.

Unit II : Solutions [10 Periods]

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, colligative properties - relative lowering of vapour pressure, Raoult's law, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, Van't Hoff factor.

Unit III : Electrochemistry [12 Periods]

Redox reactions, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells, lead accumulator, 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, fuel cells, corrosion.

Unit IV : Chemical Kinetics [10 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), concept of collision theory (elementary idea, no mathematical treatment). Activation energy, Arrhenious equation.

Unit V : Surface Chemistry [08 Periods]

Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, catalysis, homogenous and heterogenous activity and selectivity; enzyme catalysis colloidal state distinction between true solutions, colloids and suspension; lyophilic, lyophobic multimolecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation, emulsion - types of emulsions.

Unit VI : General Principles and Processes of Isolation of Elements [08 Periods]

Principles and methods of extraction - concentration, oxidation, reduction - electrolytic method and refining; occurrence and principles of extraction of aluminium, copper, zinc and iron.

Unit VII : *p*-Block Elements [12 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, Oxides of Nitrogen(Structure only) ; Phosphorus - allotropic forms, compounds of Phosphorus : Preparation and Properties of Phosphine, Halides and Oxoacids (elementary idea only).

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 : industrial process of manufacture, 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 [12 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, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.

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

Actinoids - Electronic configuration, oxidation states and comparison with lanthanoids.

Unit IX : Coordination Compounds [12 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; structure and stereoisomerism, importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).

Unit X : Haloalkanes and Haloarenes. [10 Periods]

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

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

Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

Unit XI : Alcohols, Phenols and Ethers [10 Periods]

Alcohols : Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol.

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 : Organic compounds containing Nitrogen [10 Periods]

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

Cyanides and Isocyanides - will be mentioned at relevant places in text.

Diazonium salts : Preparation, chemical reactions and importance in synthetic organic chemistry.

Unit XIV : Biomolecules [12 Periods]

Carbohydrates - Classification (aldoses and ketoses), monosaccahrides (glucose and fructose), D-L configuration oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose, glycogen); Importance of carbohydrates.

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; enzymes. Hormones - Elementary idea excluding structure.

Vitamins - Classification and functions. Nucleic Acids : DNA and RNA.

Unit XV : Polymers [08 Periods]

Classification - natural and synthetic, methods of polymerization (addition and condensation), copolymerization, some important polymers : natural and synthetic like polythene, nylon polyesters, bakelite, rubber. Biodegradable and non-biodegradable polymers.

Unit XVI : Chemistry in Everyday life [06 Periods]

Chemicals in medicines - analgesics, tranquilizers antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistamines.

Chemicals in food - preservatives, artificial sweetening agents, elementary idea of antioxidants. Cleansing agents- soaps and detergents, cleansing action.

*QUESTION PAPER DESIGN
CLASS - XII

Time : 3 Hours **Max. Marks : 70**

S. No.	Typology of Questions	Very Short Answer (VSA) (1 mark)	Short Answer-I (SA-I) (2 marks)	Short Answer-II (SA-II) (3 marks)	Value based question (4 marks)	Long Answer (LA) (5 marks)	Total Marks	% Weigh-tage
1	Remembering- (Knowledge based Simple recall questions, to know specific facts, terms, concepts, principles, or theories, Identify, define,or recite, information)	2	1	1	-	-	7	10%
2	Understanding- Comprehension -to be familiar with meaning and to understand conceptually, interpret, compare, contrast, explain, paraphrase information)	-	2	4	-	1	21	30%
3	Application (Use abstract information in concrete situation, to apply knowledge to new situations, Use given content to interpret a situation, provide an example, or solve a problem)	-	2	4	-	1	21	30%
4	High Order Thinking Skills (Analysis and Synthesis- Classify, compare, contrast, or differentiate between different pieces of information, Organize and/or integrate unique pieces of information from a variety of sources)	2	-	1	-	1	10	14%
5	Evaluation- (Appraise, judge, and/or justify the value or worth of a decision or outcome, or to predict outcomes based on values)	1	-	2	1	-	11	16%
	TOTAL	**5×1=5**	**5×2=10**	**12×3=36**	**1×4=4**	**3×5=15**	**70(26)**	**100%**

QUESTION WISE BREAK UP

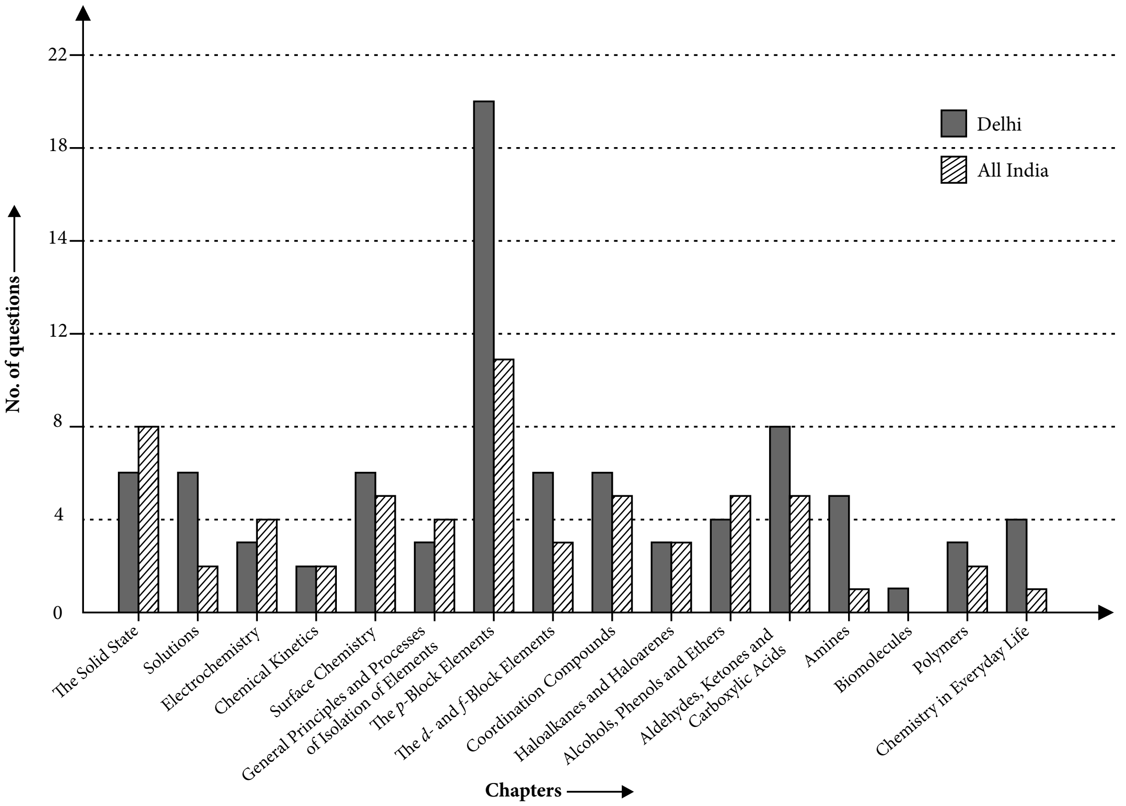
Type of Question	Mark per Question	Total No. of Questions	Total Marks
VSA	1	5	05
SA-I	2	5	10
SA-II	3	12	36
VBQ	4	1	04
LA	5	3	15
Total		**26**	**70**

1. *Internal Choice : There is no overall choice in the paper. However, there is an internal choice in one question of 2 marks weightage, one question of 3 marks weightage and all the three questions of 5 marks weightage.*
2. *The above template is only a sample. Suitable internal variations may be made for generating similar templates keeping the overall weightage to different form of questions and typology of questions same.*

** For latest details refer www.cbse.nic.in*

CBSE-BOARD
SOLVED PAPER 2017
(DELHI, ALL INDIA)

Chapterwise Analysis of CBSE Board Questions (2017)



1 The Solid State

1.2 Amorphous and Crystalline Solids

SA I (2 marks)

1. Write any two differences between amorphous solids and crystalline solids. *(2/5 Delhi)*

1.3 Classification of Crystalline Solids

VSA (1 mark)

2. Based on the nature of intermolecular forces, classify the following solids :
Silicon carbide, Argon *(1/3 AI)*

3. Based on the nature of intermolecular force, classify the following solids :
Benzene, Silver *(1/3 AI)*

4. Based on the nature of intermolecular forces, classify the following solids :
Sodium sulphate, Hydrogen *(1/3 AI)*

1.5 Number of Atoms in a Unit Cell

SA I (2 marks)

5. Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a *fcc* structure. (Atomic mass of Al = 27 g mol^{-1}) *(2/5 Delhi)*

1.8 Calculations Involving Unit Cell Dimensions

SA II (3 marks)

6. An element has atomic mass 93 g mol^{-1} and density 11.5 g cm^{-3}. If the edge length of its unit cell is 300 pm, identify the type of unit cell. *(3/5 Delhi)*

1.9 Imperfections in Solids

VSA (1 mark)

7. Give reason :
In stoichiometric defects, NaCl exhibits Schottky defect and not Frenkel defect. *(1/5 Delhi)*

8. ZnO turns yellow on heating. Why? *(1/3 AI)*

9. AgCl shows Frenkel defect while NaCl does not. Give reason. *(1/3 AI)*

10. What happens when $CdCl_2$ is doped with AgCl? *(1/3 AI)*

1.10 Electrical Properties

VSA (1 mark)

11. Give reason :
Silicon on doping with phosphorus forms *n*-type semiconductor. *(1/5 Delhi)*

12. What is meant by groups 12-16 compounds? Give an example. *(1/3 AI)*

13. What type of semiconductor is formed when Ge is doped with Al? *(1/3 AI)*

1.11 Magnetic Properties

VSA (1 mark)

14. Give reason :
Ferrimagnetic substances show better magnetism than antiferromagnetic substances. *(1/5 Delhi)*

2 Solutions

2.2 Expressing Concentration of Solutions

VSA (1 mark)

15. Define the following term :
Molality (*m*) *(1/2 Delhi)*

16. Define the following term :
Molarity (*M*) *(1/2 Delhi)*

2.5 Ideal and Non-ideal Solutions

VSA (1 mark)

17. Define the following term :
Ideal solution *(1/2 Delhi)*

SA I (2 marks)

18. Write two differences between ideal solutions and non-ideal solutions. *(2/5 AI)*

2.6 Colligative Properties and Determination of Molar Mass

VSA (1 mark)

19. Define the following term :
Colligative properties *(1/2 Delhi)*

SA II (3 marks)

20. A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if freezing point of pure water is 273.15 K.
(Given : Molar mass of sucrose = 342 g mol^{-1}, molar mass of glucose = 180 g mol^{-1}) *(Delhi)*

21. 30 g of urea (M = 60 g mol^{-1}] is dissolved in 846 g of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg. *(3/5 AI)*

2.7 Abnormal Molar Masses

SA I (2 marks)

22. Define the following terms :
(i) Abnormal molar mass
(ii) van't Hoff factor (i) *(Delhi)*

3 Electrochemistry

3.4 Conductance of Electrolytic Solutions

SA I (2 marks)

23. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}.
(Given : $\lambda°(H^+)$ = 349.68 S cm^{2}mol^{-1} and $\lambda°(CH_3COO^-)$ = 40.9 S cm^2 mol^{-1}) *(Delhi)*

3.5 Electrolytic Cells and Electrolysis

SA I (2 marks)

24. Calculate the mass of Ag deposited at cathode when a current of 2 ampere was passed through a solution of $AgNO_3$ for 15 minutes.
(Given : Molar mass of Ag = 108 g mol^{-1}, 1 F = 96500 C mol^{-1}) *(2/3 Delhi)*

SA II (3 marks)

25. (a) The cell in which the following reaction occurs :

$$2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}$$

has $E°_{cell}$ = 0.236 V at 298 K. Calculate the standard Gibbs energy of the cell reaction. (Given : 1 F = 96,500 C mol^{-1})

(b) How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours? (Given : 1 F = 96,500 C mol^{-1}) *(AI)*

3.6 Batteries

SA I (2 marks)

26. Write the name of the cell which is generally used in hearing aids. Write the reactions taking place at the anode and the cathode of this cell. *(AI)*

27. Write the name of the cell which is generally used in inverters. Write the reactions taking place at the anode and the cathode of this cell. *(AI)*

28. Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and the cathode of this cell. *(AI)*

3.7 Fuel Cells

VSA (1 mark)

29. Define fuel cell. *(1/3 Delhi)*

4 Chemical Kinetics

4.2 Factors Influencing Rate of a Reaction

VSA (1 mark)

30. For a reaction $R \longrightarrow P$, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction? *(Delhi)*

4.3 Integrated Rate Equations

SA II (3 marks)

31. Following data are obtained for the reaction:

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

***t*/s**	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(a) Show that it follows first order reaction.
(b) Calculate the half-life.
(Given : log 2 = 0.3010, log 4 = 0.6021) *(Delhi)*

32. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.
(Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021) *(AI)*

4.5 Temperature Dependence of the Rate of a Reaction

VSA (1 mark)

33. What is the effect of adding a catalyst on
(a) activation energy (E_a), and
(b) Gibbs energy (ΔG) of a reaction? *(AI)*

5 Surface Chemistry

5.1 Adsorption

VSA (1 mark)

34. Write one similarity between physisorption and chemisorption. *(Delhi)*

5.2 Catalysis

VSA (1 mark)

35. Write one difference of the following:
Homogeneous catalysis and heterogeneous catalysis *(1/3 Delhi)*

5.3 Colloids

VSA (1 mark)

36. Write one difference of the following:
Solution and colloid *(1/3 Delhi)*

5.4 Classification of Colloids

VSA (1 mark)

37. Write one difference in each of the following:
Lyophobic sol and lyophilic sol *(1/3 Delhi)*

38. What type of colloid is formed when a liquid is dispersed in a solid? Give an example. *(AI)*

39. What type of colloid is formed when a solid is dispersed in a liquid? Give an example. *(AI)*

40. What type of colloid is formed when a gas is dispersed in a liquid? Give an example. *(AI)*

SA I (2 marks)

41. Write one difference between each of the following :
(i) Multimolecular colloid and macromolecular colloid
(ii) Sol and gel *(2/3 Delhi)*

42. Write one difference in each of the following:
(a) Multimolecular colloid and associated colloid
(b) Coagulation and peptization *(2/3 AI)*

43. (a) Write the dispersed phase and dispersion medium of milk.
(b) Write the chemical method by which $Fe(OH)_3$ sol is prepared from $FeCl_3$.
(2/3 AI)

5.5 Emulsions

VSA (1 mark)

44. Write one difference between each of the following :
O/W emulsion and W/O emulsion *(1/3 Delhi)*

6 General Principles and Processes of Isolation of Elements

6.2 Concentration of Ores

VSA (1 mark)

45. Write the principle of the following :
Froth floatation process *(1/3 AI)*

SA I (2 marks)

46. (a) Out of PbS and $PbCO_3$ (ores of lead), which one is concentrated by froth floatation process preferably?

(b) What is the significance of leaching in the extraction of aluminium? *(2/3 Delhi)*

47. (a) Write the role of dilute NaCN in the extraction of silver.

(b) What is the role of the collectors in the froth floatation process? Give an example of a collector. *(2/3 AI)*

6.4 Thermodynamic Principles of Metallurgy

VSA (1 mark)

48. Why does copper obtained in the extraction from copper pyrites have a blistered appearance? *(1/3 AI)*

6.7 Refining

VSA (1 mark)

49. Write the principle of method used for the refining of germanium. *(1/3 Delhi)*

50. Write the principle of electrolytic refining. *(1/3 AI)*

SA II (3 marks)

51. Write the principles of the following methods:
(i) Vapour phase refining
(ii) Zone refining
(iii) Chromatography *(Delhi)*

7 The *p*-Block Elements

7.1 Group 15 Elements

VSA (1 mark)

52. Give reason:
Nitrogen does not form pentahalide. *(1/3 Delhi)*

7.2 Dinitrogen

VSA (1 mark)

53. What happens when $(NH_4)_2Cr_2O_7$ is heated? *(1/2 Delhi)*

7.4 Oxides of Nitrogen

VSA (1 mark)

54. Give reasons for the following :
N_2O_5 is more acidic than N_2O_3. *(1/3 AI)*

7.5 Nitric Acid

VSA (1 mark)

55. Write the formula of the compound of phosphorus which is obtained when conc. HNO_3 oxidises P_4. *(AI)*

56. Write the formula of the compound of sulphur which is obtained when conc. HNO_3 oxidises S_8. *(AI)*

57. Write the formula of the compound of iodine which is obtained when conc. HNO_3 oxidises I_2. *(AI)*

7.6 Phosphorus – Allotropic Forms

VSA (1 mark)

58. Give reason for the following :
Red phosphorus is less reactive than white phosphorus. *(1/3 AI)*

7.8 Phosphorus Halides

VSA (1 mark)

59. What happens when PCl_5 is heated?
Write the equation involved. *(1/2 Delhi)*

7.9 Oxoacids of Phosphorus

VSA (1 mark)

60. What happens when H_3PO_3 is heated?
Write the equation. *(1/2 Delhi)*

61. Draw the structure of the following :
H_3PO_2 *(1/2 Delhi)*

62. Draw the structure of the following :
$H_4P_2O_7$ *(1/2 Delhi)*

7.10 Group 16 Elements

VSA (1 mark)

63. Give reason:
Thermal stability decreases from H_2O to H_2Te. *(1/3 Delhi)*

7.16 Oxoacids of Sulphur

VSA (1 mark)

64. Draw the structure of the following :
$H_2S_2O_7$ *(1/2 Delhi)*

65. Draw the structure of the following :
H_2SO_3 *(1/2 AI)*

66. Draw the structure of the following :
$H_2S_2O_8$ *(1/2 AI)*

7.17 Sulphuric Acid

SA I (2 marks)

67. What happens when
(i) conc. H_2SO_4 is added to Cu?
(ii) SO_3 is passed through water?
Write the equations. *(Delhi)*

7.18 Group 17 Elements

VSA (1 mark)

68. Give reason:
Fluoride ion has higher hydration enthalpy than chloride ion. *(1/3 Delhi)*

69. Complete the following chemical equation :
$F_2 + 2Cl^- \rightarrow$ *(1/2 Delhi)*

70. Give reason for the following :
Electron gain enthalpies of halogens are largely negative. *(1/3 AI)*

7.19 Chlorine

VSA (1 mark)

71. Complete the following reaction :
$NH_3 + 3Cl_{2(excess)} \longrightarrow$ *(1/2 Delhi)*

72. Complete the following reaction:
$Cl_2 + H_2O \longrightarrow$ *(1/2 Delhi)*

7.20 Hydrogen Chloride

VSA (1 mark)

73. What happens when
HCl is added to MnO_2? *(1/2 Delhi)*

7.21 Oxoacids of Halogens

VSA (1 mark)

74. Draw the structure of the following :
$HClO_3$ *(1/2 AI)*

7.22 Interhalogen Compounds

VSA (1 mark)

75. Draw the structure of the following :
ClF_3 *(1/2 AI)*

76. Draw the structure of the following :
BrF_5 *(1/2 AI)*

7.23 Group 18 Elements

VSA (1 mark)

77. Complete the following reaction :
$XeF_6 + 2H_2O \longrightarrow$ *(1/2 Delhi)*

78. Draw the structure of the following :
XeF_6 *(1/2 Delhi)*

79. Draw the structure of the following :
XeF_4 *(1/2 Delhi)*

80. Complete the following reaction:
$XeF_6 + 3H_2O \longrightarrow$ *(1/2 Delhi)*

81. Draw the structures of the following :
$XeOF_4$ *(1/2 Delhi)*

82. Complete the following chemical equations :
$2XeF_2 + 2H_2O \rightarrow$ *(1/2 Delhi)*

8 The *d*- and *f*-Block Elements

8.3 General Properties of the Transition Elements (*d*-Block)

VSA (1 mark)

83. Write the formula of an oxo-anion of chromium (Cr) in which it shows the oxidation state equal to its group number. *(Delhi)*

84. Write the formula of an oxoanion of manganese (Mn) in which it shows the oxidation state equal to its group number. *(Delhi)*

SA I (2 marks)

85. Account for the following :

(i) Transition metals show variable oxidation states.

(ii) Zn, Cd and Hg are soft metals. *(2/5 AI)*

SA II (3 marks)

86. Account the following :

(i) Transition metals form large number of complex compounds.

(ii) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.

(iii) $E°$ value for the Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V) as compared to Cr^{3+}/Cr^{2+}. *(3/5 Delhi)*

87. (i) How is the variability in oxidation states of transition metals different from that of the *p*-block elements?

(ii) Out of Cu^+ and Cu^{2+}, which ion is unstable in aqueous solution and why?

(iii) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali. Why? *(3/5 Delhi)*

88. Following are the transition metal ions of 3*d* series :

$Ti^{4+}, V^{2+}, Mn^{3+}, Cr^{3+}$

(Atomic numbers : Ti = 22, V = 23, Mn = 25, Cr = 24)

Answer the following :

(i) Which ion is most stable in aqueous solution and why?

(ii) Which ion is strong oxidising agent and why?

(iii) Which ion is colourless and why? *(3/5 AI)*

8.4 Some Important Compounds of Transition Elements

SA I (2 marks)

89. Complete the following equations :

(i) $2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow$

(ii) $KMnO_4 \xrightarrow{\text{Heat}}$ *(2/5 AI)*

8.6 The Actinoids

VSA (1 mark)

90. Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements. *(1/5 Delhi)*

91. Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons. *(1/5 Delhi)*

9 Coordination Compounds

9.3 Nomenclature of Coordination Compounds

VSA (1 mark)

92. Write the IUPAC name of the following complex: $[Cr(NH_3)_3Cl_3]$. *(1/3 Delhi)*

93. Write the IUPAC name of the following complex: $[Co(NH_3)_5(CO_3)]Cl$. *(1/3 Delhi)*

SA I (2 marks)

94. Using IUPAC norms write the formulae for the following :

(a) Sodium dicyanidoaurate(I)

(b) Tetraamminechloridonitrito-N-platinum(IV) sulphate *(AI)*

95. Using IUPAC norms write the formulae for the following :

(a) *Tris*(ethane-1,2,diamine)chromium(III) chloride

(b) Potassium tetrahydroxozincate(II) *(AI)*

96. Using IUPAC norms write the formulae for the following :

(a) Potassium trioxalatoaluminate(III)

(b) Dichlorido*bis*(ethane-1,2-diamine) cobalt(III) *(AI)*

9.4 Isomerism in Coordination Compounds

VSA (1 mark)

97. What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$? *(1/3 Delhi)*

98. What type of isomerism is shown by the complex $[Co(en)_3]Cl_3$? *(1/3 Delhi)*

99. What type of isomerism is shown by the complex $[Co(NH_3)_5(SCN)]^{2+}$? *(1/3 AI)*

9.5 Bonding in Coordination Compounds

VSA (1 mark)

100. Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless?
(At. no. of Ni = 28) *(1/3 Delhi)*

101. Write the hybridisation and magnetic character of $[Co(C_2O_4)_3]^{3-}$.
(At. no. of Co = 27) *(1/3 Delhi)*

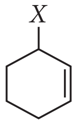
SA I (2 marks)

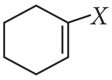
102. (a) Why is $[NiCl_4]^{2-}$ paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic?
(Atomic number of Ni = 28)
(b) Why are low spin tetrahedral complexes rarely observed? *(2/3 AI)*

10 Haloalkanes and Haloarenes

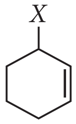
10.1 Classification

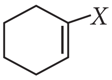
VSA (1 mark)

103. Out of 

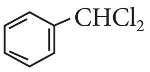
and 

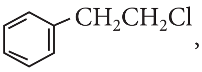
, which is an example of allylic halide? *(AI)*

104. Out of 

and 

, which is an example of vinylic halide? *(AI)*

105. Out of 

and 

, which is an example of a benzylic halide? *(AI)*

10.2 Nomenclature

VSA (1 mark)

106. Write the structure of 1-bromo-4-chlorobut-2-ene. *(Delhi)*

107. Write the structure of 3-bromo-2-methylprop-1-ene. *(Delhi)*

10.6 Chemical Reactions

SA II (3 marks)

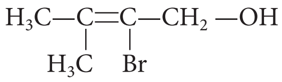
108. Following compounds are given to you:
2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane
(i) Write the compound which is most reactive towards S_N2 reaction.
(ii) Write the compound which is optically active.
(iii) Write the compound which is most reactive towards β-elimination reaction. *(Delhi)*

11 Alcohols, Phenols and Ethers

11.2 Nomenclature

VSA (1 mark)

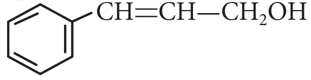
109. Write the IUPAC name of the following compound :



$H_3C-\underset{H_3C}{\underset{|}{C}}=\underset{Br}{\underset{|}{C}}-CH_2-OH$

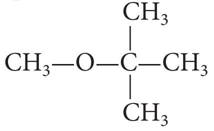
(AI)

110. Write the IUPAC name of the following compound :



(AI)

111. Write the IUPAC name of the following compound :



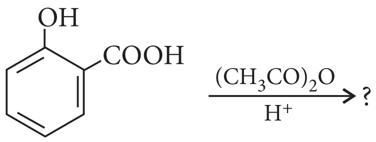
$CH_3-O-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

(AI)

11.4 Alcohols and Phenols

SA I (2 marks)

112. Write the product(s) in the following reactions:

(i) 

(ii) $CH_3-CH=CH-CH_2-OH \xrightarrow{PCC} ?$

(2/5 Delhi)

113. Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Ethanol and phenol

(ii) Propanol and 2-methylpropan-2-ol

(2/5 Delhi)

114. (a) Arrange the following compounds in the increasing order of their acid strength :

p-cresol, *p*-nitrophenol, phenol

(b) Write the mechanism (using curved arrow notation) of the following reaction :

$$CH_2{=}CH_2 \xrightarrow{H_3O^+} CH_3-\overset{+}{C}H_2 + H_2O$$ *(AI)*

115. Write the structure of the products when Butan-2-o1 reacts with the following :

(a) CrO_3 (b) $SOCl_2$ *(AI)*

LA (5 marks)

116. (a) Write the formula of reagents used in the following reactions :

(i) Bromination of phenol to 2,4,6- tribromophenol

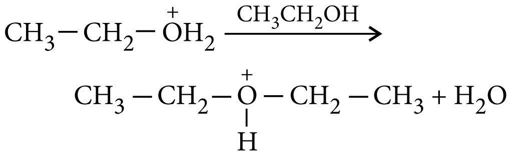
(ii) Hydroboration of propene and then oxidation to propanol.

(b) Arrange the following compound groups in the increasing order of their property indicated:

(i) *p*-nitrophenol, ethanol, phenol (acidic character)

(ii) propanol, propane, propanal (boiling point)

(c) Write the mechanism (using curved arrow notation) of the following reaction :



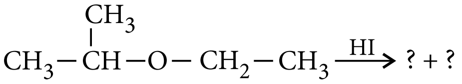
$$CH_3-CH_2-\overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH} CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3+H_2O$$

(Delhi)

11.6 Ethers

VSA (1 mark)

117. Write the product in the following reaction :



$$CH_3-\overset{CH_3}{CH}-O-CH_2-CH_3 \xrightarrow{HI} ?+?$$

(1/5 Delhi)

12 Aldehydes, Ketones and Carboxylic Acids

12.2 Preparation of Aldehydes and Ketones

VSA (1 mark)

118. Write the equation involved in the following reaction:

Etard reaction. *(1/2 Delhi)*

119. Do the following conversion in not more than two steps:

Benzoic acid to benzaldehyde *(1/3 Delhi)*

120. Write the reaction involved in the following :

Stephen reduction *(1/5 AI)*

121. Write the product in the following reaction :

$$CH_3-CH=CH-CN \xrightarrow[\text{(b) } H_2O]{\text{(a) DIBAL–H}} ?$$

(1/5 AI)

12.4 Chemical Reactions

VSA (1 mark)

122. Write the equation involved in the following reaction :

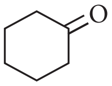
Wolff–Kishner reduction *(1/2 Delhi)*

123. Do the following conversion in not more than two steps:

Propanone to propene *(1/3 Delhi)*

SA I (2 marks)

124. (a) Write the product in the following reaction:



$+ \ HCN \longrightarrow ?$

(b) Give simple chemical test to distinguish between the following pair of compounds :

Butanal and Butan-2-one *(2/5 AI)*

125. Write the equations involved in the following reactions.

(i) Clemmensen reduction

(ii) Cannizzaro reaction *(Delhi)*

12.7 Methods of Preparation of Carboxylic Acids

VSA (1 mark)

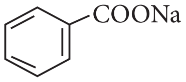
126. Do the following conversion in not more than two steps:
Ethyl benzene to benzoic acid *(1/3 Delhi)*

12.9 Chemical Reactions

SA I (2 marks)

127. Write the reactions involved in the following:
(i) Hell—Volhard—Zelinsky reaction
(ii) Decarboxylation reaction *(Delhi)*

128. (a) Write the product in the following reaction:



$+ \text{NaOH} \xrightarrow[\Delta]{\text{CaO}} ?$

(b) Give simple chemical test to distinguish between the following pair of compounds :
Benzoic acid and Phenol *(2/5 AI)*

129. How will you convert the following in not more than two steps :
(i) Acetophenone to benzoic acid
(ii) Ethanoic acid to 2-hydroxyethanoic acid *(2/5 AI)*

SA II (3 marks)

130. Write the structures of compounds *A*, *B* and *C* in each of the following reactions :

(i) $$\begin{tikzcd} C_6H_5Br \arrow[r, "Mg/dry\ ether"] & A \arrow[r, "(a)\ CO_{2(g)}", "(b)\ H_3O^+"'] & B \arrow[d, "PCl_5"] \\ & & C \end{tikzcd}$$

(ii) $$\begin{tikzcd} CH_3CN \arrow[r, "(a)\ SnCl_2/HCl", "(b)\ H_3O^+"'] & A \arrow[r, "dil.\ NaOH"] & B \arrow[d, "\Delta"] \\ & & C \end{tikzcd}$$

(Delhi)

13 Amines

13.3 Nomenclature

VSA (1 mark)

131. Write IUPAC name of the following compound:
$(CH_3CH_2)_2NCH_3$ *(Delhi)*

132. Write the structure of 2,4-dinitrochlorobenzene. *(Delhi)*

133. Write the IUPAC name of the following compound:
$CH_3NHCH(CH_3)_2$ *(Delhi)*

134. Write IUPAC name of the following compound:
$(CH_3)_2N — CH_2CH_3$ *(Delhi)*

13.6 Chemical Reactions (Amines)

SA II (3 marks)

135. Give reasons :
(i) Acetylation of aniline reduces its activation effect.
(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.
(iii) Although $—NH_2$ is *o*/*p* directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline. *(Delhi)*

13.9 Chemical Reactions (Diazonium salts)

SA II (3 marks)

136. Write the structures of compounds *A*, *B* and *C* in the following reactions :

(a) $CH_3—COOH \xrightarrow{NH_3/\Delta} A \xrightarrow{Br_2/KOH_{(aq)}} B$
$\xrightarrow{CHCl_3 + \text{alc. KOH}} C$

(b) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Fe/HCl} B$
$\xrightarrow{CH_3COCl/\text{pyridine}} C$

(AI)

14 Biomolecules

14.4 Vitamins

VBQ (4 marks)

137. After watching a programme on TV about the presence of carcinogens (cancer causing agents) potassium bromate and potassium iodate in bread and other bakery products, Ritu a class XII student decided to aware others about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct canteen contractor to stop selling sandwiches, pizza, burgers and other bakery products to the students. Principal took an immediate action and instructed the canteen contractor to replace the bakery products with some proteins and vitamins rich food like fruits, salads, sprouts, etc. The decision was welcomed by the parents and students. After reading the above passage, answer the following questions :

(i) What are the values (at least two) displayed by Ritu?

(ii) Which polysaccharide component of carbohydrates is commonly present in bread?

(iii) Write the two types of secondary structure of proteins.

(iv) Give two examples of water soluble vitamins. *(Delhi)*

15 Polymers

15.2 Types of Polymerisation

VSA (1 mark)

138. Write the structure of the monomers used for getting the following polymer :
Nylon-6, 6 *(1/3 AI)*

SA I (2 marks)

139. Write the structures of the monomers used for getting the following polymers :
(i) Dacron (ii) Buna-N *(2/3 Delhi)*

140. Write the structures of the monomers used for getting the following polymers :
(i) Nylon-6 (ii) Teflon *(2/3 Delhi)*

SA II (3 marks)

141. Write the structures of the monomers used for getting the following polymers:
(i) Neoprene
(ii) Melamine-formaldehyde polymer
(iii) Buna-S *(Delhi)*

15.5 Polymers of Commercial Importance

VSA (1 mark)

142. Write the structures of the monomers used for getting the following polymer :
Polyvinyl chloride (PVC) *(1/3 AI)*

16 Chemistry in Everyday Life

16.3 Therapeutic Action of Different Classes of Drugs

VSA (1 mark)

143. Define the following :
Antacids *(1/3 AI)*

SA I (2 marks)

144. Define the following :
(i) Broad spectrum antibiotics
(ii) Antiseptic *(2/3 Delhi)*

145. Define the following :
(i) Narrow spectrum antibiotics
(ii) Disinfectants *(2/3 Delhi)*

146. Define the following :
(i) Limited spectrum antibiotics
(ii) Tranquilizers *(2/3 Delhi)*

16.5 Cleansing Agents

VSA (1 mark)

147. Define the following :
Cationic detergents *(1/3 Delhi)*

Detailed Solutions

1. Differences between crystalline and amorphous solids are as follows :

	Crystalline solid	Amorphous solid
1.	It has definite characteristic geometrical shape.	It has irregular shape.
2.	It has sharp melting point. *e.g.*, Sodium chloride (NaCl).	It melts over a range of temperature. *e.g.*, Plastic.

2. Silicon carbide : Covalent or network solid.
Argon : Non-polar molecular solid.

3. Benzene : Non-polar molecular solid.
Silver : Metallic solid

4. Sodium sulphate : Crystalline solid
Hydrogen : Non-polar molecular solid.

5. As 27 g of Al will contain 6.023×10^{23} atoms

$\therefore$ 8.1 g Al will contain

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

$= 1.8069 \times 10^{23}$ atoms

In *fcc*, 4 atoms are present in one unit cell

$\therefore$ 1.8069×10^{23} atoms will be present in

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

6. Given, atomic mass (M) = 93 g mol^{-1},
density (d) = 11.5 g cm^{-3},
edge length (a) = 300 pm = 300×10^{-10} cm
Z = ?

We know that, $d = \dfrac{Z \times M}{N_A \times a^3}$

or, $Z = \dfrac{d \times N_A \times a^3}{M}$

$$= \frac{11.5 \times 6.022 \times 10^{23} \times (3 \times 10^{-8})^3}{93} = 2.01 \approx 2$$

So, type of the unit cell is *bcc*.

7. Since Schottky defect is shown by highly ionic compounds having small difference in the size of cations and anions, whereas Frenkel defect is shown by compounds having large difference in the size of cations and anions. Therefore, NaCl exhibits Schottky defect.

8. Initially ZnO is white in colour at room temperature but on heating it loses oxygen which creates anion vacancy defect and it turns yellow.

$$\text{ZnO} \xrightarrow{\text{heating}} \text{Zn}^{2+} + \frac{1}{2}\text{O}_2 + 2e^-$$

9. Frenkel defect is shown by those ionic substances which have large difference in the size of ions. Hence, AgCl shows frenkel defect but NaCl does not.

10. When $CdCl_2$ is added to AgCl, a cationic vacancy defect is created *i.e.*, an Ag^+ ion from the lattice is absent from its position due to presence of adjacent Cd^{2+} ion.

11. Since group 15 elements (*e.g.*, phosphorus) have one electron excess to group 14 elements (*e.g.*, silicon) after forming four covalent bonds. Thus, the extra free electron is responsible for the formation of n-type semiconductor.

12. Groups 12-16 compounds are formed by the combination of elements of group-12 and group-16. In groups 12-16 compounds, the bonds are not perfectly covalent and the ionic character depends upon the electronegativities of the two elements, *e.g.*, ZnS.

13. When germanium (Ge) is doped with aluminium (Al), p-type semiconductor is formed.

14. Ferrimagnetic substances have a net dipole moment due to unequal parallel and antiparallel alignment of magnetic moments whereas antiferromagnetic substances have net magnetic moment zero due to compensatory alignment of magnetic moments. Therefore, ferrimagnetic substances show better magnetism than antiferromagnetic substances.

15. Molality (m) is defined as the number of moles of the solute per kilogram of the slovent and is expressed as :

$$\text{Molality } (m) = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

16. Molarity : It is the number of moles of the solute dissolved per litre of the solution. It is denoted by M.

$$\therefore \quad \text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{n}{V} \times 1000 = = \frac{W_2 \times 1000}{M_2 \times V} \left(\therefore n_2 = \frac{W_2}{M_2} \right)$$

17. A solution which obeys Raoult's law of vapour pressure for all compositions is called ideal solution. In this solution $\Delta V_{\text{mix}} = 0$, $\Delta H_{\text{mix}} = 0$

$A \ldots\ldots B$ interaction $= A \ldots\ldots A$ and $B \ldots\ldots B$ interactions.

18. The two differences between ideal solutions and non ideal solutions are as follows :

(i) In ideal solutions $\Delta V_{\text{mixing}} = 0$ and $\Delta H_{\text{mix}} = 0$ whereas in non ideal solutions, $\Delta V_{\text{mix}} \neq 0$ and $\Delta V_{\text{mix}} \neq 0$.

(ii) In ideal solutions, each component obeys Raoult's law at all temperatures and concentrations whereas in non ideal solutions, they do not obey Raoult's law.

19. Properties which depend upon the number of solute particles irrespective of their nature relative to the total number of particles present in the solution are called colligative properties.

20. Molality (m) of sucrose solution

$$= \frac{w \times 1000}{M \times \text{Mass of solvent}} = \frac{10}{342} \times \frac{1000}{90} = 0.325 \text{ m}$$

ΔT_f for sucrose solution

$= T_f^\circ - T_f = (273.15 - 269.15)$ K $= 4$ K

$\because \quad \Delta T_f = K_f \times m$

$$\therefore \quad K_f = \frac{\Delta T_f}{m} = \frac{4 \text{ K}}{0.325 \text{ m}} = 12.308 \text{ K/m}$$

$$\text{Molality of glucose solution} = \frac{10}{180} \times \frac{1000}{90} = 0.617 \text{ m}$$

$\Delta T_f = K_f \times m$

$\therefore \quad \Delta T_f = 12.308 \text{ K/m} \times 0.617 \text{ m} = 7.59 = 7.6 \text{ K}$

$\therefore$ Freezing point of glucose solution,

$T_f^\circ - \Delta T_f = (273.15 - 7.60) \text{ K} = 265.55 \text{ K}$

21. Given, weight of urea (w_2) = 30 g

Weight of water (w_1) = 846 g

Vapour pressure of water $p_1^\circ = 23.8$ mm Hg

$$n_B = \frac{30}{60} = 0.5, \quad n_A = \frac{846}{18} = 47$$

$$\text{Mole fraction of water } (x_A) = \frac{n_A}{n_A + n_B}$$

$$= \frac{47}{47 + 0.5} = \frac{47}{47.5} = 0.99$$

$P_A = p_A^\circ \times x_A = 23.8 \times 0.99 = 23.5$ mm Hg.

22. (i) The molar mass which is either lower or higher than the expected or normal value is known as abnormal molar mass.

(ii) van't Hoff factor (i) is defined as the ratio of the experimental (observed) value of colligative property to the calculated value of colligative property.

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$$\text{or, } i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

23. Degree of dissociation $(\alpha) = \dfrac{\Lambda_m}{\Lambda_m^\circ}$

$$\alpha = \frac{39.05 \text{ S cm}^2 \text{mol}^{-1}}{(349.68 + 40.9) \text{ S cm}^2 \text{mol}^{-1}} = 0.1$$

24. Given : $I = 2$ A, $t = 15$ min $= 15 \times 60$ s $= 900$ s

$w = ?$

$Q = I \times t = 2 \times 900 = 1800$ C

Reaction for deposition of Ag is as follows :

$$\begin{array}{ccccc} \text{Ag}^+ & + & 1e^- & \longrightarrow & \text{Ag} \\ & & 1 \text{ F} & & 1 \text{ mol} \\ & & 1 \times 96500 \text{ C} & & 108 \text{ g} \end{array}$$

Thus, 1×96500 C of electricity is required to deposit 108 g of Ag.

$\therefore$ 1800 C of electricity would deposit

$$= \frac{108 \times 1800}{1 \times 96500} = 2.014 \text{ g of Ag}$$

25. (a) Given cell reaction is

$2\text{Fe}^{3+}_{(aq)} + 2\text{I}^-_{(aq)} \longrightarrow 2\text{Fe}^{2+}_{(aq)} + \text{I}_{2(s)}$

No. of electron transferred (n) = 2

Now, from the relationship of Gibbs energy and E°_{cell},

$\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$

$\Rightarrow \quad \Delta_r G^\circ = -2 \times 96500 \text{ C mol}^{-1} \times 0.236 \text{ V}$

$= -45548 \text{ J mol}^{-1} = -45.548 \text{ kJ mol}^{-1}$

(b) Given, $I = 0.5$ A, $t = 2$ hrs.

Number of electrons = ?

Total charge (Q) = $I \times t$

$= 0.5 \times 2 \times 60 \times 60 = 3600$ C

$$\therefore \quad \text{Number of electrons} = \frac{\text{Total charge}}{\text{Charge of one electron}}$$

$$= \frac{3600}{1.6 \times 10^{-19}} = 2.25 \times 10^{22} \text{ electrons.}$$

26. The mercury cell is generally used in hearing aids.

Reaction at cathode :

$\text{HgO} + \text{H}_2\text{O} + 2e^- \longrightarrow \text{Hg} + 2\text{OH}^-$

Reaction at anode :

$\text{Zn(Hg)} + 2\text{OH}^- \longrightarrow \text{ZnO} + \text{H}_2\text{O} + 2e^-$

27. The cell which is generally used in inverters is secondary cell *i.e.*, lead storage battery.

At cathode : $PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

At anode : $Pb_{(s)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$

28. Mercury cell is generally used in transistors.

At cathode : $HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^-$

At anode : $Zn(Hg) + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$

29. Those galvanic cells which give us direct electrical energy by the combustion of fuels like hydrogen, methane, methanol, etc are called fuel cells.

30. Half-life of first order reaction is independent of the initial concentration of reactants.

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

31. (a) The formula of rate constant for first order reaction is

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

$$k_1 = \frac{2.303}{300\text{ s}}\log\frac{(1.6\times10^{-2})\text{ mol L}^{-1}}{(0.8\times10^{-2})\text{ mol L}^{-1}} = 2.3\times10^{-3}\text{ s}^{-1}$$

Similarly, $k_2 = \frac{2.303}{600\text{ s}}\log\frac{(1.6\times10^{-2})\text{ mol L}^{-1}}{(0.4\times10^{-2})\text{ mol L}^{-1}}$
$= 2.3 \times 10^{-3}\text{ s}^{-1}$

Unit and magnitude of rate constant shows the given reaction is of first order.

(b) The formula for half-life for first order reaction is

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.3\times10^{-3}\text{ s}^{-1}} = 301.30\text{ s}$$

32. According to the 1st order kinetics

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A_t]}$$

[where, k = rate constant, $[A_0]$ = initial conc., $[A_t]$ = conc. after time t]

$$\Rightarrow \quad k = \frac{2.303}{20\text{ min}}\log\frac{[100]}{[75]} \Rightarrow k = 0.014\text{ min}^{-1}$$

Similarly, for 2nd process, $0.014 = \frac{2.303}{t}\log\left(\frac{100}{25}\right)$
$t = 99$ min

33. (a) A catalyst lowers the activation energy (E_a) by providing an alternate pathway or reaction mechanism.

(b) Catalyst does not affect the Gibbs energy (ΔG) of a reaction.

34. Physical adsorption and chemical adsorption both increase with increase in surface area of the adsorbent.

35. Homogeneous catalysis : Catalyst is present in the same phase as reactants.

Heterogeneous catalysis : Catalyst is present in a different phase as that of reactants.

36. Solution : In true solution, the size of the particles is about 10^{-10} m.

Colloid : In a colloid, the size of the particles is between 10^{-7} to 10^{-9} m.

37. Difference between lyophilic and lyophobic colloids.

Lyophobic colloid	Lyophilic colloid
These are solvent repelling.	These are solvent attracting.

38. When a liquid is dispersed in a solid, 'gel' is formed, *e.g.*, butter.

39. When a solid is dispersed in a liquid, a colloid is formed which is known as 'sol' *e.g;* paints.

40. When a gas is dispersed in a liquid, foam is formed, *e.g.*, froth.

41.

(i)	**Multimolecular Colloids**	**Macromolecular Colloids**
	Atoms or molecules of these colloids are held together by weak van der Waals forces.	Due to long chain, the van der Waals forces holding them are stronger.
(ii)	**Sol**	**Gel**
	Dispersed phase is solid whereas dispersion medium is liquid.	Dispersed phase is liquid whereas dispersion medium is solid.

42. (a) Difference between multimolecular colloid and associated colloid :

Multimolecular colloid	Associated colloid
The particles of this type of colloids are aggregates of atoms or molecules with diameter less than 1 nm. *e.g.*, sulphur sol consists of colloidal particles which are aggregate of S_8 molecules.	They are substances which at low concentration behave as true solution and at higher concentration exhibit colloidal behaviour.

(b) Difference between coagulation and peptization :

Coagulation	Peptization
It is the process of settling of colloidal particles	It is the process responsible for the formation of stable dispersion of colloidal particles in dispersion medium.

43. (a) Dispersed phase and dispersion medium of milk are liquid and liquid respectively.

(b) Hydrolysis is the chemical method by which $Fe(OH)_3$ sol is prepared from $FeCl_3$.

$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_{3(sol)} + 3HCl$

44.

O/W emulsion	**W/O emulsion**
Oil is dispersed phase and water is the dispersion medium.	Water is dispersed phase and oil is the dispersion medium.

45. Froth floatation process : This method is based on the principle that the ore particles are preferentially wetted by oil while gangue particles are wetted by water. This principle is applied mainly to concentrate sulphide ores.

46. (a) Sulphide ores are concentrated by froth floatation process preferebly, hence, PbS is concentrated more preferebly than $PbCO_3$ by this method.

(b) The significance of leaching in the extraction of aluminium is to concentrate pure alumina (Al_2O_3) from bauxite ore.

47. (a) In the extraction of silver, silver metal is leached with a dilute solution of NaCN in the presence of air from which the metal is obtained.

$$4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4\,Na[Ag(CN)_2] + 4\,NaOH$$

(b) The role of collectors in the froth floatation process is to enhance non-wettability of the ore particles *e.g.*, pine oil.

48. Copper obtained in the extraction from copper pyrites has a blistered appearance due to the evolution of SO_2.

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$

49. Germanium is refined by zone refining method which is based on the principle that the impurities are more soluble in the molten state than in the solid state of the metal.

50. In this process, impure metal is made the anode and a strip of pure metal is made the cathode. A solution of a soluble salt of the same metal is taken as the electrolyte and net result is the transfer of metal in pure form from the anode to the cathode.

51. (i) Vapour phase refining : In this method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal.

(ii) Zone refining : This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal.

(iii) Chromatography : Chromatographic method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The adsorbed components are removed using suitable eluent.

52. Nitrogen cannot expand its octet due to absence of *d*-orbitals.

53. When orange red crystals of ammonium dichromate are heated, these crystals decompose violently evolving nitrogen and green coloured chromic oxide is formed.

$$\underset{\text{(Orange red)}}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} \underset{\text{(Green)}}{Cr_2O_3} + N_2 + 4H_2O$$

54. Oxidation state of N in $N_2O_5 = +5$

Oxidation state of N in $N_2O_3 = +3$

As the oxidation number of central element increases, acidic strength increases. Hence, N_2O_5 is more acidic than N_2O_3.

55. H_3PO_4 (phosphoric acid) is obtained when conc. HNO_3 oxidises P_4.

$P_4 + 20HNO_{3(conc.)} \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

56. When conc. HNO_3 oxidises S_8, it forms sulphuric acid.

$S_8 + 48HNO_3 \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$

57. Iodic acid (HIO_3) is formed when conc. HNO_3 oxidises I_2.

$$I_2 + 10HNO_3 \longrightarrow \underset{\text{Iodic acid}}{2HIO_3} + 10NO_2 + 4H_2O$$

58. White phosphorus is made up of discrete P_4 tetrahedra which are subjected to very high angular strain as the angles are 60°. Red phosphorus is a polymer of P_4 tetrahedra, which has much less angular strain. This high angular strain makes white phosphorus unstable and highly reactive.

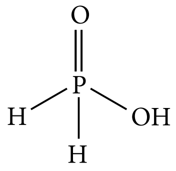
59. PCl_5 on heating, sublimes but it decomposes into phosphorus trichloride and chlorine on stronger heating.

$PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$

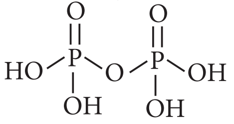
60. When phosphorous acid (H_3PO_3) is heated, it forms orthophosphoric acid and phosphine.

$4H_3PO_3 \xrightarrow{200\ °C} 3H_3PO_4 + PH_3$

61.

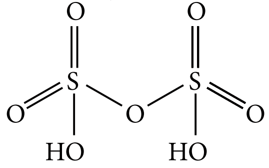


62. $H_4P_2O_7$ (Pyrophosphoric acid) :

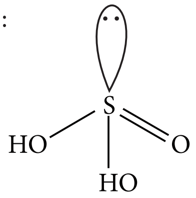


63. As the size of central atom increases, $M—H$ bond becomes weaker and longer and hence, thermal stability decreases while going from H_2O to H_2Te.

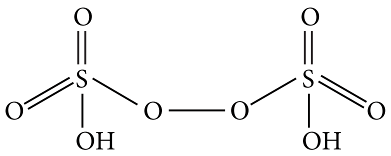
64. $H_2S_2O_7$ (Pyrosulphuric acid)



65. H_2SO_3 :



66. $H_2S_2O_8$:



67. (i) When conc. H_2SO_4 reacts with Cu, CuO is formed which gets further converted into $CuSO_4$.

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(ii) When SO_3 is passed through water, it dissolves SO_3 to give H_2SO_4.

$SO_3 + H_2O \longrightarrow H_2SO_4$

68. As the size of halogen increases down the group from F to I, the hydration enthalpy of corresponding halide ion decreases. Hence F^- ion has higher hydration enthalpy (524 kJ mol^{-1}) than Cl^- ion (378 kJ mol^{-1}).

69. $F_2 + 2Cl^- \rightarrow 2F^- + Cl_2$

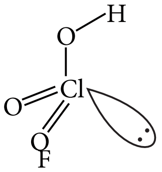
70. Halogens have the smallest size in their respective periods and therefore have high effective nuclear charge. As a result, they readily accept one electron to acquire noble gas configuration. Hence, electron gain enthalpies of halogens are largely negative.

71. $NH_3 + 3Cl_{2(excess)} \longrightarrow \underset{\substack{\text{Nitrogen}\\ \text{trichloride}\\ \text{(explosive)}}}{NCl_3} + 3HCl$

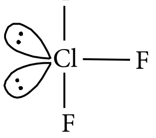
72. $Cl_2 + H_2O \longrightarrow \underset{\substack{\text{Hydrochloric}\\ \text{acid}}}{HCl} + \underset{\substack{\text{Hypochlorous}\\ \text{acid}}}{HOCl} \longrightarrow 2HCl + \underset{\substack{\text{Nascent}\\ \text{oxygen}}}{[O]}$

73. When HCl is added to MnO_2, Cl_2 gas is formed.
$MnO_2 + 4HCl \rightarrow Cl_2 + MnCl_2 + 2H_2O$

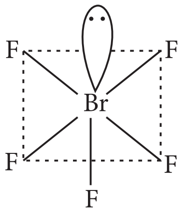
74. $HClO_3$:



75. ClF_3:

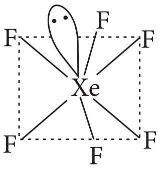


76. BrF_5 ;

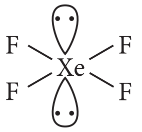


77. $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$

78. XeF_6 : (Xenon hexafluoride)

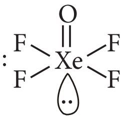


79.



80. $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

81. $XeOF_4$:



82. $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$

83. Oxo-anion of chromium in which it shows +6 oxidation state equal to its group number is $Cr_2O_7^{2-}$ (dichromate ion).

84. Formula of oxoanion of manganese is MnO_4^-.
Oxidation state of Mn in this oxoanion = + 7
Group number of Mn is 7.

85. (i) Transition metals show variable oxidation states because the difference of energy in the $(n-1)$ d and ns orbitals is very less. Hence, electrons from both the energy levels can be used for bond formation.

(ii) In Zn, Cd and Hg, all the electrons in d-subshell are paired. Hence, the metallic bonds are weak. That is why they are soft metals with low melting and boiling points.

86. (i) Transition metals form a large number of complex compounds due to following reasons :

- Comparatively smaller size of metal ions.
- High ionic charges.
- Availability of d-orbitals for bond formation.

(ii) As oxidation number of transition metals in their oxides increases, their acidic character increases due to lack of d-electrons. In the lowest oxide, oxidation state is lower and hence, it becomes basic and in highest oxide, oxidation state is higher and therefore, it becomes acidic or amphoteric.

(iii) Much larger third ionisation energy of Mn(where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance.

87. (i) Variability of oxidation states of transition metals arises due to incomplete filling of d-orbitals and it differs from each other by unity *e.g.*, $V^{(V)}$, $V^{(IV)}$, $V^{(III)}$, $V^{(II)}$. In p-block elements oxidation states differ generally by a unit of two. *e.g.*, Sn(II), Sn(IV), PCl_3, PCl_5, etc.

(ii) $Cu^{2+}_{(aq)}$ is much more stable than $Cu^{+}_{(aq)}$. This is because $\Delta_{hyd}H$ for $Cu^{2+}_{(aq)}$ is much more negative than that for $Cu^{+}_{(aq)}$ and hence it more than compensates for the second ionisation enthalpy of copper. Therefore, copper(I) compounds are unstable in aqueous solution and undergo disproportionation as follows :

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

(iii) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when an alkali is added because on addition of an alkali, the concentration of H^+ ions decreases and hence, the reaction proceeds in the forward direction producing yellow solution containing CrO_4^{2-} ions.

$$\underset{\text{orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{yellow}}{2CrO_4^{2-}} + H_2O$$

88. (i) Ti^{4+} has highest oxidation state among the given ions. Ti^{4+} has stable inert gas configuration and hence, most stable in aqueous solution.
On the other hand, V^{2+}, Mn^{3+}, Cr^{3+} have unstable electronic configuration and hence, are less stable.

(ii) Due to presence of highest oxidation state of Ti, it acts as the strongest oxidising agent among the given ions.

(iii) Due to absence of unpaired electron in Ti^{4+}, it is a colourless ion.
E.C. of Ti^{4+} = $[Ar]3d^04s^0$

89. (i) $2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$

(ii) $2KMnO_4 \xrightarrow{\text{heat}} K_2MnO_4 + MnO_2 + O_2$

90. Similarity : The elements of both the series are electropositive in nature. They are reactive metals and act as strong reducing agents.
Difference : Lanthanoids except promethium are non-radioactive elements, while all actinoids are radioactive elements.

91. Chemistry of actinoids is more complicated than lanthanoids because

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

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

92. IUPAC name of the complex $[Cr(NH_3)_3Cl_3]$ is triamminetrichloridochromium(III).

93. Pentaamminecarbonatocobalt(III) chloride

94. (a) $Na[Au(CN)_2]$
Sodium dicyanidoaurate(I)

(b) $[Pt(NH_3)_4(Cl)(NO_2)]SO_4$
Tetraamminechloridonitrito-N-platinum(IV) sulphate

95. (a) $[Cr(en)_3]Cl_3$
Tris(ethane-1,2-diamine)chromium(III) chloride
(b) $K_2[Zn(OH)_4]$
Potassium tetrahydroxozincate(II)

96. (a) $K_3[Al(C_2O_4)_3]$
Potassium trioxalatoaluminate(III)
(b) $[CoCl_2(en)_2]^+$
Dichlorido*bis*(ethane–1,2-diamine)cobalt(III) ion

97. Coordination isomerism.

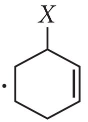
98. The complex, $[Co(en)_3]Cl_3$ shows optical isomerism.

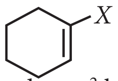
99. The complex $[Co(NH_3)_5(SCN)]^{2+}$ shows linkage isomerism as SCN^- is an ambidentate ligand.

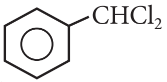
100. $[Ni(H_2O)_6]^{2+}$ is a high spin complex (Δ_o small) while $[Ni(CN)_4]^{2-}$ is a low spin square planar complex.
In $[Ni(H_2O)_6]^{2+}$ *d-d* transitions are taking place on absorbing low energy radiation (red component of spectrum) from visible region showing green as the complementary colour.
In $[Ni(CN)_4]^{2-}$ complex, *d-d* transitions do not take place in the visible region of spectrum, *d-d* transitions take place in the UV region and hence, complex is colourless.

101. The complex $[Co(C_2O_4)_3]^{3-}$ has d^2sp^3-hybridisation and it is diamagnetic in nature due to the absence of unpaired electrons.

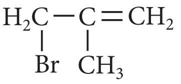
102. (a) Due to the presence of weak field ligand, *i.e.*, Cl^- in the complex $[NiCl_4]^{2-}$, two unpaired electrons are present in 3*d*-orbitals of Ni-atom hence, this complex is paramagnetic in nature. On the other hand, due to the presence of strong field ligand *i.e.*, CN^- in the complex $[Ni(CN)_4]^{2-}$, no unpaired electron is present in 3*d*-orbitals of Ni-atom (as strong field ligand causes pairing of electrons), hence, it is diamagnetic in nature.
(b) In tetrahedral coordination entity formation, the *d*-orbital splitting is smaller. Consequently, the orbital splitting energies are not sufficiently large to force pairing and therefore, low spin configurations are rarely observed.

103.  is an allylic halide as the halogen is attached to sp^3 hybridised carbon atom which is next to carbon-carbon double bond.

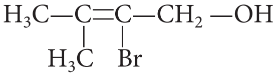
104.  is a vinylic halide as the halogen is attached to sp^2 hybridised carbon.

105.  is a benzylic halide as the halide group is attached to sp^3-hybridised carbon atom next to aromatic ring.

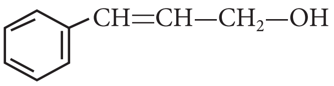
106. The structure of 1-bromo-4-chlorobut-2-ene is
$Cl—\overset{4}{C}H_2—\overset{3}{C}H{=}\overset{2}{C}H—\overset{1}{C}H_2—Br$

107. Structure of 3-bromo-2-methylprop-1-ene
is 
$H_2\underset{Br}{C}-\underset{CH_3}{C}=CH_2$

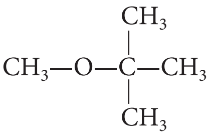
108. (i) 1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane
(ii) 2-Bromopentane
(iii) 2-Bromo-2-methylbutane

109. 
$H_3C—\underset{H_3C}{C}{=}\underset{Br}{C}—CH_2—OH$

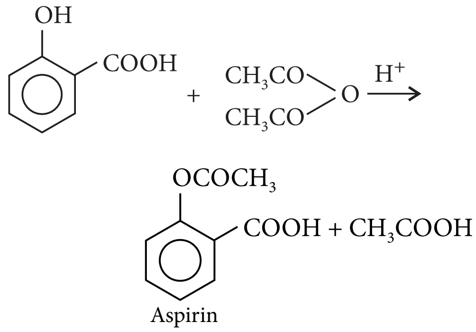
2-Bromo-3-methylbut-2-en-1-ol.

110. 

IUPAC name : 3-Phenylprop-2-en-1-o1

111. 
$CH_3—O—\underset{CH_3}{\overset{CH_3}{C}}—CH_3$

IUPAC name : 2-Methoxy-2-methylpropane

112. (i) 

Aspirin

(ii) $\underset{\text{But-2-en-1-ol}}{CH_3-CH=CH-CH_2OH} \xrightarrow{PCC} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$

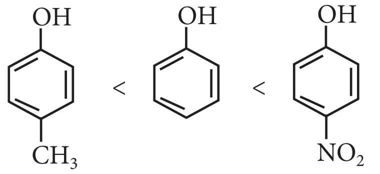
113. (i) Distinction between ethanol and phenol.
$FeCl_3$ test : Phenol gives a violet colouration with

$FeCl_3$ solution while ethanol does not.

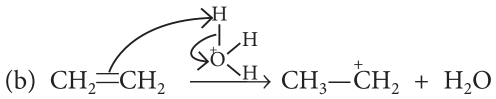
$$\underset{\text{Phenol}}{3C_6H_5OH} + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{(C_6H_5O)_3Fe} + 3HCl$$

$$C_2H_5OH + FeCl_3 \longrightarrow \text{No violet colouration.}$$

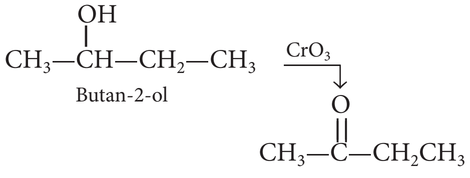
(ii) On oxidation in presence of acidic $KMnO_4$, 1° alcohol (propanol) will give aldehyde while 3° alcohol (2-methylpropan-2-ol) will give a ketone.

114. (a) 

p-Cresol   Phenol   *p*-Nitrophenol

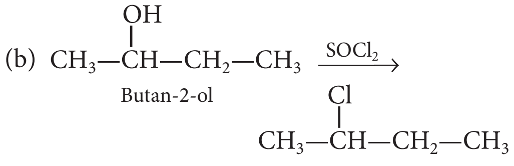
(b) 

$$CH_2{=}CH_2 \longrightarrow CH_3-\overset{+}{C}H_2 + H_2O$$

115. (a) 

$$\underset{\text{Butan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-CH_3} \xrightarrow{CrO_3} CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3$$

Butan-2-one

(b) 

$$\underset{\text{Butan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-CH_3} \xrightarrow{SOCl_2} CH_3-\overset{\overset{Cl}{|}}{C}H-CH_2-CH_3$$

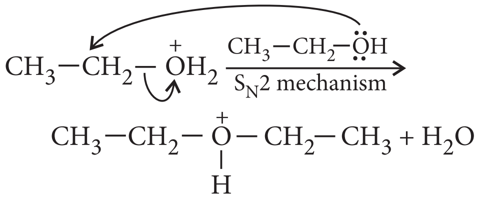
2-Chlorobutane

116. (a) (i) Br_2/H_2O

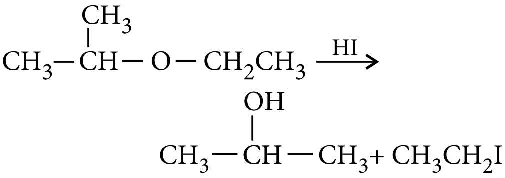
(ii) BH_3 in THF/H_2O_2

(b) (i) *p*-nitrophenol > phenol > ethanol

(ii) Propanol > propanal > propane

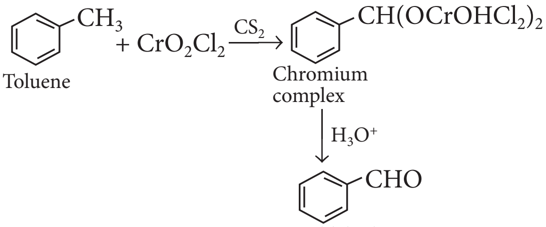
(c) 

$$CH_3-CH_2-\overset{+}{O}H_2 \xrightarrow[S_N2\text{ mechanism}]{CH_3-CH_2-\ddot{O}H} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_2-CH_3 + H_2O$$

117. 

$$CH_3-\overset{\overset{CH_3}{|}}{C}H-O-CH_2CH_3 \xrightarrow{HI} CH_3-\overset{\overset{OH}{|}}{C}H-CH_3 + CH_3CH_2I$$

118. Etard reaction :

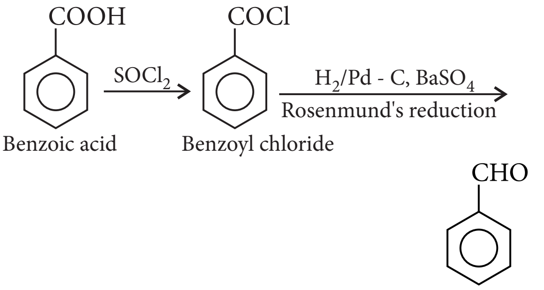


Toluene

Chromium complex

Benzaldehyde

119.



Benzoic acid

Benzoyl chloride

Rosenmund's reduction

Benzaldehyde

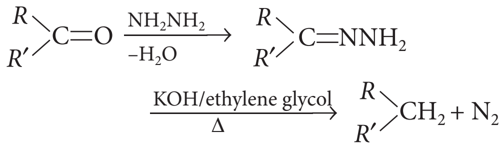
120. Stephen reduction :

Nitriles when react with $SnCl_2$ in the presence of HCl, get reduced to corresponding imines which on hydrolysis give corresponding aldehydes.

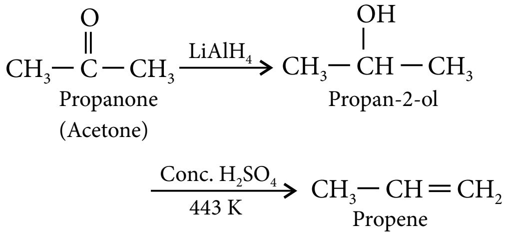
$$R-CN + SnCl_2 + HCl \longrightarrow R-CH{=}NH \xrightarrow{H_3O^+} R-CHO$$

121. $CH_3-CH{=}CH-CN \xrightarrow{\text{(a) DIBAL–H}} CH_3-CH{=}CH-CH{=}NH \xrightarrow{\text{(b) } H_2O} CH_3-CH{=}CH-CHO$

122. Wolff-Kishner reduction :



$$\begin{matrix}R\\R'\end{matrix}\!\!>C{=}O \xrightarrow[-H_2O]{NH_2NH_2} \begin{matrix}R\\R'\end{matrix}\!\!>C{=}NNH_2 \xrightarrow[\Delta]{\text{KOH/ethylene glycol}} \begin{matrix}R\\R'\end{matrix}\!\!>CH_2 + N_2$$

123. 

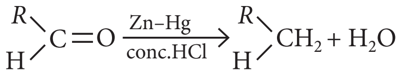
$$\underset{\substack{\text{Propanone}\\\text{(Acetone)}}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3} \xrightarrow[443\text{ K}]{\text{Conc. }H_2SO_4} \underset{\text{Propene}}{CH_3-CH{=}CH_2}$$

124. (a)

Cyclohexanone Cyclohexane cyanohydrin

(b) Butanal respond to Fehling test and silver mirror test but Butan-2-one does not respond.

125. (i) Clemmensen reduction :



$$\begin{matrix}R\\H\end{matrix}\!\!>C{=}O \xrightarrow[\text{conc.HCl}]{\text{Zn–Hg}} \begin{matrix}R\\H\end{matrix}\!\!>CH_2 + H_2O$$

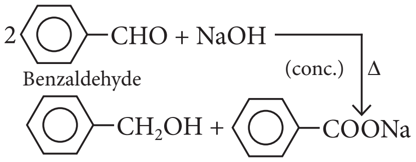
(ii) Cannizzaro reaction :

$$2H-\overset{\overset{\displaystyle O}{||}}{C}-H + KOH_{(conc.)} \xrightarrow{\Delta} CH_3OH$$

Formaldehyde Methanol

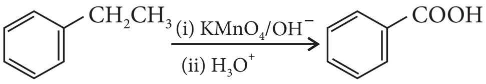
$+ HCOOK$

Potassium formate



Benzene

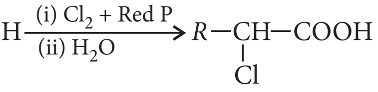
126.



Ethylbenzene Benzoic acid

127. (i) Carboxylic acids having α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus.

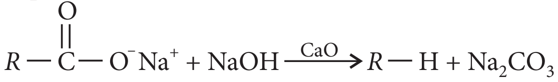
e.g.,



$$RCH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Cl_2 + \text{Red P}} R-\underset{\underset{\displaystyle Cl}{|}}{CH}-COOH$$

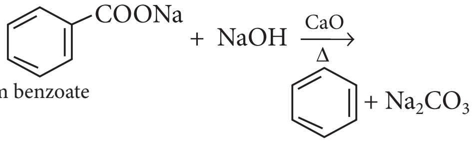
α-Chloro acid

(ii) Sodium or potassium salt of carboxylic acids on heating with soda lime (NaOH and CaO), loses a molecule of carbon dioxide and alkanes are obtained as products.



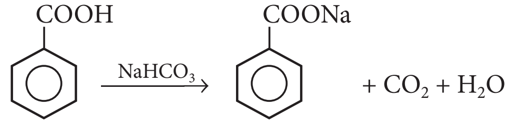
$$R-\overset{\overset{\displaystyle O}{||}}{C}-O^-Na^+ + NaOH \xrightarrow{CaO} R-H + Na_2CO_3$$

128. (a)

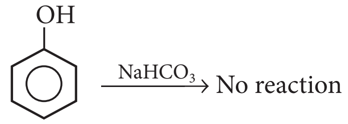


Sodium benzoate

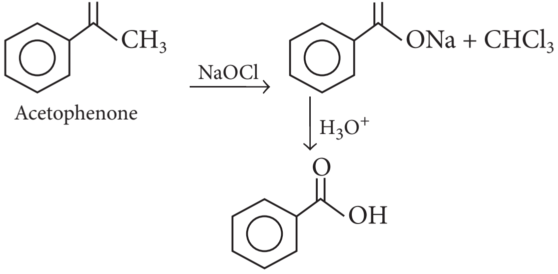
(b) Benzoic acid will react with $NaHCO_3$ to yield sodium benzoate with effervescence of CO_2 whereas phenol does not react with $NaHCO_3$.



Sodium benzoate



129. (i) Acetophenone to benzoic acid :



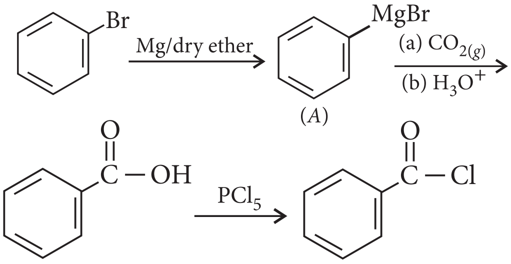
Benzoic acid

(ii) Ethanoic acid to 2-hydroxyethanoic acid.

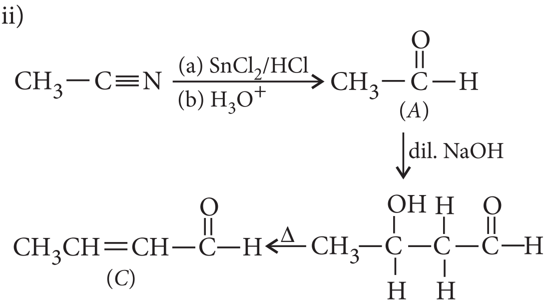
$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[H_2O]{Cl_2/\text{Red P}} \underset{\text{2-Chloroethanoic acid}}{Cl—CH_2—COOH}$$

$$\xrightarrow{NaOH} \underset{\text{2-Hydroxyethanoic acid}}{HO—CH_2—COOH}$$

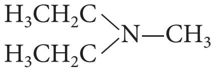
130. (i)



(ii)

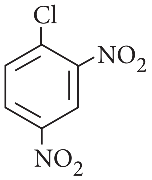


131.



IUPAC name : *N*-Ethyl-*N*-methylethanamine

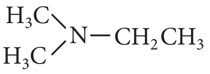
132.



2, 4-Dinitrochlorobenzene

133. *N*-Methylpropan-2-amine (2° amine)

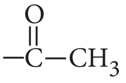
134.



$(H_3C)_2N{-}CH_2CH_3$

N,N-Dimethylethanamine

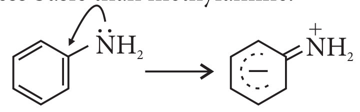
135. (i) After acetylation of aniline, acetanilide is formed in which due to the presence of



$-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ group having –*I* effect, electron density on N-atom decreases and hence, activation effect of aniline gets reduced.

(ii) In aniline, lone pair of electrons of nitrogen is not free for donation because it is involved in resonance. But, in case of methylamine, lone pair of electrons on nitrogen is free for donation. So, aniline is less basic than methylamine.

(a)



(b) $R \rightarrow \ddot{N}H_2$

(iii) Nitration is carried out with conc. HNO_3 in the presence of conc. H_2SO_4. In the presence of these acids, the – NH_2 group of aniline gets protonated and is converted into – $\overset{+}{N}H_3$ group. This positively charged group acts as a strong electron withdrawing and *meta* directing group. Hence, the incoming electrophile goes to *m*-position.

136. (a)

$$\begin{tikzcd}
CH_3{-}COOH \arrow[r, "NH_3/\Delta"] & \underset{(A)}{\underset{\text{Acetamide}}{CH_3CONH_2}} \arrow[d, "Br_2/KOH_{(aq)}", "\substack{\text{Hoffmann}\\\text{bromamide}\\\text{degradation}}"'] \\
\underset{(C)}{\underset{\substack{\text{Methyl}\\\text{isocyanide}}}{CH_3{-}NC}} & \underset{(B)}{\underset{\text{Methylamine}}{CH_3NH_2}} \arrow[l, "CHCl_3 + \text{alc. } KOH", "\substack{\text{Carbylamine}\\\text{reaction}}"']
\end{tikzcd}$$

(b)

$$\begin{tikzcd}
C_6H_5N_2^+BF_4^- \arrow[r, "NaNO_2/Cu", "\Delta"'] & \underset{(A)}{\underset{\text{Nitrobenzene}}{C_6H_5NO_2}} \arrow[d, "Fe/HCl", "\text{Reduction}"'] \\
\underset{(C)}{\underset{\text{Acetanilide}}{C_6H_5NHCOCH_3}} & \underset{(B)}{\underset{\text{Aniline}}{C_6H_5NH_2}} \arrow[l, "CH_3COCl", "\text{Pyridine}"']
\end{tikzcd}$$

137. (i) The two values displayed by Ritu are health consciousness and implementation of her knowledge for the welfare of others.

(ii) Starch is present in bread.

(iii) There are two types of secondary structure of proteins :

(a) α-helix

(b) β-pleated sheet structure

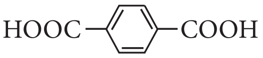
(iv) The two examples of water soluble vitamins are vitamin B complex and vitamin C.

138. Monomers used for getting nylon–6,6, are $HOOC(CH_2)_4COOH$ (adipic acid) and $H_2N(CH_2)_6NH_2$ (hexamethylenediamine).

139. (i) Monomers of dacron :

$HOCH_2{-}CH_2{-}OH$ and

Ethylene glycol



Terephthalic acid

(ii) Monomers of Buna–N :

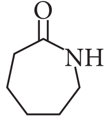
$CH_2{=}CH{-}CH{=}CH_2$

1,3-Butadiene

$H_2C{=}CH{-}CN$

Acrylonitrile

140. (i) Monomer of nylon-6 : Caprolactam;



(ii) Monomer of teflon : Tetrafluoroethene;

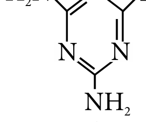
$(CF_2 = CF_2)$

141. (i) Neoprene is formed by the free radical polymerisation of chloroprene.

$CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2$

2-Chloro-1,3-butadiene

(ii) Melamine-formaldehyde polymer is formed by condensation polymerisation of melamine and formaldehyde.

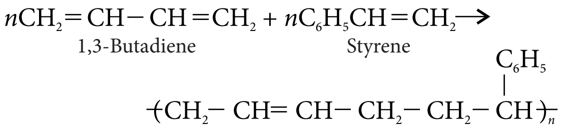


+ HCHO

Formaldehyde

Melamine

(iii) 1,3-Butadiene and styrene are the monomers of Buna-S.



$$\underset{\text{1,3-Butadiene}}{nCH_2{=}CH-CH{=}CH_2} + \underset{\text{Styrene}}{nC_6H_5CH{=}CH_2} \longrightarrow$$

$$\left(CH_2-CH{=}CH-CH_2-CH_2-\overset{\overset{\displaystyle C_6H_5}{|}}{CH} \right)_n$$

142. Monomer used for getting the polymer polyvinyl chloride (PVC) is vinyl chloride ($CH_2{=}CHCl$).

143. Antacids : The compounds which reduce or neutralise acidity and raise the pH to appropriate level in stomach are known as antacids *e.g.*, ranitidine.

144. (i) The antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are called broad spectrum antibiotics.

(ii) Antiseptic : The chemicals which kill or prevent the growth of microorganisms and are applied to the living tissues are called antiseptics.

145. (i) Narrow spectrum antibiotics : The antibiotics that are specifically effective against a limited group of microorganisms are known as narrow spectrum antibiotics.

(ii) Disinfectants : The chemical substances which kill microorganisms or stop their growth but harmful to human tissues are known as disinfectants.

146. (i) The antibiotics which are effective against a single organism or disease are called limited spectrum antibiotics.

(ii) The class of chemical compounds which are used for the treatment of stress, or even severe mental diseases, are known as tranquilizers. They are neurologically active drugs.

147. Cationic detergents : These are quaternary ammonium salts of amines with acetate, chlorides or bromides as anions. Cationic part has long hydrocarbon chain and positive charge lies on nitrogen atom.

e.g., cetyl trimethyl ammonium bromide.

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Name of the Unit	Total Weigh-tage	VSA (1 mark)	SA-I (2 marks)	SA-II (3 marks)	VBQ (4 marks)	LA (5 marks)	Weigh-tage
The Solid Sate	23	1(1) Remembering	---	3(1) Understanding	---		4(2)
Solutions		---	2(1) Remembering	3(1) Evaluation	---	---	5(2)
Electrochemistry		---	---	---	---	5(1) Application	5(1)
Chemical Kinetics		---	2(1) Application	3(1) Application	---	---	5(2)
Surface Chemistry		1(1) Remembering	---	3(1) Evaluation	---	---	4(2)
General Principles and Processes of Isolation of Elements	19	---	---	3(1) Application	---	---	3(1)
The *p*-Block Elements		---	2(1) Understanding	3(1) Application	---	---	5(2)
The *d*- and *f*-Block Elements		1(1) HOTS	---	---	---	5(1) Understanding	6(2)
Coordination Compounds		---	2(1) Application	3(1) HOTS	---	---	5(2)
Haloalkanes and Haloarenes	28	1(1) Evaluation	---	3(1) Understanding	---	---	4(2)
Alcohols, Phenols and Ethers		1(1) HOTS	---	3(1) Understanding	---	---	4(2)
Aldehydes, Ketones and Carboxylic Acids		---	---	---	---	5(1) HOTS	5(1)
Amines		---	2(1) Understanding	3(1) Application	---	---	5(2)
Biomolecules			---	3(1) Remembering	---	---	3(1)
Polymers		---	---	3(1) Understanding	---	---	3(1)
Chemistry in Everyday Life		---	---	---	4(1) Value based question	---	4(1)
Total		**5(5)**	**10(5)**	**36(12)**	**4(1)**	**15(3)**	**70(26)**

Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Define Kraft temperature.

2. The electronic configuration of a transition element in +3 oxidation state is $[Ar]3d^7$. Find out its atomic number.

3. Draw the structure of 4-*tert*-butyl-3-iodoheptane.

4. Give the equation of reaction for the preparation of phenol from cumene.

5. Name the type of semiconductor obtained when silicon is doped with boron.

6. The two complexes of nickel, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$, have different structures but possess same magnetic behaviour. Explain.

OR

A chloride of fourth group cation in qualitative analysis gives a green coloured complex [*A*] in aqueous solution which when treated with ethane-1,2-diamine (*en*) gives pale - yellow solution [*B*] which on subsequent addition of ethane-1,2-diamine turns to blue/purple [*C*] and finally to violet [*D*]. Write the structures of complexes [*A*], [*B*], [*C*] and [*D*].

7. Account for the following :

(i) XeF_2 is linear molecule without a bend.

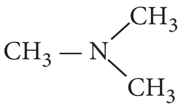
(ii) The electron gain enthalpy with negative sign for fluorine is less than that of chlorine, still fluorine is a stronger oxidising agent than chlorine.

8. Derive the relationship between relative lowering of vapour pressure and mole fraction of the volatile liquid.

9. After 24 hours, only 0.125 g out of the initial quantity of 1 g of a radioactive isotope remains behind. What is its half-life period?

10. Write the IUPAC names of the following :

$C_6H_5CH_2NH_2$,



$CH_3-N(CH_3)_2$

11. The edge length of a unit cell of a metal having molar mass 75 g/mol is 5 Å which crystallises in a cubic lattice. If the density is 2 g/cm^3, then find the radius of the metal atom.

12. (i) A mixture of *X* and *Y* was loaded in the column of silica. It was eluted by alcohol water mixture. Compound *Y* eluted in preference to compound *X*. Compare the extent of adsorption of *X* and *Y* on column.

(ii) Why copper matte is put in silica lined converter? Write the reactions involved?

(iii) Name the method used for the refining of Zr.

13. (i) Complete the following chemical equations :

(a) $NH_4Cl_{(aq.)} + NaNO_{2\,(aq.)} \longrightarrow$

(b) $P_4 + 3NaOH + 3H_2O \longrightarrow$

(ii) Why is $K_{a_2} << K_{a_1}$ for H_2SO_4 in water?

14. Write the correct formulae for the following coordination compounds :

(i) $CrCl_3.6H_2O$ (violet with 3 chloride ions precipitated as AgCl)

(ii) $CrCl_3.6H_2O$ (light green colour, with 2 chloride ions precipitated as AgCl)

(iii) $CrCl_3.6H_2O$ (dark green colour, with 1 chloride ion precipitated as AgCl)

15. Give reasons for the following observations :

(i) *p*-Dichlorobenzene has higher melting point than those of *o*- and *m*-isomers.

(ii) Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(iii) The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkene is the major product.

16. (i) Why does leather get hardened after tanning?

(ii) On the basis of Hardy-Schulze rule explain why the coagulating power of phosphate is higher than chloride.

(iii) Do the vital functions of the body such as digestion get affected during fever? Explain your answer.

17. Calculate the mass of a non-volatile solute (molar mass 40 g/mol) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

OR

At 300 K, 36 g of glucose ($C_6H_{12}O_6$) present per litre in its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of another glucose solution is 1.52 bar at the same temperature, calculate the concentration of the other solution.

18. Carry out the following conversions :

(i) Phenol to benzoquinone

(ii) Propanone to 2-methylpropan-2-ol

(iii) Propene to propan-2-ol

19. (i) Illustrate the following reactions :

(a) Hoffmann bromamide degradation reaction

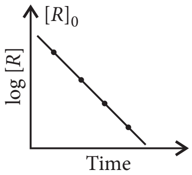
(b) Coupling reaction

(ii) Write a chemical test to distinguish between aniline and methylamine.

20. (i) Name the common types of secondary structure of proteins and give one point of difference.

(ii) Give one structural difference between amylose and amylopectin.

21. Observe the graph in diagram and answer the following questions :



(i) If slope is equal to -2.0×10^{-6} sec^{-1}, what will be the value of rate constant?

(ii) How does the half-life of zero order reaction relate to its rate constant?

22. (i) Classify the following as addition and condensation polymers : Terylene, Bakelite, Polyvinyl chloride, Polythene.

(ii) Explain the difference between Buna-N and Buna-S.

23. Ali's brother likes taking medicines. He sometimes even takes cough syrups even when he is not ill. One such day, he took cough syrup when he was healthy. After some time he started feeling nausea, headache and his body started itching. Ali's father did not take him to the doctor and wanted to give medicine on his own. Ali insisted that his father should not give medicine to his brother on his own but should take him to a doctor.

After reading the above passage, answer the following questions :

(i) Mention the values shown by Ali.

(ii) Why did his body start itching and what kind of medicine will doctor prescribe him?

(iii) Why medicines should not be taken without consulting doctor?

(iv) Give one point of difference between agonist and antagonist.

24. (i) State the relationship amongst cell constant of a cell, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solution related to conductivity of its solution?

(ii) A voltaic cell is set up at 25°C with the following half cell; Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50 M). Calculate the cell voltage.

$(E^{\circ}_{Ni^{2+}/Ni} = -0.25\text{ V},\ E^{\circ}_{Al^{3+}/Al} = -1.66\text{ V})$

OR

(i) Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

(ii) State Faraday's laws of electrolysis. How much charge in terms of Faraday is required for reduction of 1 mol of $Cr_2O_7^{2-}$ to Cr^{3+}?

25. (i) Is the variability in oxidation number of transition elements different from that of non-transition elements? Illustrate with examples.

(ii) Give reasons :

(a) *d*-block elements exhibit more oxidation states than *f*-block elements.

(b) Orange solution of potassium dichromate turns yellow on adding sodium hydroxide to it.

(c) Zirconium (Z = 40) and Hafnium (Z = 72) have almost similar atomic radii.

OR

(i) Describe the preparation of potassium permanganate from pyrolusite ore. Write balanced chemical equation for one reaction to show the oxidising nature of potassium permanganate.

(ii) Draw the structures of chromate and dichromate ions.

26. (i) A ketone *A* which undergoes haloform reaction gives compound *B* on reduction. *B* on heating with sulphuric acid gives compound *C*, which forms mono-ozonide *D*. The compound *D* on hydrolysis in presence of zinc dust gives only acetaldehyde. Write the structures and IUPAC names of *A*, *B* and *C*. Write down the reactions involved.

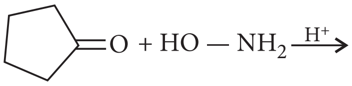
(ii) Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents :

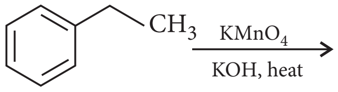
(a) PhMgBr and then H_3O^+.

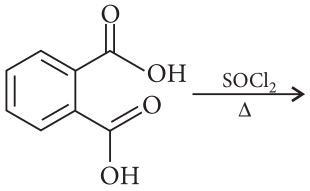
(b) Tollens' reagent.

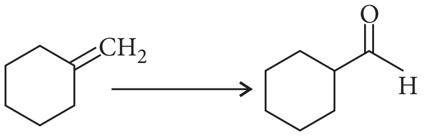
OR

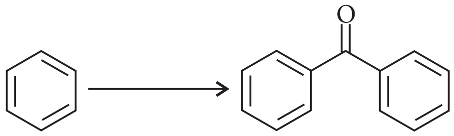
Complete each synthesis by giving missing starting material, reagent or products :

(a) 

(b) 

(c) 

(d) 

(e) 

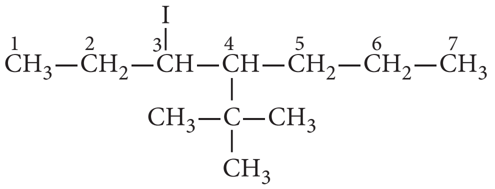
Detailed Solutions

1. The temperature above which formation of micelles takes place is called Kraft temperature.

2. Atomic number = Total number of electrons in neutral atom

= 18 + 7 + 3 = 28

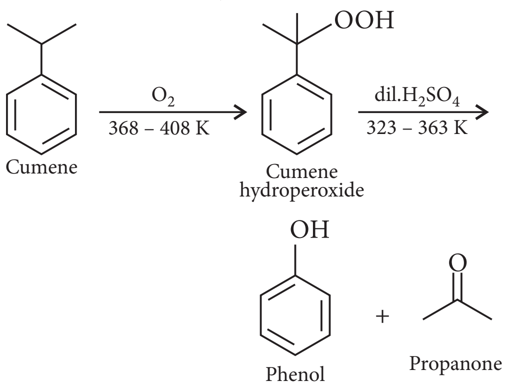
3.



$$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{\underset{}{C}}H(I)-\overset{4}{C}H(C(CH_3)_3)-\overset{5}{C}H_2-\overset{6}{C}H_2-\overset{7}{C}H_3$$

4-*tert*-butyl-3-iodoheptane

4.

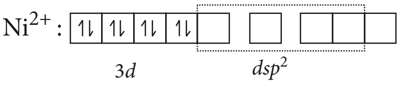


5. When silicon is doped with boron, *p*-type semiconductor is obtained.

6. $[Ni(CN)_4]^{2-}$ contains Ni^{2+} ion ($3d^8$ system) dsp^2 hybridisation and square planar geometry.

Ni^{2+} : [Ar] $3d^84s^04p^0$

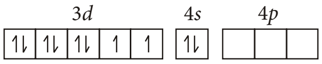
Ni^{2+} in the presence of strong field (CN^-) ligand



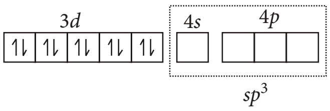
$[Ni(CO)_4]$ contains Ni^0 ($3d^84s^2$ system)

sp^3 hybridisation and tetrahedral geometry,

Ni(0) : $3d^84s^2$



In the presence of strong field ligand (CO) two electrons of 4*s* orbital shift to 3*d* orbitals.



It has no unpaired electrons hence, it is diamagnetic. Thus, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$ have different structures but same magnetic behaviour.

OR

Aqueous solution of $NiCl_2$ gives a green colour due to the formation of following complex :

$$NiCl_2 + 6H_2O \rightarrow \underset{(A)}{[Ni(H_2O)_6]^{2+}_{(aq)}} + 2Cl^-$$

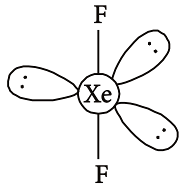
When ethane-1,2-diamine (*en*) is added to above complex, the colour changes to pale-blue, which on further addition of ethane-1,2-diamine changes to blue/purple and finally to violet. This occurs due to the following ligand replacement reactions :

$$\underset{(A)}{[Ni(H_2O)_6]^{2+}_{(aq)}} + en_{(aq)} \longrightarrow \underset{\text{Pale blue }(B)}{[Ni(H_2O)_4(en)]^{2+}_{(aq)}} + 2H_2O$$

$$[Ni(H_2O)_4(en)]^{2+}_{(aq)} + en_{(aq)} \longrightarrow \underset{\text{Blue/purple }(C)}{[Ni(H_2O)_2(en)_2]^{2+}_{(aq)}} + 2H_2O$$

$$[Ni(H_2O)_2(en)_2]^{2+}_{(aq)} + en_{(aq)} \longrightarrow \underset{\text{Violet }(D)}{[Ni(en)_3]^{2+}_{(aq)}} + 2H_2O$$

7. (i) The electronic arrangement in XeF_2 is trigonal bipyramidal. The shape is linear because the lone pairs prefer to occupy the equatorial positions. The molecule XeF_2 has 3 lone-pairs and 2 bond-pairs.



(ii) Fluorine has higher standard reduction potential than chlorine, so it is more easily reduced and hence, it is a stronger oxidising agent than chlorine.

8. Let us assume a binary solution in which the mole fraction of the solvent be x_1 and that of the solute be x_2, p_1 be the vapour pressure of the solvent and p_1° be the vapour pressure of the solvent in pure state.

According to Raoult's law : $p_1 = x_1p_1^\circ$ ...(i)

The decrease in vapour pressure of the solvent (Δp_1) is given by :

$\Rightarrow\ \Delta p_1 = p_1^\circ - p_1$

$\Rightarrow\ \Delta p_1 = p_1^\circ - p_1^\circ x_1$ [using equation (i)]

$\Rightarrow\ \Delta p_1 = p_1^\circ(1 - x_1)$

Since we have assumed the solution to be binary solution, $x_2 = 1 - x_1$

$\Rightarrow\ \Delta p_1 = p_1^\circ x_2 \ \Rightarrow\ x_2 = \Delta p_1/p_1^\circ$

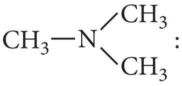
9. $a = 1$ g, $a - x = 0.125$ g, $t = 24$ hours

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

$$k = \frac{2.303}{24}\log\frac{1}{0.125} = 0.0866\ \text{hr}^{-1}$$

$$\text{Also, } t_{1/2} = \frac{0.693}{k};\ t_{1/2} = \frac{0.693}{0.0866} = 8\ \text{hours}$$

10. $C_6H_5CH_2NH_2$: 1-Phenylmethanamine



$CH_3{-}N(CH_3)_2$: *N, N*-Dimethylmethanamine

11. $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

$$Z = \frac{2 \times (5 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{75} = 2$$

∴ The cubic lattice is body-centred.

For *bcc* lattice, $r = \dfrac{\sqrt{3}}{4}a$;

$$r = \frac{\sqrt{3}}{4} \times 5 = 2.165\ \text{Å}$$

12. (i) Extent of adsorption is inversely proportional to elution. Hence, *X* is more strongly adsorbed than *Y*.

(ii) Copper matte contains small amount of FeO as impurity which is removed as $FeSiO_3$ slag when reacts with silica. Therefore, it is put in silica lined converter.

$$FeO + SiO_2 \longrightarrow \underset{\text{(slag)}}{FeSiO_3}$$

(iii) van Arkel method is used for refining of Zr.

13. (i) (a) $NH_4Cl_{(aq)} + NaNO_{2(aq)} \longrightarrow N_{2(g)} + 2H_2O_{(l)} + NaCl_{(aq)}$

(b) $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$

(ii) H_2SO_4 is a very strong acid in water because of its first ionisation to H_3O^+ and HSO_4^-. The ionisation of HSO_4^- to H_3O^+ and SO_4^{2-} is very less as it is difficult to remove a proton from a negatively charged ion. Therefore, $K_{a_2} << K_{a_1}$.

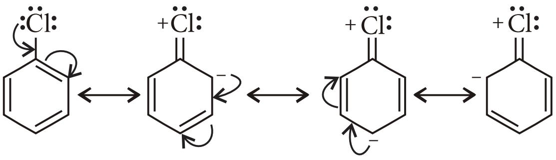
14. (i) $[Cr(H_2O)_6]Cl_3$

(ii) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

(iii) $[Cr(H_2O)_4(Cl)_2]Cl \cdot 2H_2O$

15. (i) The melting point of *p*-dichlorobenzene is higher than that of *o*-and *m*-isomers. This is because, *p*-isomer has symmetrical structure and therefore, its molecules can easily pack closely in crystal lattice. Hence, it has stronger intermolecular forces of attraction than *o*- and *m*-isomers.

(ii) In haloarenes the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



C – Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarenes is difficult than in haloalkanes and therefore, they are less reactive towards nucleophilic substitution reaction.

(iii) Alkoxide ion present in alcoholic KOH is not only a strong nucleophile but also a strong base. So, it reacts with alkyl halide to give alkene as the major product.

$$R{-}CH_2{-}CH_2{-}Cl \xrightarrow{\text{alc. KOH}} R{-}CH{=}CH_2$$

On the other hand, aqueous KOH is a good nucleophile and when it reacts with alkyl chloride it forms alcohol.

$$R{-}CH_2{-}CH_2Cl \xrightarrow{aq.\ \text{KOH}} R{-}CH_2{-}CH_2{-}OH$$

16. (i) Animal hides are colloidal in nature having positively charged particles. When soaked in tannin which contains negatively charged colloidal particles, mutual coagulation occurs, which results in the hardening of leather.

(ii) Greater the valency of flocculating ion added, greater is its power to cause precipitation. Valency of phosphate ion is three while that of chloride is one. Hence, phosphate has higher coagulating power than chloride.

(iii) The optimum temperature range for enzymatic activity is 298-310 K. Hence, beyond this temperature range (during fever), the activity of enzymes may be affected.

17. Vapour pressure of pure liquid = $p°$

80% of $p° = p_s = 80 \times p°/100 = 0.8\,p°$

$p_s = p° \times x_{\text{solute}}$

Mass of solute = x g

Mass of solvent = 114 g

Molar mass of solute = 40 g/mol

Molar mass of solvent (octane) = 114 g/mol

Number of moles of solute = $x/40 = 0.025x$

Number of moles of solvent = 114/114 = 1 mole

Mole fraction of solvent = $1/(1 + 0.025x)$

$0.8p° = p° \times 1/(1 + 0.025x)$

or, $(1 + 0.025x)\,0.8p° = p°$ ...(i)

On dividing equation (i) by $0.8p°$ we get,

$1 + 0.025x = 1.25$

On subtracting both side by 1 we get, $0.025x = 0.25$

Now, dividing by 0.025, we get $x = 10$ g

OR

From formula of osmotic pressure, $\pi V = CRT$

where, π = osmotic pressure

V = Volume of solution, C = Concentration

R = gas constant, T = Temperature

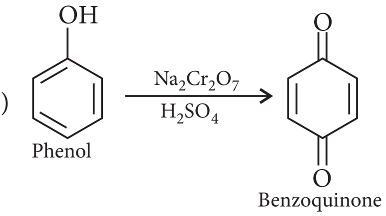
So, $4.98 = 36/180 \times R \times 300 = 60R$ ...(i)

$1.52 = C \times R \times 300$ ...(ii)

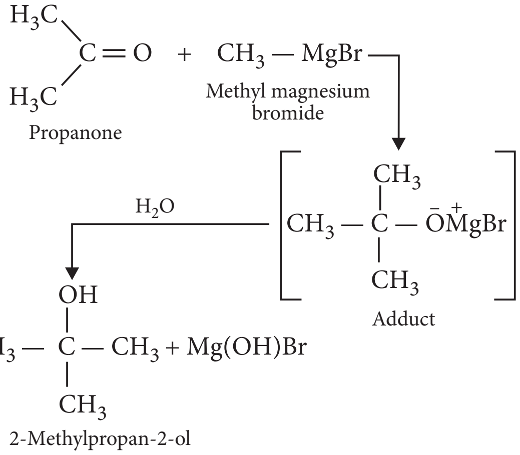
Putting the value of R from (i) in (ii) we get,

$C = 0.061$ M

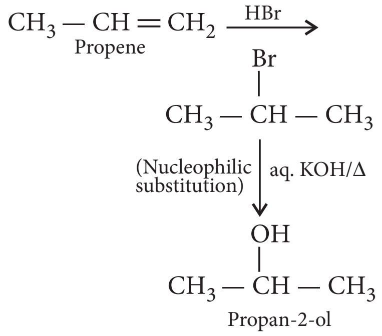
18. (i)



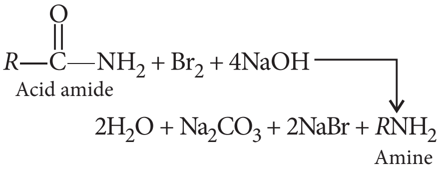
(ii)



(iii)



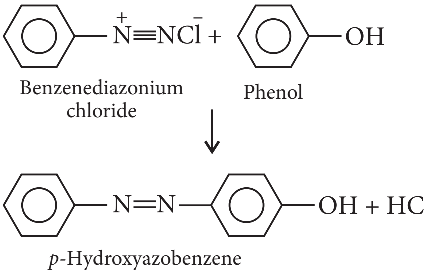
19. (i) (a) Hoffmann bromamide degradation :



$$R{-}\overset{O}{\overset{\|}{C}}{-}NH_2 + Br_2 + 4NaOH \longrightarrow 2H_2O + Na_2CO_3 + 2NaBr + RNH_2$$

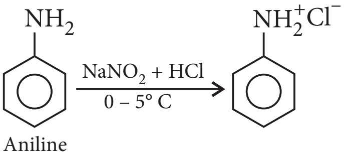
Acid amide on reaction with bromine and alkali such as NaOH, an amine is formed which has one carbon atom lesser than the initial amide molecule.

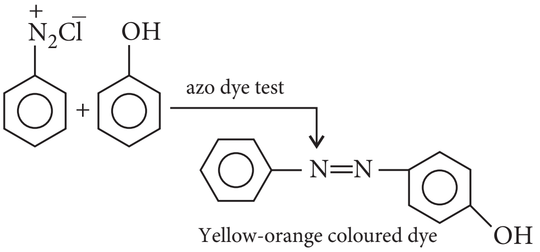
(b) Coupling reaction :



When arenediazonium chloride reacts with electron rich species like phenol, it undergoes coupling reaction to form p-hydroxyazobenzene.

(ii)





$\underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow[\text{dye test}]{\text{azo}}$ No reaction

Aniline will give azo dye test whereas methylamine will not.

20. (i) α - helix structure : In this type of structure, the long peptide chains undergo formation of H - bonding between the $\overset{\overset{\displaystyle \mathrm{O}}{\|}}{—\mathrm{C}—}$ and $\overset{\overset{\displaystyle \mathrm{H}}{|}}{—\mathrm{N}—}$ bonds of different peptide groups within the same chain. As a result the polypeptide chain gets coiled up to form a right handed helix.

β-pleated sheet : n this structure, the long peptide chains lie side by side to form a flat sheet. Each chain is held by the two neighbouring chains by H-bonds (N – H .... O═C).

(ii) Amylose is a straight chain polymer of *D*-glucose whereas amylopectin is branched polymer.

21. (i) From the graph, it is clear that it is first order kinetics.

For first order,

$$\log[R] = \frac{-kt}{2.303} + \log[R]_0$$

Comparing it with general straight line equation,

$y = mx + c$

$$\text{Slope}(m) = -\frac{k}{2.303}$$

$k = -2.303 \times -2.0 \times 10^{-6}\ \text{s}^{-1} = 4.606 \times 10^{-6}\ \text{s}^{-1}$

(ii) Half-life of zero order reaction is directly proportional to initial concentration as shown,

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

22. (i) Addition polymers : Polyvinyl chloride, polythene

Condensation polymers : Terylene, Bakelite

(ii) Buna-N is a copolymer of 1,3-butadiene and acrylonitrile and Buna-S is a copolymer of 1,3-butadiene and styrene.

23. (i) Caring, empathetic, awareness, application of knowledge at right place.

(ii) Because of production of histamine his body starts itching. So, doctor will prescribe antihistamine.

(iii) Medicines should not be taken without consulting doctor because medicines can be potent poisons which depends upon how vital that medicine is and in how much quantity it is taken.

(iv) An agonist is a chemical that binds to a receptor and activates the receptor to produce a biological response whereas antagonist is a drug that blocks a receptor.

24. (i) Conductivity of the solution is the ratio of cell constant and resistance of a cell and can be written as

$$\kappa = \frac{G}{R}$$

Molar conductivity of a solution is related to conductivity as,

$$\Lambda_m = \frac{1000 \times \kappa}{C}$$

(ii) $$E_{\text{Ni}^{2+}/\text{Ni}} = -0.25 - \frac{0.0591}{2}\log\frac{1}{0.50} = -0.259\ \text{V}$$

$$E_{\text{Al}^{3+}/\text{Al}} = -1.66 - \frac{0.0591}{3}\log\frac{1}{0.001} = -1.719\ \text{V}$$

$$E_{\text{cell}} = -0.259\ \text{V} - (-1.719\ \text{V}) = 1.46\ \text{V}$$

OR

(i) $$E_{\text{H}^+/1/2\text{H}_2} = E^\circ_{\text{H}^+/1/2\text{H}_2} - \frac{0.0591}{n}\log\frac{1}{[\text{H}^+]}$$

$$E_{\text{H}^+/1/2\text{H}_2} = 0 - \frac{0.0591}{1}\log\frac{1}{10^{-10}} = -0.591\ \text{V}$$

(ii) Faraday's first law of electrolysis states that, the chemical deposition due to flow of current through an electrolyte is directly proportional to the quantity of electricity (coulombs) passed through it, *i.e.*, $w \propto Q$ or $w = ZQ$.

Faraday's second law of electrolysis states that, when the same quantity of electricity is passed through several electrolytes, the mass of the substances deposited are proportional to their respective chemical equivalent or equivalent weight.

$$\text{Cr}_2\text{O}_7^{2-} + 3e^- \longrightarrow \text{Cr}^{3+}$$

Charge carried by 3 moles of electrons

$= 3 \times (1.6021 \times 10^{-19}\ \text{C}) \times (6.022 \times 10^{23})$

$= 3 \times 96487\ \text{C} = 3\text{F}$

25. (i) Variability of oxidation states of transition metals arises due to incomplete filling of *d*-orbitals and it differs from each other by unity *e.g.*, $V^{(V)}$, $V^{(IV)}$, $V^{(III)}$, $V^{(II)}$. In *p*-block elements oxidation states differ generally by a unit of two. *e.g.*, Sn(II), Sn(IV), PCl_3, PCl_5, etc.

(ii) (a) *d*-block elements exhibit more oxidation states because of comparable energy gap between $(n-1)d$ and *ns* subshell whereas *f*-block elements have large energy gap between $(n-2)f$ and $(n-1)d$ subshell.

(b) When an alkali such as NaOH is added to orange solution of potassium dichromate, it turns yellow due to the formation of chromate.

$$\underset{\text{Orange}}{K_2Cr_2O_7} + 2NaOH \longrightarrow K_2CrO_4 + \underset{\text{Yellow}}{Na_2CrO_4} + H_2O$$

(c) Due to lanthanoid contraction, Zr (230 pm) and Hf (225 pm) have almost same atomic radii.

OR

(i) Preparation of potassium permanganate : Potassium permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidising agent like KNO_3 to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.

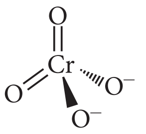
$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

$$3K_2MnO_4 + 4HCl \longrightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4KCl$$

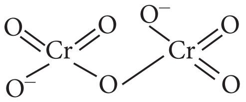
A reaction to show oxidising nature of potassium permaganate is,

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(ii)



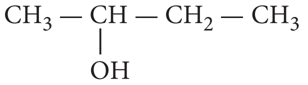
Chromate ion



Dichromate ion

26. (i) $\underset{\text{2-butene}}{CH_3CH{=}CHCH_3}$ (*C*)

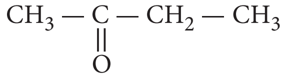
The compound *C* is obtained by dehydration of *B*, thus the latter should be



$$\underset{\underset{\text{2-butanol}}{OH}}{CH_3-\underset{|}{CH}-CH_2-CH_3}$$

(*B*)

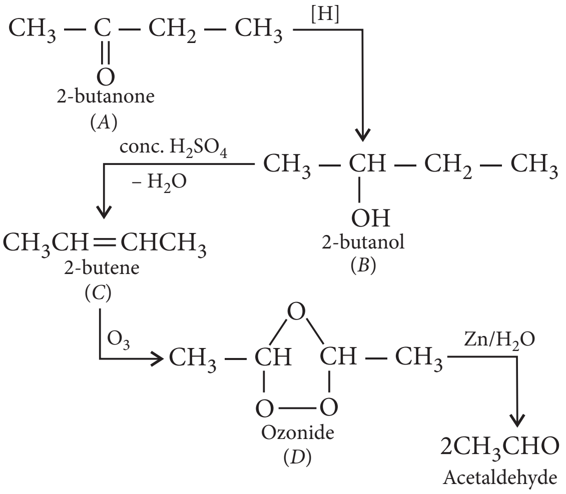
Finally, *B* is obtained by the reduction of *A*. Hence compound *A* should be



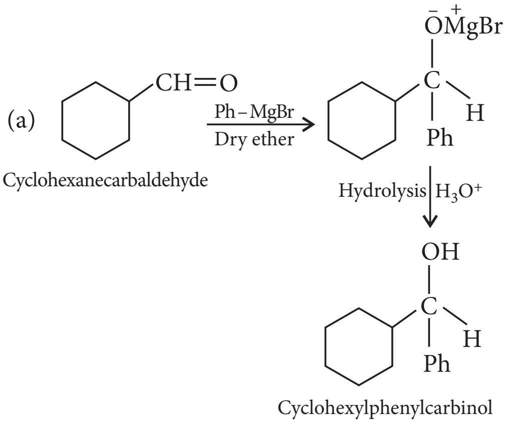
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$$

2-butanone (*A*)

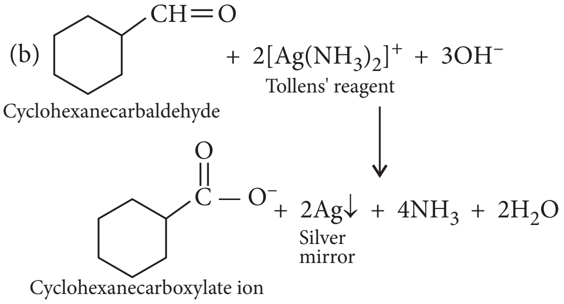
The equations involved are as follows :



(ii) (a)

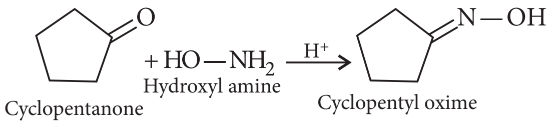


(b)

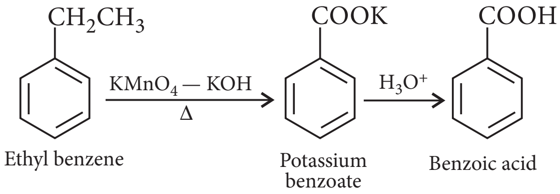


OR

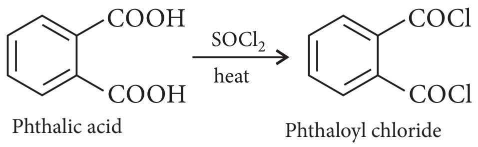
(a)


O
+ HO—NH₂
Hydroxyl amine
H⁺
N—OH
Cyclopentanone
Cyclopentyl oxime

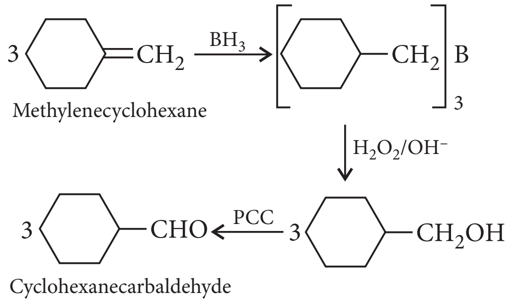
(b)


CH₂CH₃
KMnO₄ — KOH
Δ
COOK
H₃O⁺
COOH
Ethyl benzene
Potassium benzoate
Benzoic acid

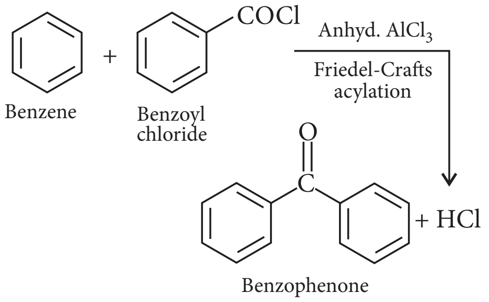
(c)


COOH
COOH
SOCl₂
heat
COCl
COCl
Phthalic acid
Phthaloyl chloride

(d)


3
=CH₂
BH₃
CH₂
B
3
Methylenecyclohexane
H₂O₂/OH⁻
3
CHO
PCC
3
CH₂OH
Cyclohexanecarbaldehyde

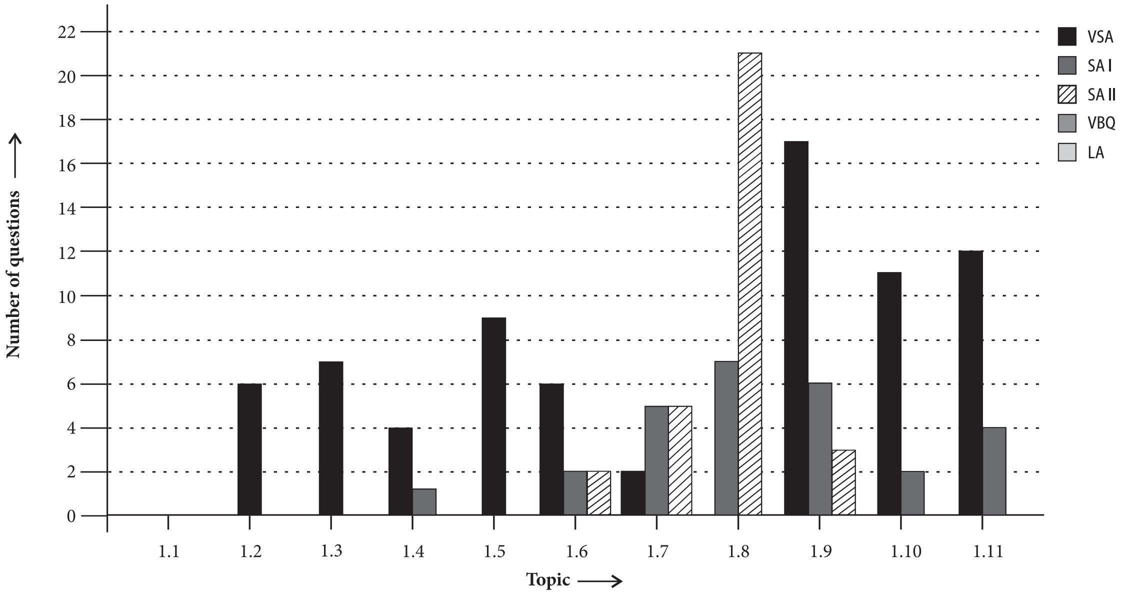
(e)


+
COCl
Anhyd. AlCl₃
Friedel-Crafts acylation
Benzene
Benzoyl chloride
O
C
+ HCl
Benzophenone

01

The Solid State

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)

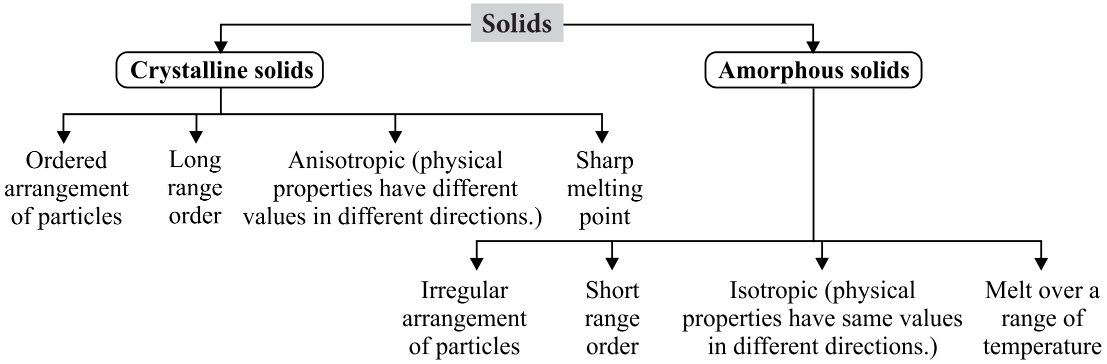


- Maximum total weightage is of *Calculations Involving Unit Cell Dimensions.*
- Maximum VSA type questions were asked from *Imperfections in Solids.*
- Maximum SA I and SA II type questions were asked from *Calculations Involving Unit Cell Dimensions.*

QUICK RECAP

- **Solids :** They have definite mass, volume and shape due to the fixed position of their constituent particles, small intermolecular distances and strong intermolecular forces between them.

- **Solids :** They can be classified as crystalline or amorphous on the basis of the nature of order present in the arrangement of their constituent particles.



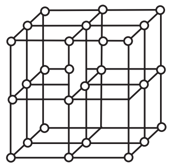
- **Types of crystalline solids :** Classification of crystalline solids on the basis of nature of intermolecular forces :

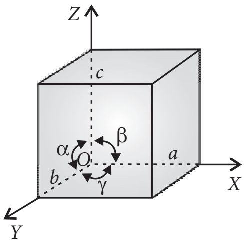
	Ionic solid	Metallic solid	Covalent solid	Molecular solid
1.	**Constituent particles are held by :** Ionic bonds	Metallic bonds	Covalent bonds	Weak van der Waals forces or hydrogen bonds
2.	**Constituent particles :** Ions	Metal ions and sea of electrons	Non-metal atoms	Atoms or molecules
3.	**Physical nature :** Hard and brittle	Hard, malleable and ductile	Hard	Soft
4.	**Electrical conductivity :** Insulator	Conductor	Insulator except graphite	Insulator
5.	**Melting point :** High	Fairly high	Very high	Low
6.	**Examples :** NaCl, ZnS, CaF_2, MgO, etc.	Fe, Cu, Ag, Na, Mg, etc.	Diamond, graphite, quartz, carborundum, AlN, etc.	Ice, I_2, P_4, S_8, naphthalene, camphor, solid CO_2 (dry ice), etc.

- **Crystal lattice :** The regular three dimensional arrangement of constituent particles in a crystal is called *crystal lattice.*

- **Lattice points :** Constituent particles (atoms, molecules or ions) of a solid crystal are represented as points which are known as *lattice points* or *lattice sites.*

- **Unit cell :** The smallest repeating pattern which represents structure of a crystalline solid is called *unit cell.*


A portion of a three dimensional cubic lattice and its unit cell



- It is the smallest portion of a crystal lattice which when repeated in different directions generates the *entire lattice.*
- A unit cell has characteristic dimensions along the three edges *a*, *b* and *c* and interfacial angles α (between *b* and *c*), β (between *a* and *c*) and γ (between *a* and *b*).
- On the basis of primitives or axial distances and interfacial angles there are *seven crystal systems* and *fourteen Bravais lattices.*

Seven primitive unit cells or crystal systems

Crystal system	Axial distances or edge lengths	Axial angles	Examples
Cubic (*most symmetrical*)	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Cu, Zinc blende, KCl, NaCl
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Sn(White tin), SnO_2, TiO_2, $CaSO_4$
Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°; \beta \neq 90°$	Monoclinic sulphur, $PbCrO_4$, $Na_2SO_4.10H_2O$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°; \gamma = 120°$	Graphite, ZnO, CdS
Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$CaCO_3$ (Calcite), HgS (Cinnabar)
Triclinic (*most unsymmetrical*)	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4\cdot5H_2O$, H_3BO_3

Unit cell constant (*Z*) for different types of unit cells

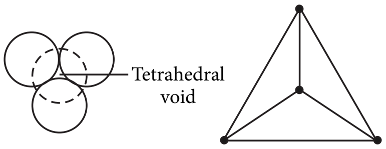
Type of unit cell	Simple cubic	*bcc*	*ccp/fcc*	*hcp*
No. of particles (*Z*)	$8\times\frac{1}{8}=1$	$8\times\frac{1}{8}+1=2$	$8\times\frac{1}{8}+6\times\frac{1}{2}=4$	$12\times\frac{1}{6}+2\times\frac{1}{2}+3=6$

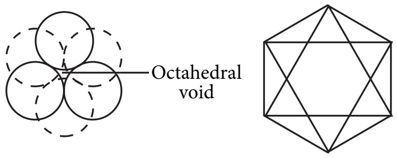
Packing in solids

	Arrangement	Space occupied	C. No.	Relation between *d, a* and *r*	Examples
Simple cubic packing (*scp*)	*AAA* ... type	52.4%	6	$d = a = 2r, r = \frac{a}{2}$	Po
Hexagonal close packing (*hcp*)	*ABABAB* ... type	74%	12	$a = 2r$ $h = 2\times\sqrt{\frac{2}{3}}\,a$	Mg, Zn, Mo, V, Cd
Cubic close packing (*ccp*) or Face centred cubic (*fcc*)	*ABCABC* ... type	74%	12	$d = 2r = \frac{a}{\sqrt{2}}$, $r = \frac{a}{2\sqrt{2}}$	Cu, Ag, Au, Ni, Pt, etc.

Body centred cubic packing (*bcc*)	The spheres in square close packing are slightly opened up, in second layer, the spheres are at the top of hollows and third layer is exactly over the first layer and so on.	68%	8	$d = 2r = \frac{\sqrt{3}a}{2}$, $r = \frac{\sqrt{3}a}{4}$	Li, Na, K, Rb, Cs, Ba, Cd, Fe, Mn, etc.

- In a unit cell some empty space exists between spheres, this is called *void space* or *hole*, also called *interstitial void*, or *interstices*.
- Two types of interstitial voids are present in three dimensional close packing systems :
  - **Tetrahedral voids :** These are holes or interstices surrounded by four spheres present at the corners of a tetrahedron.
  - **Octahedral voids :** These are holes surrounded by six spheres located on a regular octahedron.





- If N is the number of close packed spheres, then the number of octahedral voids generated = N, the number of tetrahedral voids generated = $2N$
- Radius (r) of tetrahedral void = 0.225 R; Radius (r) of octahedral void = 0.414 R where R is the radius of the spheres in close packing.
- **Radius ratio rules :** For the stability of an ionic compound, each cation should be surrounded by maximum number of anions and *vice versa* for maximum electrostatic forces of attraction.

$$\text{Radius ratio} = \frac{\text{Radius of the cation } (r_+)}{\text{Radius of the anion } (r_-)}$$

Radius ratio	C. No.	Structural arrangement	Example
0.155 – 0.225	3	Planar triangular	Boron trioxide (B_2O_3)
0.225 – 0.414	4	Tetrahedral	Sphalerite (ZnS)
0.414 – 0.732	6	Octahedral	Rock salt (NaCl)
0.732 – 1.0	8	Body centred cubic	Caesium chloride (CsCl)

- **Calculations involving unit cell dimensions :**

  $\rho = \frac{Z \times M}{a^3 \times N_A} \times 10^{-30}$ g cm^{-3} where Z = no. of atoms per unit cell, a = edge length in pm, ρ = density of solid, M = molar mass and N_A = Avogadro's no.
- **Imperfections in solids :** Any deviation from the perfectly ordered arrangement of constituent particles in a crystal is called *imperfection* or *defect*.

Imperfections/Defects in Solids

Point defects
Deviations from ideal arrangement around a point or an atom.

Line defects
Deviations from ideal arrangement in entire rows of lattice points.

Stoichiometric/Intrinsic/Thermodynamic defects
Do not disturb stoichiometry of solid.

Impurity defects
Arise when foreign atoms are present at lattice site *e.g.*, $SrCl_2$, $CdCl_2$, AgCl etc.

Non-stoichiometric defects
Disturb stoichiometry of solids.

Vacancy defect : Arises when lattice sites are vacant. Decreases density, shown by non-ionic solids.

Interstitial defect : Arises when constituent particles occupy interstitial site. Increases density, shown by non-ionic solids.

Frenkel defect : Smaller ion (usually cation) dislocates from its normal site to an interstitial site. Does not change density, shown by ionic solids, *e.g.*, ZnS, AgCl, AgBr, AgI, etc.

Schottky defect : Arises when equal number of cations and anions are missing. Decreases density, shown by ionic solids, *e.g.*, NaCl, KCl, CsCl, AgBr, etc.

Metal excess defect

Metal deficiency defect
Arises when metal shows variable valency *e.g.*, Fe^{2+}, Fe^{3+}

Due to anionic vacancies
A negative ion is missing from its lattice site, leaving a 'hole' which is occupied by an electron to maintain electrical neutrality, *e.g.*, LiCl, NaCl

Due to the presence of extra cations
Usually arises when metal oxides are heated, *e.g.*, ZnO.

- **Electrical properties :** The electrical conductivity of solids varies from 10^{-20} to 10^{7} $ohm^{-1}\ m^{-1}$. So on the basis of electrical conductivity solids are classified as :

Solids

Conductors
Allow the passage of electric current.
Conductivity : $10^{4} - 10^{7}$ $ohm^{-1}m^{-1}$

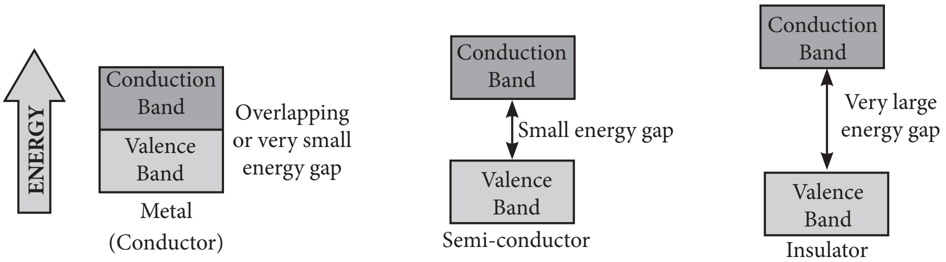
Semi-conductors
Conduct electricity due to presence of impurities.
Conductivity : 10^{-6} to 10^{4} $ohm^{-1}m^{-1}$

Insulators
Do not allow the passage of electric current.
Conductivity : $10^{-20} - 10^{-10}$ $ohm^{-1}\ m^{-1}$

Metallic conductor
Conducts electricity in solid as well as molten state. *e.g.*, Cu, Ag.

Electrolytic conductor
Conducts electricity only in molten state or aqueous solution. *e.g.*, NaCl, KCl.

- **Distinction among metals, insulators and semi-conductors :**



Electrical conductivity of semi-conductors increases with rise in temperature because more electrons can jump to the conduction band.

- **Doping :** It is a process of adding an appropriate amount of suitable impurity to increase the conductivity of intrinsic semiconductors.
- **By doping with electron rich impurities**, *e.g.*, group 14 elements like Si or Ge with group 15 elements like P, As etc. Free electrons become available which increase conductivity. Such solids are called *n-type semiconductors*.
- **By doping with electrons deficit impurities**, *e.g.*, group 14 elements like Si or Ge with group 13 elements like B, Al or Ga. As a result, holes are created. Electrons move to occupy the holes. Thus, holes move towards negatively charged plate as if they carry positive charge. These are called *p-type semiconductors*.
- **Magnetic properties :**

Solids

Paramagnetic

- Possess permanent dipole and attracted by magnetic field.
- They contain unpaired electrons.

e.g., Cu^{2+}, Fe^{3+}, Cr^{3+}, O_2, etc.

Diamagnetic

- Weakly repelled by magnetic field.
- These materials have all paired electrons.

e.g., NaCl, water, benzene, etc.

Ferromagnetic

- Strongly attracted by magnetic field and show permanent magnetism even when magnetic field is removed.
- Magnetic moment of domains in the same direction, ↑↑↑↑

e.g., Fe, Co, Ni, CrO_2, etc.

Antiferromagnetism

- Expected to possess paramagnetism or ferromagnetism but magnetic moment of domains in a compensatory way so as to give a net zero magnetic moment, ↑↓↑↓

e.g., MnO, etc.

Ferrimagnetism

- Expected to have large magnetism but actually have small net magnetic moment as magnetic moment of domains are aligned in parallel and anti-parallel directions in unequal number. ↑↑↓↑↑↓

e.g., Fe_3O_4, $MgFe_2O_4$ and $ZnFe_2O_4$, etc.

- These substances lose ferrimagnetism on heating and become paramagnetic.

Previous Years' CBSE Board Questions

1.2 Amorphous and Crystalline Solids

VSA (1 mark)

1. Why are crystalline solids anisotropic? (*AI 2014C*)

2. Some of the glass objects recovered from ancient monuments look milky instead of being transparent. Why? *(1/3, AI 2012C)*

3. "Crystalline solids are anisotropic in nature." What does this statement mean? *(Delhi, Foreign 2011)*

4. Why is glass considered supercooled liquid? *(AI 2008C)*

5. Assign reason for the following :

Some of the very old glass objects appear slightly milky instead of being transparent. *(1/3, AI 2007)*

1.3 Classification of Crystalline Solids

VSA (1 mark)

6. Give an example each of a molecular solid and an ionic solid. *(AI 2016)*

7. Which one of the following is an example of molecular solid :

CO_2 or SiO_2? *(1/3, Foreign 2014)*

8. Write a feature which will distinguish a metallic solid from an ionic solid. *(Delhi 2010)*

9. What type of interactions holds the molecules together in a polar molecular solid? *(AI 2010)*

10. Write a distinguishing feature of metallic solids. *(AI 2010)*

11. How do metallic and ionic substances differ in conducting electricity? *(AI 2009)*

12. "Stability of a crystal is related to the magnitude of its melting point." How? *(AI 2009C)*

1.4 Crystal Lattices and Unit Cells

VSA (1 mark)

13. Define primitive unit cells. *(AI 2015,Delhi 2009)*

14. How will you distinguish between the following pair of terms :
Crystal lattice and unit cell? *(AI 2014)*

15. Define crystal lattice. *(AI 2010C)*

SA I (2 marks)

16. Name the parameters that characterise a unit cell. *(AI 2009C)*

1.5 Number of Atoms in a Unit Cell

VSA (1 mark)

17. How many atoms per unit cell (Z) are present in *bcc* unit cell? *(Delhi 2014C, 2007)*

18. How many atoms constitute one unit cell of a face-centred cubic crystal? *(Delhi 2013,AI 2009)*

19. Calculate the number of atoms in a face centred cubic unit cell. *(Delhi 2013C)*

20. How many atoms are there in one unit cell of a body centred cubic crystal? *(Foreign 2011)*

21. What is the total number of atoms per unit cell in a face centred cubic (*fcc*) structure? *(Delhi 2008)*

22. How many effective sodium ions are located at the edge centre of a unit cell in a sodium chloride crystal? *(Delhi 2008C)*

23. Find out the number of atoms per unit cell in a face-centred cubic structure having only single atom at its lattice points. *(AI 2007)*

1.6 Close Packed Structures

VSA (1 mark)

24. What is the formula of a compound in which the element Y forms *ccp* lattice and atoms of X occupy 1/3rd of tetrahedral voids? *(Delhi 2015)*

25. What is the formula of a compound in which the element Y forms *ccp* lattice and atoms of X occupy 2/3rd of octahedral voids? *(Foreign 2015)*

26. How will you distinguish between the following pair of terms :
Tetrahedral and octahedral voids? *(AI 2014)*

27. An ionic compound AB_2 possesses CaF_2 type crystal structure. Write the coordination number of A^{2+} and B^- ions in crystals AB_2. *(AI 2009C)*

28. What is the coordination number of each type of ions in a rock-salt type crystal structure? *(Delhi, AI 2008)*

SA I (2 marks)

29. A compound forms *hcp* structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids? *(AI 2013C)*

30. An alloy of gold and cadmium crystallises with a cubic structure in which gold atoms occupy the corners and cadmium atoms fit into the face centres. Assign formula for this alloy. *(AI 2011C)*

SA II (3 marks)

31. The radius of Na^+ ion is 95 pm and that of Cl^- ion is 181 pm. Predict whether the coordination number of Na^+ ion is 6 or 4. *(Delhi 2010)*

32. In a face centred lattice of X and Y, X atoms are present at the corners while Y atoms are at face centres.
(a) What is the formula of the compound?
(b) What would be the formula of the compound if
  (i) one of the X atom is missing from a corner in each unit cell.
  (ii) two atoms of X are missing from the corners.
  (iii) one atom of X from a corner is replaced by Z atom (also monovalent)? *(Delhi 2008)*

1.7 Packing Efficiency

VSA (1 mark)

33. Express the relationship between atomic radius (r) and the edge length (a) in the *bcc* unit cell. *(Foreign 2014)*

34. Express the relationship between atomic radius (r) and the edge length (a) in the *fcc* unit cell. *(Foreign 2014)*

SA I (2 marks)

35. Aluminium crystallises in a *fcc* structure. Atomic radius of the metal is 125 pm. What is the length of the side of the unit cell of the metal? *(AI 2013, Foreign 2011)*

36. Calculate the packing efficiency of a metal for a simple cubic lattice. *(AI 2011)*

37. Chromium metal crystallises in a body centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius of chromium. *(Delhi 2010C)*

38. The edge of the face-centred cubic unit cell of aluminium is 404 pm. Calculate the radius of aluminium atom. *(Delhi 2010C)*

SA II (3 marks)

39. Tungsten crystallises in body centred cubic unit cell. If the edge of the unit cell is 316.5 pm, what is the radius of tungsten atom? *(Delhi 2012)*

40. Silver crystallises in face cented cubic unit cell. Each side of this unit cell has a length of 400 pm. Calculate the radius of the silver atom. (Assume the atom just touch each other on the diagonal across the face of the unit cell, that is each face atom is touching the four corner atoms). *(Delhi 2011)*

41. Aluminium crystallises in a cubic close-packed structure. Radius of atom in the metal is 125 pm.
(i) What is the length of the side of the unit cell?
(ii) How many unit cells are there in 1 cm^3 of aluminium? *(Foreign 2011)*

42. Silver crystallises with face-centred cubic unit cell. Each side of this unit cell has a length of 409 pm. What is the radius of silver atom? Assume the atoms just touch each other on the diagonal across the face of the unit cell. *(Foreign 2011, AI 2009)*

1.8 Calculations Involving Unit Cell Dimensions

SA I (2 marks)

43. An element with density 11.2 g cm^{-3} forms a *fcc* lattice with edge length of 4×10^{-8} cm. Calculate the atomic mass of the element.
(Given : $N_A = 6.022 \times 10^{23}$ mol^{-1}) *(Delhi 2014)*

44. An element with density 2.8 g cm^{-3} forms a *fcc* unit cell with edge length 4×10^{-8} cm. Calculate the molar mass of the element.
(Given : $N_A = 6.022 \times 10^{23}$ mol^{-1}) *(AI 2014)*

45. An element crystallises in structure having *fcc* unit cell of an edge 200 pm. Calculate the density if 200 g of this element contains 24×10^{23} atoms. *(AI 2013C)*

46. The unit cell of an element of atomic mass 108 u and density 10.5 g cm^{-3} is a cube with edge length, 409 pm. Find the type of unit cell of the crystal.
[Given : Avogadro's constant = 6.023×10^{23} mol^{-1}] *(Delhi 2012C)*

47. An element *X* crystallises in *fcc* structure. 208 g of it has 4.2832×10^{24} atoms. Calculate the edge of the unit cell, if density of *X* is 7.2 g cm^{-3}. *(Delhi 2012C)*

48. Explain how we can determine the atomic mass of an unknown metal if you know its density and the dimension of unit cell of its crystal. *(AI 2011)*

49. A copper crystal has a face-centred cubic lattice structure. Atomic radius of the copper atom is 128 pm. Calculate the density of copper.
Atomic mass of copper = 63.5 *(AI 2011C)*

SA II (3 marks)

50. An element crystallises in a *fcc* lattice with cell edge of 250 pm. Calculate the density if 300 g of this element contains 2×10^{24} atoms. *(Delhi 2016)*

51. An element crystallises in a *bcc* lattice with cell edge of 500 pm. The density of the element is 7.5 g cm^{-3}. How many atoms are present in 300 g of the element? *(AI 2016)*

52. An element with molar mass 27 g mol^{-1} forms a cubic unit cell with edge length 4.05×10^{-8} cm. If its density is 2.7 g cm^{-3}, what is the nature of the cubic unit cell? *(Delhi 2015)*

53. An element *X* (molar mass = 60 g mol^{-1}) has density of 6.23 g cm^{-3}. Identify the type of cubic unit cell, if the edge length of the unit cell is 4×10^{-8} cm. *(Foreign 2015)*

54. The density of copper is 8.95 g cm^{-3}. It has a face centred cubic structure. What is the radius of copper atom? (Atomic mass Cu = 63.5 g mol^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1}) *(Delhi 2014C, AI 2010)*

55. Iron has a body centred cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.87 g cm^{-3}. Use this information to calculate Avogadro's number.
(Gram atomic mass of Fe = 56 g mol^{-1}). *(AI 2014C, 2012, 2009, Delhi 2012, 2009)*

56. An element occurs in *bcc* structure. It has a cell edge length of 250 pm. Calculate the molar mass if its density is 8.55 g cm^{-3}. Also calculate the radius of an atom of this element. *(Delhi 2013C)*

57. Niobium crystallises in body-centred cubic structure. If its density is 8.55 g cm^{-3}, calculate atomic radius of niobium, given its atomic mass 93 u. *(Delhi 2013C)*

58. 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, $N_A = 6.02 \times 10^{23}$ mol^{-1}) *(AI 2012)*

59. The density of lead is 11.35 g cm^{-3} and crystallise with *fcc* unit cell. Estimate the radius of lead atom.
(At. mass of lead = 207 g mol^{-1} and
$N_A = 6.02 \times 10^{23}$ mol^{-1}) *(Delhi 2011)*

60. The well known mineral fluorite is chemically calcium fluoride. It is known that in one unit cell of this mineral there are 4Ca^{2+} ions and 8F^- ions and that Ca^{2+} ions are arranged in a *fcc* lattice. The F^- ions fill all the tetrahedral holes in the face centred cubic lattice of Ca^{2+} ions. The edge of the unit cell is 5.46×10^{-8} cm in length. The density of the solid is 3.18 g cm^{-3}. Use this information to calculate Avogadro's number. (Molar mass of CaF_2 = 78.08 g mol^{-1}) *(Delhi 2010)*

61. The density of copper metal is 8.95 g cm^{-3}. If the radius of copper atom be 127.8 pm, is the copper unit cell simple cubic, body-centred cubic or face-centred cubic?
(Given : atomic mass of Cu = 63.54 g mol^{-1} and $N_A = 6.02 \times 10^{23}$ mol^{-1}) *(AI 2010, 2008)*

62. Silver crystallises in *fcc* lattice. If the edge length of the unit cell is 4.077×10^{-8} cm and density of the crystal is 10.5 g cm^{-3}, calculate the atomic mass of silver.
($N_A = 6.02 \times 10^{23}$ atoms mol^{-1}) *(AI 2010)*

63. Copper crystallises in face-centred cubic lattice and has density of 8.930 g cm^{-3} at 293 K. Calculate the radius of copper atom.
[Atomic mass of Cu = 63.55 u,
$N_A = 6.02 \times 10^{23}$ mol^{-1}] *(AI 2010C)*

64. Copper crystallises into an *fcc* lattice with edge length 3.61×10^{-8} cm. Calculate the density of copper. [Given : Cu = 63.5 g mol^{-1}, $N_A = 6.022 \times 10^{23}$ mol^{-1}] *(Delhi 2009C)*

1.9 Imperfections in Solids

VSA (1 mark)

65. Define the following term :
Schottky defect *(1/3, AI 2015)*

66. Which stoichiometric defect does not change the density of the crystal? *(1/2, AI 2014)*

67. What type of stoichiometric defect is shown by KCl and why? *(1/2, Foreign 2014)*

68. What type of stoichiometric defect is shown by NaCl? *(Delhi 2014C)*

69. What type of stoichiometric defect is shown by AgCl? *(Delhi 2013)*

70. What type of point defect is produced when AgCl is doped with $CdCl_2$? *(Delhi 2013)*

71. Account for the following :
Schottky defects lower the density of related solids. *(1/2, AI 2013, 2007)*

72. What change occurs when AgCl is doped with $CdCl_2$? *(1/2, AI 2013)*

73. Which type of ionic substances show Schottky defect in solids? *(Delhi 2013C)*

74. Which stoichiometric defect increases the density of a solid? *(AI 2012)*

75. What type of stoichiometric defect is shown by AgBr and AgI? *(AI 2012C)*

76. What type of defect can arise when a solid is heated? *(AI 2012C)*

77. Which stoichiometric defect in crystals increases the density of a solid? *(Delhi 2011)*

78. Why is Frenkel defects not found in pure alkali metal halides? *(Delhi 2010)*

79. Give an example of an ionic compound which shows Frenkel defect. *(AI 2010C)*

80. Which point defect of its crystals decreases the density of a solid? *(AI 2009)*

SA I (2 marks)

81. Examine the given defective crystal.

A^+	B^-	A^+	B^-	A^+
B^-	○	B^-	A^+	B^-
A^+	B^-	A^+	○	A^+
B^-	A^+	B^-	A^+	B^-

Answer the following questions :
(i) What type of stoichiometric defect is shown by the crystal?
(ii) How is the density of the crystal affected by this defect?
(iii) What type of ionic substances show such defect? *(Delhi 2014)*

82. (i) What type of non-stoichiometric point defect is responsible for the pink colour of LiCl?
(ii) What type of stoichiometric defect is shown by NaCl? *(AI 2014)*

83. If NaCl is doped with 10^{-3} mole percen $SrCl_2$, what will be the concentration of cation vacancies? ($N_A = 6.02 \times 10^{23}$ mol^{-1}) *(AI 2013C)*

84. Explain the following terms with suitable examples :
(i) Schottky defect
(ii) Interstitial defect *(Delhi 2010C)*

85. Account for following :
(i) Zinc oxide on heating becomes yellow.
(ii) Frenkel defect does not change the density of AgCl crystals. *(AI 2008C)*

86. How would you account for the following?
(a) Frenkel defects are not found in alkali metal halides.
(b) Schottky defects lower the density of related solids. *(Delhi 2008)*

SA II **(3 marks)**

87. What are point defects? Describe two types of point defects. *(Delhi 2008)*

88. Explain the following terms with suitable examples :
(a) Crystal defects
(b) Metal deficiency defects *(Delhi 2008C)*

89. A metal crystallises in a face centred cubic unit cell with $a = 0.560$ nm. Calculate the density of the metal if it contains 0.1% schottky defects. Given : Atomic mass of metal = 40 g mol^{-1}) *(AI 2008C)*

1.10 Electrical Properties

VSA **(1 mark)**

90. What type of semiconductor is formed when silicon is doped with As? *(1/3, Foreign 2014)*

91. What type of semiconductor is obtained when silicon is doped with boron? *(1/3, Delhi, AI 2013)*

92. Account for the following :
Conductivity of silicon increases on doping it with phosphorus. *(AI 2013)*

93. What is meant by 'doping' in semiconductor? *(Delhi 2012)*

94. How may the conductivity of an intrinsic semiconductor be increased? *(AI 2012)*

95. What are *n*-type semiconductors? *(AI 2012)*

96. What is meant by an 'intrinsic semiconductor'? *(Foreign 2011)*

97. Impurity doped silicon is a semiconductor. *(Delhi 2008)*

98. Assign reason for the following :
Phosphorus doped silicon is a semiconductor. *(AI 2007)*

99. Explain the following with suitable examples :
Piezoelectric effect *(Delhi 2007)*

SA I **(2 marks)**

100. What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanism. *(AI 2013C)*

101. What is a semiconductor? Describe the two main types of semiconductors. *(Delhi 2013C)*

1.11 Magnetic Properties

VSA **(1 mark)**

102. What type of magnetism is shown by a substance if magnetic moments of domains are arranged in same direction? *(Delhi 2016)*

103. Define the following term :
Ferromagnetism *(1/2, AI 2015)*

104. Write the type of magnetism observed when the magnetic moments are oppositely aligned and cancel out each other. *(AI 2014)*

105. Write the type of magnetism observed when the magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers. *(AI 2014)*

106. What is meant by 'antiferromagnetism'? *(AI 2014C)*

107. What type of substances would make better magnets, ferromagnetic or ferrimagnetic? *(1/3, Foreign 2014, Delhi 2013)*

108. What type of magnetism is shown in the following alignment of magnetic moments?
$\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$ *(1/3, Delhi 2013)*

109. What type of substances exhibits antiferromagnetism? *(Delhi 2008)*

110. What are diamagnetic susbtances? *(AI 2008C)*

111. Account for the following :
Fe_3O_4 is ferrimagnetic at room temperature but becomes paramagnetic at 850 K. *(1/3, AI 2008C)*

112. Explain the following with suitable example :
Paramagnetism *(Delhi 2007)*

SA I **(2 marks)**

113. Explain the following terms with suitable examples :
Ferromagnetism and ferrimagnetism *(Delhi 2012C)*

114. Explain the following terms with suitable example of each.
(a) Ferromagnetism
(b) Antiferromagnetism *(Delhi 2011C)*

115. How is ferromagnetism different from paramagnetism? *(Delhi 2011C)*

116. Explain the following terms with one suitable example of each.
(a) Ferromagnetism
(b) Paramagnetism *(Delhi 2010C)*

Detailed Solutions

1. Crystalline solids are anisotropic in nature because of different arrangements of particles in different directions. Some of their physical properties like electrical conductivity, refractive index, etc., shows different values in different directions in the same crystals.

2. Some of the glass objects from ancient monuments look milky instead of being transparent because it undergoes heating during the day and cooling at night *i.e.*, annealing over a number of years. As a result, it acquires some crystalline character. They become a bit opaque.

3. *Refer to answer 1.*

4. Glass is considered as super cooled liquid because glass is an amorphous solid and has tendency to flow very slowly like liquids.

5. *Refer to answer 2.*

6. Molecular solids : HCl, SO_2, H_2O (*any one*)
Ionic solids : KCl, $CuSO_4$, ZnS (*any one*)

7. Carbon dioxide (CO_2) is a molecular solid.
Quartz (SiO_2) is a covalent solid.

8. (i) Metallic solids are malleable and ductile whereas ionic solids are hard and brittle.
(ii) In solid state, ionic solids are electrical insulators because ions are not free to move about, *e.g.* NaCl, Na_2SO_4, etc. while metals are good electrical conductors in solid state because of the presence of free electrons *e.g.* copper, nickel etc. (*any one*)

9. Strong dipole-dipole interactions

10. Malleable, ductile, lustrous and conductor of heat and electricity.

11. *Refer to answer 8.*

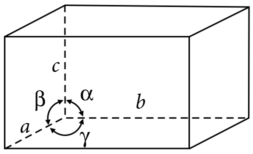
12. The crystalline solids have sharp melting points. Melting point of a solid is related to the force of attraction between its molecules. Higher the melting point of a crystalline substance, greater is the force between the constituent particles and hence, greater is the stability.

13. A unit cell in which constituent particles (lattice points) are present only at the corner positions is called primitive or simple unit cell.

14. Arrangement of lattice points in three dimensional space is called crystal lattice.
The smallest repeating unit which represents arrangement of lattice points in a crystal lattice is called unit cell.

15. *Refer to answer 14.*

16. A unit cells is characterised by the two types of parameters :



(i) Dimensions along the three edges represented as a, b and c.
(ii) Angles between edges α, β and γ.
Hence, a unit cell is represented by six parameters a, b, c, α, β and γ.

17. In a body centred cubic unit cell.
(i) 8 corners × $\frac{1}{8}$ per corner atom = 8 × $\frac{1}{8}$
= 1 atom
(ii) 1 body centre atom = 1 × 1 = 1 atom
∴ Total number of atoms per unit cell
= 1 + 1 = 2 atoms

18. In face centred cubic unit cell
(i) No. of atoms contributed from the corners of the unit cell
= 8 corner atoms × $\frac{1}{8}$ atom per unit cell
$= 8\times\frac{1}{8} = 1$ atom
(ii) No. of atoms contributed from the faces
= 6 face centred atoms × $\frac{1}{2}$ atoms per unit cell
$= 6\times\frac{1}{2} = 3$ atoms
∴ Total no. of atoms per unit cell = 4 atoms

19. *Refer to answer 18.*

20. *Refer to answer 17.*

21. *Refer to answer 18.*

22. Na units in edge $= 12\times\frac{1}{4} = 3$

23. *Refer to answer 18.*

24. No. of Y atoms per unit cell $= \frac{1}{8}\times 8+\frac{1}{2}\times 6=4$

No. of tetrahedral voids = 2 × 4 = 8

$\therefore$ No. of X atoms $= \frac{1}{3}\times 8=\frac{8}{3}$

Formula of the compound $= X_{\frac{8}{3}}Y_4 = X_2Y_3$

25. No. of Y atoms per unit cell in *ccp* lattice

$$= \frac{1}{8}\times 8+\frac{1}{2}\times 6=4$$

[$\because$ *ccp* is same as face-centred cubic packing. Thus, no. of atoms = 4]

No. of octahedral voids = No. of atoms present in *ccp* lattice

No. of octahedral voids occupied by atoms

$$= \frac{2}{3}\times 4 = \frac{8}{3}$$

Therefore, formula of the compound $= X_{\frac{8}{3}}Y_4 = X_2Y_3$

26. A void surrounded by four atoms whose centre when joined forms tetrahedron is tetrahedral void.

Number of tetrahedral voids = 2 × Number of atoms.

A void surrounded by six atoms whose centre when joined forms an octahedron is called octahedral voids.

Number of octahedral voids = Number of atoms.

27. Coordination number of $A^{2+} = 8$

Coordination number of $B^{-} = 4$

28. In a rock salt type crystal structure, coordination number is 6 : 6

$\Rightarrow$ Coordination number of $M^{+} = 6$

Coordination number of $A^{-} = 6$

29. Number of atoms in 0.5 mol *hcp* lattice

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

$\therefore$ Number of octahedral voids = Number of atoms

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

Number of tetrahedral voids = 2 × Number of atoms

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

Total number of voids = Number of octahedral voids + Number of tetrahedral voids

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

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

30. When the particles are present not only corners but also at the centre of each face of the unit cell. It is called face-centred unit cell.

Number of atoms in a unit cell of the face-centred-cubic (*fcc*) $\Rightarrow$ 8 atoms on the corners (gold) and 6 atoms of cadmium on the face (one of each face).

Contribution by atoms (gold) on the corners

$$= \frac{1}{8}\times 8=1$$

Contribution by atom (cadmium) on the faces

$$= \frac{1}{2}\times 6=3$$

Number of atoms present in the unit cell = 1 + 3 = 4

Hence, formula for the given alloy = $AuCd_3$

31. Radius of Na^{+} = 95 pm

Radius of Cl^{-} = 181 pm

Radius ratio, $\frac{r_+}{r_-} = \frac{r(Na^+)}{r(Cl^-)} = \frac{95}{181} = 0.524$

The radius ratio lies between 0.414 – 0.732.

Hence, Na^{+} ions prefer to occupy octahedral holes having coordination number 6.

32. (a) No. of X atoms in the unit cell $= 8\times\frac{1}{8}=1$

No. of Y atoms in the unit cell $= 6\times\frac{1}{2} = 3$

Formula = XY_3

(b) (i) If one X atom is missing, no. of X atoms $= \frac{7}{8}$

Formula $= X_{\frac{7}{8}}Y_3$ or X_7Y_{24}

(ii) If two X atoms are missing, no. of X atoms $= \frac{6}{8}$

Formula $= X_{\frac{3}{4}}Y_3$ or XY_4

(iii) No. of X atoms $= \frac{7}{8}$, No. of Z atoms $= \frac{1}{8}$

No. of Y atoms = 3.

Formula $= X_{\frac{7}{8}}Y_3Z_{\frac{1}{8}}$ or $X_7Y_{24}Z$

33. In *bcc* unit cell $r = \frac{\sqrt{3}}{4}a$

34. In *fcc* unit cell $r = \frac{a}{2\sqrt{2}}$

35. For *fcc* (or *ccp*), $a = 2\sqrt{2}r$

$= 2 \times 1.414 \times 125 \text{ pm} = 354 \text{ pm}$

36. Packing efficiency

$$= \frac{Z \times \text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100$$

$$= \frac{Z \times \frac{4}{3}\pi r^3}{a^3} \times 100$$

For a simple cubic lattice, $a = 2r$ and $Z = 1$

$$\therefore \quad \text{Packing efficiency} = \frac{1 \times \frac{4}{3}\pi r^3}{(2r)^3} \times 100$$

$$= \frac{\pi}{6} \times 100 = 52.4\%$$

37. Atomic radius for *bcc* lattice $r = \frac{\sqrt{3}a}{4}$

or $\quad r = \frac{1.732 \times 287 \text{ pm}}{4} = 124.27 \text{ pm}$

38. Edge of the face-centred cubic unit cell, $a = 404$ pm

$$\therefore \quad \text{Radius, } r = \frac{a}{2\sqrt{2}} = \frac{404}{2\sqrt{2}} = \frac{202}{\sqrt{2}}$$

$$= \frac{202}{\sqrt{2}} \times \frac{\sqrt{2}}{\sqrt{2}} = \frac{202\sqrt{2}}{2} = 101\sqrt{2}$$

$$= 101 \times 1.414 = 142.814 \text{ pm}$$

39. Given : Structure = *bcc*, $a = 316.5$ pm, $r = ?$

Using formula, $r = \frac{\sqrt{3}a}{4} = \frac{1.732 \times 316.5}{4} = 137.04 \text{ pm}$

40. $a = 400$ pm

For *fcc*, $r = \frac{a}{2\sqrt{2}}$

$$\therefore \quad r = \frac{400}{2\sqrt{2}} = \frac{400}{2\sqrt{2}} \times \frac{\sqrt{2}}{\sqrt{2}} = \frac{400\sqrt{2}}{4} = 100\sqrt{2}$$

$\Rightarrow \quad r = 100 \times 1.414 = 141.4$ pm

41. (i) For *fcc* (or *ccp*), $a = 2\sqrt{2}r = 2 \times 1.414 \times 125 \text{ pm}$
$= 354 \text{ pm}$

(ii) $a = 354 \text{ pm} = 3.54 \times 10^{-8}$ cm

Volume of one unit cell = $a^3 = (3.54 \times 10^{-8} \text{ cm})^3$
$= 4.436 \times 10^{-23} \text{ cm}^3$

$$\text{Number of unit cells} = \frac{\text{Total volume}}{\text{Volume of one unit cell}}$$

$$= \frac{1 \text{ cm}^3}{4.44 \times 10^{-23} \text{ cm}^3} = 2.25 \times 10^{22}$$

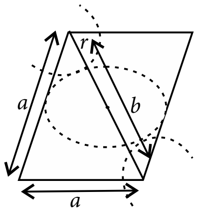
42. As the atoms just touch each other on the diagonal across the face of unit cell, therefore

$b^2 = a^2 + a^2 = 2a^2$

$b = \sqrt{2}a$ ...(i)

Also $b = r + 2r + r = 4r$ ...(ii)

From (i) and (ii), we get



$$4r = \sqrt{2}a \Rightarrow r = \frac{\sqrt{2}}{4}a;$$

$$r = \frac{1.414 \times 409 \text{ pm}}{4}$$

$= 144.58$ pm

43. Given : $d = 11.2 \text{ g cm}^{-3}$, $Z = 4$, $a = 4 \times 10^{-8}$ cm, $M = ?$, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

$$M = \frac{d \times a^3 \times N_A}{Z} = \frac{11.2 \times (4 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{4}$$

$$= 108 \text{ g mol}^{-1}$$

44. Given, Density of solid, $d = 2.8 \text{ g cm}^{-3}$

For *fcc* unit cell, $Z = 4$

Edge length, $a = 4 \times 10^{-8}$ cm,

Molar mass, $M = ?$

$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Using formula, $d = \frac{Z \times M}{N_A \times a^3}$

or $\quad M = \frac{d \times N_A \times a^3}{Z}$

Substituting these values, we get

$$M = \frac{2.8 \text{ g cm}^{-3} \times 6.022 \times 10^{23} \text{ mol}^{-1} \times (4 \times 10^{-8} \text{ cm})^3}{4}$$

or $\quad M = \frac{2.8 \times 6.022 \times 6.4}{4} = 26.98 \text{ g mol}^{-1}$

45. Edge length = 200 pm

Volume of the unit cell = $(200 \times 10^{-10} \text{ cm})^3$
$= 8 \times 10^{-24} \text{ cm}^3$

In a *fcc* unit cell there are four atoms per unit cell.

$$\therefore \quad \text{Mass of unit cell} = \frac{200 \times 4}{24 \times 10^{23}} = 33.3 \times 10^{-23} \text{g}$$

$$\text{Density} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{33.3 \times 10^{-23} \text{g}}{8 \times 10^{-24} \text{cm}^3}$$

$$= 41.6 \text{ g cm}^{-3}$$

46. Atomic mass, $M = 108$ u, $d = 10.5\,\text{g/cm}^3$, $a = 409$ pm

We know, $d = \dfrac{Z \times M}{a^3 \times 10^{-30} \times N_A}$ [$\because$ a is in pm]

$$Z = \frac{d \times a^3 \times 10^{-30} \times N_A}{M}$$

$$Z = \frac{10.5 \times (409)^3 \times 10^{-30} \times 6.022 \times 10^{23}}{108} = 4$$

47. For *fcc* structure $Z = 4$, $d = 7.2\,\text{g/cm}^3$

Let a be the edge length in pm

We know that density, $d = \dfrac{Z \times M}{a^3 \times 10^{-30}}$

Mass per atom, $M = \dfrac{208}{4.2832 \times 10^{24}}$,

$$a^3 = \frac{Z \times M}{d \times 10^{-30}}$$

$$= \frac{4 \times 208}{7.2 \times 4.2832 \times 10^{24} \times 10^{-30}}$$

$= 26.97 \times 10^6\,\text{pm}^3 \Rightarrow a = (27 \times 10^6)^{1/3} = 300$ pm

48. We can determine the atomic mass of an unknown metal by using the formula of density of its unit cell.

d (Density)

$$= \frac{Z(\text{No. of atoms per unit cell}) \times M(\text{Atomic mass})}{a^3(\text{Cell edge}) \times N_A\ (\text{Avogadro's number})}$$

By knowing density d, dimension of unit cell we can calculate M, the atomic mass of metal as for a given unit cell, Z is fixed and N_A is a universal constant.

49. For *fcc*, $Z = 4$

$$r = \frac{a}{2\sqrt{2}} \quad \text{or} \quad a = 2\sqrt{2}\,r$$

$a = 2 \times 1.414 \times 128$ pm $= 362$ pm

$a = 362 \times 10^{-10}$ cm

$$d = \frac{Z \times M}{a^3 \times N_A} = \frac{4 \times 63.5\,\text{g/mol}}{(362 \times 10^{-10}\,\text{cm})^3 \times (6.02 \times 10^{23}\,\text{mol}^{-1)}}$$

$= 8.9\,\text{g cm}^{-3}$

50. Molar mass of element (M)

$$= \frac{300 \times 6.02 \times 10^{23}}{2 \times 10^{24}} = 90.3\,\text{g mol}^{-1}$$

Density $(d) = \dfrac{Z \times M}{a^3 \times N_A}$

$$= \frac{4 \times 90.3}{(250 \times 10^{-10})^3 \times 6.02 \times 10^{23}} = 38.4\,\text{g cm}^{-3}$$

51. Given, edge length $a = 500$ pm $= 500 \times 10^{-10}$ cm

Mass of substance = 300 g

Number of atoms = ?

Density, $d = 7.5\,\text{g cm}^{-3}$

Using formula $d = \dfrac{Z \times M}{N_A \times a^3}$

or $M = \dfrac{d \times N_A \times a^3}{Z}$

or

$$M = \frac{7.5\,\text{g cm}^{-3} \times 6.022 \times 10^{23}\,\text{mol}^{-1} \times (500 \times 10^{-10}\,\text{cm})^3}{2}$$

or $M = 282.28\,\text{g mol}^{-1}$

Number of atoms $= \dfrac{6.022 \times 10^{23} \times 300}{282.28}$

$= 6.40 \times 10^{23}$ atoms

52. $M = 27\,\text{g mol}^{-1}$, $a = 4.05 \times 10^{-8}$ cm, $d = 2.7\,\text{g cm}^{-3}$

$$d = \frac{Z \times M}{N_A \times a^3} \quad \therefore \quad Z = \frac{d \times N_A \times a^3}{M}$$

$$Z = \frac{2.7 \times 6.022 \times 10^{23} \times (4.05 \times 10^{-8})^3}{27} = 4$$

As $Z = 4$, hence cubic unit cell is face centred cubic unit cell.

53. Given, $d = 6.23\,\text{g cm}^{-3}$, $a = 4 \times 10^{-8}$ cm,

$M = 60\,\text{g mol}^{-1}$

$N_A = 6.023 \times 10^{23}$, $Z = ?$

Using formula $d = \dfrac{Z \times M}{N_A \times a^3}$ or $Z = \dfrac{d \times N_A \times a^3}{M}$

$$Z = \frac{6.23\,\text{g cm}^{-3} \times 6.023 \times 10^{23} \times (4 \times 10^{-8}\,\text{cm})^3}{60\,\text{g mol}^{-1}}$$

or $Z = 4.0$

Hence, structure is *fcc*.

54. Let us assume $Z = 4$ (copper has *fcc*)

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

$$8.95 = \frac{4 \times 63.5}{a^3 \times 6.02 \times 10^{23}}$$

$a^3 = 47.145 \times 10^{-24}\,\text{cm}^3$

$$a = \sqrt[3]{47.145 \times 10^{-24}}$$

$a = 3.612 \times 10^{-8}$ cm $= 361.2$ pm

For *fcc*, $4r = \sqrt{2}a$

It shows Cu has *fcc* structure,

$$r = \frac{a}{2\sqrt{2}} = \frac{361.2}{2 \times 1.414} = 127.7\,\text{pm}$$

55. Given : For *bcc*, $Z = 2$

$a = 286.65 \text{ pm} = 2.87 \times 10^{-8} \text{ cm}$

$d = 7.874 \text{ g cm}^{-3}$, $N_A = ?$

Using formula $d = \dfrac{Z \times M}{N_A \times a^3}$

or, $N_A = \dfrac{Z \times M}{d \times a^3} = \dfrac{2 \times 56 \text{ g mol}^{-1}}{7.87 \times (2.87 \times 10^{-8} \text{ cm})^3}$

or, $N_A = 6.022 \times 10^{23}$

56. $a = 250$ pm

$d = 8.55 \text{ gm}^{-3}$; $Z = 2$

$$d = \frac{Z \times M}{a^3 \times N_A \times 10^{-30}}$$

$$M = \frac{d \times a^3 \times N_A \times 10^{-30}}{Z}$$

$$= \frac{8.55 \times 250 \times 250 \times 250 \times 6.02 \times 10^{23} \times 10^{-30}}{2}$$

$M = 40.21$ u

bcc unit cell body diagonal is equal to 4 times the radius of atom.

$\therefore \quad 4r = \sqrt{3}a = \sqrt{3} \times 250$

$4r = 1.732 \times 250 \Rightarrow r = 108$ pm

57. Given density (d) = 8.55 g cm^{-3}

Atomic radius (r) = ?

Atomic mass (M) = 93 u = 93 g mol^{-1}

For *bcc* structure $Z = 2$

Using formula $d = \dfrac{Z \times M}{N_A \times a^3}$ or $a^3 = \dfrac{Z \times M}{N_A \times d}$

or $\quad a^3 = \dfrac{2 \times 93 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1} \times 8.55 \text{ g cm}^{-3}}$

or $\quad a^3 = 36.1 \times 10^{-24} \text{ cm}^3$

or $\quad a = 3.304 \times 10^{-8} \text{ cm} = 330.4$ pm

Again for *bcc* $r = \dfrac{\sqrt{3}a}{4} = \dfrac{1.732 \times 330.4}{4}$ pm

or $\quad r = 143.1$ pm

58. Given : Structure *fcc*, hence $Z = 4$, $r = 127.8$ pm, $M = 63.55$ u, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$, $d = ?$

Using formula, $d = \dfrac{Z \times M}{N_A \times a^3}$

We get

$$d = \frac{4 \times 63.55 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1} \times (2\sqrt{2} \times 127.8 \times 10^{-10})^3}$$

$= 8.940 \text{ g/cm}^3$

59. $d = \dfrac{Z \times M}{a^3 \times N_A} \Rightarrow a^3 = \dfrac{Z \times M}{d \times N_A}$ ...(i)

For *fcc* unit cell, $Z = 4$

Given, $M = 207 \text{ g mol}^{-1}$, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$

$d = 11.35 \text{ g cm}^{-3}$

Substituting these value in equation (i), we get

$$a^3 = \frac{4 \times 207 \text{g mol}^{-1}}{11.35 \text{ g cm}^{-3} \times 6.02 \times 10^{23} \text{mol}^{-1}}$$

$$a^3 = \frac{4 \times 207 \times 10}{11.35 \times 6.02 \times 10^{24}} \text{ cm}^3$$

$$\Rightarrow \quad a = \left(\frac{8280}{11.35 \times 6.02}\right)^{1/3} \times 10^{-8} \text{ cm}$$

$\therefore \quad a = 4.949 \times 10^{-8} \text{ cm} \Rightarrow a = 494.9$ pm

For *fcc*, $r = \dfrac{a}{2\sqrt{2}}$

$\therefore \quad r = \dfrac{494.9}{2\sqrt{2}} \text{ pm} = \dfrac{494.9\sqrt{2}}{4} \text{ pm} = \dfrac{494.9 \times 1.414}{4}$ pm

$\therefore \quad r = 174.95$ pm

60. Given for *fcc* lattice $Z = 4$, $d = 3.18 \text{ g cm}^{-3}$

$a = 5.46 \times 10^{-8}$ cm, $N_A = ?$

Using formula $d = \dfrac{Z \times M}{N_A \times a^3}$

or, $\quad N_A = \dfrac{4 \times 78.08 \text{ g mol}^{-1}}{3.18 \text{ g cm}^{-3} \times (5.46 \times 10^{-8} \text{ cm})^3}$

or, $\quad N_A = 6.033 \times 10^{23} \text{ mol}^{-1}$

61. Given : $d = 8.95 \text{ g cm}^{-3}$, $r = 127.8$ pm,

$M = 63.54 \text{ g mol}^{-1}$

$N_A = 6.02 \times 10^{23} \text{ mo1}^{-1}$

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

For *fcc*, $r = \dfrac{a}{2\sqrt{2}} \Rightarrow a = 2\sqrt{2}r$

$$Z = \frac{8.95 \text{ g cm}^{-3} \times (2\sqrt{2} \times 127.8 \times 10^{-10})\text{cm}^3 \times 6.02 \times 10^{23} \text{mol}^{-1}}{63.54 \text{ g mol}^{-1}}$$

$Z = 4$

Hence, copper is the face-centred cubic unit cell.

62. Given, edge length $a = 4.077 \times 10^{-8}$ cm
density $d = 10.5$ g cm^{-3}
For *fcc* lattice $Z = 4$, Atomic mass $M = ?$

Using formula $d = \dfrac{Z \times M}{N_A \times a^3}$

or, $M = \dfrac{d \times N_A \times a^3}{Z}$

$$\text{or} \quad M = \frac{10.5\text{ g cm}^{-3} \times 6.022 \times 10^{23}\text{ atoms mol}^{-1} \times (4.077 \times 10^{-8}\text{ cm})^3}{4\text{ atoms}}$$

or $M = 107.12$ g mol^{-1}

63. *Refer to answer 54.*

64. In *fcc* lattice, $Z = 4$ atoms,
Given, $M = 63.5$ g mol^{-1}, $N_A = 6.022 \times 10^{23}$ mol^{-1}
$a = 3.61 \times 10^{-8}$ cm

Density, $d = \dfrac{Z \times M}{a^3 \times N_A}$

$$= \frac{4 \times 63.5}{(3.61 \times 10^{-8})^3 \times 6.022 \times 10^{23}}$$

$$= \frac{254}{47.046 \times 10^{-24} \times 6.022 \times 10^{23}}$$

$$= \frac{254}{283.311 \times 10^{-1}} = \frac{254}{28.33} = 8.965 \text{ g cm}^{-3}$$

65. Schottky defect : The defect in which cations and anions are missing in the stoichiometric ratio of compound is called Schottky defect. Schottky defect is actually vacancy defect in ionic solids. In this defect, electrical neutrality is maintained. In this defect, density of solid decreases. Schottky defect is shown by ionic solids in which the cation and anion are of almost similar sizes.
Examples **:** NaCl, KCl, CsCl, AgBr, etc.

66. Frenkel defect does not change the density of the solid.

67. *Refer to answer 65.*

68. *Refer to answer 65.*

69. Frenkel defect

70. Addition of $CdCl_2$ to AgCl crystal causes impurity defect.
In this defect also one Cd^{2+} ion replaces two Ag^+ ions from the crystal. One site is occupied by one Cd^{2+} ion and other site remains vacant.

71. Schottky defects occur when cations and anions are missing from their lattice site. Mass of unit cell decreases which decreases the density of the solid.

72. *Refer to answer 70.*

73. *Refer to answer 65.*

74. Interstitial defect

75. Frenkel defect is shown by ionic solids in which difference in size of cations and anions is large. Examples : ZnS, AgI and AgBr.

76. On heating a solid vacancy defect is produced in the crystal. This is because on heating, some lattice sites become vacant.

77. *Refer to answer 74.*

78. Frenkel defects is not found in alkali metal halides because the ions cannot get into the interstitial sites due to their larger size.

79. *Refer to answer 75.*

80. Schottky defect.

81. (i) Schottky defect

(ii) Density of the crystal decreases.

(iii) This defect is shown by ionic substances in which the cation and anion are of almost similar sizes.

82. (i) Metal excess defect is responsible for pink colour of LiCl. It is also known as anion vacancy defect.
(ii) NaCl crystal shows Schottky defect.

83. The number of cation vacancies created in the lattice of NaCl is equal to the number of divalent Sr^{2+} ions added.
Concentration of $Sr^{2+} = 10^{-3}$ mol%

$$= \frac{10^{-3}}{100} = 10^{-5} \text{ mol}$$

1 mole of $Sr^{2+} = 6.023 \times 10^{23} Sr^{2+}$ ions
10^{-5} mol of $Sr^{2+} = 6.023 \times 10^{23} \times 10^{-5}$
$= 6.023 \times 10^{18}$ Sr^{2+} ions.
Hence, the concentration of cation vacancies is 6.023×10^{18}.

84. (i) *Refer to answer 65.*

(ii) **Interstitial defect :** The defect in which some constituent particles occupy the interstitial site in the crystal is called interstitial defect. This defect increases density of solid. *e.g.*, non-ionic solids.

85. (i) Zinc oxide is white in colour at room temperature. On heating, it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{Heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Now, there is excess of zinc in the crystal and excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(ii) Due to Frenkel defect, no ions are missing from the crystal as a whole. Thus, there is no change in density.

86. (a) *Refer to answer 78.*

(b) *Refer to answer 71.*

87. Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline solid. Types of point defects are :

Stoichiometric defects : These are the point defects that do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects.

In non-ionic solids :

(i) **Vacancy defect :** Some of the lattice sites are vacant, decreases the density of the substance.

(ii) **Interstitial defect :** Some constituent particles (atoms or molecules) occupy an interstitial site, increases the density of the substance.

In ionic solids :

(i) **Frenkel defect or dislocation defect :** The smaller ion (usually cation) is dislocated from its normal site to an interstitial site.

It does not change the density of the solid and is shown by ionic substances in which there is a large difference in the size of ions, *e.g.*, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^+ ions.

(ii) **Schottky defect :** Equal number of cations and anions are missing. It decreases the density of the substance and is shown by ionic substances in which the cation and anion are of almost similar sizes *e.g.*, NaCl, KCl, CsCl and AgBr. AgBr shows both, Frenkel as well as Schottky defects.

Non-stoichiometric defects : When the ratio of the cations to the anions becomes different from that indicated by the ideal chemical formula, the defects are called non-stoichiometric defects.

Metal excess defect :

(i) Due to anionic vacancies *e.g.*, on heating crystals of NaCl in presence of Na vapour, some anions (Cl^-) leave lattice sites which are occupied by electrons called ***F*-centres** giving colour to crystals.

(ii) Due to presence of extra cations at interstitial sites *e.g.*, on heating, white ZnO turns yellow as it loses oxygen and Zn^{2+} ions and the electrons occupy interstitial sites.

Metal deficiency defect : There are many solids which are difficult to prepare in the stoichiometric composition and less amount the metal as compared to the stoichiometric proportion (*any two*).

88. (a) Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects.

(b) This type of defects generally occurs when metal shows variable valency. The defect arises due to the missing of cation from its lattice site and the presence of the cation having higher charge in the adjacent lattice site, *e.g.*, Fe_xO.

89. Due to Schottky defects, the vacant spaces will increase resulting in decrease in number of atoms per unit cell.

$$Z = \left(4 - \frac{4 \times 0.1}{100}\right) = 3.996$$

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

$$= \frac{3.996 \times (40\text{ g mol}^{-1})}{(0.560 \times 10^{-7})^3 \times (6.022 \times 10^{23}\text{ mol}^{-1})}$$

$= 1.51\text{ g cm}^{-3}$

90. n-type semiconductor is formed when silicon is doped with arsenic.

91. p-type semiconductor is obtained when silicon is doped with boron.

92. Silicon when doped with phosphorus, which contains five valence electrons, they occupy some of the lattice sites in silicon crystal. Four out of five electrons are used in the formation of four covalent bonds with the four neighboring silicon atoms.

The fifth electron is extra and becomes delocalised. These delocalised electrons increases the conductivity of doped silicon.

93. Addition of an appropriate amount of suitable impurity in a crystalline solid is called doping.
Doping is done to increase the conductivity of intrinsic semiconductors.

94. The conductivity of intrinsic semiconductor like silicon is too low to be of practical use. This conductivity is increased by adding an appropriate amount of suitable impurity like Al or As which is electron deficient or electron rich. So, the electrical conductivity of silicon is increased.

95. A semiconductor in which doped impurity has more valence electrons than the pure element is called *n*-type semiconductor. *e.g.,* Ge or Si (Group-14) doped with P or As (Group-15).

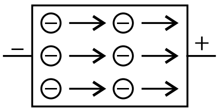
96. Pure substance which acts as semiconductor is called intrinsic semiconductor. *e.g.,* Si and Ge at high temperature.

97. *Refer to answer 94.*

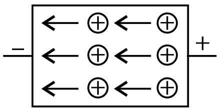
98. Phosphorus is pentavalent. When phosphorus is doped in silicon it increases the number of electrons which increases the conductivity of doped silicon and makes it semiconductor.

99. Piezoelectric effect : When the electricity is produced by applying mechanical stress on some polar crystals, it is known as piezoelectric effect. Quartz shows this property.

100. The solids which have conductivities between 10^{-6} to 10^4 $\text{ohm}^{-1}\ \text{m}^{-1}$ are called semiconductors.
e.g., Germanium and silicon. The two main types of semiconductors are as follows :
(i) ***n*-type semiconductor :** When a silicon crystal is doped with atoms of group-15 elements, such as P, As, Sb or Bi then only four of the five valence electrons of each impurity atom participate in forming covalent bonds and fifth electron is almost free to conduct electricity. Group-14 elements doped with a group-15 elements are called *n*-type semiconductors.
(ii) ***p*-type semiconductor :** When a silicon crystal is doped with atoms of group-13 elements, such as B, Al, Ga or In. Each impurity atoms form only three covalent bonds with the host atom. The place where the fourth electron is missing is caused a hole which move through the crystal like a positive charge and hence increases its conductivity. Group-14 elements doped with group-13 elements are called *p*-type semiconductors.



n-type semiconductor



p-type semiconductor

101. *Refer to answer 100.*

102. Ferromagnetism

103. Ferromagnetism : Materials which are strongly attracted by magnetic field are called ferromagnetic materials and the property thus exhibited is caused ferromagnetism.
e.g., Fe, Co, Ni show ferromagnetism at room temperature.

104. Antiferromagnetism

105. Ferrimagnetism

106. Antiferromagnetism : Paramagnetic substances which show very poor magnetic effect are antiferromagnetic and this property is called antiferromagnetism.
Examples : MnO, Fe_2O_3, Cr_2O_3.

107. Ferromagnetic substances because these substances become a permanent magnet.

108. Ferromagnetism

109. *Refer answer 106.*

110. Substances which are weakly repelled by magnetic field are called diamagnetic and this property is called diamagnetism. Diamagnetism is shown by those substances in which all electrons are paired.
Examples : NaCl, H_2O, C_6H_6, Zn^{2+}

111. On heating at 850 K, the magnetic domains undergo realignment and become paramagnetic.

112. Paramagnetism : Materials which are weakly attracted by magnetic fields are called paramagnetic materials and this property is called paramagnetism.
Paramagnetic substances contain unpaired electrons.
e.g., TiO, CuO, O_2 and VO_2, etc.

113. Ferromagnetism : Substances which are very strongly attracted by the magnetic field are called ferromagnetic and this property is called ferromagnetism.

Examples : Iron, cobalt, nickel, gadolinium and CrO_2.

These substances can be permanently magnetised *i.e.,* they retain magnetic property even in absence of applied magnetic field.

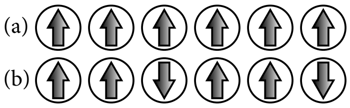
In ferromagnetic substance all the domains (tiny magnet formed by grouping of metal ions in small region) are oriented in the direction of the applied magnetic field and produce a strong magnetic effect. This ordered orientation of domain persists even when the magnetic field is removed.

Ferrimagnetism : Substances which are weakly attracted by the magnetic field as compared to ferromagnetic substances are called ferrimagnetic and this property is called ferrimagnetism.

Examples : Fe_3O_4 (Magnetite, Ferrites - $MgFe_2O_4$, $ZnFe_2O_4$.

Ferrimagnetism is observed when the magnetic domains are aligned in parallel and antiparallel directions in unequal numbers. Hence, net magnetic moment is never zero.

These substances lose ferrimagnetism and become paramagnetic on heating.



Schematic alignment of magnetic moments in (a) ferromagnetic (b) ferrimagnetic.

114. (a) *Refer to answer 113.*
(b) *Refer to answer 106.*

115. *Refer to answers 113 and 112.*

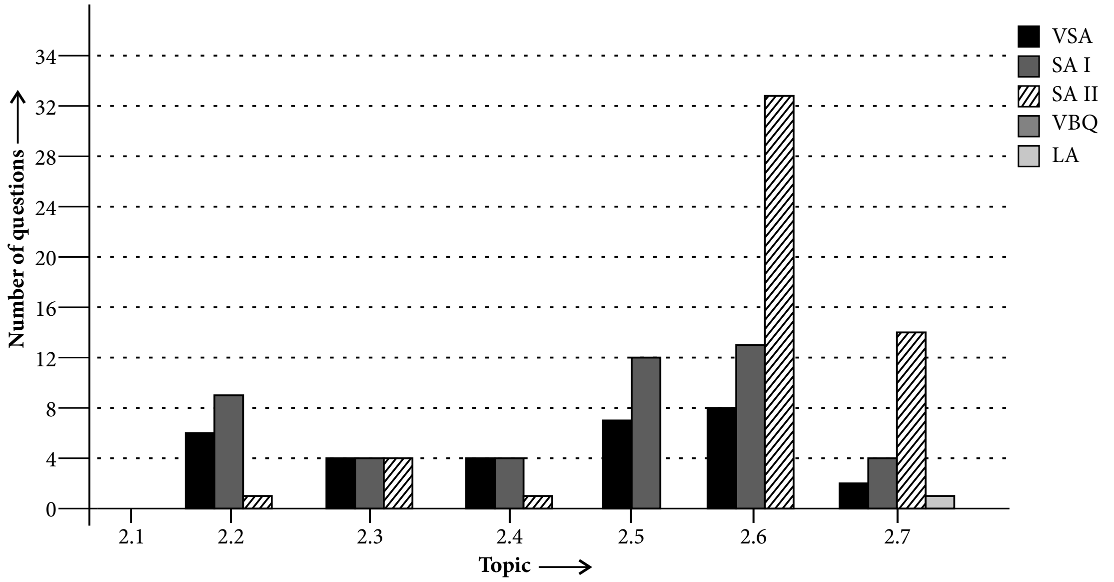
116. (a) *Refer to answer 113.*
(b) *Refer to answer 112.*

02

Solutions

2.1 Types of Solutions
2.2 Expressing Concentration of Solutions
2.3 Solubility
2.4 Vapour Pressure of Liquid Solutions
2.5 Ideal and Non-ideal Solutions
2.6 Colligative Properties and Determination of Molar Mass
2.7 Abnormal Molar Masses

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



- Maximum total weightage is of *Colligative Properties and Determination of Molar Mass.*
- Maximum VSA type questions were asked from *Colligative Properties and Determination of Molar Mass.*
- Maximum SA I and SA II type questions were asked from *Colligative Properties and Determination of Molar Mass.*

QUICK RECAP

- **Solution :** A perfectly homogeneous mixture of two or more components is called *solution*.
- **Solute :** The component which is present in lesser amount or whose physical state is changed during the formation of solution is called *solute*.

- **Solvent :** The component which is present in larger amount and determines the physical state of the solution is called *solvent*.
- **Types of solution :** Depending upon the nature of solute and solvent, solutions are classified as follows :
  - **Gaseous solutions :** Solutions in which gas acts as solvent are known as *gaseous solutions*.

Solute	Solvent	Examples
Solid	Gas	Iodine vapours in air, dust or smoke particles in air.
Liquid	Gas	Water vapours in air (humidity)
Gas	Gas	Air

  - **Liquid solutions :** Solutions in which liquids are present in larger amount.

Solute	Solvent	Examples
Solid	Liquid	Salt/sugar in water
Liquid	Liquid	Alcohol in water
Gas	Liquid	Aerated drinks, O_2 in water

  - **Solid solutions :** Solutions in which solids are present in larger amount.

Solute	Solvent	Examples
Solid	Solid	Alloys, copper dissolved in gold
Liquid	Solid	Hg in Ag, Hg in Zn (Amalgam)
Gas	Solid	Solution of hydrogen in palladium.

- **Different methods for expressing concentration of solution :**

Method of expressing	Formula
Mass percentage	$\left(\frac{w}{W}\right)\% = \frac{w_2}{(w_1+w_2)}\times 100$
Volume percentage	$\left(\frac{v}{V}\right)\% = \frac{V_2}{(V_1+V_2)}\times 100$
Mass by volume percentage	$\left(\frac{w}{V}\right)\% = \frac{w_2}{V_{\text{solution(in mL)}}}\times 100$
Mass fraction	$x_1 = \frac{w_1}{w_1+w_2}$ or $x_2 = \frac{w_2}{w_1+w_2}$
Strength (g L^{-1})	$\frac{w_{2\text{(in g)}}}{V_{\text{solution (in mL)}}}\times 1000$
Parts per million (ppm)	$\frac{w_2}{(w_1+w_2)}\times 10^6$
Molarity, (M) (mol L^{-1})	$\frac{w_2\times 1000}{M_2\times V_{\text{solution(in mL)}}}$
Molality, (m) (mol kg^{-1})	$\frac{w_2\times 1000}{M_2\times w_{1\text{(in g)}}}$
Mole fraction, (x)	$x_1 = \frac{n_1}{n_1+n_2}$ or $x_2 = \frac{n_2}{n_1+n_2}$, ($x_1 + x_2 = 1$) In case of gases only, $y_1 = \frac{p_1}{p_1+p_2}$ or $y_2 = \frac{p_2}{p_1+p_2}$, ($y_1 + y_2 = 1$)

- **Solubility :** Maximum amount of substance that can be dissolved in a specified amount of solvent at a specified temperature is called its *solubility*.
- **Factors affecting solubility of a solid in a liquid :**
  - **Nature of solute and solvent :** Polar solutes dissolve in polar solvents and non-polar solutes in non-polar solvents. (*i.e.*, like dissolves like).
  - **Effect of temperature :**
    - If the dissolution process is endothermic ($\Delta_{sol}H > 0$), the solubility **increases** with **rise** in temperature.
    - If dissolution process is exothermic ($\Delta_{sol}H < 0$), the solubility decreases with **rise** in temperature.

  - **Effect of pressure :** Pressure does not have any significant effect on solubility of solids in liquids as these are highly incompressible.

- **Factors affecting solubility of a gas in a liquid :**
  - **Effect of pressure : Henry's law** states that "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution"

    $p = K_H\, x$ where, K_H is the Henry's law constant and is different for different gases at a particular temperature.

    Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.
  - **Effect of temperature :** As dissolution is an exothermic process, then according to Le Chatelier's principle, the solubility should decrease with increase of temperature.

- **Raoult's law :** It states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. $p_1 = p_1^\circ x_1$ and $p_2 = p_2^\circ x_2$ where p_1° and p_2° are vapour pressures of pure components 1 and 2 respectively, at the same temperature.

- **Dalton's law of partial pressures :**

$$P_{\text{total}} = p_1 + p_2 = x_1 p_1^\circ + x_2 p_2^\circ$$
$$= (1 - x_2)p_1^\circ + x_2 p_2^\circ$$
$$= p_1^\circ + (p_2^\circ - p_1^\circ)x_2$$

- If y_1 and y_2 are the mole fractions of the components 1 and 2 respectively in the vapour phase then, $p_1 = y_1 P_{\text{total}}$ and $p_2 = y_2 P_{\text{total}}$

- **Raoult's law for solid-liquid solutions :** It states that relative lowering in vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute.

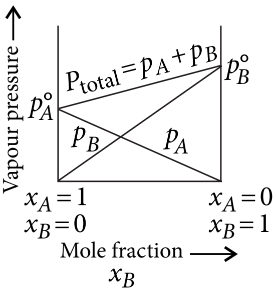
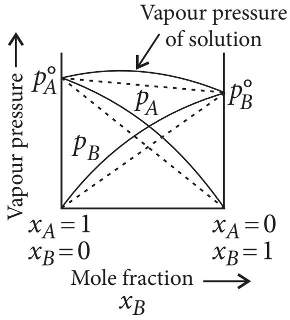
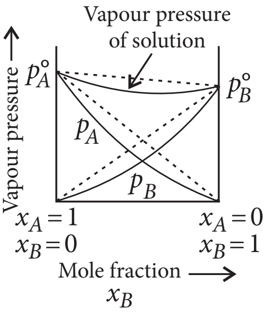
$$\frac{p^\circ - p_s}{p^\circ} = x_2 \text{ where,}$$

p° = vapour pressure of pure solvent

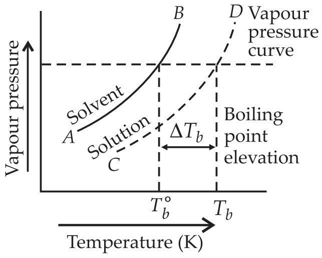
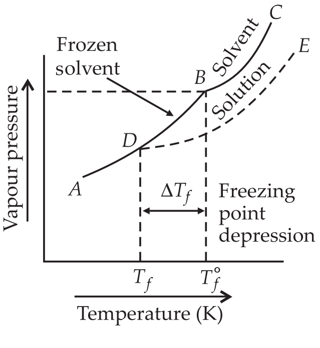
p_s = vapour pressure of solution

x_2 = mole fraction of solute.

- **Ideal and non-ideal solutions :**

Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
		
$A - B$ interactions ≈ $A - A$ and $B - B$ interactions	$A - B$ interactions << $A - A$ and $B - B$ interactions	$A - B$ interactions >> $A - A$ and $B - B$ interactions
$\Delta H_{\text{mix}} = 0, \Delta V_{\text{mix}} = 0$	$\Delta H_{\text{mix}} > 0, \Delta V_{\text{mix}} > 0$	$\Delta H_{\text{mix}} < 0, \Delta V_{\text{mix}} < 0$
e.g., dilute solution, benzene + toluene, *n*-hexane + *n*-heptane	*e.g.*, acetone + ethanol, acetone + CS_2, water + methanol	*e.g.*, acetone + aniline, acetone + chloroform, $CH_3OH + CH_3COOH$

- **Azeotropes :** The mixtures of liquids which boil at constant temperature like a pure liquid and possess same composition of components in liquid as well as vapour phase are called *constant boiling mixtures* or *azeotropic mixtures*.
  - **Minimum boiling azeotropes :** They formed by those liquid pairs which show positive deviations from ideal behaviour *e.g.*, ethanol-water mixture.
  - **Maximum boiling azeotropes :** They are formed by those liquid pairs which show negative deviations from ideal behaviour *e.g.*, nitric acid-water mixture.
- **Colligative properties :** Properties which depend only on the number of solute particles dissolved in a definite amount of the solvent and not on the nature of the solute are called *colligative properties*.

Colligative properties	Expression
Relative lowering of vapour pressure : When a non-volatile solute is dissolved in a solvent, vapour pressure of the solution is lower than that of the pure solvent which is known as *lowering of vapour pressure*. Relative lowering of vapour pressure is equal to the mole fraction of the solute in the solution.	$\frac{p_1^\circ - p_1}{p_1^\circ} = x_2 = \frac{n_2}{n_1 + n_2}$ $= \frac{n_2}{n_1} = \frac{w_2 \times M_1}{M_2 \times w_1}$ ($\because$ for dilute solutions, $n_2 << n_1$)
Elevation in boiling point : The boiling point of a solution containing a non-volatile solute is always higher than the boiling point of the pure solvent. This increase in boiling point is termed as *elevation in boiling point*. 	$\Delta T_b = T_b - T_b^\circ$ $\Delta T_b \propto m$ or $\Delta T_b = K_b m$ $= K_b \left(\frac{w_2 \times 1000}{M_2 \times w_1 \text{(in g)}} \right)$ or $M_2 = \frac{K_b \times w_2 \times 1000}{\Delta T_b \times w_1 \text{(in g)}}$ K_b is called *boiling point elevation constant or molal elevation constant or Ebullioscopic constant*, having unit K kg mol^{-1}.
Depression in freezing point : The freezing point of a solution containing a non-volatile solute is always less than the freezing point of the pure solvent. This decrease in freezing point is termed as *depression in freezing point*. 	$\Delta T_f = T_f^\circ - T_f$ $\Delta T_f \propto m$ or $\Delta T_f = K_f m$ $= K_f \left(\frac{w_2 \times 1000}{M_2 \times w_1 \text{(in g)}} \right)$ or $M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1 \text{(in g)}}$ K_f is known as *freezing point* depression constant or *molal depression constant* or *Cryoscopic constant*, having unit K kg mol^{-1}.
Osmosis and osmotic pressure : The movement of solvent molecules from less concentrated solution to more concentrated solution through semipermeable membrane is termed as *osmosis*. The hydrostatic pressure which develops on account of osmosis is called *osmotic pressure* or the excess pressure that must be applied on the solution to prevent osmosis is called *osmotic pressure*.	$\pi = CRT = \left(\frac{n_2}{V} \right) RT$, $\pi V = \frac{w_2 RT}{M_2}$ or $M_2 = \frac{w_2 RT}{\pi V}$

- Two solutions having same osmotic pressure at a given temperature are called *isotonic solutions*.
- If one solution is of lower osmotic pressure, it is called *hypotonic* with respect to the more concentrated solution. The more concentrated solution is said to be *hypertonic* with respect to the dilute solution.
- If a pressure higher than the osmotic pressure is applied on the solution, the solvent will flow from the solution into the pure solvent through the semipermeable membrane and the process is called *reverse osmosis*. It is used in *desalination of sea water*.

Abnormal molecular mass : When the molecular mass of a substance determined by any of the colligative properties comes out to be different than the expected value, the substance is said to show *abnormal molecular mass*.

- Abnormal molecular masses are observed when the solution is non-ideal (not dilute) or the solute undergoes *association* or *dissociation*.

van't Hoff Factor : It is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.

$$i = \frac{\text{Observed value of the colligative property}}{\text{Calculated value of the colligative property}}$$

$$i = \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$$

$$i = \frac{\begin{array}{c}\text{(Total number of moles of particles}\\ \text{after association / dissociation)}\end{array}}{\begin{array}{c}\text{(Total number of moles of particles}\\ \text{before association / dissociation)}\end{array}}$$

- If $i > 1$, solute undergoes dissociation in the solution and if $i < 1$, solute undergoes association in the solution.

$$\alpha_{\text{dissociation}} = \frac{i-1}{n-1}$$

$$\alpha_{\text{association}} = \frac{1-i}{1-\frac{1}{n}}$$

- For substances undergoing association or dissociation in the solution, the various expressions for the colligative properties are modified as follows :

$$\frac{p_1^\circ - p_1}{p_1^\circ} = ix_2\ ;\ \Delta T_b = iK_bm;\ \Delta T_f = iK_fm;$$

$$\pi = iCRT$$

Previous Years' CBSE Board Questions

2.2 Expressing Concentration of Solutions

VSA (1 mark)

1. Define the following term :
Molarity *(1/5 AI 2014)*

2. Define the following term :
Mole fraction *(1/2 Delhi 2012, AI 2012, 2009)*

3. What is meant by molality of a solution? *(1/5 AI 2009)*

4. State the main advantage of molality over molarity as the unit of concentration. *(Delhi 2009C)*

SA I (2 marks)

5. Calculate the molarity of 9.8% (*w*/*W*) solution of H_2SO_4 if the density of the solution is 1.02 g mL^{-1}.
(Molar mass of H_2SO_4 = 98 g mol^{-1}) *(2/5 Foreign 2014)*

6. Differentiate between molarity and molality of a solution. How can we change molality value of a solution into molarity value? *(Delhi 2014C)*

7. Define :
(i) Mole fraction (ii) Molality *(2/5 AI 2014 C)*

8. A solution of glucose ($C_6H_{12}O_6$) in water is labelled as 10% by weight. What would be the molality of the solution?
(Molar mass of glucose = 180 g mol^{-1}) *(2/5 AI 2013)*

9. Differentiate between molarity and molality in a solution. What is the effect of temperature change on molarity and molality in a solution? *(2/5 Delhi 2011, 2009, 2/5 AI 2011)*

10. Differentiate between molarity and molality of a solution. Explain how molarity value of a solution can be converted into its molality? *(Foreign 2011)*

11. Define the term, 'molarity of a solution'. State one disadvantage in using the molarity as the unit of concentration. *(2/3 AI 2010C)*

12. An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_4(OH)_2$) and 200 g of water. Calculate the molality of the solution. If the density of this solution be 1.072 g mL^{-1} what will be the molality of the solution? *(Delhi 2007)*

SA II (3 marks)

13. A solution of glucose (molar mass = 180 g mol^{-1}) in water is labelled as 10% (by mass). What would be the molality and molarity of the solution?
(Density of solution = 1.2 g mL^{-1}) *(3/5 AI 2014)*

2.3 Solubility

VSA (1 mark)

14. Gas (*A*) is more soluble in water than gas (*B*) at the same temperature. Which one of the two gases will have the higher value of K_H (Henry's constant) and why? *(1/2 AI 2016)*

15. Explain the following :
Henry's law about dissolution of a gas in a liquid. *(1/5 AI 2012)*

16. State the following :
Henry's law about partial pressure of a gas in a mixture. *(1/5 Delhi, AI 2011)*

SA I (2 marks)

17. State Henry's law and mention two of its important applications. *(2/5, AI 2013C, 2012C)*

18. Explain why aquatic species are more comfortable in cold water rather than in warm water. *(Delhi 2012C)*

19. State Henry's law correlating the pressure of a gas and its solubility in a solvent and mention two applications for the law. *(Delhi 2008)*

SA II **(3 marks)**

20. The partial pressure of ethane over a saturated solution containing 6.56×10^{-2} g of ethane is 1 bar. If the solution contains 5.0×10^{-2} g of ethane, then what will be the partial pressure of the gas? *(Delhi 2013C, AI 2012C)*

21. If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 k bar. *(AI 2012C)*

22. What concentration of nitrogen should be present in a glass of water at room temperature? Assume a temperature of 25°C, a total pressure of 1 atmosphere and mole fraction of nitrogen in air of 0.78.
[K_H for nitrogen = 8.42×10^{-7} M/mm Hg] *(3/5 AI 2009)*

2.4 Vapour Pressure of Liquid Solutions

VSA **(1 mark)**

23. Define Raoult's law. *(1/5 AI 2014C)*

24. State the following :
Raoult's law in its general form in reference to solutions. *(1/5 Delhi, 1/2 AI 2011)*

25. State 'Raoult's law' for a solution of volatile liquids. *(AI 2009C)*

SA I **(2 marks)**

26. State Raoult's law for the solution containing volatile components. What is the similarity between Raoult's law and Henry's law? *(Delhi 2014, AI 2013)*

27. State Raoult's law for a solution containing volatile components. Name the solution which follows Raoult's law at all concentrations and temperatures. *(2/5 Foreign 2014)*

28. State Raoult's law. How is it formulated for solutions of non-volatile solutes? *(Delhi 2012C)*

SA II **(3 marks)**

29. The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase. *(3/5 AI 2013C)*

2.5 Ideal and Non-ideal Solutions

VSA **(1 mark)**

30. In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes? *(1/2 AI 2016)*

31. Some liquids on mixing form 'azeotropes'. What are 'azeotropes'? *(Delhi 2014)*

32. Define the following term :
Azeotrope *(1/5 Foreign 2014)*

33. Define the following term :
Ideal solution *(1/5 AI 2013, 2012, 1/2 Delhi 2012)*

34. How is it that alcohol and water are miscible in all proportions ? *(AI 2007)*

SA I **(2 marks)**

35. What is meant by positive deviations from Raoult's law? Give an example. What is the sign of $\Delta_{mix}H$ for positive deviation? *(Delhi 2015)*

36. Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example. *(Delhi 2015)*

37. What is meant by negative deviation from Raoult's law? Give an exmaple. What is the sign of $\Delta_{mix}H$ for negative deviation? *(Foreign 2015)*

38. Define azeotropes. What type of azeotrope is formed by negative deviation from Raoult's law? Give an example. *(Foreign 2015)*

39. What type of deviation is shown by a mixture of ethanol and acetone? Give reason. *(2/5 AI 2014)*

40. What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{mix}H$ related to positive and negative deviations from Raoult's law? *(AI 2013 C)*

41. Explain why a solution of chloroform and acetone shows negative deviation from Raoult's law. *(2/5 Delhi 2011C)*

42. Non-ideal solutions exhibit either positive or negative deviations from Raoult's law. What are these deviations and why are they caused? Explain with one example for each type. *(Delhi 2010)*

43. What type of intermolecular attraction exists in each of the following pairs of compounds:
(i) *n*-hexane and *n*-octane
(ii) methanol and acetone *(Delhi 2010C)*

44. State Raoult's law for solutions of volatile liquids. Taking suitable examples explain the meaning of positive and negative deviations from Raoult's law. *(Delhi, AI 2008)*

45. What is meant by negative deviation from Raoult's law? Draw a diagram to illustrate the relationship between vapour pressure and mole fractions of components in a solution to represent negative deviation. *(AI 2008C)*

2.6 Colligative Properties and Determination of Molar Mass

VSA (1 mark)

46. What are isotonic solutions? *(Delhi 2014)*

47. Define the following term :
Molal elevation constant (K_b) *(1/5 AI 2014)*

48. How is the vapour pressure of a solvent affected when a non-volatile solute is dissolved in it? *(1/2 Delhi 2014C)*

49. Define the following term :
Osmotic pressure *(1/5 AI 2013)*

50. Define the following term :
Isotonic solutions *(1/2 Delhi 2012)*

51. Explain the following :
Boiling point elevation constant for a solvent. *(AI 2012)*

52. What is meant by colligative properties? *(1/5 AI 2009)*

53. State the condition resulting in reverse osmosis. *(AI 2007)*

SA I (2 marks)

54. (i) Out of 1 M glucose and 2 M glucose, which one has a higher boiling point and why?
(ii) What happens when the external pressure applied becomes more than the osmotic pressure of solution? *(2/5 Delhi 2016)*

55. Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing
(i) 1.2% sodium chloride solution?
(ii) 0.4% sodium chloride solution? *(2/5 Delhi 2016)*

56. Why does a solution containing non-volatile solute have higher boiling point than the pure solvent? Why is elevation of boiling point a colligative property? *(AI 2015)*

57. Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K. (K_f = 5.12 K kg mol^{-1}). *(Delhi 2014)*

58. 18 g of glucose, $C_6H_{12}O_6$ (Molar mass = 180 g mol^{-1}) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil?
(K_b for water = 0.52 K kg mol^{-1}, boiling point of pure water = 373. 15 K) *(Delhi 2013)*

59. An aqueous solution of sodium chloride freezes below 273 K. Explain the lowering in freezing point of water with the help of a suitable diagram. *(Delhi 2013C)*

60. Define the terms osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property? Explain. *(2/5 Delhi 2011)*

61. List any four factors on which the colligative properties of a solution depend. *(2/5 AI 2011C)*

62. Define the terms, 'osmosis' and 'osmotic pressure'. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions? *(AI 2010)*

63. Outer hard shells of two eggs are removed. One of the egg is placed in pure water and the other is placed in saturated solution of sodium chloride. What will be observed and why? *(AI 2010C)*

64. Find the boiling point of a solution containing 0.520 g of glucose ($C_6H_{12}O_6$) dissolved in 80.2 g of water.
[Given : K_b for water = 0.52 K/m] *(AI 2010C)*

65. Define the term 'osmotic pressure'. Describe how the molecular mass of a substance can be determined on the basis of osmotic pressure measurement. *(Delhi, AI 2008)*

SA II (3 marks)

66. Calculate the freezing point of the solution when 31 g of ethylene glycol ($C_2H_6O_2$) is dissolved in 500 g of water.
(K_f for water = 1.86 K kg mol^{-1}) *(AI 2015)*

67. A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution. *(3/5 AI 2014)*

68. Calculate the boiling point elevation for a solution prepared by adding 10 g of $CaCl_2$ to 200 g of water. (K_b for water = 0.52 K kg mol^{-1}, molar mass of $CaCl_2$ = 111 g mol^{-1}) *(2/3 Foreign 2014)*

69. Define the following terms :
(i) Osmotic pressure
(ii) Colligative properties *(Foreign 2014)*

70. Some ethylene glycol, $HOCH_2CH_2OH$, is added to your car's cooling system along with 5 kg of water. If the freezing point of water-glycol solution is –15.0°C, what is the boiling point of the solution?
(K_b = 0.52 K kg mol^{-1} and K_f = 1.86 K kg mol^{-1} for water) *(Delhi 2014C)*

71. 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is 5.12 K kg mol^{-1}. Find the molar mass of the solute. *(AI 2013, 2008)*

72. A 5% solution (by mass) of cane-sugar in water has freezing point of 271 K. Calculate the freezing point of 5% solution (by mass) of glucose in water if the freezing point of pure water is 273.15 K.
[Molecular masses : Glucose $C_6H_{12}O_6$: 180 amu; Cane-sugar $C_{12}H_{22}O_{11}$: 342 amu] *(3/5 AI 2013C)*

73. A solution of glycerol ($C_3H_8O_3$) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C while pure water boils at 100°C. What mass of glycerol was dissolved to make the solution?
(K_b for water = 0.512 K kg mol^{-1}) *(Delhi 2012, 2010, AI 2012)*

74. 15.0 g of an unknown molecular material was dissolved in 450 g of water. The resulting solution was found to freeze at –0.34°C. What is the molar mass of this material?
(K_f for water = 1.86 K kg mol^{-1}) *(Delhi 2012, 3/5, AI 2012, 2010)*

75. A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further 18 g of water is added to this solution. The new vapour pressure becomes 2.9 kPa at 298 K. Calculate
(i) the molecular mass of solute and
(ii) vapour pressure of water at 298 K. *(Delhi 2012C)*

76. Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250.00 g of water. (K_b for water = 0.512 K kg mol^{-1}), (Molar mass of NaCl = 58.44 g) *(3/5 Delhi 2011)*

77. A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming the gene fragment is a non-electrolyte, determine its molar mass. *(3/5 Delhi, AI 2011)*

78. What would be the molar mass of a compound if 6.21 g of it dissolved in 24.0 g of chloroform to form a solution that has a boiling point of 68.04°C. The boiling point of pure chloroform is 61.7°C and the boiling point elevation constant, K_b for chloroform is 3.63°C/m. *(3/5 Delhi 2011)*

79. What mass of NaCl must be dissolved in 65.0 g of water to lower the freezing point of water by 7.50°C? The freezing point depression constant (K_f) for water is 1.86°C/m. Assume van't Hoff factor for NaCl is 1.87.
(Molar mass of NaCl = 58.5 g mol^{-1}). *(AI 2011)*

80. The molecular masses of polymers are determined by osmotic pressure method and not by measuring other colligative properties. Give two reasons. *(3/5 AI 2011C)*

81. Calculate the boiling point of one molar aqueous solution (density 1.06 g mL^{-1}) of KBr. [Given : K_b for H_2O = 0.52 K kg mol^{-1}, atomic mass : K = 39, Br = 80] *(3/5 AI 2011C)*

82. A solution prepared by dissolving 1.25 g of oil of winter green (methyl salicylate) in 99.0 g of benzene has a boiling point of 80.31°C. Determine the molar mass of this compound. (B.pt. of pure benzene = 80.10°C and K_b for benzene = 2.53°C kg mol^{-1}) *(Delhi 2010)*

83. What mass of ethylene glycol (molar mass = 62.0 g mol^{-1}) must be added to 5.50 kg of water to lower the freezing point of water from 0°C to – 10.0°C?
(K_f for water 1.86 K kg mol^{-1}) *(AI 2010)*

84. 100 mg of a protein is dissolved in just enough water to make 10.0 mL of solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25°C, what is the molar mass of the protein? (R = 0.0821 L atm mol^{-1} K^{-1} and 760 mm Hg = 1 atm.) *(Delhi, 3/5, AI 2009)*

85. Calculate the amount of sodium chloride which must be added to one kilogram of water so that the freezing point of water is depressed by 3 K. [Given : K_f = 1.86 K kg mol^{-1}, atomic mass : Na = 23.0, Cl = 35.5] *(3/5, Delhi, AI 2009C)*

86. x g of a non-electrolytic compound (molar mass = 200) is dissolved in 1.0 L of 0.05 M NaCl aqueous solution. The osmotic pressure of this solution is found to be 4.92 atm at 27°C. Calculate the value of x. Assume complete dissociation of NaCl and ideal behaviour of the solution. (R = 0.082 L atm mol^{-1} K^{-1}) *(AI 2009C)*

87. Calculate the freezing point of a solution containing 18 g glucose, $C_6H_{12}O_6$ and 68.4 g sucrose, $C_{12}H_{22}O_{11}$ in 200 g of water. The freezing point of pure water is 273 K and K_f for water is 1.86 K m^{-1}. *(AI 2009C)*

88. Calculate the temperature at which a solution containing 54 g of glucose, ($C_6H_{12}O_6$), in 250 g of water will freeze.
(K_f for water = 1.86 K mol^{-1} kg) *(Delhi 2008)*

89. A solution containing 8 g of a substance in 100 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 K kg mol^{-1}) *(AI 2008)*

90. A 0.1539 molal aqueous solution of cane sugar (mol. mass = 342 g mol^{-1}) has a freezing point of 271 K while the freezing point of pure water is 273.15 K. What will be the freezing point of an aqueous solution containing 5 g of glucose (mol. mass = 180 g mol^{-1}) per 100 g of solution. *(AI 2007)*

2.7 Abnormal Molar Masses

VSA (1 mark)

91. Define the following term :
Van't Hoff factor *(1/5 Delhi 2012, AI 2009)*

SA I (2 marks)

92. What is van't Hoff factor? What types of values can it have if in forming the solution the solute molecules undergo
(i) Dissociation (ii) Association? *(2/5 AI 2014C)*

93. Assuming complete dissociation, calculate the expected freezing point of a solution prepared by dissolving 6.00 g of Glauber's salt, $Na_2SO_4 \cdot 10H_2O$ in 0.100 kg of water.
(K_f for water = 1.86 K kg mol^{-1}, atomic masses : Na = 23, S = 32, O = 16, H = 1) *(2/5, AI 2014C)*

94. A 1.00 molal aqueous solution of trichloroacetic acid (CCl_3COOH) is heated to its boiling point. The solution has the boiling point of 100.18°C. Determine the van't Hoff factor for trichloroacetic acid.
(K_b for water = 0.512 K kg mol^{-1}) *(Delhi 2012)*

95. What is van't Hoff factor? What possible value can it have if the solute molecules undergo dissociation? *(2/5 Delhi 2011C)*

SA II (3 marks)

96. Calculate the freezing point of solution when 1.9 g of $MgCl_2$(M = 95 g mol^{-1}) was dissolved in 50 g of water, assuming $MgCl_2$ undergoes complete ionization.
(K_f for water = 1.86 K kg mol^{-1}) *(Delhi 2016)*

97. When 2.56 g of sulphur was dissolved in 100 g of CS_2, the freezing point lowered by 0.383 K. Calculate the formula of sulphur (S_x).
(K_f the CS_2 = 3.83 K kg mol^{-1}, atomic mass of sulphur = 32 g mol^{-1}) *(3/5 Delhi 2016)*

98. Calculate the boiling point of solution when 4 g of $MgSO_4$ (M = 120 g mol^{-1}) was dissolved in 100 g of water, assuming $MgSO_4$ undergoes complete ionization.
(K_b for water = 0.52 K kg mol^{-1}) *(AI 2016)*

99. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated).
(Given : Molar mass of benzoic acid = 122 g mol^{-1}, K_f for benzene = 4.9 K kg mol^{-1}) *(Delhi 2015)*

100. Calculate the mass of NaCl (molar = 58.5 g mol^{-1}) to be dissolved in 37.2 g of water to lower the freezing point by 2°C, assuming that NaCl undergoes complete dissociation.
(K_f for water = 1.86 K kg mol^{-1}) *(Foreign 2015)*

101. Determine the osmotic pressure of a solution prepared by dissolving 2.5×10^{-2} g of K_2SO_4 in 2 L of water at 25°C, assuming that it is completely dissociated.
(R = 0.0821 L atm K^{-1} mol^{-1}, molar mass of K_2SO_4 = 174 g mol^{-1}) *(Delhi 2013)*

102. Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2 K (the K_f for water = 1.86 K kg mol^{-1}). *(Delhi 2012)*

103. Calculate the freezing point of an aqueous solution containing 10.50 g of $MgBr_2$ in 200 g of water. (Molar mass of $MgBr_2$ = 184 g mol^{-1}) (K_f for water = 1.86 K kg mol^{-1})
(3/5 Delhi 2011)

104. A 0.561 m solution of an unknown electrolyte depresses the freezing point of water by 2.93°C. What is van't Hoff factor for this electrolyte? The freezing point depression constant (K_f) for water is 1.86°C kg mol^{-1}. *(Foreign 2011)*

105. Phenol associates in benzene to a certain extent to form a dimer. A solution containing 20 g of phenol in 1.0 kg of benzene has its freezing point lowered by 0.69 K. Calculate the fraction of phenol that has dimerised
[Given K_f for benzene = 5.1 K m^{-1}]
(3/5 Delhi 2011C)

106. An aqueous solution containing 12.48 g of barium chloride in 1.0 kg of water boils at 373.0832 K. Calculate the degree of dissociation of barium chloride.
[Given K_b for H_2O = 0.52 K m^{-1};
Molar mass of $BaCl_2$ = 208.34 g mol^{-1}]
(3/5, Delhi 2011C)

107. A decimolar solution of potassium ferrocyanide $K_4[Fe(CN)_6]$ is 50% dissociated at 300 K. Calculate the value of van't Hoff factor for potassium ferrocyanide. *(Delhi 2010C)*

108. The boiling point elevation of 0.30 g acetic acid in 100 g benzene is 0.0633 K. Calculate the molar mass of acetic acid from this data. What conclusion can you draw about the molecular state of the solute in the solution?
[Given K_b for benzene = 2.53 K kg mol^{-1}]
(AI 2008C)

109. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g of benzene is lowered by 0.45°C. Calculate.
(i) the molar mass of acetic acid from this data
(ii) van't Hoff factor
[For benzene, K_f = 5.12 K kg mol^{-1}]
What conclusion can you draw from the value of van't Hoff factor obtained?
(AI 2008C)

LA (5 marks)

110. (i) The depression in freezing point of water observed for the same molar concentration of acetic acid, trichloroacetic acid and trifluroacetic acid increases in the order as stated above. Explain.
(ii) Calculate the depression in freezing point of water when 20.0 g of $CH_3CH_2CHClCOOH$ is added to 500 g of water.
[Given : $K_a = 1.4 \times 10^{-3}$, K_f = 1.86 K kg mol^{-1}]
(Delhi 2008C)

Detailed Solutions

1. Number of moles of solute dissolved in one litre solution is called molarity. It is denoted by *M*.

$$M = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litre}}$$

2. Mole fraction is the ratio of number of moles of solute or solvent and total number of moles of solution. It is denoted by *x*.

$$x_{\text{solute}} = \frac{n_2}{n_1 + n_2},\ x_{\text{solvent}} = \frac{n_1}{n_1 + n_2}$$

3. Molality of a solution can be defined as the number of moles of solute dissolved in one kg solvent. It is denoted by *m*.

$$m = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \frac{n_2}{W_1}$$

4. Molality is independent of temperature, whereas molarity is a function of temperature.

5. Mass of solute = 9.8 g
Mass of solution = 100 g
Density of solution = 1.02 g mL^{-1}

$$\therefore \quad \text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}}$$

$$= \frac{100\text{ g}}{1.02\text{ g mL}^{-1}} = 98.039\text{ mL}$$

$$= 0.098\text{ L}$$

$$\text{Number of moles of solute, } n = \frac{9.8\text{ g}}{98\text{ g}} = 0.1\text{ mol}$$

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$$

$$= \frac{0.1\text{ mol}}{0.098\text{ L}} = 1.02\text{ M}$$

6.

Molarity	Molality
Number of moles of solute dissolved in one litre solution is called molarity.	Number of moles of solute dissolved in one kg solvent is called molality.
$M = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litre}}$	$m = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$
Molarity depends on temperature as volume depends on temperature. Molarity decreases with rise in temperature.	Molality is independent of temperature as mass does not change with temperature.

7. (i) *Refer to answer 2.*
(ii) *Refer to answer 3.*

8. Mass of solution = 100 g
Mass of solute = 10 g

$$\text{Mass of solvent} = 100 - 10 = 90\text{ g} = \frac{90}{1000}\text{ kg}$$

$$= 0.09\text{ kg}$$

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

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

9. *Refer to answer 6.*

10. *Refer to answer 6.*

If M_B is the molar mass of solute, *d* is the density of solution then molarity (*M*) value of a solution can be converted into its molality (*m*) by using the following formula,

$$m = \frac{1000 \times M}{(1000 \times d) - (M \times M_B)}$$

11. *Refer to answer 1.*

Disadvantage in using molarity as the unit of concentration is that it depends upon temperature.

12. Mass of the solute, $C_2H_4(OH)_2$ = 222.6 g
Molar mass of solute, $C_2H_4(OH)_2$ = 62 g mol^{-1}

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

Mass of the solvent = 200 g = 0.200 kg

$$\text{Volume of solution} = \frac{422.6\text{ g}}{1.072\text{ g mL}^{-1}} = 394.2\text{ mL}$$

$$= 0.3942\text{ L}$$

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \frac{3.59}{0.2}$$

$$= 17.95\text{ m}$$

$$\text{Molarity} = \frac{3.59\text{ moles}}{0.3942\text{ L}} = 9.11\text{ mol L}^{-1}$$

13. Given : Mass of solute, $W_2 = 10$ g
Mass of solvent, $W_1 = 90$ g
Molar mass of solute, $M_2 = 180$ g mol^{-1}
Density of solution = 1.2 g mL^{-1}

(i) Molality $= \dfrac{W_2 \times 1000}{M_2 \times W_1} = \dfrac{10 \times 1000}{180 \times 90}$

$= 0.62$ mol kg^{-1}

(ii) Volume of solution = $\dfrac{\text{mass}}{\text{density}} = \dfrac{100\,\text{g}}{1.2\,\text{g}\,\text{mL}^{-1}}$

Molarity $= \dfrac{w_2 \times 1000}{M_2 \times V}$

$$M = \frac{10 \times 1000}{180 \times \frac{100}{1.2}} = \frac{10 \times 1000 \times 1.2}{180 \times 100} = 0.66 \text{ mol L}^{-1}$$

14. According to Henry's law, the solubility of a gas is inversely proportional to the Henry's law constant (K_H) for that gas. Hence, gas (B) being less soluble, would have a higher K_H value.

15. Henry's law states that, the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

$p = K_H \cdot x$ where, K_H = Henry's law constant. Different gases have different K_H values at the same temperature.

16. *Refer to answer 15.*

17. *Refer to answer 15.*

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) To minimise the painful effects of decompression sickness in deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.

18. Increase in temperature decreases the solubility of oxygen in water. As a result, amount of dissolved oxygen decreases. It becomes more difficult to breathe as oxygen is less. Hence, the aquatic species are not comfortable in warm water.

19. Henry's law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

Refer to answers 17.

20. Applying the relationship,
$m = K_H \times p$
In the first case, 6.56×10^{-2} g $= K_H \times 1$ bar
or, $K_H = 6.56 \times 10^{-2}$ g bar^{-1}

In the second case,
5.0×10^{-2} g $= (6.56 \times 10^{-2}$ g bar$^{-1}) \times p$

$$p = \frac{5.0 \times 10^{-2}\text{ g}}{6.56 \times 10^{-2}\text{ g bar}^{-1}} = 0.762 \text{ bar}$$

21. According to Henry's law, $p_{N_2} = K_H \times x_{N_2}$

$$x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{0.987 \text{ bar}}{76480 \text{ bar}} = 1.29 \times 10^{-5}$$

If n moles of N_2 are present in 1 L (*i.e.*, 55.55 moles),

$x_{N_2} = \dfrac{n}{n + 55.55} \simeq \dfrac{n}{55.55}$ of water

$\therefore \quad \dfrac{n}{55.55} = 1.29 \times 10^{-5}$

or $\quad n = 1.29 \times 10^{-5} \times 55.55$ moles
$= 71.659 \times 10^{-5}$ moles $= 0.716$ millimoles

22. $T = 25°\text{C} + 273 = 298$ K
Total pressure (P_{total}) = 1 atm
p_{N_2} = mol fraction of N_2 in air × P_{total} = 0.78 × 1 atm
= 0.78 atm = 0.78 × 760 mm = 592.8 mm
As K_H is in the units of M(mm)$^{-1}$, Henry's law is applied in the form :
Conc. in solution $= K_H\, p_{N_2} = 8.42 \times 10^{-7}$ M (mm)$^{-1}$ $\times 592.8$ mm
$= 4.99 \times 10^{-4}$ M

23. **Raoult's law :** For a solution of volatile liquids, the partial pressure of each component in the solution is directly proportional to its mole fraction. Thus, for any component, partial vapour pressure,
$p \propto x \Rightarrow p = p° . x$
where $p°$ = vapour pressure of pure component
x = mole fraction of that component

24. *Refer to answer 23.*

25. *Refer to answer 23.*

26. *Refer to answer 23.*

Henry's law : If gas is the solute and liquid is the solvent, then according to Henry's law,

$p = K_H \cdot x$

i.e., partial pressure of the volatile component (gas) is directly proportional to the mole fraction of that component (gas) in the solution.

Hence, Raoult's law and Henry's law has been identical except that their proportionality constant are different. It is equal to $p°$ for Raoult's law and K_H for Henry's law.

Therefore, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to vapour pressure of pure component $p°$.

27. *Refer to answer 23.*

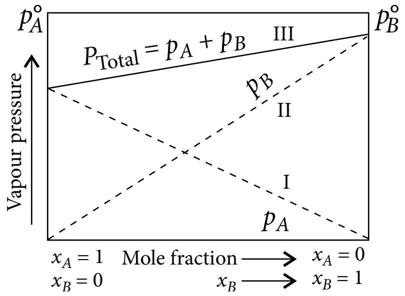
Let a solution consists of two volatile liquids *A* and *B* with their mole fraction x_A and x_B respectively. If p_A and p_B are their partial vapour pressures, then,

$p_A \propto x_A \Rightarrow p_A = p_A^\circ x_A$ and $p_B \propto x_B \Rightarrow p_B = p_B^\circ x_B$

where p_A° and P_B° represent the vapour pressures of pure liquid components *A* and *B*.

$P_{\text{total}} = p_A + p_B$

A plot of p_A or p_B against x_A or x_B for a solution will be a straight line.



Ideal solutions obey Raoult law at all concentrations and temperature.

28. *Refer to answer 23.*

Raoult's law for solution containing non-volatile solute : It states that partial vapour pressure of a solution of non-volatile solute, p_{solution} is directly proportional to the mole fraction of the solvent in the solution.

Mathematically,

$p_{\text{solution}} = p^\circ_{\text{solvent}} \times x_{\text{solvent}}$

where p°_{solvent} = vapour pressure of the pure solvent at the given temperature.

or, $$\frac{p^\circ - p_{\text{sol}}}{p^\circ} = x_2$$

29. Given : p_A° = 450 mm Hg, p_B° = 700 mm Hg, P_{Total} = 600 mm Hg, x_A = ?

Applying Raoult's law, $p_A = x_A \times p_A^\circ$

$p_B = x_B \times p_B^\circ = (1 - x_A)p_B^\circ$

$P_{\text{Total}} = p_A + p_B = x_A \times p_A^\circ + (1 - x_A)p_B^\circ$

$= p_B^\circ + (p_A^\circ - p_B^\circ)x_A$

Substituting the given values, we get

$600 = 700 + (450 - 700)x_A$ or, $250x_A = 100$

or $$x_A = \frac{100}{250} = 0.40$$

Thus, composition of the liquid mixture will be

$x_A = 0.40$

$x_B = 1 - 0.40 = 0.60$

Calculation of composition in the vapour phase,

$p_A = x_A \times p_A^\circ = 0.40 \times 450$ mm Hg = 180 mm Hg

$p_B = x_B \times p_B^\circ = 0.60 \times 700$ mm Hg = 420 mm Hg

Mole fraction of *A* in the vapour phase

$$= \frac{p_A}{p_A + p_B} = \frac{180}{180 + 420} = 0.30$$

Mole fraction of *B* in the vapour phase = 1 – 0.30
= 0.70

30. Non-ideal solutions that show negative deviation from Raoult's law form maximum boiling azeotropes.

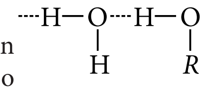
31. Azeotropes are the binary mixtures of solutions that have the same composition in liquid and vapour phases and that have constant boiling points.

It is not possible to separate the components of azeotropes by fractional distillation.

32. *Refer to answer 31.*

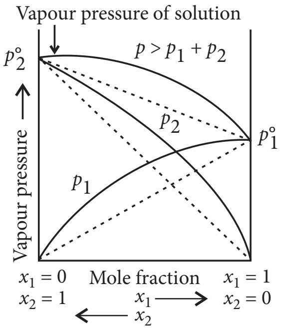
33. A solution which obeys Raoult's law at all concentrations and temperatures is called an ideal solution.

34. Both alcohol and water are polar in nature hence, they are miscible in all proportions. Water and ethanol molecules attract each other because of the formation of H-bonds. This property also makes them miscible.



$$\cdots\underset{\text{H}}{\underset{|}{\text{H—O}}}\cdots\underset{R}{\underset{|}{\text{H—O}}}$$

35. **Positive deviation :** For non-ideal solutions, if the vapour pressure is higher, then it is said to exhibit positive deviation. *A*—*B* interactions are weaker than *A*—*A* or *B*—*B* interactions. Due to this, vapour pressure increases which results in positive deviation. In positive deviation, intermolecular force decreases, volume increases, vapour pressures increases. enthalpy increases. Therefore, ΔH_{mix} = +ve, ΔV_{mix} = + ve. *e.g.*, ethanol + acetone and carbon disulphide + acetone show positive deviation.

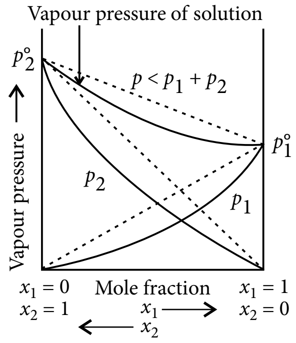


Plot for non-ideal solution showing positive deviation

36. *Refer to answer 31.*

A minimum boiling azeotrope is formed by solutions showing a large positive deviation from Raoult's law at a specific composition. For example an ethanol-water mixture containing approximately 95% ethanol by volume.

37. **Negative deviation :** For non-ideal solution, if the vapour pressure is lower, then it is said to exhibit negative deviation. $A—B$ interactions are stronger than $A—A$ and $B—B$ interactions. Due to this, vapour pressure decreases which results in negative deviation. In negative deviation, intermolecular force increases, volume decreases, vapour pressure decreases and heat is released. Therefore, ΔH_{mix} = –ve, ΔV_{mix} = – ve Example, phenol + aniline and chloroform + acetone show negative deviation.



Plot for non-ideal solution showing negative deviation

38. *Refer to answer 31.*

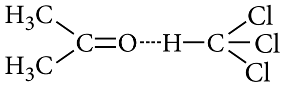
A maximum boiling azeotrope is formed by solutions showing a large negative deviation from Raoult's law at a specific compostion.

For example Chloroform – acetone mixture.

39. A mixture of ethanol and acetone shows positive deviation from Raoult's law. Pure ethanol possesses hydrogen bonding. Introduction of acetone between the molecules of ethanol results in breaking of some of these hydrogen bonds. Due to weakening of interactions, the solution shows positive deviation from Raoult's law.

40. *Refer to answers 35 and 37.*

41. A mixture of chloroform and acetone shows negative deviation from Raoult's law because chloroform molecule forms H-bonding with acetone molecule. As a result of this $A—B$ interaction becomes stronger than $A—A$ and $B—B$ interactions. This leads to the decrease in vapour pressure and resulting in negative deviation.



42. *Refer to answers 35 and 37.*

43. (i) n-Hexane and n-octane : London dispersion forces as both the molecules are non-polar.

(ii) Methanol and acetone : Dipole-dipole interactions as both the molecules are polar.

44. *Refer to answers 23, 35 and 37.*

45. *Refer to answer 37.*

46. Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.

47. Molal elevation constant may be defined as the elevation in boiling point when the molality of the solution is unity (*i.e.*, 1 mole of the solute is dissolved in 1 kg (1000 g) of the solvent). The units of K_b are therefore, degree/molality *i.e.*, K/m or °C/m or K kg mol^{-1}.

48. When a non-volatile solute is added to a solvent, the vapour pressure of the solvent (above the resulting solution) is lower than the vapour pressure above the pure solvent.

49. Osmotic pressure is the extra pressure which is applied on the solution to just prevent the flow of solvent into the solution through a semi-permeable membrane.

50. *Refer to answer 46.*

51. Ebullioscopic constant is the boiling point elevation constant when one mole of solute is dissolved in 1000 g of solvent. It is denoted by K_b.

52. Colligative properties are the properties of solution which depend upon the number of solute particles and not upon the nature of the solute.

53. Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution side.

54. (i) The elevation in boiling point of a solution is a colligative property which depends on the number of moles of solute added. Higher the concentration of solute added, higher will be the elevation in boiling point. Thus, 2 M glucose has higher boiling point than 1 M glucose solution.

(ii) When the external pressure applied becomes more than the osmotic pressure of solution then the solvent molecules from the solution pass through the semipermeable membrane to the solvent side and the process is called reverse osmosis.

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

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

56. The boiling point of the solution is always higher than that of the pure solvent. As the vapour pressure of the solution is lower than that of the pure solvent and vapour pressure increases with increase in temperature. Hence, the solution has to be heated more to make the vapour pressure equal to the atmospheric pressure.

Elevation of boiling point is a colligative property because it depends on number of solute particles present in a solution.

57. Given : $W_2 = ?$, $M_2 = 256 \text{ g mol}^{-1}$, $\Delta T_f = 0.48 \text{ K}$

$W_1 = 75 \text{ g}$, $K_f = 5.12 \text{ K kg mol}^{-1}$

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_f \times M_2 \times W_1}{K_f \times 1000} = \frac{0.48 \times 256 \times 75}{5.12 \times 1000} = 1.8 \text{ g}$$

58. Given $W_1 = 1 \text{ kg} = 1000 \text{ g}$, $W_2 = 18 \text{ g}$, $M_2 = 180 \text{ g mol}^{-1}$

$T_b^\circ = 373.15 \text{ K}$, $K_b = 0.52 \text{ K Kg mol}^{-1}$, $T_b = ?$

Using formula,

$$\Delta T_b = K_b \times \frac{W_2 \times 1000}{M_2 \times W_1}$$

or $$\Delta T_b = \frac{0.52 \text{ K} \times 18 \times 1000}{180 \times 1000} = 0.052 \text{ K}$$

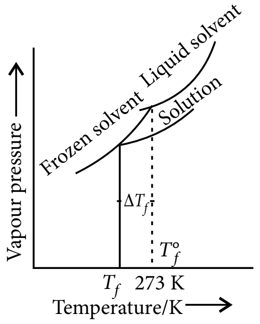
$$\Delta T_b = T_b - T_b^\circ$$

$$0.052 = T_b - 373.15$$

$$T_b = 373.15 + 0.052 = 373.202 \text{ K}$$

59. When a non-volatile solute is added to a solvent, the freezing point of the solution is always lower than that of pure solvent as the vapour pressure of the solvent decreases in the presence of non-volatile solute.

Plot for the lowering in freezing point of water when NaCl is added to it is shown as :



60. Osmosis : The spontaneous movement of the solvent molecules from the pure solvent or from a dilute solution to a concentrated solution through a semi-permeable membrane is called osmosis.

Osmotic Pressure : The minimum excess pressure that has to be applied on the solution to prevent the passage of solvent molecules into it through semipermeable membrane is called osmotic pressure.

Osmotic pressure is a colligative property because it depends on the number of solute particles and not on their nature.

61. (i) Number of particles of solute
(ii) Association or dissociation of solute
(iii) Concentration of solute
(iv) Temperature

62. *Refer to answer 60.*

The osmotic pressure method has the advantage over other methods because

(i) osmotic pressure can be measured at room temperature and the molarity of the solution is used instead of molality.

(ii) its magnitude is large as compared to other colligative properties even for very dilute solutions.

63. The egg placed in pure water will swell because the concentration of proteins is high inside the egg as compared to water. Therefore, endosmosis occurs and water diffuses through the semipermeable membrane. The egg which is placed in sodium chloride solution will shrink due to osmosis of water out of the egg.

64. Given, $W_2 = 0.520 \text{ g}$,

$W_1 = 80.2 \text{ g}$, $K_b = 0.52 \text{ K m}^{-1}$

M_2 of $C_6H_{12}O_6 = 6 \times 12 + 12 \times 1 + 6 \times 16$

$= 180 \text{ g mol}^{-1}$

$$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{0.52 \times 0.520 \times 1000}{180 \times 80.2} = 0.019 \text{ K}$$

Boiling point of solution, $T_b = T_b^\circ + \Delta T_b$

$= 373 \text{ K} + 0.019 \text{ K} = 373.019 \text{ K}$

65. *Refer to answer 49.*

Relation between osmotic pressure and molar mass,

$\pi V = n_2 RT$

$$\pi V = \frac{W_2 RT}{M_2} \qquad \left[\because n_2 = \frac{W_2}{M_2}\right]$$

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

where π is osmotic pressure and

M_2 is molar mass of solute.

66. Mass of ethylene glycol ($C_2H_6O_2$), $W_2 = 31$ g

Mass of water, $W_1 = 500$ g

M_2 (Mol. mass of $C_2H_6O_2$) = 62 g mol^{-1},

$K_f = 1.86$ K kg mol^{-1}, $T_f = ?$

Using formula, $\Delta T_f = K_f \times \dfrac{W_2 \times 1000}{M_2 \times W_1}$

$$= 1.86 \times \frac{31 \times 1000}{62 \times 500} = 1.86 \text{ K}$$

$$\Delta T_f = T_f^\circ - T_f$$

or $T_f = T_f^\circ - \Delta T_f = 273 - 1.86 = 271.14 \text{ K}$

67. Mass of urea = 15 g

Molar mass of urea = 60 g mol^{-1}

Molar mass of glucose = 180 g mol^{-1}

Mass of glucose = ?

For isotonic solution, osmotic pressure, $\pi_1 = \pi_2$

$n_1 = n_2$ (when volume is same)

or $\dfrac{W_1}{M_1} = \dfrac{W_2}{M_2} \Rightarrow \dfrac{15}{60} = \dfrac{W_2}{180}$

$\Rightarrow \quad W_2 = \dfrac{15 \times 180}{60} = 45 \text{ g}$

68. Mass of $CaCl_2$ (W_2) = 10 g

Mass of water (W_1) = 200 g

Molar mass of $CaCl_2$ (M_2) = 111 g mol^{-1}

Molal Elevation constant = 0.512 K kg mol^{-1}

$$m = \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$m = \frac{10}{111} \times \frac{1000}{200} = 0.450 \text{ m}$$

$\Delta T_b = K_b\, m = 0.512 \times 0.450 = 0.2306$ K

69. (i) *Refer to answer 61.*

(ii) *Refer to answer 52.*

70. $T_f = -15°\text{C}$, $K_f = 1.86$ K kg mol^{-1}

$\Delta T_f = T_f^\circ - T_f = 0 - (-15°\text{C}) = 15°\text{C} = 288 \text{ K}$

$\Delta T_f = K_f \times m$

$$288 = 1.86 \times \frac{W_2}{0.062 \times 5}$$

$W_2 = 48$ kg

$\Delta T_b = K_b \times m$

$$\Delta T_b = 0.52 \times \frac{48}{0.062 \times 5}$$

$\Delta T_b = 80.51$ K

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

$80.51 = T_b - 373$

$T_b = 80.51 + 373 = 453.51$ K

71. $W_2 = 1.00$ g, $W_1 = 50$ g, $K_f = 5.12$ K kg mol^{-1}, $\Delta T_f = 0.40$ K

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{W_1 \times \Delta T_f} = \frac{5.12 \times 1 \times 1000}{50 \times 0.40}$$

$= 256$ g mol^{-1}

72. Molality of sugar solution

$$= = \frac{W_2 \times 1000}{M_2 \times W_1} = \frac{5}{342} \times \frac{1000}{95} = 0.154 \text{ m}$$

$\Delta T_f = T_f^\circ - T_f = 273.15 - 271 = 2.15$ K

$\Delta T_f = K_f \times m \quad \therefore \; K_f = \dfrac{\Delta T_f}{m} = \dfrac{2.15}{0.154}$

Molality of glucose solution

$$= = \frac{W_2 \times 1000}{M_2 \times W_1} = \frac{5}{180} \times \frac{1000}{95} = 0.292 \text{ m}$$

$\therefore \quad \Delta T_f (\text{Glucose}) = K_f \times m = \dfrac{2.15}{0.154} \times 0.292 = 4.08$

$\therefore \quad$ Freezing point of glucose solution =

$= 273.15 - 4.08 = 269.07$ K

73. $W_1 = 500$ g

Boiling point of solution (T_b) = 100.42°C

K_b for water = 0.512 K kg mol^{-1}

$M_2(C_3H_8O_3) = (3 \times 12) + (8 \times 1) + (3 \times 16)$

$= 92$ g mol^{-1}

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

$= 373.42 \text{ K} - 373 \text{ K} = 0.42 \text{ K}$

$$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_b \times M_2 \times W_1}{K_b \times 1000} = \frac{0.42 \times 92 \times 500}{0.512 \times 1000} = 37.73 \text{ g}$$

74. $W_1 = 450$ g, $W_2 = 15.0$ g
$\Delta T_f = T_f^\circ - T_f = 273 \text{ K} - 272.66 \text{ K} = 0.34 \text{ K}$
$K_f = 1.86 \text{ K kg mol}^{-1}$

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}$$

$$M_2 = \frac{1.86 \times 15 \times 1000}{0.34 \times 450} = 182.35 \text{ g mol}^{-1}$$

75. The relative lowering of vapour pressure is given by the following expression,
$(p^\circ_{\text{solvent}} - p_{\text{solution}})/p^\circ_{\text{solvent}} = n_2/(n_1 + n_2)$
for dilute solutions, $n_2 << n_1$, therefore
$(p^\circ_{\text{solvent}} - p_{\text{solution}})/p^\circ_{\text{solvent}} = n_2/n_1$
$= (W_2 \times M_1)/(M_2 \times W_1)$
$(p^\circ_{\text{solvent}} - 2.8)/p^\circ_{\text{solvent}} = (30 \times 18)/(M_2 \times 90)$
$(p^\circ_{\text{solvent}} - 2.8)/p^\circ_{\text{solvent}} = 6/M_2$ ...(1)
Similarly for second case we get,
$(p^\circ_{\text{solvent}} - 2.9)/p^\circ_{\text{solvent}} = (30 \times 18)/(M_2 \times 108)$
$(p^\circ_{\text{solvent}} - 2.9)/p^\circ_{\text{solvent}} = 5/M_2$ ...(2)
On solving eq. (1) and (2), we get
$(p^\circ_{\text{solvent}} - 2.8)/(p^\circ_{\text{solvent}} - 2.9) = 6/5$
$\therefore \quad p^\circ_{\text{solvent}} = 3.4 \text{ k}P_a$
i.e., vapour pressure of water at 298 K is 3.4 kp_a
Substituting the value of p°_{solvent} in (1) we get,
$(3.4 - 2.8)/3.4 = 6/M_2$
or $0.6/3.4 = 6/M_2$
$\therefore \quad M_2 = 34$ g

76. $i = 2$, $K_b = 0.512 \text{ K kg mol}^{-1}$, $W_B = 15$ g
$M_B = 58.44 \text{ g mol}^{-1}$, $W_A = 250$ g

$$\Delta T_b = \frac{i \times K_b \times W_B \times 1000}{M_B \times W_A}$$

$$\Delta T_b = \frac{2 \times 0.512 \times 15 \times 1000}{58.44 \times 250} = 1.05 \text{ K}$$

Therefore, boiling point of aqueous solution,
$T_b = T_b^\circ + \Delta T_b = 373.15 \text{ K} + 1.05 \text{ K} = 374.20 \text{ K}$

77. $W_B = 8.95 \text{ mg} = 8.95 \times 10^{-3}$ g,
$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$, $V = 35 \times 10^{-3}$ L
$T = (25 + 273) \text{ K} = 298 \text{ K}$, $\pi = \frac{0.335}{760}$ atm
Substituting these values in the equation,

$$M_B = \frac{W_B \times R \times T}{\pi \times V}$$

$$M_B = \frac{8.95 \times 10^{-3} \text{ g} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{\frac{0.335}{760} \text{ atm} \times 35 \times 10^{-3} \text{ L}}$$

$M_B = 14193.29 \text{ g mol}^{-1}$

78. $W_2 = 6.21$ g, $W_1 = 24.0$ g
$T_b = 68.04$ °C, $T_b^\circ = 61.7$ °C
and $K_b = 3.63$ °C/m
$\Delta T_b = T_b - T_b^\circ = 68.04 \text{ °C} - 61.7 \text{ °C} = 6.34 \text{ °C}$

$$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$

or $$M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

$$M_2 = \frac{3.63 \text{°C m}^{-1} \times 6.21 \text{ g} \times 1000}{6.34 \text{°C} \times 24.0 \text{ g}} = 148.15 \text{ g mol}^{-1}$$

79. $W_1 = 65.0$ g, $\Delta T_f = 7.50$°C,
$K_f = 1.86$°C/m, $i = 1.87$ and $M_2 = 58.5 \text{ g mol}^{-1}$

$$\Delta T_f = \frac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_f \times M_2 \times W_1}{i \times K_f \times 1000} = \frac{7.50 \text{°C} \times 58.5 \text{ g mol}^{-1} \times 65 \text{ g}}{1.87 \times 1.86 \text{°C/m} \times 1000} = 8.199 \text{ g}$$

80. *Refer to answer 63.*

81. Concentration of the solution = 1 molar
Density of the solution = 1.06 g mL^{-1}
M_2, molar mass of KBr = 39 + 80 = 119 g mol^{-1}
K_b for H_2O = 0.52 K kg mol^{-1}

Molality, $$m = \frac{M \times 1000}{1000 \times d - M \times M_2}$$

$$m = \frac{1 \times 1000}{1000 \times 1.06 - 1 \times 119} = 1.0626 \text{ mol kg}^{-1}$$

$\Delta T_b = K_b m = 0.52 \text{ K kg mol}^{-1} \times 1.0626 \text{ mol kg}^{-1}$
$\Delta T_b = 0.5525 \text{ K} \approx 0.553 \text{ K}$
$T_b = T_b^\circ + \Delta T_b = 373 \text{ K} + 0.553 \text{ K} = 373.553 \text{ K}$

82. $W_2 = 1.25$ g, $W_1 = 99.0$ g
$\Delta T_b = T_b - T_b^\circ = (80.31 - 80.10)\text{°C} = 0.21\text{°C} = 0.21 \text{ K}$
$\Delta T_b = K_b \cdot m$

$$\Delta T_b = K_b \times \frac{W_2 \times 1000}{M_2 \times W_1}, \; M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

$$= \frac{2.53 \times 1.25 \times 1000}{0.21 \times 99} = \frac{3162.5}{20.79} = 152.11 = 152 \text{ g mol}^{-1}$$

83. M_2 (ethylene glycol) = 62 g mol^{-1},
$W_1 = 5.50$ kg = 5500 g, $\Delta T_f = T_f^\circ - T_f = 0°\text{C} - (-10°\text{C})$
$= 10°\text{C} = 10$ K

and $K_f = 1.86$ K kg mol^{-1}

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_f \times M_2 \times W_1}{K_f \times 1000} = \frac{10 \times 62 \times 5500}{1.86 \times 1000} = 1833.33 \text{ g}$$
$$= 1.833 \text{ kg}$$

84. $W_2 = 100$ mg = 0.1 g,
$V = 10.0$ mL = 0.01 L,

$\pi = 13.3$ mm Hg $= \frac{13.3}{760}$ atm

$T = 25°\text{C} = 273 + 25 = 298$ K

$R = 0.0821$ L atm mol^{-1} K^{-1}

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

$$M_2(\text{Protein}) = \frac{W_2 RT}{\pi V}$$

$$= \frac{0.1 \text{ g} \times 0.0821 \text{ L atm mol}^{-1}\text{K}^{-1} \times 298 \text{ K}}{\frac{13.3}{760} \text{ atm} \times 0.01 \text{ L}}$$

$M_2 = 13980.45$ g mol^{-1}

85. $W_1 = 1$ kg = 1000 g, $\Delta T_f = 3$ K
$K_f = 1.86$ K kg mol^{-1}
$M_2(\text{NaCl}) = 23 + 35.5 = 58.5$ g mol^{-1}

$$\Delta T_f = \frac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_f \times M_2 \times W_1}{i \times K_f \times 1000}$$

[For NaCl, $i = 2$ because 1 mole of NaCl on dissociation gives 2 moles of ions]

$$W_2 = \frac{3 \times 58.5 \times 1000}{2 \times 1.86 \times 1000} = 47.18 \text{ g}$$

86. Total moles in solution

$$= \frac{x}{200} + 0.05 \times 2 = \frac{x}{200} + 0.1 \qquad (\because \; i = 2 \text{ for NaCl})$$

$pV = nRT$

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

$$\frac{x}{200} + 0.1 = \frac{4.92 \text{ atm} \times 1 \text{ L}}{0.082 \text{ L atm K}^{-1}\text{mol}^{-1} \times 300 \text{ K}} = 0.20$$

$$\frac{x}{200} = 0.20 - 0.1 = 0.1$$

$x = 0.1 \times 200 = 20$ g

87. Molar mass of glucose, $C_6H_{12}O_6$
$= 6 \times 12 + 12 \times 1 + 6 \times 16 = 180$ g mol^{-1}
Molar mass of sucrose, $C_{12}H_{22}O_{11}$
$= 12 \times 12 + 22 \times 1 + 11 \times 16 = 342$ g mol^{-1}

$$n_{\text{glucose}} = \frac{18}{180} = 0.1, \; n_{\text{sucrose}} = \frac{68.4}{342} = 0.2$$

Total moles of solute, $n_2 = 0.1 + 0.2 = 0.3$

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$\Delta T_f = \frac{K_f \times n_2 \times 1000}{W_1}$$

$$= \frac{1.86 \text{ K m}^{-1} \times 0.3 \text{ mol} \times 1000}{200 \text{ g}} = 2.79 \text{ K}$$

Freezing point of aqueous solution, $T_f = T_f^\circ - \Delta T_f$
$= 273 - 2.79 = 270.21$ K

88. M_2 (glucose, $C_6H_{12}O_6$) = 180 g mol^{-1}
$W_2 = 54$ g, $W_1 = 250$ g, $K_f = 1.86$ K kg mol^{-1}

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{1.86 \times 54 \times 1000}{180 \times 250} = 2.23 \text{ K}$$

Freezing point of solution, $T_f = T_f^\circ - \Delta T_f$
$= 273 \text{ K} - 2.23 \text{ K} = 270.77$ K

89. $T_b = 36.86°\text{C}$, $T_b^\circ = 35.60°\text{C}$
$\Delta T_b = T_b - T_b^\circ = 36.86 - 35.60 = 1.26°\text{C}$

$$m = \frac{W_2}{M_2} \times \frac{1000}{W_1} = \frac{8}{M_2} \times \frac{1000}{100} = \frac{80}{M_2}$$

$\Delta T_b = K_b \cdot m$

$$1.26 = 2.02 \times \frac{80}{M_2}$$

$$M_2 = \frac{80 \times 2.02}{1.26} = 128.25 \text{ g mol}^{-1}$$

90. Molality = 0.1539 m,
$\Delta T_f = T_f^\circ - T_f = 273.15 - 271 = 2.15$ K

$$\therefore \quad \Delta T_f = K_f \cdot m \text{ or } K_f = \frac{\Delta T_f}{m} = \frac{2.15}{0.1539}$$

Again mass of solute, $W_2 = 5$ g
Molar mass of solute, $M_2 = 180$ g mol^{-1}
Mass of solution = 100 g
$\therefore$ Mass of solvent, $W_1 = 95$ g

$$\text{Using, } \Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{2.15 \times 5 \times 1000}{0.1539 \times 180 \times 95} = 4.08 \text{ K}$$

$\therefore$ Freezing point of solution, $T_f = T_f^\circ - \Delta T_f$
$= 273.15 - 4.08 = 269.07$ K

91. **van't Hoff factor :** It is defined as the ratio of the experimental value of colligative property to the calculated value of the colligative property and is used to find out the extent of dissociation or association. Mathematically, it is represented as

$$i = \frac{\text{Experimental (or observed value) of colligative property}}{\text{Calculated (or normal value) of colligative property}}$$

92. *Refer to answer 91.*
(i) van't Hoff factor (i) > 1 for solutes undergoing dissociation
(ii) van't Hoff factor (i) < 1 For soutes undergoing association

93. Molecular mass of $Na_2SO_4 \cdot 10H_2O$
$= [2 \times 23 + 32 + 16 \times 4 + 10 \times (2 \times 1 + 16)]$
$= (46 + 32 + 64 + 180)$ g mol^{-1} = 322 g mol^{-1}
$Na_2SO_4 \cdot 10H_2O$ ionises as :
$$Na_2SO_4 \cdot 10H_2O \rightleftharpoons 2Na^+ + SO_4^{2-} + 10H_2O$$
$\Rightarrow$ $i = 3$

$$m = \frac{n_B}{W_A} = \frac{W_B}{M_B \times W_A} = \frac{6.00 \text{ g}}{322 \text{ g mol}^{-1} \times 0.1 \text{ kg}}$$
$$= 0.186 \text{ mol kg}^{-1} = 0.186 \text{ m}$$

Also, $\Delta T_f = i\,K_f \cdot m$
$= 3 \times 1.86$ K m^{-1} $\times$ 0.186 m = 1.04 K
$\Rightarrow$ $T_f = T_f^\circ - \Delta T_f = (273 - 1.04)$ K = 271.96 K

94. Molality of solution, $m = 1.00$ m
Boiling point of solution, $T_b = 100.18$°C = 373.18 K
Boiling point of water (solvent), $T_b^\circ = 100.00$°C = 373 K
$\Delta T_b = T_b - T_b^\circ = 373{\cdot}18$ K $- 373$ K $= 0{\cdot}18$ K
$\Delta T_b = i\,K_b \cdot m$
$0.18 \text{ K} = i \times K_b \cdot m$
$0.18 \text{ K} = i \times 0.512$ K kg mol^{-1} $\times$ 1 mol kg^{-1}

$$i = \frac{0.18 \text{ K}}{0.512 \text{ K kg mol}^{-1} \times 1 \text{ mol kg}^{-1}} = 0.35$$

95. *Refer to answer 91 and 92 (i).*

96. $\Delta T_f = iK_f \cdot m$
i for $MgCl_2 = 3$

$$\text{Molality, } m = \frac{W_2 \times 1000}{M_2 \times W_1} = \frac{1.9 \times 1000}{95 \times 50} = 0.4 \text{ m}$$

$\Delta T_f = 3 \times 1.86 \times 0.4 = 2.232$ K
Freezing point of solution, , $T_f = T_f^\circ - \Delta T_f$
$= 273 - 2.232$ K = 270.77 K

97. $W_2 = 2.56$ g, $W_1 = 100$ g, $\Delta T_f = 0.383$ K
$K_f = 3.83$ K kg mol^{-1}, $\Delta T_f = K_f \times m$

$$\Rightarrow \quad \Delta T_f = K_f \times \frac{W_2}{M_2} \times \frac{1000}{W_1}$$

$$\Rightarrow \quad M_2 = \frac{W_2 \times 1000}{\Delta T_f \times W_1} \times K_f = \frac{2.56 \times 1000}{0.383 \times 100} \times 3.83$$
$$= 256 \text{ g mol}^{-1}$$

$$\because \quad i = \frac{\text{Normal atomic mass}}{\text{Observed atomic mass}} = \frac{32}{256} = \frac{1}{8}$$

Sulphur exists as S_8.

98. $W_2 = 4$ g, $M_2 = 120$ g mol^{-1}
$W_1 = 100$ g, $K_b = 0.52$ K kg mol^{-1}
For complete dissociation, $i = 2$
Using formula, $\Delta T_b = iK_b m$

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

$\therefore$ $T_b = T_b^\circ + \Delta T_b = 100 + 0.34 = 100.34$°C

99. $W_2 = 3.9$ g, $W_1 = 49$ g, $\Delta T_f = 1.62$ K, $M_2 = 122$ g mol^{-1}, $K_f = 4.9$ K kg mol^{-1}

$$\Delta T_f = i\,K_f m = i \times K_f \times \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$\Rightarrow \quad 1.62 = \frac{i \times 4.9 \times 3.9 \times 1000}{122 \times 49}$$

$$\Rightarrow \quad i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000} = 0.506$$

As $i < 1$, solute is associated.

100. $\Delta T_f = iK_f m = \dfrac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$

$$2 = \frac{2 \times 1.86 \times W_2 \times 1000}{58.5 \times 37.2}$$

$\Rightarrow$ $W_2 = 1.17$ g

101. Mass of K_2SO_4, $W_2 = 2.5 \times 10^{-2}$ g
Molar mass of K_2SO_4, $M_2 = 174 \text{ g mol}^{-1}$
$V = 2$ L, $T = 25°C = 298$ K
$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

We know, osmotic pressure, $\pi = \dfrac{W_2RT}{M_2V}$

$$\pi = \frac{2.5 \times 10^{-2} \times 0.0821 \times 298}{174 \times 2}$$

$$= \frac{61.1645 \times 10^{-2}}{348} = 0.1758 \times 10^{-2} \text{ atm}$$

102. $\Delta T_f = 2$ K, $K_f = 1.86 \text{ K kg mol}^{-1}$,
$W_1 = 1$ kg, $\Delta T_f = i\,K_f\,m$, $M_2(\text{KCl}) = 74.5 \text{ g mol}^{-1}$

$i = 2$ for KCl

$$\Delta T_f = \frac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$2 = \frac{2 \times 1.86 \times W_2 \times 1000}{74.5 \times 1000}$$

$\Rightarrow \quad W_2 = 40.05$ g

103. $W_2 = 10.50$ g, $W_1 = 200$ g
$M_2(MgBr_2) = 184 \text{ g mol}^{-1}$
$K_f = 1.86 \text{ K kg mol}^{-1}$
$MgBr_{2(aq)} \longrightarrow Mg^{2+}_{(aq)} + 2Br^{-}_{(aq)}$, $i = 3$

$$\Delta T_f = iK_f m, \quad \Delta T_f = \frac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$\Delta T_f = \frac{3 \times 1.86 \times 10.50 \times 1000}{184 \times 200} = 1.592 \text{ K}$$

Freezing point of solution, $T_f = T_f^\circ - \Delta T_f = 273 - 1.592$
$= 271.408$ K

104. $m = 0.561$ m, $\Delta T_f = 2.93°C$ and
$K_f = 1.86°C \text{ kg mol}^{-1}$
$\Delta T_f = iK_f m$

$$i = \frac{\Delta T_f}{K_f m} = \frac{2.93°C}{1.86°C \text{ kg mol}^{-1} \times 0.561 \text{ m}} = 2.807$$

105. Here, $n = 2$ because phenol forms dimer on association.
$W_2 = 20$ g, $W_1 = 1$ kg $= 1000$ g, $\Delta T_f = 0.69$ K, $K_f = 5.1 \text{ K m}^{-1}$

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1} = \frac{5.1 \times 20 \times 1000}{0.69 \times 1000} = 147.82$$

$M_{2(\text{observed})} = 147.82$

$M_{2(\text{calculated})}$
$C_6H_5OH = 6 \times 12 + 6 \times 1 + 16 = 94 \text{ g mol}^{-1}$

$$i = \frac{M_{2(\text{calculated})}}{M_{2(\text{observed})}} = \frac{94}{147.82} = 0.635$$

$2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$

$$\alpha = \frac{i-1}{\left(\frac{1}{n}-1\right)} = \frac{0.635-1}{\left(\frac{1}{2}-1\right)} = \frac{0.365}{0.5} = 0.73 = 73\%$$

106. Here, $n = 3$ because 1 molecule of $BaCl_2$ on dissociation gives three ions.
$W_2 = 12.48$ g, $W_1 = 1.0$ kg $= 1000$ g
$T_b = 373.0832$ K, K_b for $H_2O = 0.52 \text{ K m}^{-1}$
and $M_2(BaCl_2) = 208.34 \text{ g mol}^{-1}$
$\Delta T_b = T_b - T_b^\circ = 373.0832 \text{ K} - 373 \text{ K} = 0.0832$ K

$$M_{2(\text{observed})} = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

$$M_{2(\text{observed})} = \frac{0.52 \times 12.48 \times 1000}{0.0832 \times 1000} = 78$$

$M_{2(\text{observed})} = 78 \text{ g mol}^{-1}$

$$i = \frac{M_{2(\text{calculated})}}{M_{2(\text{observed})}} = \frac{208.34 \text{ g mol}^{-1}}{78 \text{ g mol}^{-1}} = 2.67$$

$$\alpha = \frac{i-1}{n-1} = \frac{2.67-1}{3-1} = \frac{1.67}{2} = 0.835 = 83.5\%$$

107. $C = \dfrac{1}{10}$ M
$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$
$\therefore \quad n = 5$

Degree of dissociation, $\alpha = \dfrac{50}{100} = 0.5$

$$\alpha = \frac{i-1}{n-1}, \; 0.5 = \frac{i-1}{5-1}, \; 0.5 = \frac{i-1}{4}$$

$\Rightarrow \quad i - 1 = 2 \quad \therefore \quad i = 3$

So, osmotic pressure, $\pi = iCRT$

$$= 3 \times \frac{1}{10} \times 0.0821 \times 300 = 90 \times 0.0821 = 7.389 \text{ atm}$$

108. $M_2 = \dfrac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1} = \dfrac{2.53 \times 0.30 \times 1000}{0.0633 \times 100}$
$= 120 \text{ g mol}^{-1}$

$\therefore \quad$ Molar mass of $CH_3COOH = 60$ g/mol

$$i = \frac{M_{2(\text{calculated})}}{M_{2(\text{observed})}} = \frac{60}{120} = \frac{1}{2} = 0.5$$

Here, $i < 1$, therefore the solute acetic acid is associated in benzene.

109. (i) $M_2 = \dfrac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1} = \dfrac{5.12 \times 0.2 \times 1000}{0.45 \times 20}$

$= 113.77 \text{ g/mol}^{-1}$

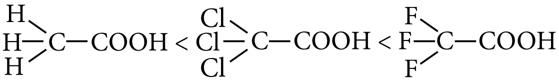
(ii) Molar mass of acetic acid = 60 g/mol

$$i = \frac{M_{2(\text{calculated})}}{M_{2(\text{observed})}} = \frac{60}{113.77} = 0.52$$

$i < 1$, the solute acetic acid is associated in benzene.

110. (i) The depression in freezing point is in the order :

Acetic acid < trichloroacetic < trifluoroacetic acid



$H_3C{-}COOH < Cl_3C{-}COOH < F_3C{-}COOH$

Fluorine has the highest electron withdrawing inductive effect ($-I$ effect) so trifluoroacetic acid is the strongest acid and acetic acid is the weakest acid. Therefore, trifluoroacetic acid ionises to the greater extent and acetic acid ionises to the minimum extent. Greater the number of ions produced, greater is the depression in freezing point.

(ii) Molar mass of $CH_3CH_2CHClCOOH$

$= 4 \times 12 + 7 \times 1 + 35.5 + 2 \times 16 = 122.5 \text{ g mol}^{-1}$

Number of moles of $CH_3CH_2CHClCOOH$

$$= \frac{20}{122.5} = 0.1632 \text{ mol}$$

$$\text{Molality of solution} = \frac{\text{Moles of solute} \times 1000}{\text{Mass of solvent (g)}}$$

$$m = \frac{0.1632 \times 1000}{500} = 0.3264 \text{ m}$$

$$CH_3CH_2CHClCOOH_{(aq)} \rightleftharpoons CH_3CH_2CHClCOO^-_{(aq)} + H^+_{(aq)}$$

Initial conc.	C	0	0
Equili. conc.	$C - C\alpha$	$C\alpha$	$C\alpha$

where, α is the degree of dissociation of acid.

$$K_a = \frac{(C\alpha)^2}{C(1-\alpha)} = C\alpha^2 \qquad (\because 1 >>> \alpha)$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} = 0.065$$

$\alpha = \dfrac{i-1}{n-1} \Rightarrow 0.065 = \dfrac{i-1}{2-1}$ [$\because$ For the given acid $n = 2$ because 1 molecule gives 2 particles on dissociation.]

$i = 1 + 0.065 = 1.065$

$\Delta T_f = iK_f m$

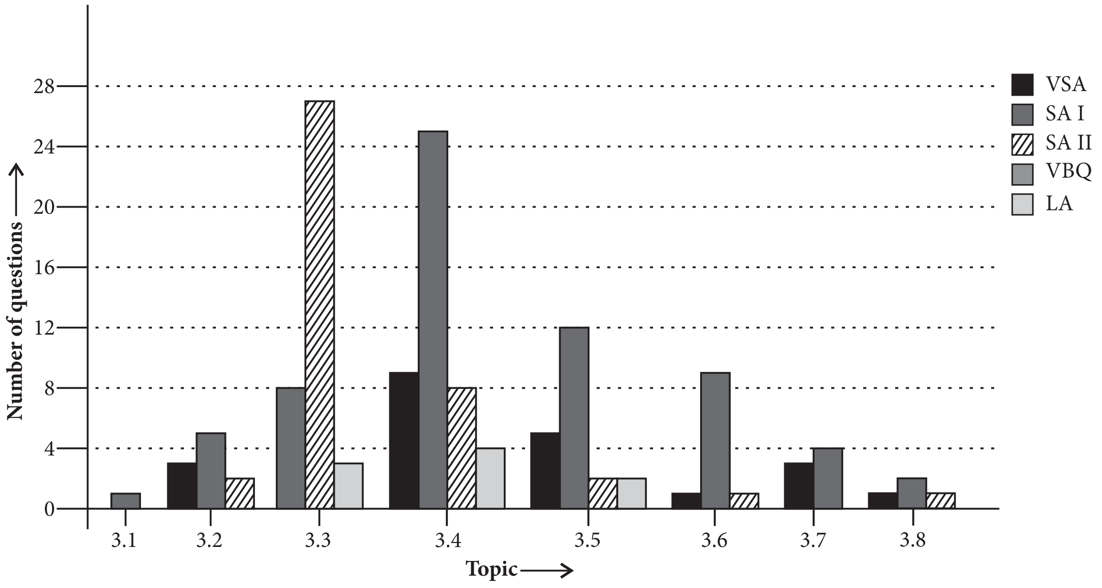
$= 1.065 \times 1.86 \times 0.3264$

$\Delta T_f = 0.6465 \approx 0.65 \text{ K}$

03

Electrochemistry

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



- ⏩ Maximum total weightage is of *Nernst Equation.*
- ⏩ Maximum VSA and SA I type questions were asked from *Conductance of Electrolytic Solutions*.
- ⏩ Maximum SA II type questions were asked from *Nernst Equation*.

QUICK RECAP

⏩ **Electrochemistry :** It is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

Differences between electrochemical cell and electrolytic cell :

Electrochemical cell (Galvanic or Voltaic cell)	Electrolytic cell
1. It is a device which converts chemical energy into electrical energy.	1. It is a device which converts electrical energy into chemical energy.
2. It is based upon the redox reaction which is spontaneous. *i.e.*, $\Delta G = -\text{ve}$	2. The redox reaction is non-spontaneous and takes place only when electrical energy is supplied. *i.e.*, $\Delta G = +\text{ve}$
3. Two electrodes are usually set up in two separate beakers.	3. Both the electrodes are suspended in the solution or melt of the electrolyte in the same beaker.
4. The electrolytes taken in the two beakers are different.	4. Only one electrolyte is taken.
5. The electrodes taken are of different materials.	5. The electrodes taken may be of the same or different materials.
6. The electrode on which oxidation takes place is called the *anode* (or –ve pole) and the electrode on which reduction takes place is called the *cathode* (or +ve pole)	6. The electrode which is connected to the –ve terminal of the battery is called the *cathode*; the cations migrate to it which gain electrons and hence, a reduction takes place, the other electrode is called the *anode*.
7. To set up this cell, a salt bridge/porous pot is used.	7. No salt bridge is used in this case.

- **Nernst equation :** For a reduction reaction, $M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)}$;

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}_{(aq)}]}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}_{(aq)}]}$$

- For concentration cell, EMF at 298 K is given by

$$E_{\text{cell}} = \frac{2.303RT}{nF}\log\frac{C_2}{C_1} \text{ where } C_2 > C_1$$

- **Applications of Nernst equation :**
  - **To calculate electrode potential of a cell :**

$$aA + bB \xrightarrow{ne^-} xX + yY$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

  - **To calculate equilibrium constant :**

At equilibrium, $E_{\text{cell}} = 0$

$$E^\circ_{\text{cell}} = \frac{0.0591}{n}\log K_c \quad \text{at 298 K}$$

- **Relation between cell potential and Gibbs energy change :**

$\Delta G^\circ = -nFE^\circ_{\text{cell}}$; $\Delta G^\circ = -2.303\, RT \log K_c$

- **Conductance in electrolytic solutions :**

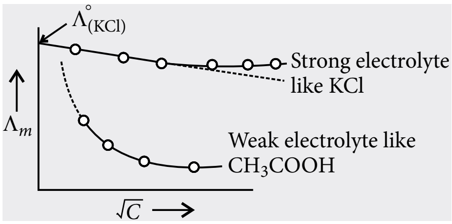
Property	Formula	Units	Effect of dilution
Conductance (G)	$\frac{1}{R} = \frac{a}{\rho l} = \frac{\kappa a}{l}$	Ohm^{-1} (Ω^{-1})/Siemens (S)	Increases as larger number of ions are produced.
Specific conductance (κ) or conductivity	$\frac{1}{\rho}$ or $G\frac{l}{a}$	Ohm^{-1} cm^{-1}/S m^{-1}	Decreases as number of ions per cm^3 decreases.
Equivalent conductivity (Λ_{eq})	$\kappa \times V$ or $\kappa \times \frac{1000}{N}$	Ω^{-1} cm^2 eq^{-1}/S m^2 eq^{-1}	Increases with dilution due to large increase in V.
Molar conductivity (Λ_m)	$\kappa \times V$ or $\kappa \times \frac{1000}{M}$	Ω^{-1} cm^2 mol^{-1}/S m^2 mol^{-1}	Increases with dilution due to large increase in V.

Limiting molar conductivity : When concentration approaches zero *i.e.* ; at infinite dilution, the molar conductivity is known as *limiting molar conductivity* (Λ_m°).

Variation of molar conductivity with concentration :

For a strong electrolyte it is shown by *Debye-Huckel Onsager equation* as follows :

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



Here, Λ_m°= Molar conductivity at infinite dilution (Limiting molar conductivity)

Λ_m = Molar conductivity at V-dilution

A = Constant which depends upon nature of solvent and temperature

C = Concentration

Plot of Λ_m against $C^{1/2}$ is a straight line with intercept equal to Λ_m° and slope equal to '$-A$'.

Thus, Λ_m^c decreases linearly with $\sqrt{C}$, when C = 0, $\Lambda_m^c = \Lambda_m^\circ$ and Λ_m° can be determined experimentally.

- **For weak electrolytes :** There is a very large increase in conductance with dilution especially near infinite dilution as no. of ions increases. Λ_m^c increases as C decreases but does not reach a constant value even at infinite dilution. Hence, their Λ_m° cannot be determined experimentally.
- **For a strong electrolyte :** there is only a small increase in conductance with dilution. This is because a strong electrolyte is completely dissociated in solution and so, the number of ions remain constant and on dilution, inter-ionic attractions decreases as ions move far apart.

Kohlrausch's law of independent migration of ions : It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. $\Lambda_m^\circ = \upsilon_+\lambda_+^\circ + \upsilon_-\lambda_-^\circ$ where λ_+° and λ_-° are the limiting molar conductivities of the cation and anion respectively and υ_+ and υ_- are stoichiometric no. of cations and anions respectively in one formula unit of the electrolyte.

Applications of Kohlrausch's law :

- **Calculation of molar conductivity of weak electrolytes :**

$$\Lambda_m^\circ (CH_3COOH) = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$$

$$= \left(\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}\right) + \left(\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+}\right) - \left(\lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}\right)$$

$$= \Lambda_m^\circ (HCl) + \Lambda_m^\circ (CH_3COONa) - \Lambda_m^\circ (NaCl)$$

- **Calculation of degree of dissociation :**

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\Lambda_m^\circ}$$

$$= \frac{\text{Molar conductivity at concentration } c}{\text{Molar conductivity at infinite dilution}}$$

- **Calculation of dissociation constant (K_c) of weak electrolyte :**

	$AB \rightleftharpoons$	A^+	+ B^-
Initial conc.	c	0	0
Conc. at equil.	$(c - c\alpha)$	$c\alpha$	$c\alpha$

$$K_c = \frac{c\alpha \times c\alpha}{(c - c\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

Electrolysis : It is the process of decomposition of an electrolyte by passing electricity through its aqueous solution or molten state.

- **Faraday's first law of electrolysis :** The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt). $w \propto Q$ or $w = ZQ = Z \times I \times t$ where Z is electrochemical equivalent of the substance deposited and $Z = \frac{\text{Eq. wt. of substance}}{96500}$.
- **Faraday's second law of electrolysis :** The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights.

$\frac{w_1}{w_2} = \frac{E_1}{E_2}$ where E is the equivalent weight.

Products of electrolysis :

Electrolyte	Products		Reactions involved	
	At cathode	At anode	At cathode	At anode
Molten NaCl	Na metal	Cl_2 gas	$Na^+_{(l)} + e^- \longrightarrow Na_{(l)}$	$Cl^-_{(l)} \longrightarrow \frac{1}{2}Cl_{2(g)} + e^-$
Aqueous NaCl	H_2 gas	Cl_2 gas	$H_2O_{(l)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} + OH^-_{(aq)}$	$Cl^-_{(aq)} \longrightarrow \frac{1}{2}Cl_{2(g)} + e^-$
Dil. H_2SO_4	H_2 gas	O_2 gas	$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$	$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$
Conc. H_2SO_4	H_2 gas	$S_2O_8^{2-}$	$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$	$2SO^{2-}_{4(aq)} \longrightarrow S_2O^{2-}_{8(aq)} + 2e^-$

Some commercial cells :

- **Primary cells :** Cells once exhausted cannot be used again *e.g.*, dry cell and mercury cell.
- **Secondary cells :** Rechargeable cell which can be used again and again *e.g.*, nickel-cadmium cell and lead storage battery.
- **Fuel cells :** Cells which can convert the energy of combustion of fuels such as H_2, CO, CH_4, etc. into electrical energy *e.g.*, $H_2 - O_2$ fuel cell.

Dry cell, lead accumulator and fuel cell :

	Dry cell	Lead storage battery	Fuel cell
Anode	Zinc	Lead	Porous carbon containing catalysts (H_2 passed)
Cathode	Graphite	Lead dioxide	Porous carbon containing catalysts (O_2 passed)
Electrolyte	MnO_2 + C (touching cathode) $NH_4Cl + ZnCl_2$ (touching anode)	H_2SO_4 (38%)	Conc. aqueous KOH
Anode reaction	$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$	$Pb_{(s)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$	$H_{2(g)} + 2OH^-_{(aq)} \longrightarrow 2H_2O_{(l)} + 2e^-$
Cathode reaction	$MnO_{2(s)} + NH^+_{4(aq)} + e^- \longrightarrow MnO(OH)_{(s)} + NH_{3(g)}$	$PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+ + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$	$O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$

Corrosion : The slow eating away of metals when exposed to the atmosphere is called *corrosion*.

Corrosion of iron (Rusting) : It is an electrochemical phenomenon which occurs in the presence of moisture and oxygen.

At anode : $2Fe_{(s)} \longrightarrow 2Fe^{2+}{}_{(aq)} + 4e^-$

At cathode : $O_{2(g)} + 4H^+{}_{(aq)} + 4e^- \longrightarrow 2H_2O_{(l)}$

Overall reaction : $2Fe_{(s)} + O_{2(g)} + 4H^+{}_{(aq)} \longrightarrow 2Fe^{2+}{}_{(aq)} + 2H_2O_{(l)}$.

Methods used for prevention of corrosion : Barrier protection, sacrificial protection, anti-rust solutions.

Previous Years' CBSE Board Questions

3.1 Electrochemical Cells

SA I (2 marks)

1. Define electrochemical cell. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell? *(2/5, AI 2016)*

3.2 Galvanic Cells

VSA (1 mark)

2. Represent the galvanic cell in which the reaction $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ takes place. *(1/3, Delhi 2013C)*

3. What is the necessity to use a salt bridge in a Galvanic cell? *(Delhi 2011C)*

SA I (2 marks)

4. On the basis of standard electrode potential values stated for acid solutions, predict whether Ti^{4+} species may be used to oxidise Fe^{II} to Fe^{III}.
Reactions :
$Ti^{4+} + e^- \rightarrow Ti^{3+}$; + 0.01
$Fe^{3+} + e^- \rightarrow Fe^{2+}$; + 0.77 *(AI 2007)*

5. Two half-reactions of an electrochemical cell are given below :
$MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}, E^\circ = +1.51V$
$Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e^-, E^\circ = +0.15$ V
Construct the redox equation from the standard potential of the cell and predict if the reaction is reactant favoured or product favoured. *(Delhi 2011, AI 2010, 2009)*

6. Given that the standard electrode potential (E°) of metals are :
$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V,
$Cu^{2+}/Cu = 0.34$ V,
$Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$ V,
$Fe^{2+}/Fe = -0.44$ V.
Arrange these metals in an increasing order of their reducing power *(AI 2010)*

7. Formulate the galvanic cell in which the following reaction takes place :
$Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$
State :
(i) Which one of its electrodes is negatively charged.
(ii) The reaction taking place at each of its electrode.
(iii) The carriers of current within this cell. *(Delhi 2008)*

SA II (3 marks)

8. A cell is prepared by dipping copper rod in 1 M copper sulphate solution and zinc rod in 1 M zinc sulphate solution. The standard reduction potential of copper and zinc are 0.34 V and −0.76 V respectively.
(i) What will be the cell reaction?
(ii) What will be the standard electromotive force of the cell?
(iii) Which electrode will be positive? *(Delhi 2011C)*

9. Depict the galvanic cell in which the reaction $Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$ takes place. Further show :
(i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell.
(iii) Individual reaction at each electrode. *(Delhi 2010C)*

3.3 Nernst Equation

SA I (2 marks)

10. Calculate $\Delta_r G^\circ$ for the reaction :
$Mg_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$
Given $E^\circ_{cell} = +2.71$ V, 1 F = 96500 C mol^{-1} *(2/3,AI 2014)*

11. Equilibrium constant (K_c) for the given cell reaction is 10. Calculate E°_{cell}.
$A_{(s)} + B^{2+}_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + B_{(s)}$ *(2/3,Foreign 2014)*

12. The standard electrode potential (E°) for Daniell cell is +1.1 V. Calculate the ΔG° for the reaction.
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
(1 F = 96500 C mol^{-1}) *(AI 2013)*

13. The standard electrode potential for Daniell cell is 1.1 V. Calculate the standard Gibbs energy for the cell reaction.
(F = 96,500 C mol^{-1}) *(Delhi 2013C)*

14. A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential.
[$E^\circ_{Zn^{2+}/Zn} = -0.76$ V] *(Delhi 2012C)*

15. Determine the value of equilibrium constant (K_c) and ΔG° for the following reactions :
$Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$, $E^\circ = 1.05$ V
(1 F = 96500 C mol^{-1})
(Delhi 2011, Foreign 2011)

16. Calculate the emf for the given cell at 25° C :
$Cr|Cr^{3+}$ (0.1 M) || Fe^{2+} (0.01 M)| Fe
Given :

$$E^\circ_{Cr^{3+}/Cr} = -0.74\text{ V},\ E^\circ_{Fe^{2+}/Fe} = -0.44\text{V}$$

(2/5, Delhi 2009C)

SA II (3 marks)

17. Calculate e.m.f. of the following cell at 298 K
$2Cr_{(s)} + 3Fe^{2+}(0.1M) \rightarrow 2Cr^{3+}(0.01M) + 3Fe_{(s)}$
Given : $E^\circ_{(Cr^{3+}|Cr)} = -0.74$ V, $E^\circ_{(Fe^{2+}|Fe)} = -0.44$ V
(Delhi 2016)

18. Calculate E°_{cell} for the following reaction at 298 K.
$2Al_{(s)} + 3Cu^{2+}(0.01M) \rightarrow 2Al^{3+}(0.01M) + 3Cu_{(s)}$
Given : $E_{cell} = 1.98$ V *(3/5,AI 2016)*

19. Calculate emf of the following cell at 25°C:
$Fe|Fe^{2+}(0.001\text{ M})||H^+(0.01\text{ M})|H_{2(g)}(1\text{ bar})|Pt_{(s)}$
$E^\circ(Fe^{2+}|Fe) = -0.44$ V, $E^\circ(H^+|H_2) = 0.00$ V
(Delhi 2015)

20. Calculate the emf of the following cell at 25°C
$Zn|Zn^{2+}$ (0.001 M) || H^+(0.01M)| $H_{2(g)}$ (1 bar) | $Pt_{(s)}$

$$E^\circ_{(Zn^{2+}/Zn)} = -0.76\text{ V},\ E^\circ_{(H^+/H_2)} = 0.00\text{ V}$$

(Foreign 2015)

21. For the cell reaction
$Ni_{(s)}|Ni^{2+}_{(aq)}||Ag^+_{(aq)}|Ag_{(s)}$
Calculate the equilibrium constant at 25°C. How much maximum work would be obtained by operation of this cell?

$$E^\circ_{(Zn^{2+}/Zn)} = -0.25\text{ V and } E^\circ_{Ag^+/Ag} = 0.80\text{V}$$

(3/5, Delhi 2015C)

22. Calculate the standard cell potential of the galvanic cell in which the following reaction takes place :
$Fe^{2+}_{(aq)} + Ag^+_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Ag_{(s)}$
Calculate the $\Delta_r G^\circ$ and equilibrium constant of the reaction also,

$$\left(E^\circ_{Ag^+/Ag} = 0.80\text{ V};\ E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\text{ V}\right)$$

(3/5, Delhi 2015C)

23. Calculate the emf of following cell at 298 K :
$Mg_{(s)}$ | Mg^{2+}(0.1 M) || Cu^{2+}(0.01 M)|$Cu_{(s)}$
[Given : $E^\circ_{cell} = +2.71$ V, 1 F = 96500 C mol^{-1}]
(3/5, Delhi 2014)

24. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The Gibbs energy change for the decomposition reaction
$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$ is 960 kJ.
(F = 96500 C mol^{-1}) *(3/5,Delhi 2014C)*

25. Calculate the emf of the following cell at 298 K :
$Fe_{(s)}|Fe^{2+}(0.001\text{ M})||H^+(1\text{ M})|H_{2(g)}$ (1 bar), $Pt_{(s)}$
(Given $E^\circ_{cell} = +0.44$ V) *(Delhi 2013)*

26. Calculate the emf of the following cell at 25°C :
$Ag_{(s)}|Ag^+(10^{-3}\text{ M})||Cu^{2+}(10^{-1}\text{ M})|Cu_{(s)}$
Given : $E^\circ_{cell} = +0.46$ V and $\log 10^n = n$.
(AI 2013)

27. In the button cell, widely used in watches, the following reaction takes place.
$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$
Determine E° and ΔG° for the reaction.
(Given : $E^\circ_{Ag^+/Ag} = +0.80$ V, $E^\circ_{Zn^{2+}/Zn} = -0.76$ V)
(3/5, Delhi 2012)

28. A voltaic cell is set up at 25°C with the following half cells :
Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50 M)
Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.
$E^\circ_{Ni^{2+}/Ni} = -0.25$ V and $E^\circ_{Al^{3+}/Al} = -1.66$ V.
($\log 8 \times 10^{-6} = -5.09$) *(3/5, AI 2012, 2011, 3/5, Foreign 2011, 3/5, Delhi 2009)*

29. The cell in which the following reaction occurs :
$2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}$
has E°_{cell} = 0.236 V at 298 K, Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.
(Antilog of 6.5 = 3.162×10^6 ; of 8.0 = 10×10^8 ; of 8.5 = 3.162×10^8)
(Delhi 2012C)

30. Calculate the potential for half-cell containing 0.10 M $K_2Cr_2O_{7(aq)}$, 0.20 M $Cr^{3+}{}_{(aq)}$ and 1.0×10^{-4} M $H^+_{(aq)}$. The half cell reaction is :
$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$
and the standard electrode potential is given as E° = 1.33 V. *(3/5, AI 2011)*

31. For the cell
$Zn_{(s)} \mid Zn^{2+}\ (2\ M) \parallel Cu^{2+}\ (0.5\ M) \mid Cu_{(s)}$
(a) Write equation for each half-reaction.
(b) Calculate the cell potential at 25°C
Given :
$$E^\circ_{Zn^{2+}/Zn} = -0.76\ V\ ;\ E^\circ_{Cu^{2+}/Cu} = +0.34 V$$
(Delhi 2011C)

32. Calculate the equilibrium constant, *K* for the reaction at 298 K,
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + Cu_{(s)}$
Given : $\Delta G^\circ = -\ 212.300\ kJ\ mol^{-1}$
$$E^\circ_{Zn^{2+}/Zn} = -0.76\ V\ ;\ E^\circ_{Cu^{2+}/Cu} = +\ 0.34\ V$$
(AI 2011C)

33. A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell.
Given :
$$E^\circ_{Ag^+/Ag} = +0.80\ V,\ E^\circ_{Cu^{2+}/Cu} = +\ 0.34\ V$$
(3/5, Delhi 2010, AI 2009)

34. A voltaic cell is set up at 25° with the following half cells :
$Ag^+(0.001\ M) \mid Ag$ and $Cu^{2+}\ (0.10\ M) \mid Cu$
What would be the voltage of this cell?
(E°_{cell} = 0.46 V) *(AI 2009)*

35. A voltaic cell is set up at 25°C with the following half-cells :
$Al \mid Al^{3+}\ (0.001\ M)$ and $Ni \mid Ni^{2+}\ (0.50\ M)$
Calculate the cell voltage
$$[E^\circ_{Ni^{2+}|Ni} = -0.25\ V,\ E^\circ_{Al^{3+}|Al} = -\ 1.66\ V]$$
(3/5, Delhi 2009)

36. Calculate the equilibrium constant for the reaction
$Fe_{(s)} + Cd^{2+}_{(aq)} \rightleftharpoons Fe^{2+}_{(aq)} + Cd_{(s)}$
Given :
$$[E^\circ_{Cd^{2+}|Cd} = -\ 0.40\ V,\ E^\circ_{Fe^{2+}|Fe} = -\ 0.44\ V]$$
(3/5, Delhi 2009, 2009C, 3/5, AI 2009)

37. One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. Its other half-cell consists of a zinc electrode dipping in 1.0 M solution of $Zn(NO_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver nitrate solution used.
$$[E^\circ_{Zn^{2+}|Zn} = -\ 0.76\ V,\ E^\circ_{Ag^+|Ag} = +\ 0.80\ V]$$
(3/5, Delhi 2009)

38. Calculate the standard cell potential of a galvanic cell in which the following reaction takes place :
$2Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Cd_{(s)}$
Calculate $\Delta_r G^\circ$ and equilibrium constant, *K* of the above reaction at 25°C.
Given :
$$E^\circ_{Cr^{3+}/Cr} = -\ 0.74\ V,\ E^\circ_{Fe^{2+}/Fe} = -\ 0.44\ V$$
($F = 96{,}500\ C\ mol^{-1}$) *(Delhi 2008C)*

39. (i) Formulate the electrochemical cell representing the reaction ;
$2Cr_{(s)} + 3Fe^{2+}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 3Fe_{(s)}$
(ii) Calculate E°_{cell}.
(iii) Calculate E_{cell} at 25°C if
$[Cr^{3+}]$ = 0.1 M and $[Fe^{2+}]$ = 0.01 M
Given :
$$E^\circ_{Cr^{3+}/Cr} = -\ 0.74\ V,\ E^\circ_{Fe^{2+}/Fe} = -\ 0.44\ V$$
(3/5, AI 2008C)

LA (5 marks)

40. Calculate e.m.f and ΔG for the following cell
$Mg_{(s)} \mid Mg^{2+}\ (0.001\ M) \parallel Cu^{2+}\ (0.0001\ M) \mid Cu_{(s)}$
$$E^\circ_{(Mg^{2+}/Mg)} = -2\cdot 37\ V,\ E^\circ_{(Cu^{2+}/Cu)} = +0.34\ V$$
(AI 2015)

41. Calculate the standard electrode potential of Ni^{2+}/Ni electrode if emf of the cell

$Ni_{(s)}|Ni^{2+}(0.01\,M)||Cu^{2+}(0.1\,M)|Cu_{(s)}$ is 0.059 V.

[Given : $E^{\circ}_{Cu^{2+}/Cu} = +0.34$ V] *(Delhi 2009C)*

42. Calculate the cell emf and $\Delta_r G^{\circ}$ for the cell reaction at 25°C

$Zn_{(s)} \,|\, Zn^{2+}\,(0.1\ M) \,||\, Cd^{2+}\,(0.01\ M)|\, Cd_{(s)}$

Given :

$E^{\circ}_{Zn^{2+}/Zn} = -0.763$ V, $E^{\circ}_{Cd^{2+}/Cd} = -0.403$ V

1 F = 96,500 C mol^{-1}, $R = 8.314$ J K^{-1} mol^{-1}

(AI 2009C)

3.4 Conductance of Electrolytic Solutions

VSA (1 mark)

43. Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration? *(1/2, Delhi 2015)*

44. State Kohlrausch's law of independent migration of ions. Write its one application. *(1/2, Foreign 2015)*

45. Define the following term :

Molar conductivity (Λ_m) *(1/5, Delhi 2015C)*

46. Define the following term :

Kohlrausch's law of independent migration of ions. *(1/5, Delhi 2015C)*

47. Define the following term : Limiting molar conductivity *(1/5, Delhi 2014)*

48. State and explain Kohlrausch's law. *(1/3, Delhi 2013C)*

49. Express the relation between conductivity and molar conductivity of a solution held in a cell? *(Delhi 2011)*

50. Express the relation among the conductivity of solution in the cell, the cell constant and the resistance of solution in the cell. *(Delhi 2011)*

51. Express the relation between the conductivity and the molar conductivity of a solution. *(AI 2008)*

SA I (2 marks)

52. Define the term degree of dissociation. Write an expression that relates the molar conductivity of a weak electrolyte to its degree of dissociation. *(2/5, Delhi 2015C)*

53. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration. *(2/5, AI 2015C)*

54. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? *(AI 2014)*

55. Define the terms conductivity and molar conductivity for the solution of an electrolyte. Comment on their variation with temperature. *(Delhi 2014C)*

56. The resistance of 0.01 M NaCl solution at 25°C is 200 Ω. The cell constant of the conductivity cell used is unity. Calculate the molar conductivity of the solution. *(2/3, AI 2014C)*

57. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with change in temperature. *(AI 2014C)*

58. The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity. *(Delhi 2013, 2008, AI 2007)*

59. The conductivity of 0.001 M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2/mol. *(2/3, Delhi 2013C, 2012C)*

60. Express the relation among cell constant, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solution related to its conductivity? *(AI 2012, 2010, 2/5,Delhi 2009)*

61. The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution. *(AI 2012, 2010C)*

62. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}? *(Delhi 2010C, 2009C, 2008, 2007)*

63. Define molar conductivity of a substance and describe how for weak and strong electrolytes, molar conductivity changes with concentration of solute. How is such change explained? *(2/5, Delhi 2009)*

64. Define the term molar conductivity. How is it related to conductivity of the related solution? *(2/5, Delhi 2009)*

65. State Kohlrausch's law of independent migration of ions. How can the degree of dissociation of acetic acid in a solution be calculated from its molar conductivity data? *(2/5, AI 2008C)*

66. Explain with examples the terms weak and strong electrolytes. *(Delhi 2007)*

SA II (3 marks)

67. The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).
Given : $\lambda°$ (H^+) = 349.6 S cm^2 mol^{-1} and $\lambda°(CH_3COO^-)$ = 40.9 S cm^2 mol^{-1} *(3/5, AI 2016)*

68. The conductivity of 0·20 mol L^{-1} solution of KCl is 2.48×10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).
Given $\lambda°$ (K^+) = 73.5 S cm^2 mol^{-1}
and $\lambda°$ (Cl^-) = 76.5 S cm^2 mol^{-1}. *(AI 2015)*

69. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29×10^{-2} Ω^{-1} cm^{-1}. *(3/5, AI 2014)*

70. The value of $\Lambda°_m$ of $Al_2(SO_4)_3$ is 858 S cm^2 mol^{-1}, while $\lambda°$ SO_4^{2-} is 160 S cm^2 mol^{-1} calculate the limiting ionic conductivity of Al^{3+}. *(AI 2013C)*

71. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity. *(AI 2012)*

72. When a certain conductance cell was filled with 0.1 M KCl, it has a resistance of 85 ohms at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.
[Specific conductance of 0.1 M KCl
= 1.29×10^{-2} ohm^{-1} cm^{-1}] *(AI 2012C)*

73. Calculate the degree of dissociation of acetic acid at 298 K, given that :
Λ_m (CH_3COOH) = 11.7 S cm^2 mol^{-1}
$\Lambda°_m(CH_3COO^-)$ = 49.9 S cm^2 mol^{-1}
$\Lambda°_m(H^+)$ = 349.1 S cm^2 mol^{-1} *(Delhi 2011C)*

74. The resistance of a conductivity cell when filled with 0.05 M solution of an electrolyte X is 100 ohms at 40°C. The same conductivity cell filled with 0.01 M solution of electrolyte Y has a resistance of 50 ohms. The conductivity of 0.05 M solution of electrolyte X is 1.0×10^{-4} S cm^{-1}. Calculate
(i) Cell constant
(ii) Conductivity of 0.01 M Y solution
(iii) Molar conductivity of 0.01 M Y solution *(3/5, AI 2008C)*

LA (5 marks)

75. (a) Define molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and a strong electrolyte.
(b) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}? *(AI 2012)*

76. (a) State Kohlrausch's law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch's law.
(b) Calculate $\Lambda°_m$ for acetic acid.
Given that
$\Lambda°_m(HCl)$ = 426 S cm^2 mol^{-1}
$\Lambda°_m(NaCl)$ = 126 S cm^2 mol^{-1}
$\Lambda°_m(CH_3COONa)$ = 91 S cm^2 mol^{-1} *(Delhi 2010)*

77. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity if Λ°_m for acetic acid is 390.5 S cm^2 mol^{-1}. What is its dissociation constant? *(Delhi, AI 2008)*

3.5 Electrolytic Cells and Electrolysis

VSA (1 mark)

78. Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution :

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}, \quad E^\circ = +0.80 \text{ V}$$

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}, \quad E^\circ = 0.00 \text{ V}$$

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why? *(1/2, Delhi 2015)*

79. How much charge is required for the reduction of 1 mol of Zn^{2+} to Zn? *(Delhi 2015)*

80. Following reactions occur at cathode during the electrolysis of aqueous copper (II) chloride solution :

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad E^\circ = +0.34 \text{ V}$$

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} \qquad E^\circ = 0.00 \text{ V}$$

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why? *(1/2, Foreign 2015)*

81. State the Faraday's first law of electrolysis. *(Delhi 2015C)*

82. How much charge is required for the reduction of 1 mole of Cu^{2+} to Cu? *(Delhi 2007)*

SA I (2 marks)

83. State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu. *(2/5, Delhi 2014)*

84. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 ampere for 20 minutes. What mass of nickel will be deposited at the cathode?
(Given : At. mass of Ni = 58.7 g mol^{-1},
1F = 96500 C mol^{-1}) *(Foreign 2014)*

85. Predict the products of electrolysis in each of the following :

(i) An aqueous solution of $AgNO_3$ with platinum electrodes.

(ii) An aqueous solution of H_2SO_4 with platinum electrodes. *(2/5, Delhi 2014C)*

86. How much electricity in terms of Faradays is required to produce 20 g of calcium from molten $CaCl_2$? *(2/3, Delhi 2013C)*

87. Silver is uniformly electrodeposited on a metallic vessel of surface area of 900 cm^2 by passing a current of 0.5 ampere for 2 hours. Calculate the thickness of silver deposited. Given : the density of silver is 10.5 g cm^{-3} and atomic mass of Ag = 108 amu. *(2/3, AI 2013C)*

88. How many coulombs are required to reduce 1 mole $Cr_2O_7^{2-}$ to Cr^{3+}? *(2/3, Delhi 2012C)*

89. How many moles of mercury will be produced by electrolysing 1.0 M $Hg(NO_3)_2$ solution with a current of 2.00 A for 3 hours? *(2/5, AI 2011)*

90. A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode? *(AI 2009)*

91. Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode. Write overall reaction.

Given :

$$E^\circ_{Na^+/Na} = -2.71 \text{ V}, E^\circ_{H_2O/H_2} = -0.83 \text{ V},$$

$$E^\circ_{Cl_2/Cl^-} = +1.36 \text{ V}, E^\circ_{H^+/H_2/H_2O} = +1.23 \text{ V}$$

(2/5, Delhi 2009C)

92. Consider the reaction :

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 8H_2O$$

What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$? *(AI 2008)*

93. Explain why electrolysis of an aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode.

$$E^\circ_{Na^+/Na} = -2.71 \text{ V}, E^\circ_{H_2O/H_2} = -0.83 \text{ V}$$

$$E^\circ_{Cl_2/2Cl^-} = +1.36 \text{ V},$$

$$E^\circ_{2H^+/\frac{1}{2}O_2/H_2O} = +1.23 \text{ V}$$

(2/5, Delhi 2008C)

94. Predict the products of electrolysis obtained at the electrodes in each if the electrodes used are of platinum?
(i) An aqueous solution of $AgNO_3$.
(ii) An aqueous solution of H_2SO_4. *(AI 2007)*

SA II (3 marks)

95. Calculate the strength of the current required to deposit 1.2 g of magnesium from molten $MgCl_2$ in 1 hour.
[1 F = 96,500 C mol^{-1} ;
Atomic mass : Mg = 24.0] *(3/5, Delhi 2009C)*

96. A solution of $CuSO_4$ is electrolysed for 16 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode? *(AI 2007)*

LA (5 marks)

97. Three electrolytic cells *A*, *B* and *C* containing solutions of zinc sulphate, silver nitrate and copper sulphate, respectively are connected in series. A steady current of 1.5 ampere is passed through them until 1.45 g of silver is deposited at the cathode of cell *B*. How long did the current flow? What mass of copper and what mass of zinc were deposited on the concerned electrodes? (Atomic masses of Ag = 108, Zn = 65.4, Cu = 63.5) *(Delhi, AI 2008)*

3.6 Batteries

VSA (1 mark)

98. Define : Secondary batteries *(1/5, Delhi 2015C)*

SA I (2 marks)

99. From the given cells :
Lead storage cell, Mercury cell, Fuel cell and Dry cell
Answer the following :
(i) Which cell is used in hearing aids?
(ii) Which cell was used in Apollo Space Programme?
(iii) Which cell is used in automobiles and invertors?
(iv) Which cell does not have long life? *(Delhi 2016)*

100. What type of battery is mercury cell? Why is it more advantageous than dry cell? *(2/5, AI 2015)*

101. What type of a battery is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it. *(2/5, Delhi 2012)*

102. Write the reactions taking place at cathode and anode in lead storage battery when the battery is in use. What happens on charging the battery? *(AI 2012C)*

103. What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery. *(2/5, AI 2011, 2009, 2/5, Delhi 2009)*

104. Mention the reactions occurring at (i) anode, (ii) cathode, during working of a mercury cell. Why does the voltage of a mercury cell remain constant during its operation? *(Delhi 2011C)*

105. Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery. *(2/5, Delhi 2010)*

SA II (3 marks)

106. What is a nickel-cadmium cell? State its one merit and one demerit over lead storage cell. Write the overall reaction that occurs during discharging of this cell. *(AI 2010C)*

3.7 Fuel Cells

VSA (1 mark)

107. Define : Fuel cell *(1/5, Delhi 2015C, 2014)*

108. Name the type of cell which was used in Apollo space programme for providing electrical power. *(1/3, AI 2014)*

SA I (2 marks)

109. Write two advantages of $H_2 — O_2$ fuel cell over ordinary cell. *(2/3, Foreign 2014)*

110. What are fuel cells? Explain the electrode reactions involved in the working of
$H_2 — O_2$ fuel cell. *(2/3, Delhi 2013C, 2009)*

111. Give an example of a fuel cell and write the cathode and anode reactions for it. *(AI 2011C)*

3.8 Corrosion

VSA (1 mark)

112. Using the $E°$ values of A and B predict which is better for coating the surface of iron

$$\left[E^{\circ}_{(\text{Fe}^{2+}/\text{Fe})} = -0.44\right]$$

to prevent corrosion and why?

$$E^{\circ}_{(A^{2+}/A)} = -2.37\text{ V}; E^{\circ}_{(B^{2+}/B)} = 0.14\text{ V}$$

(AI 2016)

SA II (2 marks)

113. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere. *(Delhi 2011)*

114. Corrosion is essentially an electrochemical phenomenon. Explain the reactions occurring during corrosion of iron kept in an open atmosphere. *(2/5, AI 2009)*

SA II (3 marks)

115. What is corrosion? Explain the electrochemical theory of rusting of iron and write the reactions involved in the rusting of iron. *(Delhi 2012C)*

Detailed Solutions

1. The device which converts the chemical energy liberated during the chemical reaction to electrical energy is called electrochemical cell. If external potential applied becomes greater than E°_{cell} of electrochemical cell then the cell behaves as an electrolytic cell and the direction of flow of current is reversed.

2. Representation of the galvanic cell for the given reaction is :

$$\underset{\text{Anode}}{\text{Zn} \mid \text{Zn}^{2+}_{(aq)}} \underset{\substack{\text{Salt}\\\text{bridge}}}{\|} \underset{\text{Cathode}}{\text{Cu}^{2+}_{(aq)} \mid \text{Cu}}$$

3. The salt bridge allows the movement of ions from one solution to the other without mixing of the two solutions. Moreover, it helps to maintain the electrical neutrality of the solutions in the two half cells.

4. Because standard electrode potential of Ti^{4+}/Ti^{3+} is less than that of Fe^{3+}/Fe^{2+} so, it cannot oxidise Fe^{II} to Fe^{III}.

5. At anode : $Sn^{2+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2e^-] \times 5$

At cathode : $MnO^-_{4(aq)} + 8H^+{}_{(aq)} + 5e^- \longrightarrow$

$$Mn^{2+}_{(aq)} + 4H_2O_{(l)}] \times 2$$

Net cell reaction :

$2MnO^-_{4(aq)} + 5Sn^{2+}_{(aq)} + 16H^+_{(aq)} \longrightarrow$

$$2Mn^{2+}_{(aq)} + 5Sn^{4+}_{(aq)} + 8H_2O_{(l)}$$

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.51\text{ V} - 0.15\text{ V} = 1.36\text{ V}.$

Since, cell potential is positive therefore the reaction is product favoured.

6. The reducing power increases with decreasing value of electrode potential. Hence, the order is Ag < Cu < Fe < Cr < Mg < K.

7. The cell reaction is

$Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$

The cell is represented as

$Zn_{(s)} \mid Zn^{2+}_{(aq)} \| Ag^+_{(aq)} \mid Ag_{(s)}$

(i) Anode *i.e.*, zinc electrode will be negatively charged.

(ii) At anode :

$Zn_{(s)} \longrightarrow Zn^{2+}{}_{(aq)} + 2e^-$ (oxidation)

At cathode :

$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$ (Reduction)

(iii) Ions are the carriers of current within the cell.

8. (i) The cell reactions are :

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ (Anode)

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ (Cathode)

Net reaction :

$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

(ii) $E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}} = 0.34\text{ V} - (-0.76\text{ V}) = 1.10\text{ V}$

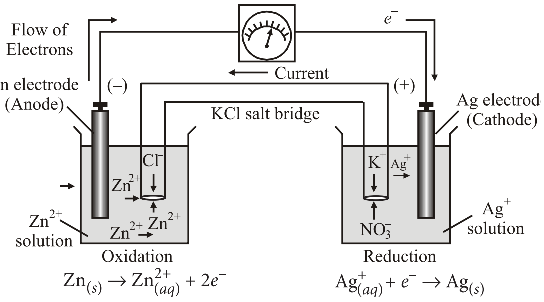
(iii) Copper electrode will be positive on which reduction takes place.

9. The reaction is

$Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$

Cell can be represented as

$Zn \mid Zn^{2+}_{(aq)} \| Ag^+_{(aq)} \mid Ag$



(i) The zinc electrode is negatively charged (anode) as it pushes the electrons into the external circuit.

(ii) Ions are the current carriers within the cell.

(iii) The reactions occurring at two electrodes are :

At zinc electrode (anode) : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

At silver electrode (cathode) : $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$

10. **(a)** Given : $E^\circ_{\text{cell}} = 2.71\text{ V}$

For the reaction,

$Mg_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$

$n = 2, \Delta_r G^\circ = ?$

Using formula, $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$

$\Delta_r G^\circ = -2 \times 96500\text{ C mol}^{-1} \times 2.71\text{ V}$

or $\Delta_r G^\circ = 523.03\text{ kJ mol}^{-1}$

11. $A_{(s)} + B^{2+}_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + B_{(s)}$

Here, $n = 2$

using formula,

$$E^\circ_{\text{cell}} = \frac{0.059}{n}\log K_c$$

$$E^\circ_{\text{cell}} = \frac{0.059}{2}\log 10$$

$E^\circ_{\text{cell}} = 0.0295\text{ V}$

12. Here $n = 2$, $E^\circ_{cell} = 1.1$ V
$F = 96500 \text{ C mol}^{-1}$
$\Delta_r G^\circ = -nFE^\circ_{cell}$
$\Delta_r G^\circ = -2 \times 1.1 \times 96500 = -212300 \text{ J mol}^{-1}$
$= -212.3 \text{ kJ mol}^{-1}$

13. *Refer to answer 12.*

14. The electrode reaction written as reduction reaction is
$Zn^{2+} + 2e^- \longrightarrow Zn \ (n = 2)$
Applying Nernst equation, we get,

$$\left[E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{0.0591}{2}\log\frac{1}{Zn^{2+}}\right]$$

As 0.1 M $ZnSO_4$ solution is 95% dissociated, this means that in the solution,

$$[Zn^{2+}] = \frac{95}{100} \times 0.1 = 0.095 \text{ M}$$

$$\therefore \quad E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2}\log\frac{1}{0.095}$$

$= -0.76 - 0.02955 (\log 1000 - \log 95)$
$= -0.76 - 0.0295 (3 - 1.9777) = -0.79021$ V

15. $Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}, E^\circ = 1.05$ V
Here, $n = 2$

Using formula, $\log K_c = \frac{nE^\circ_{cell}}{0.059}$

or $\log K_c = \frac{2 \times 1.05}{0.059} = 35.5932$

$K_c = \text{antilog } 35.5932$ or $K_c = 3.92 \times 10^{35}$
Again, $\Delta G^\circ = -nFE^\circ_{cell}$
$\Delta G^\circ = -2 \times 96500 \times 1.05 = -202650$ J
$\Delta G^\circ = -202.65$ kJ

16. $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left} = -0.44 - (-0.74) = 0.30$ V

$$E_{cell} = 0.30 - \frac{0.0591}{6}\log\frac{(0.1)^2}{(0.01)^3}$$

$= 0.30 - 0.0394 = 0.26$ V

17. *Refer to answer 16.*

18. Given cell,
$2Al_{(s)} + 3Cu^{2+} (0.01 \text{ M}) \longrightarrow 2Al^{3+}(0.01 \text{ M}) + 3Cu_{(s)}$
$E_{cell} = 1.98$ V, $E^\circ_{cell} = ?$
Using Nernst equation at 298 K

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{6}\log\frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$

$$1.98 \text{ V} = E^\circ_{cell} - \frac{0.0591}{6}\log\frac{[10^{-2}]^2}{[10^{-2}]^3}$$

$$1.98 \text{ V} = E^\circ_{cell} - \frac{0.0591}{6}\log 10^2$$

$$1.98 \text{ V} = E^\circ_{cell} - \frac{0.0591}{6} \times 2$$

$$\therefore \quad E^\circ_{cell} = 1.98 + \frac{0.0591}{6} = 1.99 \text{ V}$$

19. The cell reaction is
$Fe_{(s)} + 2H^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_{2(g)}$
$E^\circ_{cell} = 0.00 - (-0.44) = 0.44$ V

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}]}{[H^+]^2}$$

$$= 0.44 - \frac{0.0591}{2}\log\frac{0.001}{(0.01)^2}$$

$= 0.44 - 0.02955 = 0.41045$ V

20. The cell reaction is
$Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$
$E^\circ_{cell} = 0.00 - (-0.76) = 0.76$ V

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[H^+]^2}$$

$$= 0.76 - \frac{0.0591}{2}\log\frac{(0.001)}{(0.01)^2}$$

$= 0.76 - 0.02955 = 0.730$ V

21. At anode : $Ni \longrightarrow Ni^{2+} + 2e^-$
At cathode : $[Ag^+ + e^- \longrightarrow Ag] \times 2$
Cell reaction : $Ni + 2Ag^+ \longrightarrow Ni^{2+} + 2Ag$
$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
$= E^\circ_{Ag^+/Ag} - E^\circ_{Ni^{2+}/Ni} = 0.80 \text{ V} - (-0.25)$
$E^\circ_{cell} = 1.05$ V

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_c$$

$$\log K_c = \frac{E^\circ_{cell} \times n}{0.0591} = \frac{1.05 \times 2}{0.0591}$$

$\log k_c = 35.53$
$K_c = \text{antilog } 35.53 = 3.38 \times 10^{35}$

22. $E^\circ_{cell} = +0.80 \text{ V} - 0.77 \text{ V} = +0.03$ V
$\Delta_r G^\circ = -nFE^\circ_{cell} = -1 \times 96500 \times 0.03$
$= -2895 \text{ J mol}^{-1} = -2.895 \text{ kJ mol}^{-1}$
$\Delta G^\circ = -2.303 \ RT \log K_c$
$-2895 = -2.303 \times 8.314 \times 298 \times \log K$
or $\log K_c = 0.5074$
$K_c = \text{Antilog } (0.5074) = 3.22$

23. The cell reaction can be represented as :

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

Given: $E^\circ_{cell} = +2.71\ V, T = 298\ K$

According to the Nernst equation :

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Mg^{2+}_{(aq)}]}{[Cu^{2+}_{(aq)}]}$$

$$= 2.71 - \frac{0.0591}{2}\log\frac{0.1}{0.01} = 2.6805\ V$$

24. $Al_2O_3\ (2Al^{3+} + 3O^{2-}) \longrightarrow 2Al + \frac{3}{2}O_2,\ n = 6e^-$

$\therefore\ \frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2,\ n = \frac{2}{3} \times 6e^- = 4e^-$

$\Delta G = 960 \times 1000 = 960000$

Now, $\Delta G = -nFE^\circ_{cell}$

$E^\circ_{cell} = -\frac{\Delta G}{nF} = \frac{-960000}{4\times 96500}$

$E^\circ_{cell} = -2.487\ V$

Minimum potential difference needed to reduce Al_2O_3 is −2.487 V.

25. $Fe_{(s)}\,|\,Fe^{2+}(0.001\,M)\,||\,H^+(1\,M)\,|H_{2(g)}(1\,bar)\,|\,Pt_{(s)}$

Reactions :

Anode : $Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$

Cathode : $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

Cell reaction : $Fe_{(s)} + 2H^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_{2(g)}$

$n = 2.$

Using Nernst equation at 298 K

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}]\times p_{H_2}}{[H^+]^2}$$

For the given cell,

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{H^+/H_2} - E^\circ_{Fe^{2+}/Fe}$

$= 0 - (-0.44) = +\,0.44\ V$

Given $[Fe^{2+}] = 0.001\ M$; $[H^+] = 1\ M$; $P_{H_2} = 1$ bar

Putting in Nernst equation

$E_{cell} = 0.44 - 0.0295\log\frac{0.001\times1}{1^2}$

$= 0.44 - 0.0295\log 10^{-3}$

$= 0.44 - [(0.0295) \times (-3)]$

$= 0.44 + 0.0885 = 0.53\ V$

26. The cell may be represented as

$Ag_{(s)}\,|Ag^+\,(10^{-3}\,M)||Cu^{2+}\,(10^{-1}\,M)|\,Cu_{(s)}$

Using formula $E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Ag^+]^2}{[Cu^{2+}]}$

$E_{cell} = 0.46\ V - 0.0295\log\frac{(10^{-3})^2}{10^{-1}}$

$= 0.46 - 0.0295\log 10^{-5} = 0.46 - 0.0295\,(-5)$

$= 0.46 + 0.0295 \times 5 = 0.6075\ V$

27. The cell reaction in button cell :

$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$

(i) Calculation of E°_{cell}

Reactions :

Anode : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

Cathode :

$Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \longrightarrow 2Ag_{(s)} + 2OH^-_{(aq)} + 2e^-$

$n = 2$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{Ag_2O/Ag} - E^\circ_{Zn^{2+}/Zn}$

$= +\,0.80 - (-\,0.76)\ V = 1.56\ V$

(ii) Calculation of Δ_rG°

$\Delta_rG^\circ = -nFE^\circ_{cell}$

$= -\,2 \times 96500\ C\ mol^{-1} \times 1.56\ V$

$= -\,301080\ C\ V\ mol^{-1}$

$= -\,301080\ J\ mol^{-1} = -\,301\ kJ\ mol^{-1}$

28. At anode : $Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-] \times 2$

At cathode : $Ni^{2+} + 2e^- \rightarrow Ni_{(s)}] \times 3$

Cell reaction : $2Al_{(s)} + 3Ni^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Ni_{(s)}$

Applying Nernst equation to the above cell reaction,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2\times3}\log\frac{[Al^{3+}]^2}{[Ni^{2+}]^3}$$

Now, $E^\circ_{cell} = E^\circ_{Ni^{2+}/Ni} - E^\circ_{Al^{3+}/Al}$

$= -\,0.25\ V - (-1.66) = 1.41\ V$

$\therefore\ E_{cell} = 1.41\ V - \frac{0.0591}{6}\log\frac{(10^{-3})^2}{(0.5)^3}$

$= 1.41\ V - \frac{0.0591}{6}\log(8 \times 10^{-6})$

$= 1.41\ V - \frac{0.0591}{6}(5.09)$

$= 1.41V + 0.050\ V = 1.46\ V$

29. $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ and $2I^- \longrightarrow I_2 + 2e^-$

Hence, for the given cell reaction, $n = 2$

$\Delta_rG^\circ = -nFE^\circ_{cell} = -2\times96500\times0.236 = -45.55\ kJ\ mol^{-1}$

$\Delta_rG^\circ = -\,2.303\ RT\log K_c$

or $\log K_c = -\frac{\Delta_rG^\circ}{2.303RT}$

$$= -\frac{-45.55\ kJ\ mol^{-1}}{2.303\times8.314\times10^{-3}\ kJ\ K^{-1}mol^{-1}\times298\ K} = 7.983$$

$\therefore\ K_c = \text{Antilog}\ (7.983) = 9.616 \times 10^7$

30. For half cell reaction,

$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

Given, $E^\circ_{cell} = 1.33$ V, $n = 6$, $[Cr^{3+}] = 0.2$ M

$[Cr_2O_7^{2-}] = 0.1$ M, $[H^+] = 1 \times 10^{-4}$ M

$$\Rightarrow \quad E_{cell} = 1.33\text{V} - \frac{0.0591}{6}\log\frac{(0.20)^2}{(0.1)\,(10^{-4})^{14}}$$

$$= 1.33\text{V} - \frac{0.0591}{6}\log(4\times10^{55})$$

$$= 1.33\text{ V} - \frac{0.0591}{6}[\log 4 + \log 10^{55}]$$

$$= 1.33\text{ V} - \frac{0.0591}{6}[\log 4 + 55\log 10]$$

$$= 1.33\text{ V} - \frac{0.0591}{6}[0.602 + 55]$$

$$= 1.33\text{ V} - 0.548\text{ V} = 0.782\text{ V}$$

31. (a) Oxidation half reaction :

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

Reduction half reaction :

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

(b) $E^\circ_{cell} = 0.34 - (-0.76) = 1.10$ V

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\Rightarrow \quad E_{cell} = 1.10 - \frac{0.0591}{2}\log\frac{2}{0.5}$$

$$= 1.10 - \frac{0.0591}{2}\log\frac{2}{0.5}$$

$$= 1.10 - \frac{0.059}{2} \times 0.6021$$

$$= 1.10 - 0.0177 = 1.0823\text{ V}$$

32. $\Delta G^\circ = -RT\ln K_c = -2.303\,RT\log K_c$

$\Rightarrow -212300 = -2.303 \times 8.314 \times 298 \times \log K_c$

$$\text{or} \quad \log K_c = \frac{212300}{2.303\times8.314\times298} = 37.2074$$

$K_c = \text{Antilog } 37.2074 = 1.6 \times 10^{37}$.

33. The given cell may be represented as

$Cu_{(s)}\,|Cu^{2+}\,(0.10\text{ M})||\,Ag^+\,(C)|\,Ag_{(s)}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.80\text{ V} - 0.34\text{ V} = 0.46\text{ V}$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$\text{or,} \quad 0.422\text{ V} = 0.46\text{ V} - \frac{0.0591}{2}\log\frac{0.1}{[Ag^+]^2}$$

$$-0.038\text{ V} = -0.0295\log\frac{0.1}{[Ag^+]^2}$$

$$\text{or, }\log\frac{0.1}{[Ag^+]^2} = \frac{-0.038}{-0.0295} = 1.288$$

$$\text{or,} \quad \frac{0.1}{[Ag^+]^2} = \text{antilog } 1.288 = 19.41$$

$$\therefore \quad [Ag^+]^2 = \frac{0.1}{19.41} = 5.1519\times10^{-3}$$

$[Ag^+] = 7.1 \times 10^{-2}$ M

34. *Refer to answer 26.*

35. *Refer to answer 28.*

36. $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.40\text{V} - (-0.44\text{V}) = 0.04\text{V}$

Using formula, $\log K_c = \dfrac{nE^\circ}{0.0591}$ at 298 K

$$\text{or,} \quad K_c = \text{antilog}\,\frac{2\times0.04\text{ V}}{0.0591\text{ V}}$$

or, $K_c = \text{antilog } 1.356 = 22.38$

37. The cell may be represented as

$Zn_{(s)}\,|Zn^{2+}_{(aq)}(1\text{ M})\,||Ag^+_{(aq)}|Ag_{(s)}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.80\text{ V} - (-0.76\text{ V}) = 1.56\text{ V}$

Using formula,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$\text{or,} \quad 1.48 = 1.56 - \frac{0.0591}{2}\log\frac{1}{[Ag^+]^2}$$

or, $\log[Ag^+] = -1.354$

or, $[Ag^+] = \text{antilog}(-1.354)$

or, $[Ag^+] = 4.426 \times 10^{-2}$ M

38. $T = 273 + 25°\text{C} = 298$ K and $n = 6$

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

$\Delta_r G^\circ = -nFE^\circ_{cell} = -6\times96500\times0.34 = -196860\text{ J mol}^{-1}$

Again $\Delta_r G^\circ = -2.303\,RT\log K$

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

$\Rightarrow \quad \log K = 34.5014$

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

39. (i) The cell can be represented as

$Cr_{(s)} \mid Cr^{3+}_{(aq)} \parallel Fe^{2+}_{(aq)} \mid Fe_{(s)}$

(ii) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= -0.44 - (-0.74) = -0.44 + 0.74 = 0.30$ V

(iii) *Refer to answer 16.*

40. $Mg_{(s)} \mid Mg^{2+}(0.001\ M) \parallel Cu^{2+}(0.0001\ M) \mid Cu_{(s)}$

Reactions :

Anode : $Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e^-$

Cathode : $Cu^{2+}{}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

Net cell reaction : $Mg_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$

$\therefore \quad n = 2$

Using Nernst equation :

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

For the given cell

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Mg^{2+}/Mg}$

$= 0.34\ V - (-2.37\ V) = 2.71$ V

Given $[Mg^{2+}] = 0.001$ M, $[Cu^{2+}] = 0.0001$ M

Putting in Nernst equation at 298 K

$$E_{cell} = 2.71\ V - \frac{0.059}{2}\log\frac{0.001}{0.0001}$$

$E_{cell} = 2.71 - 0.0295 \log 10 = 2.71 - 0.03 = 2.68$ V

$\Delta_r G = -nFE_{cell}$

$= -2 \times 96500\ C\ mol^{-1} \times 2.68$

$= -517{,}240\ J\ mol^{-1} = -517.24\ kJ\ mol^{-1}$

41. We have

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{\left[Ni^{2+}_{(aq)}\right]}{\left[Cu^{2+}_{(aq)}\right]}$$

$0.059 = E^\circ_{cell} - \frac{0.059}{2}\log\left(\frac{0.01}{0.1}\right)$ [Here $n = 2$]

$0.059 = E^\circ_{cell} - \frac{0.059}{2}\log\left(\frac{1}{10}\right)$

$0.059 = E^\circ_{cell} - \frac{0.059}{2}(-\log 10)$

$0.059 = E^\circ_{cell} + \frac{0.059}{2}$

$\Rightarrow E^\circ_{cell} = 0.059 - \frac{0.059}{2}$

$\therefore \quad E^\circ_{cell} = \frac{0.059}{2} = 0.0295 \approx 0.03$

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

$0.03 = 0.34 - E^\circ_{anode}$

$E^\circ_{anode} = 0.34 - 0.03 = 0.31$ V

Hence, $E^\circ_{Ni^{2+}/Ni} = +0.31$ V

42. $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= -0.403 - (-0.763) = -0.403 + 0.763 = 0.360$ V

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log\frac{\left[Zn^{2+}_{(aq)}\right]}{\left[Cd^{2+}_{(aq)}\right]}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{\left[Zn^{2+}_{(aq)}\right]}{\left[Cd^{2+}_{(aq)}\right]}$$

$$\left[\because \frac{2.303RT}{F} = 0.059\right]$$

$$= 0.36 - \frac{0.059}{2}\log\left(\frac{0.1}{0.01}\right) = 0.36 - \frac{0.059}{2}\log 10$$

$= 0.36 - 0.0295 = 0.3305 = 0.33$ V

$\therefore \quad \Delta_r G^\circ = -nFE^\circ_{cell}$

$= -2 \times 96500 \times 0.36 = -69480\ J\ mol^{-1}$

$= -69.48\ kJ\ mol^{-1}$

43. The limiting molar conductivity of an electrolyte is defined as its molar conductivity when the concentration of the electrolyte in the solution approaches zero.

Conductivity of an electrolyte decreases with dilution because the number of current carrying particles *i.e.,* ions present per cm^3 of the solution becomes less and less on dilution.

44. Kohlrausch's law of independent migration of ions : It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

If $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are limiting molar conductivities of the sodium and chloride ions respectively then the limiting molar conductivity for sodium chloride is given by

$\Lambda^\circ_{m\ (NaCl)} = \lambda^\circ_{Na^+} \lambda^\circ_{Cl^-}$

Kohlrausch's law helps in the calculation of degree of dissociation of weak electrolyte like acetic acid.

The degree of dissociation α is given by

$$\alpha = \frac{\Lambda_m}{\overset{\circ}{\Lambda}_m}$$

where Λ_m is the molar conductivity and Λ°_m is the limiting molar conductivity.

45. Molar Conductivity : Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from one mole of the electrolyte dissolved in V cm^3 of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole solution is contained between them.

$\Lambda_m = \kappa V$

It units is S cm^{2}mol^{-1}

46. *Refer to answer 44.*

47. *Refer to answer 43.*

48. *Refer to answer 44.*

49. $\Lambda_m = \dfrac{\kappa \times 1000}{M}$ in CGS units

$\Lambda_m = \dfrac{\kappa \times 10^{-3}}{M}$ in SI units

where κ is the conductivity, M is the molar concentration and Λ_m is molar conductivity.

50. $\kappa = \dfrac{1}{R} \times \dfrac{l}{A}$

where κ is the conductivity R is resistance and l/A is the cell constant.

51. *Refer to answer 49.*

52. The fraction of the total number of molecules present in solution as ions is known as degree of dissociation.

Molar conductivity (λ_m) = $\alpha\lambda°_m$

where $\lambda°_m$ is the molar conductivity at infinite dilution.

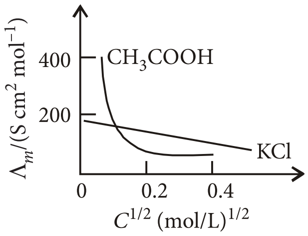
53. The reciprocal of resistivity is known as specific conductance or simply conductivity. It is denoted by κ (kappa).

$\kappa = \dfrac{1}{\rho}$ or $\kappa = G \times \dfrac{l}{a}$

Hence, conductivity of a solution is defined as the conductance of a conductor of 1 cm length and having 1 sq. cm as the area of cross section. Alternatively, it may be defined as conductance of one centimetre cube of the solution of the electrolyte. Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from 1 mole of the electrolyte dissolved in V cm^3 of the solution. It is represented by Λ_m.

$\Lambda_m = \kappa V$

Variation of conductivity and molar conductivity with concentration : Conductivity always decreases with decrease in concentration, for both weak and strong electrolytes. Because the number of ions per unit volume that carry the current in a solution decreases on dilution.



Molar conductivity vs $C^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions

Molar conductivity increases with decrease in concentration. Because that total volume, V, of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume.

54. *Refer to answers 43 and 44.*

55. *Refer to answer 53.*

Variation of conductivity and molar conductivity with temperature : Both increase with increase in temperature as degree of ionisation increases.

56. Conductivity (κ) = $\dfrac{1}{R} \times G = \dfrac{1}{200} \times 1$

$= 5 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$

Molar conductivity (Λ_m)

$$= \frac{\kappa \times 1000}{M} = \frac{5 \times 10^{-3} \times 1000}{0.01} = 500\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

57. *Refer to answer 55.*

58. Here, κ = 0.025 S cm^{-1}, Molarity = 0.20 M

Molar conductivity $\Lambda_m^c = \dfrac{\kappa \times 1000}{\text{Molarity}}$

$$= \frac{0.025 \times 1000}{0.20} = 125\ \text{S cm}^2\ \text{mol}^{-1}$$

59. C = 0.001 M, κ = 4 × 10^{-5} S cm^{-1},

Λ_m^c = 390 S cm^2/mol

$\Lambda_m^c = \dfrac{\kappa \times 1000}{C}$

Substituting the values,

$$\Lambda_m^c = \frac{4 \times 10^{-5} \times 1000}{0.001} = 40\ \text{S cm}^2/\text{mol}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{40}{390} = 0.10256$$

$$\begin{array}{ccccc} CH_3COOH & \rightleftharpoons & CH_3COO^- & + & H^+ \\ c & & 0 & & 0 \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$K_a = \frac{0.001(0.103)^2}{(1-0.103)} = \frac{1.061\times10^{-5}}{0.897} = 1.18 \times 10^{-5}$$

60. *Refer to answers 49 and 50.*

61. $\Lambda_m^c = \frac{\kappa \times 1000}{M}$

$$\Rightarrow \kappa = \frac{\Lambda_m^c \times M}{1000} = \frac{138.9 \times 1.5}{1000} = 0.20835 \text{ S cm}^{-1}$$

62. Here, conductivity (κ) = 0.146×10^{-3} S cm^{-1}, resistance (R) = 1500 Ω

$$\text{Cell constant} = \frac{\text{Conductivity}}{\text{Conductance}}$$

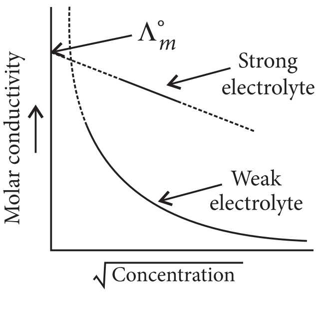
= Conductivity × Resistance

$$= \kappa \times R \qquad \left[\because \text{conductance} = \frac{1}{\text{resistance}}\right]$$

$= 0.146 \times 10^{-3} \times 1500 = 0.219$ cm^{-1}

63. Strong electrolyte : The molar conductivity of strong electrolyte decreases slightly with the increase in concentration. This increase is due to increase in attraction as a result of greater number of ions per unit volume. With dilution the ions are far apart, interionic attractions become weaker and conductance increases.

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



64. *Refer to answers 45 and 49.*

65. *Refer to answer 44.*

66. Weak electrolytes : The electrolytes which are not completely dissociated into ions in solution are called weak electrolytes *e.g.*, CH_3COOH, NH_4OH, HCN, etc.

Strong electrolytes : The electrolytes which are completely dissociated into ions in solution are called strong electrolytes. *e.g.*, HCl, KCl, NaOH, NaCl, etc.

67. Using formula, $\Lambda_m^c = \frac{\kappa \times 1000}{C}$

Given $\kappa = 3.905 \times 10^{-5}$ S cm^{-1}
$C = 0.001$ mol L^{-1}

$$\therefore \quad \Lambda_m^c = \frac{3.905 \times 10^{-5} \times 1000}{0.001} = 39.05 \text{ S cm}^2 \text{ mol}^{-1}$$

The degree of dissociation,

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{39.05}{390.5} = 0.1$$

$[\because \Lambda_m^\circ = 349.6 + 40.9 = 390.5 \text{ S cm}^2\text{mol}^{-1}]$

68. Given : Conductivity, $\kappa = 0.0248$ S cm^{-1}
Molarity, $C = 0.20$ M = 0.20 mol L^{-1}

Using formula, $\Lambda_m = \frac{1000 \times \kappa}{C}$

$$\Lambda_m^c = \frac{(1000\,\text{cm}^3\ \text{L}^{-1}) \times (0.0248 \text{ S cm}^{-1})}{(0.20 \text{ mol L}^{-1})}$$

$= 124$ S cm^2 mol^{-1}

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{124}{73.5 + 76.5} = 0.82$$

69. Resistance of 0.1 M KCl solution R = 100 Ω
Conductivity $\kappa = 1.29$ S m^{-1}
Cell constant $G^* = \kappa \times R = 1.29 \times 100 = 129$ m^{-1}
Resistance of 0.02 M KCl solution, R = 520 Ω

$$\text{Conductivity, } \kappa = \frac{\text{cell constant}}{R} = \frac{129 \text{ m}^{-1}}{520\ \Omega}$$

$= 0.248$ S m^{-1}

Concentration, $C = 0.02$ mol L^{-1}

$= 1000 \times 0.02$ mol m^{-3} = 20 mol m^{-3}

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa}{C} = \frac{0.248 \text{ S m}^{-1}}{20 \text{ mol m}^{-3}}$$

$= 0.0124$ S m^2 mol^{-1}

70. $\Lambda^\circ_m\ Al_2(SO_4)_3 = 2\lambda^\circ_m Al^{3+} + 3\lambda^\circ_m SO_4^{2-}$

⇒ $858 = 2\lambda^\circ_m Al^{3+} + 3 \times 160$

⇒ $\lambda^\circ_m Al^{3+} = \dfrac{858 - 480}{2} = 189\ \text{S cm}^2\ \text{mol}^{-1}$

71. Given : Diameter = 1 cm, length = 50 cm

$R = 5.5 \times 10^3$ ohm, $M = 0.05$ M

$\rho = ?\quad \kappa = ?\quad \Lambda_m = ?$

Area of the column,

$$a = \pi r^2 = 3.14 \times \left(\frac{1}{2}\ \text{cm}\right)^2 = \frac{3.14}{4}\ \text{cm}^2$$

Resistivity,

$$\rho = R \cdot \frac{a}{l} = 5.5 \times 10^3\ \text{ohm} \times \frac{3.14\ \text{cm}^2}{4 \times 50\ \text{cm}}$$

$= 86.35$ ohm cm

Again, conductivity, $\kappa = \dfrac{1}{\rho}$

$$= \frac{1}{86.35} = 1.158 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

and molar conductivity, $\Lambda_m = \kappa \cdot \dfrac{10^3}{M}$

$$= 1.158 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^{-1} \times \frac{10^3}{5 \times 10^{-2}}$$

$= 231.6\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

72. $\kappa = 1.29 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^{-1}$

$\kappa = \dfrac{1}{R} \times$ Cell constant

⇒ Cell constant $= \kappa \times R = 1.29\ \text{S m}^{-1} \times 85 = 109.65\ \text{m}^{-1}$

For second solution,

$\kappa = \dfrac{1}{R} \times$ Cell constant $= \dfrac{1}{96\ \Omega} \times 109.65\ \text{m}^{-1}$

$= 1.142\ \Omega^{-1}\text{m}^{-1}$

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.142\ \Omega^{-1}\text{m}^{-1} \times 1000\ \text{cm}^3}{0.052}$$

$$\Lambda_m = \frac{1.142\ \Omega^{-1}\text{cm}^{-1} \times 10^{-2} \times 1000\ \text{cm}^3}{0.052\ \text{mol}}$$

$= 219.61\ \text{S cm}^2\ \text{mol}^{-1}$

73. According to Kohlrausch's law,

$\Lambda^\circ CH_3COOH = \lambda^\circ CH_3COO^- + \lambda^\circ H^+$

Degree of dissociation, $\alpha = \dfrac{\Lambda_m}{\Lambda^\circ_m}$

$$= \frac{11.7\ \text{S cm}^2\text{mol}^{-1}}{(49.9 + 349.1)\ \text{S cm}^2\text{mol}^{-1}} = \frac{11.7}{390} = 3 \times 10^{-2}$$

74. For electrolyte X :

Molarity = 0.05 M

resistance = 100 ohms

conductivity $= 1.0 \times 10^{-4}\ \text{S cm}^{-1}$

For electrolyte Y :

Molarity = 0.01 M

resistance = 50 ohms

conductivity = ?

(i) Cell constant, G^*

= conductivity (κ) × resistance (R)

$= 100 \times 1 \times 10^{-4} = 10^{-2}\ \text{cm}^{-1}$

∴ Conductivity of solution Y is

$$\kappa = \frac{G^*}{R} = \frac{10^{-2}}{50} = 0.02 \times 10^{-2} = 2 \times 10^{-4}\ \text{S cm}^{-1}$$

Molar conductance, $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

$$= \frac{2 \times 10^{-4} \times 1000}{0.01} = 20\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

75. (a) *Refer to answers 45 and 63.*

(b) *Refer to answer 62.*

76. (a) *Refer to answer 44.*

$\Lambda^\circ_m(CH_3COOH) = \lambda^\circ_{H^+} + \lambda^\circ_{CH_3COO^-}$

(b) $\Lambda^\circ_m\ (HCl) = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}$

$\Lambda^\circ_m\ (NaCl) = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$

$\Lambda^\circ_m\ (CH_3COONa) = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+}$

$\Lambda^\circ_m(CH_3COOH) = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$

$= \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} + \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+} - \lambda^\circ_{Cl^-} - \lambda^\circ_{Na^+}$

$= \Lambda^\circ_m(HCl) + \Lambda^\circ_m(CH_3COONa) - \Lambda^\circ_m\ NaCl$

$= 426 + 91 - 126 = 391\ \text{S cm}^2\ \text{mol}^{-1}$

77. Conductivity of acetic acid,

$\kappa = 7.896 \times 10^{-5}\ \text{S cm}^{-1}$,

Λ°_m for acetic acid $= 390.5\ \text{S cm}^2\ \text{mol}^{-1}$.

Molar conductivity, $\Lambda^c_m = \dfrac{\kappa \times 1000}{\text{Molarity}}$

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

Degree of dissociation,

$$\alpha = \frac{\Lambda^c_m}{\Lambda^\circ_m} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

Dissociation constant of acetic acid,

$$K_a = \frac{C\alpha^2}{1 - \alpha} = \frac{(0.00241) \times (8.4 \times 10^{-2})^2}{1 - 0.084} = 1.86 \times 10^{-5}$$

78. The species that get reduced at cathode is the one having higher value of standard reduction potential. Hence, the reaction that will occur at cathode is $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$.

79. $\underset{1\text{ mol}}{Zn^{2+}_{(aq)}} + \underset{2\text{ mol}}{2e^-} \longrightarrow Zn_{(s)}$

One mole of Zn^{2+} requires 2 moles of electrons for reduction *i.e.*

$Q = 2 \times F = 2 \times 96500 = 193000$ C

80. The species that get reduced at cathode is the one which have higher value of standard reduction potential. Hence, the reaction that will occur at cathode is

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

81. Faraday's first law of electrolysis : During electrolysis the amount of any substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte *i.e.*,

$w \,\alpha\, Q$ or $w \propto I \times t$ $[\because Q = I \times t]$

$w = Z \times I \times t$

where, Z is a constant of proportionality known as electrochemical equivalent of the substance deposited.

82. The electrode reaction is $Cu^{2+} + 2e^- \rightarrow Cu$

$\therefore$ Quantity of charge required for reduction of 1 mole of $Cu^{2+} = 2F = 2 \times 96500 = 193000$ C

83. *Refer to answers 81 and 82.*

84. Given : Current $I = 5$ A; $t = 20 \times 60$ s, $w = ?$

$Q = I \times t = 5 \times 20 \times 60 = 6000$ C

Reaction for deposition of Ni,

$Ni^{2+} + \underset{\substack{2\text{ mol}\\2\times 96500\text{ C}}}{2e^-} \longrightarrow \underset{\substack{1\text{ mol}\\58.7\text{ g}}}{Ni}$

Thus, 2×96500 C of electricity produces 58.7 g Ni

$\therefore$ 6000 C of electricity would produce

$$= \frac{58.7 \times 6000}{2 \times 96500} = 1.825 \text{ g}$$

85. (i) **At cathode :** The following reduction reactions compete to take place at the cathode.

$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}\ ;\ E° = 0.80$ V

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}\ ;\ E° = 0.00$ V

The reaction with a higher value of $E°$ takes place at the cathode. Therefore, the deposition of silver will take place at the cathode.

Since, Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or NO_3^- ions can be oxidized at the anode. But OH^- ions having a lower discharge potential get preference and decompose to liberate O_2.

$OH^- \longrightarrow OH + e^-$

$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

(ii) At the cathode, the following reduction reaction occurs to produce H_2 gas.

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$

At the anode, the following processes are possible :

$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-\ ;\ E° = +\,1.23$ V ...(i)

$2SO^{2-}_{4(aq)} \longrightarrow S_2O^{2-}_{8(aq)} + 2e^-\ ;\ E° = +\,1.96$ V ...(ii)

For dilute sulphuric acid, reaction (i) is preferred to produce O_2 gas but for concentrated sulphuric acid, (ii) occurs.

86. Reaction for production of Ca from molten $CaCl_2$:

$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$

$Ca^{2+} + \underset{2F}{2e^-} \longrightarrow \underset{40\text{ g}}{Ca}$

Electricity required to produce 40 g = 2 F

$\therefore$ Electricity required to produce 20 g = 0.5×2 F = 1 F

87. Calculation of mass of Ag deposited

The electrode reaction is $Ag^+ + e^- \longrightarrow Ag$

The quantity of electricity passed = Current × Time

$= 0.5 \text{ (amp)} \times 2 \times 60 \times 60 \text{ (sec)} = 3600$ C

From the electrode reaction, it is clear that 96500 C of electricity deposit Ag = 108 g

3600 C of electricity will deposit Ag

$$= \frac{108}{96500} \times 3600 = 4.03 \text{ g}$$

Calculation of thickness :

Let the thickness of deposit be x cm

Mass = volume × density = Area × thickness × density

[$\because$ volume = area × thickness]

$\therefore$ $4.03 \text{ g} = 900 \text{ (cm}^2) \times x \text{ (cm)} \times 10.5 \text{ (g cm}^{-3})$

$\therefore$ $x = \dfrac{4.03}{900 \times 10.5} \text{ cm} = 4.26 \times 10^{-4}$ cm.

88. The given reaction is

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

one mole $Cr_2O_7^{2-}$ requires 6 mol of electrons for reduction. Hence, quantity of electricity required

$= 6 \text{ mol} \times 96500 \text{ C mol}^{-1} = 5.79 \times 10^5$ coulomb

89. Quantity of electricity passed

$Q = I \times t = 2.0 \text{ A} \times 3 \times 60 \times 60 \text{ s} = 21600$ C

$Hg^{2+} + \underset{2\text{ F}}{2e^-} \longrightarrow \underset{1\text{ mol}}{Hg}$

2×96500 C electricity produces 1 mole Hg

$\therefore$ 21600 C will produce $= \dfrac{21600}{2 \times 96500}$

$= 0.112$ mole of Hg

90. Current (I) = 1.5 A
Time (t) = 10 min = 10 × 60 = 600 s
Quantity of electricity passed = $I \times t$
= (1.5 A) × (600 s) = 900 C
Copper is deposited as :

$$Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$$

2 × 96500 C of current deposit copper = 63.56 g
∴ 900 C of current will deposit copper

$$= \frac{63.56}{2\times96500}\times900 = 0.296 \text{ g}$$

91. Aqueous NaCl ionises as

$$NaCl \longrightarrow Na^+ + Cl^-$$

(i) Following reactions are possible at cathode,

$$2Na^+_{(aq)} + 2e^- \longrightarrow 2Na_{(s)};\ E° = -2.71 \text{ V}$$

$$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)};\ E° = -0.83 \text{ V}$$

The reaction with higher $E°$ value will take place, hence H_2 is produced at cathode.
(ii) Following reactions may take place at anode

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^-;\ E° = 1.36 \text{ V}$$

$$H_2O_{(l)} \longrightarrow \frac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e^-;\ E° = 1.23 \text{ V}$$

The reaction with lower $E°$ value will take place, but due to over voltage. Cl_2 is liberated at anode.

92. *Refer to answer 88.*

93. *Refer to answer 91.*

94. *Refer to answer 85.*

95. Reaction for deposition of Mg from molten $MgCl_2$:

$$MgCl_2 \longrightarrow Mg^{2+} + 2Cl^-$$

$$Mg^{2+} + 2e^- \longrightarrow Mg$$

24 g of Mg is deposited by 2 × 96500 C of electricity
∴ 1.2 g of Mg will be deposited by

$$\frac{2\times96500}{24}\times1.2 = 9650 \text{ C of electricity}$$

Now, $Q = It$

$$\therefore\ I = \frac{Q}{t} = \frac{9650}{60\times60} = 2.68 \text{ A}$$

96. According to the reaction :

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

Charge = Current × time = 1.5 amp × 16 × 60 s = 1440 C
2 × 96500 C electricity deposits = 63.5 g Cu

$$\therefore\ 1440 \text{ electricity deposits} = \frac{63.5\times1440}{2\times96500} = 0.47 \text{ g}$$

97. Reaction for deposition of silver :

$$\begin{array}{lcl} Ag^+ + e^- & \longrightarrow & Ag \\ \text{1 mol} & & \text{1 mol} \\ \text{1 F = 96500 C} & & \text{108 g} \end{array}$$

108 g of silver is deposited by 96500 C of electricity
∴ 1.45 g of silver would be deposited by

$$\frac{96500\times1.45}{108} = 1295.6 \text{ C}$$

Q = 1295.6 C
Given, current strength I = 1.5 A

$$\therefore\ t = \frac{Q}{I} = \frac{1295.6}{1.5} = 863.7 \text{ s} = 14.4 \text{ min}$$

Reaction for deposition of zinc :

$$\begin{array}{lll} Zn^{2+} + & 2e^- \longrightarrow & Zn \\ & \text{2 mol} & \text{1 mol} \\ & 2\times96500 \text{ C} & 65.3 \text{ g} \end{array}$$

Thus, 2 × 96500 C electricity deposits 65.3 g Zn
∴ 1295.6 C electricity would deposit

$$= \frac{65.3\times1295.6}{2\times96500} = 0.438 \text{ g Zn}$$

Reaction for deposition of copper :

$$\begin{array}{lll} Cu^{2+} + & 2e^- \longrightarrow & Cu \\ & \text{2 mol} & \text{1 mol} \\ & 2\times96500 \text{ C} & 63.5 \text{ g} \end{array}$$

Thus, 2 × 96500 C electricity deposits 63.5 g Cu
∴ 1295.6 C electricity would deposit

$$= \frac{63.5\times1295.6}{2\times96500} = 0.426 \text{ g Cu}$$

98. Secondary batteries : The batteries which can be recharged again and again are called as secondary batteries. *e.g.*, lead storage battery.

99. (i) Mercury cell is used for low current devices like watches and hearing aids.
(ii) The hydrogen oxygen fuel cell was used in Apollo space programme.
(iii) Lead storage battery is used in automobiles and invertors.
(iv) Dry cell

100. Mercury cell is a primary battery. Hence, it can be used only once and cannot be recharged.
Advantage : The cell potential remains constant during its life time. Hence, it is useful for devices requiring constant current *e.g.*, hearing aids and watches.

101. Lead storage battery is a secondary cell.
Cell reactions during operation
At anode : $Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$
At cathode :

$$PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$

Overall reaction :

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO^{2-}_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

102. The lead storage battery is most important secondary cell. The cell reactions when the battery is in use :

At anode:

$Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

At cathode :

$PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

The overall cell reaction is

$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

Following reaction takes place during recharging

At cathode : $PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO^{2-}_{4(aq)}$

At anode : $PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow PbO_{2(s)} + SO^{2-}_{4\,(aq)} + 4H^+_{(aq)} + 2e^-$

Net reaction : $2PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)}$

103. *Refer to answer 101.*

104. Mercury Cell : It is a miniature cell which finds a frequent use these days to supply energy for watches, video cameras, hearing aids and other compact devices. In mercury cell the anode is zinc-mercury amalgam, and the cathode is a paste of mercury (II) oxide and carbon, electrolyte is a moist paste of KOH - ZnO.

The cell reactions are as follows :

Anode :

$\underset{\text{(Amalgam)}}{Zn(Hg)} + 2OH^- \longrightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$

Cathode :

$HgO_{(s)} + H_2O_{(l)} + 2e^- \longrightarrow Hg_{(l)} + 2OH^-$

Net reaction :

$Zn(Hg) + HgO_{(s)} \longrightarrow ZnO_{(s)} + Hg_{(l)}$

The cell potential remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its use.

105. *Refer to answer 101.*

106. Nickel cadmium cell is a secondary battery which consists of a cadmium anode, nickel hydroxide as cathode and sodium or potassium hydroxide acts as electrolyte.

Merit : It has longer life than lead storage battery.

Demerit : It is more expensive than lead storage battery.

The following reaction takes place during discharging :

$Cd_{(s)} + 2Ni(OH)_{3(s)} \rightarrow CdO_{(s)} + 2Ni(OH)_{2(s)} + H_2O_{(l)}$

107. Those galvanic cells which give us direct electrical energy by the combustion of fuels like hydrogen, methane, methanol etc. are called fuel cells.

108. H_2 — O_2 fuel cell was used in Appollo space programme.

109. (i) It is pollution free.

(ii) It has high efficiency of 70 - 75% and its rate can be controlled.

110. Fuel cells : *Refer to answer 107.*

The reactions taking place in hydrogen - oxygen fuel cell :

At cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

At anode : $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$

Net reaction : $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

111. *Refer to answer 111.*

112. Metals of lower electrode potential value when connected with iron protect it from oxidation and prevent corrosion. Hence, coating of metal *A* having lower electrode potential will be better than *B* which has higher $E^\circ_{(B^{2+}/B)} = -\ 0.14$ V.

113. According to electrochemical theory of rusting the impure iron surface behaves like small electrochemical cell. In this any point of iron acts as anode and other iron surface acts as cathode. Moisture having dissolved CO_2 or O_2 acts as an electrolyte. The reactions are given below.

At anode :

$$Fe \rightarrow Fe^{2+} + 2e^-; E^\circ_{Fe^{2+}/Fe} = -0.44\,V.$$

At cathode :

$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O;\ E^\circ_{H^+/O_2/H_2O} = 1.23\ V$$

Overall reaction :

$$Fe + 2H^+ + \frac{1}{2}O_2 \rightarrow Fe^{2+} + H_2O;$$

$E^\circ_{cell} = 1.67$ V

The Fe^{2+} ions are further oxidised by atmospheric oxygen to Fe^{3+} ions, which form hydrated ferric oxide (rust).

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^+$$

$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3 \cdot xH_2O$ (Rust)

114. *Refer to answer 113.*

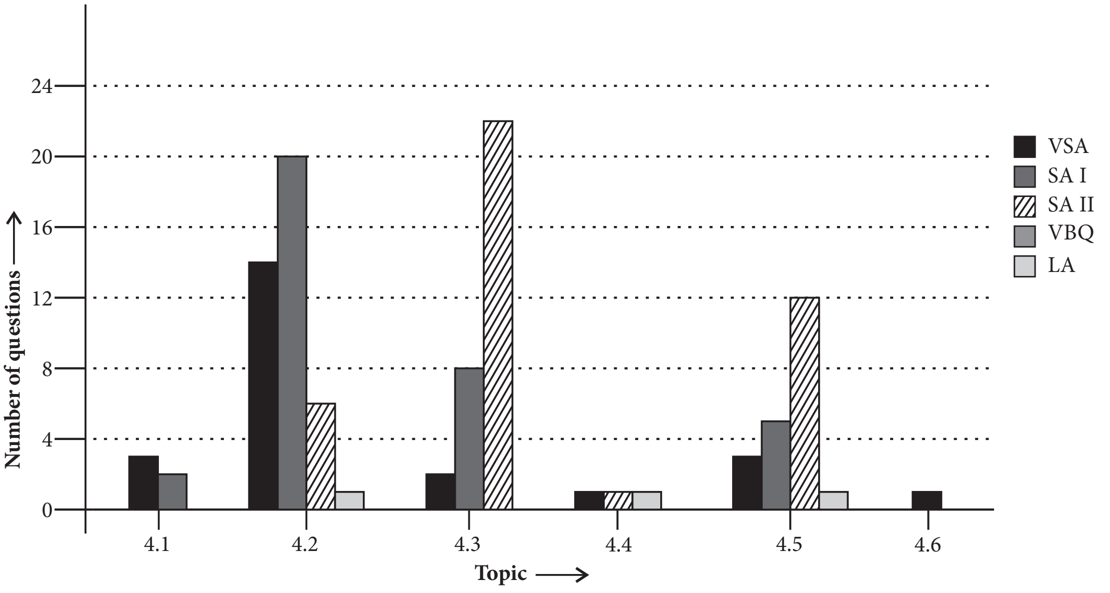
115. Corrosion is the process of slowly eating away of the metal due to attack of the atmospheric gases on the surface of the metal resulting into the formation of compounds such as oxides, sulphides, carbonates, etc. The corrosion of iron is called rusting.

Electrochemical theory of rusting of iron : *Refer to answer 113.*

04

Chemical Kinetics

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



- Maximum total weightage is of *Integrated Rate Equations.*
- Maximum SA I type questions were asked from *Factors Influencing Rate of a Reaction.*
- Maximum SA II type questions were asked from *Integrated Rate Equations.*

QUICK RECAP

- **Chemical kinetics :** It is the branch of chemistry which deals with the study of reaction rates and their mechanisms.
- **Rate of a reaction :** The rate of a reaction can be defined as the change in concentration of a reactant or a product in unit time. For the reaction,

$$R \longrightarrow P, \text{Rate} = -\frac{\Delta[R]}{\Delta t} \text{ or } +\frac{\Delta[P]}{\Delta t}$$

- **Units of rate :** Concentration time^{-1} *i.e.*, mol L^{-1} s^{-1} or atm s^{-1} for gaseous reactions.

Average rate of reaction : It is the average value during a large time interval.

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{+\Delta[P]}{\Delta t}$$

Instantaneous rate of reaction : It is the rate of a reaction at a particular instant of time *i.e.*, when Δt approaches zero.

$$r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$$

Factors influencing rate of a reaction :

- **Concentration :** Greater the concentrations of the reactants, faster is the rate of reaction.
- **Physical state of reactants :** Reactions involving gaseous reactants are faster than reactions containing solid and liquid reactants.
- **Temperature :** The rate of reaction increases with increase of temperature. For most of the reactions, rate of reaction becomes almost double with 10° C rise of temperature.
- **Presence of catalyst :** A catalyst generally increases the speed of a reaction.
- **Surface area of reactants :** For a reaction involving a solid reactant or catalyst, the greater is the surface area, the faster is the reaction.
- **Presence of light :** Photochemical reactions take place in the presence of light only.
- **Activation energy :** Lower the activation energy faster is the reaction.

Rate law and rate constant : The equation that correlates the rate of reaction with concentration of reactants is known as *rate law*.

- For a simple reaction, $A + B \rightarrow C + D$
  Rate = $k[A][B]$ where k is the *rate constant* which is equal to the rate of reaction when concentration of each of the reactant is unity.

Order and molecularity :

Molecularity of reaction	Order of reaction
It is the total number of species taking part in a chemical reaction.	It is the sum of the powers of the concentration terms of reacting species in the rate law equation.
It is a theoretical concept.	It is an experimental quantity.
It is derived from the mechanism of reaction.	It is derived from the rate expression.
It can neither be zero nor fractional. It is always a whole number.	It may be zero, fractional or an integer (may range from 0 to 3).
It is applicable only to elementary reactions. The overall molecularity of a complex reaction has no significance.	It is applicable to elementary as well as complex reactions.

Half life of reaction : The time in which the concentration of a reactant is reduced to one half of its initial concentration is called *half life of the reaction.*

$t_{1/2} \propto \frac{1}{a^{n-1}}$ where n is the order of the reaction.

Rate law, integrated rate law, half-life, units of rate constant and graph for the reactions of different orders :

Order	Rate law	Integrated rate law	Half-life	Units of rate constant	Graph
0	Rate = $k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	mol L^{-1} s^{-1}	$[A]$ *vs* t; slope = $-k$
1	Rate = $k[A]^1$	$\ln[A]_t = -kt + \ln[A]_0$	$t_{1/2} = 0.693/k$	s^{-1}	$\ln[A]$ *vs* t; slope = $-k$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k\,[A]_0$	L mol^{-1} s^{-1}	$1/[A]$ *vs* t; slope = k
2	Rate = $k[A][B]$	$kt = \frac{1}{[A]_0 - [B]_0}\ln\frac{[B]_0[A]}{[A]_0[B]}$	–	L mol^{-1} s^{-1}	$1/[A]$ *vs* t; slope = k
n	Rate = $k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}$	$t_{1/2} = \frac{2^{n-1}-1}{k(n-1)[A]_0^{n-1}}$	$(\text{mol L}^{-1})^{1-n}\,\text{s}^{-1}$	$\frac{1}{[A]^{n-1}}$ *vs* t; slope = k

Pseudo first order reactions : Those reactions which are not truly of the first order but under certain conditions become reactions of the first order are called *pseudo first order reactions.*

e.g.

- **Acid hydrolysis of ethyl acetate :**

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k'[CH_3COOC_2H_5][H_2O] = k[CH_3COOC_2H_5]$$

where $k = k'[H_2O]$

- **Acid catalysed inversion of cane sugar :**

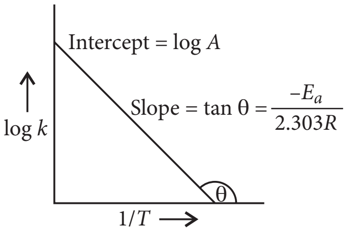
$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\text{Rate} = k[C_{12}H_{22}O_{11}]$$

Effect of temperature on rate of reaction :

- For a chemical reaction with rise in temperature by 10° C, the rate constant is nearly doubled.
- **Arrhenius equation :** $k = Ae^{-E_a/RT}$

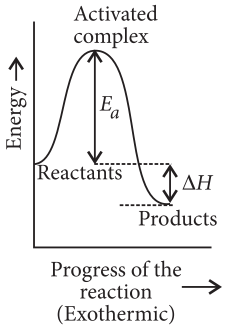
$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

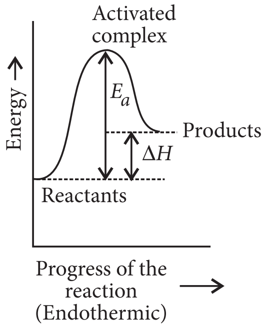


where, k = Rate constant,
A = Pre-exponential factor (frequency factor),
E_a = Activation energy,
T = Temperature

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Activation energy : The minimum amount of energy required by reactant molecules to participate in a reaction is called *activation energy* (E_a).





- Activation energy = Threshold energy – Average kinetic energy of reacting molecules
- Activation energy (E_a) $= E_{(\text{activated complex})} - E_{(\text{ground state})}$
- ΔH = Activation energy of forward reaction – Activation energy of backward reaction

Collision theory of chemical reactions :

- Reaction occurs due to collision of molecules.
- All collisions are not effective.
- *Effective collisions* are those collisions in which molecules collide with sufficient kinetic energy (called *threshold energy* which is equal to activation energy + energy possessed by reacting species) and proper orientation.
- Rate = $PZ_{AB}e^{-E_a/RT}$ where, P = probability or steric factor which takes into account the fact that in a collision, molecules must be properly oriented and Z_{AB} = collision frequency (*i.e.*, the no. of collisions per second per unit volume of the reaction mixture) of reactants, A and B.

Previous Years' CBSE Board Questions

4.1 Rate of a Chemical Reaction

VSA (1 mark)

1. Express the rate of the following reaction in terms of the formation of ammonia.
$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ *(Delhi 2013C)*

2. Define elementary step in a reaction. *(1/5, Foreign 2011)*

3. Why does the rate of a reaction not remain constant throughout the reaction process? *(AI 2009C)*

SA I (2 marks)

4. What is meant by rate of reaction? Differentiate between average rate and instantaneous rate of reaction. *(AI 2012C)*

5. Explain the difference between the average rate and instantaneous rate of chemical reaction. *(2/5, AI 2010C)*

4.2 Factors Influencing Rate of a Reaction

VSA (1 mark)

6. Define the rate constant. *(1/5, Foreign 2015, Delhi 2015C)*

7. Define the specific rate of reaction. *(AI 2014C)*

8. For a reaction $A + B \rightarrow P$, the rate law is given by,
$r = k[A]^{1/2}\,[B]^2$
What is the order of this reaction? *(AI 2013)*

9. If the rate constant of reaction is $k = 3 \times 10^{-4} s^{-1}$, then identify the order of the reaction. *(Delhi 2013C, 2011C)*

10. Define 'order of a reaction'. *(AI 2011)*

11. Identify the reaction order from the following rate constant :
$k = 2.3 \times 10^{-5}$ L mol^{-1}s^{-1} *(Delhi, AI 2011C)*

12. Distinguish between molecularity and order of a reaction. *(1/5, AI 2010C)*

13. Define the term 'order of reaction' for chemical reactions. *(Delhi, AI 2008)*

14. For the reaction, $Cl_{2(g)} + 2NO_{(g)} \rightarrow 2NOCl_{(g)}$ the rate law is expressed as
Rate = $k[Cl_2]\,[NO]^2$
What is the overall order of this reaction? *(Delhi 2007)*

15. Express the rate of the following reaction in terms of disappearance of hydrogen in the reaction :
$3H_{2(g)} + N_{2(g)} \rightarrow 2NH_{3(g)}$ *(AI 2007)*

SA I (2 marks)

16. For a reaction : $2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$
Rate = k
(i) Write the order and molecularity of this reaction.
(ii) Write the unit of k. *(Delhi 2016)*

17. For a reaction : $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$
Rate = k
(i) Write the order and molecularity of this reaction
(ii) Write the unit of k. *(AI 2016)*

18. For a reaction $A + B \longrightarrow P$, the rate is given by
Rate = $k[A][B]^2$
(i) How is the rate of reaction affected if the concentration of B is doubled?
(ii) What is the overall order of reaction if A is present in large excess? *(2/5, Delhi 2015)*

19. Define rate of reaction. Write two factors that affect the rate of reaction. *(AI 2015)*

20. Write units of rate constants for zero order and for the second order reactions if the concentration is expressed in mol L^{-1} and time in second. *(AI 2015C)*

21. Write two differences between 'order of reaction' and 'molecularity of reaction'. *(Delhi 2014, 2011C)*

22. (i) For a reaction, $A + B \rightarrow$ Product, the rate law is given by, Rate = $k[A]^1[B]^2$. What is the order of the reaction ?

(ii) Write the unit of rate constant 'k' for the first order reaction. *(Delhi 2014C)*

23. A reaction is of second order with respect to its reactant. How will its reaction rate be affected if the concentration of the reactant is (i) doubled (ii) reduced to half ? *(AI 2014C, 2012, Delhi 2009)*

24. What do you understand by the 'order of a reaction'? Identify the reaction order from each of the following units of reaction rate constant.
(i) L^{-1} mol s^{-1} (ii) L mol^{-1} s^{-1} *(Delhi 2012)*

25. Distinguish between 'rate expression' and 'rate constant' of a reaction. *(Delhi 2011)*

26. What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are :
(i) L^{-1} mol s^{-1} (ii) L mol^{-1} s^{-1} *(AI 2011)*

27. Express clearly what do you understand by 'rate expression' and 'rate constant' of a reaction *(2/5, Foreign 2011)*

28. Explain the term 'order of reaction'. Derive the unit for first order rate constant. *(Delhi 2009C)*

29. 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 k (i) for a zero order reaction and (ii) for a first order reaction? *(Delhi 2008)*

30. List the factors on which the rate of a chemical reaction depends. *(2/5, Delhi, AI 2008)*

31. Distinguish between order and molecularity of a reaction. When could order and molecularity of a reaction be the same? *(Delhi 2008C)*

SA II (3 marks)

32. A reaction is second order in A and first order in B.
(i) Write the differential rate equation.
(ii) How is the rate affected on increasing the concentration of A three times?
(iii) How is the rate affected when the concentration of both A and B are doubled? *(3/5, Delhi 2013)*

33. The reaction, $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ contributes to air pollution whenever a fuel is burnt in air at a high temperature. At 1500 K, equilibrium constant K for it is 1.0×10^{-5}. Suppose in a case $[N_2] = 0.80$ mol L^{-1} and $[O_2] = 0.20$ mol L^{-1} before any reaction occurs. Calculate the equilibrium concentrations of the reactants and the product after the mixture has been heated to 1500 K. *(AI 2012)*

34. (i) A reaction is first order in A and second order in B.
(a) Write differential rate equation.
(b) How is rate affected when concentration of B is tripled?
(c) How is rate affected when concentration of both A and B is doubled?
(ii) What is molecularity of a reaction? *(AI 2012C)*

35. $A + 2B \rightarrow 3C + 2D$. The rate of disappearance of B is 1×10^{-2} mol/L/s.
What will be (i) rate of the reaction (ii) rate of change in concentration of A and C ? *(3/5, AI 2008)*

36. The data given below is for the reaction,
$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$ at 298 K :

S. No.	**$[N_2O_5]$ (mol L^{-1})**	**Rate of disappearance of N_2O_5(mol L^{-1} min^{-1})**
1.	1.13×10^{-2}	34×10^{-5}
2.	0.84×10^{-2}	25×10^{-5}
3.	0.62×10^{-2}	18×10^{-5}

Determine for this reaction :
(i) order of reaction
(ii) rate constant
(iii) rate law. *(AI 2008C)*

37. The decomposition of NH_3 on platinum surface :
$2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$
is a zero order reaction with $k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}
What are the rates of production of N_2 and H_2? *(Delhi 2007)*

LA (5 marks)

38. The following results have been obtained during the kinetic studies of the reaction :
$2A + B \longrightarrow C + D$

Experiment No.	$[A]$	$[B]$	Inital rate of formation of D
1.	0.1 M	0.1 M	6.0×10^{-3} M min^{-1}
2.	0.3 M	0.2 M	7.2×10^{-2} M min^{-1}
3.	0.3 M	0.4 M	2.88×10^{-1} M min^{-1}
4.	0.4 M	0.1 M	2.40×10^{-2} M min^{-1}

Calculate the rate of formation of D when $[A] = 0.5$ mol L^{-1} and $[B] = 0.2$ mol L^{-1}.
(Delhi 2010C)

4.3 Integrated Rate Equations

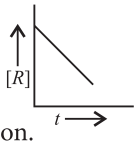
VSA (1 mark)

39. Define the half-life period of reaction ($t_{1/2}$).
(Delhi 2014)

40. If half-life period of a first order reaction is x and 3/4th life period of the same reaction is y, how are x and y related to each other?
(1/5, Delhi 2013C)

SA I (2 marks)

41. For a chemical reaction $R \rightarrow P$, the variation in the concentration $[R]$ *vs.* time (t) plot is given as



(i) Predict the order of the reaction.
(ii) What is the slope of the curve? *(AI 2014)*

42. Define half-life of a reaction. Write the expression of half-life for
(i) zero order reaction and
(ii) first order reaction. *(Foreign 2014)*

43. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.
(2/5, Delhi 2013)

44. Rate constant k for a first order reaction has been found to be 2.54×10^{-3} sec^{-1}. Calculate its 3/4th life. ($\log 4 = 0.6020$) *(Delhi 2013C)*

45. The thermal decomposition of HCO_2H is a first order reaction with a rate constant of 2.4×10^{-3} s^{-1} at a certain temperature. Calculate how long will it take for three-fourth of initial quantity of HCO_2H to decompose. ($\log 0.25 = -0.6021$)
(AI 2011)

46. In a first order reaction, the concentration of the reactant is reduced from 0.6 mol L^{-1} to 0.2 mol L^{-1} in 5 minutes. Calculate the rate constant of the reaction. *(AI 2011C)*

47. Show that for a first order reaction, the time required for half the change (half-life period) is independent of initial concentration.
(Delhi 2009C)

48. A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value. *(Delhi, AI 2008)*

SA II (3 marks)

49. For the first order thermal decomposition reaction, the following data were obtained :
$C_2H_5Cl_{(g)} \longrightarrow C_2H_{4(g)} + HCl_{(g)}$

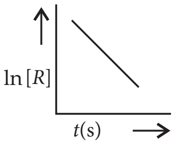
Time/sec	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant.
(Given : $\log 2 = 0.301, \log 3 = 0.4771, \log 4 = 0.6021$)
(AI 2016)

50. A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction. ($\log 2 = 0.3010$)
(3/5, Delhi 2015)

51. A first order reaction takes 10 minutes for 25% decomposition. Calculate $t_{1/2}$ for the reaction. (Given : $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$) *(3/5, Foreign 2015)*

52. For a chemical reaction $R \longrightarrow P$, the variation in the concentration, ln $[R]$ vs. time (s) plot is given as



(i) Predict the order of the reaction.
(ii) What is the slope of the curve?
(iii) Write the unit of the rate constant for this reaction. *(3/5, Foreign 2015)*

53. 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 1/10th value? *(AI 2015C, 2007)*

54. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume :
$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$

Experiment	Time/s	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

(Given : log 4 = 0.6021, log 2 = 0.3010)

(Delhi, AI, Foreign 2014)

55. Hydrogen peroxide, $H_2O_{2(aq)}$ decomposes to $H_2O_{(l)}$ and $O_{2(g)}$ in a reaction that is first order in H_2O_2 and has a rate constant $k = 1.06 \times 10^{-3}\ \text{min}^{-1}$.

(i) How long will it take for 15% of a sample of H_2O_2 to decompose?

(ii) How long will it take for 85% of the sample to decompose? *(Delhi 2014C)*

56. The first order reaction take 100 minutes for completion of 60% of the reaction. Find the time when 90% of the reaction will be completed. *(3/5, Delhi 2013C)*

57. For the reaction :

$2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)}$

The following data were collected. All the measurements were taken at 263 K.

Exp. No.	Initial [NO](M)	Initial $[Cl_2]$ (M)	Initial rate of disapp. of Cl_2 (M/min)
1.	0.15	0.15	0.60
2.	0.15	0.30	1.20
3.	0.30	0.15	2.40
4.	0.25	0.25	?

(i) Write the expression for rate law.

(ii) Calculate the value of rate constant and specify its units.

(iii) What is the initial rate of disappearance of Cl_2 in exp. 4? *(Delhi 2012)*

58. A first order reaction is 15% completed in 20 minutes. How long will it take to complete 60% of the reaction? *(3/5, Delhi 2012C)*

59. Nitrogen pentoxide decomposes according to equation :

$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$

This first order reaction was allowed to proceed at 40° C and the data below were collected :

$[N_2O_5]$ (M)	Time (min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

(i) Calculate the rate constant. Include units with answer.

(ii) What will be the concentration of N_2O_5 after 100 minutes?

(iii) Calculate the initial rate of reaction.

(Delhi 2011)

60. Nitrogen pentoxide decomposes according to the equation :

$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$

This first order reaction was allowed to proceed at 40°C and the data given below were collected :

$[N_2O_5]$ (M)	Time (min)
0.400	0.00
0.289	20.00
0.209	40.00
0.151	60.00
0.109	80.00

(i) Calculate the rate constant for the reaction. Include units with your answer.

(ii) Calculate the initial rate of reaction.

(iii) After how many minutes will $[N_2O_5]$ be equal to 0.350 M? *(3/5, Delhi 2011)*

61. A first order reaction has a rate constant value of $0.00510\ \text{min}^{-1}$. If we begin with 0.10 M concentration of the reactant, how much of the reactant will remain after 3.0 hours?

(3/5, Foreign 2011)

62. A reactant has a half-life of 10 minutes.

(i) Calculate the rate constant for the first order reaction.

(ii) What fraction of the reactant will be left after an hour of the reaction has occurred?

(Delhi 2011C)

63. The decomposition of a compound is found to follow a first order rate law. If it takes 15 minutes for 20 per cent of original material to react, calculate

(i) the rate constant.
(ii) the time at which 10% of the original material remains unreacted.

(3/5, Delhi 2010C)

64. The half-life for a first order reaction is 5×10^4 s. What percentage of the initial reactant will react in 20 hours? *(3/5, AI 2009C)*

65. A first order reaction is 20% complete in 5 minutes. Calculate the time taken for the reaction to be 60% complete. *(AI 2009C)*

66. The half-life for decay of radioactive ^{14}C is 5730 years. An archaeological artifact containing wood has only 80% of the ^{14}C activity as found in living trees. Calculate the age of the artifact. *(Delhi, AI 2008)*

4.4 Pseudo First Order Reaction

VSA (1 mark)

67. Define the following term :
Pseudo first order reaction *(1/2, Delhi 2014)*

SA II (3 marks)

68. In a pseudo first order hyrolysis of ester in water, the following results are obtained :

***t* in seconds**	0	30	60	90
[Ester]M	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

(3/5, AI 2010C)

LA (5 marks)

69. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained :

***t*/s**	0	30	60
$[CH_3COOCH_3]$/mol L^{-1}	0.60	0.30	0.15

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.
(ii) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
(Given : log 2 = 0.3010, log 4 = 0.6021)

(Delhi 2015)

4.5 Temperature Dependence of the Rate of a Reaction

VSA (1 mark)

70. Define the following :
Energy of activation of reaction.

(1/5, Foreign 2015, AI 2014C, 2008)

SA I (2 marks)

71. How does a change in temperature affect the rate of a reaction? How can this effect on the rate constant of reaction be represented quantitatively? *(AI 2014C)*

72. With the help of diagram, explain the physical significance of energy of activation (E_a) in chemical reactions. *(AI 2013C)*

73. With the help of a labelled diagram explain the role of activated complex in a reaction.

(2/5, Delhi 2012C)

74. The rate of most of the reactions becomes double when their temperature is raised from 298 K to 308 K. Calculate their activation energy.
[Given $R = 8.314$ J mol^{-1} K^{-1}] *(Delhi 2011C)*

75. Define "order of a reaction" and "activation energy of a reaction". *(AI 2009)*

SA II (3 marks)

76. The rate constant for the first order decomposition of H_2O_2 is given by the following equation :

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} \mathrm{K}$$

Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.
(Given : $R = 8.314$ J K^{-1} mol^{-1}) *(Delhi 2016)*

77. The rate constant of a first order reaction increases from 2×10^{-2} to 4×10^{-2} when the temperature changes from 300 K to 310 K. Calculate the energy of activation (E_a).
(log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

(Delhi 2015)

78. The rate constants of reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} respectively. Calculate the value of activation energy, E_a ($R = 8.314$ J K^{-1} mol^{-1}). *(Delhi 2015C, 2008)*

79. For a decomposition reaction, the values of k at two different temperatures are given below :

$k_1 = 2.15 \times 10^{-8}$ L/(mol.s) at 650 K

$k_2 = 2.39 \times 10^{-8}$ L/(mol.s) at 700 K

Calculate the value of E_a for the reaction.

($R = 8.314$ J K^{-1} mol^{-1}) *(AI 2014C, 2009)*

80. Rate constant 'k' of a reaction varies with temperature 'T' according to the equation :

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

where E_a is the activation energy. When a graph is plotted for log k *vs* $\frac{1}{T}$, a straight line with a slope of – 4250 K is obtained. Calculate 'E_a' for the reaction.

($R = 8.314$ J K^{-1} mol^{-1}). *(3/5, Delhi 2013)*

81. The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of activation (E_a) of the reaction assuming that it does not change with temperature.

[$R = 8.314$ J K^{-1} mol^{-1}, log 4 = 0.6021] *(AI 2013)*

82. The decomposition of A into products has a value of k as 4.5×10^3 s^{-1} at 10°C and energy of activation is 60 kJ mol^{-1}. At what temperature would k be 1.5×10^4 s^{-1}? *(3/5, Delhi 2013C)*

83. In general it is observed that the rate of a chemical reaction doubles with every 10 degree rise in temperature. If the generalisation holds good for a reaction in the temperature range 295 K to 305 K, what would be the value of activation energy for this reaction?

[$R = 8.314$ J/K^{-1} mol^{-1}] *(AI 2012C)*

84. The decomposition of phosphine,

$4PH_{3(g)} \longrightarrow P_{4(g)} + 6H_{2(g)}$

has the rate law, Rate = $k[PH_3]$.

The rate constant is 6.0×10^{-4}s^{-1} at 300 K and activation energy is 3.05×10^5 J mol^{-1}. Calculate the value of rate constant at 310 K.

[Given : $R = 8.314$ J K^{-1} mol^{-1}] *(Delhi 2008C)*

85. The first order rate constant for the decomposition of ethyl iodide by the reaction :

$$C_2H_5I_{(g)} \rightarrow C_2H_{4(g)} + HI_{(g)}$$

at 600 K is 1.6×10^{-5} s^{-1}. Its energy of activation is 209 kJ mol^{-1}.

Calculate the rate constant of reaction at 700 K. *(AI 2007)*

LA (5 marks)

86. (i) What is the physical significance of energy of activation? Explain with diagram.

(ii) In general, it is observed that the rate of a chemical reaction doubles with every 10 degree rise in temperature. If the generalisation holds good for the reaction in the temperature range of 295 K to 305 K, what would be the value of activation energy for this reaction?

[$R = 8.314$ J/K^{-1} mol^{-1}] *(Delhi 2012C)*

4.6 Collision Theory of Chemical Reactions

VSA (1 mark)

87. In some cases it is found that a large number of colliding molecules have energy more than threshold energy, yet the reaction is slow, Why? *(Delhi 2013C)*

Detailed Solutions

1. $N_{2\,(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

$$\frac{-d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

2. **Elementary step :** Each step of a complex reaction is called an elementary step.

3. The rate of a reaction does not remain constant throughout the reaction process because the rate of the reaction depends upon concentration of reactants which keeps on decreasing.

4. Change in concentration *i.e.*, either (decrease in concentration of reactant or increase in concentration of product) per unit time is called rate of reaction**.**

Rate of reaction $= \dfrac{C_2 - C_1}{t_2 - t_1} = \dfrac{\Delta C}{\Delta t}$

The ratio of change of concentration of reactants to the time consumed in that change is called average rate of reaction.

$$r_{av} = \frac{\Delta x}{\Delta t} = -\frac{C_2 - C_1}{t_2 - t_1}$$

The rate of reaction at a particular instant (time) is called instantaneous rate of reaction.

$$r_{ins} = \frac{dx}{dt}$$

dx = small change in concentration
dt = small time interval

5. *Refer to answer 4.*

6. Rate constant is the proportionality factor in the rate law expression for a chemical reaction. It is defined as the rate of a chemical reaction for which the concentration of each of the reacting species is unity.

7. At a given temperature, rate is equal to the rate constant of reaction when concentration of the reactant in unity. Thus rate constant is also known as specific reaction rate.

In the case of two reactants, the reaction may be written as :

$$A + B \rightarrow \text{Products}$$

$$r = \frac{dx}{dt} = k\,C_A C_B$$

where all the terms have their usual meaning as :
if $C_A = C_B = 1$ then $r = k$.

8. $A + B \rightarrow$ Product

Rate law, $r = k[A]^{1/2}\,[B]^2$

Order of reaction is sum of the powers of concentration terms,

$$\therefore \quad \text{Order of reaction} = \frac{1}{2} + 2 = \frac{5}{2} = 2.5$$

9. First order reaction.

10. It is defined as "the sum of the powers or exponents to which the concentration terms are raised in the rate law expression."

If rate $= k[A]^m\,[B]^n$, then order $= m + n$.

11. Second order reaction :

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

12. Distinction between order and molecularity of a reaction : (*any one*)

Order of a reaction	Molecularity of a reaction
1. It is the sum of powers of the concentration of the reactants in the rate law expression.	1. It is the number of reacting species(atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.
2. It need not be a whole number.	2. It is always a whole number.

Generally, in a complex reaction the order of reaction is equal to the molecularity of the slowest step.

13. *Refer to answer 10.*

14. Rate $= k[Cl_2]\,[NO]^2$

Hence order of the reaction = 1 + 2 = 3

15. Rate $= \dfrac{-1}{3}\dfrac{d[H_2]}{dt}$

16. (i) The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.
In this reaction, platinum metal acts as a catalyst.

At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.

However, two molecules of ammonia react to give products thus, the molecularity is two.
(ii) For a zero order reaction, unit of rate constant is mol L^{-1} sec^{-1}.

17. (i) Rate = k
Experimentally, it is found that the rate of reaction is independent of the concentration of H_2 and Cl_2. Hence, it is a zero order reaction.
Molecularity = 2
(ii) Unit of k = mole $litre^{-1}$ sec^{-1}

18. (i) From the rate law equation, order of reaction w.r.t. B is 2. Hence, if concentration of B is doubled, rate will become four times.
(ii) If A is present in large excess, rate of reaction will be independent of concentration of A and hence, order of reaction will be 2.

19. *Refer to answer 4.*

Following factors affect the rate of a chemical reaction :
(i) Concentration of reactants : Higher the concentration of reactants, faster would be the rate of reaction.

Rate = $k\,C^n$, where C = concentration of reactant.

(ii) Temperature : The rate of reaction increases with the temperature. For every 10°C rise in temperature rate of reaction increases 2 to 3 times.

20. Unit of rate constant (k), for zero order reaction.
Rate = $k[A]^0 \Rightarrow k = \text{mol L}^{-1}\ \text{s}^{-1}$
Unit of rate constant (k), for second order reaction
Rate = $k[A]^2 \Rightarrow k = \text{mol}^{-1}\ \text{L s}^{-1}$

21. *Refer to answer 12.*

22. (i) Order of reaction is sum of powers of concentration terms,
∴ Order of reaction = 1 + 2 = 3
(ii) *Refer to answer 28.*

23. Let the concentration of the reactant $[A] = a$
Order of reaction = 2 so that
Rate of reaction = $k\,[A]^2$ ...(1)
$= ka^2$
(i) Given that concentration of the reactant is doubled
So, that $[A] = 2a$,
Putting the value in equation (1) we get
New rate of reaction, $R_1 = k(2a)^2 = 4ka^2$
Hence, rate of reaction will increased to 4 times.
(ii) Given that concentration of the reactant is reduced to half
So that $[A] = (1/2)a$
Putting the value in equation (1), we get
New rate of reaction $R_2 = k((1/2)a)^2$
$= (1/4)ka^2$
Hence, rate of reaction will reduced to 1/4.

24. Order of a reaction : *Refer to answer 10.*
(i) L^{-1}mol s^{-1} – Zero order reaction
(ii) L mol^{-1} s^{-1} – Second order reaction

25. Rate expression is a way of expressing rate of reaction in terms of concentration of reactants, *e.g.*, for a general reaction, $aA + bB \longrightarrow cC + dD$
Rate = $k[A]^x\,[B]^y$
Rate constant (k) is equal to the rate of reaction when molar concentration of reactant is unity. Its units depends upon the order of reaction.

26. *Refer to answers 25 and 24.*

27. *Refer to answer 25.*

28. Order of a reaction : *Refer to answer 10.*
Unit for first order rate constant :
For first order reaction,

$$\text{Rate} = \frac{dx}{dt} = k[A]$$

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k.\ \text{mol L}^{-1} \Rightarrow k = \frac{1}{\text{sec}} = \text{sec}^{-1}.$$

29. *Refer to answer 6.*
Unit for k :
(i) For a zero order reaction : mol L^{-1} s^{-1}
(ii) For a first order reaction : s^{-1}.

30. Factors affecting the rate of a chemical reaction :
(i) Concentration of reactants : In general the rate of a reaction increases when concentration of reactants is increased.
Rate = kC^n

(ii) Temperature : Most of the chemical reactions are accelerated by increase in temperature.

(iii) Catalyst : Rate of a reaction increases in presence of a catalyst.

(iv) Nature of reactants : Reactions involving ionic reactants are fast as compared to those involving covalent reactants.

(v) Surface area of the reactants : In case of solid reactants, the rate of reaction increases with the surface area of the particles of the reactants.

(vi) Light : In case of photochemical reactions, the rate of reaction increases with increasing the intensity of light.

31. *Refer to answer 12.*

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

(i) Differential rate equation is

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

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

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

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

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

New concentration of $B = [2B]$

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

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

33. Given reaction is

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}\ ;\ K = 1.0 \times 10^{-5}$$

Initially : 0.80 mol L^{-1} 0.20 mol L^{-1} 0

At equil.: $0.80 - x$ $0.20 - x$ $2x$

According to law of mass action,

$$K = \frac{[NO]^2}{[N_2][O_2]}$$

$$\text{or} \quad 1.0 \times 10^{-5} = \frac{(2x)^2}{(0.80 - x)(0.20 - x)}$$

x is very small hence can be neglected in the denominator. Thus,

$$1.0 \times 10^{-5} = \frac{4x^2}{0.8 \times 0.2} \text{ or } 1.0 \times 10^{-5} = \frac{4x^2}{0.16}$$

or, $4x^2 = 1.0 \times 10^{-5} \times 0.16$ or $4x^2 = 16 \times 10^{-7}$

or, $x^2 = 4 \times 10^{-7}$ or $x = 6.32 \times 10^{-4}$

$\therefore$ $[N_2] = 0.80 - 0.000632 = 0.7994$ mol L^{-1}

$[O_2] = 0.20 - 0.000632 = 0.199$ mol L^{-1}

$[NO] = 2x = 2 \times 0.000632 = 0.001264$ mol L^{-1}

34. (i) (a) Differential rate equation of reaction is

$$\frac{dx}{dt} = k[A]^1[B]^2 = k[A][B]^2$$

When conc. of B is tripled, it means conc. of B becomes $[3 \times B]$

$\therefore$ New rate of reaction, $\dfrac{dx'}{dt} = k[A][3B]^2$

$$= 9k[A][B]^2 = 9\left(\frac{dx}{dt}\right)$$

i.e., the rate of reaction will become 9 times.

(i) When conc. of A is doubled and that of B is also doubled, then conc. of A becomes $[2A]$ and that of B becomes $[2B]$.

$\therefore$ Now rate of reaction, $\dfrac{dx'}{dt} = k[2A][2B]^2$

$= 8k\,[A][B]^2$

i.e., the rate of reaction will become 8 times.

(ii) Molecularity of a reaction is the number of reacting particles which collide simultaneously to bring about the chemical change. It is a theoretical concept.

35. (i) Rate $= -\dfrac{1}{2}\dfrac{d[B]}{dt} = \dfrac{1}{2} \times 1 \times 10^{-2}$

$= 0.5 \times 10^{-2}$ mol/L/s.

(ii) $\text{Rate} = \dfrac{-d[A]}{dt} = \dfrac{-1}{2}\dfrac{d[B]}{dt} = +\dfrac{1}{3}\dfrac{d[C]}{dt}$

Rate of change in concentration of A,

$$= \frac{-d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

$= 0.5 \times 10^{-2}$ mol/L/s.

Rate of change in concentration of C,

$$= +\frac{d[C]}{dt} = -\frac{3}{2}\frac{d[B]}{dt} = \frac{3}{2} \times 10^{-2}$$

$= 1.5 \times 10^{-2}$ mol/L/s.

36. (i) Let rate law for the disappearance of N_2O_5 is

Rate = $k[N_2O_5]^a$

$$\text{Then } \frac{r_1}{r_2} = \frac{34 \times 10^{-5}}{25 \times 10^{-5}} = \frac{k\,(1.13 \times 10^{-2})^a}{k(0.84 \times 10^{-2})^a}$$

$$\text{or, } \frac{34}{25} = \left(\frac{113}{84}\right)^a \quad \text{or } a = 1$$

Thus, order of reaction = 1

(ii) $r = k[N_2O_5]$ or, $34 \times 10^{-5} = k \times 1.13 \times 10^{-2}$

$$\text{or,} \quad k = \frac{34 \times 10^{-5}}{1.13 \times 10^{-2}} = 3.0 \times 10^{-2}\ \text{min}^{-1}$$

(iii) Rate law = $k[N_2O_5]$

37. The reaction is

$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

Here : $k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

The order of reaction is 0 *i.e.*,

Rate = k [Reactant]^0

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

$$\text{Rate of reaction} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt}$$

The rate of formation of $N_2 = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

$$\text{Again, } 2.5 \times 10^{-4} = \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\therefore \quad \frac{d[H_2]}{dt} = 7.5 \times 10^{-4} \text{ mol L}^{-1}\text{ s}^{-1}$$

Therefore, rate of formation of H_2

$= 7.5 \times 10^{-4}$ mol L^{-1} s^{-1}

38. Suppose order with respect to A is m and with respect to B is n. Then the rate law will be

Rate = $k[A]^m[B]^n$

Substituting the value of experiments 1 to 4, we get

Expt. 1 : Rate = $6.0 \times 10^{-3} = k\,(0.1)^m\,(0.1)^n$ ...(i)

Expt. 2 : Rate = $7.2 \times 10^{-2} = k\,(0.3)^m\,(0.2)^n$ ...(ii)

Expt. 3 : Rate = $2.88 \times 10^{-1} = k\,(0.3)^m\,(0.4)^n$ ...(iii)

Expt. 4 : Rate = $2.4 \times 10^{-2} = k\,(0.4)^m\,(0.1)^n$ ...(iv)

Comparing equation (i) and equation (iv),

$$\therefore \quad \frac{(\text{Rate})_1}{(\text{Rate})_4} = \frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{k(0.1)^m\,(0.1)^n}{k(0.4)^m\,(0.1)^n}$$

$$\text{or, } \frac{1}{4} = \frac{(0.1)^m}{(0.4)^m} = \left(\frac{1}{4}\right)^m \quad \therefore m = 1$$

Comparing equation (ii) and equation (iii)

$$\frac{(\text{Rate})_2}{(\text{Rate})_3} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k(0.3)^m\,(0.2)^n}{k(0.3)^m\,(0.4)^n}$$

$$\text{or, } \left(\frac{1}{2}\right)^2 = \frac{(0.2)^n}{(0.4)^n} = \left(\frac{1}{2}\right)^n \quad \therefore n = 2$$

$\therefore$ Rate law expression is : Rate = $k[A][B]^2$

The rate constant can be calculated from the given data of any experiment using expression :

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

$$\text{From Expt. 1, } k = \frac{6.0 \times 10^{-3}}{0.1 \times (0.1)^2} = 6.0$$

$\therefore$ Rate constant $k = 6.0$ mol^{-2} L^2 min^{-1}

$$\text{Unit of } k,\ \frac{dx}{dt} = k[A]^1[B]^2 = 6.0[0.5][0.2]^2$$

$= 6 \times 5 \times 4 \times 10^{-3}$

$= 1.2 \times 10^{-1}$ mol L^{-1} min^{-1}

39. The time taken for half of the reaction to complete, *i.e.*, the time in which the concentration of a reactant is reduced to half of its original value Is called half-life period of the reaction.

$$t = t_{1/2} \text{ when } [R] = \frac{[R_0]}{2}$$

40. For a first order reaction, $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{x}$

For $\dfrac{3}{4}$th life period, $a = a$

$$a - x = a - \frac{3}{4}a = \frac{1}{4}a$$

$$\therefore \quad k = \frac{2.303}{y}\log\frac{a}{(a-x)}$$

$$\frac{0.693}{x} = \frac{2.303}{y}\log\frac{a}{a/4}$$

$$\frac{0.693}{x} = \frac{2.303}{y}2\log 2$$

$$\frac{0.693}{x} = \frac{0.693 \times 2}{y}$$

$y = 2x$

41. (i) The reaction is of zero order.

(ii) Slope of the straight line graph gives 'k'

$$= -k = \frac{d[R]}{dt}$$

42. *Refer to answer 39.*

(i) For zero order reaction rate constant is given by :

$$k = \frac{[R]_0 - [R]}{t}, \quad \text{At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$k = \frac{[R]_0 - \frac{[R]_0}{2}}{t_{1/2}} \Rightarrow k = \frac{[R]_0}{2t_{1/2}} \Rightarrow t_{1/2} = \frac{[R]_0}{2k}$$

In zero order reaction, $t_{1/2}$ is directly proportional to $[R]_0$.

(ii) For first order reaction,

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

$$\therefore k = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]_0/2} \quad \text{or, } t_{1/2} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} \Rightarrow t_{1/2} = \frac{0.693}{k}$$

In first order reaction, $t_{1/2}$ is independent of initial concentration.

43. For first order reaction, $t = \frac{2.303}{k}\log\frac{[R_0]}{[R_t]}$

For 99% completion of reaction

$t = t_{0.99}$, $[R]_0 = 1$, $[R]_t = (1 - 0.99) = 0.01 = 10^{-2}$

$$t_{0.99} = \frac{2.303}{k}\log\frac{1}{10^{-2}} = \frac{2.303}{k}\log 10^2 = \frac{2.303}{k}\times 2 \quad \text{...(i)}$$

For 90% completion of reaction

$t = t_{0.90}$, $[R]_0 = 1$, $[R]_t = (1-0.9) = 0.1 = 10^{-1}$

$$t_{0.90} = \frac{2.303}{k}\log\frac{1}{10^{-1}} = \frac{2.303}{k}\log 10 = \frac{2.303}{k} \quad \text{...(ii)}$$

Comparing equations (i) and (ii),

$t_{0.99} = 2 \times t_{0.90}$

44. The integrated rate equation for first order reaction is

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

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

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

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

$t_{3/4} = 546$ s

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

45. For a first order reaction,

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

Given $k = 2.4\times10^{-3}$ s^{-1}

$[R] = \frac{[R]_0}{4}$, $t = ?$

Substituting these values in the equation, we get

$$t = \frac{2.303}{2.4\times10^{-3}\text{ s}^{-1}}\log\frac{[R]_0}{[R]}$$

$$t = \frac{2.303}{2.4\times10^{-3}\text{ s}^{-1}}\log 4 = \frac{2.303}{2.4\times10^{-3}}\times 0.6021\text{ s}$$

$t = 577.7$ s $= 578$ s.

46. $a = 0.6$ mol/L, $(a - x) = 0.4$ mol/L

$t = 5$ min

$$k = \frac{2.303}{5\text{ min}}\log\frac{0.6}{0.4} = 0.0811\text{ min}^{-1}$$

47. *Refer to answer 42(ii).*

48. Here $t = 40$ min, $t_{1/2} = ?$

Let $a = 100$ ∴ $x = 30\%$ of $100 = 30$

Using the formula,

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

$$\Rightarrow\ 40 = \frac{2.303}{k}\log\frac{100}{100-30}$$

$$40 = \frac{2.303}{k}\log\frac{100}{70}$$

$$\Rightarrow\ 40 = \frac{2.303}{k}(\log 10 - \log 7)$$

$$40 = \frac{2.303}{k}(1 - 0.8451)$$

$$\Rightarrow 40 = \frac{2.303}{k}\times 0.1549 \Rightarrow k = \frac{0.357}{40} = 0.0089\text{ min}^{-1}$$

$$\therefore\ t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0089} = 77.86\text{ min.}$$

49. The given reaction is

$$\begin{array}{llll} & C_2H_5Cl_{(g)} & \longrightarrow C_2H_{4(g)} & +\ HCl_{(g)} \\ \text{At time } t = 0 & 0.30\text{ atm} & 0 & 0 \\ \text{At time } t = 300\text{ sec} & 0.30 - x & x & x \end{array}$$

Total pressure $= 0.30 - x + x + x = 0.50$

or $0.30 + x = 0.50$

∴ $x = 0.50 - 0.30 = 0.20$

∴ Initial pressure, $P_0 = 0.30$ atm

Pressure of C_2H_5Cl after 300 sec, $P_t = 0.30 - 0.20 = 0.10$ atm

Using formula for first order reaction,

$$k = \frac{2.303}{t}\log\frac{P_0}{P_t}$$

$$k = \frac{2.303}{300}\log\frac{0.30}{0.10}$$

$$k = \frac{2.303}{300}\log 3 = \frac{2.303\times0.4771}{300} = 3.66\times10^{-3}\text{ sec}^{-1}$$

50. $t_{50\%}$ or $t_{1/2} = 30$ minutes

$$\Rightarrow\ k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231\text{ min}^{-1}$$

$$t_{90\%} = \frac{2.303}{k}\log\frac{100}{100-90} = \frac{2.303}{0.0231}\log 10$$

$= 99.69$ minutes

51. For a first order reaction,

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

$$k = \frac{2.303}{10}\log\frac{100}{100-25}$$

$$k = \frac{2.303}{10}\times 0.124 = 0.02$$

$$\therefore \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.02} = 34.65\text{ min}$$

52. (i) The reaction is of 1st order.

(ii) For first order reaction

$\ln[R] = -kt + \ln[R]_0$

comparing *eqn.* $y = m \times x + c$

we get a straight line with slope = $-k$ and intercept equal to $\ln[R]_0$.

(iii) Unit of rate constant for first order reaction

$$\frac{\text{mol L}^{-1}}{\text{s}}\times\frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$$

53. $t = \dfrac{2.303}{k}\log\dfrac{[R]_0}{[R]}$

$\Rightarrow \; k = 60\,\text{s}^{-1},\ [R] = \dfrac{1}{10}[R]_0$

or, $[R]_0 = 10\,[R]$

$$t = \frac{2.303}{60}\log\frac{10[R]}{[R]} \Rightarrow t = \frac{2.303}{60}\log 10$$

$$\Rightarrow \; t = \frac{2.303\times 1}{60}$$

$t = 0.0384$ second

54. The given reaction is

$$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$

	$SO_2Cl_{2(g)}$	$SO_{2(g)}$	$Cl_{2(g)}$
At $t = 0$	0.4 atm	0	0
At time t	$(0.4 - x)$ atm	x atm	x atm

Total pressure at time t will be

$P_T = (0.4 - x) + x + x = 0.4 + x$

$x = (P_T - 0.4)$

Pressure of SO_2Cl_2 at time t will be

$p_{SO_2Cl_2} = 0.4 - x = 0.4 - (P_T - 0.4) = 0.8 - P_T$

At time $t = 100$ s, $P_T = 0.7$ atm

$\therefore \; p_{SO_2Cl_2} = 0.8 - 0.7 = 0.1$ atm

According to first order kinetic equation

$$k = \frac{2.303}{t}\log\frac{p_{SO_2Cl_2(\text{initial})}}{p_{SO_2Cl_2(\text{after reaction})}}$$

$$= \frac{2.303}{100}\log\left(\frac{0.4}{0.1}\right) = 1.3\times 10^{-2}\ \text{s}^{-1}$$

55. (i) $t = \dfrac{2.303}{k}\log\dfrac{[A]_0}{[A]}$

Given $k = 1.06\times 10^{-3}\ \text{min}^{-1}$, $\dfrac{[A]_0}{[A]} = \dfrac{100}{85}$

$$t = \frac{2.303}{1.06\times 10^{-3}\ \text{min}^{-1}}\log\frac{100}{85}$$

$$t = \frac{2303}{1.06}[2\log 10 - \log 85]\text{min}$$

$$t = \frac{2303}{1.06}[2\times 1 - 1.9294] = \frac{2303\times 0.0706}{1.06}$$

$t = 153.39$ min $= 153.4$ min.

(ii) Given $k = 1.06\times 10^{-3}\ \text{min}^{-1}$, $\dfrac{[A]_0}{[A]} = \dfrac{100}{15}$

$$t = \frac{2.303}{1.06\times 10^{-3}\ \text{min}^{-1}},\ \log\frac{100}{15}$$

$$= \frac{2303}{1.06}[2\log 10 - \log 15]\text{min}$$

$$= \frac{2303}{1.06}[2\times 1 - 1.1761] = \frac{2303\times 0.8231}{1.06}\text{min} = 1788\text{ min}$$

56. For the first order reaction,

Rate constant, $k = \dfrac{2.303}{100}\log\dfrac{a}{a-x}$

For 60% completion of the reaction, if $a = 100\%$

$a - x = 100 - 60 = 40\%$

Then, $k = \dfrac{2.303}{100}\log\dfrac{100}{40}$ ...(i)

For 90% completion of the reaction,

$a = 100\%$

and $a - x = 100 - 90 = 10\%$

Then, $k = \dfrac{2.303}{t}\log\dfrac{100}{10}$ ...(ii)

Substituting the value of k in eq. (ii),

we have, $\dfrac{2.303}{100}\log\dfrac{100}{40} = \dfrac{2.303}{t}$ $[\because \log 10 = 1]$

or $\dfrac{1}{t} = \dfrac{1}{100}\log\dfrac{100}{40}$

$$\frac{1}{t} = \frac{0.3979}{100}$$

$$t = \frac{100}{0.3979}$$

$t = 251$ min

57. Given reaction :

$$2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)}$$

Exp. No.	**Initial [NO] (M)**	**Initial [Cl_2] (M)**	**Initial rate of disapp. of Cl_2 (M/min)**
1.	0.15	0.15	0.60
2.	0.15	0.30	1.20
3.	0.30	0.15	2.40
4.	0.25	0.25	?

(i) Let rate of this reaction $r = k[\text{NO}]^m[\text{Cl}_2]^n$

then $\frac{r_1}{r_2} = \frac{0.60}{1.20} = \frac{k(0.15)^m(0.15)^n}{k(0.15)^m(0.30)^n}$

or $\frac{1}{2} = \left(\frac{1}{2}\right)^n \Rightarrow n = 1$

Again from $\frac{r_2}{r_3} = \frac{1.20}{2.40} = \frac{k(0.15)^m(0.30)^1}{k(0.30)^m(0.15)^1}$

or $\frac{1}{2} = \left(\frac{1}{2}\right)^m \cdot \frac{2}{1}$ or $\frac{1}{4} = \left(\frac{1}{2}\right)^m \Rightarrow m = 2$

Hence, expression for rate law is

$r = k[\text{NO}]^2\,[\text{Cl}_2]^1$

(ii) Substituting the values in experiment (1),

$0.60\ \text{M min}^{-1} = k(0.15\ \text{M})^2\ (0.15\ \text{M})^1$

or $k = \frac{0.60\ \text{M min}^{-1}}{0.0225 \times 0.15\ \text{M}^3} = 177.77\ \text{M}^{-2}\ \text{min}^{-1}$

(iii) $r = 177.7\ \text{M}^{-2}\ \text{min}^{-1} \times (0.25\ \text{M})^2\ (0.25\ \text{M})$

$= 2.77\ \text{M min}^{-1}$

58. $k = \frac{2.303}{20\,\text{min}} \log \frac{100}{100-15}$

$\frac{2.303}{20\,\text{min}} \log \frac{100}{100-15} = \frac{2.303 \times 0.0706}{20} \text{min}$

$t = \frac{2.303}{k} \log \frac{100}{100-60} = \frac{2.303 \times 20}{2.303 \times 0.0706} \log \frac{100}{40}$

$= \frac{20}{0.0706} \times 0.3979 = 112.7$ min

59. (i) When $t = 20$ min, $[R] = 0.289\ \text{mol L}^{-1}$

$[R]_0 = 0.400\ \text{mol L}^{-1}$

For a first order reaction,

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

$$\therefore\ k = \frac{2.303}{20} \log \frac{0.400}{0.289}$$

$$\Rightarrow k = \frac{2.303}{20} \log \frac{4.00}{2.89}$$

$$\Rightarrow k = \frac{2.303}{20} [\log 4.00 - \log 2.89]$$

$$\Rightarrow k = \frac{2.303}{20} [0.6021 - 0.4609]$$

$$\Rightarrow k = \frac{2.303}{20} \times 0.1412$$

$\Rightarrow k = 2.303 \times 0.00706$

$\Rightarrow k = 1.626 \times 10^{-2}\ \text{min}^{-1}$

(ii) $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

Here, $[R]_0 = 0.400\ \text{mol L}^{-1}$, $t = 100$ min,
$k = 1.626 \times 10^{-2}\ \text{min}^{-1}$, $[R] = ?$

$$\therefore\ 100 = \frac{2.303}{1.626 \times 10^{-2}} \log \frac{0.400}{[R]}$$

$$\frac{100 \times 1.626 \times 10^{-2}}{2.303} = \log \frac{0.4}{[R]}$$

$$0.7060 = \log \frac{0.4}{[R]}$$

or Antilog $(0.7060) = \frac{0.4}{[R]}$

$$5.082 = \frac{0.4}{[R]} \Rightarrow [R] = \frac{0.4}{5.082} = 0.079\ \text{M}$$

(iii) Initial rate, *i.e.*, rate of reaction when $t = 0$

When $t = 0.00$ min, $[R] = 0.400\ \text{mol L}^{-1}$

Also, $k = 1.626 \times 10^{-2}\ \text{min}^{-1}$

$\therefore$ Initial rate $= k[R]$

$= 1.626 \times 10^{-2}\ \text{min}^{-1} \times 0.400\ \text{mol L}^{-1}$

$= 6.504 \times 10^{-3}\ \text{mol L}^{-1}\ \text{min}^{-1}$

60. (i) *Refer answer 59(i).*

(ii) *Refer answer 59(iii).*

(iii) $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

Here, $k = 1.6259 \times 10^{-2}\ \text{min}^{-1}$, $[R]_0 = 0.400$ M,
$[R] = 0.350$ M

Substituting these values in the equation, we get

$$t = \frac{2.303}{1.6259 \times 10^{-2}} \log \frac{0.400}{0.350}$$

$$= \frac{2.303}{1.6259 \times 10^{-2}} [\log 40 - \log 35]$$

$= 141.583\ [1.6021 - 1.5441] = 141.583 \times 0.0580$

$= 8.21$ min

61. Given : $k = 5.10 \times 10^{-3}\ \text{min}^{-1}$,
$t = 3 \times 60\ \text{min} = 180\ \text{min}$
$[R]_0 = 0.1\ \text{M}$
Substituting these values in the equation

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

We get, $$180\,\text{min} = \frac{2.303}{5.1\times 10^{-3}\ \text{min}^{-1}}\log\frac{0.1}{[R]}$$

$$\log\frac{0.1}{[R]} = \frac{180\,\text{min}\times 5.1\times 10^{-3}\ \text{min}^{-1}}{2.303} = 0.398$$

$$\frac{0.1}{[R]} = \text{Antilog } 0.398 = 2.50$$

$[R] = 0.1/2.5 = 0.04\ \text{M}$

62. (i) $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{10} = 0.0693$

(ii) $N = N_0\left(\dfrac{1}{2}\right)^n$

where, $n = \dfrac{\text{Total time}}{t_{1/2}} = \dfrac{60}{10} = 6$

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^6 = \frac{1}{64} \qquad \text{...(1)}$$

[where N_0 = initial amount of reactant and N = amount of reactant left after time, t].

63. 20% decomposition means that x = 20% of $a = 0.20\,a$

For first order reaction, $k = \dfrac{2.303}{t}\log\dfrac{a}{a-x}$

$$= \frac{2.303}{15}\log\frac{a}{a-0.20a} = \frac{2.303}{15}\log\frac{a}{0.80a}$$

$$= \frac{2.303}{15}\log 1.25$$

$$= \frac{2.303}{15}\times 0.0969 = 0.0148\,\text{min}^{-1}$$

64. Here $t_{1/2} = 5\times 10^4$ s and t = 2 hours
= 2 × 60 × 60 = 7200 s

$$k = \frac{0.693}{t_{1/2}} \text{ and } k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$$\therefore \quad \frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$$\frac{0.693}{5\times 10^4} = \frac{2.303}{7200}\log\frac{[A]_0}{[A]}$$

$$\therefore \quad \log\frac{[A]_0}{[A]} = \frac{0.693}{5\times 10^4}\times\frac{7200}{2.303} = \frac{4989.6}{11.515\times 10^4}$$

$$= \frac{4989.6}{115150} = 0.0433$$

$$\frac{[A]_0}{[A]} = \text{antilog } 0.0433 = 1.105$$

$$\Rightarrow \frac{[A]}{[A_0]} = \frac{1}{1.105}\times 100 = 90.49\%$$

65. For the first order reaction :

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

Let $[A]_0 = x$
then $[A] = x - 20\%$ of $x = x - 0.20\,x = 0.80\,x$

$$\therefore \quad k = \frac{2.303}{5}\log\frac{x}{0.80x}$$

$$k = \frac{2.303}{5}\log 1.25 \qquad \text{...(i)}$$

In second case, let $[A]_0 = x$ then
$[A] = x - 60\%$ of $x = x - 0.60\,x = 0.40\,x$

$$\therefore \quad k = \frac{2.303}{t}\log\frac{x}{0.40x}$$

$$k = \frac{2.303}{t}\log 2.5 \qquad \text{...(ii)}$$

From (i) and (ii), we have

$$\frac{2.303}{t}\log 2.5 = \frac{2.303}{5}\log 1.25$$

$$\frac{\log 2.5}{t} = \frac{\log 1.25}{5} \Rightarrow t = \frac{5\times\log 2.5}{\log 1.25}$$

$$\therefore \quad t = \frac{5\times 0.3979}{0.0969} = 20.53\text{ minutes}$$

66. Radioactive decay follows first order kinetics.
Let $[A]_0 = 100$
$\therefore \quad [A] = 100 \times 80\% = 80$

Decay constant $(k) = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{5730}$

$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]} = \frac{2.303}{0.693/5730}\log\frac{100}{80}$$

$$= \frac{2.303\times 5730}{0.693}\times\log 1.25 = \frac{2.303\times 5730}{0.693}\times 0.0969$$

$$= \frac{1278.7108}{0.693} = 1845.18 \approx 1845\,\text{years}$$

67. A reaction of second order which obeys the first order rate law is known as pseudo first order reaction.

e.g., Inversion of cane sugar :

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Rate = $k[C_{12}H_{22}O_{11}]^1[H_2O]^0$

68. (i) Average rate of reaction between the time interval 30 to 60 seconds is

$$r_{av} = \frac{-[0.17-0.31]}{60-30} = \frac{0.14}{30}$$

$= 4.67 \times 10^{-3}\ s^{-1}$ [Taking only difference]

(ii) $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$

At $t = 30$ s,

$$k = \frac{2.303}{30}\log\frac{0.55}{0.31} = \frac{2.303}{30}\times 0.249 = 1.91\times 10^{-2}\,s^{-1}$$

At $t = 60$ s,

$$k = \frac{2.303}{60}\log\frac{0.55}{0.17} = \frac{2.303}{90}\times 0.5099 = 1.96\times 10^{-2}\,s^{-1}$$

At $t = 90$ s

$$k = \frac{2.303}{90}\log\frac{0.55}{0.085}$$

$$k = \frac{2.303}{90}\times 0.8109 = 2.07\times 10^{-2}\,s^{-1}$$

$\therefore$ Average value of k

$$= \frac{1.91\times 10^{-2} + 1.96\times 10^{-2} + 2.07\times 10^{-2}}{3} = 1.98\times 10^{-2} s^{-1}$$

69. (i) For a first order reaction,

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

When $t = 30$ s

$$k = \frac{2.303}{30}\log\frac{0.60}{0.30} = \frac{2.303}{30}\times 0.3010 = 0.0231\ s^{-1}$$

When $t = 60$ s

$$k = \frac{2.303}{60}\log\frac{0.60}{0.15} = \frac{2.303}{60}\times 0.602 = 0.0231\ s^{-1}$$

As the value of k is constant at different time intervals, the reaction is first order w.r.t. ester when $[H_2O]$ is constant. Hence, it is pseudo first order reaction.

(ii) Average rate $= -\frac{C_2 - C_1}{t_2 - t_1} = \frac{-(0.15-0.30)}{60-30}$

$$= \frac{0.15}{30} = 5\times 10^{-3}\ \text{mol L}^{-1}\text{s}^{-1}$$

70. The minimum extra energy which must be supplied to the reactants to enable them to cross over the potential energy barrier between reactants and products is called activation energy. It is denoted by E_a.

$E_a = E_T - E_R$

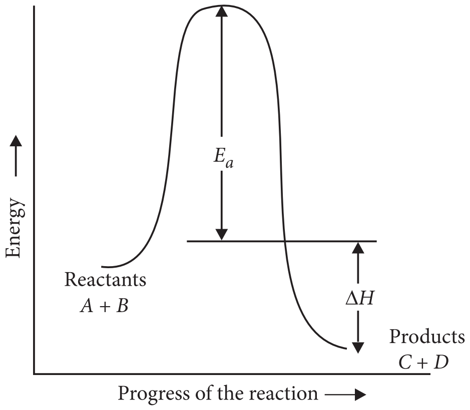
71. The rate constant is nearly doubled with a rise in temperature by 10° for a chemical reaction.

The temperature effect on the rate constant can be represented quantitatively by Arrherius equation :

$k = Ae^{-E_a/RT}$

where $k \rightarrow$ Rate constant
$A \rightarrow$ Arrhenius factor
$R \rightarrow$ Gas constant
$T \rightarrow$ Temperature
$E_a \rightarrow$ Energy of activation for the reaction.

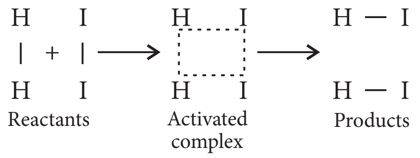
72. The energy required to form activated complex is called activation energy. It is the difference between the threshold energy and the average energy possessed by the reacting molecules.



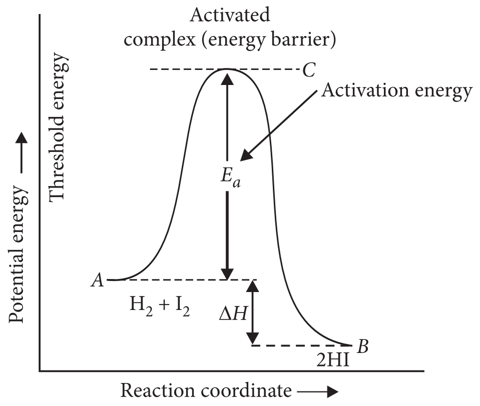
Activation energy (E_a) = Threshold energy – Average energy possessed by reacting molecules.

73. When the colliding molecules possess the kinetic energy equal to E_a, the atomic configuration of species formed at this stage is different from the reactant as well as the products. This stage is called the activated state and the specific configuration bearing state is called activated complex.

For example, in the reaction between $H_{2(g)}$ and $I_{2(g)}$, activated complex has configuration in which H—H and I—I bonds are breaking and H—I bonds, are forming as shown below.



Potential energy diagram of this reaction is shown below :



74. Here $k_2 = 2k_1$, $T_1 = 298$ K, $T_2 = 308$ K

$E_a = ?$

$$\therefore \quad \log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{2k_1}{k_1} = \frac{E_a}{2.303R}\left[\frac{308-298}{308\times298}\right]$$

$$\log 2 = \frac{E_a}{2.303R}\left[\frac{10}{91784}\right]$$

$$0.3010 = \frac{1.089\times10^{-4}E_a}{2.303\times8.314}$$

$$E_a = \frac{0.3010\times2.303\times8.314}{1.089\times10^{-4}} = 52922.77\,\text{J mol}^{-1}$$

75. (i) Order of a reaction : *Refer to answer 10.*

(ii) Activation energy of a reaction : *Refer to answer 70.*

76. For first order reaction, $t_{1/2} = \dfrac{0.693}{k}$

$$t_{1/2} = 200\,\text{min} = 200\times60 = 12000\text{ s}$$

$$\Rightarrow \quad k = \frac{0.693}{12000\text{ s}} = 5.8\times10^{-5}\,\text{s}^{-1}$$

Also, for first order decomposition of H_2O_2, rate constant is

$$\log k = 14.2 - \frac{1.0\times10^4}{T}\text{K}$$

Comparing the above equation with the Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\Rightarrow \quad E_a = 2.303\times8.314\times1.0\times10^4 = 1.91\times10^5\text{ J mol}^{-1}$$

77. Given, $T_1 = 300$ K, $T_2 = 310$ K

$k_1 = 2\times10^{-2}$, $k_2 = 4\times10^{-2}$, $E_a = ?$

Using Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\text{or} \quad \log\frac{4\times10^{-2}}{2\times10^{-2}} = \frac{E_a}{2.303\times8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$$

$$\text{or} \quad \log 2 = \frac{E_a}{2.303\times8.314}\times\left[\frac{310-300}{310\times300}\right]$$

$$\text{or} \quad E_a = \frac{0.301\times2.303\times8.314\times310\times300}{10}$$

$$= 53598\text{ J mol}^{-1} = 53.598\text{ kJ mol}^{-1}$$

78. $k_1 = 0.02\text{ s}^{-1}$, $k_2 = 0.07\text{ s}^{-1}$

$T_1 = 500$ K, $T_2 = 700$ K

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_2T_1}\right]$$

$$\log\frac{0.07}{0.02} = \frac{E_a}{2.303R}\left[\frac{700-500}{700\times500}\right]$$

$$E_a = \frac{0.544\times2.303\times8.314\times700\times500}{200}$$

$$= 18228.07\text{ J mol}^{-1}$$

79. $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$E_a = \left(\frac{2.303\times R\times T_1\times T_2}{T_2 - T_1}\right)\log\frac{k_2}{k_1}$$

$$E_a = \frac{2.303\times8.314\,\text{J mol}^{-1}\,\text{K}^{-1}\times650\,\text{K}\times700\,\text{K}}{700\,\text{K} - 650\,\text{K}} \times\log\frac{2.39\times10^{-8}}{2.15\times10^{-8}}$$

$$E_a = \frac{19.147\times650\times700}{50}(\log 23.9 - \log 2.15)\text{ J mol}^{-1}$$

$= 174237.7\ (1.3783 - 0.3324)$ J mol^{-1}

$= 174237.7 \times 1.0459$ J mol^{-1}

$= 1822235.2$ J mol^{-1} $= 182.24$ kJ mol^{-1}

80. Given : Slope, $m = -4250$ K,

$R = 8.314$ J K^{-1} mol^{-1}

$E_a = ?$

Using formula,

$$\log k = \log A - \frac{E_a}{2.303\,R}\left(\frac{1}{T}\right)$$

Comparing with $y = mx + c$ [straight line equation]

$$-\frac{E_a}{2.303\,R} = \frac{-\,4250}{1}$$

$E_a = 2.303 \times 8.314 \text{ J K}^{-1}\text{ mol}^{-1} \times 4250 \text{ K}$

$= 81{,}375.35 \text{ J mol}^{-1} = 81.37 \text{ kJ mol}^{-1}$

81. Since the rate of a reaction quadruples when temperature changes from 293 K to 313 K.

$\therefore\quad k_2 = 4k_1$

$T_1 = 293$ K and $T_2 = 313$ K

According to Arrhenius equation

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Putting the values

$$\log\frac{4k_1}{k_1} = \frac{E_a}{2.303 \times 8.314 \text{ J K}^{-1}\text{ mol}^{-1}}\left[\frac{(313 - 293)\text{K}}{293\text{K} \times 313\text{ K}}\right]$$

$$0.6021 = \frac{E_a \times 20}{2.303 \times 8.314 \text{ JK}^{-1}\text{ mol}^{-1} \times 293 \text{ K} \times 313 \text{ K}}$$

$$\therefore\quad E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20} \text{ J mol}^{-1}$$

$= 52863.3 \text{ J mol}^{-1} = 52.86 \text{ kJ mol}^{-1}$

82. $k_1 = 4.5 \times 10^3 \text{ s}^{-1}, T_1 = 10 + 273 \text{ K}, k_2 = 1.5 \times 10^4 \text{ s}^{-1}$

$T_2 = ?\ E_a = 60 \text{ kJ mol}^{-1}$

From Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\text{or} \log\frac{1.5\times10^4}{4.5\times10^3} = \frac{60000 \text{ J mol}^{-1}}{2.303\times8.314 \text{ JK}^{-1}\text{ mol}^{-1}}\left[\frac{T_2 - 283}{283T_2}\right]$$

$$\text{or } \log 3.333 = 3133.63\left[\frac{T_2 - 283}{283T_2}\right]$$

$$\text{or}\quad \frac{0.5228}{3133.63} = \frac{T_2 - 283}{283T_2}$$

or $\quad 0.0472T_2 = T_2 - 283$ or $0.9528T_2 = 283$

$$\text{or}\quad T_2 = \frac{283}{0.9528} = 297\text{K} \text{ or } (297 - 273)°\text{C} = 24°\text{C}$$

83. $T_1 = 295$ K, $k_1 = k$ (say)

$T_2 = 305$ K, $k_2 = 2k$, $E_a = ?$

Using Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{2k}{k} = \frac{E_a}{2.303 \times 8.314} \times \frac{305 - 295}{295 \times 305}$$

$$E_a = \frac{2.303 \times 8.314 \times 295 \times 305 \times \log 2}{10}$$

$$= \frac{2.303 \times 8.314 \times 295 \times 305 \times 0.3010}{10}$$

$= 51855.2 \text{ J mol}^{-1}$

84. $k_1 = 6.0 \times 10^{-4} \text{ s}^{-1}, T_1 = 300 \text{ K}, E_a = 3.05 \times 10^5 \text{ J mol}^{-1}$

$k_2 = ?$, $T_2 = 310$ K

Using Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\text{or, } \log\frac{k_2}{k_1} = \frac{3.05 \times 10^5 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1}\text{ mol}^{-1}} \times \left[\frac{310 - 300}{300 \times 310}\right]$$

$$\log\frac{k_2}{k_1} = \frac{3.05\times10^5 \text{ J mol}^{-1} \times 10 \text{ K}}{1780684.2 \text{ JK}^{-1}\text{mol}^{-1}}$$

$$\log\frac{k_2}{k_1} = 1.71 \Rightarrow \frac{k_2}{k_1} = \text{antilog}(1.71)$$

$$\frac{k_2}{6\times10^{-4}} = 51.28$$

$k_2 = 3.07 \times 10^{-2} \text{ s}^{-1}$

85. Here $T_1 = 600$ K, $T_2 = 700$ K

$E_a = 209 \text{ kJ/mol} = 209000 \text{ J mol}^{-1}$

$k_1 = 1.6 \times 10^{-5} \text{ s}^{-1}$

Using formula,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log k_2 - \log k_1 = \frac{209000}{2.303 \times 8.314}\left[\frac{700 - 600}{700 \times 600}\right]$$

$\log k_2 - \log(1.60 \times 10^{-5}) = 2.598$

$\log k_2 = 2.598 + \log(1.6 \times 10^{-5})$

$\log k_2 = -\,4.796 + 2.598 = -\,2.198$

$k_2 = \text{Antilog}(-\,2.198)$

or, $\ k_2 = 6.34 \times 10^{-3} \text{ s}^{-1}$

86. (i) *Refer to answer 72.*

(ii) *Refer to answer 83.*

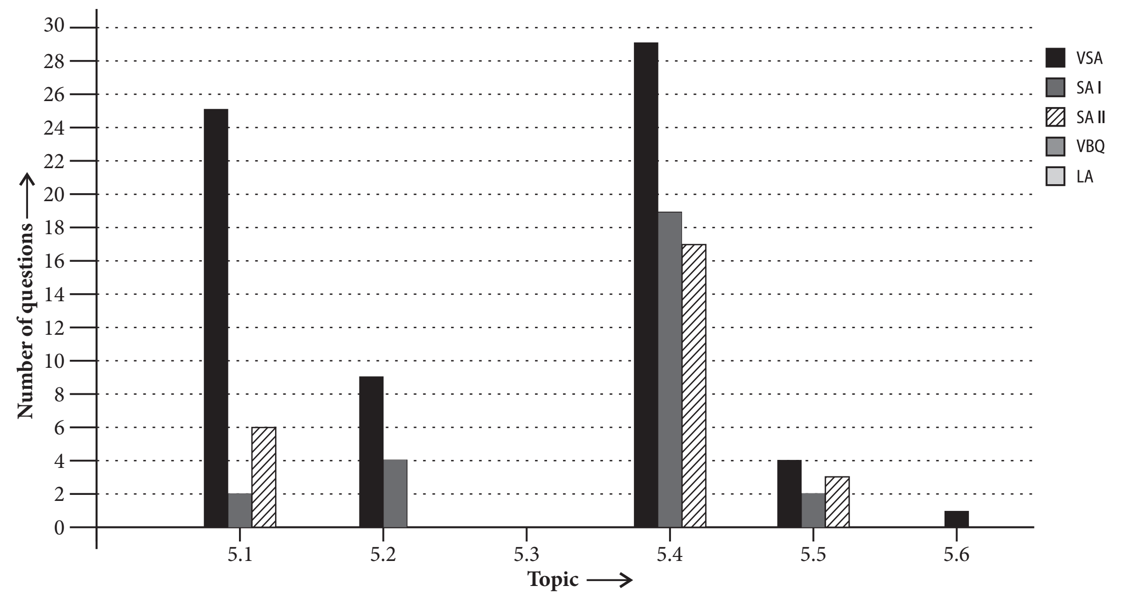
87. It is due to improper orientation. Energy more than threshold energy and proper orientation are the two main factors which are responsible for a reaction to occur.

05

Surface Chemistry

5.1 Adsorption
5.2 Catalysis
5.3 Colloids
5.4 Classification of Colloids
5.5 Emulsions
5.6 Colloids Around Us

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



- Maximum total weightage is of *Classification of Colloids.*
- Maximum VSA type questions were asked from *Classification of Colloids.*
- Maximum SA I and SA II type questions were asked from *Classification of Colloids.*

QUICK RECAP

- **Surface chemistry :** It deals with phenomena that occur at the surfaces or interfaces.
- **Adsorption :** It is the process of accumulation of molecular species at the surface rather than in the bulk of a solid or liquid.
- **Adsorbate :** The molecular species or substance, which concentrates or accumulates at the surface.
- **Adsorbent :** The material on the surface of which the adsorption takes place.

- **Desorption :** The process of removing an adsorbed substance from the surface.
- **Sorption :** The term used when both absorption and adsorption occur simultaneously.

Distinction between adsorption and absorption

Adsorption	Absorption
It is a surface phenomenon, *i.e.*, it occurs only at the surface of the adsorbent.	It is a bulk phenomenon, *i.e.*, occurs throughout the body of the material.
In this phenomenon, the concentration on the surface of adsorbent is different from that in the bulk.	In this phenomenon, the concentration is same throughout the material.
Its rate is high in the beginning and then decreases till equilibrium is attained.	Its rate remains same throughout the process.

- ΔG, ΔH and ΔS all are – ve for adsorption.
- **Types of adsorption :** Depending on forces which hold the adsorbate on the surface of adsorbent, adsorption is divided into two classes :
  - **Physical adsorption :** When the particles are held to the surface by the physical forces like van der Waals forces, the adsorption is called *physical adsorption* or *physisorption*.
  - **Chemical adsorption :** When the particles are held to the surface by the chemical forces or by chemical bonds, the adsorption is called *chemical adsorption* or *chemisorption*.

Differences between Physisorption and Chemisorption

Property	Physisorption	Chemisorption
Enthalpy	Low enthalpy, is the order of 20-40 kJ mol^{-1}	High enthalpy, is the order of 80-240 kJ mol^{-1}
Reversibility	Reversible process	Irreversible process
Effect of temperature	With the increase in temperature, extent of adsorption decreases because adsorption is a exothermic process and kinetic energy of gas molecules increases with temperature.	Chemisorption first increases with temperature upto a certain extent and then decreases. A gas adsorbed at low temperature by physical adsorption may change into chemisorption at high temperature.
Selectivity	Not selective in nature. Does not depend upon the nature or chemical properties of gas and adsorbent.	Highly selective in nature. Depends upon the nature of gas and adsorbent.
Nature and state of adsorbate	The extent of adsorption depends upon the ease of liquefaction of the gas.	The state of adsorbed molecules may be different from that in the bulk.
Activation energy	No appreciable energy needed.	High activation energy needed.
Pressure	Increase in pressure increases adsorption.	Increase in pressure decreases adsorption.
Layers	Multimolecular layer.	Mono-molecular layer.

- **Factors affecting adsorption of gases on solids :**
  - **Nature of adsorbent :** Greater are the strained forces on the surface, more is the ease with which adsorption takes place on the surface. The activated adsorbents have high adsorbing power.
  - **Surface area of adsorbent :** Greater the surface area, more is the adsorption.
  - **Nature of gas being adsorbed :** Easily liquefiable gases like NH_3, HCl, Cl_2, SO_2, CO_2, etc. (whose critical temperature is high) are adsorbed to greater extent.

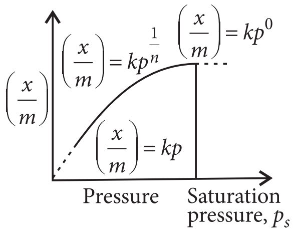
- **Pressure :** Adsorption increases with increase in pressure. The effect of pressure is large at low temperature.
- **Temperature :** Since adsorption is an exothermic process so according to Le-Chatelier's principle adsorption decreases with increase in temperature.

Freundlich adsorption isotherm : The plot of $\frac{x}{m}$ *vs* pressure at constant temperature is called *Freundlich adsorption isotherm*,
where, m = mass of the adsorbent x = mass of the adsorbate

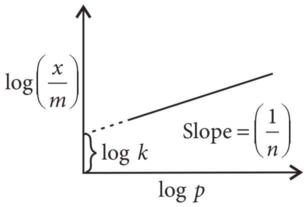
For low pressure, $\frac{x}{m} \propto p$

For high pressure, $\frac{x}{m} \propto p^0$

For intermediate pressures, $\frac{x}{m} \propto p^{1/n}$ $(n > 1)$



$$\log\frac{x}{m} = \log k + \frac{1}{n}\log p$$



Similarly, for adsorption of solutes from solutions, $\frac{x}{m} = k.C^{1/n}$ where, C is the equilibrium concentration, *i.e.*, when adsorption is complete.

Plot of $\log\frac{x}{m}$ *vs* log C is linear.

Promoters : The substances that enhance the activity of a catalyst *e.g.*, Mo acts as a promoter in Haber's process.

Poisons : The substances that decrease the activity of a catalyst.

- **Activity :** It is the capacity of a catalyst to increase the speed of the chemical reaction.
- **Selectivity :** It is the ability of a catalyst to direct a reaction to yield a particular product.

Catalysis : Substances which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as *catalysts*, and the phenomenon is known as *catalysis* :

Homogeneous Catalysis

The process in which the reactants and the catalyst are in the same phase.
e.g., oxidation of SO_2 to SO_3 by NO as catalyst (lead chamber process), hydrolysis of methyl acetate by HCl, hydrolysis of sugar by H_2SO_4.

Shape-selective Catalysis

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules. *e.g.*, Zeolites (have honey–comb like structures).

Heterogeneous Catalysis

The process in which the reactants and the catalyst are in different phases. *e.g.*, oxidation of SO_2 to SO_3 by Pt, manufacture of NH_3 from N_2 and H_2 by Fe (Haber's process), oxidation of NH_3 to NO by Pt (Ostwald's process), hydrogenation of vegetable oils by Ni.

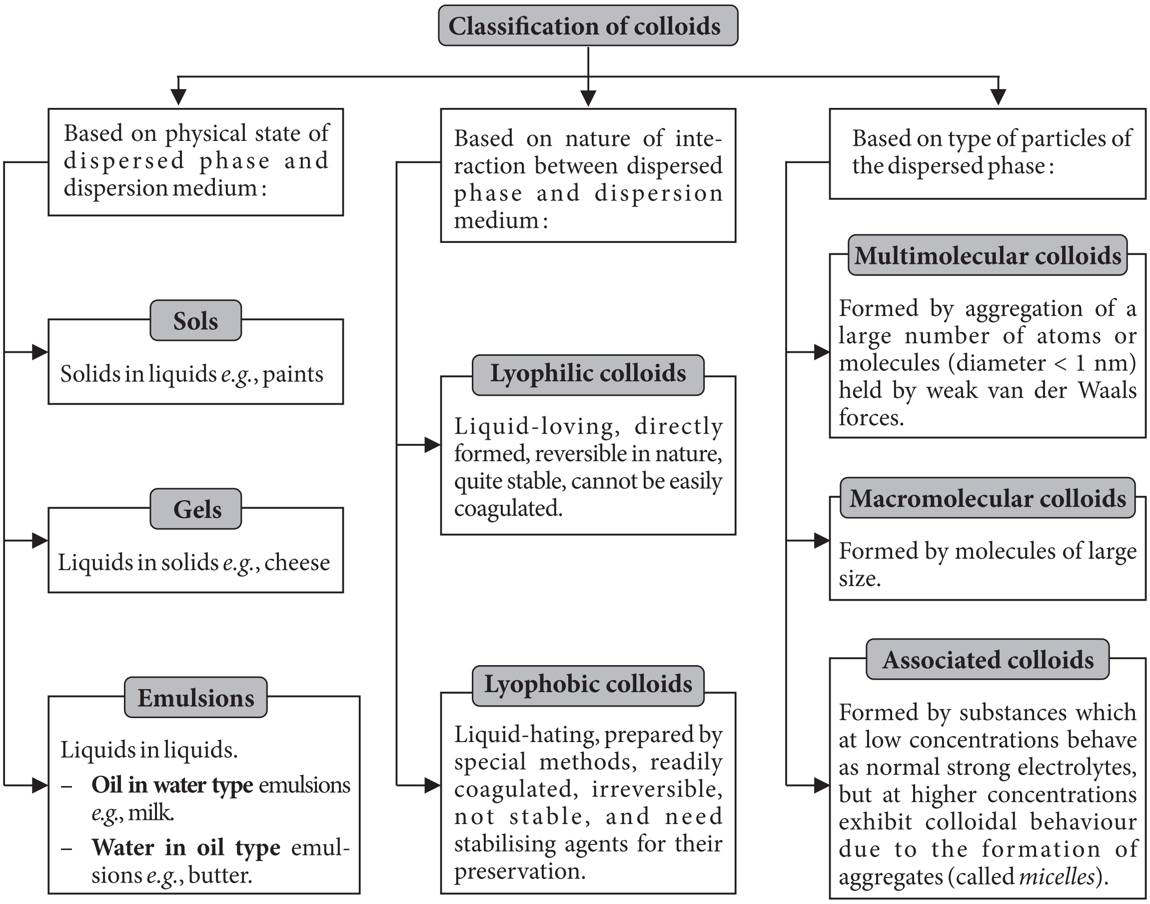
Enzyme Catalysis

Many biochemical reactions are catalysed by complex nitrogeneous organic compounds (proteins or enzymes) which are also called *biochemical catalysts* and the phenomenon is known as *biochemical catalysis*.

Some Enzymatic Reactions

	Enzyme	Source	Enzymatic reaction
1.	Invertase	Yeast	Sucrose → glucose and fructose
2.	Zymase	Yeast	Glucose → ethyl alcohol and carbon dioxide
3.	Diastase	Malt	Starch → maltose
4.	Maltase	Yeast	Maltose → glucose
5.	Urease	Soyabean	Urea → ammonia and carbon dioxide
6.	Pepsin	Stomach	Proteins → Amino acids

A colloid is a heterogeneous system in which one substance (dispersed phase) is dispersed as very fine particles in another substance called *dispersion medium*. The range of diameters of colloidal particles is between 1 and 1000 nm (10^{-9} to 10^{-6} m).



Classification of colloids

Based on physical state of dispersed phase and dispersion medium :

Sols
Solids in liquids *e.g.*, paints

Gels
Liquids in solids *e.g.*, cheese

Emulsions
Liquids in liquids.
- **Oil in water type** emulsions *e.g.*, milk.
- **Water in oil type** emulsions *e.g.*, butter.

Based on nature of interaction between dispersed phase and dispersion medium :

Lyophilic colloids
Liquid-loving, directly formed, reversible in nature, quite stable, cannot be easily coagulated.

Lyophobic colloids
Liquid-hating, prepared by special methods, readily coagulated, irreversible, not stable, and need stabilising agents for their preservation.

Based on type of particles of the dispersed phase :

Multimolecular colloids
Formed by aggregation of a large number of atoms or molecules (diameter < 1 nm) held by weak van der Waals forces.

Macromolecular colloids
Formed by molecules of large size.

Associated colloids
Formed by substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates (called *micelles*).

Properties of colloidal solutions :

- **Colligative properties :** Colloids show colligative properties like relative lowering of vapour pressure, elevation of boiling point, etc. and magnitude of colligative properties of colloids is much less than true solutions due to larger size of colloidal particles.
- **Tyndall effect (Optical property) :** Scattering of light by colloidal particles due to which the path of light beam becomes visible.
- **Brownian movement (Mechanical property) :** Zig zag movement of colloidal particles due to the unbalanced bombardment by the molecules of dispersion medium.

- **Charge on colloidal particles :** Colloidal particles always carry an electric charge and nature of charge (+ve or –ve) is same on all the particles in a given colloidal solution. The charge is due to preferential adsorption of ions from solution.

Positively charged sols	Negatively charged sols
Hydrated metallic oxides. *e.g.*, $Al_2O_3 \cdot xH_2O$, $Fe_2O_3 \cdot xH_2O$, metal hydroxides, $Fe(OH)_3$, $Al(OH)_3$, basic dye stuff like Prussian blue, haemoglobin (blood).	Metallic particles. *e.g.*, Cu, Ag, Au Metal sulphides - *e.g.* As_2S_3, CdS, Acidic dyes like eosin, congo red etc, sols of gelatin, gum, starch, etc.

- **Electrophoresis (Electrical property) :** Movement of colloidal particles towards one of the electrodes on passage of electricity through colloidal solution. The direction depends on the type of charge on colloidal particles.
- **Coagulation of colloids :** Precipitation of colloidal solution by induced aggregation of colloidal particles.
  - **Lyophobic sols:** They can be coagulated by electrophoresis, boiling, persistent dialysis, mixing of oppositely charged sols and addition of electrolytes.
  - **Hardy–Schulze rules :**
    - In case of electrolytes, the ion carrying charge opposite to that of colloidal particles is effective in causing coagulation and greater the valency of the ion causing coagulation, greater is the coagulating power.
    - The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called *coagulating value*. The smaller the quantity needed, the higher will be the coagulating power of an ion.
  - **Lyophilic sols :** They can be coagulated by addition of electrolytes and addition of a suitable solvent.

Emulsions : Colloids in which both dispersed phase and dispersion medium are in liquid state.

- **Types of emulsions :**
  - **Oil in water :** Dispersed phase is oil, *e.g.*, milk, body lotion.
  - **Water in oil :** D ispersed phase is water, *e.g.*, butter, cold cream.
- **Emulsification :** Process of making an emulsion.
- **Emulsifying agent :** Used to stabilize the emulsion *e.g.*, soaps and detergents.
- **Demulsification :** Separating the two components of an emulsion. Methods used are boiling, freezing, changing pH.

Previous Years' CBSE Board Questions

5.1 Adsorption

VSA (1 mark)

1. Differentiate between adsorption and absorption. *(1/3, Delhi 2016)*
2. Physisorption is reversible while chemisorption is irreversible. Why ? *(Foreign 2015)*
3. Define the following term :
   Adsorption
   (1/3 Delhi 2015C, 2014C, 1/2, AI 2013)
4. In reference to Freundlich adsorption isotherm write the expression for adsorption of gases on solids in the form of an equation. *(1/3, Delhi 2014)*
5. What is the effect of temperature on chemisorption? *(AI 2014)*
6. Why is adsorption always exothermic? *(AI 2014, 2009C)*
7. What type of forces are responsible for the occurrence of physisorption? *(1/3, Foreign 2014)*
8. Write the expression for the Freundlich adsorption isotherm for the adsorption of gases on solids, in the form of an equation. *(1/3, Foreign 2014)*
9. Define the following term :
   Sorption *(1/3, Delhi 2014C)*
10. Of physisorption or chemisorption, which has a higher enthalpy of adsorption? *(AI 2013, 2008)*
11. Out of NH_3 and CO_2, which gas will be adsorbed more readily on the surface of activated charcoal and why? *(Delhi 2012C)*
12. Adsorption of a gas on surface of solid is generally accompanied by a decrease in entropy, still it is a spontaneous process. Explain. *(1/3, Delhi 2012C)*
13. Write two applications of adsorption. *(AI 2012C)*
14. Physisorption is multi-layered, while chemisorption is mono-layered. *(1/3, Delhi 2012C)*
15. Why is a finely divided substance more effective as an adsorbent? *(AI 2011C, Delhi 2010 C)*
16. What is the basic difference between adsorption and absorption? *(AI 2010C)*
17. What are physisorption and chemisorption? *(AI 2010C)*
18. Name the two types of adsorption phenomenon. *(Delhi 2009C)*
19. Why does physisorption decrease with the increase of temperature ? *(Delhi 2008C)*
20. In chemisorption why x/m initially increases and then decreases with rise in temperature? *(Delhi 2008C)*

SA I (2 marks)

21. Give reasons for the following observations:
    (i) NH_3 gas absorbs more readily than N_2 gas on the surface of charcoal.
    (ii) Powdered substances are more effective adsorbents. *(2/3, Foreign 2015)*
22. Write the differences between physisorption and chemisorption with respect to the following :
    (i) Specificity
    (ii) Temperature dependence
    (iii) Reversibility and
    (iv) Enthalpy change *(Delhi 2013)*

SA II (3 marks)

23. Giving appropriate examples, explain how the two types of processes of adsorption (physisorption and chemisorption) are influenced by the prevailing temperature, the surface area of adsorbent and the activation energy of the process? *(AI 2014C)*
24. What is an adsorption isotherm? Describe Freundlich adsorption isotherm. *(Delhi 2013, AI 2012C)*
25. What is an 'adsorption isotherm' ? *(Delhi 2010C)*
26. How do the size of particles of adsorbent, pressure of gas and temperature influence the extent of adsorption. *(Delhi 2009C)*
27. Define adsorption. Write any two features which distinguish physisorption from chemisorption. *(Delhi 2007)*

5.2 Catalysis

VSA (1 mark)

28. Give reasons for the following observation :
It is necessary to remove CO when ammonia is prepared by Haber's process. *(1/3 Delhi 2015)*

29. Define the following term :
Shape selective catalysis
(1/3, Delhi 2015C, 2009C, 1/2, AI 2012, 2011, 2010, 2007)

30. What are biocatalysts ? Give an example. *(Foreign 2014)*

31. Give an example of 'shape-selective catalyst'. *(Delhi 2010)*

SA I (2 marks)

32. Name the two groups into which phenomenon of catalysis can be divided. Give an example of each group with the chemical equation involved. *(Delhi 2012)*

33. Explain how the phenomenon of adsorption find application in the following processes :
(i) Production of vaccum
(ii) Heterogeneous catalysis *(Foreign 2011)*

34. Distinguish between homogeneous and heterogeneous catalysis. What role does adsorption play in heterogeneous catalysis? *(AI 2008C)*

35. Explain the following term giving a suitable example.
Homogeneous catalysis *(Delhi 2007)*

5.4 Classification of Colloids

VSA (1 mark)

36. Write the main reason for the stability of colloidal sols. *(Delhi, AI 2016)*

37. Out of $BaCl_2$ and KCl, which one is more effective in causing coagulation of a negatively charged colloidal sol? Give reason. *(Delhi 2015)*

38. Write the dispersed phase and dispersion medium of butter. *(AI 2015, Foreign 2014)*

39. In reference to surface chemistry, define dialysis. *(Delhi 2015C, 2014C, AI 2014C, 2007)*

40. Define the following term :
Electrophoresis *(1/3, Delhi 2015C)*

41. Give one example each of sol and gel. *(Delhi 2014)*

42. Give one example each of lyophobic sol and lyophilic sol. *(Delhi 2014)*

43. What are the dispersed phase and dispersion medium in milk? *(Delhi 2014)*

44. Name of the temperature above which the formation of micelles takes place. *(Foreign 2014)*

45. Based on the type of dispersed phase, what type of colloid is micelles. *(Foreign 2014)*

46. What is the difference between lyophobic sol and lyophilic sol ? *(Delhi 2014C)*

47. Which aerosol depletes ozone layer? *(AI 2013)*

48. To which colloidal system does milk belong ? *(AI 2013C)*

49. Which complex ion is formed when undecomposed AgBr is washed with hypo solution in photography ? *(AI 2013C)*

50. Define peptization. *(AI 2012)*

51. How can a colloidal solution and true solution of the same colour be distinguished from each other *(Delhi 2012C)*

52. How is a sol different from an emulsion ? *(AI 2012C)*

53. What are lyophobic colloids? Give an example for them. *(AI 2011)*

54. Define the term 'Tyndall effect'. *(AI 2010, Delhi 2009)*

55. What causes brownian movement in a colloidal solution? *(Delhi 2008)*

56. Describe 'electrophoresis' briefly. *(AI 2008)*

57. What happens when gelatin is added to gold solution? *(AI 2007)*

58. Explain the following terms giving a suitable example :
Emulsification *(Delhi 2007)*

SA I (2 marks)

59. (i) Out of $MgCl_2$ and $AlCl_3$, which one is more effective in causing coagulation of negatively charged sol and why ?
(ii) Out of sulphur sol and proteins, which one forms multimolecular colloids? *(2/3, Delhi 2016)*

60. Give reasons for the following observations :
(i) Leather gets hardened after tanning.
(ii) Lyophilic sol is more stable than lyophobic sol. *(2/3, Delhi 2015)*

61. (i) Based on type of particles of dispersed phase, give one example each of associated colloid and multimolecular colloid
(ii) Write an important characteristic of lyophilic sols. *(2/3, Delhi 2014)*

62. Define the following terms :
(i) Peptization
(ii) Sol *(2/3, Delhi 2014C)*

63. Define the following terms :
(i) Tyndall effect
(ii) Electrophoresis *(2/3, Delhi 2014C)*

64. Write the dispersed phase and dispersion medium of the following colloidal systems :
(i) Smoke
(ii) Milk *(Delhi 2013)*

65. What is the difference between multimolecular and macromolecular colloids? Give one example of each. *(Delhi 2013)*

66. How are the following colloidal solutions prepared?
(a) Sulphur in water (b) Gold in water *(Delhi 2013C)*

67. Explain the following terms giving one example for each.
(i) Micelles (ii) Aerosol *(Delhi, AI 2012)*

68. Explain the cleaning action of soap. Why do soaps not work in hard water? *(AI 2012)*

69. (i) Same substances can act both as colloids and crystalloids. Explain
(ii) What will be the charge on AgI colloidal particles when it is prepared by adding small amount of $AgNO_3$ solution to KI solution in water? What is responsible for the development of this charge ? *(2/3, Delhi 2012C)*

70. Define the following terms giving an example of each :
(i) Emulsion
(ii) Hydrosol *(Foreign 2011)*

71. Define the following terms :
(i) Aerosol
(ii) Coagulation of colloids. *(Foreign 2011)*

72. What is meant by coagulation of a colloidal solution? Name any method by which coagulation of lyophobic sols can be carried out. *(AI 2010)*

73. Define the following :
(i) Peptization
(ii) Reversible sols *(AI 2010)*

74. Explain the following terms :
(i) Electrophoresis (ii) Dialysis *(AI 2009C)*

75. Explain the following terms :
(i) Tyndall effect (ii) Coagulation *(AI 2009C)*

76. Distinguish between micelles and colloidal particles. Give one example of each. *(AI 2008C)*

SA II (3 marks)

77. Define the following terms :
(i) Lyophilic colloid (ii) Zeta potential
(iii) Associated colloids *(AI 2016)*

78. Define the following terms :
(i) Brownian movements
(ii) Peptization
(iii) Multimolecular colloids *(AI 2015)*

79. Describe the following processes :
(i) Dialysis
(ii) Electrophoresis
(iii) Tyndall effect *(AI 2015C, 2011C)*

80. What are the characteristics of the following colloids? Give one example of each.
(i) Multimolecular colloids
(ii) Lyophobic sols
(iii) Emulsions *(AI 2013)*

81. Explain what is observed when :
(i) A beam of light is passed through a colloidal solution.
(ii) NaCl solution is added to hydrated ferric oxide sol.
(iii) Electric current is passed through a colloidal solution. *(AI 2013C, 2009, Delhi 2008C)*

82. What is meant by coagulation of a colloidal solution? Describe briefly any three methods by which coagulation of lyophobic sols can be carried out. *(Delhi 2012)*

83. Classify colloids where the dispersion medium is water. State their characteristics and write an example of each of these classes. *(AI 2011)*

84. Distinguish between multimolecular, macromolecular and associated colloids. Give one example of each. *(Delhi 2011C)*

85. Explain the following terms :
(i) Electrophoresis
(ii) Coagulation
(iii) Tyndall effect *(AI 2010C)*

86. What is the difference between multimolecular and macromolecular colloids? Give one example of each type. How are associated colloids different from these two types of colloids ? *(Delhi 2009)*

87. How are the following colloids different from each other in respect of dispersion medium and dispersed phase? Give one example of each type.
(i) An aerosol
(ii) A hydrosol
(iii) An emulsion *(Delhi 2009)*

88. What are lyophilic and lyophobic sols? Give one example of each type. Which one of these two types of sols is easily coagulated and why? *(Delhi, AI 2008)*

89. Explain what is observed when
(i) KCl, an electrolyte, is added to hydrated ferric oxide sol,
(ii) an electric current is passed through a colloidal solution,
(iii) a beam of light is passed through a colloidal solution. *(AI 2008)*

5.5 Emulsions

VSA (1 mark)

90. What are emulsions? Give an example. *(Delhi 2015C)*

91. Give one example each of 'oil in water' and 'water in oil' emulsion. *(Delhi 2014)*

92. What is an emulsion? *(Delhi 2014C, 2010, AI 2012, Foreign 2011)*

93. What are emulsions? Name an emulsion in which water is a dispersed phase. *(AI 2014C)*

94. Explain the following :
Artificial rain is caused by spraying salt over clouds. *(1/3, Delhi 2012C)*

SA I (2 marks)

95. What is the difference between oil/water (O/W) type and water/oil (W/O) type emulsions? Given an example of each type. *(Delhi 2013)*

96. What are emulsions? State one application of emulsification. *(Delhi 2009C)*

SA II (3 marks)

97. What are emulsions? What are their different types? Give one example of each type. *(AI 2014, Delhi 2013C)*

98. (i) What is the difference between a colloidal solution and an emulsion? Give one example of each.
(ii) What are emulsifiers ? *(Delhi 2008C)*

5.6 Colloids Around Us

VSA (1 mark)

99. Give reasons for the following observations :
A delta is formed at the meeting point of sea water and river water *(1/3, Foreign 2015, 2014)*

Detailed Solutions

1. Adsorption is a surface phenomenon. In this process the adsorbate is concentrated on the surface of the adsorbent and does not penetrate into the bulk whereas, absorption of a substance takes place throughout the bulk of the material. In adsorption, concentration of adsorbate is high on the surface of adsorbent, while during absorption concentration is uniform throughout. *e.g.*, water vapour is adsorbed by silica gel whereas absorbed by anhydrous calcium carbide.

2. Physisorption takes place (any one) with the help of non-covalent bonding between an adsorbate and an adsorbent; it makes the process reversible. Chemisorption, on the other hand, takes place with the help of covalent bonding; it makes the process irreversible.

3. Adsorption is the phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting in higher concentration of the molecules on the surface.

4. $\frac{x}{m} = kp^{1/n} (n > 1)$

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log p$$

where $\frac{x}{m}$ is the mass of gas adsorbed per gram of the adsorbent and p is the pressure of gas.

5. **Effect of temperature :** Chemisorption is an exothermic process. Hence, according to Le Chatelier principle, rate of adsorption decreases with rise in temperature. [redacted]

6. In adsorption, there is always a decrease in residual unbalanced forces on the surface. This results in decrease in surface energy which appears as heat. Hence, adsorption is unconditionally an exothermic process.

7. The forces operating in these cases are weak van der Wals' forces.

8. *Refer to answer 4.*

9. The term sorption is used to describe both the processes adsorption and absorption.

10. Chemisorption has higher enthalpy of adsorption.

11. NH_3 gas will be adsorbed more readily on the surface because it has higher critical temperature than CO_2 gas.

Due to the greater attraction of the gas molecules on the surface of the adsorbent, greater will be the adsorption.

12. For the process to be spontaneous ΔG must be negative.

As ΔS is negative, ΔG can be negative only if ΔH is negative and greater than $T\Delta S$.

13. Applications of adsorption :

(i) Deionisation of water

(ii) In chromatographic analysis.

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

15. A finely divided substance is more effective as adsorbent because

(i) It has more surface area so more adsorption occurs.

(ii) The number of active sites (active centres) becomes more and the extent of adsorption increases.

16. *Refer to answer 1.*

17. **Physisorption :** The phenomenon in which adsorbate and adsorbent are held by van der Waals' forces.

It is reversible in nature. *e.g.,* setting a layer of dust particles on the furniture.

Chemisorption : The phenomenon in which adsorbate and adsorbent are held by chemical bonds.

It is irreversible in nature. *e.g.,* painting on a furniture.

18. The two types of adsorption phenomenon are chemisorption or chemical adsorption and physisorption or physical adsorption.

19. Since, adsorption is exothermic and according to Le-chatelier's principle, low temperature is favourable for physical adsorption hence, physisorption decreases with increase in temperature.

Solid + Gas $\rightleftharpoons$ Gas adsorbed on solid + heat

20. *Refer to answer 5.*

21. (i)

Higher the critical temperature of gas, more readily it can get adsorbed on the surface of an adsorbent due to stronger van der Waals' forces.

NH_3 (132°C) has a higher critical temperature than dinitrogen (–147°C). Thus, NH_3 gas adsorbs more readily than N_2 gas on the surface of charcoal.

(ii) *Refer to answer 15.*

22.

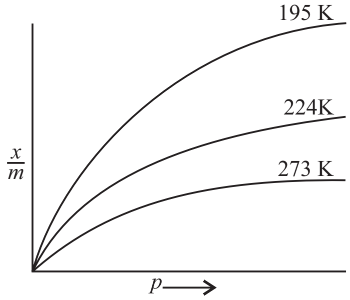
S. No.	Criteria	Physisorption	Chemisorption
(i)	Specificity	It is not specific in nature.	It is highly specific in nature.
(ii)	Temperature dependence	It decreases with increase in temperature. Thus, low temperature is favourable for physisorption.	It increases with increase in temperature. Thus, high temperature is favourable for chemisorption.
(iii)	Reversibility	Reversible in nature.	Irreversible in nature.
(iv)	Enthalpy change	Low enthalpy of adsorption	High enthalpy of adsorption

23. Effect of temperature : Physisorption decreases with increase of temperature and chemisorption first increases then decreases with increase of temperature.

Surface area : Greater the surface area, greater is the physisorption and chemisorption.

Activation energy : In physisorption, no appreciable activation energy is needed. In chemisorption, sometimes high activation energy is needed.

24. Adsorption isotherm : It is the variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature.



Adsorption isotherm

Freundlich adsorption isotherm : It is an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.

$$\frac{x}{m} = kp^{1/n} (n > 1) \qquad \ldots(i)$$

when, $n = 1, \Rightarrow \frac{x}{m} = kp$ or $\frac{x}{m} \propto p$

where x is the mass of gas adsorbed on mass m of the adsorbent at pressure p. k and n are constants which depend on the nature of the adsorbent and the gas at the particular temperature.

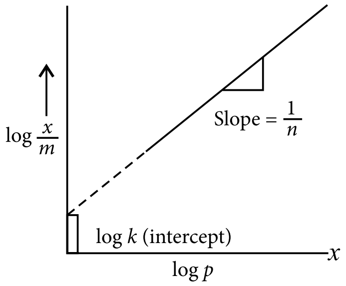
These curves indicate that on increasing temperature, physical adsorption decreases at a fixed pressure.

Taking log in Eq. (i), gives

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

The validity of Freundlich isotherm can be verified by plotting $\frac{x}{m}$ on y-axis and $\log p$ on x-axis.

If it comes to be a straight line, the Freundlich isotherm is valid.



Freundlich isotherm

25. *Refer to answer 24.*

26. Size of adsorbent particles : Smaller the size of adsorbent particles, larger is the surface area and hence, higher is the adsorption.

Pressure : Increase in pressure forces gas molecules to come closer to the surface of adsorbent leading to increase in the amount of adsorption.

Temperature : Adsorption is an exothermic reaction hence is favoured at lower temperature, at higher temperature the *K.E.* of adsorbate is high and hence extent of adsorption is low.

27. *Refer to answers 3 and 22.*

28. CO is a catalytic poison. It reacts with iron to form iron carbonyl thus inhibiting the activity of catalyst.

29. The catalytic reaction that [redacted] pore structure of the catalyst and the size of the reactant and product molecules is called shape selective catalysis.

30. Enzymes are termed as biocatalysts as they help in catalysis of biological reactions.

For example, Inversion of cane sugar with the help of invertase enzyme.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11(aq)}} + H_2O_{(l)} \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_{6(aq)}} + \underset{\text{Fructose}}{C_6H_{12}O_{6(aq)}}$$

31. Zeolites (ZSM - 5) are good shape selective catalysts which convert alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

32. Catalysis is divided into following two groups.

Homogeneous catalysis : When reactants and the catalysts are in the same phase *i.e.,* liquid or gas, the catalysis is known as homogeneous catalysis.

e.g., $2H_2O_{2(aq)} \xrightarrow{I^-_{(aq)}} 2H_2O_{(l)} + O_{2(g)}$

or $\frac{3}{2}O_{2(g)} \xrightarrow{NO_{(g)}} O_{3(g)}$

Heterogeneous catalysis: When reactants and the catalysts are in different phases, the catalysis is known as heterogeneous catalysis. In most cases, the catalyst is solid, while reactants are either liquid or gases. Here, the catalyst is usually a metal or an oxide in finely divided form *e.g.,*

$$\text{Vegetable oils } (l) + H_{2(g)} \xrightarrow{Ni_{(s)}} \text{Vegetable ghee}_{(s)}$$

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{Pt_{(s)}} 4NO_{(g)} + 6H_2O_{(g)}$$

33. (i) **Production of Vacuum :** Adsorption can be applied to create condition of high vacuum. Vessel which has already been exhausted by vacuum pump is connected to a bulb containing charcoal. The remaining traces of air inspite of low pressure are adsorbed by the charcoal almost completely.

(ii) **Role of adsorption in heterogeneous catalysis**

The reactant molecules in gaseous state or in solutions are adsorbed on the surface of the solid catalyst by physisorption or chemisorption. As result, the concentration of the reactant molecules on the surface increases and hence, the rate of reaction increases.

34. *Refer to answers 32 and 33(ii).*

35. *Refer to answer 32.*

36. The main reason for the stability of colloids is the electrostatic stabilisation *i.e.*, equal and same type of charge on the colloidal particles which causes repulsion between them and prevents the coagulation of the sol.

37. $BaCl_2$ is more effective in causing coagulation of negatively charged colloidal sol.

Because greater the valency of the coagulating ion, greater is its power to bring about coagulation.

38. Dispersed phase : Liquid

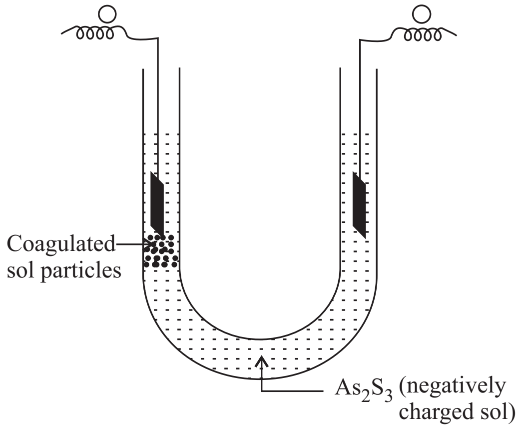
Dispersion medium : Solid

39. Dialysis : It is the process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane.

A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flowing.

The molecules and ions diffuse through membrane into the water and pure colloidal solution is left behind.

40. The movement of colloidal particles under an applied electric potential is called electrophoresis. Positively charged colloidal particles move towards the cathode, while negatively charged particles move towards the anode.



Electrophoresis

41.

Type of colloid	Dispersed phase	Dispersion medium	Examples
Sol	Solid	Liquid	Paints or Cell fluids
Gel	Liquid	Solid	Cheese or Butter or Jellies

42. A colloidal sol in which dispersed phase and dispersion medium attract each other is called lyophilic colloid. *e.g.,* gum. A colloidal sol in which dispersed phase and dispersion medium repel each other is called lyophobic colloid. *e.g.,* gold solution.

43. Liquid fat is the dispersed phase and water is the dispersion medium.

44. The formation of micelles takes place only above a particular temperature called Kraft temperature (T_k).

45. Associated colloids

46. Lyophilic sols : The colloidal solution in which particles of the dispersed phase have a strong affinity for the dispersion medium.

These colloidal sols, even if precipitated, change back to the colloid form simply by adding dispersion medium. So, lyophilic sols are reversible in nature. *e.g.,* glue, starch, rubber, etc.

Lyophobic sols : The colloidal solution in which particles of the dispersed phase have no or very little affinity for dispersion medium.

These are irreversible in nature *i.e.*, once precipitated, they have little tendency to get back into the colloidal form on simply adding dispersion medium *e.g.,* As_2S_3 solution. Lyophobic sols need stabilising agents for their preservation.

47. CFC (Chlorofluorocarbon)

48. Emulsion

49. The developed film is immersed in sodium thiosulphate (hypo) solution which removes unchanged silver bromide as a complex ion.

This is known as fixing.

$$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

After fixing, the film is not sensitive to light.

50. Peptization is the process of conversion of a precipitate into colloidal state in the presence of some electrolyte.

51. When a powerful beam of light is passed through true and colloidal solutions each kept in a glass vessel then, colloidal solution exhibits tyndall effect whereas true solution does not.

52. Sol is a type of colloid in which the dispersed phase is solid and the dispersion medium is a liquid.

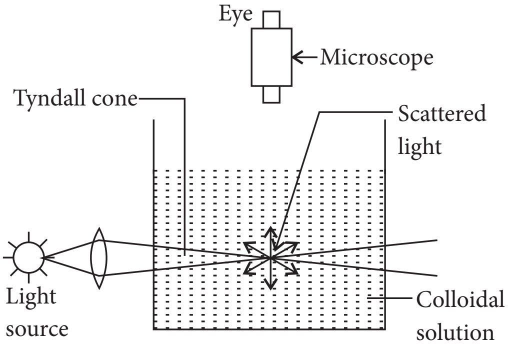
Examples include mud, milk of magnesia.

Emulsion is a type of colloid in which the dispersed phase is liquid and dispersion medium is also a liquid.

Examples include milk, face cream etc.

53. *Refer to answer 46.*

54. When a beam of light is passed through a colloidal solution and viewed perpendicular to the path of incident light, the path of beam is illuminated by a bluish light. This phenomenon is called Tyndall effect. This is due to the fact that colloidal particles scatter light in all the directions in space.



55. The continuous rapid zig-zag motion of the colloidal particles in the dispersion medium is called Brownian movement.

Unbalanced bombardment of the particles of dispersed phase by molecules of dispersion medium causes Brownian motion.

This stabilises the sol.

56. *Refer to answer 40.*

57. Gold solution which is lyophobic solution starts behaving like a lyophilic colloid when gelatin is added to it.

58. Emulsification : The process of making emulsion is known as emulsification. To stabilise an emulsion, an emulsifying agent or emulsifier is added. Soaps and detergents are most frequently used emulsifiers.

59. (i) According to Hardy-Schulze rule, for negatively charged sol greater the valency of positive ion added to it, greater is its coagulation power.

In $AlCl_3$, Al has +3 charge which is more than Mg with +2 charge in $MgCl_2$. Thus, $AlCl_3$ is more effective in causing coagulation of negatively charged sol.

(ii) Proteins are macromolecules which cannot form multimolecular colloids while sulphur sol have smaller S_8 molecules which can form multimolecular colloids.

60. **(i)** Animal hides are colloidal in nature. When a hide, which has positively charged particles is soaked in tannin, containing negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather.

(ii) Lyophilic sol is more stable than lyophobic sol because It is highly hydrated in the solution.

61. (i) Associated colloid : Soap
Multimolecular colloid : Sulphur sol

(ii) Lyophilic sols are reversible sols. These are quite stable and cannot be easily precipitated.

62. *(i) Refer to answer 50.*

(ii) Sol is a type of colloid in which dispersed phase is solid and dispersion medium is liquid *e.g.*, paints

63. *(i) Refer to answer 54.*

(ii) Refer to answer 40.

64. (i) Dispersed phase of smoke = Solid
Dispersion medium of smoke = Gas

(ii) Dispersed phase of milk = Liquid
Dispersion medium of milk = Water (liquid)

65.

S.No.	Multimolecular Colloids	Macromolecular colloids
1.	When a large number of small molecules or atoms (diameter < 1 nm) of a substance combine together in a dispersion medium to form aggregates, having size in the colloidal range, the colloidal solutions thus, formed are known as multimolecular colloids.	When substances which possess very high molecular masses are dispersed in suitable dispersion medium, the colloidal solutions thus, formed are called macromolecular colloids.
2.	*e.g.*, gold sol, sulphur sol, etc.	*e.g.*, cellulose, starch, etc.

66. (i) Sulphur sol is prepared by the oxidation of H_2S with SO_2.

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} \underset{\text{(Sol)}}{3S} + 2H_2O$$

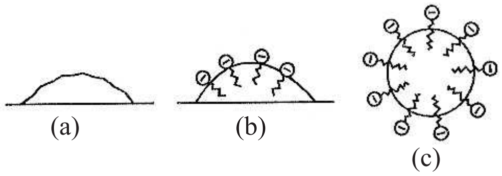
(ii) Gold sol is prepared by Bredig's arc process or by the reduction of $AuCl_3$ with HCHO.

$$2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{\text{Oxidation}} \underset{\text{(Sol)}}{2Au} + 3HCOOH + 6HCl$$

67. (i) Aggregated particles of associated colloids at high concentration are called micelles. *e.g.*, soaps.

(ii) Colloid of a liquid in a gas is called aerosol *e.g.*, fog, sprays etc.

68. The cleansing action of soap is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part is in the oil droplet and hydrophilic part interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus, soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.



Hard water contains calcium and magnesium ions. These ions form insoluble calcium and magnesium salts when sodium or potassium soaps are dissolved in hard water. These insoluble soaps separate as scum in water and are useless as cleansing agent.

69. (i) The same substance can act as both colloid and crystalloid. It depends on the size of the particles.

When the size of the particles lies between 1 to 1000 nm, it behaves as a colloid. If particle size is less than 1 nm, it exists as a true solution and behave like a crystalloid.

(ii) When $AgNO_3$ solution is added to aqueous KI solution, a negatively charged sol of AgI is formed.

This is due to selective adsorption of I^- ions from the dispersion medium.

$$AgI + \underset{\text{Dispersion medium}}{I^-} \longrightarrow \underset{\text{Negative sol}}{[AgI]I^-}$$

70. (i) **An emulsion :** It is a colloidal system when both the dispersed phase and the dispersion medium are in the liquid state. *e.g.*, milk.
(ii) **A hydrosol :** It is a colloidal solution of a solid in water as the dispersion medium. *e.g.*, starch solution.

71. (i) *Refer to answer 67 (ii).*
(ii) **Coagulation :** The process of aggregating together the colloidal particles into large sized particle which ultimately settle down under the force of gravity as a precipitate is called coagulation.

72. **Coagulation :** *Refer to answer 71 (ii).*
Coagulation of lyophobic sol can be carried out by adding electrolyte.

73. *(i) Refer to answer 50.*
(ii) **Reversible sols :** Lyophilic colloids are also known as reversible sols. These sols are directly formed by mixing substances like gum, gelatin, starch etc with a suitable liquid. These sols are stable and cannot be easily coagulated.

74. *(i) Refer to answer 40.*
(ii) Refer to answer 39.

75. *(i) Refer to answer 54.*
(ii) *Refer to answer 71 (ii).*

76. **Micelles :** When small particles (ions) of an electrolyte molecule form the aggregate particles which behave like colloidal particles, these aggregated particles are known as micelles.
Examples : Soap and detergents.
Colloidal particles : Colloidal particles have an enormous surface area per unit mass as a result of their small size. Its size ranges between 1 nm to 100 nm. *e.g.*, sulphur sol.

77. (i) *Refer to answer 46.*

(ii) The difference of potential between fixed layer and diffused layer of a colloidal sol is known as electrokinetic or zeta potential. It is given by

$$Z = \frac{4\pi\eta u}{K}$$

Z - Zeta potential
η - Co-efficient of viscosity of sol
u - Velocity of sol particles; K - Dielectric constant.

(iii) **Associated colloids :** The substances which at low concentration, behave as normal strong electrolytes but at higher concentration exhibit colloidal behaviour due to the formation of aggregated particles, are known as associated colloids.

These are also known as micelles. The formation of micelles takes place only above a particular temperature, called the Kraft temperature and above a particular concentration, called the Critical Micelle Concentration (CMC), *e.g.*, surface active agents such as soaps and synthetic detergents.

78. (i) **Brownian movement :** When the colloidal particles are observed under the ultramicroscope, the particles are seen to be in constant motion in zig-zag path.

This zig-zag motion of dispersed phase particles is called Brownian movement.

Importance : Avogadro's number can be calculated with the help of Brownian movement.
(ii) *Refer to answer 50.*
(iii) **Multimolecular colloids :** A colloid in which large number of small molecules combine to form a particle of colloidal size is called multimolecular colloid *e.g.*, sulphur sol.

79. (i) *Refer to answer 39.*
(ii) *Refer to answer 40.*
(iii) *Refer to answer 54.*

80. (i) *Refer to answer 78 (iii).*
(ii) *Refer to answer 46.*
(iii) *Refer to answer 70 (i).*

81. (i) Scattering of light by the colloidal particles takes place and the path of light becomes visible (Tyndall effect).

(ii) The positively charged colloidal particles of ferric hydroxide sol get coagulated by the oppositely charged Cl^- ions provided by NaCl.

(iii) On passing electric current through a sol, colloidal particles start moving towards oppositely charged electrodes where they lose their charge and get coagulated (electrophoresis).

82. The process of setting of colloidal particles is called coagulation of the sol. It is also known as precipitation. Following are the three methods by which coagulation of lyophobic sols can be carried out :

(i) **Electrophoresis:** In this process, the colloidal particles move towards oppositely charged electrodes and get discharged resulting in coagulation.

(ii) **Mixing of two oppositely charged sols:** When equal proportions of oppositely charged sols are mixed, they neutralise each other resulting in coagulation.

(iii) **Dialysis:** By this method, electrolytes present in sol are removed completely and colloid becomes unstable resulting in coagulation.

83. (i) **Sol:** When solids is dispersed in water, it is called sol, *e.g.*, gold sol starch sol.

(ii) **Emulsion:** When liquid is dispersed in water, it is called emulsion, *e.g.*, milk.

(iii) **Foam :** When gas is dispersed in water, it is called foam or froth, *e.g.*, soap lather, whipped cream.

84. *Refer to answers 65 and 77 (iii).*

85. *(i) Refer to answer 40.*

(ii) Refer to answer 71 (ii).

(iii) Refer to answer 54.

86. *Refer to answer 65.*

Refer to answer 77 (iii).

87. *(i) Refer to answer 67 (ii).*

(ii) Refer to answer 70 (ii).

(iii) Refer to answer 70 (i).

88. *Refer to answer 46.*

Hydrophobic solutions get easily coagulated on the addition of small amount of electrolyte or by heating or even shaking as they are not stable.

89. *Refer to answer 81.*

90. *Refer to answer 70 (i).*

91. Oil in water emulsion : Milk

Water in oil emulsion : Butter

92. *Refer to answer 70 (i).*

93. *(i) Refer to answer 70 (i).*

(ii) Butter is an emulsion in water acts a dispersed phase and oil acts as the dispersion medium.

94. Clouds are colloidal dispersion of water particles in air. These water particles carry some charge over them. On spraying oppositely charged colloidal dust or sand particles over a cloud from an aeroplane, the colloidal water particles present in the cloud will get neutralized and as a result they will come closer and will grow in size to form bigger water drops and ultimately will coagulate or precipitate causing artificial rain.

95. The two types of emulsions are :

(i) Oil-in-water type in which small droplets of an oil are dispersed in water.

Example : Milk, cod liver oil.

(ii) Water-in-oil type in which water droplets are dispersed in an oil medium.

Example : Butter.

96. *(i) Refer to answer 70 (i).*

(ii) **Application of emulsification** Cleansing action of soaps is due to the emulsification of oils and fats. Actually, soaps help in emulsification of oils and fats.

97. *Refer to answer 70(i).*

Types of emulsions :

Oil dispersed in water *e.g.*, milk.

Water dispersed in oil *e.g.*, butter.

98. (i) **Colloidal solution :** These are the solutions in which the diameter of dispersed phase particles may range from 1 to 1000 nm. These are intermediate of true solutions and suspensions. The colloidal particles do not settle down under the force of gravity even on long standing. A colloid is a heterogeneous system, *e.g.*, gold sol, sulphur sol, soap, etc. Emulsions are one of the types of colloidal system, in which both the dispersed phase and dispersion medium are liquids, *e.g.*, milk.

(ii) **Emulsifiers :** The substances which are added to stabilise the emulsion are called emulsifiers. *e.g.*, various kinds of soaps, lyophilic colloids (proteins, gum etc.).

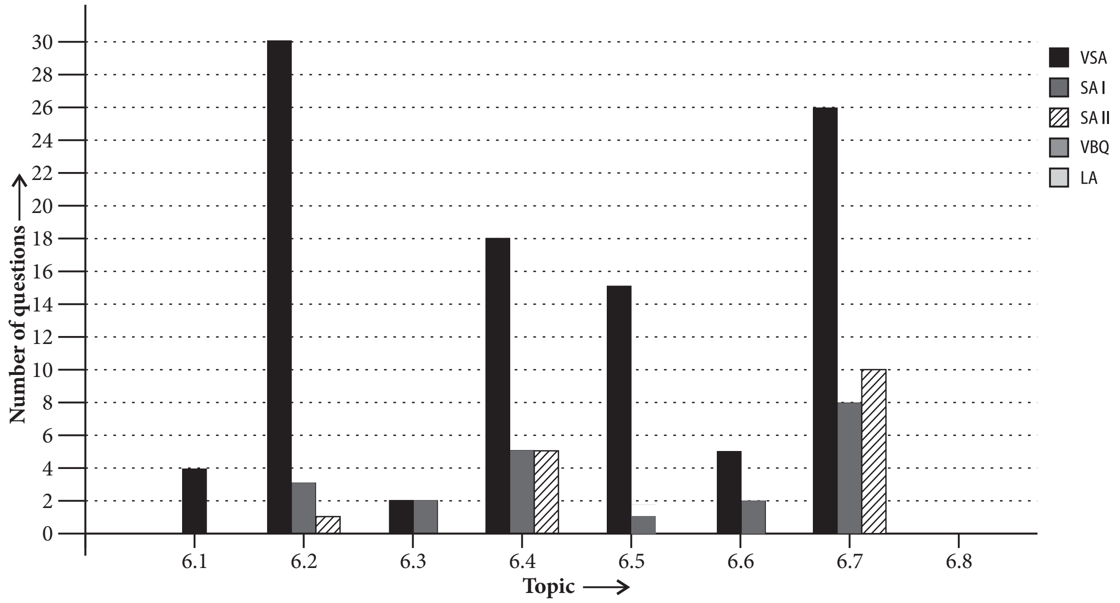
99. Sea water contains a lot of electrolytes. River contains colloids of sand and clay. When they meet the electrolytes neutralise the charge on colloidal particles which results in the precipitation of sand, clay etc. thus, resulting in a delta formation.

06

General Principles and Processes of Isolation of Elements

6.1 Occurrence of Metals
6.2 Concentration of Ores
6.3 Extraction of Crude Metal from Concentrated Ore
6.4 Thermodynamic Principles of Metallurgy
6.5 Electrochemical Principles of Metallurgy
6.6 Oxidation Reduction
6.7 Refining
6.8 Uses of Aluminium, Copper, Zinc and Iron

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



- Maximum total weightage is of *Refining*.
- Maximum VSA type questions were asked from *Concentration of Ores*.
- Maximum SA I and SA II type questions were asked from *Refining*.

QUICK RECAP

- **Minerals :** Naturally occurring chemical substances in the earth's crust obtainable by mining.
- **Ores :** The minerals from which metal can be extracted profitably and conveniently.
- **Metallurgy :** The entire scientific and technological process used for isolation of the metal from its ore.

Concentration of ore : Removal of gangue from ore is known as *concentration* or *dressing* of ore.

- Depending upon the nature of the ore and the impurities present, different methods are used for concentration of ore.

Method	Principle and ores specification	Process
Hydraulic washing	It is based on the difference in the specific gravities of the gangue and the ore particles and is mostly used for oxide ores.	The powdered ore is agitated with water. The heavier ore particles settle down while lighter impurities are washed away.
Electromagnetic separation	It is based on the difference in magnetic properties of the gangue and ore particles and is used for magnetite (Fe_3O_4), haematite (Fe_2O_3), wolframite ($FeWO_4$), chromite ($FeO\cdot Cr_2O_3$), etc.	The powdered ore containing impurity is dropped on a belt which rotates around a magnetic roller. The magnetic particles fall nearer to the roller while non-magnetic particles fall farther off.
Froth floatation process	It is based on the difference in wetting properties of gangue and ore particles and is mostly used for sulphide ores.	Powdered ore is mixed with pine oil and water and violently agitated with air. Ore particles rise to the surface in the form of froth and impurities remain in water.
Leaching	It is based on the difference in chemical properties of gangue and ore particles and is used for extraction of Au, Ag and pure alumina from bauxite ore.	*Baeyer's process* : $Al_2O_3\cdot 2H_2O + 2NaOH + H_2O \longrightarrow 2Na[Al(OH)_4]$ $2Na[Al(OH)_4] + 2CO_2 \longrightarrow Al_2O_3\cdot xH_2O + 2NaHCO_3$ $Al_2O_3\cdot xH_2O \xrightarrow{1200°C} Al_2O_3 + xH_2O$ *Mac Arthur Forest cyanide process* : $4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$ $2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$

Extraction and isolation of metals :

- **Calcination :** It is the process of heating the ore (like carbonate and hydrated oxide) strongly below its melting point either in the absence of air or in the limited supply.
- **Roasting :** It is the process of heating the ore strongly below the melting point in a sufficient supply of air to bring about its oxidation and remove volatile impurities.

Reduction or conversion of ores to metals : The ore obtained after calcination or roasting is reduced to metal and choice of reducing agent depends upon the nature of ore.

- Carbon or carbon monoxide is used for oxides of Fe, Cu, Zn, Mg, Co, etc. and the process is called *smelting*.
- Electropositive metals like Na, Al, Mg or hydrogen are used for reduction of ores of Mn, Cr, Ti, Mo, W, etc.
- Water gas is used for nickel ores.
- Auto–reduction process is used for ores of Pb, Hg, Cu, etc.
- Electrolytic reduction is used for highly electropositive metals.
- Hydrometallurgy or displacement method is used for Ag, Au, etc.

Refining of metals : Purification of crude metals by removing the impurities present in it is called *refining*.

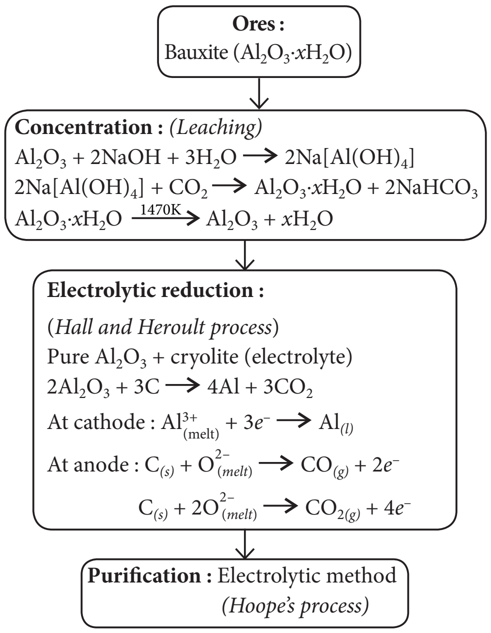
- Different methods are used depending upon the differences in properties of the metal and the impurity.

Refining/purification of the crude metal

Methods	Metals purified
Liquation	Used for low melting metals like Sn, Pb, Hg, Bi, etc.
Distillation	Used for volatile metals like Zn, Hg, Cd, etc. or metals containing non-volatile impurities.
Poling	Used for metals which contain impurities of their own oxides. *e.g.*, Cu.
Cupellation	Used for metals containing easily oxidisable impurities. *e.g.*, Ag containing Pb impurities.
Electrolytic refining	Used for metals like Cu, Ag, Au, Al which get deposited at cathode and impurities get deposited at anode. Solution of a soluble metal salt acts as the electrolyte.
Mond's process	Used for refining of Ni. $4CO + \underset{\text{Impure}}{Ni} \xrightarrow{60°-80°C} Ni(CO)_4 \xrightarrow{180°C} \underset{\text{Pure}}{Ni} + 4CO$
Zone refining	Used to produce extremely pure metals (semiconductors) like Si, Ge, Ga, B and In.
van Arkel method	Used for ultra-pure metals like Ti, Zr which are used in space technology. $\underset{\text{Impure}}{Ti_{(s)}} + 2I_{2(g)} \xrightarrow{523\text{ K}} TiI_{4(g)} \xrightarrow{1673\text{ K}} \underset{\text{Pure}}{Ti_{(s)}} + 2I_{2(g)}$ $\underset{\text{Impure}}{Zr} + 2I_2 \xrightarrow{870\text{ K}} ZrI_{4(g)} \xrightarrow{1800\text{ K}} \underset{\text{Pure}}{Zr_{(s)}} + 2I_{2(g)}$
Chromatographic methods	Based on the principle that different components of a mixture are differently adsorbed on an adsorbent *e.g.*, lanthanoids are purified by using ion exchange as adsorbent.

Extraction of Fe, Cu, Al and Zn

Extraction of Al



Ores : Bauxite ($Al_2O_3 \cdot xH_2O$)

Concentration : *(Leaching)*

$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4]$

$2Na[Al(OH)_4] + CO_2 \longrightarrow Al_2O_3 \cdot xH_2O + 2NaHCO_3$

$Al_2O_3 \cdot xH_2O \xrightarrow{1470K} Al_2O_3 + xH_2O$

Electrolytic reduction :

(*Hall and Heroult process*)

Pure Al_2O_3 + cryolite (electrolyte)

$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$

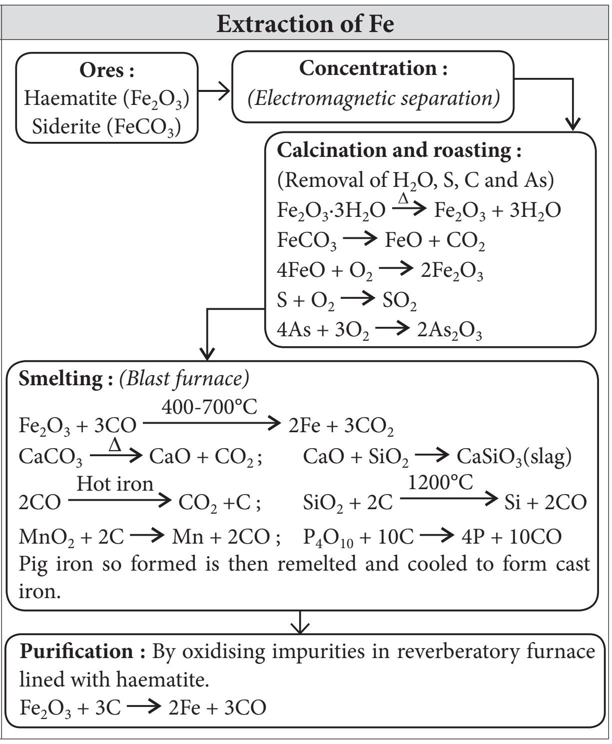
At cathode : $Al^{3+}_{(melt)} + 3e^- \longrightarrow Al_{(l)}$

At anode : $C_{(s)} + O^{2-}_{(melt)} \longrightarrow CO_{(g)} + 2e^-$

$C_{(s)} + 2O^{2-}_{(melt)} \longrightarrow CO_{2(g)} + 4e^-$

Purification : Electrolytic method *(Hoope's process)*

Extraction of Fe



Ores : Haematite (Fe_2O_3) Siderite ($FeCO_3$)

Concentration : *(Electromagnetic separation)*

Calcination and roasting :

(Removal of H_2O, S, C and As)

$Fe_2O_3 \cdot 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$

$FeCO_3 \longrightarrow FeO + CO_2$

$4FeO + O_2 \longrightarrow 2Fe_2O_3$

$S + O_2 \longrightarrow SO_2$

$4As + 3O_2 \longrightarrow 2As_2O_3$

Smelting : *(Blast furnace)*

$Fe_2O_3 + 3CO \xrightarrow{400\text{-}700°C} 2Fe + 3CO_2$

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$; $CaO + SiO_2 \longrightarrow CaSiO_3(\text{slag})$

$2CO \xrightarrow{\text{Hot iron}} CO_2 + C$; $SiO_2 + 2C \xrightarrow{1200°C} Si + 2CO$

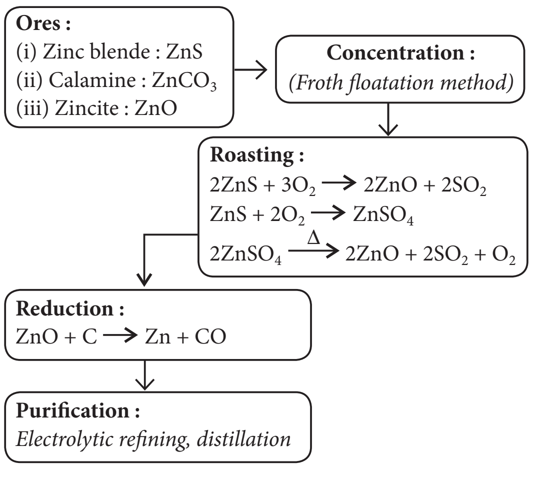
$MnO_2 + 2C \longrightarrow Mn + 2CO$; $P_4O_{10} + 10C \longrightarrow 4P + 10CO$

Pig iron so formed is then remelted and cooled to form cast iron.

Purification : By oxidising impurities in reverberatory furnace lined with haematite.

$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$

Extraction of Zn



Ores :
(i) Zinc blende : ZnS
(ii) Calamine : $ZnCO_3$
(iii) Zincite : ZnO

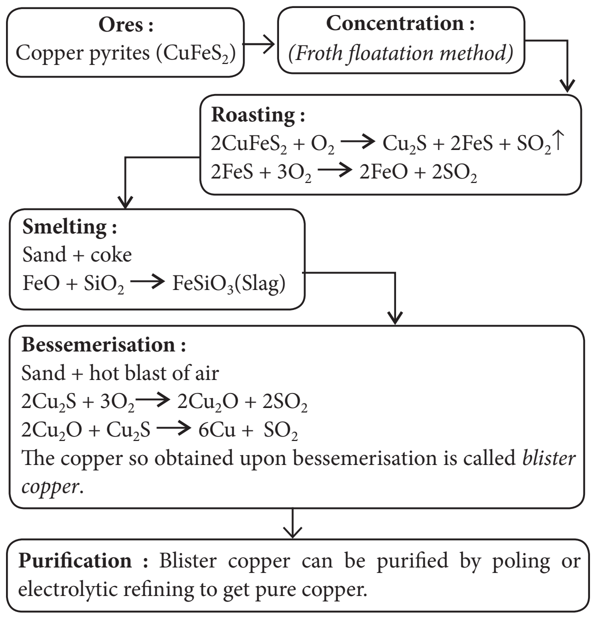
Concentration :
(Froth floatation method)

Roasting :
$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$
$ZnS + 2O_2 \longrightarrow ZnSO_4$
$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$

Reduction :
$ZnO + C \longrightarrow Zn + CO$

Purification :
Electrolytic refining, distillation

Extraction of Cu



Ores :
Copper pyrites ($CuFeS_2$)

Concentration :
(Froth floatation method)

Roasting :
$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2\uparrow$
$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

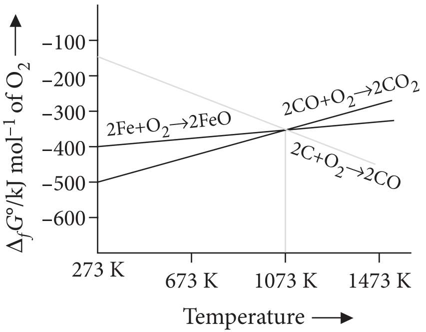
Smelting :
Sand + coke
$FeO + SiO_2 \longrightarrow FeSiO_3$(Slag)

Bessemerisation :
Sand + hot blast of air
$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$
$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$
The copper so obtained upon bessemerisation is called *blister copper*.

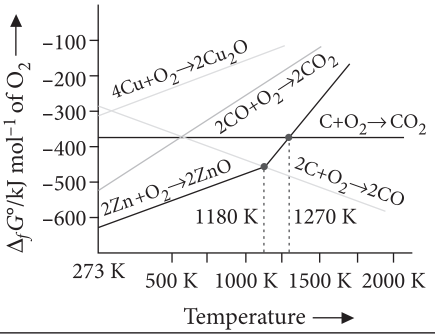
Purification : Blister copper can be purified by poling or electrolytic refining to get pure copper.

Thermodynamic and electrochemical principles of extraction :

- **Thermodynamic principles :**
  - Thermodynamics help in understanding the conditions of temperature and selecting suitable reducing agent in a metallurgical process.
  - **Gibb's Helmholtz equation** is used to check the feasibility of a reduction process.
  - $\Delta G° = \Delta H° - T\Delta S°$, if $\Delta G° < 0$, the reduction is feasible.
  - For a reaction, enthalpy change is fixed but temperature factor can be controlled and it can be the deciding factor for feasibility of that reaction.
- **Coupled reactions :** If reactants and products of two reactions are put together in a system and the net ΔG of two possible reactions is –ve, the overall reaction will take place. These reactions are called *coupled reactions*.
- **Ellingham diagram :** It consists of plots of $\Delta_f G°$ *vs*. temperature for the formation of oxides of elements.



Ellingham diagram for formation of FeO from Fe, CO from C and CO_2 from CO



Ellingham diagram showing the formation of Cu_2O from Cu, ZnO from Zn, CO from C and CO_2 from C and CO.

- It provides a sound idea about selecting a reducing agent in reduction of oxides.
- Such diagrams help in predicting the feasibility of thermal reduction of an ore. ΔG must be –ve at a given temperature for a reaction to be feasible.

Electrochemical principles :

- Electrolysis is used to carry out the reduction of a molten metal salt.
- The electrochemical principles of this method can be understood through the equation, $\Delta G^\circ = -nFE^\circ$
- More reactive metals have large negative values of the electrode potentials so, their reduction is difficult.
- If the difference of two E° values corresponds to a positive E° and consequently, negative ΔG°, then the less reactive metal will come out of the solution and the more reactive metal will go to the solution.

Previous Years' CBSE Board Questions

6.1 Occurrence of Metals

VSA (1 mark)

1. Name the chief ores of aluminium and zinc. *(AI 2014 C)*
2. Differentiate between a mineral and an ore. *(AI 2011)*
3. Name the principal ore of aluminium. *(1/3, AI 2009, 2007)*

6.2 Concentration of Ores

VSA (1 mark)

4. In the extraction of Al, impure Al_2O_3 is dissolved in conc. NaOH to form sodium aluminate and leaving impurities behind. What is the name of this process? *(1/3, Delhi 2016)*
5. Write the principle of the following method.
   Froth floatation method *(1/2, Delhi 2014)*
6. Describe the role of the following :
   NaCN in froth floatation process *(1/2, AI 2014)*
7. What is the function of collectors in the froth floatation process for the concentration of ores. *(Foreign 2014)*
8. Name the depressant which is used to separate ZnS and PbS ores in froth floatation process. *(Foreign 2014)*
9. What role is played by CO_2 in getting pure alumina ($Al_2 O_3$) in the extraction of aluminium? *(Delhi 2014 C)*
10. Describe the underlying principle of froth floatation process of concentration of ores. *(1/2, Delhi 2014 C)*
11. What are the collectors used in froth floatation process? Name a substance that can be used as such. *(AI 2014 C)*
12. Describe the underlying principle of recovery of silver from the solution obtained by leaching silver ore with a solution of NaCN. *(1/2, AI 2014 C)*
13. What is the role of CO_2 in the extractive metallurgy of aluminium from its ore? *(AI 2014 C)*
14. Which solution is used for the leaching of silver metal in the presence of air in the metallurgy of silver? *(1/2, Delhi 2013)*
15. Which of the following ores can be concentrated by froth floatation method and why?
    Fe_2O_3, ZnS, Al_2O_3 *(1/2, Delhi 2013)*
16. Name the method used for removing gangue from sulphide ores. *(1/2, AI 2013)*
17. Explain the role of the following :
    NaCN in the extraction of silver from silver ore. *(1/2, Delhi 2013 C, AI 2010 and 2009)*
18. What is the role of collectors in froth floatation process? *(AI 2012)*
19. What is the role of depressants in the froth floatation process of dressing of ores? *(Delhi 2012 C)*
20. State the principle on which the following process operates :
    Recovery of silver after the silver ore has been leached with NaCN. *(1/3, Delhi, Foreign 2011)*
21. Describe the principle controlling the following process :
    Froth floatation method of concentration of a sulphide ore. *(1/2, AI 2011)*
22. Why is it that only sulphide ores are concentrated by froth floatation process? *(AI 2011)*
23. What type of ores can be concentrated by magnetic separation method? *(AI 2011)*
24. Describe the principle controlling the following process :
    Preparation of pure alumina (Al_2O_3) from bauxite ore. *(1/2, AI 2011)*
25. Write the reactions involved in the following process :
    Leaching of bauxite ore to prepare pure alumina. *(1/2, Foreign 2011)*

26. Describe the principle involved in the following process of metallurgy :
Froth floatation method. *(1/3, AI 2010)*

27. Why is the froth floatation method selected for the concentration of sulphide ores. *(Delhi 2009)*

28. Describe the leaching of aluminium ore. *(1/2, AI 2009)*

29. State briefly the principle which serves as basis for the following operation in metallurgy :
Froth floatation process *(1/3, Delhi 2008)*

30. Describe the role of the following :
Depressant in froth floatation process *(1/3, Delhi 2008 C)*

SA I (2 marks)

31. Write the chemical reactions involved in the extraction of silver from silver ore. *(Foreign 2014)*

32. How can you obtain pure alumina (Al_2O_3) from a bauxite ore? Give necessary reaction involved. *(AI 2010 C, 2009 C)*

SA II (3 marks)

33. Write the principle behind the froth floatation process. What is the role of collectors in this process? *(AI 2014)*

6.3 Extraction of Crude Metal from Concentrated Ore

VSA (1 mark)

34. Answer the following :
Differentiate between roasting and calcination. *(1/3, AI 2015 C)*

35. What is meant by the term 'pyrometallurgy'? *(AI 2009)*

SA I (2 marks)

36. Define the following terms :
(i) Roasting
(ii) Calcination *(Delhi 2014 C)*

37. Giving examples differentiate between calcination and roasting. *(AI 2013 C)*

6.4 Thermodynamic Principles of Metallurgy

VSA (1 mark)

38. What is the role of coke in the extraction of iron from its oxides? *(1/3, Delhi 2016)*

39. What is the role of limestone in the extraction of iron from its oxides? *(1/3, Delhi 2016)*

40. What is the role of silica in the extraction of copper? *(1/3, Delhi 2015)*

41. Which form of the iron is the purest form of commercial iron? *(1/3, Delhi 2015)*

42. What is 'copper matte'? *(1/3, Foreign 2015)*

43. Describe the role of the following :
SiO_2 in the extraction of copper from copper matte *(1/2, AI, Foreign 2014, Delhi 2010)*

44. What is the function of SiO_2 in the metallurgy of copper? *(Delhi 2014 C)*

45. Out of C and CO, which is a better reducing agent at the lower temperature range in the blast furnace to extract iron from the oxide ore? *(1/2, Delhi 2013)*

46. What is the composition of 'copper matte'? *(Delhi 2013)*

47. Give reason for the following :
Zinc oxide can be reduced to metal by heating with carbon but Cr_2O_3 cannot be reduced by heating with carbon. *(1/2, Delhi 2013 C)*

48. Although thermodynamically feasible, in practice, magnesium metal is not used for reduction of alumina in the metallurgy of aluminium. Why? *(AI 2012 C)*

49. Describe the principle controlling the following process :
Preparation of cast iron from pig iron. *(1/2, AI 2011)*

50. Copper matte is charged into a silica lined converter in extraction of copper. What is the role of silica lining here? *(AI 2010 C)*

51. Describe the role of the following :
Silica in the extraction of copper from copper pyrites ore. *(1/3, Delhi 2008 C)*

52. The reaction $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$; $\Delta G° = -421$ kJ is thermodynamically feasible as is apparent from the Gibbs energy value. Why does it not take place at room temperature? *(1/3, Delhi, AI 2008 C)*

SA I (2 marks)

53. (i) What is the role of silica in the extraction of copper?
(ii) How is 'cast iron' different from 'pig iron'? *(2/3, AI 2015)*

54. How is wrought iron different from steel? *(AI 2013)*

55. Why is copper matte put in silica lined converter? *(Delhi 2012 C)*

56. Describe how the following changes are brought about :
(i) Pig iron into steel
(ii) Zinc oxide into metallic zinc. *(2/3, Delhi 2010)*

57. Give reasons for the following :
(i) Zinc oxide can be reduced to the metal by heating with carbon but not Cr_2O_3.
(ii) Extraction of copper directly from sulphide ores is less favourable than that from its oxide ore through reduction. *(2/3, Delhi 2009 C)*

SA II (3 marks)

58. Write down the reactions taking place in different zones in the blast furnace during the extraction of iron. How is pig iron different from cast iron? *(Delhi 2015 C)*

59. Write the reactions taking place in different zones of the blast furnace to obtain iron. *(AI 2015 C)*

60. Write down the reactions which occur in upper, middle and lower zones in the blast furnace during the extraction of iron from iron ore. *(Delhi 2011 C)*

61. What chemical principle is involved in choosing a reducing agent for getting the metal from its oxide ore? Consider the metal oxides, Al_2O_3 and Fe_2O_3, and justify the choice of reducing agent in each case. *(AI 2008)*

62. What are the chief ores of zinc? Write chemical reactions taking place in the extraction of zinc from zinc blende. *(AI 2008)*

6.5 Electrochemical Principles of Metallurgy

VSA (1 mark)

63. What is the role of cryolite in the extraction of aluminium? *(1/3, AI 2016, 2015 C, Delhi, AI 2013, Delhi 2012, AI 2010, Delhi 2008 C)*

64. Which reducing agent is employed to get copper from the leached low grade copper ore? *(Delhi 2014)*

65. Write the role of graphite rod in the electrometallurgy of aluminium. *(1/2, Delhi, Foreign 2012)*

66. How is copper extracted from a low grade ore of it? *(AI 2012)*

67. Which method is employed for extracting copper from low grade ores and scraps? *(AI 2012 C)*

68. Describe the role of cryolite in the extraction of aluminium from pure alumina. *(1/2, AI 2009)*

69. Give reason for the following :
Alumina is dissolved in cryolite for electrolysis instead of being electrolysed directly. *(1/3, Delhi 2009 C)*

70. Which of the two scraps, zinc or iron would be preferred for the recovery of copper from the leached copper ore and why? *(Delhi 2009 C)*

SA I (2 marks)

71. Write all the reactions involved in the extraction of aluminium from bauxite ore. *(2/3, AI 2008 C)*

6.6 Oxidation Reduction

VSA (1 mark)

72. What is the role of dilute NaCN in the extraction of gold? *(1/3, Foreign 2015)*

73. What is the role of zinc metal in the extraction of silver? *(AI 2014)*

74. Write the reaction involved in the following process :
Recovery of gold after gold ore has been leached with NaCN solution. *(1/2, Foreign 2011)*

75. Describe the role of NaCN in the extraction of gold from gold ore. *(1/3, Delhi 2010)*

76. Why is electrolytic reduction preferred over chemical reduction for the isolation of certain metals? *(AI 2009)*

SA I (2 marks)

77. The extraction of gold by leaching with NaCN involves both oxidation and reduction. Justify giving chemical equations. *(AI 2012 C)*

78. How is chemical reduction different from electrolytic reduction? Name a metal each which is obtained by
(i) electrolytic reduction,
(ii) chemical reduction. *(AI 2010 C)*

6.7 Refining

VSA (1 mark)

79. Name the method of refining of metals such as germanium. *(1/3, Delhi 2016)*

80. Name the method of refining of nickel. *(1/3, AI 2016, 2014)*

81. Indicate the principle behind the method used for the refining of zinc. *(1/3, Delhi 2015)*

82. What is the principle behind the zone refining of metals?
(1/3, AI 2015, Foreign 2014, Delhi 2013 C, AI 2012 C)

83. Indicate the principle behind the method used for the refining of nickel. *(1/3, Foreign 2015)*

84. What is meant by the term 'chromatography'? *(1/3, AI 2015 C)*

85. Name the method used for refining of copper metal. *(AI 2014)*

86. Write the role of the following :
CO in the purification of nickel *(1/2, Foreign 2014)*

87. Write the role of the following :
Iodine in the refining of zirconium. *(1/2, Foreign 2014)*

88. Describe the underlying principle of the following process :
Vapour phase refining of metals. *(1/2, Delhi 2014 C)*

89. Describe the underlying principle of the following process :
Electrolytic refining of a crude metal. *(1/2, AI 2014 C)*

90. Name the methods used for the vapour phase refining of impure titanium and nickel metals. *(Delhi 2013 C)*

91. Explain the role of the following :
Iodine in the refining of titanium. *(1/2, Delhi 2013 C, AI 2010)*

92. Write the chemical reaction which takes place in Mond's process for refining of nickel. *(Delhi 2013 C)*

93. Describe the following :
The role of carbon monoxide in the refining of crude nickel. *(1/2, Delhi 2012)*

94. Name the methods used for refining of following metals.
(i) Nickel (ii) Titanium *(Delhi 2012 C)*

95. What types of metals are usually purified by the method of zone refining? Give an example. *(Delhi 2012 C)*

96. Describe the principle controlling the following process :
Vapour phase refining of titanium metal. *(1/2, AI 2011)*

97. Write the reactions involved in the following process :
Refining of zirconium by van Arkel method. *(1/2, Foreign 2011)*

98. Describe how the following change is brought about :
Impure titanium into pure titanium. *(1/3, Delhi 2010)*

99. Describe the role of iodine in the refining of zirconium. Write chemical equations for the involved reactions. *(1/3, Delhi 2010)*

SA I (2 marks)

100. Write the principle of the following method : Vapour phase refining. *(Delhi 2014)*

101. Describe the principle involved in each of the following processes.
(i) Zone refining of a metal
(ii) Vapour phase refining of metals. *(AI 2014, 2013)*

102. Give an example of zone refining of metals. *(Delhi 2013)*

103. Describe the principle involved in each of the following processes.
(i) Mond process for refining of nickel.
(ii) Column chromatography for purification of rare elements. *(Delhi 2012)*

104. Describe the principle controlling each of the following processes :
(i) Zone refining of metals
(ii) Electrolytic refining of metals *(AI 2011)*

105. Describe the underlying principle of each of the following metal refining methods :
(i) Electrolytic refining of metals
(ii) Vapour phase refining of metals. *(AI 2009)*

106. State briefly the principles which serve as basis for the following operations in metallurgy :
(i) Zone refining
(ii) Refining by liquation *(2/3, Delhi 2008)*

SA II (3 marks)

107. Outline the principles of refining of metals by the following methods :
(i) Distillation
(ii) Zone refining
(iii) Electrolysis *(Delhi 2015 C)*

108. Outline the principles behind the refining of metals by the following methods :
(i) Zone refining method
(ii) Chromatographic method *(Delhi 2014)*

109. Explain the principle of the method of electrolytic refining of metals. Give one example. *(AI 2014)*

110. Which methods are usually employed for purifying the following metals?
(i) Nickel (ii) Germanium
Mention the principle behind each one of them. *(AI 2012)*

111. State the principle on which each of the following process operates :
(i) Electrolytic refining of a metal.
(ii) Vapour phase refining of a metal. *(Delhi 2011, Foreign 2010)*

112. State the principles of the following methods of refining crude metals :
(i) Zone refining
(ii) Liquation method
(iii) Chromatographic method *(AI 2011 C)*

113. State the principle involved in refining of metals by each of the following methods :
(i) Zone refining
(ii) Vapour phase refining
(iii) Electrolytic refining *(Delhi 2010 C, Delhi 2008)*

114. What is meant by the term, 'Chromatography' What criterion is followed for the selection of the stationary phase in chromatography? *(Delhi 2010 C)*

Detailed Solutions

1. The chief ore of aluminium is bauxite and that of zinc is zinc blende or sphalerite.

2. The naturally occurring chemical substances present in the earth's crust which can be obtained by mining are called minerals. Those minerals from which metals can be extracted economically are called ores.

3. *Refer to answer 1.*

4. Leaching

5. The principle behind this method is that the sulphide ore is preferentially wetted by oils while gangue is preferentially wetted by water. Then on agitation froth is formed that carries mineral particles and can be skimmed off.

6. NaCN is used as a depressant in froth floatation process which selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

7. Collectors enhance non-wettability of the mineral particles. Pine oil can be used as collectors.

8. NaCN is used to separate ZnS and PbS ores in froth floatation process.

9. The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated.

$$2Na[Al(OH)_4]_{(aq)} + CO_{2(g)} \rightarrow Al_2O_3.xH_2O_{(s)} + 2NaHCO_{3(aq)}.$$

10. *Refer to answer 5.*

11. *Refer to answer 7.*

12. During leaching Ag is oxidised to Ag^+ which then combines with CN^- ions (from NaCN) to form soluble complex $[Ag(CN)_2]^-$. Silver is then recovered from this complex by displacement method using more electropositive zinc metal.

$$2[Ag(CN)_2]^-_{(aq)} + Zn_{(s)} \rightarrow 2Ag_{(s)} + [Zn(CN)_4]^{2-}_{(aq)}$$

13. *Refer to answer 9.*

14. Dilute solution of NaCN or KCN in the presence of air (for O_2).

15. ZnS (Froth floatation method is used to remove gangue from sulphide ores).

16. Froth floatation method.

17. *Refer to answer 12.*

18. *Refer to answer 7.*

19. *Refer to answer 6.*

20. *Refer to answer 12.*

21. *Refer to answer 5.*

22. This is because the sulphide ore particles becomes lighter when preferentially wetted by oil and rise to surface along with the froth, whereas gangue particles are preferentially wetted by water become heavier and settle down.

23. If either the ore or the gangue particles are capable of being attracted by magnetic field, then such ore is concentrated by magnetic separation method.

24. Al_2O_3 present in bauxite is soluble in concentrated NaOH solution whereas impurities are not, Al_2O_3 is reprecipitated from the solution.

25. (i) Leaching of bauxite ore to prepare pure alumina :

$$Al_2O_3 + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2Na[Al(OH)_4]_{(aq)}$$

$$2Na[Al(OH)_4]_{(aq)} + CO_{2(g)} \rightarrow Al_2O_3{\cdot}xH_2O_{(s)} + 2NaHCO_{3(aq)}$$

$$Al_2O_3{\cdot}xH_2O_{(s)} \xrightarrow{1470\text{ K}} Al_2O_{3(s)} + xH_2O_{(g)}$$

26. *Refer to answer 5.*

27. *Refer to answer 22.*

28. *Refer to answer 25.*

29. *Refer to answer 5.*

30. *Refer to answer 6.*

31. $$\underset{\text{Argentite}}{Ag_2S} + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

$$4Na_2S + 2H_2O + 5O_2 \rightarrow 2Na_2SO_4 + 4NaOH + 2S$$

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag$$

32. *Refer to answer 25.*

33. Froth floatation method : The method has been in use for removing gangue from sulphide ores. In this process, a suspension of the powdered ore is made with water. To it collectors and froth stabilisers are added.

Collectors (*e.g.*, pine oils, fatty acids, xanthates, etc.) enhance non wettability of the mineral particles and froth stabilisers (*e.g.*, cresols, aniline) stabilise the froth.

The mineral particles become wet by oils while the gangue particles by water. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and skimmed off.

34.

Roasting	**Calcination**
1. It is the process of heating the ore below its melting point with excess of air.	1. It is the process of heating the ore below its melting point in the absence or limited supply of air.
2. Sulphide ore is converted into oxide form. $2\,ZnS + 3O_2 \xrightarrow{Heat} 2ZnO + 2SO_2\uparrow$ and volatile impurities are removed as oxides SO_2, As_2O_3 etc.	2. Carbonate ores are converted into oxide. $ZnCO_3 \xrightarrow{Heat} ZnO + CO_2\uparrow$ and water and organic impurities are removed.

35. The process of extraction of metal from its ore by heating the ore with a suitable reducing agent is known as pyrometallurgy.

36. *Refer to anwer 34.*

37. *Refer to anwer 34.*

38. Coke reduces iron oxide to iron.

$$FeO_{(s)} + C_{(s)} \rightarrow Fe_{(s/l)} + CO_{(g)}$$

39. Limestone decomposes to form CaO and CO_2. CaO thus formed acts as a flux and combines with silica (present as impurity) to form fusible calcium silicate slag.

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + \underset{\text{(Silica)}}{SiO_2} \rightarrow \underset{\text{(slag)}}{CaSiO_3}$$

40. During the metallurgy of copper from copper pyrites, $CuFeS_2$, its roasting gives FeO besides Cu_2O and SO_2.

$$\underset{\text{(Copper pyrites)}}{4CuFeS_{2(s)}} + 11O_{2(g)} \rightarrow 4FeO_{(s)} + 2Cu_2O_{(s)} + 8SO_{2(g)}$$

To remove FeO, SiO_2 is added to form slag.

$$\underset{\text{(Basic oxide)}}{FeO_{(s)}} + \underset{\text{(Acidic oxide)}}{SiO_{2(s)}} \rightarrow \underset{\text{Slag}}{FeSiO_{3(l)}}$$

41. Wrought iron is the purest form of commercial iron.

42. Copper matte is mixture of Cu_2S and FeS.

43. *Refer to answer 40.*

44. *Refer to answer 40.*

45. Ellingham diagram for oxides of metals and carbon shows

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{i}$$

$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)} \tag{ii}$$

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)} \tag{iii}$$

that at 673 K, $\Delta_f G°(CO_2) < \Delta_f G°(CO)$ hence formation of CO_2 gas is more favourable than CO gas. Hence, out of C and CO, CO is a better reducing agent.

46. Cu_2S and FeS.

47. Carbon is suitable reducing agent for reduction of zinc oxide. Reduction of Cr_2O_3 by carbon is not thermodynamically favourable.

48. Below the temperature (1623K) corresponding to the point of intersection of Al_2O_3 and MgO curves in ellingham diagram magnesium can reduce alumina. But magnesium is a much costlier metal than aluminium and hence the process will be uneconomical.

49. Pig iron is melted with scrap iron and coke using hot air blast. Due to this, impurities such as C, S and P present in the pig iron are removed as CO_2, SO_2 and P_2O_5 and carbon content is reduced to about 3%.

50. The copper matte containing Cu_2S and FeS is put in silica lined converter. Some silica is also added and hot air blast is blown to convert remaining FeS to FeO, which is removed as slag with silica.

51. *Refer to answer 40.*

52. In solid state chance of contact between reactants is negligible.

Some thermodynamically feasible reactions also require some activation energy for initiation.

Hence, the reaction does not take place at room temperature.

53. *(i) Refer to Answer 40.*

(ii) Impure iron obtained from blast furnace is known as pig iron and cast into pigs (blocks). It contains 4-5 percent of carbon along with some phosphorus, silicon, manganese and sulphur.

Cast iron contains a less percentage of carbon (1.8 to 3 percent) made by melting pig iron with scrap iron and coke using hot air blast.

54. Wrought iron is the purest form of iron. Steel is an alloy of iron which contains requisite amount of C, Mn, Ni, Cr, etc.

55. *Refer to answer 50.*

56. (i) Pig iron is mixed with scrap iron and heated in a furnace. After removal of impurities required quantity of spiegel is added to make steel.

(ii) Zinc oxide is mixed with coke and clay and brickettes are made. The brickettes are heated at 1673 K to give metallic zinc.

$$ZnO_{(s)} + C_{(s)} \xrightarrow{1673\text{ K}} Zn_{(s)} + CO_{(g)}$$

57. (i) *Refer to answer 47.*

(ii) Free energy change for the reduction of copper sulphide to copper by carbon is positive.

whereas, $\Delta_r G°$ for the reduction of copper oxide to copper by carbon is negative and hence feasible.

58. Reduction of iron oxide in blast furnace :

(i) Lower zone of the blast furnace :

$$C + O_2 \longrightarrow CO_2 + \text{heat}$$
$$C + CO_2 \longrightarrow 2CO$$

Coke is burnt to give temperature up to 2200 K at lower part of the blast furnace.

(ii) Middle zone of the blast furnace : CO and heat move up in the furnace. The temperature range in the middle zone of the blast furnace is 900-1500 K.

$$FeO + CO \longrightarrow Fe + CO_2$$

Lime stone is also decomposed to CaO which removes silicate impurity of the ore as slag.

$$CaCO_3 \xrightarrow{1100\text{ K}} CaO + CO_2$$
$$C + CO_2 \longrightarrow 2CO$$
$$CaO + SiO_2 \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

(iii) Upper zone of the blast furnace : Temperature range in this zone is 500-800 K.

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$
$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

Impure iron obtained from blast furnace is known as pig iron and cast into pigs (blocks). It contains 4-5 percent of carbon along with some phosphorus, silicon, manganese and sulphur.

Cast iron contains a less percentage of carbon (1.8 to 3 percent) made by melting pig iron with scrap iron and coke using hot air blast.

59. *Refer to answer 59.*

60. *Refer to answer 59.*

61. Thermodynamic factor helps us in choosing a suitable reducing agent for the reduction of a particular metal oxide to the metallic state.

Any metal will reduce the oxides of other metals if $\Delta_f G°$ of the oxide of the element is less than $\Delta_f G°$ of the metal oxide to be reduced.

Thus, both Al and Zn can reduce Fe_2O_3 and Mg can reduce Al_2O_3 to Al.

62. The chief ores of zinc are

(i) Zinc blende, ZnS

(ii) Calamine, $ZnCO_3$

(iii) Zincite, ZnO.

Extraction of zinc : From zinc blende zinc is extracted by roasting followed by reduction with coke.

(a) **Roasting :** The concentrated ore is heated with oxygen at 900°C in reverberatory furnace to convert zinc sulphide to zinc oxide.

$$\underset{\text{(Zinc blende)}}{2ZnS} + 3O_2 \rightarrow \underset{\text{(Zinc oxide)}}{2ZnO} + 2SO_2$$

(b) **Reduction :** The reduction of zinc oxide is done using coke.

$$ZnO + C \xrightarrow{1673\text{ K}} Zn + CO$$

The metal is distilled off and collected by rapid chilling.

63. Purified alumina (Al_2O_3) is mixed with cryolite (Na_3AlF_6) which lowers the melting temperature of electrolyte and also increase its conductivity.

64. Scrap iron or H_2.

65. Graphite anode is used in the electrometallurgy of aluminium from alumina, Al_2O_3.

Oxygen liberated at high temperature reacts with graphite to form both CO_2 and CO gases and prevent the liberation of O_2 gas at the anode which may react with Al metal to give Al_2O_3 again.

$$\text{At anode : } C_{(s)} + O^{2-}\ (\text{melt}) \rightarrow CO_{(g)} + 2e^-$$
$$C_{(s)} + 2O^{2-}\ (\text{melt}) \rightarrow CO_{2(g)} + 4e^-$$

66. Copper is extracted by hydrometallurgy from low grade ores. It is leached out using acid or bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2.

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

67. *Refer to answer 66.*

68. *Refer to answer 63.*

69. *Refer to answer 63.*

70. Zinc scrap should be preferred because zinc is more electropositive than iron.

But zinc is costlier metal than iron so using iron scraps will be preferred.

71. Aluminium metal is extracted from bauxite ($Al_2O_3{\cdot}2H_2O$) in two steps.

Stage I (Leaching) : The ore is treated with sodium hydroxide solution. Aluminium oxide and silica dissolve to form sodium aluminate and sodium silicate respectively. Iron oxide and TiO_2 is filtered off.

$$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2Na[Al(OH)_4]_{(aq)}$$

$$2Na[Al(OH)_4]_{(aq)} \xrightarrow{CO_2} Al_2O_3 \cdot xH_2O_{(s)} + 2NaHCO_{3(aq)}$$

The hydrated alumina is filtered, dried and calcined *i.e.*, heated at 1470 K to get pure alumina.

$$\underset{\text{Aluminium hydroxide}}{Al_2O_3 \cdot xH_2O_{(s)}} \xrightarrow{1470\text{ K}} \underset{\text{Pure alumina}}{Al_2O_{3(s)}} + xH_2O_{(g)}$$

Stage II (Electrolysis) : The alumina is dissolved in molten cryolite $Na_3[AlF_6]$ and then electrolysed in a large steel tank lined with graphite which acts as cathode. The anodes are made of carbon. On passing current, molten aluminium is produced at cathode and oxygen gas is evolved at the anode which reacts with carbon anode producing CO and CO_2. The electrolytic reactions may be written as :

$$\text{Cathode : } 2Al^{3+}\ (\text{melt}) + 6e^- \rightarrow 2Al_{(l)}$$
$$\text{Anode : } C_{(s)} + O^{2-} \rightarrow CO_{(g)} + 2e^-$$
$$C_{(s)} + 2O^{2-} \rightarrow CO_{2(g)} + 4e^-$$

The anode burns away. Therefore the graphite rods must be replaced from time to time.

72. NaCN is used for leaching of gold ore in the presence of air to form soluble gold complex from which metal is displaced by adding more reactive metal.

$$4Au_{(s)} + 8CN^-_{(aq)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow 4[Au(CN)_2]^-_{(aq)} + 4OH^-_{(aq)}$$

73. (ii) Zinc in the extraction of silver : Role of zinc is to recover silver from the complex by displacement reaction. Silver ore is leached with dilute solution of NaCN in the presence of air or oxygen to form a soluble complex.

$$4Ag_{(s)} + 8CN^-_{(aq)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow \underset{\text{Soluble complex}}{4[Ag(CN)_2]^-} + 4OH^-_{(aq)}$$

$$2[Ag(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Ag$$

74. Gold is recovered from $[Au(CN)_2]^-$ complex by displacement method using a more electropositive metal zinc.

$$2[Au(CN)_2]^-_{(aq)} + Zn_{(s)} \rightarrow 2Au_{(s)} + [Zn(CN)_4]^{2-}_{(aq)}$$

75. *Refer to answer 72.*

76. Electropositive metals which cannot be reduced by chemical reduction are easily reduced electrolytically.

77. During the leaching process, Au is first oxidised to Au^+ by O_2 of the air which then combines with CN^- ions to form the soluble complex, sodium dicyanoaurate (I).

$$\underset{\text{Gold (Impure)}}{4Au_{(s)}} + 8NaCN_{(aq)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow \underset{\substack{\text{Sod. dicyanoaurate (I)}\\ \text{(Soluble complex)}}}{4Na[Au(CN)_2]_{(aq)}} + 4NaOH_{(aq)}$$

Gold is then extracted from this complex, by displacement method using a more electropositive zinc metal. In this reaction,

Zn acts as a reducing agent. It reduces Au^+ to Au while itself gets oxidized to Zn^{2+} which combines with CN^-ions to form soluble complex, sodium tetracyanozincate (II).

$$2Na[Au(CN)_2]_{(aq)} + Zn_{(s)} \longrightarrow \underset{\text{Gold}}{2Au_{(s)}} + \underset{\text{Sod. tetracyanozincate (II)}}{Na_2[Zn(CN)_4]_{(aq)}}$$

Thus, extraction of Au by leaching with NaCN involves both oxidation and reduction.

78. In chemical reduction, metal is obtained by reduction of its ore by a suitable reducing agent, whereas in electrolytic reduction, reduction is carried out by passing electric current through molten ore.
(i) Aluminium is obtained by electrolytic reduction.
(ii) Iron is obtained by chemical reduction.

79. Zone refining is used for refining of semiconductors or other metals of very high purity.

80. Mond's process : Impure nickel is treated with carbon monoxide at 60-80°C to form volatile nickel carbonyl which decomposes to give pure nickel at 180°C.

$$\underset{\text{Impure}}{Ni} + 4CO \longrightarrow Ni(CO)_4 \longrightarrow \underset{\text{Pure}}{Ni} + 4CO$$

81. Zinc is refined by electrolytic refining.
In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal. The more basic metal remains in the solution and the less basic ones go to the anode mud.
At anode : $Zn \longrightarrow Zn^{2+} + 2e^-$
At cathode : $Zn^{2+} + 2e^- \longrightarrow Zn$

82. Zone refining is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal.

83. *Refer to answer 80.*

84. The term chromatography was derived from the Greek word "chroma", meaning colour and "graphy", for writing. It was used for the first time to separate the colour pigments of plants. Chromatography is a technique for analysing or separating mixtures of gases, liquids or dissolved substances.

85. Copper is refined by electrolytic refining.

86. The role of CO is to convert impure nickel to volatile nickel tetracarbonyl whereas the impurities are left behind in the solid state. The vapour of nickel tetracarbonyl on heating at 450-470 K decomposes to give pure nickel metal and carbon monoxide.

$$\underset{\text{Impure nickel}}{Ni} + 4CO \xrightarrow{330\text{-}350K} \underset{\text{Nickel tetracarbonyl}}{Ni(CO)_4} \xrightarrow{450 - 470\ K} \underset{\text{Pure nickel}}{Ni} + 4CO_{(g)}$$

87. In this method, crude metal is heated in an evacuated vessel with iodine. The metal iodide formed is decomposed on a tungsten filament at high temperature (1800 K) to get pure metal.

$$\underset{\text{Impure}}{Zr} + 2I_2 \rightarrow ZrI_4 \rightarrow \underset{\text{Pure}}{Zr} + 2I_2$$

88. Vapour phase refining : In this method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal. So, the two requirements are :
(a) The metal should form a volatile compound with an available reagent.
(b) The volatile compound should be easily decomposable, so that the recovery is easy.

89. *Refer to answer 81.*

90. Titanium is refined by van Arkel method and nickel is refined by Mond's process.

91. Iodine forms a volatile compound with titanium which on further heating decomposes to give pure titanium.

$$\underset{\text{(Impure)}}{Ti} + 2I_{2(s)} \xrightarrow{\Delta} TiI_4 \xrightarrow{\Delta} \underset{\text{(Pure)}}{Ti} + 2I_2$$

92. $\underset{\text{Impure}}{Ni} + 4CO \xrightarrow{330\text{–}350\ K} Ni(CO)_4$

$Ni(CO)_4 \xrightarrow{450\text{–}470\ K} \underset{\text{Pure}}{Ni} + 4CO$

93. *Refer to answer 86.*

94. *Refer to answer 90.*

95. The metals such as germanium, silicon, gallium, etc. which are used as semiconductors are purified by zone refining which is based upon the principle that impurities are more soluble in the melt than in the solid state of metals.

96. In this method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal.

$$\underset{\text{Impure metal}}{Ti} + 2I_2 \xrightarrow{523\ K} TiI_4$$

$$TiI_4 \xrightarrow{1700\ K} \underset{\text{Pure metal}}{Ti} + 2I_2$$

97. Refining of zirconium by van Arkel method.

$$Zr_{(s)} + 2I_{2(s)} \xrightarrow{870\text{ K}} ZnI_{4(g)}$$

$$ZrI_{4(g)} \xrightarrow[\text{Tungsten filament}]{2075\text{ K}} \underset{\text{Pure}}{Zr_{(s)}} + 2I_{2(s)}$$

98. *Refer to answer 96.*

99. *Refer to answer 87.*

100. *Refer to answer 88.*

101. (i) *Refer to answer 82.*
(ii) *Refer to answer 88.*

102. *Refer to answer 95.*

103. (i) *Refer to answer 80.*
(ii) Chromatographic method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The adsorbed components are removed (eluted) by using suitable eluent. There are several chromatographic techniques such as paper chromatography, colum chromotagraphy, gas chromatography, etc.

104. (i) *Refer to answer 82.*
(ii) *Refer to answer 81.*

105. (i) *Refer to answer 81.*
(ii) Refer to answer 88.

106. (i) *Refer to answer 82.*
(ii) **Refining by liquation :** In this method a low melting metal like tin is heated on a sloping surface of a reverberatory furnace. Metal melts and flows down leaving impurities behind.

107. (i) **Distillation :** This process is used for volatile metals.

Impure metal is heated in a retort and its vapours are separately condensed in a receiver. The non-volatile impurities are left behind. *e.g.*, Zn, Cd, Hg, etc. are purified by this method.

(ii) *Refer to answer 82.*
(ii) *Refer to answer 81.*

108. (i) *Refer to answer 82.*
(ii) *Refer to answer 103(ii).*

109. *Refer to answer 81.*

110. (i) *Refer to answer 80.*
(ii) Refer to answer 82.

111. (i) *Refer to answer 81.*
(ii) *Refer to answer 88.*

112. (i) *Refer to answer 82.*
(ii) *Refer to answer 106(ii).*
(iii) *Refer to answer 103(ii).*

113. (i) *Refer to answer 82.*
(ii) *Refer to answer 88.*
(iii) *Refer to answer 81.*

114. The term chromatography was derived from the Greek word "chroma", meaning colour and "graphy", for writing. It was used for the first time to separate the colour pigments of plants. Chromatography is a technique for analysing or separating mixtures of gases, liquids or dissolved substances.

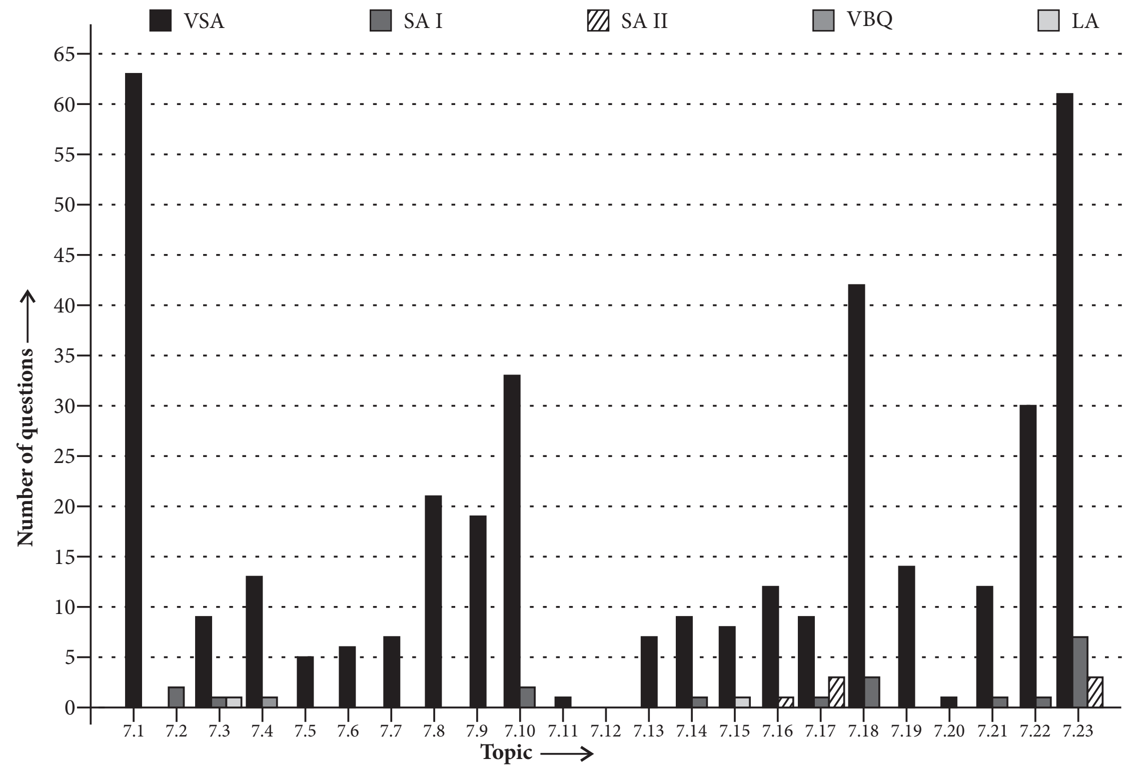
The criterion of selecting, the stationary phase depends on the different adsorbing powers of the components of a mixture to be separated.

Generally used adsorbent material is silica gel or alumina. The adsorbent can be spread over a flat glass plate (thin - layer chromatography) or taken in a glass tube (column chromatography).
In paper chromatography, the stationary phase is water held in the pores of the paper. Here, the separation depends upon the different distribution of the components between water in stationary phase and the element.

07

The *p*-Block Elements

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



- Maximum total weightage is of *Group 18 Elements.*
- Maximum VSA type questions were asked from *Group 15 Elements.*
- Maximum SA I and SA II type questions were asked from *Group 18 Elements.*

QUICK RECAP

- Elements in which the last electron enters any one of the three *p*-orbitals of their respective outermost shell are called *p-block elements.*

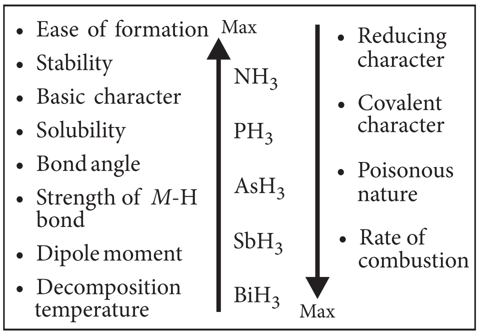
GROUP 15 ELEMENTS (NITROGEN FAMILY)

- Group 15 elements are collectively called *pnictogens.*

- **General characteristics :**

Electronic configuration	$ns^2\ np^3$
Elements	$_7N$, $_{15}P$, $_{33}As$, $_{51}Sb$, $_{83}Bi$
Physical state and metallic character	N_2 (unreactive gas), P_4 (solid non-metal), As_4 and Sb_4 (Solid metalloids), Bi (metal)
Atomic radii	Increase down the group, smaller than that of group 14 elements due to increased nuclear charge.
Melting and boiling points	M.pt. increases from N to As and then decreases whereas b. pt. increases from N to Sb and decreases very slightly.
Ionisation enthalpy	Decreases regularly down the group due to increase in size.
Electronegativity	Decreases down the group.
Allotropy	Nitrogen (α and β-Nitrogen), phosphorus (white, red, scarlet, violet, α- black, β-black), arsenic (grey, yellow, black), antimony (metallic, yellow, explosive)

- **Chemical properties :**
- Stability of +3 oxidation state increases and that of +5 decreases down the group due to *inert pair effect.*
- **Halides :** All the elements form trihalides of the type MX_3 and except nitrogen, all form pentahalides of the type MX_5.
  - **Stability :** $NF_3 > NCl_3 > NBr_3$
  - **Lewis acid strength :** $PCl_3 > AsCl_3 > SbCl_3$ and $PF_3 > PBr_3 > PI_3$
  - **Lewis base strength :** $NI_3 > NBr_3 > NCl_3 > NF_3$
  - **Bond angle :** $PF_3 < PCl_3 < PBr_3 < PI_3$ (increasing *b.p.* – *b.p.* repulsions)
- **Hydrides :** All the elements form hydrides of the type MH_3 which are covalent and pyramidal in shape. Their general trends are :

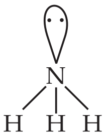
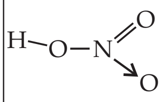
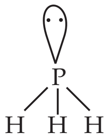
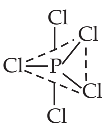


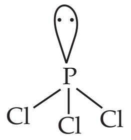
- **Oxides :** All these elements form oxides of the type X_2O_3, X_2O_4 and X_2O_5.

N_2O_3 N_2O_4 N_2O_5	P_2O_3 P_2O_4 P_2O_5	As_2O_3 As_2O_4 As_2O_5	Sb_2O_3 Sb_2O_4 Sb_2O_5	Bi_2O_3 Bi_2O_4 Bi_2O_5	↓ Acidic nature increases
→ Acidic nature decreases					

- **Preparation, properties and uses of some important compounds :**

Compound	Preparation	Properties	Uses
N_2 $N \equiv N$	$NH_4Cl + NaNO_2 \longrightarrow N_2\uparrow + 2H_2O + NaCl$ $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2\uparrow + 4H_2O + Cr_2O_3$ $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2\uparrow$	$6Li + N_2 \xrightarrow{Heat} 2Li_3N$ $3Mg + N_2 \xrightarrow{Heat} Mg_3N_2$ $N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{773\ K} 2NH_{3(g)}$ $N_{2(g)} + O_{2(g)} \xrightleftharpoons{Heat} 2NO_{(g)}$	Used in manufacture of nitric acid, ammonia, calcium cyanamide and other nitrogen compounds. Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

NH_3  	$NH_2CONH_2 + 2H_2O \longrightarrow$ $(NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$ $2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$ $(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$ *Haber's process* : $N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{773\ K} 2NH_{3(g)}$; $\Delta H_f^\circ = -46.1$ kJ/mol	$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$ $ZnSO_{4(aq)} + 2NH_4OH_{(aq)} \longrightarrow \underset{\text{(white ppt.)}}{Zn(OH)_{2(s)}} + (NH_4)_2SO_{4(aq)}$ $FeCl_{3(aq)} + NH_4OH_{(aq)} \longrightarrow \underset{\text{(brown ppt.)}}{Fe_2O_3 . xH_2O_{(s)}} + NH_4Cl_{(aq)}$ $\underset{\text{(blue)}}{Cu^{2+}_{(aq)}} + 4NH_{3(aq)} \rightleftharpoons \underset{\text{(deep blue)}}{[Cu(NH_3)_4]^{2+}_{(aq)}}$ $\underset{\text{(colourless)}}{Ag^+_{(aq)}} + Cl^-_{(aq)} \longrightarrow \underset{\text{(white ppt.)}}{AgCl_{(s)}}$ $\underset{\text{(white ppt.)}}{AgCl_{(s)}} + 2NH_{3(aq)} \longrightarrow \underset{\text{(colourless)}}{[Ag(NH_3)_2]Cl_{(aq)}}$	Used in refrigerators, manufacturing of rayon, HNO_3, $NaHCO_3$, nitrogenous fertilizers.
HNO_3  	$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$ *Ostwald's Process* : $4NH_3 + 5O_2 \xrightarrow[500\ K,\ 9\ bar]{Pt/Rh\ gauge\ catalyst} 4NO + 6H_2O$ $2NO + O_2 \rightleftharpoons 2NO_2$ $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$	$HNO_{3(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + NO^-_{3(aq)}$ $3Cu + 8HNO_3(dilute) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ $Cu + 4HNO_3(conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$ $4Zn + 10HNO_3(dilute) \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$ $Zn + 4HNO_3(conc.) \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$ $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$ $C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2$ $S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$ $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$ $NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$ $[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{(brown)}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$	Used as fertilizers, explosives, perfumes and dyes.
PH_3  	$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$ $Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$ $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2}$ $PH_4I + KOH \longrightarrow KI + H_2O + PH_3$	$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$ $3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$ $PH_3 + HBr \longrightarrow PH_4Br$	The spontaneous combustion of phosphine is technically used in *Holme's signals*. It is also used in *smoke screens*.
PCl_5  	$\underset{\text{(white or red)}}{P_4} + 10Cl_2 \longrightarrow 4PCl_5$	$PCl_5 \xrightarrow[\text{(in excess)}]{H_2O} H_3PO_4 + HCl$ $PCl_5 \xrightarrow{P_4S_{10}} PSCl_3$ $PCl_5 \xrightarrow{SO_2} SOCl_2 + POCl_3$ $PCl_5 \xrightarrow{P_4O_{10}} POCl_3$	Used as chlorinating and dehydrating agent.

PCl_3 	$P_4 + 6Cl_2 \longrightarrow 4PCl_3$ $P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$	$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$ $3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$ $3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$	Used as reagent in organic synthesis and as a precursor of PCl_5, $POCl_3$ and $PSCl_3$. It is used in the synthesis of some organic compounds, *e.g.*, C_2H_5Cl, CH_3COCl.

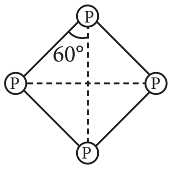
Preparation and properties of oxides of nitrogen :

Formula	O.S.	Preparation	Properties
N_2O	+1	$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$	colourless gas, neutral
NO	+2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	colourless gas, neutral
N_2O_3	+3	$2NO + N_2O_4 \xrightarrow{250\text{ K}} 2N_2O_3$	blue solid, acidic
NO_2	+4	$2Pb(NO_3)_2 \xrightarrow{673\text{ K}} 2PbO + 4NO_2 + O_2$	brown gas, acidic
N_2O_4	+4	$2NO_2 \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} N_2O_4$	colourless solid/liquid, acidic
N_2O_5	+5	$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$	colourless solid, acidic

Allotropes of phosphorus :

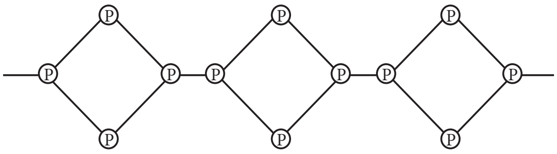
Property	White phosphorus	Red Phosphorus	Black phosphorus
Colour	White, but turns yellow on exposure	Dark red	Black
State	Waxy solid, can be cut with knife	Brittle powder	Crystalline with greasy touch
Smell	Garlic smell	Odourless	—
Density	1.84	2.1	2.69
Ignition temperature	307 K	543 K	673 K
Melting point	317 K	Sublimes in absence of air at 560 K	860 K

- White phosphorus consists of discrete tetrahedral P_4 molecule.



Structure of white phosphorus

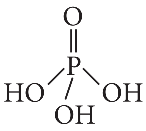
- Red phosphorus is polymeric and consists of inter linked P_4 tetrahedra.



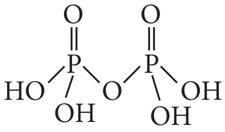
Structure of red phosphorus

- Black phosphorus is thermodynamically most stable at room temperature and has two forms : α-black phosphorus and β-black phosphorus.

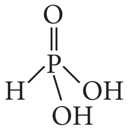
Oxoacids of phosphorus :



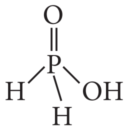
H_3PO_4
Orthophosphoric acid



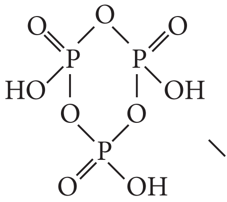
$H_4P_2O_7$
Pyrophosphoric acid



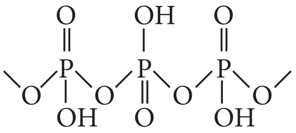
H_3PO_3
Orthophosphorous acid



H_3PO_2
Hypophosphorous acid



$(HPO_3)_3$
Cyclotrimetaphosphoric acid



$(HPO_3)_n$
Polymetaphosphoric acid

GROUP 16 ELEMENTS (OXYGEN FAMILY)

Group 16 elements are collectively called *chalcogens*.

General characteristics :

Electronic configuration	ns^2np^4
Elements	${}_8O$, ${}_{16}S$, ${}_{34}Se$, ${}_{52}Te$, ${}_{84}Po$
Physical state and metallic characters	O_2 (gas), S_8 (solid non-metal), Se and Te (solid metalloid), Po (radioactive)
Atomic radii	Increase down the group
Ionisation enthalpy	Decreases down the group
Electronegativity	Decreases down the group
Electron gain enthalpy	Increases from oxygen to sulphur and then decreases.
Melting and boiling points	Increase down the group upto Te and then decreases.
Allotropy	All elements show allotropy

Chemical properties :

- Stability of –2 oxidation state decreases down the group, stability of +4 oxidation state increases and that of +6 oxidation state decreases down the group due to *inert pair effect*.
- **Hydrides :** All the elements form stable hydrides of the type H_2M. Their general trends are :
  - **Boiling point :** $H_2O > H_2Te > H_2Se > H_2S$
  - **Volatility** : $H_2S > H_2Se > H_2Te > H_2O$
  - **Bond angle :** $H_2O > H_2S > H_2Se > H_2Te$
  - **Acidic character :** $H_2O < H_2S < H_2Se < H_2Te$
  - **Reducing power :** $H_2Te > H_2Se > H_2S > H_2O$
- **Halides :** All elements form halides of the type EX_6, EX_4 and EX_2.
- **Oxides :**

Simple oxides	MgO, Al_2O_3
Mixed oxides	Pb_3O_4, Fe_3O_4
Acidic oxides	SO_2, Cl_2O_7, CO_2, N_2O_5
Basic oxides	Na_2O, CaO, BaO
Amphoteric oxides	Al_2O_3
Neutral oxides	CO, NO, N_2O

Dioxygen (O_2) :

- **Preparation :**

$$2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$$

$$2Ag_2O_{(s)} \xrightarrow{\Delta} 4Ag_{(s)} + O_{2(g)}$$

$$2Pb_3O_{4(s)} \xrightarrow{\Delta} 6PbO_{(s)} + O_{2(g)}$$

$$2HgO_{(s)} \longrightarrow 2Hg_{(l)} + O_{2(g)}$$

$$2PbO_{2(s)} \longrightarrow 2PbO_{(s)} + O_{2(g)}$$

$$2H_2O_{2(aq)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$$

- **Properties :**
  - Dioxygen is colourless and odourless gas, soluble in water and paramagnetic in nature.
  - Dioxygen directly reacts with all metals (except noble metals like Au, Pt), non-metals (except noble gases).

$2Ca + O_2 \longrightarrow 2CaO$ (Basic oxide)

$4Al + 3O_2 \longrightarrow 2Al_2O_3$ (Amphoteric oxide)

$P_4 + 5O_2 \longrightarrow P_4O_{10}$ (Acidic oxide)

$C + O_2 \longrightarrow CO_2$ (Acidic oxide)

$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$ (Roasting)

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ (Combustion)

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$ (Catalytic oxidation)

$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$ (Catalytic oxidation)

- **Uses :**
  - For artificial respiration in hospitals and by mountaineers, pilots and divers.
  - In oxy-hydrogen and oxy-acetylene torches which are used for cutting and welding of metals.
  - Liquid dioxygen is used as a rocket fuel.

Ozone (O_3) :

- **Preparation :** $3O_2 \xrightarrow{\text{electric discharge}} 2O_3$
- **Properties :** It is a pale blue gas, dark blue liquid and violet black solid.
- **Oxidising action :**

$O_3 \longrightarrow O_2 + O$

$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$

$2I^-_{(aq)} + H_2O_{(l)} + O_{3(g)} \longrightarrow 2OH^-_{(aq)} + I_{2(g)} + O_{2(g)}$

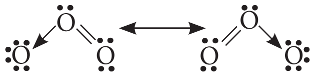
(used for estimation of O_3 by reacting I_2 with hypo.)

- **Reducing action :**

$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

$BaO_2 + O_3 \longrightarrow BaO + 2O_2$

- **Structure :**



Oxidation state of O is +1 and –1.

- **Uses :**
  - Used for bleaching ivory, flour, delicate fabrics, etc.
  - As germicide and disinfectant for sterilising water.
  - Manufacture of $KMnO_4$ and artificial silk.

Allotropes of sulphur :

- **Rhombic sulphur (α-sulphur) :** Has S_8 molecules, yellow in colour, m.pt. 385.8 K, specific gravity 2.06 g cm^{-3}, insoluble in water, soluble in CS_2.
- **Monoclinic sulphur (β-sulphur) :** Has S_8 molecules, colourless, needle-shaped crystals, m.pt. 393 K, specific gravity 1.98 g cm^{-3}, soluble in CS_2.

Sulphur dioxide (SO_2) :

- **Preparation :**
  - **By heating sulphur in air :**

    $S + O_2 \xrightarrow{\Delta} SO_2$
  - **Lab method :** By heating Cu with conc. H_2SO_4.

    $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

It is also prepared by treating a sulphite with dilute H_2SO_4.

$SO^{2-}_{3(aq)} + 2H^+_{(aq)} \longrightarrow H_2O_{(l)} + SO_{2(g)}$

- **Properties :**
  - **As reducing agent :**

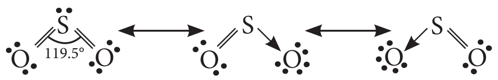
    $SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$

    $2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$
  - **As oxidising agent :**

    $2H_2S + SO_2 \longrightarrow 2H_2O + 3S\downarrow$
  - **Bleaching action :** Its bleaching action is due to reduction and is temporary.

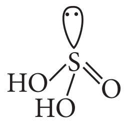
    $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$

    Coloured matter + [H] $\longrightarrow$ Colourless matter.
- **Structure :** SO_2 is a gas having sp^2 hybridisation and V-shape.

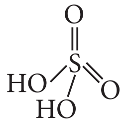


- **Uses :**
  - In the manufacture of sulphuric acid, sulphites and hydrogen sulphide.
  - As a disinfectant, fumigant and preservative.
  - For bleaching delicate articles.

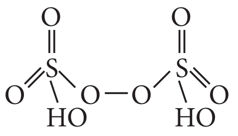
Oxoacids of sulphur :



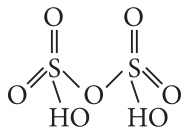
H_2SO_3
Sulphurous acid



H_2SO_4
Sulphuric acid



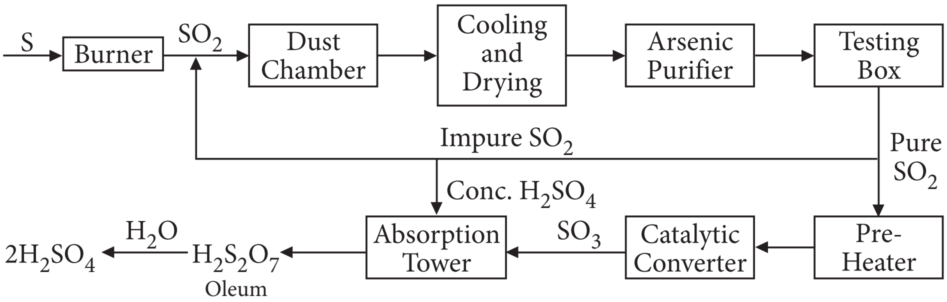
$H_2S_2O_8$
Peroxodisulphuric acid

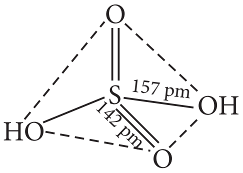
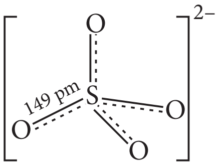


$H_2S_2O_7$
Pyrosulphuric acid (Oleum)

Sulphuric Acid (H_2SO_4) :

- **Preparation :** Contact process :



Structure	Properties	Uses
 Sulphuric acid  Sulphate ion	$H_2SO_4 \xrightarrow{NaOH} NaHSO_4 + H_2O$ $H_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2H_2O$ $H_2SO_4 \xrightarrow{Zn} ZnSO_4 + H_2$ $H_2SO_4 \xrightarrow{C_{12}H_{22}O_{11}} 12C + 11H_2O$ $H_2SO_4 \xrightarrow{S_8} SO_2 + H_2O$ $H_2SO_4 \xrightarrow{Na_2S} Na_2SO_4 + H_2S$ $H_2SO_4 \xrightarrow{BaCl_2} BaSO_4 + 2HCl$ $H_2SO_4 \xrightarrow{K_4[Fe(CN)_6]} K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO\uparrow$	It is used as oxidising agent, dehydrating agent and for the preparation of dyes, drugs, explosives, volatile acids, etc.

GROUP 17 ELEMENTS (HALOGEN FAMILY)

Group 17 elements are collectively called *halogens*.

General characteristics :

Electronic configuration	ns^2np^5
Elements	$_9F$, $_{17}Cl$, $_{35}Br$, $_{85}At$
Colour and physical state	F_2 (pale yellow gas), Cl_2 (greenish yellow gas), Br_2 (reddish brown liquid), I_2 (purple solid)
Atomic radii	Increase down the group
Ionisation enthalpy	Very high and decreases down the group.
Electronegativity	Decreases down the group.
Electron gain enthalpy	Cl > F > Br > I
Melting and boiling points	Increase down the group
Bond energy	$Cl_2 > Br_2 > F_2 > I_2$
Heat of hydration	$F^- > Cl^- > Br^- > I^-$

Chemical properties :

- F shows only – 1 oxidation state while other elements show –1, +1, +3, +5 and +7 oxidation states also.
- **General trends :**
  - **Reactivity :** $F_2 > Cl_2 > Br_2 > I_2$
  - **Boiling points :** HF > HI > HBr > HCl
  - **Melting points :** HI > HF > HBr > HCl
  - **Bond lengths :** HI > HBr > HCl > HF
  - **Bond dissociation enthalpy :** HF > HCl > HBr > HI
  - **Acidic strength :** HI > HBr > HCl > HF
  - **Thermal stability :** HF > HCl > HBr > HI
  - **Reducing power :** HI > HBr > HCl > HF
- **Oxides :**
  - Fluorine forms two oxides OF_2 and O_2F_2 called *oxygen fluorides*, other halogens form oxides in which oxidation states of these halogens range from +1 to +7.
  - The higher oxides of halogens are more stable than the lower ones.

- **Metal halides :**
  - **Ionic character :** $MF > MCl > MBr > MI$
  - For metals exhibiting more than one oxidation states, the halides in higher oxidation states will be more covalent than the one in lower oxidation states.

Chlorine (Cl_2) :

- **Preparation :**

$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$

$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

- **Manufacture :**
  - **Deacon's process :** By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ at 723 K.

    $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$
  - **Electrolytic process :** By the electrolysis of brine solution.
  - **Down's process :** Obtained as by-product during manufacture of sodium by electrolysis of fused NaCl.
- **Properties :** It is a yellowish green gas, poisonous in nature, soluble in water. Its aqueous solution is known as *chlorine water*.
  - **Bleaching action and oxidising property :**

    $Cl_2 + H_2O \longrightarrow HOCl + HCl$

    $HOCl \longrightarrow HCl + [O]$

    Coloured matter + [O] $\longrightarrow$ Colourless matter

The bleaching action of chlorine is permanent and is due to its oxidising nature.

  - **Action of hydrogen :**

    $H_2 + Cl_2 \xrightarrow[\text{Charcoal catalyst}]{\text{U.V. light}} 2HCl$
  - **Displacement reactions :**

    $2KBr + Cl_2 \longrightarrow 2KCl + Br_2$

    $2KI + Cl_2 \longrightarrow 2KCl + I_2$
  - **Action of NaOH :**

    $\underset{\text{(cold)}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$

    $\underset{\text{(hot and conc.)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$
  - **Addition reactions :**

    $SO_2 + Cl_2 \longrightarrow SO_2Cl_2$;

    $CO + Cl_2 \longrightarrow COCl_2$
- **Uses :** It is used as a bleaching agent, disinfectant and in the manufacture of $CHCl_3$, CCl_4, DDT, bleaching powder, poisonous gas phosgene ($COCl_2$), tear gas (CCl_3NO_2) and mustard gas ($ClC_2H_4SC_2H_4Cl$).

Hydrochloric acid (HCl) :

Preparation	Properties	Uses
$NaCl + H_2SO_4 \xrightarrow{420\text{ K}} NaHSO_4 + HCl$ $NaHSO_4 + NaCl \xrightarrow{823\text{ K}} Na_2SO_4 + HCl$	Colourless and pungent smelling gas, easily liquifiable, extremely soluble in water. $NH_3 + HCl \longrightarrow NH_4Cl$ $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$; $Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$ 3 parts of conc. HCl and 1 part of conc. HNO_3 is used for dissolving noble metals *e.g.*, gold, platinum $Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$; $3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$	In manufacture of Cl_2, NH_4Cl and glucose in medicine and as a laboratory reagent. For extracting glue from bones and purifying bone black.

Oxyacids of halogens :

Variation of the general properties of oxyacids of halogens

Halogen	**Hypohalous acids (O.S. of halogen = +1)**	**Halous acids (O.S. of halogen = +3)**	**Halic acids (O.S. of halogen = +5)**	**Perhalic acid (O.S. of halogen = +7)**	↓ Electronegativity decreases — ↓ Thermal stability decreases — ↓ Oxidising power decreases — ↓ Acidic strength decreases —
F	HOF	—	—	—	
Cl	HClO	$HClO_2$	$HClO_3$	$HClO_4$	
Br	HBrO	—	$HBrO_3$	$HBrO_4$	
I	HIO	—	HIO_3	HIO_4	
– Oxidation number of the central atom increases (+1, +3, +5, +7) → – Thermal stability increases → – Covalent character of *X*—O bond increases → – Oxidising power decreases → – Acidity increases → – Electronegativity of the central atoms remains the same —					

Interhalogens compounds : Halogens combine amongst themselves to form a number of interhalogens of the type XX', XX'_3, XX'_5 and XX'_7, where *X* is a larger size halogen (more electropositive) and *X′* is smaller size halogen.

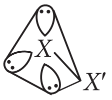
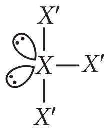
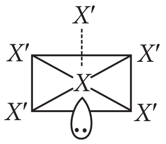
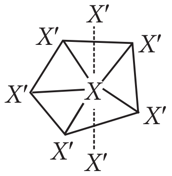
- **Preparation :**

$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{437\text{ K}} 2ClF$; $\underset{\text{(excess)}}{I_2 + 3Cl_2} \longrightarrow 2ICl_3$

$\underset{\text{(excess)}}{Cl_2 + 3F_2} \xrightarrow{573\text{ K}} 2ClF_3$; $\underset{\text{(diluted with water)}}{Br_2 + 3F_2} \longrightarrow 2BrF_3$

$\underset{\text{(equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl$; $\underset{\text{(excess)}}{Br_2 + 5F_2} \longrightarrow 2BrF_5$

- **Structures :**

Type	**Hybridisation**	**Shape**	**Structure**
XX	sp^3	Linear	
XX'_3	sp^3d	T-shaped	
XX'_5	sp^3d^2	Square pyramidal	
XX'_7	sp^3d^3	Pentagonal bipyramidal	

GROUP 18 ELEMENTS (NOBLE GASES)

These are monoatomic gases and are also known as *rare gases* or *aerogens*.

General characteristics :

Electronic configuration	ns^2np^6
Elements	$_2He$, $_{10}Ne$, $_{18}Ar$, $_{36}Kr$, $_{54}Xe$, $_{86}Rn$
Physical state	Gases
Atomic radii	Increase down the group.
Electron gain enthalpy	Positive
Melting and boiling points	Very low due to weak dispersion forces

Chemical properties : Noble gases are least reactive due to high ionization enthalpy and more positive electron gain enthalpy.

- **Xenon-fluorine compounds :**

$$\underset{\text{(excess)}}{Xe} + F_2 \xrightarrow{673\text{ K, 1 bar}} XeF_2$$

$$\underset{\text{(1 : 5 ratio)}}{Xe} + 2F_2 \xrightarrow{873\text{ K, 7 bar}} XeF_4$$

$$\underset{\text{(1 : 20 ratio)}}{Xe} + 3F_2 \xrightarrow{573\text{ K, 60–70 bar}} XeF_6$$

- **Xenon-oxygen compounds :**

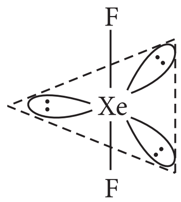
$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

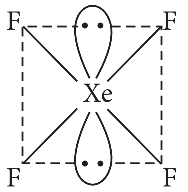
$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

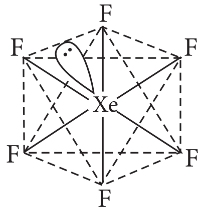
Structures of some compounds of xenon :



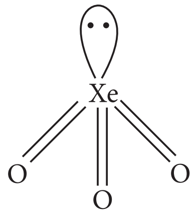
XeF_2
Linear, sp^3d



XeF_4
Square planar, sp^3d^2



XeF_6
Distorted octahedral, sp^3d^3



XeO_3
Pyramidal, sp^3

Uses :

Helium	Neon	Argon	Krypton	Xenon
– To lift weather balloons and air ships. – As breathing mixture. – For inflating the tyres of aeroplanes	– For advertising. – For filling sodium vapour lamps. – In becon light	– To create an inert atmosphere. – In geiger counters. – To date the age of rocks	– For runway and approach lights in airports. – In high efficiency miners' cap lamps.	– In electric flash bulbs for high speed photography. – Krypton and xenon are more efficient than argon in gas filled lamps.

Previous Years' CBSE Board Questions

7.1 Group 15 Elements

VSA (1 mark)

1. Arrange the following in the increasing order of property mentioned :
NH_3, PH_3, AsH_3, SbH_3, BiH_3 (Base strength)
(1/5, Delhi 2016, 2010)

2. Give reason :
Nitrogen does not form pentahalide.
(1/3, Delhi, AI 2016, 1/3, AI 2011C)

3. Account for the following :
BiH_3 is the strongest reducing agent amongst all the hydrides of group 15.
(1/5, Foreign 2015)

4. Why does $R_3P = O$ exist but $R_3N=O$ does not? (R = alkyl group) *(1/5, Delhi 2015C)*

5. Why is NH_3 more basic than PH_3?
(1/5, AI 2015C, 2014C)

6. Give reasons for the following :
$(CH_3)_3P = O$ exists but $(CH_3)_3N = O$ does not.
(1/3, AI 2014)

7. Why is the single N—N bond weaker than the single P—P bond? *(Foreign 2014)*

8. Account for the following :
Bi is a strong oxidizing agent in the +5 state.
(1/5, Foreign 2014)

9. Account for the following :
PCl_5 is known but NCl_5 is not known.
(1/5, Foreign 2014)

10. Arrange the following in the increasing order of their basic character :
NH_3, PH_3, AsH_3, SbH_3, BiH_3 *(Foreign 2014)*

11. Arrange the following group of substances in the order of the property indicated against each group :
NH_3, PH_3, AsH_3, SbH_3 – increasing order of boiling points. *(1/5, Delhi 2014C)*

12. Assign reasons for the following :
NF_3 is an exothermic compound whereas NCl_3 is not.
(1/5, AI 2014C, 2013C, 2012, 2011, 2010, 1/3, Delhi 2011, 2010)

13. Why is nitrogen gas very unreactive?
(AI 2014C)

14. Give reasons for the following : PH_3 has lower boiling point than NH_3. *(1/5, Delhi 2013)*

15. Explain the following :
$BiCl_3$ is more stable than $BiCl_5$.
(1/2, Delhi 2013C)

16. Account for the following :
Nitrogen is found in gaseous state.
(1/5, Delhi 2013C)

17. Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Why?
(1/2, AI 2013C, Delhi 2012C)

18. Account for the following :
NF_3 is an exothermic compound but NCl_3 is an endothermic compound.
(1/3, AI 2013C, 2012, 2011, 2010, 1/5, Delhi 2011, 2010)

19. Bismuth is a strong oxidising agent in the pentavalent state. Explain.
(1/3, AI 2013C, 1/5, Delhi 2012C)

20. Explain the following observations :
The molecules NH_3 and NF_3 have dipole moments which are of opposite direction.
(1/5, Delhi 2012)

21. Explain the following observation :
Phosphorus has greater tendency for catenation than nitrogen. *(1/5, AI 2012, 2010, 2009, 2008)*

22. Why is BiH_3 the strongest reducing agent amongst all the hydrides of group 15 elements?
(1/5, AI 2012C)

23. Account for the following :
Tendency to form pentahalides decreases down the group in group 15 of the periodic table.
(1/5, Delhi 2011)

24. Draw the structure of the following molecule :
NF_3 *(1/3, Foreign 2011)*

25. Explain the following :
+3 oxidation state becomes more and more stable from As to Bi in the group.
(1/5, Delhi 2011C)

26. Account for the following :
$BiCl_3$ is less covalent that PCl_3. *(1/5, Delhi 2011C)*

27. Explain the following observations giving appropriate reasons :
The stability of +5 oxidation state decreases down the group in group 15 of the periodic table. *(1/5, Delhi 2010)*

28. Why are pentahalides of a metal more covalent than its trihalides? *(AI 2010C)*

29. Account for the following :
NH_3 is clearly basic while PH_3 is only feebly basic. *(1/3, AI 2010C)*

30. Why is Bi(V) stronger oxidant than Sb(V)? *(Delhi, AI 2009)*

31. Account for the following :
NH_3 is a stronger base than PH_3. *(1/3, Delhi 2009, 2009C)*

32. Explain the following observation :
Phosphorus is much more reactive than nitrogen. *(1/3, Delhi 2009)*

33. Why is red phosphorus, less reactive than white phosphorus? *(AI 2009)*

34. Explain the following observation :
Ammonia has a higher boiling point than phosphine. *(1/5, AI 2009)*

35. Give reasons for the following observation :
The basic character of the hydrides of group 15 elements decreases with increasing atomic numbers. *(1/5, AI 2009C)*

36. Why is the bond angle in PH_3 molecule lesser than that in NH_3 molecule? *(1/3, AI 2008)*

37. Answer the following.
Of Bi (V) and Sb(V) which may be a stronger oxidising agent and why? *(1/2, AI 2008)*

38. Assign reasons for the following :
Ammonia (NH_3) has greater affinity for protons than phosphine (PH_3). *(1/5, AI 2008)*

39. Nitrogen does not form any pentahalide like phosphorus. Why? *(AI 2008C)*

40. Why is dinitrogen very unreactive as compared to phosphorus? *(AI 2008C)*

41. PH_3 has lower boiling point than NH_3. Why? *(1/3, Delhi 2008C)*

7.2 Dinitrogen

VSA (1 mark)

42. Give reasons for the following :
N_2 is less reactive at room temperature. *(1/3, AI 2015)*

43. Write the reaction of thermal decomposition of sodium azide. *(1/3, Delhi 2007)*

7.3 Ammonia

VSA (1 mark)

44. On adding NaOH to ammonium sulphate, a colourless gas with pungent odour is evolved which forms a blue coloured complex with Cu^{2+} ion. Identify the gas. *(Delhi 2016)*

45. Account for the following :
Bond angle in NH_4^+ is higher than NH_3. *(1/5, Foreign 2015)*

46. What happens when ammonium chloride is treated with $Ca(OH)_2$? *(1/5, AI 2015C)*

47. Why does NH_3 act as a Lewis base? *(AI 2014)*

48. Mention the optimum conditions for the industrial manufacture of ammonia by Haber's process. *(1/3, Foreign 2011)*

49. Complete the following reactions :
$NH_3 + NaOCl \longrightarrow$ *(1/3, AI 2009C)*

50. Complete the following chemical equation :
$Cu^{2+}_{(aq)} + \underset{\text{(excess)}}{NH_{3(aq)}} \longrightarrow$ .... *(1/3, Delhi 2008)*

51. Describe the favourable conditions for the manufacture of ammonia by Haber's process. *(1/5, AI 2008)*

52. How does ammonia react with a solution of Cu^{2+}? *(Delhi 2007)*

53. Write balanced equation when ammonia is dissolved in water. *(1/2, Delhi 2007)*

SA I (2 marks)

54. How is ammonia prepared on the large scale? Name the process and mention the optimum conditions for the production of ammonia by this process. *(2/5, AI 2014C)*

LA (5 marks)

55. How is ammonia manufactured industrially? Draw flow chart for the manufacture of ammonia. Give any two uses. *(AI 2007)*

7.4 Oxides of Nitrogen

VSA (1 mark)

56. $Pb(NO_3)_2$ on heating gives a brown gas which undergoes dimerisation on cooling? Identify the gas. *(AI 2016)*

57. Draw the structures of the following compounds: N_2O_5 *(1/3, Delhi 2014, AI 2012)*

58. Why does NO_2 dimerise? *(AI 2014, 2012C)*

59. Using VSEPR theory predict the probable structure of the following : N_2O_3 *(1/5, Delhi 2014C)*

60. What is the covalency of nitrogen in N_2O_5? *(Delhi 2013)*

61. Explain the following : NO_2 readily forms a dimer. *(1/2, Delhi 2013C, 2010)*

62. Explain the following :
The bond angles (O—N—O) are not of the same value in NO_2^- and NO_2^+. *(1/5, Delhi 2012)*

63. Give reason : Nitric oxide becomes brown when released in air *(1/5, Delhi, AI 2012C)*

64. State reasons for the following :
The N— O bond in NO_2^- is shorter than the N— O bond in NO_3^-. *(1/2, AI, Delhi 2011)*

65. Draw structures of the following species: NO_3^- *(1/5, AI 2008)*

VBQ (3 marks)

66. Mr. Rakesh, a chemistry teacher, observed some suspicious movements in his neighbourhood people and one day he saw packets of ammonium nitrate in their hand. As a chemistry teacher he knew that ammonium nitrate is used in explosives. He immediately informed the police about this. Police immediately took the required action and caught them with 3 kg of ammonium nitrate which they were using in explosives. Comment in brief :
(a) About the value/s displayed by Mr. Rakesh.
(b) Name of gas evolved on heating ammonium nitrate. Write the chemical reaction.
(c) Write two uses of ammonium nitrate. *(AI 2013C)*

7.5 Nitric Acid

VSA (1 mark)

67. Complete the following chemical reaction equations ;
$Cu + HNO_{3(dilute)} \longrightarrow$ *(1/5, Delhi 2015C, AI 2012)*

68. Complete the following chemical equations :
$I_2 + \underset{(Conc.)}{HNO_3} \longrightarrow$ *(1/5, Delhi 2011)*

69. Explain the following situations :
In the structure of HNO_3 molecule, the N—O bond (121 pm) is shorter than N—OH bond (140 pm). *(1/3, Delhi 2009)*

70. Explain the following observations :
In the structure of HNO_3, the N—O bond (121 pm) is shorter than N—OH bond (140 pm). *(1/5, AI 2009)*

7.6 Phosphorus – Allotropic Forms

VSA (1 mark)

71. Which allotrope of phosphorus is more reactive and why? *(1/5, Delhi 2015)*

72. Write the structural difference between white phosphorus and red phosphorus. *(1/3, Delhi 2014)*

73. Complete the following equations :
$P_4 + H_2O \longrightarrow$ *(1/2, AI 2014)*

74. Draw the structure of the following :
Red P_4 *(1/5, Foreign 2014)*

75. White phosphorus is more reactive than red phosphorus. *(1/5, Delhi 2012C)*

76. Explain the following giving appropriate reasons :
Red phosphorus is less reactive than white phosphorus. *(1/3, Foreign 2011)*

7.7 Phosphine

VSA (1 mark)

77. Complete the following chemical reaction equation :
$P_4 + NaOH + H_2O \longrightarrow$ *(1/5, Delhi 2015C, 2014C, 2009)*

78. Complete the following chemical equations :
$Ca_3P_2 + H_2O \longrightarrow$ *(1/3, Delhi 2014, 2008)*

79. Complete the following equation :
$HgCl_2 + PH_3 \longrightarrow$ *(1/3, AI 2011, 2009)*

7.8 Phosphorus Halides

VSA **(1 mark)**

80. Account for the following :
Solid PCl_5 is ionic in nature. *(1/5, Delhi 2016)*

81. Account for the following :
PCl_5 is more covalent than PCl_3. *(1/2, Delhi 2014)*

82. Complete the following equation :
$Ag + PCl_5 \longrightarrow$ *(1/2, AI 2014)*

83. Draw the structure of each of the following :
Solid PCl_5 *(1/2, Delhi 2014C)*

84. Draw the structure of $PCl_{5(s)}$ molecule. *(AI 2014C, 2009, 2008)*

85. Complete the following chemical equations :
$P_4 + SOCl_2 \longrightarrow$ *(1/2, AI 2014C, 1/5, Delhi 2012, 1/3, Foreign 2011)*

86. What happens when PCl_5 is heated? *(1/2, Delhi 2013, 2007)*

87. Why does PCl_3 fume in moisture? *(Delhi 2013C, 2012C)*

88. Which one of PCl_4^+ and PCl_4^- is not likely to exist and why? *(Delhi 2012)*

89. Explain the following observations :
All the bonds in PCl_5 molecule are not equivalent. *(Delhi 2012)*

90. Account for the following :
PCl_5 acts as an oxidising agent. *(1/5, AI 2012C)*

91. Explain the following observations :
All the P—Cl bonds in PCl_5 are not equivalent. *(1/5, AI 2009)*

92. Suggest a possible reason for the following observations :
In the solid state, PCl_5 behaves as an ionic species. *(1/3, AI 2009C)*

93. Assign a reason for each of the following statements :
All the bonds in PCl_5 are not equal in length. *(1/5, AI 2008)*

94. Why does PCl_5 fume in moisture? Give reaction. *(AI 2007)*

7.9 Oxoacids of Phosphorus

VSA **(1 mark)**

95. Arrange the following in the increasing order of property mentioned :
H_3PO_3, H_3PO_4, H_3PO_2 (Reducing character) *(1/5, Delhi 2016)*

96. What is the basicity of H_3PO_4? *(Delhi 2015)*

97. Draw the structure of the following :
$H_4P_2O_7$ (Pyrophosphoric acid) *(1/5, Foreign 2015)*

98. H_3PO_2 is a stronger reducing agent than H_3PO_3. *(1/3, Delhi, 1/3, AI, 1/5, Foreign 2014)*

99. What is the basicity of H_3PO_3? *(1/3, AI 2014)*

100. What happens when H_3PO_3 is heated? Write the reactions involved. *(Delhi 2013, 1/3, AI 2010C)*

101. Draw the structure of the following molecules :
$(HPO_3)_3$ *(Delhi 2013)*

102. Draw the structure of the following molecule :
H_3PO_3 *(1/2, Delhi 2013)*

103. Account for the following : H_3PO_2 has reducing nature. *(1/5, Delhi 2013C)*

104. Draw the structure of H_3PO_2 molecule. *(Delhi 2013C, 2012, AI 2013C)*

105. What is the basicity of H_3PO_2 acid and why? *(1/5, AI, 2011, 2012)*

106. Write a reaction to show the reducing behaviour of H_3PO_2. *(Delhi 2012C)*

107. Write chemical equations for the following processes : orthophosphorous acid is heated. *(1/3, Delhi 2008)*

7.10 Group 16 Elements

VSA **(1 mark)**

108. Give reasons :
SO_2 is reducing while TeO_2 is an oxidising agent. *(1/3, AI 2016)*

109. Account for the following :
There is large difference between the melting and boiling points of oxygen and sulphur. *(1/5, Delhi 2015)*

110. Give reasons for the following :
H_2Te is the strongest reducing agent amongst all the hydrides of group 16 elements. *(1/3, AI 2015)*

111. Why is dioxygen a gas but sulphur a solid? *(1/5, Delhi 2015C)*

112. Elements of group 16 generally show lower value of first ionization enthalpy compared to the corresponding elements of group 15 Why? *(1/5, AI 2015C)*

113. Arrange the following in the order of property indicated against each set :
H_2O, H_2S, H_2Se, H_2Te – increasing acidic character *(1/3, Delhi 2014)*

114. Give reasons for the following :
Oxygen has less electron gain enthalpy with negative sign than sulphur. *(1/3, AI 2014)*

115. Arrange the following group of substances in the order of the property indicated against the group :
O, S, Se, Te – increasing order of electron gain enthalpy with negative sign. *(1/5, Delhi 2014C)*

116. Assign reasons for the following :
SF_6 is kinetically inert. *(1/5, AI 2014C)*

117. Assign reasons for the following :
H_2S is more acidic than H_2O *(1/5, AI 2014C, 2011, 2009)*

118. Assign reasons for the following :
Sulphur has a greater tendency for catenation than oxygen. *(1/5, AI 2014C, 2012, 2009, 1/3, Delhi 2009)*

119. Account for the following :
Oxygen shows catenation behaviour less than sulphur. *(1/5, Delhi 2013)*

120. Account for the following :
H_2S is less acidic than H_2Te. *(1/5, Delhi 2013C, 1/3, AI 2010C)*

121. Account for the following : SF_6 in inert towards hydrolysis. *(1/5, Delhi 2013C)*

122. Account for the following :
Boiling point of water is much higher than that of hydrogen sulphide. *(1/3, AI 2013C)*

123. Explain the following observation :
Oxygen is a gas but sulphur is a solid. *(1/5, AI 2012)*

124. Account for the following :
Thermal stability of water is much higher than that of H_2S. *(1/5, Delhi 2012C)*

125. State reason for the following :
SF_6 is kinetically an inert substance. *(1/2, Delhi, AI 2011)*

126. Account for the following :
Elements of group 16 generally show lower value of first ionisation enthalpy compared to the elements in the corresponding periods of group 15. *(1/3, AI 2011C)*

127. How would you account for the following?
The value. of electron gain enthalpy with negative sign for sulphur is higher than that for oxygen. *(1/5, Delhi 2010)*

128. Explain the following situations :
SF_4 is easily hydrolysed whereas SF_6 is not easily hydrolysed. *(1/3, Delhi 2009)*

129. Give reasons for the following :
OF_6 compound is not known. *(1/3, Delhi 2009C)*

130. Give reason for the following observations : Sulphur exhibits tendency for catenation but oxygen does not do so. *(1/3, AI 2009C)*

131. Draw the structures of the following molecule :
SF_4 *(Delhi 2008)*

132. Assign reasons for the following :
SF_6 is much less reactive than SF_4. *(1/5, AI 2008)*

133. Assign a reason for each of the following statements :
The electron gain enthalpy with negative sign for oxygen (-141 kJ mol^{-1}) is less than that for sulphur (-200 kJ mol^{-1}) *(1/2, AI 2008)*

SA I (2 marks)

134. Account for the following :
(i) H_2S has lower boiling point than H_2O.
(ii) Reducing character decreases from SO_2 to TeO_2. *(2/3, Foreign 2015)*

135. Give reasons for the following :
(a) Oxygen molecule has the formula O_2 while sulphur is S_8.
(b) H_2S is less acidic than H_2Te. *(Delhi 2008C)*

7.11 Dioxygen

VSA (1 mark)

136. Complete the following reactions :
(i) $C_2H_4 + O_2 \rightarrow$
(ii) $4Al + 3O_2 \rightarrow$ *(Delhi 2008C)*

7.13 Ozone

VSA (1 mark)

137. Ozone is thermodynamically unstable? *(1/5, Delhi 2016)*

138. How the supersonic jet aeroplanes are responsible for the depletion of ozone layers? *(1/5, Delhi 2015)*

139. Account for the following :
The two O—O bond lengths in the ozone molecule are equal. *(1/3, Delhi 2014)*

140. Account for the following :
O_3 acts as a powerful oxidising agent. *(1/5, AI 2011C)*

141. Account for the following :
The two oxygen-oxygen bond lengths in ozone (O_3) molecule are same. *(1/3, AI 2011C)*

142. Draw the structure of O_3 molecule. *(Delhi 2010)*

143. Complete the following chemical reaction equations :
$I^-_{(aq)} + H_2O_{(l)} + O_{3(g)} \longrightarrow$ *(1/2, Delhi 2009)*

7.14 Sulphur – Allotropic Forms

VSA (1 mark)

144. Which allotrope of sulphur is thermally stable at room temperature? *(Foreign 2015)*

145. Account for the following :
Sulphur in vapour form exhibits paramagnetic behaviour.
(1/3, AI 2014, 2008, 1/5, Foreign, 2014, 2011 1/5, Delhi 2012, 2011C, 2008)

146. Draw the structure of the following : S_8 *(1/5, AI 2008)*

SA I (2 marks)

147. Name the two most important allotropes of sulphur. Which one of the two is stable at room temperature? What happens when the stable form is heated about 370 K? *(Foreign 2014)*

7.15 Sulphur Dioxide

VSA (1 mark)

148. What happens when :
SO_2 gas is passed through an aqueous solution Fe^{3+} salt? *(1/2, AI 2016)*

149. What happens when sulphur dioxide reacts with chlorine in the presence of charcoal? *(1/3, Delhi 2015)*

150. Predict the shape and the asked angle (90° or more or less) in the following case :
SO_3^{2-} and the angle O — S — O *(1/5, Delhi 2012)*

151. What happens when
Sulphur dioxide gas is passed through an aqueous solution of a Fe (III) salt? *(1/3, AI 2011)*

152. Complete the following chemical equation :
$Fe^{3+} + SO_2 + H_2O \longrightarrow$ *(1/5, Foreign 2011, Delhi 2011C)*

153. Why are the two S — O bonds in SO_2 molecule of equal strength? *(1/5, AI 2010C)*

154. Excess of SO_2 reacts with sodium hydroxide solution. *(1/5, Delhi 2009C)*

LA (5 marks)

155. (a) How is sulphur dioxide prepared in :
(i) Laboratory
(ii) Industrially?
(b) What happens when sulphur dioxide is passed through water and reacts with sodium hydroxide? Write balanced equation.
(c) Write its any two uses. *(Delhi 2007)*

7.16 Oxoacids of Sulphur

VSA (1 mark)

156. Write the structure of the following molecule :
H_2SO_3 *(1/2, AI 2015)*

157. Draw the structure of the following :
H_2SO_4 *(1/5, Delhi 2015C, 2014)*

158. Draw the structure of the following : $H_2S_2O_8$ *(1/5, Foreign 2014, 2011, 1/3, Delhi 2013, 2012, 1/3, AI 2009C)*

159. Draw the structure of the following molecule :
$H_2S_2O_7$ *(1/3, AI 2013, 2009, 1/5, Delhi 2012)*

160. Write the structure of the following species :
H_2SO_5. *(1/2, Delhi 2007)*

SA II (3 marks)

161. Draw the structure of
(i) H_2SO_3 (ii) H_2SO_4
(iii) $H_2S_2O_7$ *(Delhi 2007)*

7.17 Sulphuric Acid

VSA (1 mark)

162. Write the conditions to maximize the yield of H_2SO_4 by Contact process. *(1/5, Delhi 2016)*

163. Complete the following equation :
$Cu + conc.\ H_2SO_4 \longrightarrow$ *(1/3, AI 2014)*

164. Complete the following equation :
$CaF_2 + H_2SO_4 \longrightarrow$ *(1/2, AI 2014)*

165. Complete the following equation :
$C + conc.\ H_2SO_4 \longrightarrow$
(1/2, AI 2014, Delhi, Foreign 2011)

166. Why is $K_{a_2} << K_{a_1}$ for H_2SO_4 in water? *(1/2, Foreign 2014)*

167. Account for the following :
Concentrated sulphuric acid has charring action on carbohydrates. *(1/3, AI 2013C,)*

168. Complete the following equation :
$SO_3 + H_2SO_4 \longrightarrow$ *(1/5, AI 2011)*

SA I (2 marks)

169. With the help of chemical equation explain the principle of Contact process in brief for the manufacture of sulphuric acid by Contact process. *(2/3, AI 2013C)*

SA II (3 marks)

170. Describe the Contact process for the manufacture of sulphuric acid with special reference to the reaction conditions, catalysts used and yield in the process.
(3/5, Delhi 2015C)

171. Describe the conditions and the steps involved in the manufacture of sulphuric acid by Contact process. Write the necessary reactions. (No diagram is required.) *(3/5, Delhi 2012C)*

172. With the help of chemical equations explain the principle of contact process in brief for the manufacture of sulphuric acid. (No diagram).
(AI 2012C)

7.18 Group 17 Elements

VSA (1 mark)

173. Account for the following :
Acidic character increases from HF to HI.
(1/5, Delhi 2015)

174. F_2 has lower bond dissociation enthalpy than Cl_2. Why? *(1/5, Delhi 2015, 2013)*

175. Why are halogens coloured?
(1/5, Delhi 2015C, AI 2012)

176. Answer the following :
Why are halogens strong oxidising agents?
(1/5, AI 2015C)

177. Arrange the following in the order of property indicated against each set :
HF, HCl, HBr, HI – increasing bond dissociation enthalpy *(1/2, Delhi 2014)*

178. Arrange the following groups of substances in the order of the property indicated against each group :
F_2, Cl_2, Br_2, I_2 – increasing order of bond dissociation enthalpy.
(1/5, Delhi 2014C, 2011C)

179. Why is F_2 a stronger oxidising agent than Cl_2?
(AI 2014C, 2009)

180. Assign reasons for the following :
HCl is a stronger acid than HF though fluorine is more electronegative than chlorine.
(1/5, AI 2014C)

181. Account for the following :
Fluorine does not exhibit positive oxidation state. *(1/5, Delhi 2013, 2011C, 2009, 1/5, AI 2012, 2010)*

182. Fluorine exhibits only –1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation state also. Why is it so?
(Delhi 2013C)

183. HF is a weaker acid than HCl. Why?
(AI 2013C)

184. Account for the following :
HF is not stored in glass bottles but is kept in wax-coated bottles. *(1/3, AI 2013C)*

185. Explain the following observations.
Despite lower value of its electron gain enthalpy with negative sign, fluorine (F_2) is a stronger oxidising agent than Cl_2. *(1/5, AI 2012)*

186. Despite having greater polarity, hydrogen fluoride boils at a lower temperature than water. *(1/5, AI 2012)*

187. Give reason :
Bond dissociation energy of F_2 is less than that of Cl_2. *(1/5, Delhi 2012C, 2009, 1/5, AI 2012C)*

188. Explain giving reason for the following situation. In aqueous medium HCl is stronger acid than HF. *(1/2, Foreign 2011)*

189. Account for the following :
F$_2$ is a stronger oxidising agent than Cl$_2$. *(1/3, AI 2011C)*

190. Arrange HF, HCl, HBr and HI in the order of increasing acid strength. *(AI 2011C, Delhi 2009C)*

191. Account for the following :
Electron gain enthalpy with negative sign for fluorine is less than that for chlorine. *(1/3, AI 2011C, 1/3, AI 2010)*

192. How would you account for the following?
Halogens are strong oxidizing agents *(1/5, Delhi 2010, 1/3, AI 2010C)*

193. Explain the following :
The electron gain enthalpy with negative sign for fluorine is less than that for chlorine, still fluorine is a stronger oxidising agent than chlorine. *(1/3, AI 2010)*

194. Account for the following :
Fluorine always exhibits an oxidation state of –1 only in its compounds. *(1/5, Delhi 2010C)*

195. Explain the following observation :
Hydrogen fluoride has a much higher boiling point than hydrogen chloride. *(1/5, AI 2009)*

196. Suggest a possible reason for the following observations :
Fluorine forms the largest number of interhalogen compounds amongst the halogens. *(Delhi 2011C,1/3, AI 2009C)*

197. Give reasons for the following observation :
Hydrogen iodide is a stronger acid than hydrogen fluoride in aqueous solution. *(1/3, AI 2009C)*

198. Complete the following chemical equation :
$F_{2(g)} + H_2O_{(l)} \longrightarrow$ .... *(1/3, Delhi 2008)*

199. Assign reasons for the following :
The negative value of electron gain enthalpy of fluorine is less than that of chlorine. *(1/5, AI 2008)*

200. Fluorine exhibits only – 1 oxidation state in its compounds whereas other halogens exhibit many other oxidation states. Why? *(AI 2008C)*

SA I (2 marks)

201. Compare the oxidizing action of F$_2$ and Cl$_2$ by considering parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy. *(2/5, Delhi 2016)*

202. Arrange the following in order property indicated for each set.
(i) F$_2$, Cl$_2$, Br$_2$, I$_2$ increasing bond dissociation enthalpy.
(iii) HF, HCl, HBr, HI increasing acid strength *(2/3, Delhi 2010)*

203. Describe the following about halogens (Group 17 elements):
(i) Relative oxidising power of halogens.
(ii) Relative acidic strength of the hydrogen halides. *(2/3, Delhi 2010C)*

7.19 Chlorine

VSA (1 mark)

204. Write balanced equation for the following reactions :
Chlorine reacts with dry slaked lime. *(1/3, Delhi 2015C)*

205. Name two poisonous gases which can be prepared from chlorine gas. *(AI 2013)*

206. Account for the following :
Bleaching of flowers by Cl$_2$ is permanent while that of SO$_2$ is temporary? *(1/3, AI 2013C)*

207. Complete the following chemical equation :
$\underset{\text{(hot and conc.)}}{NaOH} + Cl_2 \longrightarrow$ *(1/5, Delhi 2012, 2010, 2008, 1/3, AI 2009C)*

208. Account for the following :
Chlorine water loses its yellow colour on standing. *(1/5, AI 2012C)*

209. Complete the following reaction equation :
NaOH (cold & dilute) + $Cl_2 \longrightarrow$ *(1/3, Delhi 2011C, AI 2010)*

210. Complete this reaction :
$6NaOH + 3Cl_2 \longrightarrow$ *(1/3, AI 2011C)*

211. Complete the following reaction equation :
$I_2 + H_2O + Cl_2 \longrightarrow$ *(AI 2011C, 1/5, Delhi 2010C)*

212. Write the balanced chemical equation for the reaction of Cl_2 with hot and conc. NaOH solution. Justify that this reaction is a disproportionation reaction. *(1/5, Delhi 2008C)*

7.20 Hydrogen Chloride

VSA (1 mark)

213. Iron dissolves in HCl to form $FeCl_2$ and not $FeCl_3$. *(1/5, Foreign 2015, 2014)*

7.21 Oxoacids of Halogens

VSA (1 mark)

214. Account for the following :
Fluorine forms only one oxoacid HOF. *(1/5, Delhi 2016)*

215. Account for the following
$HClO_4$ is stronger acid than HClO. *(1/5, Foreign 2015)*

216. Draw the structures of the following : $HClO_4$ *(1/2, AI 2014, 2011, 2009, 1/5 Foreign 2014)*

217. Account for the following :
Fluorine does not form oxoacids. *(1/5 AI 2012C)*

218. How would you account for the following :
The oxidising power of oxoacids of chlorine follows the order :

$$HClO_4 < HClO_3 < HClO_2 < HClO$$

(1/2, Foreign 2011)

219. Draw the structure of the following : $HClO_3$ *(1/5, AI 2009)*

220. Answer the following :
Which neutral molecule would be isoelectronic with ClO^-? *(1/2, AI 2008, 1/3, AI 2008C)*

221. Arrange $HClO_3$, $HClO_2$, HOCl and $HClO_4$ in order of increasing acid strength. Give reason for your answer. *(1/5, Delhi 2008C)*

SA I (2 marks)

222. Draw the structure of
(i) Hypochlorous acid.
(ii) Chlorous acid. *(AI 2007)*

7.22 Interhalogen Compounds

VSA (1 mark)

223. Draw the structure of : BrF_5 *(1/5, Delhi 2016)*

224. Give reasons : ICl is more reactive than I_2. *(1/3, AI 2016, 2012, 2011C, 2009)*

225. Draw the structure of the following : ClF_3 *(Delhi 2015, AI 2008, 2012)*

226. Draw the structures of the following : BrF_3 *(1/5, Delhi 2015C, 2014, 2014C, 2013,2011, 2009 1/5, AI 2014, 2011, 2008)*

227. Write the formula and describe the structure of noble gas species which is isostructural with BrO_3^- *(1/5, Delhi 2014C)*

228. Complete the following chemical equation :
$F_2(Excess) + Cl_2 \xrightarrow{300°C}$ *(1/5, AI 2014C)*

229. F_2 is more reactive than ClF_3 but ClF_3 is more reactive than Cl_2. *(1/5, Delhi 2013C)*

230. Predict the shape and the asked angle (90° or more or less) in each of the following cases.
ClF_3 and the angle F — Cl — F *(1/5, Delhi 2012)*

231. Account for the following :
$BrCl_3$ is more stable than $BrCl_5$. *(1/5, AI 2012C)*

232. Why is ICl more reactive than I_2? *(AI 2012C, 2010C)*

233. Answer the following :
Why does fluorine not play the role of a central atom in interhalogen compounds? *(AI 2011)*

234. Complete the following chemical equations:
$Br_2 + \underset{(excess)}{F_2} \longrightarrow$ *(Foreign 2011)*

235. ClF_3 molecule has a *T*-shaped structure and not a trigonal planar one. *(1/3, Delhi 2010)*

236. Flourine never acts as the central atom in polyatomic interhalogen compounds. *(1/5, AI 2010)*

237. Give one use of ClF_3. *(1/5, Delhi 2008C)*

238. How are interhalogen compounds formulated and how are they prepared? *(1/3, AI 2008C)*

SA I (2 marks)

239. How are interhalogen compounds formed? What general compositions can be assigned to them? *(AI 2013)*

7.23 Group 18 Elements

VSA **(1 mark)**

240. Draw the structure of XeF_4.
(1/5, Delhi 2016, 2014,2009C, 2008, 1/2, AI 2016, 2014, 2010)

241. What happens when XeF_4 reacts with SbF_5?
(AI 2016)

242. Write the structures of the following molecule : $XeOF_4$. *(1/5, AI 2015, 2015C, 2013, 2012, Foreign 2014)*

243. Give reasons for the following :
Helium is used in diving apparatus as a diluent for oxygen. *(1/3, AI 2015)*

244. Draw the structures of the following : XeF_2
(1/5, Foreign 2015, Delhi 2014, 2012, 2013, 2011, AI 2014, 2008)

245. Draw the structure of the following : XeO_3
(1/5, AI 2015C, 2014)

246. Complete the following equation :
$XeF_4 + O_2F_2 \longrightarrow$ *(1/2, Delhi 2014C, 2012, 1/2 AI 2014, 2012)*

247. Complete the following equation :
$XeF_2 + H_2O \longrightarrow$ *(1/2, AI 2014, 2009, 1/5, Delhi 2011, 2011C)*

248. Account for the following :
Unlike xenon, no distinct chemical compound of helium is known. *(1/5, Foreign 2014)*

249. Complete the following chemical reaction equation : $XeF_4 + H_2O \longrightarrow$
(1/2, AI 2014C, 2012, 2011, 2011C, 2008, 1/5, Delhi 2012)

250. What inspired N. Bartlett for carrying out reaction between Xe and PtF_6? *(Delhi 2013)*

251. Draw the structures of the following molecules: XeF_6 *(1/2, AI 2013, 1/5, Delhi 2012)*

252. Account for the following :
Helium is used in diving apparatus.
(1/3, AI 2013C)

253. Complete the following chemical reactions equations :
$XeF_6 + H_2O \longrightarrow$ *(1/5, Delhi 2012, 1/3, Foreign 2011, 1/2, AI 2010, 2010C)*

254. Predict the shape and asked angle (90° or more or less) in each of the following case.
XeF_2 and the angle F – Xe – F
(1/5, Delhi 2012)

255. Explain the following observations:
Helium forms no real chemical compound.
(1/5, AI 2012)

256. Noble gases have low boiling points. Why?
(Delhi 2012C, AI 2011)

257. Complete the following reaction equation :
$XeF_2 + PF_5 \longrightarrow$
(1/5, Delhi 2011C, 1/2, AI 2011C)

258. Explain the following :
XeF_2 is linear molecule without a bend.
(1/3, AI 2010)

259. Explain the following situations :
XeF_2 has a straight linear structure and not a bent angular structure. *(1/3, Delhi 2009)*

260. Explain the following observations :
The majority of known noble gas compounds are those of Xenon. *(1/3, Delhi 2009)*

261. Write balanced chemical equations for the following reaction : XeF_6 is hydrolysed
(1/3, Delhi 2009C)

262. Complete the following reaction :
$XeF_6 + KF \longrightarrow$ *(1/3, AI 2009C)*

263. Draw the structures of XeF_4 and predict their shapes. *(1/2, AI 2009C)*

264. Write the chemical equation for the following process : PtF_6 and xenon are mixed together
(1/3, Delhi 2008)

265. Assign reasons for the following :
Of the noble gases only xenon is known to form well-established chemical compounds.
(1/5, AI 2008)

266. Why do some noble gases form compounds with fluorine and oxygen only? *(Delhi 2008C)*

267. List the uses of neon and argon gases.
(2/5, AI 2007)

SA I **(2 marks)**

268. **(i)** Which noble gas is used in filling balloons for meteorological observations?
(ii) Complete the equation :
$XeF_2 + PF_5 \longrightarrow$ *(2/5, Delhi 2015)*

269. Write the balanced chemical equations for obtaining XeO_3 and $XeOF_4$ from XeF_6.
(1/5, Delhi 2013C)

270. Explain the following :
(i) Xenon does not form such fluorides as XeF_3 and XeF_5.
(ii) Out of noble gases, only Xenon is known to form real chemical compounds
(Delhi 2012C)

271. How is XeO_3 obtained? Write the related chemical equations. Draw the structure of XeO_3. *(AI 2012C)*

272. Write the formulae and the structure of noble gas species which are isostructural with
(i) ICl_4^- (ii) BrO_3^-
(Delhi 2009C)

273. Complete the following reactions :
(i) $XeF_4 + O_2F_2 \longrightarrow$
(ii) $XeF_4 + SbF_5 \longrightarrow$ *(2/3, AI 2009C)*

274. Draw structure of (i) $XeOF_4$ (ii) XeO_3.
(Delhi 2007)

SA II (3 marks)

275. (i) How does xenon atom form compounds even though the xenon atom has a closed shell electronic configuration?
(ii) Draw the structure of $XeOF_4$.
(iii) Complete and balance the following equation : $XeF_4 + H_2O \longrightarrow$
(AI 2008C)

Detailed Solutions

1. Increasing (Lewis) base strength order is :
$BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$
The reason for this order is that as we move from NH_3 to BiH_3, the size of the central atom increases. Hence lone pair is not easily available for donation. The electron density on the central atom decreases on moving from NH_3 to BiH_3 and so the basic strength also decreases.

2. Nitrogen can not expand its octet due to absence of *d*-orbitals.

3. Among hydrides of group-15 elements, the bond length increases from N – H to Bi – H with increasing size of element. Bi – H bond is longest and weakest, it can break more easily and evolve H_2 gas which acts as the reducing agent.

4. $R_3N = O$ molecule has five covalent bonds with N atom. The octet in N cannot be extended as it does not have *d* orbitals for the formation of $p\pi$-$d\pi$ bond.

In the case of $R_3P = O$, P can extend its octet since it has empty *d*-orbitals in its valence shell and form $p\pi$-$d\pi$ bond.

5. Lewis basic nature of NH_3 and PH_3 molecules is due to the presence of lone pairs on N and Bi atoms, respectively. P atom is much larger than N atom and also has empty *d* orbitals. Electron density due to lone pair on P gets diffused because of the presence of *d*-orbitals and so the lone pair is not easily available for donation. Hence PH_3 is less basic than NH_3.

6. *Refer to answer 4.*

7. The single N—N bond is weaker than the single P—P bond because of high interelectronic repulsion of the non-bonding electrons, occurring due to the small bond length.

8. On moving down the group, the stability of +5 oxidation state decreases while +3 oxidation state increases due to inert pair effect.
Thus +5 oxidation state of Bi is less stable and Bi(V) is a stronger oxidising agent.

9. Nitrogen cannot expand its valency beyond 4 due to absence of *d*-orbitals whereas phosphorus show pentavalency due to presence of *d*-orbitals.

10. *Refer to answer 1.*

11. $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$
The abnormally high boiling point of NH_3 is due to the intramolecular H-bonding. Further as we move from PH_3 to BiH_3 the molecular mass increasing. As a result, the van der walls forces of attraction increase and the boiling points increase regularly from PH_3 to BiH_3.

12. In case of nitrogen, only NF_3 is known to be stable. N–F bond strength is greater than F–F bond strength, therefore, formation of NF_3 is spontaneous. In case of NCl_3, N—Cl bond strength is lesser than Cl—Cl bond strength. Thus, energy has to be supplied during the formation of NCl_3.

13. The bond dissociation enthalpy of triple bond in $N{\equiv}N$ is very high due to $p\pi$ - $p\pi$ overlap. Hence, N_2 is less reactive at room temperature.

14. Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. Therefore, the boiling point of PH_3 is lower than NH_3.

15. $BiCl_3$ is more stable than $BiCl_5$. On moving down the group, the stability of + 5 oxidation state decreases while + 3 oxidation state increases due to inert pair effect.

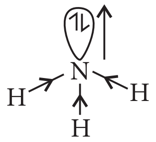
16. Nitrogen exists as a diatomic moleucle with a triple bond between two atoms. These N_2 molecules are held together by weak van der Waals force of attraction which can be easily broken by the collision of the molecules at room temperature. Therefore N_2 is a gas at room temperature.

17. *Refer to answer 2.*

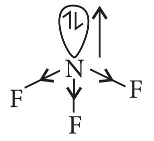
18. *Refer to answer 12.*

19. *Refer to answer 8.*

20.



In NH_3 the bond moment and lone pair moment work in same direction. Hence, net dipole moment is higher.



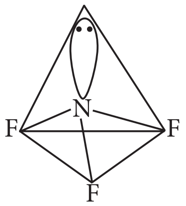
In NF_3 the bond moment and lone pair moment work in opposite direction. Hence, net dipole moment is lower.

21. The property of catenation depends upon the strength of the element - element bond. Since, P – P (213 kJ mol^{-1}) bond strength is much more than N – N (159 kJ mol^{-1}) bond strength so, phosphorus shows marked catenation properties than nitrogen.

22. *Refer to answer 3.*

23. Due to inert pair effect the stability of +5 oxidation state decreases down the group in group 15. Hence tendency to form pentahalide decreases down the group 15 of the periodic table.

24. Total no. of electrons around the central N atom = 5
No. of bond pairs = 3
No. of lone pairs = 1
Hybridisation = *sp*^{3}
Therefore, according to VSEPR theory; NF_3 should be pyramidal.



25. On moving down the group, the stability of + 5 oxidation state decreases while that of + 3 oxidation state increases due to inert pair effect.

26. $BiCl_3$ is less covalent than PCl_3 because the size of Bi^{3+} is much larger than P^{3+} (According to Fajan's rule)

27. *Refer to answer 23.*

28. In + 5 oxidation state charge/radius ratio is higher than that in + 3 oxidation state. Hence, +5 oxidation state has more polarising power than that of + 3 oxidation state and pentahalides (in O.S. + 5) are more covalent than trihalides.

29. *Refer to answer 5.*

30. On moving down the group, the stability of +5 oxidation state decreases while + 3 oxidation state increases due to inert pair effect. Thus +5 oxidation state of Bi is less stable than +5 oxidation state of Sb. Therefore, Bi(V) is a stronger oxidising agent than Sb(V).

31. Due to presence of a lone pair of electrons on N and P, both NH_3 and PH_3 act as Lewis bases and accept a proton to form an additional N—H and P—H bonds respectively

$$H_3\ddot{N} + H^+ \longrightarrow NH_4^+ \;;\; H_3\ddot{P} + H^+ \longrightarrow PH_4^+$$

However, due to smaller size of N over P, N—H bond thus formed is much stronger than the P—H bond. Therefore, NH_3 has higher proton affinity than PH_3. In other words, NH_3 is more basic than PH_3.

32. Since nitrogen forms triple bond between the two N-atoms and the phosphorus forms single bond between two P-atoms, bond dissociation energy of nitrogen (941.4 kJ mol^{-1}) is larger than the bond dissociation energy of phosphorus (213 kJ mol^{-1}). Hence, phosphorus is much more reactive than nitrogen.

33. White phosphorus is more reactive than red phosphorus under normal conditions because of angular strain in the P_4 molecule where the angles are only 60°.

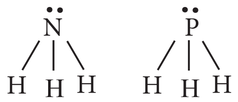
34. NH_3 molecules are held together by strong inter molecular hydrogen bonds whereas PH_3 molecules are held together by weak van der Waals bonds. Thus, NH_3 has a higher boiling point than PH_3.

35. *Refer to answer 1.*

36. The bond angle in PH_3 is much lower [93.6°] than that in NH_3 [107.8°] due to less repulsion between bond pairs.

37. *Refer to answer 30.*

38. PH_3 and NH_3 both are Lewis bases, since they have a lone pair of electrons on 'N' and 'P' atom respectively.



Because size of P is larger than N atom, therefore N atom carries more negative charge density than carried by P. Hence NH_3 has more proton affinity than PH_3.

39. *Refer to answer 9.*

40. Bond dissociation enthalpy of N_2 molecule is very high (941.4 kJ mol^{-1}) and so is least reactive at normal temperature and remains inert even in atmosphere.
Yellow phosphorus exists as P_4 molecule with a tetrahedral shape. The P – P – P bond angle is about 60° because of which the molecule is under tremendous strain and so phosphorus is reactive.

41. *Refer to answer 34.*

42. In N_2 molecule N atoms are held by triple bonds. It has very high bond dissociation energy (941.4 kJ mol^{-1}). Therefore N_2 is inert at room temperature.

43. Thermal decomposition of sodium azide gives nitrogen gas.

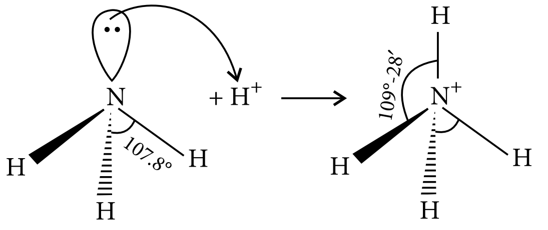
$$2NaN_3 \longrightarrow 2Na + 3N_2$$

44. $(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta}$

$$\underset{\substack{\text{(colourless and}\\ \text{pungent odoured gas)}}}{2NH_3} + Na_2SO_4 + 2H_2O$$

$$Cu^{2+} + 4NH_3 \longrightarrow \underset{\text{(Blue colour)}}{[Cu(NH_3)_4]^{2+}}$$

45. N in NH_3 in sp^3–hybridized. It has three bond pairs and one lone pair around N. Due to stronger lone pair-bond pair repulsions than bond pair-bond pair replusions. the tetrahedral angle decreases from 109° – 28′ to 107.8°. As a result, NH_3 is pyramidal. However, when it reacts with a proton, it forms NH_4^+ ion which has four bond pairs and no lone pair. Due to the absence of lone pair-bond pair repulsions and presence of four identical bond pair-bond pair interaction, NH_4^+ assumes tetrahedral geometry with a bond angle of 109° – 28′. This explains why the bond angle in NH_4^+ is higher than in NH_3.



NH_3 molecule (Pyramidal) NH_4^+ ion (Tetrahedal)

46. $2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$

47. NH_3 has a lone pair of electrons on the N-atom which it can donate to an electron acceptor. Hence, NH_3 acts as a Lewis base.

48. Optimum conditions for the production of ammonia are :

Temperature = ~ 700 K

Pressure = about 200 atm (200×10^5 Pa)

Catalyst = iron oxide with small amounts of K_2O and Al_2O_3 (as promoters).

49. $NH_3 + NaOCl \longrightarrow NaNH_2 + HClO$

50. $\underset{\text{Blue}}{Cu^{2+}_{(aq)}} + \underset{\text{(excess)}}{4NH_{3(aq)}} \longrightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]^{2+}_{(aq)}}$

51. *Refer to answer 48.*

52. *Refer to answer 50.*

53. $NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$

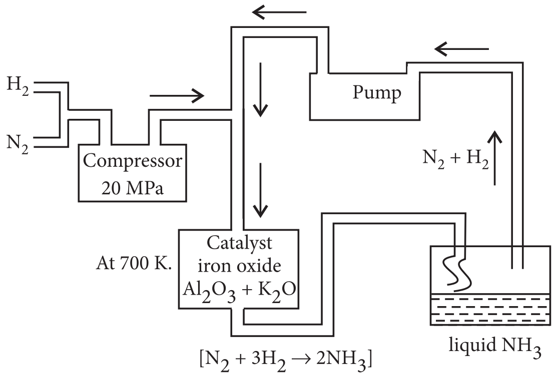
54. Ammonia is manufactured industrially by Haber's process.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$; $\Delta_r H° = -46.1$ kJ mol^{-1}

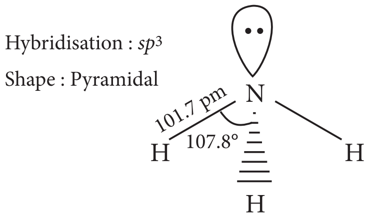
This is a reversible exothermic reaction. High pressure about 200 atm, low temperature about 700 K and use of catalyst such as iron oxide with small amounts of Al_2O_3 and K_2O would favour the formation of ammonia according to Le-Chatelier's principle.

55. *Refer to answer 54.*

The flow chart for the production of ammonia is shown below :



Structure of ammonia :



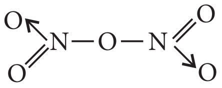
Uses of ammonia : (i) Ammonia is used to produce various nitrogenous fertilizers - for example : urea, ammonium nitrate, ammonium phosphate etc.

(ii) Liquid ammonia is used as a refrigerant.

56. $2Pb(NO_3)_2 \xrightarrow{673\text{ K}} 4NO_2 + 2PbO + O_2$

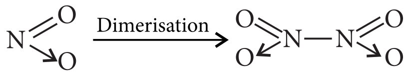
NO_2 is the brown gas

57. The structure of N_2O_5 is

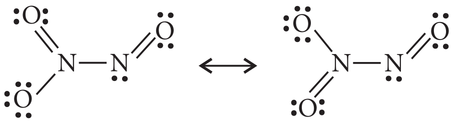


Covalence of nitrogen in N_2O_5 = 4

58. Because NO_2 contains odd number of valence electrons and on dimerisation, it is converted to stable N_2O_4 molecule with even number of electrons.

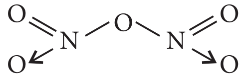


59.



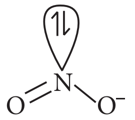
Planar structure

60. In N_2O_5 covalence of nitrogen is four.



61. *Refer to answer 58.*

62. In NO_2^- 'N' atom has sp^2-hybridisation whereas in NO_2^+, 'N' atom has sp-hybridisation.



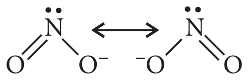
$O=\overset{\oplus}{N}=O$

Hence, bond angles are not of the same value.

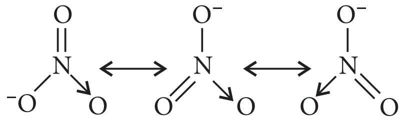
63. Nitric oxide forms brown fumes of nitrogen dioxide (NO_2) instantaneously in the presence of air.

$2NO + O_2 \longrightarrow 2NO_2$

64. In NO_2^-, the average N—O bond order is 1.5 due to two resonating structures whereas in NO_3^-, the average N—O bond order is 1.33 due to three resonating structures. Higher the bond order, shorter is the bond length.

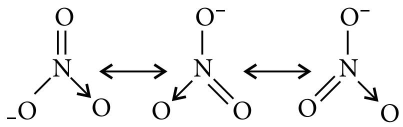


(NO_2^-)



(NO_3^-)

65.



66. (a) Mr. Rakesh displayed values like awareness care, concern alertness.

(b) Nitrous oxide (N_2O)

$NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$

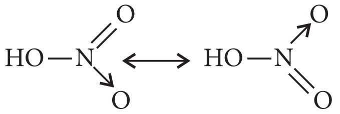
(c) (i) It is used as a fertiliser.

(ii) It is used to modify the detonation rate.

67. $3\,Cu + 8HNO_{3\,(dilute)} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

68. $I_2 + 10HNO_{3(conc.)} \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$

69. HNO_3 is supposed to exist in two resonating forms. Due to two resonating structures, N — O bond is shorter than N—OH bond.



70. *Refer to answer 69.*

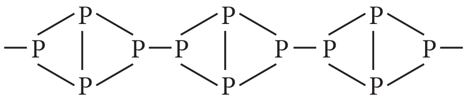
71. White phosphorus is most reactive of all the allotropes because it is unstable due to the angular strain on P_4 molecule with bond angle of 60°.

72. White phosphorus consists of discrete tetrahedral P_4 molecule.

Red phosphorus is polymeric, consisting of chains of P_4 tetrahedra linked together.

73. $P_4 + H_2O \longrightarrow$ No reaction

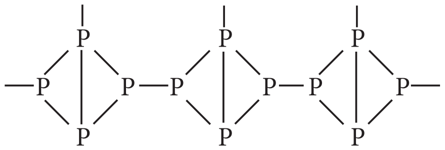
74.



Red phosphorus

White phosphorus is more reactive due to its discrete tetrahedral structure and angular strain.

75. White phosphorus consists of discrete P_4 molecules in which each phosphorus atom is tetrahedrally bonded to other three phosphorus atoms. So, white phosphorus is highly reactive. In red phosphorus, P_4 molecules are linked in an extended chain structure. So, red phosphorus is much less reactive.



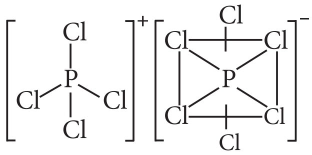
76. *Refer to answer 75.*

77. $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$

78. $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

79. $3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$

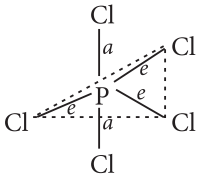
80. Phosphorus pentachloride is a salt containing the tetrahedral cation $[PCl_4]^+$ and the octahedral anion $[PCl_6]^-$ therefore, it is ionic in solid state.



81. *Refer to answer 28.*

82. $2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$

83.



In PCl_5, there are three equatorial and two axial bonds present. Since, three equatorial bonds are repelled by two bond pairs and two axial bonds are repelled by three bond pairs so, axial bonds are weaker and longer than the equatorial bonds.

84. *Refer to answer 83.*

85. $P_4 + 10SO_2Cl_2 \longrightarrow 4\ PCl_5 + 10SO_2$

86. $PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$

87. PCl_5 hydrolyses in the presence of moisture giving fumes of HCl.
$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

88. PCl_4^- because PCl_3 cannot form bond with Cl^- ions.

89. *Refer to answer 83.*

90. The oxidation state of phosphorus in PCl_5 is +5. As P has five electrons in its valence shell, it cannot increase its oxidation state beyond +5 by donating electrons. It can decrease its oxidation number from +5 to +3 or some lower value. So, PCl_5 acts as an oxidising agent.

91. *Refer to answer 83.*

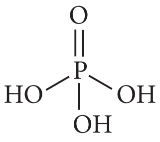
92. *Refer to answer 80.*

93. *Refer to answer 83.*

94. *Refer to answer 87.*

95. Reducing character of oxyacids of phosphorus depends on the number of P–H bonds. More the number of P–H bonds in oxyacid, more is the reducing character. H_3PO_2 has two P–H bonds, H_3PO_3 has one P–H bond and H_3PO_4 has no P–H bond. Thus, order of reducing character is $H_3PO_2 > H_3PO_3 > H_3PO_4$

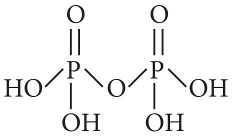
96. Basicity of oxoacids of P is equal to the number of P—OH bonds in the molecule.



H_3PO_4
Orthophosphoric acid

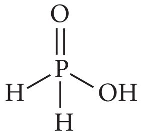
It is tribasic due to the presence of three replaceable hydrogen atoms.

97.

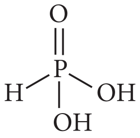


Structure of pyrophosphoric acid

98. The acids which contain P—H bond, have strong reducing properties. Hypophosphorus acid (H_3PO_2) contains two P—H bonds, whereas orthophosphorus acid (H_3PO_3) has one P—H bond. Hence, H_3PO_2 is stronger reducing agent than H_3PO_3.

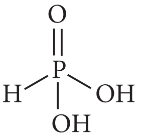


H_3PO_2



H_3PO_3

99.

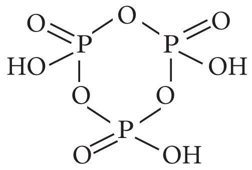


(H_3PO_3)
Orthophosphorus acid

It is dibasic due to the presence of two replaceable hydrogen atoms.

100. $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$

101.



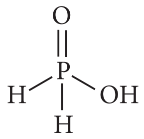
$(HPO_3)_3$

102. *Refer to answer 99.*

103. *Refer to answer 98.*

104. *Refer to answer 98.*

105.



It is monobasic acid due to the presence of one replaceable hydrogen.

106. $4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4Ag + 4HNO_3 + H_3PO_4$

107. *Refer to answer 100.*

108. The +6 oxidation state of S is more stable than +4 therefore, SO_2 acts as a reducing agent. Further, since the stability of +6 oxidation decreases from S to Te therefore, the reducing character of the dioxides decreases while their oxidising character increases. Thus, TeO_2 acts as an oxidising agent.

109. Oxygen molecules are held together by weak van der Waals' forces because of the small size and high electronegativity of oxygen. Sulphur shows catenation and the molecule is made up of 8 atoms with strong intermolecular forces. Hence, there is large difference in the melting and boiling points of oxygen and sulphur.

110. Bond dissociation enthalpy and hence thermal stability of hydrides decreases from H_2O to H_2Te. Therefore, H_2Te releases hydrogen readily. Hence, H_2Te is the strongest reducing agent amongst all the hydrides of group 16.

111. O_2 molecules are held together by weak van der Waal's forces because of the small size and high electronegativity of oxygen.

Sulphur shows catenation and the molecule is made up of eight atoms, (S_8) with strong intermolecular attractive forces. Hence, sulphur exists as solid at room temperature.

112. The first ionization enthalpy of group 16 elements is lower than those of group 15 elements despite their smaller atomic radii and higher nuclear charge. This is due to the relatively symmetrical and more stable configuration of the elements of group15 as compared to those of the elements of group 16.

113. $H_2O < H_2S < H_2Se < H_2Te$

As the atomic size increases down the group, the bond length increases and hence, the bond strength decreases. Consequently, the cleavage of *E*—H bond (*E*= O, S, Se, Te, etc.) becomes easier. As a result, the tendency to release hydrogen as proton increases *i.e.*, acidic strength increases down the group.

114. The electron gain enthalpy of oxygen is less negative than sulphur. This is due to its small size. As a result of which the electron-electron repulsion in the relatively small 2*p*-subshell are comparatively larger and hence the incoming electrons are not accepted with same ease as in case of other (sulphur) elements of this group.

115. Electron gain enthalpy of oxygen is less negative than sulphur due to compact size of oxygen atom (inter-electronic repulsion is more in O). From sulphur onwards enthalpy again becomes less negative upto Po.

$O < S > Se > Te > Po$

116. In SF_6, S atom is sterically protected by six F atoms and does not allow any reagent to attack on the S atom. Due to these reasons, SF_6 is kinetically an inert substance.

117. *Refer to answer 113.*

118. The property of catenation depends upon *E* – *E* bond strength of the element. As S – S bond is much stronger (213 kJ mol^{-1}) than O – O bond (138 kJ mol^{-1}), sulphur has greater tendency for catenation than oxygen.

119. *Refer to answer 118.*

120. *Refer to answer 113.*

121. *Refer to answer 116.*

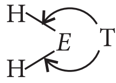
122.

	H_2O		H_2S
Boiling point	373 K	>	213 K

The abnormally high boiling point of H_2O is due to strong intermolecular H-bonding. Since, all other elements have much lower electronegativity than oxygen, they do not undergo H-bonding.

123. *Refer to answer 111.*

124. The thermal stability of the hydrides decrease from H_2O to H_2Te. This is because as the size of central element increases, the bond *E*—H become weaker and thus breaks on heating.



These bonds break on heating.

125. *Refer to answer 116.*

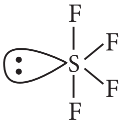
126. *Refer to answer 112.*

127. *Refer to answer 114.*

128. In SF_6, six F atoms protect the sulphur atom from attack by the reagent to such an extent that even thermodynamically most favourable reactions like hydrolysis do not occur. But in SF_4, S is not sterically protected as it is surrounded by only four F atoms hence, SF_4 is reactive.

129. OF_6 compound is not known because oxygen cannot expand its octet due to unavailability of *d*-orbital.

130. *Refer to answer 118.*

131.


SF_4 is a gas with sp^3d-hybridisation and have trigonal bipyramidal geometry and see-saw structure due to the presence of lone pair of electrons in equatorial positions.

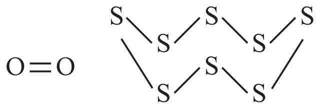
132. *Refer to answer 128.*

133. *Refer to answer 114.*

134. (i) *Refer to answer 122.*

(ii) *Refer to answer 108.*

135. (a) Due to small size oxygen forms $p\pi$ - $p\pi$ multiple bonds. As a result, oxygen exists as diatomic (O_2) molecule. Due to its bigger size sulphur does not form $p\pi$ - $p\pi$ multiple bonds. Consequently, sulphur because of its higher tendency of catenation and lower tendency for $p\pi$ - $p\pi$ multiple bonds forms octa-atomic (S_8) molecules having eight membered puckered ring structure.



(b) *Refer to answer 113.*

136. (i) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

(ii) $4Al + 3O_2 \rightarrow 2Al_2O_3$

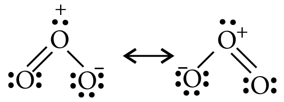
137. Ozone is thermodynamically unstable and decomposes into oxygen.

$$2O_3 \xrightarrow{\Delta} 3O_2;\ \Delta H = -\text{ve}$$

The above conversion is exothermic *i.e.*, ΔH is negative. Also, entropy increases *i.e.*, ΔS = + ve. Thus, ΔG for the decomposition of ozone is negative. Hence, it is thermodynamically unstable.

138. Nitrogen oxide emitted from the exhausts of supersonic jet aeroplanes readily combines with ozone to form nitrogen dioxide and diatomic oxygen. Since supersonic jets fly in the stratosphere near the ozone layer, they are responsible for the depletion of ozone layer.

139. The two O — O bond lengths in the ozone molecule are equal as it is a resonance hybrid of two main forms :

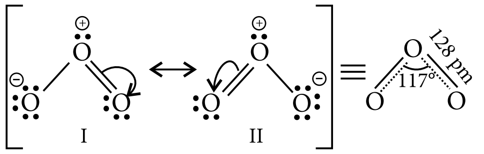


140. Ozone is a powerful oxidising agent because ozone has higher energy content than dioxygen hence, decomposes to give dioxygen and atomic oxygen.

$$\underset{\text{Ozone}}{O_{3(g)}} \longrightarrow \underset{\text{Dioxygen}}{O_{2(g)}} + \underset{\text{Atomic oxygen}}{O_{(g)}}$$

The atomic oxygen thus liberated brings about the oxidation while molecular oxygen is set free.

141. *Refer to answer 139.*

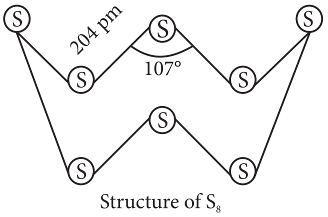
142.


(Resonating Structure) Resonance hybrid

143. $2I^-_{(aq)} + H_2O_{(l)} + O_{3(g)} \rightarrow 2OH^-_{(aq)} + I_{2(s)} + O_{2(g)}$

144. Rhombic sulphur

145. At elevated temperature, sulphur vapour exists as S_2 molecules which are paramagnetic like O_2.

146.


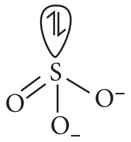
Structure of S_8

147. Sulphur exists in numerous allotropes of which yellow rhombic (α-sulphur) and monoclinic (β-sulphur) is most important. The stable form is rhombic, which transform to monoclinic sulphur, when heated above 369 K.

148. $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

149. $SO_{2(g)} + Cl_{2(g)} \rightarrow SO_2Cl_{2(l)}$

150.



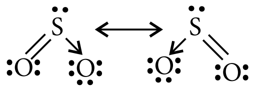
sp^3 Hybridisation

Shape : pyramidal O—S —O angle > 90°

151. *Refer to answer 148.*

152. *Refer to answer 148.*

153.



Due to resonance, the two π-bonds are equal (143 pm) and are of equal strength.

154. $2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$

155. (a) (i) It is prepared in laboratory by treating a sulphite with dil. H_2SO_4.

$$SO^{2-}_{3(aq)} + 2H^+_{(aq)} \longrightarrow H_2O_{(l)} + SO_{2(g)}$$

(ii) It is produced industrially as a by - product of the roasting of sulphide ores.

$$4FeS_{2(s)} + 11O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$$

(b) When sulphur dioxide is passed through water, it forms a solution of sulphurous acid.

$$SO_{2(g)} + H_2O_{(l)} \rightleftharpoons \underset{\text{Sulphurous acid}}{H_2SO_{3(aq)}}$$

When sulphur dioxide reacts with sodium hydroxide solution sodium, sulphite is formed.

$$2NaOH + SO_2 \longrightarrow \underset{\text{Sod. sulphite}}{Na_2SO_3} + H_2O$$

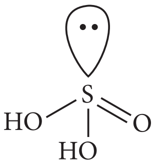
(c) Uses : (i) In refining sugar and petroleum.

(ii) In bleaching wool and silk.

(iii) As an anti - chlor, disinfectant and preservative.

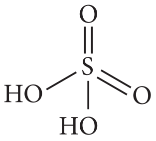
(iv) In the manufacture of sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite.

156.



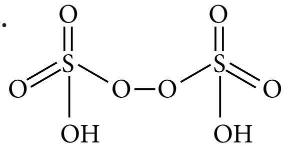
Sulphurous acid
(H_2SO_3)

157.



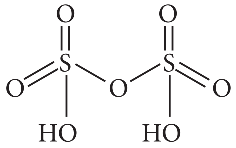
Sulphuric acid
(H_2SO_4)

158.



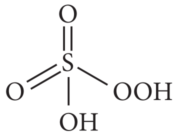
Peroxosulphuric acid
($H_2S_2O_8$)

159.



Pyrosulphuric acid (oleum)
($H_2S_2O_7$)

160.



(Caro's acid)
H_2SO_5

161. (i) *Refer to answer 156.*

(ii) *Refer to answer 157.*

(iii) *Refer to answer 159.*

162. In Contact process, the rate determining step is

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3, \Delta_f H° = -196.6 \text{ kJ mol}^{-1}$$

This reaction is reversible and exothermic *i.e.*, Δ*H* is negative. Thus, according to Le-Chatelier's principle, the conditions to maximise the yield are as follows :

(a) At lower temperature : As heat is evolved in the reaction so, at lower temperature the reaction proceeds more in forward direction.

(b) At higher pressure : As three moles of gaseous reactants give two moles of gaseous products thus, at higher pressure reaction moves in forward direction.

163. $Cu + \underset{\text{(conc.)}}{2H_2SO_4} \longrightarrow CuSO_4 + SO_2 + 2H_2O$

164. $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

165. $C + 2H_2SO_4 \text{ (conc.)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)} + 2SO_{2(g)}$

166. $H_2SO_{4(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + HSO^-_{4(aq)}$

$K_{a_1} > 10$, very large

$HSO^-_{4(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + SO^{2-}_{4(aq)}$

$K_{a_2} = 1.2 \times 10^{-2}$

K_{a_2} is smaller thanK_{a_1} because dissociation of HSO_4^- is less probable due to presence of negative charge on the ion.

167. Concentrated H_2SO_4 removes water from organic compounds hence, it has charring action on carbohydrates.

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{Sugar charcoal}}{12C} + H_2O$$

168. $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$

169. (a) **Contact process :** It involves three stages :

(i) Burning of sulphur or sulphide ore in air to generate SO_2.

$S + O_2 \rightarrow SO_2$

$4FeS_2 + 11O_2 \rightarrow 8SO_2 + 2Fe_2O_3$

(ii) Conversion of SO_2 to SO_3 by reaction with oxygen in the presence of V_2O_5 catalyst.

$$2SO_{2(g)} + O_{2\,(g)} \xrightleftharpoons{V_2O_5} 2SO_{3(g)}; \quad \Delta_r H^\circ = -196 \text{ kJ mol}^{-1}$$

(iii) The SO_3 gas from the catalytic converter is absorbed in conc. H_2SO_4 to form oleum ($H_2S_2O_7$). Dilution of oleum with water gives H_2SO_4 of desired concentration.

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (Oleum)

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

170. *Refer to answers 162 and 169.*

171. *Refer to answer 169.*

172. *Refer to answer 169.*

173. The acidic strength of the hydrohalic acids in the order :

HF < HCl < HBr < HI

This order is a result of bond dissociation enthalpies of H — *X* bond decreases from H — F to H — I as the size of halogen atom increases

174. F_2 has lower bond dissociation enthalpy than Cl_2 because F atom is very small and hence the electron-electron repulsions between the lone pairs of electrons are very large.

175. Halogens absorb radiations in visible region which results in excitation of outer electrons to higher level resulting in different colours.

176. General electronic configuration of halogens is ns^2np^5. They easily accept one electron to complete their octet. This makes them a good oxidising agent.

177. HI < HBr < HCl < HF

178. Increasing bond dissociation enthalpy order is

$I_2 < F_2 < Br_2 < Cl_2$

Bond dissociation enthalpy of F_2 is less than that of Br_2 and Cl_2 due to the lone pair - lone pair repulsions.

179. Fluorine is the strongest oxidising agent as it accept electron easily. It oxidise other halide ions in solution or even in solid phase.

$F_2 + 2X^- \longrightarrow 2F^- + X_2$ (X = Cl, Br or I)

$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$ (X = Br or I)

$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$

180. HF is the weakest acid because of its high bond dissociation energy due to small size of fluorine atom.

181. Since, fluorine is the most electronegative element, it shows only a negative oxidation state of –1, and does not show any positive oxidation state.

182. This is due to non-availability of *d*-orbitals in valence shell of fluorine.

183. *Refer to answer 180.*

184. HF acid attacks glass with the formation of fluoro silicate ions. Thus it is stored in wax-coated glass bottles to prevent the reaction.

185. *Refer to answer 179.*

186. Higher boiling point of H_2O is due to the extensive H-bonding than HF.

187. *Refer to answer 174.*

188. In aqueous medium HCl is stronger acid than HF because bond dissociation enthalpy of H—Cl is lower than that of HF

189. *Refer to answer 179.*

190. *Refer to answer 173.*

191. The electron gain enthalpy of fluorine is less negative than that of chlorine due to the small size of fluorine atom.

192. *Refer to answer 176.*

193. *Refer to answer 179.*

194. *Refer to answer 182.*

195. Hydrogen fluoride has much higher boiling point (b.p. 293 K) than hydrogen chloride (b.p. 189 K) due to strong hydrogen bonding.

196. Fuorine is the most electronegative element among halogens and it cannot exhibit any positive oxidation state. Therefore, it form largest number of interhalogen compounds.

197. *Refer to answer 173.*

198. $2F_{2(g)} + 2H_2O_{(l)} \rightarrow 4H^+_{(aq.)} + 4F^-_{(aq.)} + O_{2(g)}$

199. *Refer to answer 191.*

200. *Refer to answer 182.*

201. Oxidising power of a substance depends on the factors like bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy. Due to small size of fluorine, its electron gain enthalpy is less than that of chlorine. However, its low bond dissociation enthalpy and high hydration enthalpy compensate the low electron gain enthalpy. Fluorine because of its small size has higher hydration enthalpy than chlorine. Also, due to repulsion between electrons it has lower bond dissociation energy. Thus, fluorine has better oxidising action than chlorine.

202. (i) *Refer to answer 178.*
(ii) *Refer to answer 173.*

203. (i) From top to bottom in group - 17 oxidising power of halogens decreases
$F_2 > Cl_2 > Br_2 > I_2$.
(ii) *Refer to answer 174.*

204. $2Cl_2 + 2Ca(OH)_{2(dil.)} \xrightarrow{\text{Cold}} CaCl_2 + \underset{\text{Calcium hypochlorite}}{Ca(OCl)_2} + 2H_2O$

205. (i) Phosgene (ii) Mustard gas

206. The bleaching action of Cl_2 is due to oxidation of coloured substances to colourless substances by nascent oxygen. Since, the bleaching action of Cl_2 is due to oxidation and that of SO_2 is due to reduction, therefore, bleaching effect of Cl_2 is permanent while that of SO_2 is temporary.

207. $\underset{\text{(hot and conc.)}}{6NaOH} + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + H_2O$

208. Chlorine water on standing loses its yellow colour due to the formation of HCl and HClO.

209. $2NaOH_{\ (dil.)} + Cl_{2(aq)} \rightarrow NaCl_{(aq)} + NaClO_{(aq.)} + H_2O_{(l)}$

210. *Refer of answer 207.*

211. $I_2 + 6H_2O + 5Cl_2 \rightarrow \underset{\text{Iodic acid}}{2HIO_3} + 10HCl$

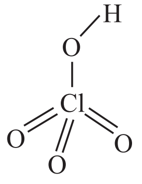
212. $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$
This reaction is a disproportionation reaction as chlorine from zero oxidation state is changed to – 1 and + 5 oxidation states.

213. Its reaction with iron produces H_2.
$Fe + 2HCl \rightarrow FeCl_2 + H_2$
Liberation of hydrogen prevents the formation of ferric chloride.

214. Fluorine forms only one oxoacid HOF. Because for the formation of other oxoacids *d* orbitals are required for the multiple $p\pi$ - $d\pi$ bonding between extra oxygen atoms and fluorine.
High electronegativity and small size of fluorine also favours only the formation of one oxoacid.

215. As the number of oxygen bonded to the central atom increases, the oxidation number of the oxidation atom increases causing a weakening of the O—H bond strength and an increase in the acidity. Hence, $HClO_4$ is stronger acid than HClO.

216.



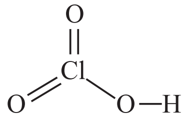
$HClO_4$ (Perchloric acid)

217. *Refer to answer 214.*

218. As the stability of the oxoanion increases, its tendency to decompose to give O_2 decreases and hence its oxidising power decreases. Since the stability of the oxoanion decreases in the order : $ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$ therefore oxidising power of their oxoacids increases in the reverse order :

$$HClO_4 < HClO_3 < HClO_2 < HClO.$$

219.

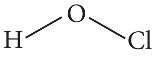


220. ClO^- has 17 + 8 + 1 = 26 electrons.
A neutral molecule with 26 electrons is OF_2 (8 + 2 × 9) = 18 + 8 = 26 electrons.

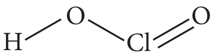
221. Acid strength of oxoacids of the same halogen increases with increase in oxidation number of the halogen.
Thus the increasing order of acid strength is

$$\underset{+1}{HOCl} < \underset{+3}{HClO_2} < \underset{+5}{HClO_3} < \underset{+7}{HClO_4}$$

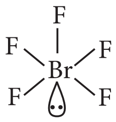
222. (i) HOCl : Hypochlorous acid



(ii) HOClO : Chlorous acid

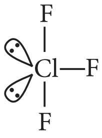


223. Geometry – Octahedral
Shape – Square pyramidal
Hybridisation – sp^3d^2

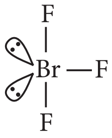


224. Interhalogen compounds are more reactive than halogens (except flourine) because $X — X'$ bond (I—Cl bond) in interhalogens is weaker than $X—X$ bond (I—I bond) in halogens except F — F bond. In other words I —Cl bond is weaker than I — I bond. That's why ICl is more reactive than I_2.

225. Hybridisation – sp^3d
Structure – Trigonal bipyramidal
Shape – Bent (*T*-shaped)
Angle F–Cl–F : less than 90°



226. Hybridisation – sp^3d
Structure – Trigonal bipyramidal
Shape – Bent -*T*



227. The central atom Br has seven electrons. Four of these electrons form two double bonds or coordinate bonds with two oxygen atoms while the fifth electron forms a single bond with O^- ion. The remaining two electrons form one lone pair. Hence, in all there are three bond pairs and one lone pair around Br atom in BrO_3^-. Therefore, according to VSEPR theory, BrO_3^- should be pyramidal.
Here, BrO_3^- has 26(7 + 3 × 6 + 1 = 26) valence electrons. A noble gas species having 26 valence electrons is XeO_3(8 + 3 × 6 = 26). Thus, like BrO_3^-, XeO_3 is also pyramidal.

228. $3F_2$ (excess) + $Cl_2 \xrightarrow{300°C} 2ClF_3$

229. Interhalogen compounds are more reactive than halogen because the $X' — X$ bond in interhalogens is weaker than $X—X$ bond in halogens. But in case of flourine, the F—F bond is weaker. This is because of the small size of fluorine atoms, the F—F bond distance is very small due to which there is appreciable inter-electronic repulsion. This repulsion weakens the bond between two fluorine atoms. Hence, F_2 is more reactive than ClF_3 but ClF_3 is more reacitve than Chlorine.

230. *Refer to answer 225.*
Angle F — Cl — F : Less than 90°

231. O.S. of Br in $BrCl_5$ is +5, whereas in case of $BrCl_3$ is +3. As Br is more stable in +3 oxidation state than +5, due to inert pair effect. Therefore, it is unstable and readily reduces from +5 to +3 oxidation state.

232. *Refer to answer 224.*

233. Fluorine does not have *d*-orbitals and its cannot show higher oxidation state. Therefore it does not play the role of a central atom in inter halogen compounds.

234. $Br_2 + 5F_2$ (excess) $\longrightarrow 2BrF_5$

235. In ClF_3, central atom Cl has three bond pairs and two lone pairs. According to VSEPR theory, the two lone pairs will occupy the equatorial position to mimimise *lp–lp* and *lp – bp* repulsion. In addition, the axial fluorine atoms will be bent towards the equatorial fluorine in order to minimise the *lp–lp* repulsions. That's why ClF_3 has a bent T shaped structure. For figure *refer to answer 226.*

236. *Refer to answer 233.*

237. ClF_3 is used for the production of UF_6 in enrichment of U^{235}.
$U_{(s)} + 3ClF_{3(l)} \rightarrow UF_{6(g)} + 3ClF_{(g)}$

238. Interhalogen compounds are formulated as XX', XX'_3, XX'_5 and XX'_7 where X is halogen of larger size and X' of smaller size.
The interhalogen compounds can be prepared by direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions, for example,

$$\underset{\text{(Equal volume)}}{Cl_2 + F_2} \xrightarrow{437\ K} 2ClF$$

$Cl_2 + \underset{\text{(Excess)}}{3F_2} \xrightarrow{573\text{ K}} 2ClF_3$

$\underset{\text{(equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl$

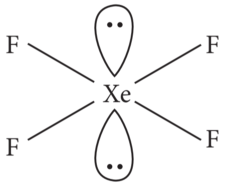
$I_2 + \underset{\text{Excess}}{3Cl_2} \rightarrow 2ICl_3$

$\underset{\text{(diluted with water)}}{Br_2 + 3F_2} \rightarrow 2BrF_3$

$Br_2 + \underset{\text{(excess)}}{5F_2} \rightarrow 2BrF_5$

239. *Refer to answer 238.*

240.

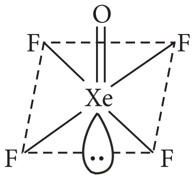


XeF_4
Shape : Square planar
Hybridisation : sp^3d^2

241. $XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$

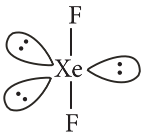
242. $XeOF_4$ is square pyramidal.

Hybridisation - sp^3d^2



243. Helium is used in diving apparatus as diluent for oxygen because of its low solubility (as compared to N_2) in blood, a mixture of oxygen and helium is used in diving apparatus used by deep sea divers.

244. XeF_2 :
Total valence electron pair
$= \frac{8+2}{2} = 5$
Bond pairs = 2
Lone pairs = 5 – 2 = 3
Hybridisation = sp^3d
Geometry = Trigonal bipyramidal
Shape = Linear

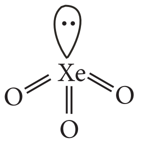


245. XeO_3 :

Hybridisation = sp^3

Geometry = Tetrahedral

Shape = Pyramidal



246. $XeF_4 + O_2F_2 \xrightarrow{143\text{ K}} XeF_6 + O_2$

247. $2XeF_{2(s)} + 2H_2O_{(l)} \longrightarrow 2Xe_{(g)} + 4HF_{(aq)} + O_{2(g)}$

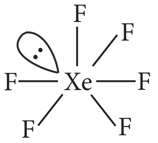
248. Extremely small size and fully filled outer orbital makes helium very stable and reistant to chemical reaction and hence, it does not form compounds unlike bigger atoms of other elements of noble gas family.

249. $6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 24HF + 3O_2 + 4Xe$

250. Neil Bartlett first prepared a red compound which is formulated as $O_2^+PtF_6^-$. He then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ/mol) is almost identical with Xe (1170 kJ/mol). He made efforts to prepare same type of compound with Xe and was successful in preparing another red compound $Xe^+PtF_6^-$.

251. XeF_6

Total valence electron pairs $= \frac{8+6}{2} = 7$
Bond pair = 6
Lone pair = 7 – 6 = 1
Hybridisation = sp^3d^3
Shape = Distorted octahedral
Geometry = Pentagonal bipyramidal



252. *Refer to answer 243.*

253. $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$

254. *Refer to answer 244.*

F — Xe — F : 180°

255. Helium has completely filled ns^2 electronic configurations in its valence shell. Due to its small size and high IE, helium is chemically unreactive. That's why it forms no real chemical compound.

256. Noble gases being monoatomic gases are held together by weak London dispersion forces, therefore they have low boiling points.

257. $XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$

258. Since there are two Xe—F covalent bonds and three one pairs in XeF_2. According to VSEPR theory, the shape of XeF_2 is linear.

259. *Refer to answer 258.*

260. Since, xenon (Xe) has least ionization energy among noble gases hence it readily forms chemical compounds particularly with O_2 and F_2.

261. *Refer to answer 253.*

262. $XeF_6 + KF \longrightarrow K^+[XeF_7]^-$

263. *Refer to answer 240.*

264. $PtF_6 + Xe \longrightarrow Xe^+[PtF_6]^-$

265. Except radon which is radioactive, Xe has least ionisation energy among noble gases and hence it readily forms chemical compounds particularly with oxygen and fluorine.

266. Fluorine and oxygen are the most electronegative elements and hence are very reactive. Therefore, they form compounds with noble gases particularly with xenon.

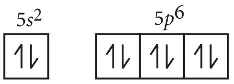
267. Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes.
Argon is used to provide an inert atmosphere in high temperature metallurgical processes and for filling electric bulbs.

268. (i) Helium is used for filling balloons for meteorological observations because it is non-inflammable.

(ii) *Refer to answer 257.*

269. $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

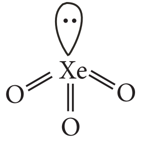
$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$

270. (i) 

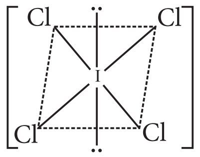
All the orbital of Xe have paired electrons. The promotion of one, two or three electrons from $5p$-filled orbitals to the $5d$-vacant orbitals will give rise to two, four and six-half filled orbitals. Therefore, xenon can combine with even number of fluorine atoms, not add. Thus, it cannot form XeF_3 and XeF_5.

(ii) *Refer to answer 265.*

271. XeO_3 can be obtained by hydrolysis of XeF_4 and XeF_6.
$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24\ HF + 3O_2$.
$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

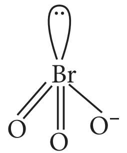
Structure – 

272. (i) Structure of ICl_4^- : I in ICl_4^- has four bond pairs and two lone pairs. Therefore, according to VSEPR theory, it should be square planar as shown. Here, ICl_4^- has $(7 + 4 \times 7 + 1) = 36$ valence electrons. A noble gas species having 36 valence electrons is $XeF_4(8 + 4 \times 7 = 36)$. Therefore, like ICl_4^-, XeF_4 is also square planar.



Square Plannar

(ii) Structure of BrO_3^- : The central atom Br has seven electrons. Four of these electrons form two double bonds or coordinate bonds with two oxygen atoms while the fifth electron forms a single bond with O^- ion. The remaining two electrons form one lone pair. Hence, in all there are three bond pairs and one lone pair around Br atom in BrO_3^-. Therefore, according to VSEPR theory, BrO_3^- should be pyramidal.



Pyramidal

Here, BrO_3^- has $26(7 + 3 \times 6 + 1 = 26)$ valence electrons. A noble gas species having 26 valence electrons is $XeO_3(8 + 3 \times 6 = 26)$. Thus, like BrO_3^-, XeO_3 is also pyramidal

273. (i) *Refer to answer 246.*

(ii) *Refer to answer 241.*

274. (i) *Refer to answer 242.*

(ii) *Refer to answer 245.*

275. (i) *Refer to answer 265.*

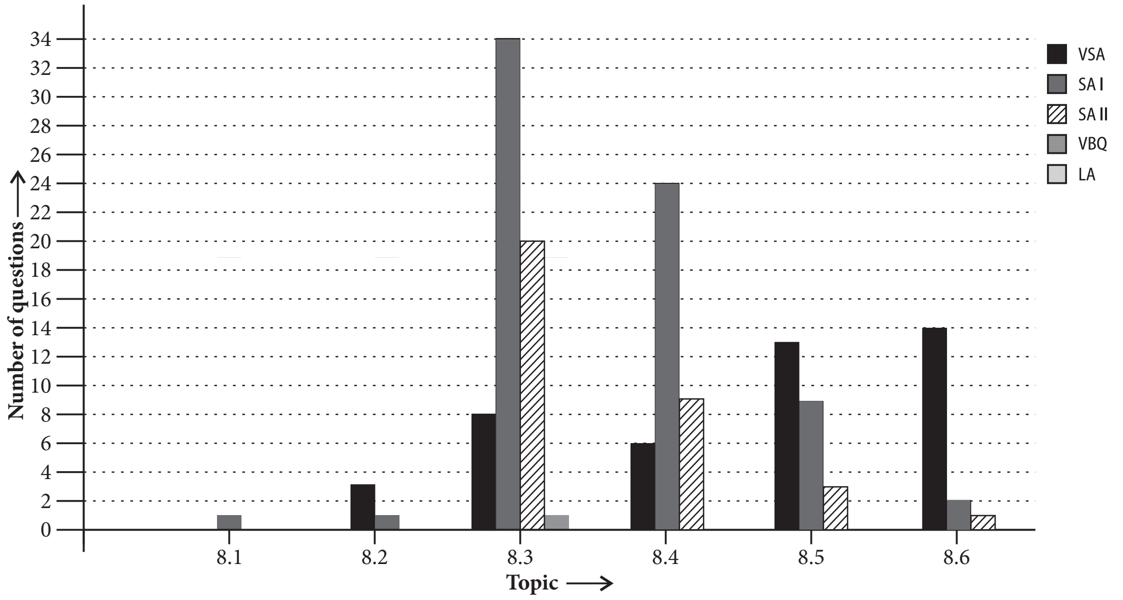
(ii) *Refer to answer 242.*

(iii) *Refer to answer 249.*

08

The *d*- and *f*-Block Elements

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



- Maximum total weightage is of *General Properties of the Transition Elements* (*d-Block*).
- Maximum VSA type questions were asked from *Actinoids.*
- Maximum SA I and SA II type questions were asked from *General Properties of the Transition Elements* (*d-Block*).

QUICK RECAP

TRANSITION ELEMENTS (*d*-BLOCK ELEMENTS)

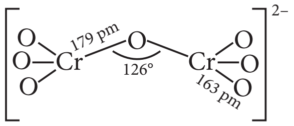
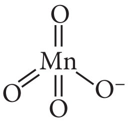
- Elements in which the last electron enters any one of the five *d*-orbitals of their respective penultimate shell are known as *transition elements* or *d-block elements*.
- Their general electronic configuration is $(n-1)d^{1-10}ns^{0-2}$.

Transition series : *d*-block consists of four transition series,
1st Transition series or 3*d* series $_{21}Sc - {}_{30}Zn$
2nd Transition series or 4*d* series $_{39}Y - {}_{48}Cd$
3rd Transition series or 5*d* series $_{57}La, {}_{72}Hf - {}_{80}Hg$
4th Transition series or 6*d* series $_{89}Ac, {}_{104}Rf - {}_{112}Cn$

General characteristics :

Melting and boiling points	High due to strong metallic bonding
Enthalpies of atomisation	High due to strong interatomic interactions
Ionisation enthalpies	Generally increases from left to right in a series
Oxidation states	Variable due to participation of *ns* and $(n-1)d$ electrons
Atomic radii	Decrease from left to right but become constant when pairing of electrons takes place
Complex formation	Form complexes due to high nuclear charge and small size and availability of empty *d*-orbitals to accept lone pair of electrons donated by ligands.
Coloured compounds	Form coloured compounds due to *d*-*d* transitions
Magnetic properties	Transition metal ions and their compounds are paramagnetic due to presence of unpaired electrons in the $(n-1)d$-orbitals and it is calculated by using the formula, $\mu = \sqrt{n(n+2)}$ where *n* is the no. of unpaired electrons.
Catalytic behaviour	Due to variable oxidation states and ability to form complexes
Interstitial compounds	Due to empty spaces in their lattices, small atoms can be easily accomodated
Alloy formation	Due to similar atomic sizes

Some important compounds :

Compounds	Preparation	Properties	Uses
Potassium dichromate ($K_2Cr_2O_7$) 	From sodium dichromate (obtained from chromite ore) $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$	Orange red, crystalline solid, oxidising agent having melting point 398°C. **Oxidising agent in acidic medium :** $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ **Oxidises :** I^- to I_2, H_2S to S, Sn^{2+} to Sn^{4+} and Fe^{2+} to Fe^{3+}	In dyeing, photography and leather industry.
Potassium permanganate ($KMnO_4$) 	From potassium manganate (obtained from pyrolusite) $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$ $2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$	Deep purple, crystalline solid, oxidising agent, having melting point 240° C. **Oxidising agent in acidic medium:** $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ **Oxidises :** I^- to I_2, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2, S^{2-} to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^- **Oxidising agent in faintly alkaline or neutral medium :** $MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$ **Oxidises :** I^- to IO_3^-, $S_2O_3^{2-}$ to SO^{2-}_4, Mn^{2+} to MnO_2	As a disinfectant, germicide, and Baeyer's reagent (alkaline $KMnO_4$).

- Volumetric titrations involving $KMnO_4$ are carried out only in the presence of dil. H_2SO_4 but not in the presence of HCl or HNO_3 because HCl is oxidised to Cl_2 and HNO_3 is itself a strong oxidising agent and partly oxidises the reducing agent. H_2SO_4 does not give any oxygen of its own to oxidise the reducing agent.

INNER TRANSITION ELEMENTS (*f*-BLOCK ELEMENTS)

- **Lanthanoids :** Last electron enters one of the 4*f*-orbitals. Cerium (at. no. 58) to lutetium (at. no. 71).
- **Actinoids :** Last electron enters one of the 4*f*-orbitals. Thorium (at. no. 90) to lawrencium (at. no. 103).

General electronic configuration : $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

General characteristics of lanthanoids :

Atomic and ionic radii	Decrease steadily on going from La to Lu.
Oxidation states	Most common oxidation state of lanthanoids is +3. Some elements exhibit +2 and +4 oxidation states due to extra stability of empty, half-filled or filled *f*-subshell. *e.g.,* Ce^{4+} acts as an oxidising agent and gets reduced to Ce^{3+}, Eu^{2+}, Yb^{2+} act as strong reducing agents and get oxidised to Eu^{3+} and Yb^{3+}.
Action of air	All the lanthanoids are silvery white soft metals and tarnish readily in moist air. They burn in oxygen of air and form oxides (Ln_2O_3 type).
Coloured ions	They form coloured ions due to *f*-*f* transitions of unpaired electrons. La^{3+} and Lu^{3+} are colourless ions due to empty ($4f^0$) or fully ($4f^{14}$) orbitals.
Magnetic properties	La^{3+}, Lu^{3+} are diamagnetic while trivalent ions of the rest of lanthanoids are paramagnetic.
Reducing agents	They readily lose electrons and are good reducing agents.
Electropositive character	Highly electropositive because low transition energies.
Alloy formation	They form alloys easily with other metals especially iron.
Tendency to form complexes	Lanthanoids do not have much tendency to form complexes due to low charge density because of their large size. The tendency to form complexes and their stability increases with increasing atomic number.

Lanthanoid contraction : In lanthanoid series, with increasing atomic number, there is progressive decrease in atomic/ionic radii (M^{3+} ions) from La^{3+} to Lu^{3+}.

- **Reason :** Due to addition of new electrons into *f*-subshell and imperfect shielding of one electron by another in the *f*-orbitals, there is greater effect of increased nuclear charge than screening effect hence contraction in size.
- **Consequences :** Their separation is difficult, they have small differences in properties and 4*d* and 5*d* transition series have almost same atomic radii (Zr and Hf have similar properties due to same size).

Uses of lanthanoids : Used in making mischmetal, an alloy of a lanthanoid metal (~ 95%) with iron (~ 5%) and traces of S, C, Ca and Al. It is used to make tracer bullets, shells and lighter flints.

General characteristics of actinoids :

Ionic radii	Like lanthanoids, ionic radii decrease regularly across to series. Actinoid contraction is greater due to poor sheilding effect of the 5*f*-electrons. Further, 5*f*-orbitals extend in space beyond 6*s* and 6*p*-orbitals whereas 4*f*-orbitals are burried deep.
Oxidation states	Like lanthanoids, most common is +3. They also show oxidation state of +4, +5, +6 and +7, *e.g.,* in Th, Pa, U and Np respectively. They show a large number of oxidation states because of very small energy gap between 5*f*, 6*d* and 7*s* subshells.

Action of air, alkalies and acids	Like lanthanoids they are also silvery white metals, tarnish rapidly in air forming oxide coating and are not attacked by alkalies and are less reactive towards acids.
Coloured ions	Are coloured due to *f-f* transition except $Ac^{3+}(5f^0)$, $Cm^{3+}(5f^7)$ and $Th^{4+}(5f^0)$ which are colourless.
Magnetic properties	They are strongly paramagnetic.
Density	All actinoids except thorium and americium have high densities.
Melting and boiling points	High melting and boiling points however there is no regular trend with rise in atomic number.
Ionisation energy	They have low ionisation energies.
Reducing agents	All actionoids are strong reducing agents.
Electropositive character	Highly electropositive metals.

- **Uses of actinoids :** Th is used in atomic reactor and treatment of cancer. U and Pu are used as fuel in nuclear reactor.
- **Differences between lanthanoids and actinoids :**

Lanthanoids	Actinoids
They show +2 and +4 oxidation states in few cases besides +3.	They show higher oxidation states of +4, +5, +6 and +7 besides +3.
Except promethium, they are non-radioactive.	All actinoids are radioactive.
They do not form oxo-cations.	They form oxo-cations like UO_2^{2+}; PuO_2^{2+}; UO_2^{+}, etc.
The compounds of lanthanoids are less basic.	Actinoid compounds are more basic.
They have less tendency of complex formation.	They have greater tendency of complex formation.

Previous Years' CBSE Board Questions

8.1 Position in the Periodic Table

SA I (2 marks)

1. What are the transition elements? Write two characteristics of the transition elements. *(Delhi 2015)*

8.2 Electronic Configurations of the *d*-Block Elements

VSA (1 mark)

2. Account for the following :
Zn is not considered as a transition element. *(1/5, AI 2014, 1/2, Delhi 2010)*

3. On what ground can you say that scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not? *(1/5, AI 2008C)*

SA I (2 marks)

4. Write down the electronic configuration of
(a) Cr^{3+} (b) Cu^+
(c) Co^{2+} (d) Mn^{2+} *(2/5, AI 2009)*

8.3 General Properties of the Transition Elements (*d*-Block)

VSA (1 mark)

5. How would you account for the following :
Transition metals form coloured compounds? *(1/3, Delhi 2015, 1/2, 2010)*

6. Zn^{2+} salts are white while Cu^{2+} salts are coloured. Why? *(AI 2015)*

7. Why do transition elements show variable oxidation states? *(Delhi 2014C)*

8. Assign reason for the following :
Copper (I) ion is not known in aqueous solution. *(1/2, Delhi 2011)*

9. Explain giving reasons :
Transition metals and their compounds generally exhibit a paramagnetic behaviour. *(1/2, AI 2011)*

10. Account for the following :
Compounds of transition elements are often coloured. *(1/2, Delhi 2008C)*

11. Why Cd^{2+} salts are white? *(AI 2007)*

SA I (2 marks)

12. Give reasons :
(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.
(ii) Transition metals show variable oxidation states. *(2/3, Delhi 2016)*

13. Account for the following :
(i) Transition metals show variable oxidation states.
(ii) Cu^+ ion is unstable in aqueous solution. *(2/3, AI 2015)*

14. Why do transition elements show variable oxidation states? In 3*d* series (Sc to Zn), which element shows the maximum number of oxidation states and why? *(Foreign 2015)*

15. How would you account for the following :
(i) Highest fluoride of Mn is MnF_4 whereas the highest oxide is Mn_2O_7.
(ii) Transition metals and their compounds show catalytic properties. *(2/3, Foreign 2015)*

16. What is meant by 'disproportionation? Give an example of a disproportionation reaction in aqueous solution. *(Delhi 2015C)*

17. Account for the following :
(i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.
(ii) The enthalpy of atomization is lowest for Zn in 3*d* series of the transition elements. *(Delhi 2014)*

18. (i) Write two characteristic of the transition elements.
(ii) Which of the 3*d*-block elements may not be regarded as the transition elements and why? *(2/3, Foreign 2014)*

19. Assign a reason for each of the following observations :
  (i) The transition metals (with the exception of Zn, Cd and Hg) are hard and have high melting and boiling points.
  (ii) The ionisation enthalpies (first and second) in the first series of the transition elements are found to vary irregularly.
(Delhi 2014C)

20. Assign a reasons for the following :
  (i) Copper(I) ion is not known to exist in aqueous solutions.
  (ii) Both O_2 and F_2 stabilize high oxidation states of transition metals but the ability of oxygen to do so exceeds that of fluorine.
(AI 2014C)

21. Give reasons for the following :
  (i) Transition metals exhibit a wide range oxidation states.
  (ii) Cobalt (II) is very stable in aqueous solutions but gets easily oxidised in the presence of strong ligands. *(2/3, AI 2014C)*

22. Assign reasons for the following :
  (i) Cu(I) ion is not known to exist in aqueous solutions.
  (ii) Transition metals are much harder than the alkali metals. *(2/3, AI 2014C)*

23. Assign reasons for the following :
  (i) Transition metals and many of their compounds act as good catalysts.
  (ii) Transition metals generally form coloured compounds. *(AI 2014C)*

24. (i) Which metal in the first transition series (3*d*-series) exhibits +1 oxidation state most frequently and why?
  (ii) Which of following cations are coloured in aqueous solutions and why?
  Sc^{3+}, V^{3+}, Ti^{4+}, Mn^{2+}
  (At. Nos. Sc = 21, V = 23, Ti = 22, Mn = 25)
(Delhi 2013)

25. How would you account for the following?
  (i) Transition metals exhibit variable oxidation states.
  (ii) Transition metals and their compounds act as catalyst. *(2/3, Delhi 2013)*

26. How would you account for the following?
  (i) Many of the transition elements are known to form interstitial compounds.
  (ii) The metallic radii of the third (5*d*) series of transition metals are virtually the same as those of the corresponding group member of the second (4*d*) series. *(2/3, Delhi 2012)*

27. How would you account for the following?
  (i) With the same *d*-orbital configuration (d^4) Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent.
  (ii) Most of the transition metal ions exhibit characteristic colours in aqueous solutions.
(2/3, Delhi 2012)

28. How would you account for the following :
  (i) The $E^\circ_{M^{2+}/M}$ for copper is positive (+0.34 V). Copper is the only metal in the first series of transition elements showing this behaviour.
  (ii) The metallic radii of the third (5*d*) series of transition metals are nearly the same as those of the corresponding members of the second (4*d*) series. *(2/3, AI 2012)*

29. Explain the following observations :
  (i) Many of the transition elements are known to form interstitial compounds.
  (ii) There is a general increase in density from titanium ($Z = 22$) to copper ($Z = 29$).
(2/3, AI 2012)

30. Explain the following observations.
  (i) With the same *d*-orbital configuration (d^4), Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent.
  (ii) There is hardly any increase in atomic size with increasing atomic numbers in a series of transition metals. *(2/3, AI 2012)*

31. Explain the following :
  (i) The enthalpies of atomization of transition metals are quite high.
  (ii) The transition metals and many of their compounds act as good catalysts.
(Delhi 2012C)

32. Give reason :
  (i) Sc (21) is a transition element but Ca (20) is not.
  (ii) The Fe^{2+} is much more easily oxidised to Fe^{3+} than Mn^{2+} to Mn^{3+}. *(2/3, AI 2012C)*

33. How is the variability in oxidation states of transition elements different from that of non-transition elements? Illustrate with examples. *(2/5, AI 2012C)*

34. Account for the following :
(i) Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state.
(ii) Cr^{2+} is reducing and Mn^{3+} oxidizing when both have d^4 configuration. *(2/5, AI 2012C)*

35. Assign reasons for each of the following :
(i) Transition metals generally form coloured compounds.
(ii) Manganese exhibits the highest oxidation state of +7 among the 3rd series of transition elements. *(Delhi 2011)*

36. How would you account for the following :
(i) Cr^{2+} is reducing in nature while with the same *d*-orbital configuration (d^4) Mn^{3+} is an oxidising agent.
(ii) In a transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series. *(AI 2011)*

37. State reasons for the following :
(i) Cu (I) ion is not stable in an aqueous solution.
(ii) Unlike Cr^{3+}, Mn^{2+}, Fe^{3+} and the subsequent other V^{2+} ions of the 3*d* series of elements, the 4*d* and the 5*d* series metals generally do not form stable cationic species. *(AI 2011)*

38. Explain giving a suitable reason for each of the following:
(i) Transition metals and their compounds are generally found to be good catalysts.
(ii) Metal-metal bonding is more frequent for the 4*d* and the 5*d* series of transition metals than that for the 3*d* series. *(AI 2011)*

39. Explain the following observations :
(i) Generally there is an increase in density of elements from titanium ($Z = 22$) to copper ($Z = 29$) in the first series of transition elements.
(ii) Transition elements and their compounds are generally found to be good catalysts in chemical reactions. *(Delhi 2010)*

40. Explain the following observations :
(i) Among the divalent cations in the first series of transition elements, manganese exhibits the maximum paramagnetism.
(ii) Cu^+ ion is not known in equeous solutions. *(2/5, Delhi 2010)*

41. Account for the following :
(i) Cu^+ ions are not stable in aqueous solution.
(ii) Most of the transition metal ions exhibit paramagnetic behaviour. *(Delhi 2010C)*

42. Account for the following :
(i) In the series Sc to Zn, the enthalpy of atomisation of zinc is the lowest.
(ii) The $E°$ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}. *(Delhi 2010C)*

43. Account for the following :
(i) The lowest oxide of a transition metal is basic, the highest is amphoteric/acidic.
(ii) Cobalt (II) is stable in aqueous solution but in the presence of complexing agents, it is easily oxidised. *(2/5, AI 2010C)*

44. How would you account for the following :
(i) Many of the transition elements and their compounds can act as good catalysts.
(ii) The metallic radii of the third (5*d*) series of transition elements are virtually the same as those of the corresponding members of the second series. *(2/3, AI 2009)*

45. How would you account for the following :
(i) Transition elements have high enthalpies of atomisation.
(ii) The transition metals and their compounds are found to be good catalysts in many processes? *(AI 2007)*

SA II (3 marks)

46. Account for the following :
(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine, if shows the highest oxidation state of +4.
(ii) Cr^{2+} is a strong reducing agent.
(iii) Cu^{2+} salts are coloured, while Zn^{2+} salts are white. *(3/5, AI 2016)*

47.

$E°_{(M^{2+}/M)}$	Cr	Mn	Fe	Co	Ni	Cu
	–0.91	–1.18	–0.44	–0.28	–0.25	+0.34

From the given data of $E°$ values, answer the following questions :

(i) Why is $E^\circ_{(Cu^{2+}/Cu)}$ value exceptionally positive?

(ii) Why is $E^\circ_{(Mn^{2+}/Mn)}$ value highly negative as compared to other elements?

(iii) Which is a stronger reducing agent Cr^{2+} or Fe^{2+}? Give reason. *(3/5, AI 2015)*

48. What is meant by disproportionation? Give on example of disproportionation reaction in aqueous solutions. *(AI 2015C)*

49. Assign suitable reasons for the following :

(i) The Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.

(ii) In the 3*d* series from Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomization of Zn is the lowest.

(iii) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured. *(Foreign 2014)*

50. Give reasons for the following :

(i) Mn^{3+} is a good oxidising agent.

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

(iii) Although 'F' is more electronegative than 'O', the highest Mn fluoride is MnF_4, whereas the highest oxide is Mn_2O_7. *(3/5, AI 2013)*

51. Give reasons :

(i) *d*-block elements exhibit more oxidation states than *f*-block elements.

(ii) The enthalpies of atomization of the transition metals are high.

(iii) The variation in oxidation states of transition metals is of different type from that of the non-transition metals. *(3/5, AI 2013C)*

52. Explain the following :

(i) Copper (I) ion is not stable in an aqueous solution.

(ii) With same (d^4) configuration Cr (II) is reducing whereas Mn (III) is oxidising.

(iii) Transition metals in general act as good catalysts. *(3/5, Foreign 2011)*

53. How would you account for the following :

(i) Metal-metal bonding is more extensive in the 4*d* and 5*d* series of transition elements than the 3*d* series.

(ii) Mn (III) undergoes disproportionation reaction easily.

(iii) Co (II) is easily oxidised in the presence of strong ligands. *(3/5, Foreign 2011)*

54. Account for the following :

(i) The transition metals and their compounds act as good catalysts.

(ii) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(iii) A transition metal exhibits higher oxidation states in oxides and fluorides. *(3/5, AI 2011C)*

55. How would you account for the following :

(i) The atomic radii of the metals of the third (5*d*) series of transition elements are virtually the same as those of the corresponding members of the second (4*d*) series.

(ii) The $E°$ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple or Fe^{3+}/Fe^{2+} couple.

(iii) The highest oxidation state of a metal is exhibited in its oxide or fluoride. *(Delhi 2010)*

56. How would you account for the following :

(i) The oxidising power of oxoanions are in the order
$VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$

(ii) The third ionization enthalpy of manganese (Z = 25) is exceptionally high.

(iii) Cr^{2+} is a stronger reducing agent than Fe^{2+}. *(3/5, AI 2010)*

57. Give reason for the following :

(i) Transition metals have high enthalpies of atomisation.

(ii) $Fe^{3+}|Fe^{2+}$ redox couple has less positive electrode potential than $Mn^{3+}|Mn^{2+}$ couple.

(iii) Copper (I) has d^{10} configuration, while copper (II) has d^9 configuration, still copper (II) is more stable in aqueous solution than copper (I). *(3/5, Delhi 2010C)*

58. Account for the following :

(i) The enthalpies of atomisation of the transition metals are high.

(ii) The lowest oxide of a transition metal is basic, the highest is amphoteric/acidic.

(iii) Cobalt (II) is stable in aqueous solution but in the presence of complexing agents, it is easily oxidised. *(3/5, AI 2010C)*

59. (a) Name the oxo-metal anion of one of the transition metals in which the metal exhibits the oxidation state equal to the group number.

(b) Account for the following :

(i) Scandium ($Z = 21$) is regarded as a transition element but zinc ($Z = 30$) is not.

(ii) $E°(M^{2+}/M)$ value for copper is +ve. *(3/5, AI 2010C)*

60. Explain the following observations :

(i) Transition elements are known to form many interstitial compounds.

(ii) With the same *d*-orbital configuration Cr^{2+} ion is reducing while Mn^{3+} ion is oxidising.

(iii) The enthalpies of atomisation of the transition elements are quite high. *(3/5, Delhi 2009)*

61. Explain the following observations :

(i) In general the atomic radii of transition elements decrease with atomic number in a given series.

(ii) The $E°_{M^{2+}|M}$ for copper is positive (+0.34 V). It is only metal in the first series of transition elements showing this type of behaviour.

(iii) The $E°$ value for $Mn^{3+}|Mn^{2+}$ couple is much more positive than for $Cr^{3+}|Cr^{2+}$ or $Fe^{3+}|Fe^{2+}$ couple. *(3/5, Delhi 2009)*

62. Explain the following observation :

(i) Cu^+ ion is unstable in aqueous solutions.

(ii) Although Co^{2+} ion appears to be stable, it is easily oxidised to Co^{3+} ion in the presence of a strong ligand.

(iii) The $E°_{Mn^{2+}|Mn}$ value for manganese is much more than expected from the trend for other elements in the series. *(3/5, Delhi 2009)*

63. Give reasons for the following observations :

(i) Cu^+ ion is not stable in aqueous solution.

(ii) Mn(II) ion shows maximum paramagnetic character amongst the bivalent ions of first transition series.

(iii) Scandium (At. no. 21) salts are white. *(3/5, Delhi 2009C)*

64. Give reasons for the following observations :

(i) Of the d^4 species, Cr^{2+} is strongly reducing whereas manganese (III) is strongly oxidising.

(ii) The enthalpies of atomisation of the transition metals are quite high.

(iii) Interstitial compounds are well-known for transition metals. *(3/5, AI 2009C)*

65. Assign reasons for the following :

(i) The enthalpies of atomisation of transition elements are high.

(ii) The transition metals and many of their compunds act as good catalyst.

(iii) The $E°$ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}. *(3/5, Delhi 2008)*

LA (5 marks)

66. The elements of 3*d* transition series are given as

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following :

(i) Write the element which shows maximum number of oxidation states. Given reason.

(ii) Which element has the highest melting point?

(iii) Which element shows only +3 oxidation state?

(iv) Which element is a strong oxidising agent in +3 oxidation state and why? *(AI 2016)*

8.4 Some Important Compounds of Transition Elements

VSA (1 mark)

67. Complete the following equation :

$2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow$ *(1/2, Delhi 2015)*

68. Complete the following equation :

$3MnO_4^{2-} + 4H^+ \longrightarrow$ *(1/3, Foreign 2015)*

69. Complete the following equation :

$MnO_4^- + 8H^+ + 5e^- \longrightarrow$ *(1/5, Delhi 2014)*

70. Complete the following chemical equations :

$SO_2 + MnO_4^- + H_2O \longrightarrow$ *(1/2, AI 2014C)*

71. Give reason :

Orange solution of potassium dichromate turns yellow on adding sodium hydroxide to it. *(1/5, AI 2013C)*

72. Complete the following chemical equation :

$Cr_2O^{2-}_{7(aq)} + H_2S_{(g)} + H^+_{(aq)} \longrightarrow$ *(1/5, AI 2010)*

SA I (2 marks)

73. When chromite ore $FeCr_2O_4$ is fused with NaOH in presence of air, a yellow coloured compound (A) is obtained which on acidification with dilute sulphuric acid gives a compound (B). Compound (B) on reaction with KCl forms a orange coloured crystalline compound (C).

(i) Write the formulae of the compounds (A), (B) and (C).

(ii) Write one use of compound (C).

(Delhi 2016)

74. Complete the following chemical equations :

(i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow$

(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow$ *(Delhi 2016)*

75. Complete the following equations.

(i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$

(ii) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow$ *(2/5, AI 2016)*

76. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with oxalic acid? Write the ionic equations for the reaction.

(AI 2015C)

77. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with (i) an iodide (ii) H_2S. *(AI 2015C)*

78. How do you prepare :

(i) K_2MnO_4 from MnO_2?

(ii) $Na_2Cr_2O_7$ from Na_2CrO_4? *(2/5, Delhi 2014)*

79. Complete the following equations :

(i) $Cr_2O_7^{2-} + 2OH^- \longrightarrow$

(ii) $MnO_4^- + 4H^+ + 3e^- \longrightarrow$ *(AI 2014)*

80. Complete the following equations :

(i) $2MnO_4^- + 5S^{2-} + 16H^+ \rightarrow$

(ii) $Cr_2O_7^{2-} + 2OH^- \rightarrow$ *(Foreign 2014)*

81. Complete the following equations :

(i) $2CrO_4^{2-} + 2H^+ \longrightarrow$

(ii) $KMnO_4 \xrightarrow{\text{Heat}}$ *(AI 2013)*

82. Complete the following chemical equations :

(i) $Cr_2O_7^{2-} + H^+ + I^-$

(ii) $MnO_4^- + NO_2^- + H^+$ *(Delhi 2012)*

83. Complete the following chemical equations :

(i) $MnO^-_{4(aq)} + S_2O^{2-}_{3(aq)} + H_2O_{(l)} \rightarrow$

(ii) $Cr_2O^{2-}_{7(aq)} + Fe^{2+}_{(aq)} + H^+_{(aq)} \rightarrow$

(AI 2011, 2/5, AI 2010)

84. Complete the following reactions in an aqueous medium :

(i) $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow$

(ii) $Cr_2O_7^{2-} + H_2S + H^+ \rightarrow$ *(2/5, Foreign 2011)*

85. Complete the following chemical equations :

(i) $Fe^{3+} + I^- \rightarrow$

(ii) $CrO_4^{2-} + H^+ \rightarrow$ *(2/5, Foreign 2011)*

86. Describe the reactions involved in the preparation of $K_2Cr_2O_7$ from chromite ore.

(2/5, AI 2011C, 2/5, Delhi 2009C)

87. How does the acidified potassium permanganate solution react with

(i) iron (II) ions and (ii) oxalic acid?

Write the ionic equations for the reactions.

(2/5, AI 2010C)

88. Complete the following chemical reaction equations :

(i) $MnO^-_{4(aq)} + C_2O^{2-}_{4(aq)} + H^+_{(aq)} \longrightarrow$

(ii) $Cr_2O^{2-}_{7(aq)} + Fe^{2+}_{(aq)} + H^+_{(aq)} \longrightarrow$

(2/5, Delhi 2009)

89. Complete the following chemical reaction equations :

(i) $MnO^-_{4(aq)} + S_2O^{2-}_{3(aq)} + H_2O_{(l)} \longrightarrow$

(ii) $Cr_2O^{2-}_{7(aq)} + H_2S + H^+_{(aq)} \longrightarrow$ *(2/5, Delhi 2009)*

90. Complete the following chemical reaction equations:

(i) $Fe^{2+}_{(aq)} + MnO^-_{4(aq)} + H^+_{(aq)} \longrightarrow$

(ii) $Cr_2O^{2-}_{7(aq)} + I^-_{(aq)} + H^+_{(aq)} \longrightarrow$ *(2/5, Delhi 2009)*

91. (i) Describe how potassium dichromate is prepared from sodium chromate.

(ii) The colour of potassium dichromate solution changes with the change of pH of the solution. Explain how.

(2/5, Delhi 2008, 2/5, AI 2008C)

92. Write complete chemical equations for

(i) Oxidation of Fe^{2+} by $Cr_2O_7^{2-}$ in acidic medium.

(ii) Oxidation of $S_2O_3^{2-}$ by MnO_4^- in neutral aqueous medium. *(AI 2008)*

93. Write the steps involved in the preparation of

(i) $K_2Cr_2O_7$ from Na_2CrO_4

(ii) $KMnO_4$ from K_2MnO_4. *(2/5, Delhi 2007)*

SA II (3 marks)

94. Complete the following chemical equations:

(i) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow$

(ii) $2CrO_4^{2-} + 2H^+ \rightarrow$

(iii) $3MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow$ *(Delhi 2013)*

95. Lokesh is a social worker. A milkman in the village has been complaining that a factory in his nearby area dumps chemical waste in his field which has become a major cause of decreasing productivity. Lokesh visited that place and found after analyis that the major waste was potassium permanganate which is being absorbed by the soil. He advised the factory people that they should treat potassium permanganate solution before dumping it into the drain.
Comment in brief
(i) About the value/s displayed by Lokesh.
(ii) Write balanced chemical equations for the two reactions showing oxidizing nature of potassium permanganate.
(VBQ) (Delhi 2013C)

96. Describe the preparation of potassium permanganate from pyrolusite ore. Write balanced chemical equation for one reaction to show the oxidizing nature of potassium permanganate. *(3/5, AI 2013C)*

97. Describe the preparation of potassium dichromate from chromite ore. What is the effect of change of pH on dichromate ion?
(3/5, AI 2012C)

98. Describe the preparation of potassium permanganate from pyrolusite ore. What happens when acidified potassium permanganate solution reacts with ferrous sulphate solution? Write balanced chemical equations. *(3/5, AI 2012C)*

99. Complete the following chemical equations :
(i) $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow$
(ii) $KMnO_4 \xrightarrow{\text{Heated}}$
(iii) $Cr_2O_7^{2-} + H_2S + H^+ \longrightarrow$ *(Delhi 2011)*

100. Describe the preparation of potassium permanganate from pyrolusite ore. Write the ionic equation for the reaction that takes place between acidified $KMnO_4$ solution and iron (II) ions. *(Delhi 2010C)*

101. Describe the oxidising actions of potassium dichromate and write the ionic equations for its reaction with (i) iodide (ii) iron (II) solution (iii) H_2S. *(Delhi 2008)*

102. (i) Describe the commercial preparation of potassium permanganate from pyrolusite ore.
(ii) Write ionic equation to represent the reaction of acidified $KMnO_4$ solution with oxalic acid. *(Delhi 2008C)*

8.5 The Lanthanoids

VSA (1 mark)

103. Account for the following :
Zr and Hf have almost similar atomic radii.
(1/5, AI 2015)

104. Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.
(1/5, Delhi 2014)

105. Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.
(1/5, AI 2014)

106. What are the different oxidation states exhibited by the lanthanoids? *(1/3, Foreign 2014)*

107. How would you account for the following :
Zr ($Z = 40$) and Hf ($Z = 72$) have almost identical radii. *(1/3, Delhi 2013, 1/5, AI 2013C,)*

108. How would you account for the following :
Among lanthanoids, Ln(III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained. *(1/3, AI 2012)*

109. Give reason :
There is a gradual decrease in the size of atoms with increasing atomic number in the series of lanthanoids. *(1/3, Delhi 2012C)*

110. What is meant by 'lanthanoid contraction'?
(AI 2011)

111. What are different oxidation states exhibited by lanthanoids? *(Delhi 2010)*

112. Explain the following observations :
La^{3+} ($Z = 57$) and Lu^{3+} ($Z = 71$) do not show any colour in solutions. *(1/5, AI 2010)*

113. Give reason for the following :
Among the Lanthanoids, Ce (III) is easily oxidised to Ce (IV). *(1/5, Delhi 2010C)*

114. Give reason for the following :
The second and third transition series elements have almost similar atomic radii.
(1/5, Delhi 2010C)

SA I (2 marks)

115. What is Lanthanoid contraction? What are its two consequences? *(Delhi 2013C)*

116. What is lanthanoid contraction and what is it due to? Write two consequences of lanthanoid contraction. *(2/5, Delhi 2013C)*

117. What is lanthanoid contraction? Mention its main consequences. *(2/3, Delhi 2012C, AI 2008C)*

118. Why is europium (II) more stable than cerium (II)? *(AI 2010)*

119. Write the electronic configuration of Ce^{3+} ion, and calculate the magnetic moment on the basis of 'spin-only' formula. [Atomic no. of Ce = 58] *(2/5, AI 2010C)*

120. What is meant by the term lanthanoid contraction? What is it due to and what consequences does it have on the chemistry of elements following lanthanoids in the periodic table? *(2/5, Delhi 2009)*

121. Name an important alloy which contains some of the lanthanoid metals. Mention its two uses. *(2/5, Delhi 2009C)*

122. What is lanthanoid contraction? List any two consequences of lanthanoid contraction. *(2/5, AI 2009C)*

SA II (3 marks)

123. What is lanthanoid contraction? What are the consequences of lanthanoid contraction? *(Delhi 2015C)*

124. What is lanthanoid contraction? What is its effect on the chemistry of the elements which follow the lanthanoids? *(3/5, AI 2011C, 3/5, Delhi 2007)*

8.6 The Actinoids

VSA (1 mark)

125. Give reasons :
Actinoids show irregularities in their electronic configurations. *(1/3, Delhi 2016)*

126. How would you account for the following:
Actinoid contraction is greater than lanthanoid contraction? *(1/3, Delhi 2015)*

127. Give reasons for the following :
Actinoids exhibit a greater range of oxidation states than lanthanoids.
(1/3, AI 2014C, 1/2, Delhi 2011, 1/5, AI 2008C)

128. Assign reasons for the following :
From element to element actinoid contraction is greater than the lanthanoid contraction.
(1/3, AI 2014C, 1/5, Delhi 2009, 1/5, Delhi 2008)

129. How would you account for the following :
Lanthanoids form primarily +3 ions, while the actinoids usually have higher oxidation states in their compounds, +4 or even +6 being typical. *(1/3, Delhi 2012)*

130. How would you account for the following :
The actinoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series. *(1/3, Delhi 2012)*

131. Explain the following observation :
The members of the actinoid series exhibit a larger number of oxidation states than the corresponding members of the lanthanoid series. *(1/3, AI 2012)*

132. Explain the following observation :
Actinoids exhibit a much larger number of oxidation states than the lanthanoids. *(1/3, AI 2012)*

133. Explain giving reasons :
The chemistry of actinoids is not as smooth as that of lanthanoids. *(1/2, AI 2011)*

134. How would you account for the following :
There is a greater range of oxidation states among the actinoids than among the lanthanoids. *(1/3, AI 2009)*

SA I (2 marks)

135. Why do actinoids show a wide range of oxidation states? Write one similarity between the chemistry of lanthanoids and actinoids. *(2/5, AI 2015)*

136. With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids. *(2/5, AI 2014)*

SA II (3 marks)

137. Compare the chemistry of the actinoids with that of lanthanoids with reference to
(i) electronic configuration
(ii) oxidation states
(iii) chemical reactivity. *(Delhi 2010C)*

Detailed Solutions

1. Elements which have incompletely filled d-orbitals in their ground state or in any one of their oxidation states are called transition elements.
Characteristics of transition elements :
(i) They show variable oxidation states.
(ii) They exhibit catalytic properties.

2. In the electronic configuration of Zn, Cd and Hg the d-orbitals are completely filled in the ground state as well as in their common oxidation state. So, they are not regarded as transition metals.

3. On the basis of incompletely filled d-orbitals :

Scandium (Z = 21), atom has incompletely filled d-orbitals ($3d^1$) in its ground state, so it is regarded as transition element.

On the other hand zinc (Z = 30) atom has completely filled d-orbitals ($3d^{10}$) in its ground state as well as most common oxidation state of +2.

4. (a) $Cr^{3+} = {}_{18}[Ar]\ 3d^3$ (b) $Cu^+ = {}_{18}[Ar]\ 3d^{10}$
(c) $Co^{2+} = {}_{18}[Ar]\ 3d^7$ (d) $Mn^{2+} = {}_{18}[Ar]\ 3d^5$

5. Due to presence of vacant d-orbitals and d-d transitions, compounds of the transition metals are generally coloured.

When an electron from a lower energy d-orbital is excited to a higher energy d-orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

6. Zn^{2+} ion has completely filled d-subshell and no d-d transition is possible. So zinc salts are white.

Configuration of Cu^{2+} is [Ar] $3d^9$. It has partly filled d-subshell and hence it is coloured due to d-d transition.

7. Transition elements can use their ns and $(n-1)d$ orbital electrons for bond formation therefore, they show variable oxidation states.
For example - Sc has $ns^2(n-1)d^1$ electronic configuration.
It utilizes two electrons from its ns subshell then its oxidation state = +2. When it utilizes both the electrons then its oxidation state = +3.

8. In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

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

Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

9. Transition metals and most of their compounds contain unpaired electrons in the $(n-1)d$ orbitals hence show paramagnetic behaviour.

10. *Refer to answer 5.*

11. It has completely filled d-orbital (d^{10}).

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

13. (i) *Refer to answer 7.*
(ii) *Refer to answer 8.*

14. Variation in oxidation state : Transition elements can use their ns and $(n-1)d$ orbital electrons for bond formation. Therefore, they show variable oxidation state.
For example - Sc has $ns^2\ (n-1)d^1$ electronic configuration.
It utilizes two electrons from its ns subshell then its oxidation state = +2. When it utilizes both the electrons then its oxidation state = +3.
Among the $3d$ series manganese (Mn) exhibits the largest number of oxidation states from +2 to +7 because it has maximum number of unparied electrons.

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

15. (i) *Refer to answer 12(i).*
(ii) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of

the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

16. Disproportionation reaction involves the oxidation and reduction of the same substance. The two examples of disproportionation reaction are :

(i) Aqueous NH_3 when treated with Hg_2Cl_2 (solid) forms mercury aminochloride disproportionatively.

$Hg_2Cl_2 + 2NH_3 \longrightarrow Hg + Hg(NH_2)Cl + NH_4Cl$

(ii) $2Cu^+ \longrightarrow Cu + Cu^{2+}$

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

(ii) Zinc (Z = 30) has completely filled d-orbital ($3d^{10}$) d-orbitals do not take part in interatomic bonding. Hence, metallic bonding is weak.

This is why it has very low enthalpy of atomisation (126 kJ mol^{-1}).

18. (i) *Refer to answer 1.*
(ii) *Refer to answer 2.*

19. (i) As we move along transition metal series from left to right (*i.e.* Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence the atomic volume decreases. At the same time, atomic mass increases. Hence, the density from titanium (Ti) to copper (Cu) increases.

(ii) Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different $3d$-configurations (*e.g.*, d^0, d^5, d^{10} are exceptionally stable).

20. (i) *Refer to answer 8.*

(ii) This is due to ability of oxygen to form multiple bonds with metals.

21. (i) *Refer to answer 7.*

(ii) The tendency to form complexes is high for Co(III) as compared to Co(II). Co^{2+} ions are very stable and are difficult to oxidise. Co^{3+} ions are less stable and are reduced by water. In contrast many Co(II) complexes are readily oxidised to Co(III) complexes and Co(III) complexes are very stable, *e.g.*,

$$[Co(NH_3)_6]^{2+} \xrightarrow{\text{Air}} [Co(NH_3)_6]^{3+}$$

This happens because the crystal field stabilisation energy of Co(III) with a $d^6(t_{2g}^6)$ configuration is higher than for Co(II) with a d^7 $(t_{2g}^6\, e_g^1)$ arrangement.

22. (i) *Refer to answer 8.*

(ii) This is attributed to the involvement of greater number of electrons from $(n-1)d$ in addition to the ns electrons in the interatomic metallic bonding.

23. (i) *Refer to answer 15(ii).*

(ii) *Refer to answer 5.*

24. (i) Copper exhibits +1 oxidation state in its compounds. Electronic configuration of Cu in the ground state is $3d^{10}\ 4s^1$. So, Cu can easily lose $4s^1$ electron to give a stable $3d^{10}$ configuration. Thus it shows +1 oxidation state.

(ii) Only those ions will be coloured which have partially filled d-orbitals facilitating d-d transition. Ions with d^0 and d^{10} will be colourless.

From electronic configuration of the ions, $V^{3+}(3d^2)$ and $Mn^{2+}(3d^5)$, are all coloured. $Ti^{4+}(3d^0)$ and $Sc^{3+}(3d^0)$ are colourless.

25. (i) *Refer to answer 7.*
(ii) *Refer to answer 15(ii).*

26. (i) Transition metals form a large number of interstitial compounds because small atoms of certain non metallic elements (H, B, C, N, etc.) get trapped in voids or vacant spaces of lattices of the transition metals. As a result of filling up of the interstitial spaces such interstitial compounds are hard and rigid.

(ii) This is due to lanthanoid contraction.

27. (i) $E°$ values for the Cr^{3+}/Cr^{2+} and Mn^{3+}/Mn^{2+} couples are

$$Cr^{3+}_{(aq)} + e^- \longrightarrow Cr^{2+}_{(aq)};\ E° = -0.41\ V$$

$$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)}\ ;\ E° = +1.551\ V$$

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

(ii) Since, transition elements contain partially filled 5-subshells. Therefore, electrons in these subshells go from lower d-subshells to higher d-subshells. This is called d-d transition. This transition takes place by absorbing energy from the visible light. The mixture of the wavelength which is not absorbed is transmitted out. This accounts for the colour of transition elements.

28. (i) Electrode potential ($E°$) value is the sum of three factors :

(a) Enthalpy of atomisation $\Delta_a H$ for $Cu_{(s)} \rightarrow Cu_{(g)}$

(b) Ionisation enthalpy $\Delta_i H$ for $Cu_{(g)} \rightarrow Cu^{2+}_{(g)}$

(c) Hydration enthalpy $\Delta_{hyd} H$ for $Cu^{2+}_{(g)} \rightarrow Cu^{2+}_{(aq)}$

In case of copper the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration.

This is why $E^\circ_{M^{2+}/M}$ for Cu is positive.

(ii) *Refer to answer 26(ii).*

29. (i) *Refer to answer 26(i).*

(ii) As we move along transition metal series from left to right (*i.e.* Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence the atomic volume decreases. At the same time, atomic mass increases. Hence the density from titanium (Ti) to copper (Cu) increases.

30. (i) *Refer to answer 27(i).*

(ii) As one proceeds along a transition series, the nuclear charge increases which tends to decrease the size but the addition of electrons in the *d*-subshell increases the screening effect which counterbalances the effect of increased nuclear charge.

31. (i) As transition metals have a large number of unpaired electrons in the *d*-orbitals of their atoms they have strong interatomic attraction or metallic bonds. Hence, they have high enthalpy of atomization.

(ii) *Refer to answer 15(ii).*

32. (i) Sc(21) is a transition element but Ca(20) is not because of incompletely filled 3*d* orbitals.

(ii) *Refer to answer 17(i).*

33. The variability in oxidation states of transition metals is due to the incomplete filling of *d*-orbitals. Their oxidation states differ from each other by unity.

For example, Fe^{3+} and Fe^{2+}, Cu^{2+} and Cu^{+}, etc.

In case of non transition elements the oxidation states normally differ by units of two. For example Pb^{2+} and Pb^{4+}, Sn^{2+} and Sn^{4+}, etc. It arises due to expansion of octet and inert pair effect.

34. (i) *Refer to answer 17(i).*
(ii) *Refer to answer 27(i).*

35. (i) *Refer to answer 5.*

(ii) As manganese has maximum number of unpaired electrons (5) in 3*d* subshell in addition to 2 electrons in the 4*s* subshell, it can use the 7 electrons for bonding purpose.

36. (i) *Refer to answer 27(i).*

(ii) Middle of the transition series contains greater number of unpaired electrons in $(n-1)d$ and *ns* orbitals.

37. (i) *Refer to answer 8.*

(ii) This is because due to lanthanoid contraction the expected increase in size does not occur hence they have very high value of ionisation enthalpies.

38. (i) *Refer to answer 15(ii).*

(ii) The metals of 4*d* and 5*d*-series have more frequent metal bonding in their compounds than the 3*d*-metals because 4*d* and 5*d*-orbitals are more exposed in space than the 3*d*-orbitals. So the valence electrons are less tightly held and form metal-metal bonding more frequently.

39. (i) *Refer to answer 29(ii).*
(ii) *Refer to answer 15(ii).*

40. (i) This is due to presence of maximum number of unpaired electrons in Mn^{2+} in ($3d^5$).
(ii) *Refer to answer 8.*

41. (i) *Refer to answer 8.*
(ii) *Refer to answer 9.*

42. (i) *Refer to answer 17(ii).*

(ii) Much larger third ionisation energy of Mn(where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance.

43. (i) Lowest oxidation compounds of transition metals are basic due to their ability to get oxidised to higher oxidation states. Whereas the higher oxidation state of metal and compounds gets reduced to lower ones and hence acts as acidic in nature.

e.g., MnO is basic whereas Mn_2O_7 is acidic.

(ii) *Refer to answer 21(ii).*

44. (i) *Refer to answer 15(ii).*
(ii) *Refer to answer 26(ii).*

45 (i) *Refer to answer 31(i).*
(ii) *Refer to answer 15(ii).*

46. (i) *Refer to answer 12(i).*

(ii) Cr^{2+} is reducing since its configuration is converted to d^3 from d^4. d^3 has half filled t_{2g} configuration with higher stability.

(iii) *Refer to answer 6.*

47. (i) *Refer to answer 28(i).*

(ii) Mn^{2+} ion has stable half-filled ($3d^5$) electronic configuration. Its ionisation enthalpy value is lower in comparison to hydration enthalpy. Hence $E^\circ_{Mn^{2+}/Mn}$ is more negative.

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

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

48. *Refer to answer 16.*

49. (i) *Refer to answer 17(i).*
(ii) *Refer to answer 17(ii).*

(iii) Only these ions are coloured which have partially filled *d*-orbitals facilitating *d-d* transitions.

Sc^{3+} with $3d^0$ configuration is colourless while Ti^{3+} ($3d^1$) is coloured.

50. (i) Mn^{2+} is more stable due to half filled d^5 configuration and Mn^{3+} easily changes to Mn^{2+} hence, it is oxidising.
(ii) The $E^\circ_{M^{2+}/M}$ values are not regular which can be explained from the irregular variation of ionisation enthalpes *i.e.*, $IE_1 + E_2$ and also the sublimation enthalpies which are relatively much less for manganese and vanadium.
(iii) *Refer to answer 12(i).*

51. (i) All transition elements except the first and the last member in each series show a large number of variable oxidation states. This is because difference of energy in the $(n - 1)d$ and ns orbitals is very little.
Hence, electrons from both the energy levels can be used for bond formation.
(ii) *Refer to answer 31(i).*
(iii) *Refer to answer 33.*

52. (i) *Refer to answer 8.*
(ii) *Refer to answer 30(i).*
(iii) *Refer to answer 15(ii).*

53. (i) *Refer to answer 38(ii).*
(ii) Mn^{3+} is less stable and changes to Mn^{2+} which is more stable due to half-filled *d*-orbital configuration. That is why, Mn^{3+} undergoes disproportionation reaction.
(iii) *Refer to answer 21(ii).*

54. (i) *Refer to answer 15(ii).*
(ii) *Refer to answer 42(i).*
(iii) *Refer to answer 12(i).*

55. (i) *Refer to answer 26(ii).*
(ii) *Refer to answer 42(ii).*
(iii) *Refer to answer 50(i).*

56. (i) Change in $Cr_2O_7^{2-}$ to Cr(III) is 3 and in MnO_4^- to Mn (II) is 5.
Change in oxidation state is large and the stability of reduced products in V(III) < Cr(III) < Mn(II). This is why oxidising power of $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$.
(ii) Third ionization enthalpy of Mn is very high because the third electron has to be removed from the stable half-filled 3*d*-orbitals [Mn^{2+} ($Z = 25$) = $3d^5$].
(iii) *Refer to answer 46(iii).*

57. (i) *Refer to answer 31(i).*
(ii) *Refer to answer 17(i).*
(iii) *Refer to answer 8.*

58. (i) *Refer to answer 31(i).*
(ii) *Refer to answer 43(i).*
(iii) *Refer to answer 43(ii).*

59. (a) Manganese shows oxidation state of +7 in its oxometal anion MnO_4^- which is equivalent to its group number 7. Cr in $Cr_2O_7^{2-}$ and CrO_4^{2-} show oxidation state +6 which is equivalent to its group number 6.
(b) (i) *Refer to answer 3.*
(ii) *Refer to answer 28(i).*

60. (i) *Refer to answer 26(i).*
(ii) *Refer to answer 27(i).*
(iii) *Refer to answer 31(i).*

61. (i) The atomic radii of transition elements decrease with the increase in atomic number as the effective nuclear charge increases because shielding effect of *d*-electron is small.
(ii) *Refer to answer 28(i).*
(iii) *Refer to answer 42(ii).*

62. (i) *Refer to answer 8.*
(ii) *Refer to answer 21(ii).*
(iii) *Refer to answer 42(ii).*

63. (i) *Refer to answer 8.*
(ii) *Refer to answer 40(i).*
(iii) *Refer to answer 49(iii).*

64. (i) *Refer to answer 26(i).*
(ii) *Refer to answer 31(i).*
(iii) *Refer to answer 26(i).*

65. (i) *Refer to answer 31(i).*
(ii) *Refer to answer 15(ii).*
(iii) *Refer to answer 42(ii).*

66. (i) Mn shows maximum no. of oxidation states from +2 to +7 because Mn has maximum number of unpaired electrons in 3*d* sub-shell.

(ii) Cr has maximum melting point, because it has 6 unpaired electrons in the valence shell, hence it has strong interatomic interaction.

(iii) Sc shows only +3 oxidation state because because after losing 3 electrons, it has noble gas electronic configuration.

(iv) Mn is strong oxidising agent in +3 oxidation state because change of Mn^{3+} to Mn^{2+} give stable half filled (d^5) electronic configuration, $E°_{(Mn^{3+}/Mn^{2+})} = 1.5$ V.

67. $2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

68. $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

69. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

70. $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$

71. When the pH of the solution of potassium dichromate is decreased, the colour of the solution changes from yellow to orange due to the conversion of CrO_4^{2-} ions into $Cr_2O_7^{2-}$ ions.

$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \rightleftharpoons \underset{\text{Orange}}{Cr_2O_7^{2-}} + H_2O$$

72. $Cr_2O_{7(aq)}^{2-} + 3H_2S_{(g)} + 8H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} + 3S_{(s)}$

73. (i) $4FeCr_2O_4 + 16NaOH + 7O_2 \longrightarrow \underset{(A)}{8Na_2CrO_4} + 2Fe_2O_3 + 8H_2O$

$2Na_2CrO_4 + H_2SO_4 \longrightarrow \underset{(B)}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$

$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{(C)}{K_2Cr_2O_7} + 2NaCl$

(ii) Potassium dichromate is used as a powerful oxidising agent in industries and for staining and tanning of leather.

74. (i) $8MnO^-_{4\,(aq)} + 3S_2O^{2-}_{3\,(aq)} + H_2O_{(l)} \rightarrow 8MnO_{2(aq)} + 6\,SO^{2-}_{4\,(aq)} + 2OH^-_{(aq)}$

(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

75. (i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$

(ii) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

76. Preparation of potassium permanganate : Potassium permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidising agent like KNO_3 to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

or, $3K_2MnO_4 + 4HCl \rightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4KCl$

$2MnO_4^{2-} + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + H_2O$

77. Potassium dichromates are strong oxidising agents.

(i) *Refer to answer 76(ii).*

(ii) *Refer to answer 73.*

78. (i) *Refer to answer 77.*

(ii) Sodium dichromate can be crystallised out from sodium chromate solution by acidifying it with sulphuric acid.

$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

79. (i) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

(ii) $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$

80. (i) $H_2S \longrightarrow 2H^+ + S^{2-}$

$5S^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$

(ii) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

81. (i) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

(ii) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

82. (i) *Refer to answer 76(ii).*

(ii) *Refer to answer 67.*

83. (i) *Refer to answer 74(i).*

(ii) $Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6Fe^{2+}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O_{(l)}$

84. (i) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

(ii) *Refer to answer 72.*

85. (i) $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

(ii) $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

86. $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

Potassium dichromate is converted to chromate if pH is increased.

$$Cr_2O_7^{2-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} CrO_4^{2-}$$

87. (i) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(ii) *Refer to answer 84(i).*

88. (i) *Refer to answer 84(i).*

(ii) *Refer to answer 83(ii).*

89. (i) *Refer to answer 74(i).*
(ii) *Refer to answer 72.*

90. (i) $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$
(ii) *Refer to answer 25(ii).*

91. (i) The yellow solution of sodium chromate is acidified with sulphuric acid to give a orange solution of sodium dichromate $Na_2Cr_2O_7$ which is crystallised.

$$\underset{\text{Sodium Chromate}}{2Na_2CrO_4} + H_2SO_4 \rightarrow \underset{\text{Sodium dichromate}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

The solution of sodium dichromate is treated with potassium chloride to obtain potassium dichromate.

$$Na_2Cr_2O_7 + 2KCl \rightarrow \underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + 2NaCl$$

(ii) *Refer to answer 71.*

92. (i) *Refer to answer 88(ii).*
(ii) *Refer to answer 74(i).*

93. (i) *Refer to answer 73(i).*
(ii) The potassium manganate is oxidised to potassium permanganate by oxidation with chlorine.

$$2K_2MnO_{4(aq)} + Cl_{2(g)} \longrightarrow 2KMnO_{4(aq)} + 2KCl_{(aq)}$$

94. (i) *Refer to answer 83(ii).*
(ii) *Refer to answer 81(i).*
(iii) *Refer to answer 84(i).*

95. (i) The values, associated with Lokesh are alertness, care, responsibility and scientific knowledge.

(ii) (a) Oxidation of Oxalate ion into CO_2

$$5C_2O_4^{2-} + MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

(b) Oxidation of Nitrite into Nitrate

$$5NO_2^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

96. *Refer to answer 76.*

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

97. *Refer to answer 91.*

98. *Refer to answer 76.*

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+}\ 4H_2O + 5Fe^{3+}$$

99. (i) *Refer to answer 84(i).*
(ii) *Refer to answer 81(ii).*
(iii) *Refer to answer 72.*

100. *Refer to answer 98.*

101. (i) *Refer to answer 75(ii).*
(ii) *Refer to answer 83(ii).*
(iii) *Refer to answer 72.*

102. (i) *Refer to answer 77.*
(ii) *Refer to answer 84(i).*

103. Due to lanthanoid contraction the elements of 4*d* and 5*d*-series have similar atomic radii *e.g.*, Zr = 145 pm and Hf = 144 pm.

104. Europium (Eu) is well known to exhibit +2 oxidation state due to its half-filled *f* orbital in +2 oxidation state.

105. Lanthanoids showing +4 oxidation state are $_{58}Ce$, $_{59}Pr$, $_{65}Tb$ and $_{66}Dy$.

106. Lanthanum and all the lanthanoids predominantly show +3 oxidation state. However, some of the lanthanoids also show +2 and +4 oxidation states in solution or in solid compounds. This irregularity arises mainly due to attainment of stable empty ($4f^0$), half-filled ($4f^7$) and fully filled ($4f^{14}$) sub shell.

e.g. $Ce^{4+} : 4f^0$, $Eu^{2+} : 4f^7$
$Tb^{4+} : 4f^7$, $Yb^{2+} : 4f^{14}$

107. *Refer to answer 103.*

108. *Refer to answer 106.*

109. As the atomic number increases, each succeeding element contains one more electron in the 4*f* orbital and one extra proton in the nucleus. The 4*f* electrons are rather ineffective in screening the outer electrons from the nucleus. As a result, there is gradual increase in the nuclear attraction for the outer electrons. Consequently, the atomic size gradually decreases. This is called lanthanoid contraction.

110. The steady decrease in the atomic and ionic radii (having the same charge) with increase in atomic number across the series from lanthanum to lutetium is known as lanthanoid contraction.

111. *Refer to answer 106.*

112. Because they have empty 4*f* subshell.

113. Ce(III) has outer configuration $4f^1 5d^0 6s^0$. It easily loses an electron to acquire the configuration $4f^0$ and forms Ce(IV). In fact this is the only (+IV) lanthanoid which exists in solution.

114. *Refer to answer 103.*

115. Lanthanoid contraction : The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by 4*f*-electrons.

Consequences of lanthanoid contraction :

(i) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.

(ii) Atomic and ionic sizes of 4*d* transition series elements and 5*d* series elements are similar. *e.g.*, atomic radii of zirconium(Zr) is same as that of hafnium Hf.

116. *Refer to answer 115.*

117. *Refer to answer 115.*

118. Europium (II) has electronic configuration $[Xe]4f^7 5d^0$ while cerium (II) has electronic configuration $[Xe]\ 4f^1\ 5d^1$. In Eu^{2+}, 4*f* subshell is half filled and 5*d*-subshell is empty. Since half filled and completely filled electronic configurations are more stable, Eu^{2+} ions is more stable than Ce^{2+} in which neither 4*f* subshell nor 5*d* subshell is half filled or completely filled.

119. Ce (Z = 58) = $[Xe]^{54}\ 4f^1\ 5d^1\ 6s^2$

$\therefore\ Ce^{3+} = [Xe]^{54}\ 4f^1\ 5d^0\ 6s^0$

Therefore, it has only one unpaired electron. *i.e.*, $n = 1$

$$\therefore\quad \mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

120. *Refer to answer 115.*

121. Mischmetal is well known alloy which consists of a lanthanoid metal (about 95%), iron (about 5%) and traces of S, C, Ca, Al etc.

Mischmetal is used in Mg based alloy to produce bullets shells and lighter flint.

122. *Refer to answer 115.*

123. *Refer to answer 115.*

124. *Refer to answer 115.*

125. The irregularities in the electronic configurations of actinoids are due to extra stabilities of the f^0 f^7 and f^{14} orbitals.

126. The actinoid contraction is more than lanthanoid contraction because 5*f*-electrons are more poorly shielding than 4*f*-electrons.

127. Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between 5*f* and 6*d* orbitals in actinoids than the energy difference between 4*f* and 5*d* orbitals in case of lanthanoids.

128. The actinoid contraction is more than lanthanoid contraction because of poor shielding by 5*f*-electrons.

129. *Refer to answer 126.*

130. *Refer to answer 126.*

131. *Refer to answer 126.*

132. *Refer to answer 126.*

133. The chemistry of actinoids is not as smooth as lanthanoid because they show greater number of oxidation states due to comparable energies of 5*f*, 6*d* and 7*s* orbitals.

134. *Refer to answer 126.*

135. *Refer to answer 126.*

Only trends of magnetic properties and colour of lanthanoids are similar to actinoids.

136. Structure : All the lanthanoids are silvery white soft metals. Hardness of Lanthanoids increases with increasing atomic number.

The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is due to irregularities in metallic radii which are greater than that of lanthanoids.

Chemical reactivity : Earlier members of lanthanoid series are quite reactive similar to calcium but with increasing atomic number they behave more like aluminium.

The actinoids are highly reactive in finely divided state.

137. (i) **Electronic configuration :** The general electronic configuration of lanthanoids is $[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$ where as that of actinoids is $[Rn]\ 5f^{1-14}\ 6d^{0-1}\ 7s^2$. Thus, lanthanoids involve the filling of 4*f*-orbitals whereas actinoids involve the filling of 5*f*-orbitals.

(ii) **Oxidation states :** Lanthanoids have principal oxidation state of +3. In addition, the lanthanoids show limited oxidation states such as +2, +3 and +4 because of large energy gap between 4*f* and 5*d* subshells. On the other hand, actinoids show a large number of oxidation states because of small energy gap between 5*f* and 6*d* subshells.

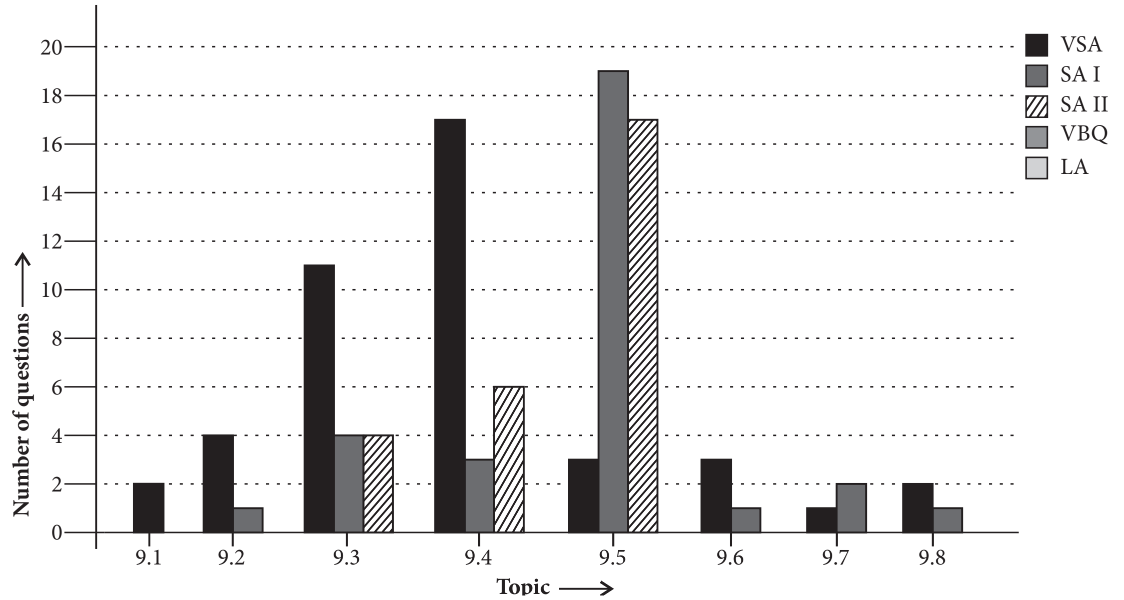
(iii) **Chemical reactivity :** (a) First few members of lanthanoids are quite reactive almost like calcium, where as actinoids are highly reactive metals especialy in the finely divided state.

(b) Lanthanoids react with dilute acids to liberate H_2 gas whereas actinoids react with boiling water to give a mixture of oxide and hydride.

09

Coordination Compounds

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



- ⏩ Maximum total weightage is of *Bonding in Coordination Compounds.*
- ⏩ Maximum VSA type questions were asked from *Isomerism in Coordination Compounds.*
- ⏩ Maximum SA I and SA II type questions were asked from *Bonding in Coordination Compounds.*

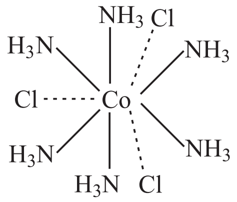
QUICK RECAP

⏩ **Werner's coordination theory :**

- ▶ It explains the nature of bonding in complexes. Metals show two different kinds of valencies:
  - – **Primary valency :** Non directional and ionisable. It is equal to the oxidation state of the central metal ion.

- **Secondary valency :** Directional and non-ionisable. It is equal to the coordination number of the metal. It is commonly satisfied by neutral and negatively charged or some times by positively charged ligands.

▶ The ionisation of the coordination compound is written as :
$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$



$[Co(NH_3)_6]Cl_3$
Representation of $CoCl_3 \cdot 6NH_3$ complex according to Werner's theory

Addition compounds : These are the compounds formed by combination of two or more simple compounds are called *addition compounds*. They are of two types :

▶ **Double salt :** A compound formed by combination of two or more simple compounds, which is stable in solid state only is called *double salt*. In solution it breaks into component ions.

e.g., $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Potash alum
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Mohr's salt
$KCl \cdot MgCl_2 \cdot 6H_2O$	Carnallite

▶ **Complex compound :** A compound formed by combination of two or more simple compounds which retain its identity in solid and solution states both is called *complex compound*.
e.g., $K_4[Fe(CN)_6]$ Potassium ferrocyanide
$[Cu(NH_3)_4]SO_4$ Cuprammine sulphate

The central metal atom or ion and ligand taken together is called *co-ordination entity*. It may be positive, negative or neutral.

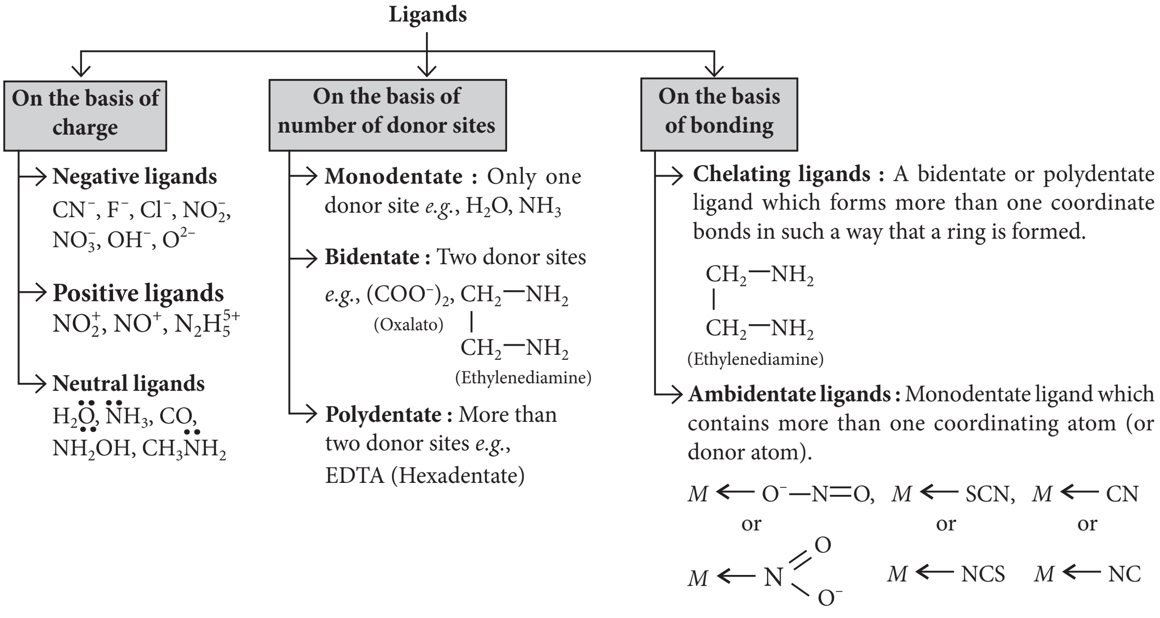
e.g., $[Cu(NH_3)_4]^{2+}$, $[Fe(CN)_6]^{4-}$, $[Ni(CO)_4]$

The atom or ion with which definite number of ligands are attached in a definite geometry are called *central atom/ion*. Any atom/ion which has high positive charge density or vacant orbitals of suitable energy may be central atom or ion. *e.g.*, transition metals, lanthanoids.

It is Lewis acid (electron acceptor).

Molecules or ions which are bound to the central atom/ion in the co-ordination entity are called *ligands*. A molecule or ion which has high negative charge or dipole or lone pair of electrons may be ligands. It is Lewis base (electron donor).

Classification of ligands :



Ligands

- **On the basis of charge**
  - **Negative ligands** CN^-, F^-, Cl^-, NO_2^-, NO_3^-, OH^-, O^{2-}
  - **Positive ligands** NO_2^+, NO^+, $N_2H_5^{5+}$
  - **Neutral ligands** $H_2\ddot{O}$, $\ddot{N}H_3$, CO, NH_2OH, CH_3NH_2
- **On the basis of number of donor sites**
  - **Monodentate :** Only one donor site *e.g.*, H_2O, NH_3
  - **Bidentate :** Two donor sites *e.g.*, $(COO^-)_2$ (Oxalato), CH_2-NH_2 | CH_2-NH_2 (Ethylenediamine)
  - **Polydentate :** More than two donor sites *e.g.*, EDTA (Hexadentate)
- **On the basis of bonding**
  - **Chelating ligands :** A bidentate or polydentate ligand which forms more than one coordinate bonds in such a way that a ring is formed.
    CH_2-NH_2 | CH_2-NH_2 (Ethylenediamine)
  - **Ambidentate ligands :** Monodentate ligand which contains more than one coordinating atom (or donor atom).
    $M \leftarrow O^--N=O$, or $M \leftarrow N(=O)O^-$; $M \leftarrow SCN$, or $M \leftarrow NCS$; $M \leftarrow CN$ or $M \leftarrow NC$

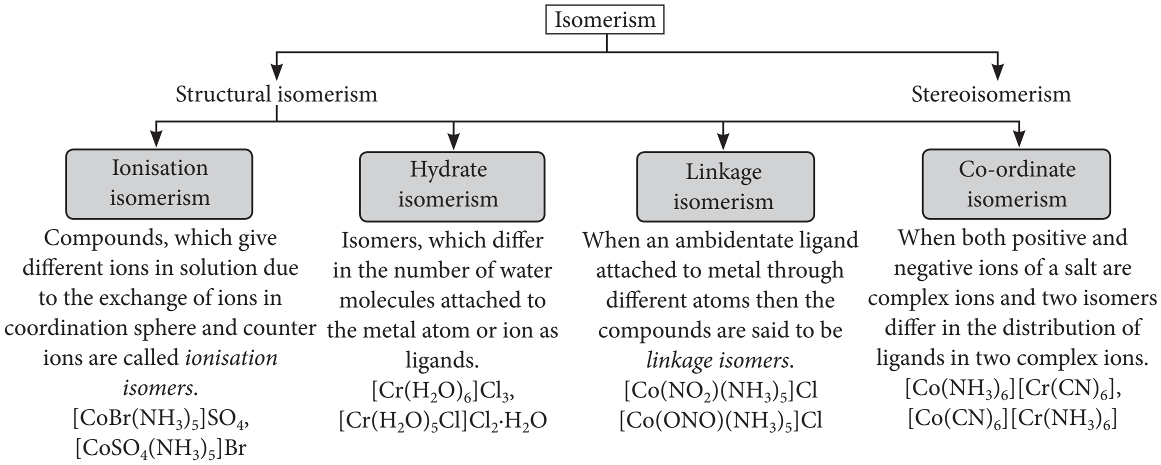
Homoleptic and heteroleptic complexes :

- **Homoleptic complexes :** Complexes in which a metal is bound to only one kind of ligand are called *homoleptic complexes.*
  e.g., $[Co(NH_3)_6]^{3+}$, $[Ti(H_2O)_6]^{3+}$, $[Cu(CN)_4]^{3-}$
- **Heteroleptic complexes :** Complexes in which the central atom is bound to different type of ligands are called *heteroleptic complexes.*
  e.g., $[Co(NH_3)_4Cl_2]$, $K_2[Fe(CN)_5NO]$, $[Fe(H_2O)_5NO]SO_4$

Nomenclature of coordination compounds :

- **Rules for writing the formula of coordination compounds :**
  - Formula of the cation whether simple or complex must be written first followed by anion.
  - The coordination sphere is written in square brackets.
  - Within the coordination sphere the sequence of symbols is, first the metal atom followed by anionic ligand then neutral ligand finally cationic ligand. Ligands of same type are arranged alphabetically.
  - Polyatomic ligands are enclosed in parentheses.
  - The number of cations or anions to be written in the formula is calculated on the basis that total positive charge must be equal to the total negative charge, as the complex as a whole is electrically neutral.
- **Rules for naming coordination compounds :**
  - The cation is named first then the anion.
  - In naming coordination sphere, ligands are named first in alphabetical order followed by metal atom and then oxidation state of metal by a roman numeral in parentheses.
  - Name of coordination compounds is started with a small letter and the complex part is written as one word.
- **Naming of ligands :**
  - Name of anionic ligands end in –*o*. *e.g.,* Cl^- : Chlorido
  - Neutral ligands (with a few exceptions) retain their names *e.g.,* NH_3 : Ammine
  - Name of cationic ligands end in – *ium*. *e.g.,* NO_2^+ : Nitronium
  - Certain ligands are represented by abbreviations in parentheses instead of their complex structural formulae. *e.g.,* ethylenediamine(*en*).
  - Ambidentate ligands are named by using different names of ligands or by placing the symbol of donor atom.
    e.g.,—SCN^- (Thiocyanato-S or Thiocyanato),
    —NCS^- (Thiocyanato-N or Isothiocyanato),
    —ONO^- (Nitrito-O or Nitrito),
    —NO_2^- (Nitrito-N or Nitro)
  - The prefixes *di-*, *tri-*, *tetra-*, *penta-* and *hexa-* are used to indicate the number of each ligand. If the ligand name includes such a prefix, the ligand name should be placed in parentheses and preceded by *bis*-(2), *tris*-(3), *tetrakis*-(4), *pentakis*-(5) and *hexakis*-(6).
  - When the coordination sphere is anionic, name of central metal ends in –*ate*.

Isomerism : Two or more substances having the same molecular formula but different structural or spatial arrangement are called *isomers* and phenomenon is called *isomerism.*

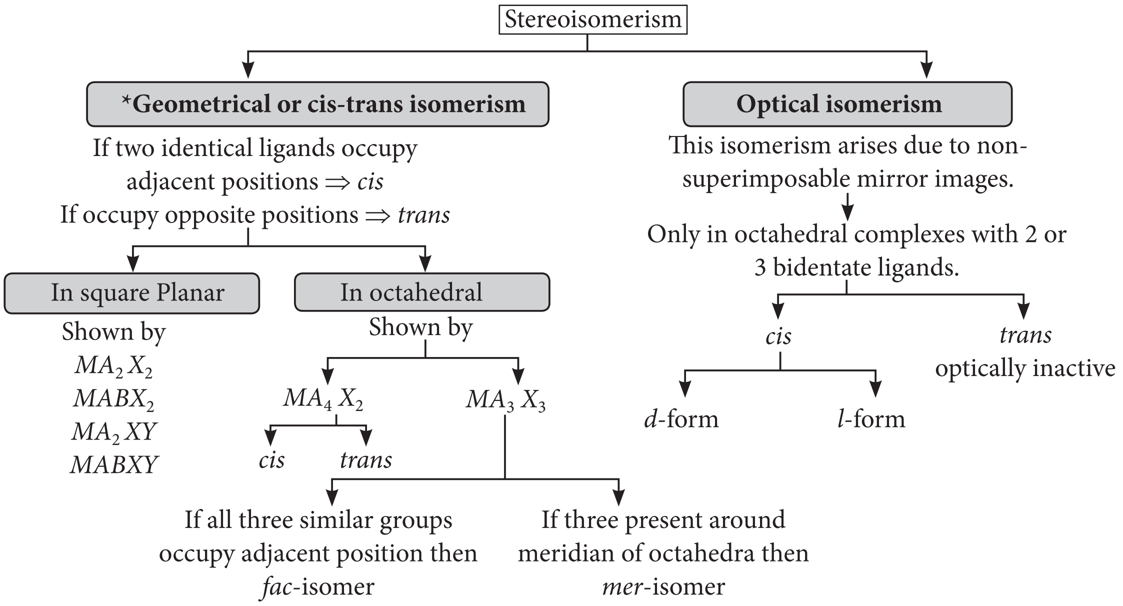


Compounds, which give different ions in solution due to the exchange of ions in coordination sphere and counter ions are called *ionisation isomers.*
$[CoBr(NH_3)_5]SO_4$, $[CoSO_4(NH_3)_5]Br$

Isomers, which differ in the number of water molecules attached to the metal atom or ion as ligands.
$[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$

When an ambidentate ligand attached to metal through different atoms then the compounds are said to be *linkage isomers.*
$[Co(NO_2)(NH_3)_5]Cl$
$[Co(ONO)(NH_3)_5]Cl$

When both positive and negative ions of a salt are complex ions and two isomers differ in the distribution of ligands in two complex ions.
$[Co(NH_3)_6][Cr(CN)_6]$, $[Co(CN)_6][Cr(NH_3)_6]$



Stereoisomerism

***Geometrical or cis-trans isomerism**

If two identical ligands occupy adjacent positions ⇒ *cis*
If occupy opposite positions ⇒ *trans*

In square Planar
Shown by MA_2X_2, $MABX_2$, MA_2XY, $MABXY$

In octahedral
Shown by MA_4X_2 (*cis*, *trans*), MA_3X_3

If all three similar groups occupy adjacent position then *fac*-isomer

If three present around meridian of octahedra then *mer*-isomer

Optical isomerism

This isomerism arises due to non-superimposable mirror images.

Only in octahedral complexes with 2 or 3 bidentate ligands.

cis: *d*-form, *l*-form

trans: optically inactive

(* Geometrical isomerism is not shown by tetrahedral complexes.)

Bonding in coordination compounds :

- **Valence bond theory :** It was developed by Pauling.
  - A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bonds with the ligands.
  - Central metal ion can use appropriate number of *s*, *p* or *d*-orbitals for hybridisation depending upon the total number of ligands.
  - The outer orbital (high spin) or inner orbital (low spin) complexes are formed depending upon whether outer *d*-orbitals or inner *d*-orbitals are used.

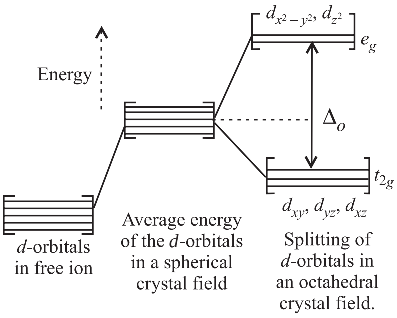
C. No.	Type of hybridisation	Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$Ni(CO)_4$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$, where $X = Cl^-, Br^-, I^-$
	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[Ni(NH_3)_4]^{2+}$
5	dsp^3	Trigonal bipyramidal	$[Fe(CO)_5]$, $[CuCl_5]^{3-}$
	sp^3d	Square pyramidal	$[SbF_5]^{2-}$
6	d^2sp^3	Octahedral (Inner orbital)	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
	sp^3d^2	Octahedral (Outer orbital)	$[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

Inner orbital complexes	Outer orbital complexes
Involves inner *d*-orbitals *i.e.*, $(n-1)d$-orbitals.	Involves outer *d*-orbitals *i.e.*, *nd*-orbitals
Low spin complexes	High spin complexes
Have less or no unpaired electrons. *e.g.*, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{4-}$	Have large number of unpaired electrons. *e.g.*, $[MnF_6]^{3-}$, $[CoF_6]^{3-}$

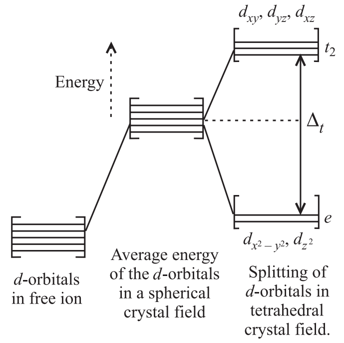
- Low spin complexes are generally diamagnetic and high spin complexes are paramagnetic.
- Paramagnetism ∝ No. of unpaired electrons.
- Magnetic moment $=\sqrt{n(n+2)}$ B.M. where n = number of unpaired electrons.

▶ **Crystal field theory :** It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. When ligands approach the central metal ion, then the five degenerate orbitals do not possess equal energy any more and results in splitting, which depends upon nature of ligand field strength.

- Greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it.
- Crystal field splitting in octahedral coordination complexes can be shown as :



- If $\Delta_o < P$ (where 'P' is energy required for forced pairing of electrons) then the electrons will remain unpaired and a high spin complex is formed.
- If $\Delta_o > P$, then pairing of electrons takes place and a low spin complex is formed.
- Crystal field splitting in tetrahedral complexes can be shown as :



- Difference in energy between e and t_2 level is less in tetrahedral complexes.

  $\Delta_t = \frac{4}{9}\Delta_o.$

- **Spectrochemical series :** Arrangement of ligands in the order of increasing field strength.

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O$$
$$< NCS^- < edta^{4-} < NH_3 < en < NO_2^- < CN^- < CO$$
$$\text{Weak field ligands} \xrightarrow{\text{Increasing order of CFSE } (\Delta_o)} \text{Strong field ligands}$$

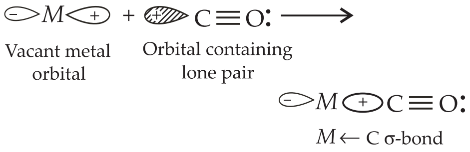
Colour of coordination compounds : The magnitude of CFSE (Δ_o) for most of the complexes is of the same order as the energy of a photon of visible light. Hence, whenever *d-d* transition takes place, it imparts colour to the complex. The colour of the complex is the colour complementary to the wavelength absorbed.

Bonding in metal carbonyls :

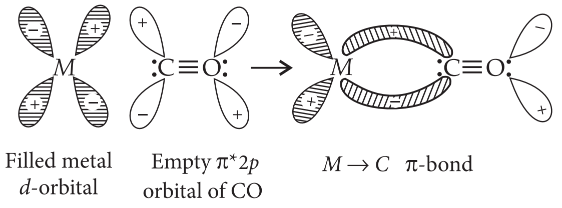
▶ Metal–carbon bond in metal carbonyls possesses both σ- and π-characters.

▶ Its formation involves the following steps :

- Overlap of filled π_{2p} orbital of CO with suitable empty metal *d*-orbital resulting in the formation of sigma bond.



- π-overlap involving filled metal *d*-orbital with an empty antibonding π^*2p orbital of same CO. This results in formation of $M \rightarrow$ C π-bond. This is also called *back bonding*.



Stability of complexes : The formation of the complex in a solution is a reversible and exothermic process.

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

$$K = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$

where, K = stability constant

- Higher the value of stability constant (K), higher will be the stability of complex.
- Higher the polarising power of metal ion and basicity of ligand, higher will be the stability of complex.

Applications of coordination compounds :

- Coordination compounds are of great importance in biological system. *e.g.*, chlorophyll, haemoglobin, vitamin B_{12}, etc. are coordinate compounds of Mg, Fe and Co respectively.
- Coordination compounds are used for qualitative and quantitative analysis, extraction of metals, electroplating, photography and as dyes.
- *cis*-platin is used in cancer treatment, EDTA is often used for treatment of lead poisoning.
- Coordination compounds are used as catalyst.

Previous Years' CBSE Board Questions

9.1 Werner's Theory of Coordination Compounds

VSA (1 mark)

1. When a co-ordination compound $CrCl_3 \cdot 6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write structural formula of the complex. *(1/2, Delhi 2016)*

2. When a coordination compound $CoCl_3 \cdot 6NH_3$ is mixed with $AgNO_3$, 3 moles of AgCl are precipitated per mole of the compound. Write structural formula of the complex. *(1/2, AI 2016)*

9.2 Definition of Some Important Terms Pertaining to Coordination Compounds

VSA (1 mark)

3. What do you understand by 'denticity of a ligand'? *(Foreign 2011)*

4. Giving a suitable example, explain the following: Ambidentate ligand *(1/3, AI 2009)*

5. What is meant by chelate effect? *(1/3, AI 2009C)*

6. What is a ligand? Give an example of a bidentate ligand. *(1/3, Delhi 2008)*

SA I (2 marks)

7. Explain the following terms giving a suitable example in each case :
(i) Ambident ligand
(ii) Denticity of a ligand *(2/3, AI 2011)*

9.3 Nomenclature of Coordination Compounds

VSA (1 mark)

8. When a co-ordination compound $CrCl_3 \cdot 6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write IUPAC name of the complex. *(1/2, Delhi 2016)*

9. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$. *(1/3, AI 2014)*

10. Write down the formula of : Tetraamineaquachloridocobalt(III)chloride. *(AI 2012C)*

11. Name the following coordination compound : $K_3[CrF_6]$ *(Foreign 2011)*

12. Write the IUPAC name of $[PtCl(NH_2CH_3)(NH_3)_2]Cl$. *(Delhi 2011C, 2010C)*

13. Write the IUPAC name of $[Pt(NH_3)_4Cl_2]Cl_2$. *(AI 2011C)*

14. Write the IUPAC name of $[Cr(NH_3)_6\,[Co(CN)_6]$. *(AI 2011C)*

15. Write the IUPAC name of $[Co(NH_3)_5Cl]Cl_2$. (Atomic no. of Co = 27) *(Delhi 2010C)*

16. Using the IUPAC norms, write the systematic name of following : $[CoCl(NO_2)(NH_3)_4]Cl$ *(Delhi 2008C)*

17. Using the IUPAC norms, write the systematic name of the following : $[Co(NH_3)_6]\,[Cr(CN)_6]$ *(Delhi 2008C)*

SA I (2 marks)

18. (i) Write down the IUPAC name of the following complex : $[Cr(NH_3)_2Cl_2(en)]Cl$ (*en* = ethylenediamine)
(ii) Write the formula for the following complex : Pentaamminenitrito-O-cobalt (III). *(Delhi 2015)*

19. Using IUPAC norms write the formulae for the following coordination compounds :
(i) Hexaamminecobalt(III)chloride
(ii) Potassiumtetrachloridonickelate(II) *(AI 2015)*

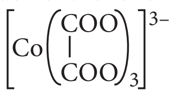
20. (i) Write down the IUPAC name of the following complex. $[Cr\,(en)_3]Cl_3$
(ii) Write the formula for the following complex. Potassium trioxalato chromate (III) *(Foreign 2015)*

21. Name the following coordination compounds according to IUPAC system of nomenclature :
(i) $[Co(NH_3)_4(H_2O)Cl]Cl_2$
(ii) $[CrCl_2(en)_2]Cl$, (en = ethane – 1,2-diamine) *(Delhi 2010)*

SA II (3 marks)

22. Write the IUPAC name of the following :
(i) $[Co(NH_3)_6]Cl_3$ (ii) $[NiCl_4]^{2-}$
(iii) $K_3[Fe(CN)_6]$ *(AI 2015C)*

23. Write down the IUPAC name for each of the following complexes :
(i) $[Co(NH_3)_5Cl]Cl_2$ (ii) $K_3[Fe(CN)_6]$
(iii) $[NiCl_4]^{2-}$ *(Delhi 2014C)*

24. Write the IUPAC name and draw the structure of each of the following complex entities :
(i)  $\left[\mathrm{Co}\left(\begin{array}{c}\mathrm{COO}\\ | \\ \mathrm{COO}\end{array}\right)_3\right]^{3-}$ (ii) $[Cr(CO)_6]$
(iii) $[PtCl_3(C_2H_4)]$
(At. nos. Cr = 25, Co = 27, Pt = 78) *(AI 2014C)*

25. Write the IUPAC names of the following coordination compounds :
(i) $[Cr(NH_3)_3Cl_3]$
(ii) $K_3[Fe(CN)_6]$
(iii) $[CoBr_2(en)_2]^+$, (en = ethylenediamine) *(Delhi 2013)*

9.4 Isomerism in Coordination Compounds

VSA (1 mark)

26. Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically active. *(1/3, Delhi 2016)*

27. Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically inactive. *(AI 2016)*

28. Draw the geometrical isomers of complex $[Pt(NH_3)_2Cl_2]$. *(1/3, Delhi 2015, 2007)*

29. Write down the IUPAC name of the complex $[Pt(en)_2Cl_2]^{2+}$. What type of isomerism is shown by this complex? *(AI 2015)*

30. Draw the geometrical isomers of complex $[Pt(en)_2Cl_2]^{2+}$. *(1/3, Foreign 2015)*

31. What type of isomerism is exhibited by the complex $[Co(en)_3]^{3+}$? (en = ethane-1,2-diamine) *(1/3, AI 2014)*

32. What type of isomerism is shown by the following complex :
$[Co(NH_3)_6][Cr(CN)_6]$ *(Foreign 2014)*

33. What type of isomerism is exhibited by the following complex :
$[Co(NH_3)_5SO_4]Cl$ *(Foreign 2014)*

34. What type of isomerism is exhibited by the complex $[Co(NH_3)_5NO_2]^{2+}$? *(Foreign 2014)*

35. Indicate the types of isomerisms exhibited by the complex $[Co(NH_3)_5(NO_2)](NO_3)_2$. (At no. Co = 27) *(AI 2012C)*

36. Give IUPAC name of ionisation isomer of $[Ni(NH_3)_3NO_3]Cl$. *(AI 2012C)*

37. Give an example of linkage isomerism. *(Delhi 2010)*

38. Give an example of coordination isomerism. *(Delhi 2010)*

39. Give an example of ionization isomerism. *(Delhi 2010)*

40. Giving a suitable example, explain the following: Linkage isomerism *(1/3, AI 2009)*

41. Square planar complexes (of MX_2L_2 type) with coordination number of 4 exhibit geometrical isomerism whereas tetrahedral complexes with similar composition, do not. Why? *(1/3, Delhi 2009C)*

SA I (2 marks)

42. Name the following coordination compounds and draw their structures.
(i) $[CoCl_2(en)_2]Cl$
(ii) $[Pt(NH_3)_2Cl(NO_2)]$
(At. No. Co = 27, Pt = 78) *(Foreign 2011)*

43. Draw the structure of isomers, if any and write the name of the following complexes :
(i) $[Cr(NH_3)_4Cl_2]^+$
(ii) $[Co(en)_3]^{3+}$ *(Foreign 2011)*

44. Write the name and draw the structures of each of the following complex compounds :
(i) $[Co(NH_3)_4(H_2O)_2]Cl_3$
(ii) $[Pt(NH_3)_4][NiCl_4]$ *(2/5, Delhi 2007)*

SA II **(3 marks)**

45. Indicate the types of isomerism exhibited by the following complexes :
(i) $[Co(NH_3)_5(NO_2)]^{2+}$
(ii) $[Co(en)_3]Cl_3$ (*en* = ethylene diamine)
(iii) $[Pt(NH_3)_2Cl_2]$ *(Delhi 2015C)*

46. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. What type of isomerism does it exhibit? *(Delhi 2014)*

47. Draw the structures of optical isomers of each of the following complex ions :
$[Cr(C_2O_4)]^{3-}$,$[PtCl_2(en)_2]^{2+}$, $[Cr(NH_3)_2Cl_2(en)]^+$ *(Delhi 2014C)*

48. Write the types of isomerism exhibited by the following complexes :
(i) $[Co(NH_3)_5Cl]SO_4$ (ii) $[Co(en)_3]^{3+}$
(iii) $[Co(NH_3)_6]$ $[Cr(CN)_6]$ *(Delhi 2013)*

49. Name the following coordination entities and draw the structures of their stereoisomers :
(i) $[Co(en)_2Cl_2]^+$ (*en* = ethane-1,2-diamine)
(ii) $[Cr(C_2O_4)_3]^{3-}$
(iii) $[Co(NH_3)_3Cl_3]$
(Atomic numbers Cr = 24, Co = 27) *(AI 2012)*

50. Write the structures and names of all the stereoisomers of the following compounds :
(i) $[Co(en)_3]Cl_3$ (ii) $[Pt(NH_3)_2Cl_2]$
(iii) $[Fe(NH_3)_4Cl_2]Cl$ *(AI 2011)*

9.5 Bonding in Coordination Compounds

VSA **(1 mark)**

51. Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic? (At. no. : Cr = 24, Co = 27, Ni = 28) *(1/3, AI 2014)*

52. Explain the following term giving a suitable example :
Crystal field splitting in an octahedral field. *(1/3, AI 2011)*

53. Giving a suitable example, explain the following:
Crystal field splitting *(1/3, AI 2009)*

SA I **(2 marks)**

54. For the complex $[Fe(CN)_6]^{3-}$, write the hybridization type, magnetic character and spin nature of the complex. (At. number : Fe = 26). *(2/3,Delhi 2016)*

55. For the complex $[Fe(H_2O)_6]^{3+}$, write the hybridization magnetic character and spin of the complex. (At number Fe = 26) *(2/3,AI 2016)*

56. (i) On the basis of crystal field theory, write the electronic configuration of d^4 ion if $\Delta_o < P$.
(ii) Write the hybridization and magnetic behaviour of the complex $[Ni(CO)_4]$.
(At. no. of Ni =28) *(2/3, Delhi 2015)*

57. Write the hybridization and shape of the following complexes :
(i) $[CoF_6]^{3-}$ (ii) $[Ni(CN)_4]^{2-}$
(Atomic number : Co = 27, Ni = 28) *(AI 2015)*

58. Write the state of hybridization, shape and IUPAC name of the complex $[CoF_6]^{3-}$. (Atomic no. of Co = 27) *(Foreign 2014)*

59. Write the state of hybridization, shape and IUPAC name of the complex $[Ni(CN)_4]^{2-}$. (Atomic no. of Ni = 28) *(Foreign 2014)*

60. Write the state of hybridization, shape and IUPAC name of the complex $[Co(NH_3)_6]^{3+}$. (Atomic no. of Co = 27) *(Foreign 2014)*

61. Give the formula of each of the following coordination entities :
(i) Co^{3+} ion is bound to one Cl^-, one NH_3 molecule and two bidentate ethylene diamine (*en*) molecules.
(ii) Ni^{2+} ion is bound to two water molecules and two oxalate ions.
Write the name and magnetic behaviour of each of the above coordination entities.
(At. nos. Co = 27, Ni = 28) *(2/3, Delhi 2012)*

62. State a reason for each of the following situations:
(i) Co^{2+} is easily oxidised to Co^{3+} in presence of a strong ligand.
(ii) The molecular shape of $Ni(CO)_4$ is not the same as that of $[Ni(CN)_4]^{2-}$.
(2/3, Delhi 2012)

63. Using valence bond theory, explain the geometry and magnetic behaviour of $[Co(NH_3)_6]^{3+}$. (At. no. of Co = 27) *(2/3, Delhi 2012C)*

64. Using valence bond theory of complexes, explain the geometry and magnetic nature of $[Ni(CN)_4]^{2-}$. (At. no. of Ni = 28) *(2/3, Delhi 2012C)*

65. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain (At. no. Fe = 26) *(Delhi 2012C)*

66. Give the name, the stereochemistry and the magnetic behaviour of the following complexes:
(i) $[Co(NH_3)_5Cl]Cl_2$ (ii) $K_2[Ni(CN)_4]$ *(Foreign 2011)*

67. Describe the shape and magnetic behaviour of following complexes :
(i) $[Co(NH_3)_6]^{3+}$ (ii) $[Ni(CN)_4]^{2-}$.
(At. no. Co = 27, Ni = 28) *(Delhi 2010)*

68. Using the valence bond theory predict the geometry and magnetic behaviour of $[CoF_6]^{3-}$.
[At. no. of Co =27] *(Delhi 2010C)*

69. Describe the type of hybridization, shape and magnetic property of $[Co(NH_3)_4Cl_2]^+$.
[Given : At. no. of Co = 27] *(2/3, Delhi 2009C)*

70. Write the IUPAC name and indicate the shape of the complex ion $[Co(en)_2Cl(ONO)]^+$.
[At. no. Co = 27] *(2/3, Delhi 2009C)*

71. Using the valence bond approach, deduce the shape and magnetic character of $[Co(NH_3)_6]^{3+}$ ion.
[Given : Atomic no. of Co = 27] *(Delhi 2008C)*

72. Explain as to how the two complexes of nickel, $[Ni(CN)_4]^{2-}$ but $Ni(CO)_4$ have different structures but do not differ in their magnetic behaviour. (Ni = 28) *(2/3, Delhi 2008)*

SA II (3 marks)

73. For the complex $[NiCl_4]^{2-}$, write
(i) the IUPAC name
(ii) the hybridization type
(iii) the shape of the complex.
(Atomic no. of Ni = 28) *(AI 2013)*

74. What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when
(i) $\Delta_o > P$ (ii) $\Delta_o < P$ *(AI 2013)*

75. Write the name, the structure and the magnetic behaviour of each one of the following complexes :
(i) $[Pt(NH_3)Cl(NO_2)]$ (ii) $[Co(NH_3)_4Cl_2]Cl$
(iii) $Ni(CO)_4$
(At. nos. Co = 27, Ni = 28, Pt = 78) *(Delhi 2012)*

76. Name the following coordination entities and describe their structures.
(i) $[Fe(CN)_6]^{4-}$ (ii) $[Cr(NH_3)_4Cl_2]^+$
(iii) $[Ni(CN)_4]^{2-}$ *(AI 2012)*

77. Write the name, stereochemistry and magnetic behaviour of the following : (At. nos. Mn = 25, Co = 27, Ni = 28)
(i) $K_4[Mn(CN)_6]$ (ii) $[Co(NH_3)_5Cl]Cl_2$
(iii) $K_2[Ni(CN)_4]$ *(Delhi 2011)*

78. For the complex $[Fe(en)_2Cl_2]Cl$, identify the following :
(i) Oxidation number of iron
(ii) Hybrid orbitals and shape of the complex
(iii) Magnetic behaviour of the complex
(iv) Number of its geometrical isomers
(v) Whether there may be optical isomer also.
(vi) Name of the complex. *(Delhi 2011, 2009)*

79. Write the state of hybridization, the shape and the magnetic behaviour of the following complex entities :
(i) $[Cr(NH_3)_4Cl_2]Cl$ (ii) $[Co(en)_3]Cl_3$
(iii) $K_2[Ni(CN)_4]$ *(AI 2011)*

80. Write the name, the state of hybridization, the shape and the magnetic behaviour of the following complexes :
$[CoCl_4]^{2-}$, $[Ni(CN)_4]^{2-}$, $[Cr(H_2O)_2(C_2O_4)_2]^-$
(At. no. : Co = 27, Ni = 28, Cr = 24) *(AI 2010)*

81. Write the IUPAC name, deduce the geometry and magnetic behaviour of the complex $K_4[Mn(CN)_6]$.
[Atomic no. of Mn = 25] *(AI 2010C)*

82. Compare the following complexes with respect to their shape, magnetic behaviour and the hybrid orbitals involved :
(i) $[CoF_4]^{2-}$
(ii) $[Cr(H_2O)_2(C_2O_4)_2]^-$
(iii) $[Ni(CO)_4]$
(Atomic number : Co = 27, Cr = 24, Ni = 28) *(Delhi 2009)*

83. Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units :
$[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $Ni(CO)_4$
(At. nos. : Co = 27, Cr = 24, Ni = 28) *(AI 2009)*

84. Explain the following :
(i) Low spin octahedral complexes of nickel are not known.
(ii) The π-complexes are known for transition elements only.
(iii) CO is a stronger ligand than NH_3 for many metals. *(AI 2009)*

85. Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units :
(i) $[Ni(CN)_4]^{2-}$ (ii) $[NiCl_4]^{2-}$
(iii) $[CoF_6]^{3-}$
[At. nos. : Ni = 28; Co = 27] *(AI 2009)*

86. What will be the correct order for the wave lengths of absorption in the visible region for the following :
$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$ *(AI 2008)*

87. (a) What is the basis of formation of the spectrochemical series?
(b) Draw the structures of geometrical isomers of the following coordination complexes :
$[Co(NH_3)_3Cl_3]$ and $[CoCl_2(en)_2]^+$
(*en* = ethylenediamine and atomic number of Co is 27) *(AI 2008)*

88. Describe for any two of the following complex ions, the type of hybridization, shape and magnetic property :
(i) $[Fe(H_2O)_6]^{2+}$ (ii) $[Co(NH_3)_6]^{3+}$
(iii) $[NiCl_4]^{2-}$
[At. Nos. Fe = 26, Co = 27, Ni = 28] *(AI 2007)*

9.6 Bonding in Metal Carbonyls

VSA (1 mark)

89. Out of NH_3 and CO, which ligand forms a more stable complex with a transition metal and why? *(1/3, AI 2015)*

90. State a reason for the following situation :
CO is a stronger complexing reagent than NH_3. *(1/3, Delhi 2012)*

91. Why is CO a stronger ligand than Cl^-? *(Foreign 2011)*

SA I (2 marks)

92. Draw the structures of :
(i) $Ni(CO)_4$ (ii) $Fe(CO)_5$ *(AI 2007)*

9.7 Stability of Coordination Compounds

VSA (1 mark)

93. Which of the following is more stable complex and why?
$[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ *(Delhi 2014)*

SA I (2 marks)

94. How is the stability of a co-ordination compound in solution decided? How is the dissociation constant of a complex defined? *(AI 2012C)*

95. What do you understand by stepwise stability constant and overall stability constant of a coordination compound? How are these two constants related? *(AI 2011C)*

9.8 Importance and Applications of Coordination Compounds

VSA (1 mark)

96. Give two examples of coordination compounds used in industries. *(1/3, Delhi 2012C)*

97. Give names of two complexes which are used in medicines. *(1/3, Delhi 2012C)*

SA I (2 marks)

98. Describe with an example of each, the role of coordination compounds in :
(a) Biological systems
(b) Analytical chemistry
(c) Medicinal chemistry *(Delhi 2009C)*

Detailed Solutions

1. For one mole of the compound, two moles of AgCl are precipitated which indicates that two ionisable chloride ions in the complex. Hence, its structural formula is $[CrCl(H_2O)_5]Cl_2{\cdot}H_2O$

2. Structural formula : $[Co(NH_3)_6]Cl_3$

3. **Denticity :** The number of coordinating groups present in a ligand is called the denticity of ligand. For example, bidentate ligand ethane-1, 2-diamine has two donor nitrogen atoms which can link to central metal atom.

$$H_2\ddot{N}{-}CH_2{-}CH_2{-}\ddot{N}H_2$$

Ethane-1, 2-diamine

4. **Ambidentate ligand :** A unidentate ligand which can coordinate to central metal atom through two different atoms is called ambidentate ligand. For example NO_2^- ion can coordinate either through nitrogen or through oxygen to the central metal atom/ion.

5. When a di– or polydentate ligand uses its two or more donor atoms to bind a single metal ion. It is said to be a chelate ligand. Chelating ligands form more stable complexes than monodentate analogs. This is called chelating effect.

6. The ions or molecules bonded to the central atom in the coordination entity are called ligands. Ethylene diammine is a bidentate ligand.

7. (i) *Refer to answer 4.*
(ii) *Rerfer to answer 3.*

8. IUPAC name of the complex $[CrCl(H_2O)_5]Cl_2{\cdot}H_2O$ is : pentaaquachloridochromium (III) chloride.

9. IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$ is tetraamminedichloridochromium (III) chloride.

10. $[Co(NH_3)_4(H_2O)(Cl)]Cl_2$

11. Potassium hexafluoridochromate(III).

12. Diamminechlorido(methylamine)platinum(II) chloride.

13. Tetraamminedichloridoplatinum (IV) chloride.

14. Hexaamminechromium(III) hexacyanocobaltate(III).

15. Pentaamminechloridocobalt(III) chloride.

16. Tetraamminechloridonitrito-N-cobalt(III) chloride.

17. Hexaamminecobalt(III)hexacyanochromate(III)

18 (i) Diamminedichlorido(ethane-1,2-diamine) chromium(III) chloride.
(ii) $[Co(NH_3)_5(ONO)]^{2+}$

19. (i) $[Co(NH_3)_6]Cl_3$
(ii) $K_2[NiCl_4]$

20. *Tris*(ethylenediammine)chromium(III) chloride
(ii) $K_3[Cr(ox)_3]$

21. (i) Hexaamminecobalt(III) chloride
(ii) Tetrachloridonickelate(II)ion
(iii) Potassiumhexacyanoferrate(III)

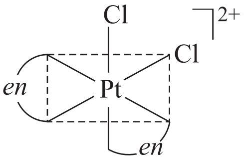
22. (i) Tetraammineaquachloridocobalt(III) chloride
(ii) Dichlorido*bis*(ethane-1,2-diamine)cobalt(III) chloride

23. (i) Pentaamminechloridocobalt(III)chloride
(ii) *Refer to answer 22(iii).*
(iii) *Refer to answer 22(ii).*

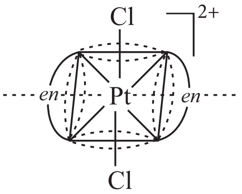
24. (i) Trioxalatocobaltate (III)
(ii) Hexacarbonylchromium (0)
(iii) Trichloroetheneplatinum (III)

25. (i) Triamminetrichloridochromium (III)
(ii) *Refer to answser 22(iii).*
(iii) Dibromido*bis*(ethane-1,2-diamine)cobalt (III) ion

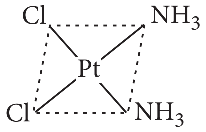
26. *cis*-isomer of the complex $[Pt(en)_2Cl_2]^{2+}$ is optically active



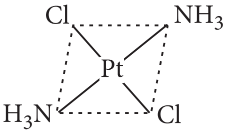
27. *Trans*-isomer is optically inactive due to the presence of plane of symmetry.



28.

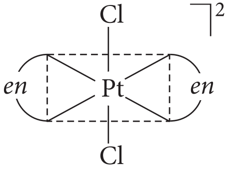


Cis-Diamminedichlorido platinum (II)

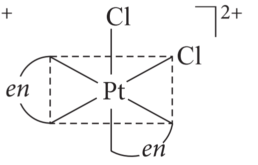


trans-Diamminedichlorido platinum (II)

29. IUPAC name - Dichlorido*bis*(ethane-1,2-diamine) platinum(IV) ion. This complex shows geometrical and optical isomerism.

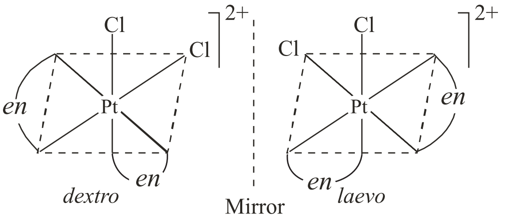


Trans

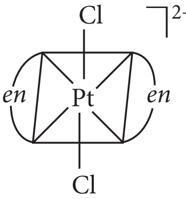


Cis

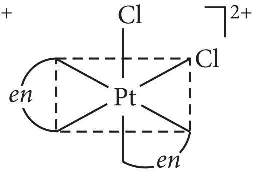
cis-isomer is optically active.



30.

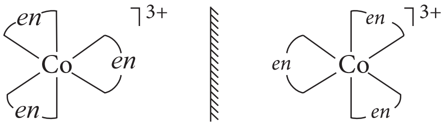


trans-isomer



cis-isomer

31. Optical isomerism :



dextro Mirror *laevo*

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

32. Coordination isomerism : Its coordination isomer $[Cr(NH_3)_6][CO(CN)_6]$, in which NH_3 ligands are bound to Cr^{3+} and CN ligands to Co^{3+}.

33. Ionisation isomerism : $[Co(NH_3)_5SO_4]Cl$ and $[CO(NH_3)_5\,Cl]\,SO_4$

34. Linkage isomerism : $[Co(NH_3)_5NO_2]^{2+}$ and $[Co(ONO)\,(NH_3)_5]^{2+}$

35. (i) Ionisation isomers :

$[Co(NH_3)_5(NO_2)](NO_3)_2$ and

$[Co(NH_3)_5(NO_3)](NO_2)(NO_3)$

(ii) Linkage isomers :

$[Co(NH_3)_5(NO_2)](NO_3)_2$ and $[Co(NH_3)_5(ONO)](NO_3)_2$

36. Ionisation isomer of $[(Ni(NH_3)_3NO_3]Cl$ is $[Ni(NH_3)_3Cl]NO_3$. The IUPAC name of this complex is triamminechloridonickel(II) nitrate.

37. $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$

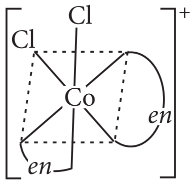
38. $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr\,(NH_3)_6]\,[Co(CN)_6]$

39. $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5\,Br]\,SO_4$

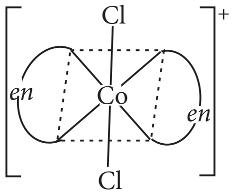
40. Linkage isomerism : Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS^- which may bind through the nitrogen to give *M*-NCS or through sulphur to give *M*-SCN. This behaviour was seen in the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($-NO_2$).

41. The tetrahedral complexes do not show geometrical isomerism because the relative positions of the atoms with respect to each other will be the same.

42. (i) Dichlorido*bis* (ethane-1, 2-diamine)cobalt(III) chloride.

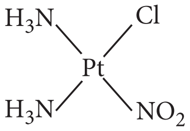


Octahedral
cis-$[CoCl_2(en)_2]^+$

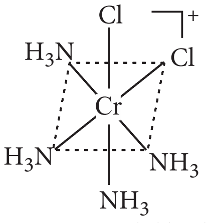


Octahedral
trans-$[CoCl_2(en)_2]^+$

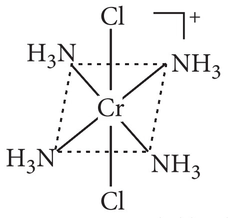
(ii) Diamminechloridonitrito-N-platinum (II)



43. (i) Geometrical isomers of $[Cr(NH_3)_4Cl_2]^+$ – Tetraamminedichloridochromium (III) ion

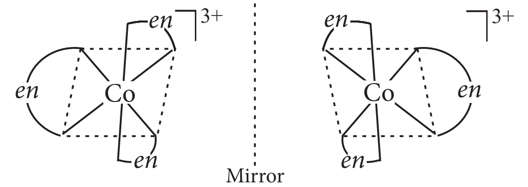


cis-Tetraamminedichlorido chromium (III) ion



trans-Tetraamminedichlorido chromium (III) ion

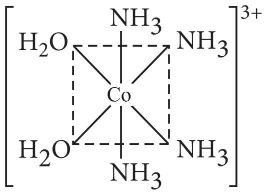
(ii) Optical isomers of $[Co(en)_3]^{3+}$ – *Tris*(ethane-1,2-diamine)cobalt (III) ion.



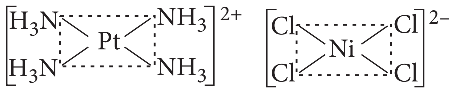
Tris(ethane-1, 2-diamine cobalt (III) ion *dextro*

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

44. (i) Tetraamminediaquacobalt (III) chloride.



(ii) Tetraammineplatinum(II)tetrachloridonickelate(II)

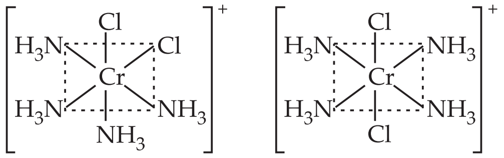


45. (i) *Refer to answer 34.*

(ii) *Refer to answer 43 (ii).*

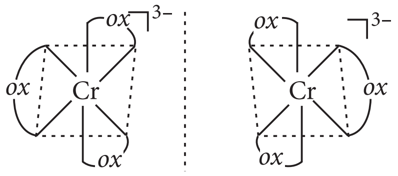
(iii) *Refer to answer 28.*

46. Tetraamminedichloridochromium(III)ion. It exhibits geometrical isomerism.



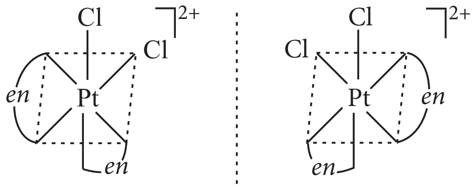
cis-form *trans-form*

47. $[Cr(C_2O_4)]^{3-}$:



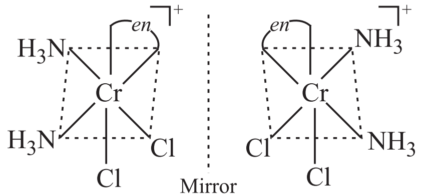
$[Cr(ox)_3]^{3-}$ *dextro* $[Cr(ox)_3]^{3-}$ *laevo*

$[PtCl_2(en)_2]^{2+}$:



dextro *laevo*

$[Cr(NH_3)_2Cl_2(en)]^+$:



dextro *laevo*

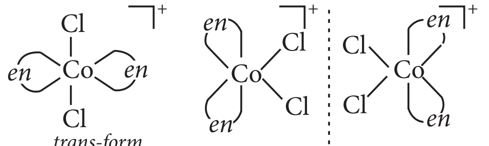
48. (i) *Refer to answer 33.*

(ii) *Refer to answer 31.*

(iii) *Refer to answer 32.*

49. (i) $[CoCl_2(en)_2]^+$: Dichlorido*bis*(ethane-1,2-diamine) cobalt(III) ion

It will exist in two geometrical isomeric forms :

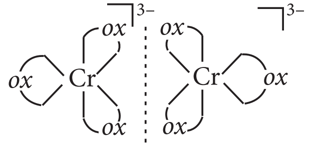


trans-form

cis-form exists in two enantiomeric forms (*d* and *l*)

(ii) $[Cr(C_2O_4)_3]^{3-}$: Trioxalatochromium(III) ion

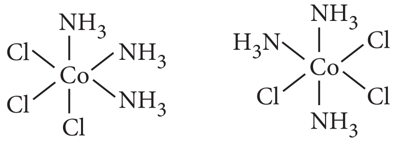
It will show optical isomerism.



Two enantiomeric forms (*d* and *l*)

(iii) $[Co(NH_3)_3Cl_3]$: Triamminetrichloridocobalt(III)

It will exist in two geometrical isomeric forms:

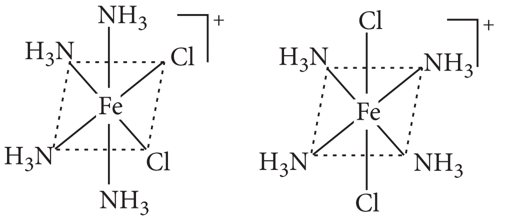


Facial (*fac*) *Meridional* (*mer*)

50. (i) $[Co(en)_3]Cl_3$: *Refer to answer 43(ii).*

(ii) $[Pt(NH_3)_2Cl_2]$: *Refer to answer 28.*

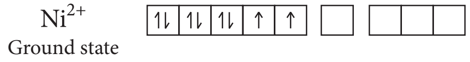
(iii) $[Fe(NH_3)_4Cl_2]Cl$



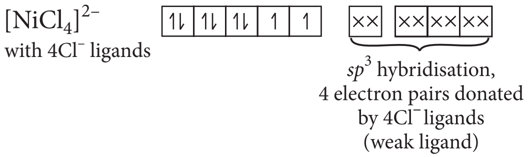
Cis-tetraamminedichlorido iron (III)

Trans-tetraamminedichlorido iron (III)

51. $[NiCl_4]^{2-}$ contains Ni^{2+} ion with $3d^8$ configuration.

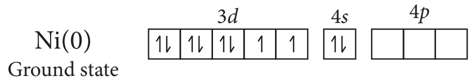


Cl⁻ is a weak field ligand. Hence, outer 4*s* and 4*p*-orbitals are used in hybridisation.

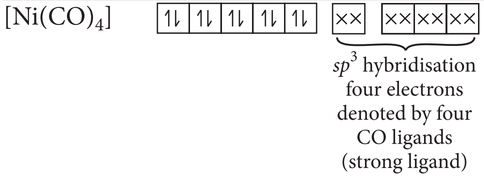


It has two unpaired electrons hence, it is paramagnetic.

$[Ni(CO)_4]$ contains Ni(0) – $3d^8 4s^2$ configuration.

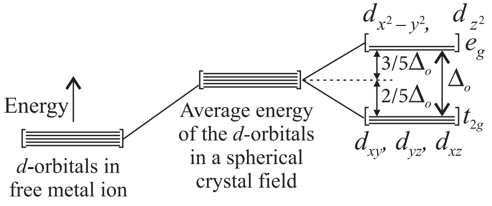


CO is a strong field ligand hence, 4*s*-electrons will shift to 3*d*-orbital making 4*s*-orbital vacant.



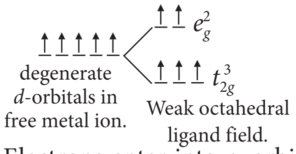
The complex has all paired electrons hence, it is diamagnetic.

52. The splitting of the degenerate *d*-orbitals into three orbitals of lower energy, t_{2g} set and two orbitals of higher energy e_g set due to the interaction of ligand in an octahedral crystal field is known as crystal field splitting in an octahedral field.



d-orbital splitting in an octahedral crystal field.

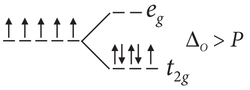
$[Mn(H_2O)_6]^{2+}$ contains Mn^{2+} – $3d^5$ configuration C.N. = 6, octahedral structure, H_2O is a weak field ligand, hence $\Delta_o < P$



Electrons enter into e_g orbital before pairing. It has five unpaired electrons.

$[Mn(CN)_6]^{4-}$ contains Mn^{2+} ion $3d^5$ configuration.

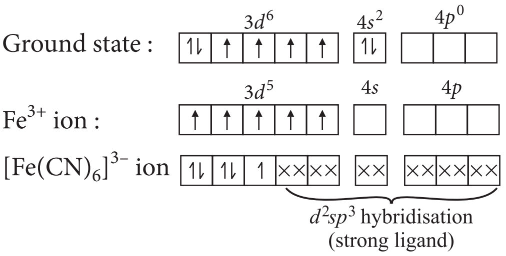
C.N. = 6, octahedral geometry, CN⁻ is strong field ligand, $\Delta_o > P$



Hence, pairing of electrons in t_{2g} orbitals takes place. It has only one unpaired electron.

53. *Refer to answer 52.*

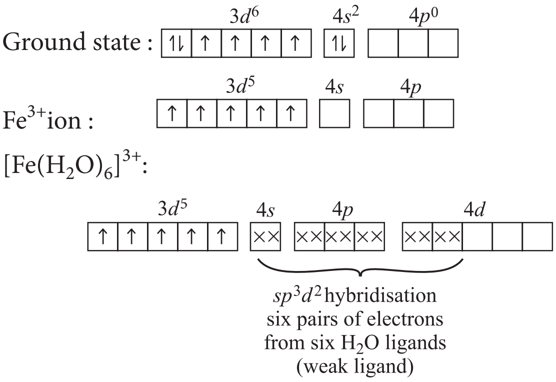
54. Fe atom ($Z = 26$)



The complex ion has inner orbital octahedral geometry (low spin) and is paramagnetic due to the presence of one unpaired electron.

55. $[Fe(H_2O)_6]^{3+}$:

Fe atom ($Z = 26$)

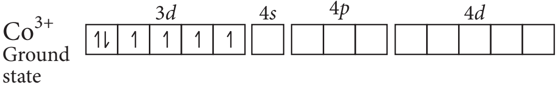


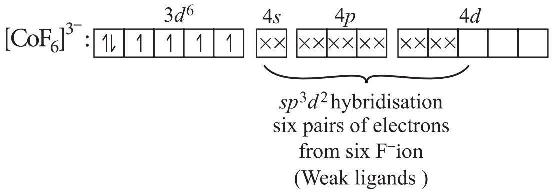
The complex ion has outer orbital octahedral geometry (high spin) and is paramagnetic due to the presence of five unpaired electrons.

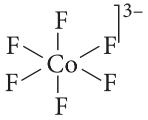
56. (i) For d^4 ion, if $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\, e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

(ii) *Refer to answer 51.*

57. (i) Oxidation state of Co ion in $[CoF_6]^{3-}$ is +3.



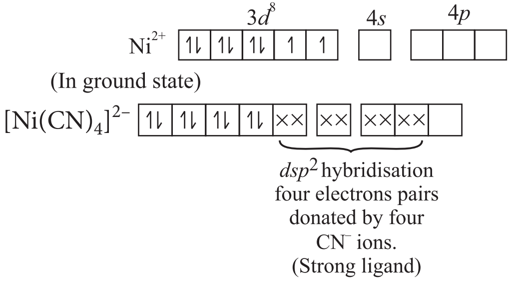




Structure – Outer orbital octahedral complex

Nature – Paramagnetic

(ii) In $[Ni(CN)_4]^{2-}$: Ni is present as Ni(II) with $3d^8$ configuration



The complex ion has square planar geometry and is diamagnetic in nature.

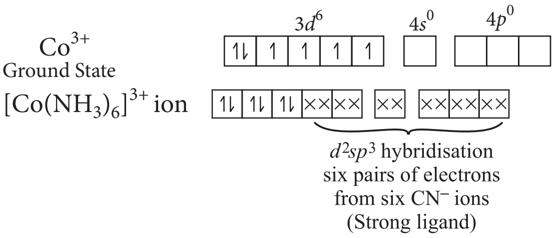
58. *Refer to answer 57(i).*

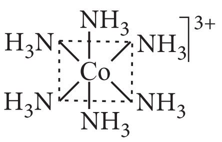
IUPAC Name : Hexafluoridocobaltate(III) ion

59. *Refer to answer 57(ii).*

IUPAC name : Tetracyanidonickelate(II) ion

60. Oxidation of cobalt in$[Co(NH_3)_6]^{3+}$ is +3.





Hybridisation – d^2sp^3

Structure – Octahedral (low spin)

Nature – Diamagnetic

IUPAC name : Hexaamminecobalt(III) ion

61. (i) $[Co(en)_2Cl(NH_3)]^{2+}$

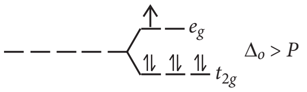
Amminechlorido*bis*(ethane-1,2-diamine)cobalt(III) ion

In presence of strong NH_3 and *en* ligand, Co^{3+} ($3d^6$) forms low spin complex. Hence, complex is diamagnetic.

(ii) $[Ni(ox)_2(H_2O)_2]^{2-}$: Diaquadioxalato nickelate(II) ion

In the presence of weak *ox* and H_2O ligand, Ni(II) forms high spin complex (sp^3d^2 hybridisation). It is paramagnetic.

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



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

(ii) *Refer to answers 57(ii) and 51.*

63. *Refer to answer 60.*

64. *Refer to answer 57 (ii).*

65. In presence of CN^-, the 3*d* electrons pair up leaving only one unpaired electron, the hybridisation is d^2sp^3 forming an inner orbital octahedral complex whereas in the presence of H_2O, 3*d* electrons do not pair up. The hydridisation is sp^3d^2 forming an outer orbital octahedral complex containing five unpaired electrons. Hence, it is strongly paramagnetic.

66. (i) $[Co(NH_3)_5Cl]Cl_2$: Pentaamminechlorido cobalt (III) chloride.

Co(III) : $[Ar]3d^64s^0$: d^2sp^3 hybridisation leads to octahedral shape.

Magnetic behaviour : Diamagnetic.

Stereochemistry : Complex $[Co(NH_3)_5Cl]Cl_2$ do not exhibit geometrical and optial isomerism.

(ii) $K_2[Ni(CN)_4]$: Potassiumtetracyanonickelate(II)

Ni(II) : [Ar] $3d^84s^0$ – dsp^2 hybridisation leads to square planar shape.

Magnetic behaviour : Diamagnetic.

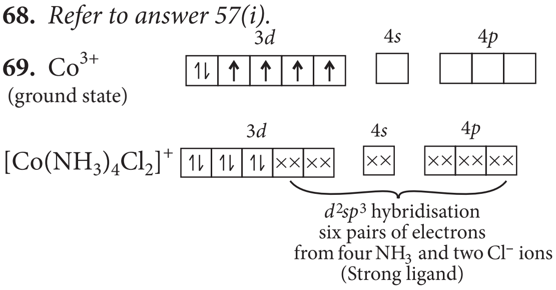
Stereochemistry : Complex $[Ni(CN)_4)$ do not exhibit geometrical isomerism and optical isomerism because all the possible arrangement are equivalent.

67. (i) *Refer to answer 60.*

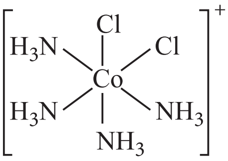
(ii) *Refer to answer 57(ii).*

68. *Refer to answer 57(i).*

69.

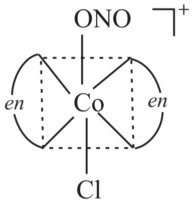


In this complex, Co is d^2sp^3 hybridised because NH_3 is strong field ligand.



cis-form

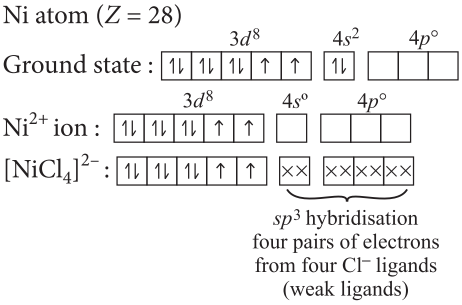
70. IUPAC name : Chlorido*bis*(ethylenediamine) nitrito-O-cobalt(III) ion. Shape is octahedral.



71. *Refer to answer 60.*

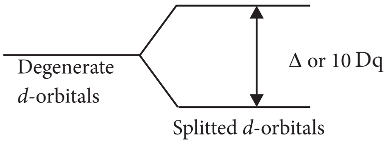
72. *Refer to answers 57 (ii) and 56 (ii).*
Thus, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$ have different structures but same magnetic behaviour.

73. (i) Tetrachloridonickelate(II) ion
Ni atom (Z = 28)



The complex ion has tetrahedral geometry and is paramagnetic due to the presence of unpaired electrons

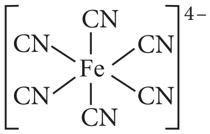
74. (i) The difference of energy between two states of splitted d-orbitals is called crystal field splitting energy. It is denoted by Δ or 10 Dq.
For octahedral Δ_o, for tetrahedral it is Δ_t and for square planar Δ_{sp}.



(ii) When $\Delta_o > P$, $t_{2g}^4\, e_g^0$.
When $\Delta_o < P$, $t_{2g}^3\, e_g^1$.

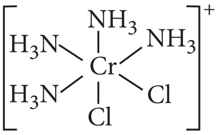
75. (i) $[Pt(NH_3)_2Cl(NO_2)]$: Diamminechloridonitrito-N-platinum(II)
It is square planar and diamagnetic.
(ii) $[Co(NH_3)_4Cl_2]Cl$: Tetraamminedichloridocobalt (III) chloride
It is octahedral and diamagnetic.
(iii) $Ni(CO)_4$: Tetracarbonylnickel(0)
It is tetrahedral and diamagnetic

76. (i) $[Fe(CN)_6]^{4-}$: Hexacyanidoferrate(II) ion
Hybridisation - d^2sp^3
Structure : Inner orbital octahedral complex



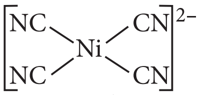
Octahedral

(ii) $[Cr(NH_3)_4Cl_2]^+$: Tetraamminedichloridochromium (III) ion
Hybridisation - d^2sp^3
Structure : Inner orbital octahedral complex



Octahedral

(iii) $[Ni(CN)_4]^{2-}$: Tetracyanidonickelate(II) ion
Hybridisation - dsp^2
Structure - Square planar



Square planar

77.

Formulae	Name of the Complex	Hybridisation of metal ion involved	Geometry of complex (stereochemistry)	Magnetic behaviour
$K_4[Mn(CN)_6]$	Potassium hexacyanomanganate(II)	d^2sp^3	Octahedral	Paramagnetic
$[Co(NH_3)_5Cl]Cl_2$	Pentaamminechloridocobalt(III) chloride	d^2sp^3	Octahedral	Diamagnetic
$K_2[Ni(CN)_4]$	Potassiumtetracyanidonikelate (II)	dsp^2	Square planar	Diamagnetic

None of these complexes will show stereoisomerism.

78. (i) $[Fe(en)_2Cl_2]Cl$

$x + 0 \times 2 + (-1) \times 2 + (-1) \times 1 = 0 \quad \therefore \quad x = 3$

Oxidation number of iron = 3

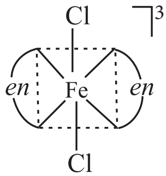
(ii) d^2sp^3 hybridisation and octahedral shape.

(iii) Paramagnetic due to presence of one unpaired electron.

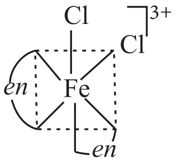
(iv) 2, *cis* and *trans* isomers.

(v) *cis*-$[Fe(en)_2Cl_2]$ has optical isomer.

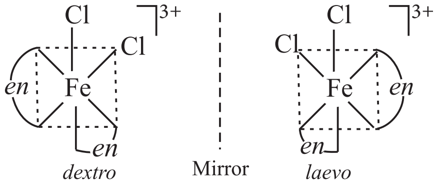
(vi) dichlorido*bis*(ethane-1,2-diamine)iron(III) chloride



Trans-bis(ethane-1,2-diamine) dichloridoiron(III) chloride



Cis-bis(ethane-1,2-diamine) dichloridoiron(III) chloride



79.

Complex	Central metal ion/ atom	Hybridisation of metal ion involved	Geometry of complex	Magnetic behaviour
$[Cr(NH_3)_4Cl_2]Cl$	Cr^{3+}	d^2sp^3	Octahedral	Paramagnetic
$[Co(en)_3]Cl_3$	Co^{3+}	d^2sp^3	Octahedral	Diamagnetic
$K_2[Ni(CN)_4]$	Ni^{2+}	dsp^2	Square planar	Diamagnetic

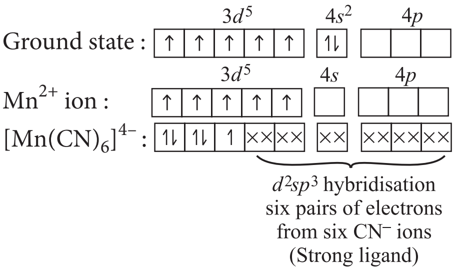
80. $[CoCl_4]^{2-}$ Tetrachloridocobaltate(II) ion

$[Ni(CN)_4]^{2-}$ Tetracyanonickelate(II) ion

$[Cr(H_2O)_2(C_2O_4)_2]^-$ Diaquadioxalatochromate(III) ion

Complexes	Hybridisation	Shape	Magnetic behaviour
$[CoCl_4]^{2-}$	sp^3	Tetrahedral	Paramagnetic
$[Ni(CN)_4]^{2-}$	dsp^2	Square planar	Diamagnetic
$[Cr(H_2O)_2(C_2O_4)_2]^-$	d^2sp^3	Octahedral	Paramagnetic

81. Mn atom ($Z = 25$)



IUPAC name : Potassium hexacyanomanganate (II)

Geometry : Octahedral

No. of unpaired electrons, $n = 1$

Magnetic behaviour : paramagnetic.

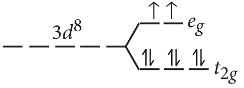
82.

Complexes	Shape	Magnetic behaviour	Hybridisation
$[CoF_4]^{2-}$	Tetrahedral	Paramagnetic	sp^3
$[Cr(H_2O)_2(C_2O_4)_2]$	Octahedral	Paramagnetic	d^2sp^3
$[Ni(CO)_4]$	Tetrahedral	Diamagnetic	sp^3

83.

Complexes	Magnetic behaviour	Hybridisation	Shape
$[Co(NH_3)_6]^{3+}$	Diamagnetic	d^2sp^3	Octahedral
$[Cr(NH_3)_6]^{3+}$	Paramagnetic	d^2sp^3	Octahedral
$[Ni(CO)_4]$	Diamagnetic	sp^3	Tetrahedral

84. (i) Nickel forms octahedral complexes mainly in +2 oxidation state which has $3d^8$ configuration. In presence of strong field ligand also it has two unpaired electrons in e_g orbital.



Hence, it does not form low spin octahedral complexes.

(ii) The transition metals/ions have empty *d* orbitals into which the electron pairs can be donated by ligands containing π electrons.

For example : $CH_2{=}CH_2$ and C_6H_6, $C_5H_5^-$.

(iii) Co is stronger ligand than NH_3 because CO has vacant molecular orbitals with which it can form π-bond with metal through back donation.

85.

Complexes	Magnetic behaviour	Hybridisation	Shape
$[Ni(CN)_4]^{2-}$	Diamagnetic	dsp^2	Square planar
$[NiCl_4]^{2-}$	Paramagnetic	sp^3	Tetrahedral
$[CoF_6]^{3-}$	Paramagnetic	sp^3d^2	Octahedral

86. All the complex ions are derived from Ni^{2+} ion with different ligands. From the position of the ligands in the spectrochemical series the order of field strength is

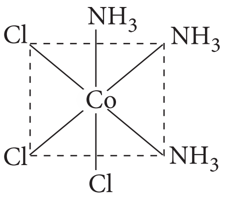
$$H_2O < NH_3 < NO_2^-$$

That means Δ_o for NO_2^- is maximum and so it would absorb the radiation of shorter wavelength having high energy. So, the order of absorption of the correct wavelengths is

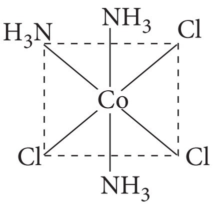
$[Ni(H_2O)_6]^{2+}$ > $[Ni(NH_3)_6]^{2+}$ > $[Ni(NO_2)_6]^{4-}$
(λ about 700 nm) (about 500 nm) (< 500 nm)

87. (a) The arrangement of ligands in order of their increasing field strength *i.e.* increasing crystal field splitting energy (CFSE) value is called spectrochemical series.

(b) (i) The facial and meridional isomers of $[Co(NH_3)_3Cl_3]$ may be represented as

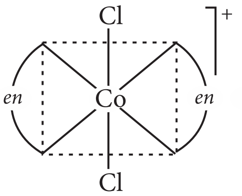


Facial - isomer

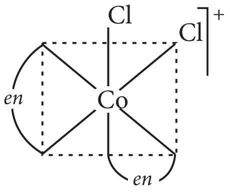


Meridional

(ii) $[CoCl_2(en)_2]^+$ ion exists in two geometrical isomers as shown below :

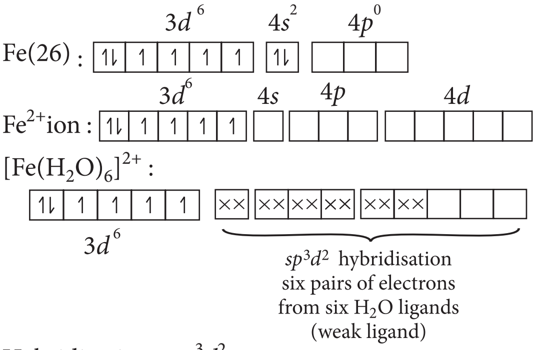


trans - form



cis - form

88. (i) $[Fe(H_2O)_6]^{2+}$



Hybridization - sp^3d^2
Shape - Octahedral.
Magnetic property - Paramagnetic.
(ii) *Refer to answer 60.*
(iii) $[NiCl_4]^{2-}$: *Refer to answer 51.*

89. In CO both lone pair of electrons and vacant π* orbitals are present. Hence, it acts as electron pair σ donor as well as π acceptor by back bonding. Hence, *M*—CO bond is stronger.

$$M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} CO$$

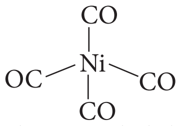
NH_3 is electron pair donor only. Accumulation of negative charge on the metal ion takes place, hence *M*—NH_3 bond is weaker.

$M \leftarrow NH_3$

90. *Refer to answer 89.*

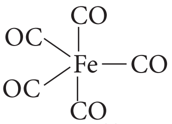
91. Because CO has vacant molecular orbitals with which it can form π-bond with metal through back donation.

92. (i) $Ni(CO)_4$:



Shape - Tetrahedral

(ii) $Fe(CO)_5$:



Shape - Trigonal bipyramidal

93. $[Co(en)_3]^{3+}$ is more stable complex than $[Co(NH_3)_6]^{3+}$ due to chelate effect as it forms rings.

94. The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the equilibrium constant for the association, quantitatively expresses the stability.

The instability constant or dissociation constant of coordination compound is defined as the reciprocal of the formation constant.

95. Stability constant of each step of complex formation reaction is called stepwise stability constant. It is denoted by *K*. Stability constant of overall complex formation reaction is called overall stability constant. It is denoted by β.

The stepwise and overall stability constant are therefore related as follows:

$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$ or more generally,

$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \ldots K_n$

96. (i) EDTA is used for water softening and in purification of metals.
(ii) Wilkinson's catalyst is used as catalyst for hydrogenation.

97. *cis*-Platin is used in the treatment of cancer.
EDTA is used in lead poisoning.

98.(a) **Biological systems :** Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which act as oxygen carrier is a coordination compound of iron. Vitamin B_{12}, cyanocobalamine, the anti-pernicious anaemia factor, is a coordination compound of cobalt.
(b) **Analytical Chemistry :** Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α-nitroso-β-naphthol, cupron, etc.

(c) Medicinal Chemistry : There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal system. Thus, excess of copper and iron are removed by the chelating ligands D-penicillamine and desferrioxime-B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are : *cis*-platin and related compounds.

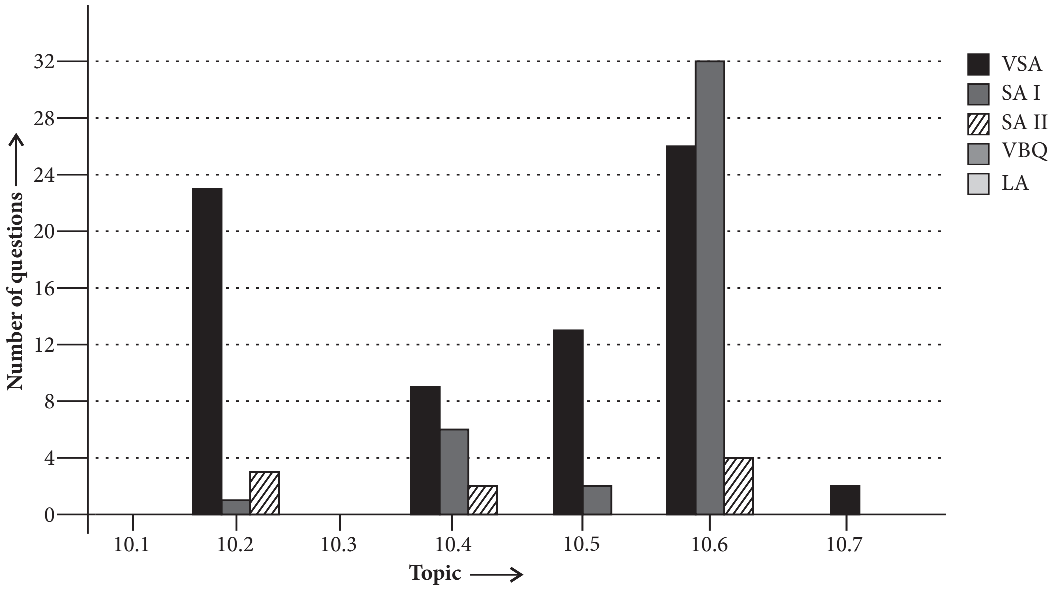
◆

10

Haloalkanes and Haloarenes

10.1 Classification
10.2 Nomenclature
10.3 Nature of C—*X* Bond
10.4 Methods of Preparation
10.5 Physical Properties
10.6 Chemical Reactions
10.7 Polyhalogen Compounds

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



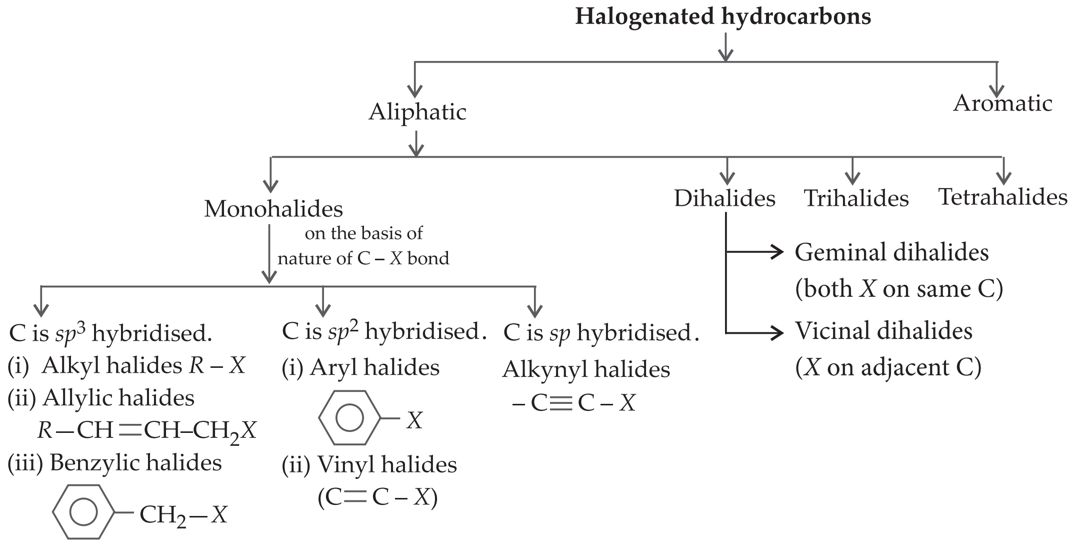
- Maximum total weightage is of *Chemical Reactions.*
- Maximum VSA type questions were asked from *Chemical Reactions.*
- Maximum SA I and SA II type questions were asked from *Chemical Reactions.*

QUICK RECAP

HALOALKANES

- **Alkyl halides :** General formula is RX, where R = alkyl group.

Classification :



General methods of preparation :

- **From alcohols :** Alkyl halides can be prepared from alcohols in a number of ways :
  - **Action of hydrogen halides :**

$$R\text{–OH} \xrightarrow{\text{HCl/anhyd. ZnCl}_2} R\text{Cl} + H_2O$$

$$R\text{–OH} \xrightarrow[\text{or KBr + conc. }H_2SO_4\text{ reflux}]{\text{HBr/}H_2SO_4\text{ reflux}} R\text{–Br} + H_2O$$

$$R\text{–OH} \xrightarrow[\text{or KI + }H_3PO_4\text{ reflux}]{\text{HI reflux}} R\text{–I} + H_2O$$

- Order of reactivity of halogen acids towards the above reaction is :

  HI > HBr > HCl

- Order of reactivity of different alcohols towards the above reaction is :

  allyl benzyl > tertiary > secondary > primary

  - **Action of phosphorus halides :**

$$R\text{–OH} \xrightarrow{PCl_5} R\text{–Cl} + POCl_3 + HCl$$

$$R\text{–OH} \xrightarrow{PCl_3} R\text{–Cl} + H_3PO_3$$

$$R\text{–OH} \xrightarrow[(P + Br_2)]{PBr_3} R\text{–Br} + H_3PO_3$$

$$R\text{–OH} \xrightarrow[(P + I_2)]{PI_3} R\text{–I} + H_3PO_3$$

  - **Action of thionyl chloride (Darzen's process) :**

$$R\text{—OH} + SOCl_2 \xrightarrow{\text{Pyridine}} R\text{—Cl} + SO_2\uparrow + HCl\uparrow$$

- **Halogenation of alkanes :**

$$R\text{—H} + X_2 \xrightarrow[\text{or 250 – 400°C}]{h\upsilon} RX + HX$$

  - Abstraction of hydrogen for a particular halogen follows the order allylic > 3° > 2° > 1° > CH_4
  - Reactivity of halogens for the above reaction follows the order :

    $F_2 > Cl_2 > Br_2 > I_2$

- **Halide exchange method :**

$$R\text{—Cl} + \text{NaI} \xrightarrow{\text{dry acetone}} R\text{—I} + \text{NaCl}$$

This is known as *Finkelstein reaction.*

  - Fluoroalkanes can also be prepared by halide exchange method by reacting alkyl chloride with inorganic fluorides. This is known as *Swart's reaction.*

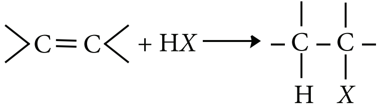
$$\underset{}{2CH_3CH_2Cl} + \underset{\text{Mercurous fluoride}}{Hg_2F_2} \longrightarrow 2CH_3CH_2F + \underset{\text{Mercurous chloride}}{Hg_2Cl_2}$$

- **Action of hydrogen halides on ethers :**

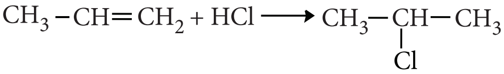
$$R\text{—O—}R + 2HX \longrightarrow 2R - X + H_2O$$

- **Addition of hydrogen halides to alkene :**

Alkenes add on a molecule of hydrogen halide to form alkyl halide.

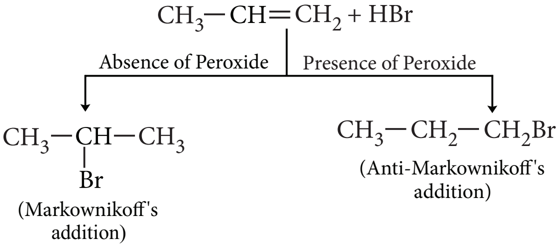


$$>C=C< + HX \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}-$$



$$CH_3-CH=CH_2 + HCl \longrightarrow CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$

- Reaction follows electrophilic addition mechanism and takes place as per Markownikoff's rule. However, in presence of peroxide addition of HBr takes place as per anti-Markownikoff's rule.



Anti-Markownikoff's rule is also known as *Peroxide effect* or *Kharasch effect*. HCl and HI do not show peroxide effect.

Physical properties :

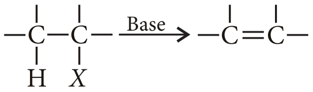
- Alkyl halides being polar in nature are insoluble in water as they cannot break H-bonding already existing in water.
- They have higher melting and boiling points. For the same alkyl group boiling point follows the order as :

  $R—I > R—Br > R—Cl > R—F$
- Decreasing order of boiling points among the isomeric alkyl halides follows the order :
  1° > 2° > 3° alkyl halides
- Decreasing order of density among the alkyl halides is $RI > RBr > RCl > RF$.
  For alkyl iodide decreasing order of density is as follows :
  $CH_3I > CH_3CH_2I > CH_3CH_2CH_2I$.
- Bond strength of C—X bond follows the order
  $CH_3—F > CH_3—Cl > CH_3—Br > CH_3—I$

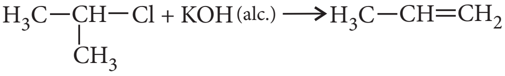
  i.e., bond strength of C—X bond decreases as the size of halogen atoms increases.
- Correct stability order of RX is as follows :
  $R—F > R—Cl > R—Br > R—I$

Chemical properties :

- **Dehydrohalogenation :**

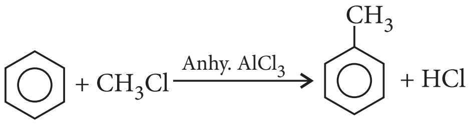


$$-\underset{\displaystyle H}{\underset{|}{\overset{|}{C}}}-\underset{\displaystyle X}{\underset{|}{\overset{|}{C}}}- \xrightarrow{\text{Base}} -\overset{|}{C}=\overset{|}{C}-$$



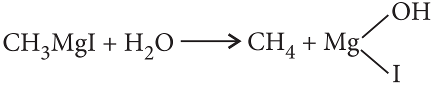
$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-Cl + KOH\,(\text{alc.}) \longrightarrow H_3C-CH=CH_2$$

- **Friedel Crafts reacton :**



- **Reaction with Mg metal :**

$$CH_3I + Mg \xrightarrow{\text{Ether}} CH_3MgI$$

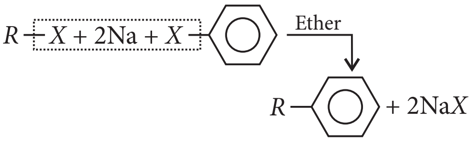


$$CH_3MgI + H_2O \longrightarrow CH_4 + Mg\begin{matrix}OH\\ I\end{matrix}$$

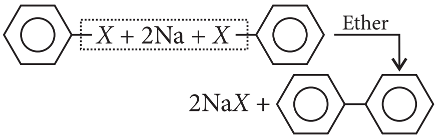
- **Wurtz reaction :**

$$R\boxed{-X + 2Na + X-}R \xrightarrow{\text{Ether}} R-R + 2NaX$$

- **Wurtz Fittig reaction :**



- **Fittig reaction :**



- **Reduction of alkyl halides :**

$$R—X + [H] \xrightarrow{\text{Zn/HCl}} R—H + ZnX_2$$

HALOARENES

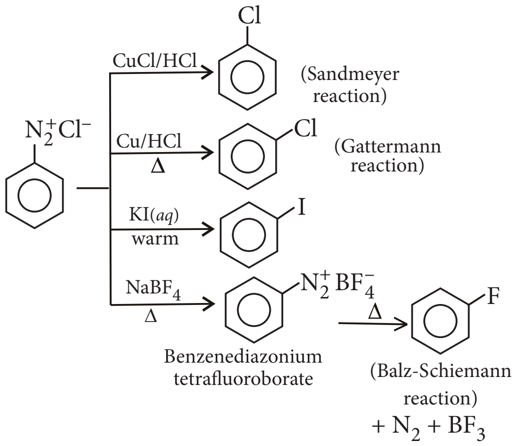
Aryl halides : General formula is ArX, where Ar = aryl group.

General methods of preparation :

- **By Raschig process :**

$$2C_6H_6 + 2HCl + O_2 \xrightarrow[500\text{ K}]{CuCl_2} 2C_6H_5Cl + 2H_2O$$

- **From benzenediazonium salt :**



- **By direct halogenation of benzene :**

$$C_6H_6 \xrightarrow{Cl_2/FeCl_3} C_6H_5Cl$$

$$C_6H_6 \xrightarrow{Br_2/FeBr_3} C_6H_5Br$$

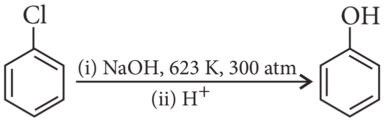
$$C_6H_6 \xrightarrow{I_2/HIO_3} C_6H_5I$$

Physical properties :

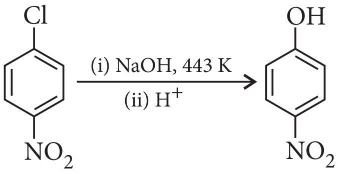
- Aryl halides are colourless stable liquids with pleasant odour.
- These are insoluble in water but readily miscible with organic solvents.
- Most of them are steam volatile, heavier than water.
- Their boiling points are higher than corresponding alkyl halides. The boiling points rise gradually from fluoro to iodo compounds.

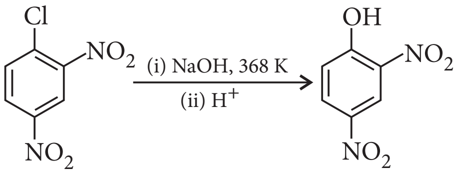
Chemical properties :

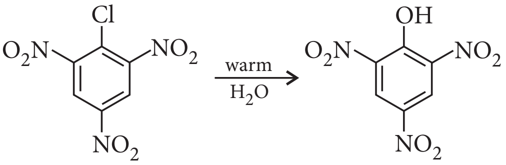
- **Nucleophilic substitution reactions :**



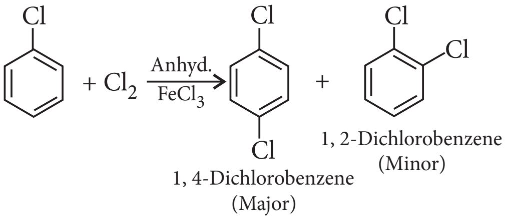
The presence of an electron withdrawing group (—NO_2) at *ortho*- and *para*-positions increases the reactivity of haloarenes.



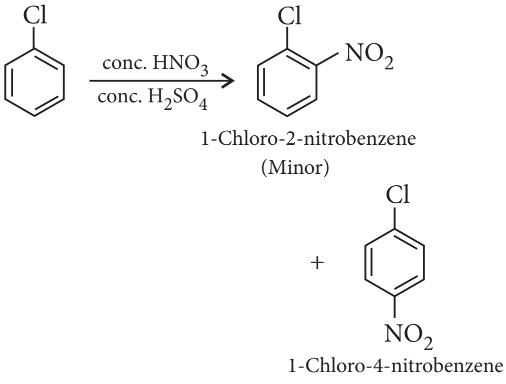




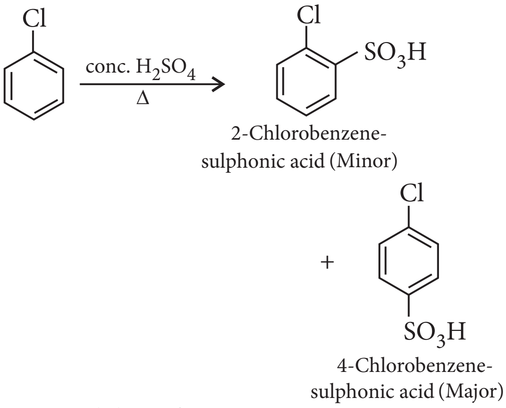
- **Electrophilic substitution reactions :**
  - **Halogenation :**



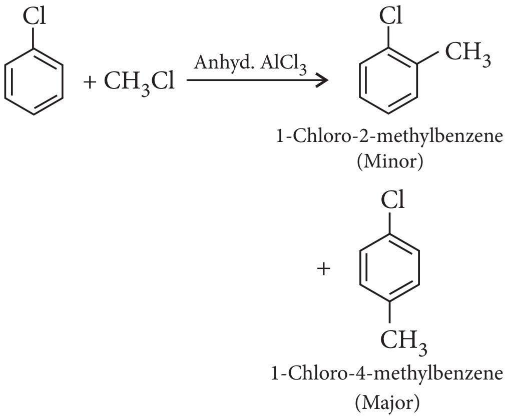
  - **Nitration :**

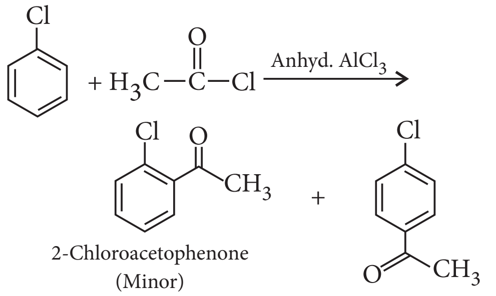


  - **Sulphonation :**



  - **Friedel-Crafts reaction :**

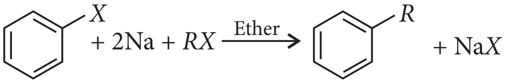




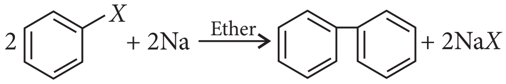
2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)

- **Reaction with metals :**



- **Fitting reaction :**



Diphenyl

S_N1 and S_N2 mechanisms : The nucleophilic substitution can proceed via S_N1 mechanism or S_N2 mechanism.

Unimolecular (S_N1)	**Bimolecular (S_N2)**
It is first order reaction.	It is second order reaction.
Generally carried out in polar protic solvents like water, alcohol and acetic acid.	Carried out in polar aprotic solvents like acetone, DMSO, acetonitrile, or DMF.
Takes place in two steps through carbocation as the intermediate.	Takes place in one step through transition state.
Rate of reaction : 3° > 2° > 1° > $\overset{+}{C}H_3$ (fastest) (slowest) Greater the stability of carbocation, faster will be the reaction.	Rate of reaction : CH_3 > 1° > 2° > 3° halides (fastest) (slowest) Less the steric hindrance in T.S., faster will be the reaction.
Tends to proceed with weak nucleophiles, *e.g.*; CH_3OH, H_2O, CH_3CH_2OH, etc.	Tends to proceed with strong nucleophiles, *e.g.*; CH_3O^-, CN^-, OH^-, etc.
Configuration is retained but in front attack inversion takes place (racemisation and inversion).	Inversion of configuration takes place (Walden inversion).

- Primary allylic and primary benzylic halides show higher reactivity in S_N1 reactions than other primary alkyl halides due to the greater stabilisation of allylic and benzylic carbocation intermediates by resonance.
- Vinylic and aryl halides are unreactive in nucleophilic substitution reactions. This is because of double bond character of C — X bond due to resonance.

Optical isomerism/Enantiomerism :

- Optical isomer is known as *dextrorotatory isomer* (latin : *dexter* means right) (*d*-form or +ve) if it rotates the plane polarised light to the right (clockwise) and *laevorotatory isomer* (latin : *laevo* means left) (*l*-form or –ve) if it rotates the plane polarised light to the left (anticlockwise).
- An equimolar mixture of the *d*- form and *l*-form will be optically inactive and is called *racemic mixture* (or *dl- form or* (±)*-mixture*).
- The process of conversion of an enantiomer into racemic mixture is known as *racemisation*.
- **Chirality :** The compound is said to have chirality if the central carbon atom is attached to four different groups and this centre is called *chiral* (*asymmetric*) *centre* or *stereogenic centre* or *stereocentre*.
- **Achirality :** The compound is said to have achirality if the central carbon atom have atleast two identical groups and this centre is called *achiral* (*symmetric*).
- If molecule has a plane of symmetry it is *achiral* (*not chiral*) and if molecule has no plane of symmetry it is *chiral*.
- **Enantiomers/*d* and *l* isomers :** They are the optical isomers which are non-superimposable mirror images (or dissymmetric).
- **Diastereomers :** They are the optical isomers which are not mirror images of each other. They have different physical properties and magnitude of specific rotation.
- **Meso compounds :** These compounds which have two or more even number of chiral carbon atoms and have an internal plane of symmetry. They are optically inactive due to internal compensation.

Uses and environmental effects of some important compounds :

Compounds	Uses	Effects
Chloroform ($CHCl_3$)	– Its major use is in the production of Freon refrigerant, R-22. – It is used as a solvent for resins, rubbers, oils and fats, alkaloids, iodine and many other substances. – In the past, it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage. – It is used in preparation of chloretone (drug) and chloropicrin (insecticide). – It is used to preserve anatomical species.	– It is oxidised to poisonous gas, carbonyl chloride, known as *phosgene*. $2CHCl_3 + O_2 \xrightarrow{\text{Light}} 2COCl_2 + 2HCl$ Phosgene gas causes liver and kidney damage. – Inhaling chloroform vapours depresses the CNS, causes dizziness, fatigue and headache.
Iodoform (CHI_3)	– It is used as an antiseptic in dressing of wounds due to liberation of iodine. – It is used as methylating agent in organic synthesis.	– It has strong smell.
Freons	– They are used as refrigerants, blowing agents, propellants in medical applications and degreasing solvent.	– Freons cause disruption of ozone layer by initiating radical chain reactions in stratosphere. – This anthropogenic compound is a greenhouse gas and its effect is more than CO_2.
DDT	– In 1940, it was used as a pesticide.	– It is a persistent organic pollutant, strongly absorbed by soil. – It is lipophilic so has a high potential to bioaccumulate. – It may be directly genotoxic but may also induce enzymes to produce other genotoxic intermediates and DNA adducts.

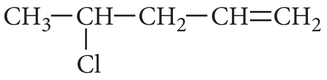
Previous Years' CBSE Board Questions

10.2 Nomenclature

VSA (1 mark)

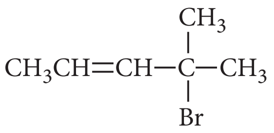
1. Draw the structure of 2-bromopentane. *(Delhi 2014C)*

2. Write the IUPAC name of



$CH_3-\underset{\substack{|\\ Cl}}{CH}-CH_2-CH=CH_2$ *(Delhi 2013)*

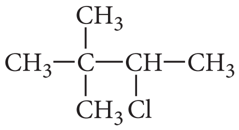
3. Write the IUPAC name of



$CH_3CH=CH-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ Br}}{C}}-CH_3$ *(Delhi 2013)*

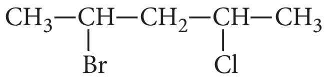
4. Write the IUPAC name of $(CH_3)_2CHCH(Cl)CH_3$. *(Delhi 2013)*

5. Write the IUPAC name of the following compound:



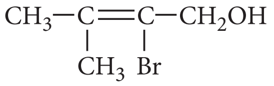
$CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-\underset{\substack{|\\ Cl}}{CH}-CH_3$ *(AI 2013)*

6. Write the IUPAC name of the following compound:



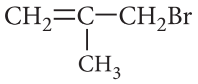
$CH_3-\underset{\substack{|\\ Br}}{CH}-CH_2-\underset{\substack{|\\ Cl}}{CH}-CH_3$ *(AI 2013)*

7. Write IUPAC name of the following :



$CH_3-\underset{\substack{|\\ CH_3}}{C}=\underset{\substack{|\\ Br}}{C}-CH_2OH$ *(AI 2013C, 2012C, Foreign 2011)*

8. Give the IUPAC name of the following compound :



$CH_2=\underset{\substack{|\\ CH_3}}{C}-CH_2Br$ *(Delhi 2012, AI 2011)*

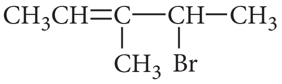
9. Write the IUPAC name of the following compound : $(CH_3)_3CCH_2Br$ *(Delhi 2011)*

10. Write the IUPAC name of the following compound : $CH_2=CHCH_2Br$ *(AI 2011)*

11. Write the structure of the following compound: 1, 4-dibromobut-2-ene *(Delhi 2011C)*

12. Write the structure of the following compound: 2-(2-Bromophenyl)butane *(Delhi 2011C)*

13. Give IUPAC name of the following organic compound :



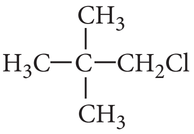
$CH_3CH=\underset{\substack{|\\ CH_3}}{C}-\underset{\substack{|\\ Br}}{CH}-CH_3$ *(Delhi 2011C)*

14. Write the structure of the following compound: 2-(2-chlorophenyl)-1-iodooctane *(AI 2011C)*

15. Write the structure of the following compound: 1-bromo-4-*sec*-butyl-2-methylbenzene *(AI 2011C)*

16. Write the structure of the compound : 4-*tert*-butyl-3-iodoheptane *(AI 2010C)*

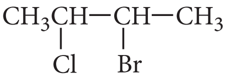
17. Write the IUPAC name of the following compound :



$H_3C-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-CH_2Cl$ *(AI 2010C)*

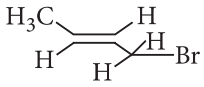
18. Write the structure of the compound 1-chloro-4-ethylcyclohexane. *(AI 2010C)*

19. Write the IUPAC name of the following compound :



$CH_3\underset{\substack{|\\ Cl}}{CH}-\underset{\substack{|\\ Br}}{CH}-CH_3$ *(Delhi 2008)*

20. State the IUPAC name of the following compound :



21. Write the IUPAC name of $ClCH_2C\equiv CCH_2Br$. *(AI 2008C)*

SA I (2 marks)

22. Write the IUPAC names of the following compounds :
(i) $CH_2=CHCH_2Br$ (ii) $(CCl_3)_3CCl$ *(AI 2014C)*

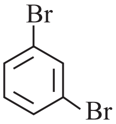
SA II (3 marks)

23. Give the IUPAC names of the following compounds :

(i)

$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-CH_3$

(ii)



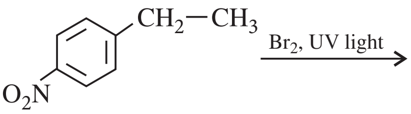
(iii) $CH_2=CH-CH_2-Cl$ *(AI 2015C)*

10.4 Methods of Preparation

VSA (1 mark)

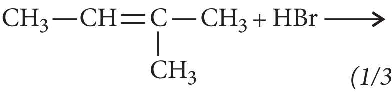
24. How do you convert:
Propene to 1-iodopropane ? *(1/3, AI 2016)*

25. Write the major products in the following :



(1/3, AI 2016)

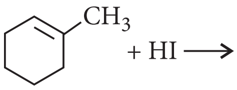
26. Write the structure of the major product in the following reaction :



$CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3+HBr\longrightarrow$ *(1/3, AI 2015)*

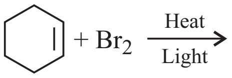
27. A hydrocarbon C_5H_{12} gives only one monochlorination product. Identify the hydrocarbon. *(Delhi 2013C)*

28. Draw the structure of major monohalogen product formed in the following reaction :



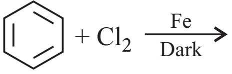
(Delhi 2012C)

29. Draw the structure of major monohalogen product in the following reaction :



(Delhi 2012C)

30. Draw the structure of major monohalo product in the following reaction :



(Delhi 2012C)

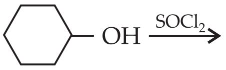
31. What happens when bromine attacks
$CH_2=CH-CH_2-C\equiv CH$? *(AI 2012)*

32. Complete the following chemical equation :
$CH_3CH_2CH=CH_2+HBr\xrightarrow{\text{Peroxide}}\ldots$
(1/2, Delhi 2008)

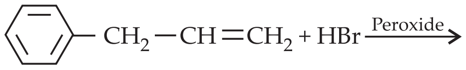
SA I (2 marks)

33. Draw the structure of major monohalo product in each of the following reactions :

(i)



(ii)



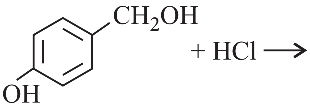
(Delhi 2014)

34. Write the mechanism of the following reaction :
$CH_3CH_2OH\xrightarrow{HBr}CH_3CH_2Br+H_2O$
(AI 2014)

35. Complete the following reaction equations :

(i)

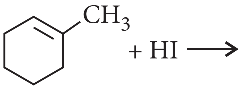
(ii)



(Delhi 2009)

36. Complete the following reaction equations :

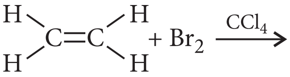
(i)



(ii) $CH_3CH_2CH=CH_2+HBr\longrightarrow$
(AI 2009)

37. Complete the following reaction equation :
(i) $C_6H_5N_2Cl+KI\longrightarrow$

(ii)

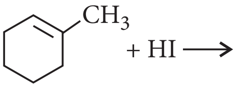


(Delhi, AI 2008)

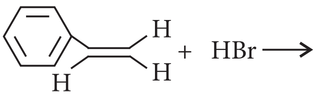
SA II (3 marks)

38. Compute the following reaction equations:

(i)

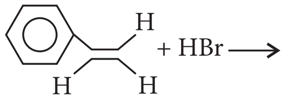


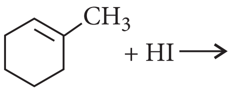
(ii)



(iii) $CH_3CH_2CH=CH_2+HBr\longrightarrow$
(Foreign 2011)

39. Complete the equation for the following reactions :

(i) 

(ii) 

(iii) 

(Delhi 2011C)

10.5 Physical Properties

VSA **(1 mark)**

40. Give reason :
n-Butyl bromide has higher boiling point than *t*-butyl bromide. *(1/3, Delhi 2015)*

41. Why are alkyl halides insoluble in water? *(1/3, Foreign 2015)*

42. Why does *p*-dichlorobenzene have a higher m.p. than its *o*- and *m*-isomers? *(1/2, Delhi 2013, 1/3, AI 2009C)*

43. Explain the following :
Alkyl halides, though polar, are immiscible with water. *(1/3, Delhi 2013C, 1/3, AI2010C)*

44. Answer the following :
Haloalkanes easily dissolve in organic solvents, why? *(1/3, Delhi 2011)*

45. Out of ethyl bromide and ethyl chloride which has higher boiling point and why? *(1/3, AI 2007)*

SA I **(2 marks)**

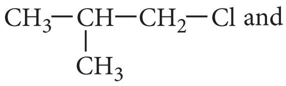
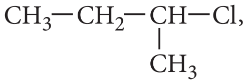
46. Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride? *(1/3, Delhi 2016, 2013C, 2011 C, 1/2 Delhi, 2010C, 1/3, AI 2010C)*

(ii) alkyl halides, though polar, are immiscible with water? *(2/3, AI 2013C, 2012C)*

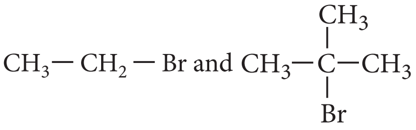
10.6 Chemical Reactions

VSA **(1 mark)**

47. Out of 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-Cl$ and 
$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-Cl$, which is more reactive towards S_N1 reaction and why? *(Delhi 2016)*

48. Write the structure of an isomer of compound C_4H_9Br which is most reactive towards S_N1 reaction. *(AI 2016)*

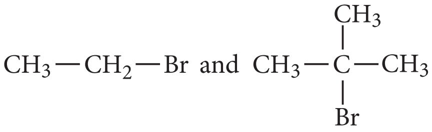
49. Which would undergo S_N2 reaction faster in the following pair and why?



CH_3-CH_2-Br and $CH_3-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_3$

(Delhi 2015)

50. Which would undergo S_N1 reaction faster in the following pair :

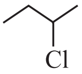
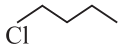


CH_3-CH_2-Br and $CH_3-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_3$

(AI 2015)

51. Which would undergo S_N2 reaction faster in the following pair and why?
CH_3-CH_2-Br and CH_3-CH_2-I *(Foreign 2015)*

52. Identify the chiral molecule in the following pair:

(AI 2014)

53. Which halogen compound in each of the following pairs will react faster in S_N2 reaction:

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3CCl$ or CH_3Cl

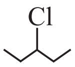
(Delhi 2014C, AI 2014)

54. What happens when CH_3-Br is treated with KCN? *(Delhi 2013)*

55. What happens when ethyl chloride is treated with aqueous KOH? *(Delhi 2013)*

56. Why is (±)-butan-2-ol is optically inactive? *(1/2, Delhi 2013)*

57. Which compound in the following pair undergoes faster S_N1 reaction?

 and 

(Delhi 2013, 2013C, 2012C)

58. How may methyl bromide be preferentially converted to methyl isocyanide? *(Delhi 2013C)*

59. Account for the following :
Grignard's reagents should be prepared under anhydrous conditions.
(1/3, Delhi 2013C, 1/3, AI 2012C)

60. Predict the order of reactivity of four isomeric bromobutanes in S_N1 reaction. *(Delhi 2012C)*

61. Predict the order of reactivity of the following compounds in S_N1 reaction.
$C_6H_5CH_2Br$, $C_6H_5C(CH_3)(C_6H_5)Br$,
$C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$
(Delhi 2012C)

62. Give a chemical test of distinguish between C_2H_5Br and C_6H_5Br. *(AI 2012C)*

63. Which will react faster in S_N2 displacement, 1-bromopentane or 2-bromopentane and why? *(Foreign 2011)*

64. Which will react faster in S_N1 displacement reaction :
1-Bromobutane or 2-bromobutane and why?
(Foreign 2011)

65. A solution of KOH hydrolyses $CH_3CHClCH_2CH_3$ and $CH_3CH_2CH_2CH_2Cl$. Which one of these is more easily hydrolysed? *(Delhi 2010)*

66. Explain the following reactions with an example:
Friedel-Crafts reaction. *(1/2, Delhi 2010)*

67. Why is the following occur :
Chloroform is stored in closed dark coloured bottles completely filled so that air is kept out.
(1/2, Delhi 2010C)

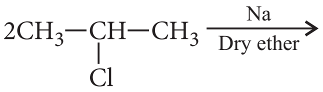
68. Explain why in the pair, $(CH_3)_3CCl$ and CH_3Cl will react faster in S_N2 reaction with OH^-? *(1/3, AI 2010C)*

SA I (2 marks)

69. Give reasons :
(i) C—Cl bond length in chlorobenzene is shorter than C—Cl bond length in $CH_3—Cl$.
(ii) S_N1 reactions are accompanied by racemization in optically active alkyl halides.
(2/3, Delhi 2016)

70. How do you convert?
(i) Chlorobenzene to biphenyl
(ii) 2-bromobutane to but-2-ene
(2/3, AI 2016)

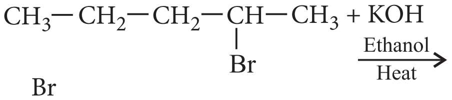
71. Write the major product(s) in the following :

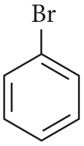
(i) 
$2CH_3-\underset{\underset{Cl}{|}}{C}H-CH_3 \xrightarrow[\text{Dry ether}]{\text{Na}}$

(ii) $CH_3-CH_2-Br \xrightarrow{\text{AgCN}}$ *(2/3, AI 2016)*

72. Give reasons:
(i) Racemic mixture is optically inactive.
(ii) The presence of nitro group $(—NO_2)$ at *o/p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. *(2/3, Delhi 2015)*

73. Write the structure of the major product in each of the following reactions :

(i) 
$CH_3-CH_2-CH_2-\underset{\underset{Br}{|}}{C}H-CH_3 + KOH \xrightarrow[\text{Heat}]{\text{Ethanol}}$

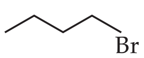
(ii) 

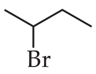
$+ CH_3Cl \xrightarrow{\text{anhyd. AlCl}_3}$

(2/3, AI 2015)

74. (i) Why is butan-1-ol optically inactive but butan-2-ol is optically active?
(ii) Although chlorine is an electron withdrawing group, yet it is *ortho-*, *para-*directing in electrophilic aromatic substitution reactions. Why?
(2/3, Foreign 2015, Delhi 2012)

75. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?

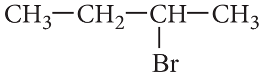
(a) 

(b) 

(ii) Out of S_N1 and S_N2, which reaction occurs with
(a) inversion of configuration
(b) racemisation? *(2/3, Delhi 2014)*

76. Write chemical equations when
(i) ethyl chloride is treated with aqueous KOH.
(ii) chlorobenzene is treated with CH_3COCl in presence of anhydrous $AlCl_3$.
(Foreign 2014)

77. (i) Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism and why?



$CH_3-CH_2-\underset{Br}{\underset{|}{C}H}-CH_3$

$CH_3-CH_2-CH_2-CH_2-Br$

(ii) Racemisation occurs in S_N1 reactions. Why? *(Foreign 2014)*

78. Write chemical equations when
- (i) methyl chloride is treated with $AgNO_2$.
- (ii) bromobenzene is treated with CH_3Cl in the presence of anhydrous $AlCl_3$. *(Foreign 2014)*

79. What are ambident nucleophiles? Explain with an example. *(2/3, AI 2014C)*

80. Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction. Give two reasons for the same. *(Delhi 2013)*

81. Account for the following:
- (i) The C—Cl bond length in chlorobenzene is shorter than that in CH_3-Cl.
- (ii) Chloroform is stored in closed dark brown bottles. *(Delhi 2013)*

82. Give reasons for the following :
- (i) Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.
- (ii) $C-X$ bond length in halobenzene is smaller than $C-X$ bond length in CH_3-X. *(2/3, AI 2013)*

83. Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Explain. *(2/3, Delhi 2012C)*

84. Answer the following :
- (i) What is known as a racemic mixture? Give an example.
- (ii) Of the two bromoderivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in S_N1 substitution reaction and why? *(2/3, Delhi 2011)*

85. Write the mechanism of the following reaction :

$$n\text{-BuBr} + \text{KCN} \xrightarrow{\text{EtOH, H}_2\text{O}} n\text{-BuCN}$$

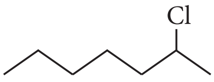
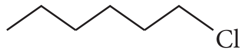
(1/3, Delhi, 2011C)

86. How are the following conversions carried out?
- (i) Benzyl chloride to benzyl alcohol,
- (ii) Methyl magnesium bromide to methylpropan-2-ol. *(2/3, Delhi 2010)*

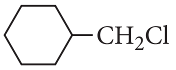
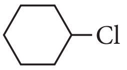
87. Which compound in the following couple will react faster in S_N2 displacement and why?
- (i) 1-Bromopentane or 2-bromopentane
- (ii) 1-Bromo-2-methylbutane or 2-bromo-2-methylbutane. *(2/3, Delhi 2010)*

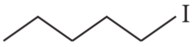
88. (a) Why is sulphuric acid not used during the reaction of alcohols with KI in the conversion of an alcohol to the alkyl iodide?

(b) Why are haloarenes less reactive than haloalkanes towards nucleophilic substitution reactions? *(Delhi 2010C)*

89. How would you account for the following :
- (i) Grignard reagents are prepared strictly under anhydrous conditions ?
- (ii)  undergoes faster S_N1 reaction than  ? *(Delhi 2010C)*

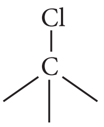
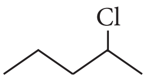
90. Which one in the following pairs of substances undergoes S_N2 substitution reaction faster and why?

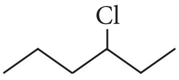
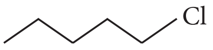
(i)  or 

(ii)  or 

(Delhi 2009)

91. Which one in the following pairs undergoes S_N1 substitution reaction faster and why?

(i)  or 

(ii)  or 

(AI 2009)

92. Suggest a possible reason for the following observations :
- (i) The order of reactivity of haloalkanes is $RI > RCl > RBr$.

(ii) Neopentyl chloride $(CH_3)_3CCH_2Cl$ does not follow S_N2 mechanism.

(2/3, Delhi 2009C)

93. Give reasons for the following observations :

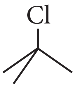
(i) Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reactions.

(ii) The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkene is the major product.

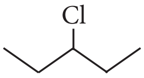
(2/3, AI 2009C)

94. (i) Why is it that haloalkanes are more reactive than haloarenes towards nucleophiles.

(ii) Which one of the following reacts faster in an S_N1 reaction and why?



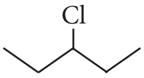
or



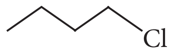
(Delhi 2008)

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

(ii) Which one of the following two substances undergoes S_N1 reaction faster and why?



or



(AI 2008)

96. Discuss the mechanism of S_N1 reaction of haloalkanes. *(Delhi 2008C)*

97. What is Saytzeff rule? Illustrate with suitable example. *(2/5, AI 2007)*

98. Give one example of each of the following reactions :

(i) Wurtz reaction

(ii) Wurtz-Fittig reaction. *(2/5, Delhi 2007)*

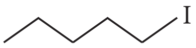
SA II (3 marks)

99. Answer the following questions:

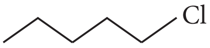
(i) What is meant by chirality of a compound? Give an example.

(ii) Which one of the following compounds is more easily hydrolysed by KOH and why?
$CH_3CHClCH_2CH_3$ or $CH_3CH_2CH_2Cl$

(iii) Which one undergoes S_N2 substitution reaction faster and why?



or



(AI 2012)

100. Rearrange the compounds of each of the following sets in order of reactivity towards S_N2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane,3-bromo-2-methylbutane

(iii) 1-Bromobutane, 1-Bromo-2, 2-dimethyl propane, 1-Bromo-2-methylbutane

(AI 2011)

101. (a) Write a chemical test to distinguish between :

(i) Chlorobenzene and benzyl chloride

(ii) Chloroform and carbon tetrachloride

(b) Why is methyl chloride hydrolysed more easily than chlorobenzene? *(Delhi 2011C)*

102. Differentiate between S_N1 and S_N2 mechanisms and give examples. *(AI 2010)*

10.7 Polyhalogen Compounds

VSA (1 mark)

103. State one use each of DDT and iodoform.

(Delhi 2010)

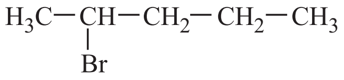
104. Write the balanced equation for the following:

(i) When chloroform is oxidised by air.

(ii) Chloroform reacts with chlorine.

(2/5, Delhi 2007)

Detailed Solutions

1. 
$H_3C-\underset{Br}{\underset{|}{C}H}-CH_2-CH_2-CH_3$

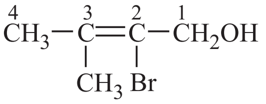
2. 4-Chloropent-1-ene

3. 4-Bromo-4-methylpent-2-ene

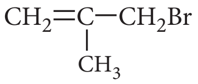
4. 2-Chloro-3-methyl butane

5. 3-Chloro-2,2-dimethyl butane

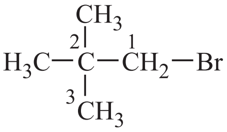
6. 2-Bromo-4-chloropentane

7. 
$\overset{4}{C}H_3-\underset{CH_3}{\overset{3}{C}}=\underset{Br}{\overset{2}{C}}-\overset{1}{C}H_2OH$

2-Bromo-3-methylbut-2-en-1-ol

8. 
$CH_2=\underset{CH_3}{C}-CH_2Br$

3-Bromo-2-methylpropene

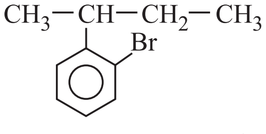
9. 
$H_3C-\overset{CH_3}{\underset{\overset{3}{C}H_3}{\overset{2}{C}}}-\overset{1}{C}H_2-Br$

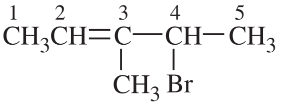
1-Bromo-2,2-dimethylpropane

10. $CH_2=CHCH_2Br$

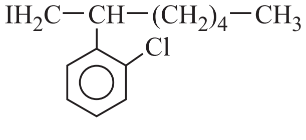
3-Bromoprop-l-ene

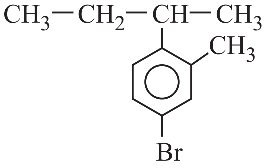
11. 
$H_2\underset{Br}{C}-CH=CH-\underset{Br}{CH_2}$

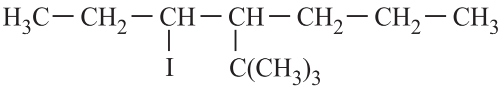
12. 

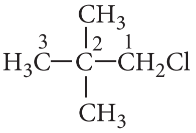
13. 
$\overset{1}{C}H_3\overset{2}{C}H=\underset{CH_3}{\overset{3}{C}}-\underset{Br}{\overset{4}{C}H}-\overset{5}{C}H_3$

4-Bromo-3-methylpent-2-ene

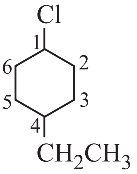
14. 

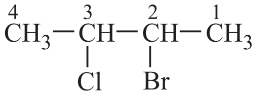
15. 

16. 
$H_3C-CH_2-\underset{I}{CH}-\underset{C(CH_3)_3}{CH}-CH_2-CH_2-CH_3$

17. 
$\overset{3}{H_3C}-\overset{CH_3}{\underset{CH_3}{\overset{2}{C}}}-\overset{1}{C}H_2Cl$

1-Chloro-2,2-dimethylpropane

18. 

19. 
$\overset{4}{C}H_3-\underset{Cl}{\overset{3}{C}H}-\underset{Br}{\overset{2}{C}H}-\overset{1}{C}H_3$

2-Bromo-3-chlorobutane

20. 1-Bromobut-2-ene

21. $Cl\overset{4}{C}H_2-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{C}H_2-Br$

1-Bromo-4-chlorobut-2-yne

22. (i) *Refer to answer 10.*

(ii) 2-(Trichloromethyl)-1, 1, 1, 2, 3, 3-3-heptachloropropane

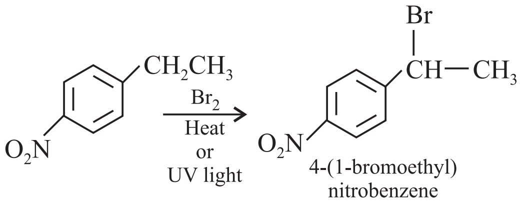
23. (i) 2-Bromobutane

(ii) 1,3-Dibromobenzene

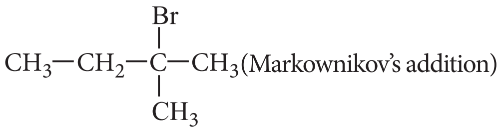
(iii) 3-Chloropropene

24. $\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2Br$

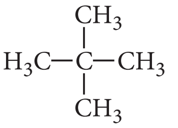
$\xrightarrow[\text{Acetone}]{\text{NaI}} \underset{\text{1-Iodopropane}}{CH_3-CH_2-CH_2I}$

25. 

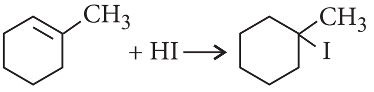
4-(1-bromoethyl) nitrobenzene

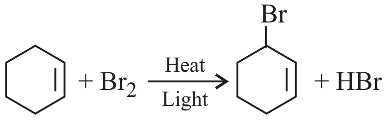
26. 
$CH_3-CH_2-\overset{Br}{\underset{CH_3}{C}}-CH_3$ (Markownikov's addition)

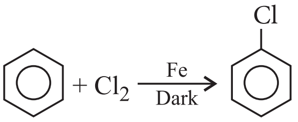
2-Bromo-2-methylbutane

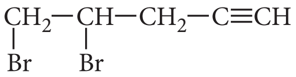
27. 
$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

2,2-Dimethylpropane

28. 

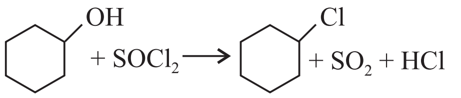
29. 

30. 

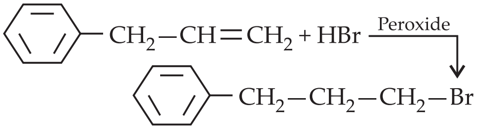
31. 
$\underset{Br}{CH_2}-\underset{Br}{CH}-CH_2-C\equiv CH$

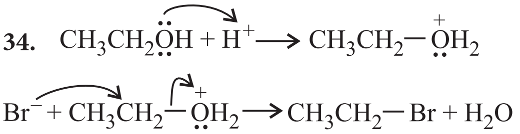
32\. $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow[\text{Anti Markownikoff's addition}]{\text{Peroxide}} CH_3CH_2CH_2CH_2Br$

1-Bromobutane

33. (i) 

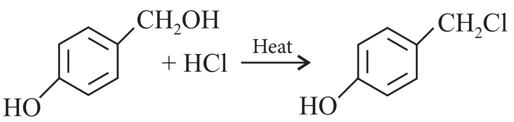
Chlorocyclohexane

(ii) 

34. 
$CH_3CH_2\ddot{\underset{\cdot\cdot}{O}}H + H^+ \longrightarrow CH_3CH_2-\overset{+}{\underset{\cdot\cdot}{O}}H_2$

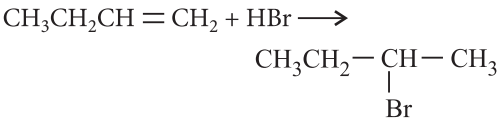
$Br^- + CH_3CH_2-\overset{+}{\underset{\cdot\cdot}{O}}H_2 \longrightarrow CH_3CH_2-Br + H_2O$

35. (i) *Refer to answer 33 (i).*

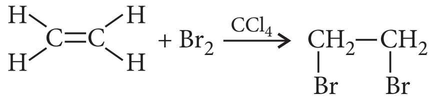
(ii) 

4-Chloromethylphenol

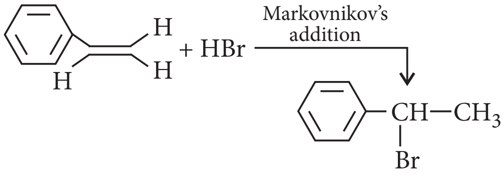
36. (i) *Refer to answer 28.*

(ii) 
$CH_3CH_2CH{=}CH_2 + HBr \longrightarrow CH_3CH_2-\underset{Br}{CH}-CH_3$

37. (i) $C_6H_5N_2Cl + KI \longrightarrow C_6H_5I + N_2 + KCl$

(ii) 

38. (i) *Refer to answer 28.*

(ii) 

(iii) *Refer to answer 36 (ii).*

39. (i) *Refer to answer 38(ii).*

(ii) *Refer to answer 28.*

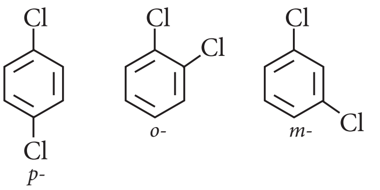
(iii) *Refer to answer 33(i).*

40. *n*-Butyl bromide, being a straight chain molecule have strong intermolecular forces whereas *t*-butyl bromide being a branched chain molecule have weaker intermolecular forces due to smaller surface area.

Hence, boiling point of *n*-butyl bromide is higher than that of *t*-butyl bromide.

41. Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H – bond among water molecules is much higher than energy released by water halide interaction.

42. *p*-Dichlorobenzene has higher melting point than those of *o*-and *m*-isomers because it is more symmetrical and packing is better in solid form. Hence, it has stronger intermolecular force of attraction than *o*-and *m*-isomers.



43. *Refer to answer 41.*

44. Haloalkanes dissolve in organic solvents because the intermolecular attractions between haloalkanes and organic solvent molecules have the same strength as in the separate haloalkanes and solvent molecules.

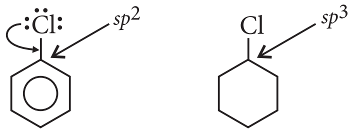
45. The boiling point of ethyl bromide is higher due to the greater magnitude of the van der Waals forces which depend upon molecular size and mass.

46. (i) There are two reasons :

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

(b) In chlorobenzene C—Cl bond has some double bond character so its bond length is smaller.

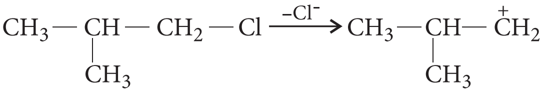
Hence dipole moment is smaller than cyclohexyl chloride which has a longer C—Cl single bond.



Chlorobenzene Cyclohexyl chloride

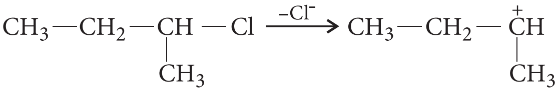
(ii) *Refer to answer 41.*

47. The S_N1 reaction proceeds through carbocation formation thus, the compound which forms more stable carbocation will be more reactive.



$CH_3—\underset{CH_3}{\underset{|}{CH}}—CH_2—Cl \xrightarrow{-Cl^-} CH_3—\underset{CH_3}{\underset{|}{CH}}—\overset{+}{CH_2}$

1-Chloro-2-methylpropane (1° Carbocation)

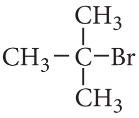


$CH_3—CH_2—\underset{CH_3}{\underset{|}{CH}}—Cl \xrightarrow{-Cl^-} CH_3—CH_2—\underset{CH_3}{\underset{|}{\overset{+}{CH}}}$

2-Chlorobutane (2° Carbocation)

As, 2° carbocation is more stable than 1° carbocation thus, 2-chlorobutane is more reactive towards S_N1 reaction.

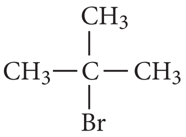
48.



$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-Br$

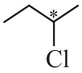
Tertiary butyl bromide
or 2-Bromo-2-methylpropane

49. $CH_3—CH_2—Br$ would undergo S_N2 reaction faster due to formating of less steric hindrance.



50. $CH_3—\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}—CH_3$ will undergo S_N1 reaction faster due to stable carbocation.

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

52.  is a chiral molecule.

53. (i) CH_3I will give faster S_N2 reaction.
(ii) CH_3Cl will give faster S_N2 reaction.

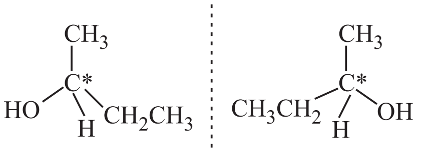
54. CH_3CN is formed by nucleophilic substitution reaction.

$CH_3Br + KCN \rightarrow CH_3CN + KBr$

55. When ethyl chloride is treated with aqueous KOH, ethanol is formed,

$CH_3CH_2Cl + KOH_{(aq)} \longrightarrow CH_3CH_2OH + KCl$

56. The (±)-Butan-2-ol is optically inactive because it exist in two enantiomeric forms which are non-superimposable mirror images of each other. Both the isomers are present in equal amounts therefore, it does not rotate the plane of polarized light and is optically inactive.



50% – (+) Butan-2-ol 50% – (–) Butan-2-ol

57. Tertiary halide  reacts faster than the secondary halide because of the greater stability of *tert*-carbocation.

58. KCN is predominantly ionic and provides cyanide ions in solution

$\underset{\text{Methyl bromide}}{CH_3Br} + KCN \longrightarrow \underset{\text{Methyl cyanide}}{CH_3C\equiv N} + KBr$

AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as main product.

$\underset{\text{Methyl bromide}}{CH_3Br} + AgCN \longrightarrow \underset{\text{Methyl isocyanide}}{CH_3N \overrightarrow{=} C} + AgBr$

59. Grignard reagents react with water to form alkanes.

$R—Mg—X + H_2O \longrightarrow R—H + Mg\genfrac{}{}{0pt}{}{X}{OH}$

So, they must be prepared under anhydrous conditions.

60.

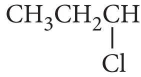
$(CH_3)_3CBr > CH_3CH_2\underset{Br}{\underset{|}{CH}}—CH_3 >$
$(CH_3)_2CHCH_2Br > CH_3CH_2CH_2CH_2Br$

61. $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$

62. C_2H_5Br reacts with $AgNO_3$ to give yellow precipitate of AgBr while C_6H_5Br will not.

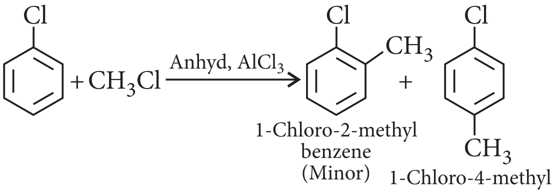
63. 1-Bromopentane is a primary alkyl halide, hence reacts faster in S_N2 displacement than secondary halide 2-bromopentane.

64. 2-Bromobutane will react faster in S_N1 displacement reaction because it will form more stable secondary carbocation intermediate.

65. 

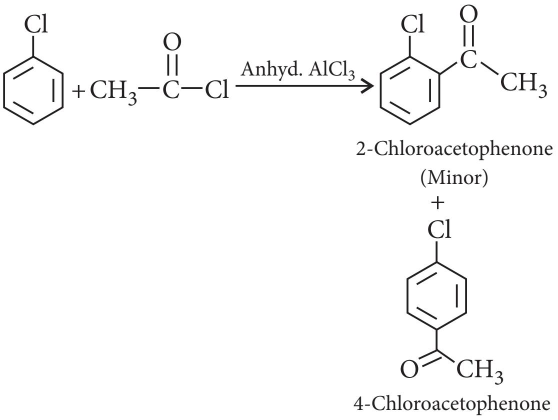
$CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$ hydrolyses easily with KOH because it is secondary halide.

66. Haloarenes can undergo both freidal craft alkylation (with alkyl halide) or freidal craft acylation (with acid halide) in presence of Lewis acid catalyst to give a mixture of *o*- and *p*-haloalkyl benzene or *o*- and *p*-haloacylbenzene.



1-Chloro-2-methyl benzene (Minor)

1-Chloro-4-methyl benzene (Major)



2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)

67. Chloroform when exposed to air and sunlight changes to phosgene which is a poisonous gas.

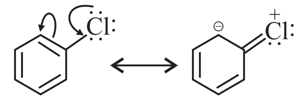
$$CHCl_3 + \frac{1}{2}O_2 \rightarrow COCl_2 + HCl$$

It is kept in dark coloured bottles to prevent the oxidation.

68. CH_3Cl will react faster in S_N2 reaction with OH^-.

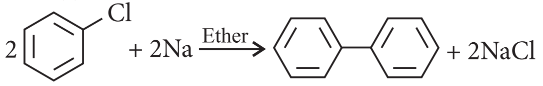
69. (i) In halobenzene C—X bond has partial double bond character due to resonance while $CH_3—X$ bond is single bond.

Thus bond length of C—X bond in halobenzene is smaller than that in $CH_3—X$.

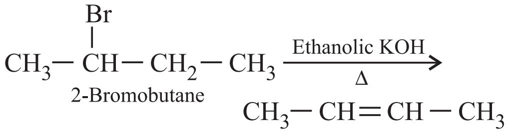


(iii) In S_N1 reaction carbocation intermediate is formed which is a planar molecule so,an incoming nucleophile can attack from either side and a equilmolar mixture of two components are formed and resulting mixture is optically inactive.

70. **(i)**

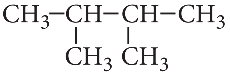


Chlorobenzene Diphenyl

(ii) 

$$CH_3-\overset{\displaystyle Br}{\overset{|}{C}}H-CH_2-CH_3 \xrightarrow[\Delta]{\text{Ethanolic KOH}} CH_3-CH=CH-CH_3$$

2-Bromobutane But-2-ene

71. (i) 

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_3$

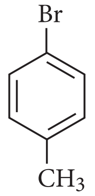
(ii) CH_3CH_2NC

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

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

73. (i) $CH_3—CH_2—CH=CH—CH_3$ (Saytzeff rule)

Pent-2-ene

(ii)  (Friedel—Crafts alkylation)

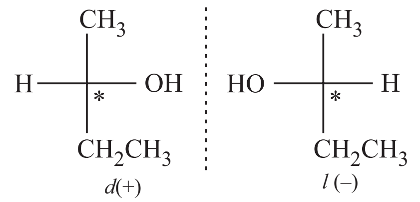
4-Bromotoluene

74. (i) Butan-1-ol is achrial, *i.e.*, does not have chiral 'C' atom which is attached to four different groups, therefore, it is optically inactive.

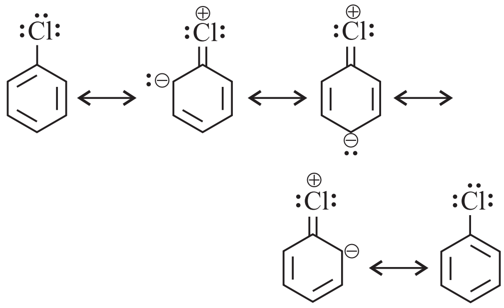
$$CH_3-CH_2-CH_2-CH_2OH$$

Butan-1-ol
(Optically inactive)
(No chiral carbon)

Butan-2-ol is chiral, *i.e.*, has chiral 'C' atom, attached to four different groups.

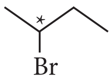


d(+) *l* (–)
Butan-2-ol

(ii)


Although Cl is electron withdrawing (*I* effect) but still *o*-and *p*-directing as due to +*R* effect, electrons density is maximum at *o*-and *p*-positions.

75. (i) (a)  undergoes faster S_N2 reaction.



(b) is chiral.

(ii) (a) S_N2 reaction occurs with inversion of configuration.

(b) S_N1 reaction occurs with racemisation.

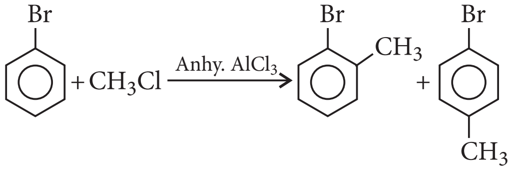
76. (i) *Refer to answer 55.*

(ii) *Refer to answer 66.*

77. (i) 1-Bromobutane is 1° alkyl halide while 2-bromobutane is 2° alkyl halide. Due to steric hindrance in 2° alkyl halides, 1° alkyl halide will react faster than 2° alkyl halide in S_N2 reaction.

(ii) Carbocations are formed in S_N1 reaction which are planar species, thus, racemisation occurs.

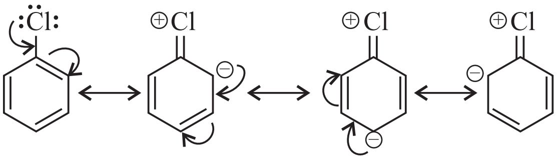
78. (i) $CH_3Cl + AgNO_2 \longrightarrow CH_3NO_2 + AgCl$

(ii)


79. A nucleophile which can attack from more than one centres, is known as ambident nucleophile.
e.g., $^{-}\ddot{C}\equiv N:$ Cyanide ion

80. Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.

(i) Resonance effect : In haloarenes the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.

(ii) Difference in hybridisation of carbon atom in C—*X* bond.

81. (i) *Refer to answer 69(i).*
(ii) *Refer to answer 67.*

82. (i) *Refer to answer 51.*
(ii) *Refer to answer 69(i).*

83. In haloarenes –ve charge gets localised on arenes using resonance, therefore they undergo electrophilic substitution.
Haloalkanes have electrophilic carbon centre due to polarity of $C \rightarrow X$ bond.

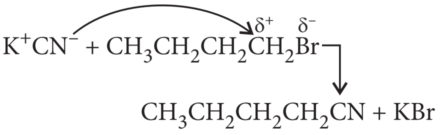
84. (i) An equimolar mixture of a pair of enantiomers is called racemic mixture. A racemic mixture is optically inactive due to external compensation.
Example :

$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3$$

Butan-2-ol

(ii) Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, the $C_6H_5CH(C_6H_5)Br$ is more reactive than $C_6H_5(CH_3)Br$ for S_N1 reaction because its carbocation is resonance stabilised by two phenyl groups.

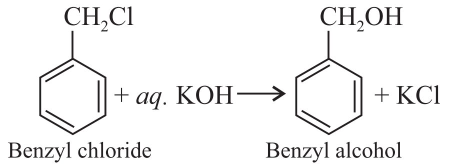
85. Normal butyl bromide will give S_N2 reaction :



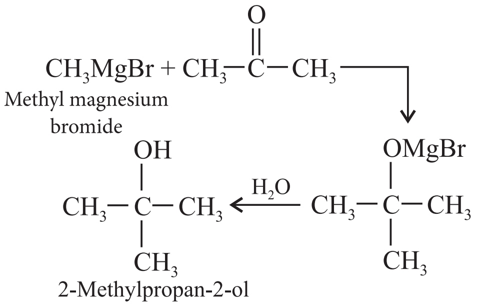
$$K^+CN^- + CH_3CH_2CH_2\overset{\delta+}{C}H_2\overset{\delta-}{Br} \longrightarrow CH_3CH_2CH_2CH_2CN + KBr$$

n-Butyl cyanide

86. (i)



(ii)



87. (i) 1-Bromopentane, as it is a primary alkyl halide.

(ii) 1-Bromo-2-methylbutane, as it is a primary alkyl halide.

88. (i) H_2SO_4 is an oxidant. KI reacts with H_2SO_4 and give HI and H_2SO_4 oxidises HI to I_2.

$2KI + H_2SO_4 \rightarrow 2KHSO_4 + 2HI$

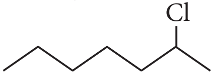
$2HI + H_2SO_4 \rightarrow 2H_2O + I_2 + SO_2$

Thus HI will not be available for reaction with alcohol to form alkyl iodide.

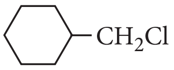
This is why sulphuric acid is not used during the reaction of alcohols with KI.

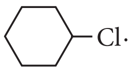
(ii) *Refer to answer 80.*

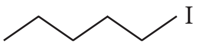
89. (i) *Refer to answer 59.*

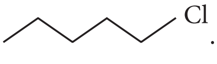
(ii) 

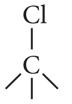
undergoes faster S_N1 reaction.

90. (i) 

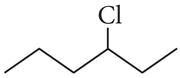
is primary halide and therefore, undergoes S_N2 reaction faster than the secondary halide 
.

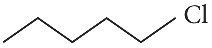
(ii) As iodide is a better leaving group because of its large size, therefore, 

undergoes S_N2 reaction faster than 
.

91. (i) 

: Tertiary halide reacts faster than secondary halide because of the greater stability of *tert.* carbocation.

(ii) 

reacts faster than 

because of greater stability of secondary carbocation than primary.

92. (i) Among the various halides with same alkyl group the order of reactivity is *R*I > *R*Br > *R*Cl.

Due to increasing bond strength of C—I, C—Br and C—Cl the reactivity decreases.

(ii) Neopentyl chloride being a primary halide reacts slowly through S_N1 and the carbon carrying halogen is sterically more hindered. Hence it does not follow S_N2 mechanism.

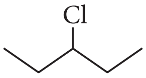
93. (i) *Refer to answer 80.*

(ii) In aqueous solution, KOH is almost completely involved to give OH^- ion which being a better nucleophile gives a substitution reaction on alkyl halides to form alcohol. But an alcoholic solution of KOH containing alkoxide (RO^-) ions which being a much stronger base than OH^- ion preferentially snatches a H^+ ion from an alkyl chloride to form alkenes.

94. (i) *Refer to answer 80.*

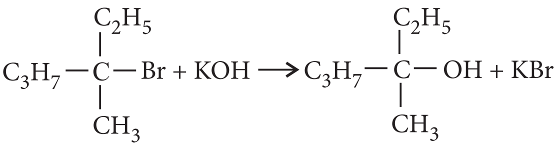
(ii) *Refer to answer 57.*

95. (i) *Refer to answer 80.*

(ii) Due to greater stability of 2° carbocation over 1° carbocation, 

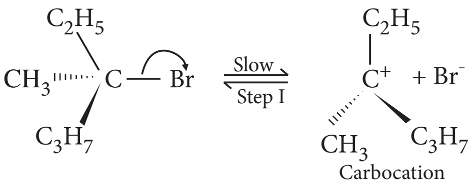
will react faster than 
Cl in S_N1 reaction.

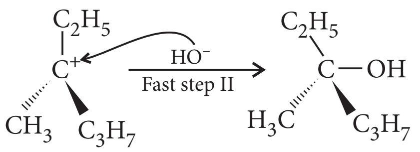
96. In S_N1 mechanism of substitution reaction, the rate of reaction depends upon the concentration of only one reactant. It is two steps reactants.



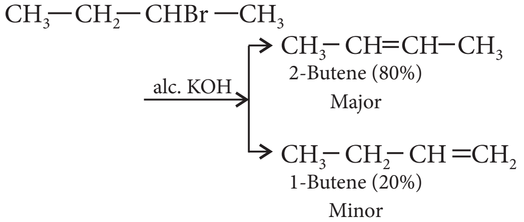
$$C_3H_7-\overset{\overset{C_2H_5}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br + KOH \longrightarrow C_3H_7-\overset{\overset{C_2H_5}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH + KBr$$

Mechanism :





97. **Saytzeff rule :** In elimination reaction alkene having the lesser number of hydrogen on the double bonded carbon atom is formed. This generalisation is known as Saytzeff rule for example.

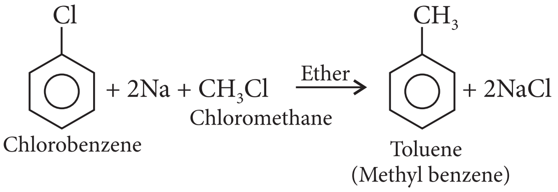


$$CH_3-CH_2-CHBr-CH_3 \xrightarrow{\text{alc. KOH}} \underset{\text{2-Butene (80\%) Major}}{CH_3-CH{=}CH-CH_3} + \underset{\text{1-Butene (20\%) Minor}}{CH_3-CH_2-CH{=}CH_2}$$

98. (i) **Wurtz reaction :** It converts alkyl halide into higher alkane in presence of sodium metal and dry ether.

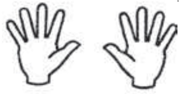
$$\underset{\text{Chloromethane}}{CH_3Cl} + 2Na + CH_3Cl \xrightarrow{\text{Ether}} 2NaCl + \underset{\text{Ethane}}{C_2H_6}$$

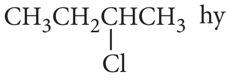
(ii) **Wurtz-Fittig reaction :** It converts aryl halide into alkyl arenes in presence of sodium metal and ether.

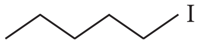
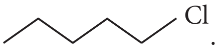


99. (i) **Chiral object :** An object which has no plane of symmetry (cannot be divided into two identical halves) is called chiral (Greek; Chiral-Hand) or dissymmetric or asymmetric. A Chiral object is not superimposable on its mirror image.

e.g., left and right hand of a person are mirror images of each other and are not superimposable.



(ii)  $CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_3$ hydrolyses easily with KOH because it is secondary halide.

(iii) As iodide is a better leaving group because of its large size, therefore,  undergoes S_N2 reaction faster than .

100. (i) 1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane.

(ii) 1-Bromo-3-methylbutane > 3-Bromo-2-methylbutane > 2-Bromo-2-methylbutane

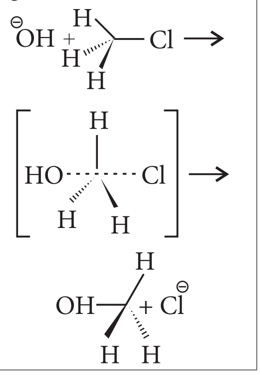
(iii) 1-Bromobutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane

101. (a) (i) Benzyl chloride gives white precipiate with $AgNO_3$ solution while chlorobenzene does not .

(ii) $CHCl_3$ with aniline in presence of alc. KOH gives foul smelling isocyanides whereas CCl_4 does not.

(b) CH_3Cl is hydrolysed easily than C_6H_5Cl as chlorobenzene has partial double bond character between C — Cl bond which is difficult to break.

102.

	S_N1 mechanism	S_N2 mechanism
1.	It is two step process, carbocation interme-diate is formed.	It is single step process. No intermediate is formed.
2.	It obeys 1st order kientics. Rate = k [Reactant]	It obeys 2nd order kinetics. Rate = k[Reactant] [Nuclephile]
3.	Order of reactivity 3° > 2° > 1°.	Order of reactivity 1° > 2° > 3°.
4.	Optically inactive product is formed (racemic mixture).	Inversion of configuration takes place.
5.	*e.g.,* $(CH_3)_3CBr + OH^-$ 2-Bromo-2-methyl propane ↓ $(CH_3)_3COH + Br^-$ 2-Methylpropan-2-ol	*e.g.,* 

103. (ii) DDT is used as an insecticide and iodoform is used as a mild antiseptic.

104. (i) $\underset{\text{Chloroform}}{2CHCl_3 + O_2} \xrightarrow{\text{Light}} \underset{\text{Carbonyl chloride}}{2COCl_2} + 2HCl$

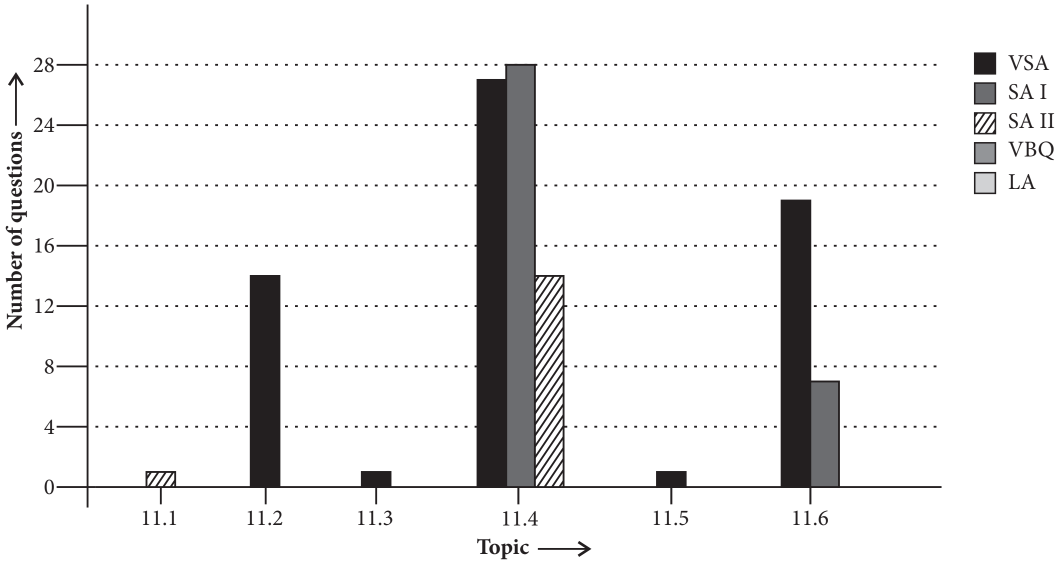
(ii) $\underset{\text{Chloroform}}{CHCl_3} + Cl_2 \longrightarrow \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl$

11

Alcohols, Phenols and Ethers

11.1 Classification
11.2 Nomenclature
11.3 Structures of Functional Groups
11.4 Alcohols and Phenols
11.5 Some Commercially Important Alcohols
11.6 Ethers

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



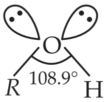
- Maximum total weightage is of *Alcohols and Phenols.*
- Maximum VSA type questions were asked from *Alcohols and Phenols.*
- Maximum SA I and SA II type questions were asked from *Alcohols and Phenols.*

QUICK RECAP

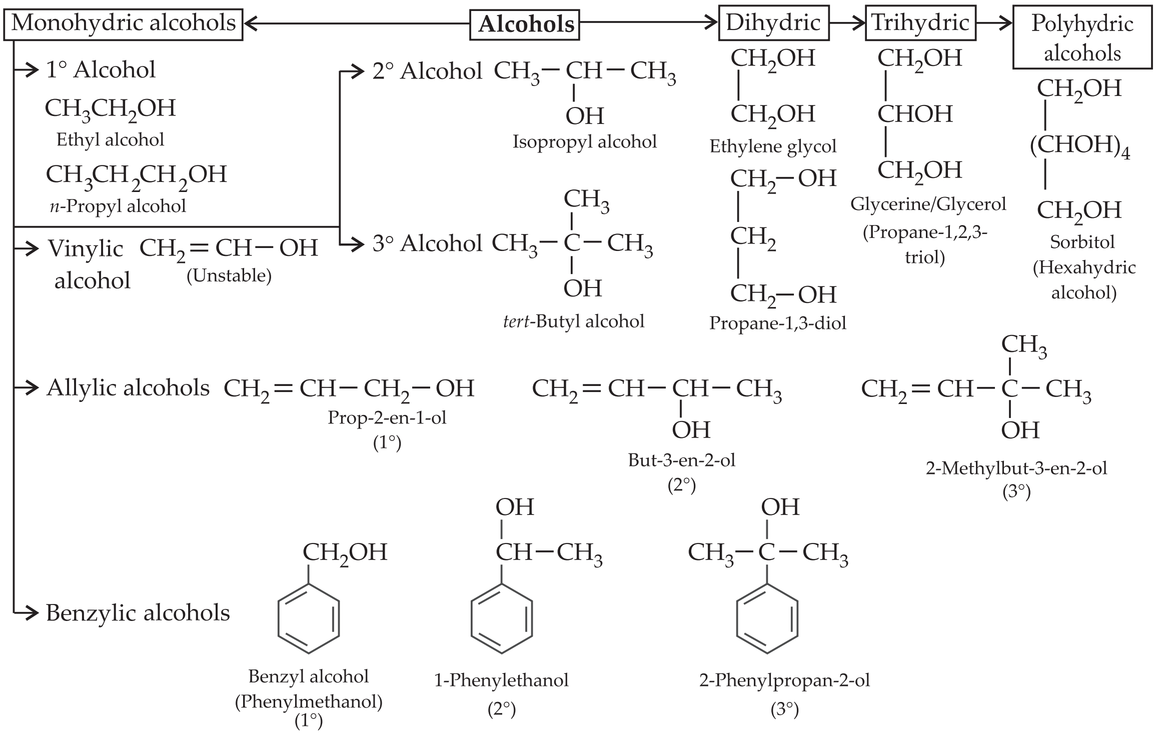
ALCOHOLS

- **General formula :** Alcohols are the hydroxy derivatives of alkanes having general formula $C_nH_{2n+1}OH$.
- **Nomenclature :** In common system, alcohols are named as *alkyl alcohol*. According to IUPAC system, alcohols are called '*alkanols*', by replacing '*-e*' of alkane by '*-ol*'.
- **Structure :** In alcohols, $R-OH$, the O atom of hydroxyl group is attached to C-atom

by a sigma (σ) bond formed by the overlap of sp^3 hybridised orbital of C-atom with sp^3 hybridised orbital of O atom.

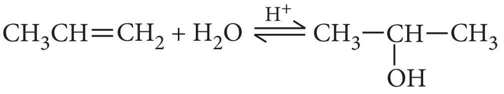


Classification : Alcohols are classified as monohydric, dihydric, trihydric and polyhydric alcohols depending upon the number of hydroxyl (—OH) groups present in the molecule.



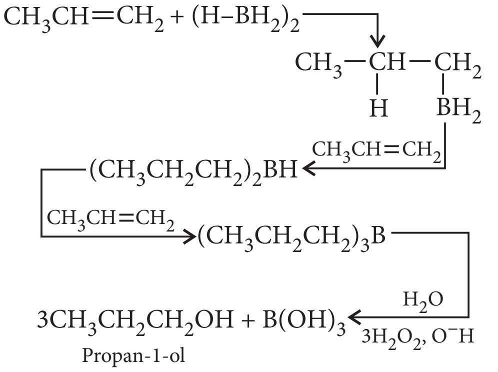
Preparation :

- **From alkenes :**
  – **By acid catalysed hydration :**



$$CH_3CH{=}CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_3$$

  – **By hydroboration-oxidation :**

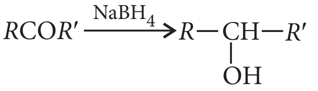


$$CH_3CH{=}CH_2 + (H{-}BH_2)_2 \longrightarrow CH_3{-}\underset{\displaystyle H}{\underset{|}{C}H}{-}\underset{\displaystyle BH_2}{\underset{|}{C}H_2}$$

$$\xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_2BH \xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_3B \xrightarrow[3H_2O_2,\ O^-H]{H_2O} \underset{\text{Propan-1-ol}}{3CH_3CH_2CH_2OH} + B(OH)_3$$

- **From carbonyl compounds :**
  – **By reduction of aldehydes and ketones :**

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$



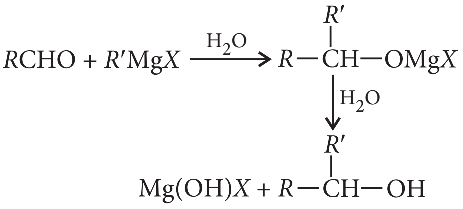
$$RCOR' \xrightarrow{NaBH_4} R{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}R'$$

  – **By reduction of carboxylic acids and esters :**

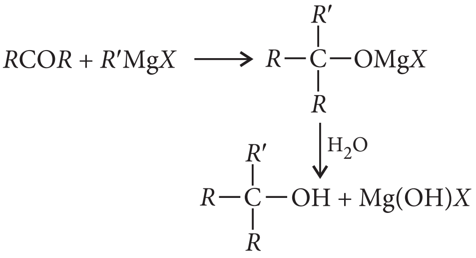
$$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2OH$$

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[Catalyst]{H_2} RCH_2OH + R'OH$$

  – **From Grignard reagents :**



$$RCHO + R'MgX \xrightarrow{H_2O} R{-}\overset{\displaystyle R'}{\overset{|}{C}H}{-}OMgX \xrightarrow{H_2O} Mg(OH)X + R{-}\overset{\displaystyle R'}{\overset{|}{C}H}{-}OH$$



$$RCOR + R'MgX \longrightarrow R-\overset{R'}{\underset{R}{C}}-OMgX \xrightarrow{H_2O} R-\overset{R'}{\underset{R}{C}}-OH + Mg(OH)X$$

Physical properties :

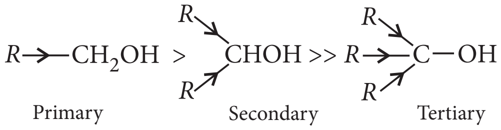
- **Physical state :** Lower alcohols are colourless liquids with characteristic smell while higher alcohols are colourless, odourless waxy solids.
- **Solubility :** Solubility of alcohols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with increase in size of alkyl groups and solubility increases with increase in branching and the order is 1° < 2° < 3°.
- **Boiling points :** The boiling points of alcohols increase with increase in the number of carbon atoms as van der Waals forces increase and the boiling points decrease with increase of branching in carbon chain due to decrease in van der Waals forces with decrease in surface area and the order is 1° > 2° > 3°.

Chemical properties : Alcohols react both as nucleophiles (when the bond between O – H is broken) and electrophiles (when the bond between C – O is broken).

- **Reactions involving cleavage of O—H bond :**
  - **Acidity of alcohols (reaction with metals) :**

$$2ROH + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2RONa} + H_2$$

  - The acid strength of alcohols decreases in the following order :



$$\underset{\text{Primary}}{R\rightarrow CH_2OH} > \underset{\text{Secondary}}{R_2CHOH} >> \underset{\text{Tertiary}}{R_3C-OH}$$

  - **Esterification :**

$ROH + (R'CO)_2O$ or $R'COCl \longrightarrow RCOOR'$

- **Reactions involving cleavage of C—O bond :**
  - **Reaction with hydrogen halides :**

$ROH + HX \longrightarrow RX + H_2O$

  - **Lucas test :** Lucas reagent is a solution of conc. HCl with anhyd. $ZnCl_2$.
  - With Lucas reagent,

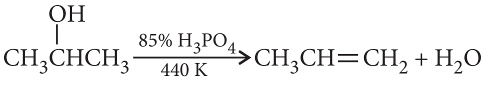
Primary alcohols – No cloudiness
Secondary alcohols – Cloudiness in 5 minutes
Tertiary alcohols – Cloudiness immediately

  - **Reaction with phosphorus trihalides :**

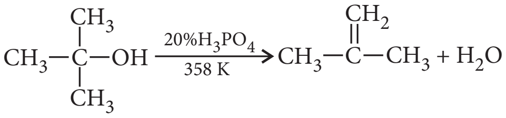
$ROH + PCl_3 \longrightarrow RCl + H_3PO_3$

  - **Dehydration :**

$$C_2H_5OH \xrightarrow[443\text{ K}]{H_2SO_4} CH_2{=}CH_2 + H_2O$$



$$CH_3\overset{OH}{C}HCH_3 \xrightarrow[440\text{ K}]{85\%\ H_3PO_4} CH_3CH{=}CH_2 + H_2O$$

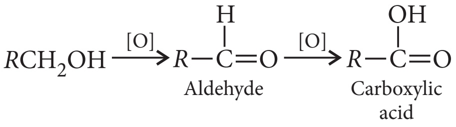


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[358\text{ K}]{20\%H_3PO_4} CH_3-\overset{CH_2}{\overset{\|}{C}}-CH_3 + H_2O$$

Thus, the relative ease of dehydration of alcohols follows the following order :

Tertiary > Secondary > Primary

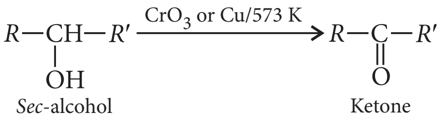
  - **Oxidation :**



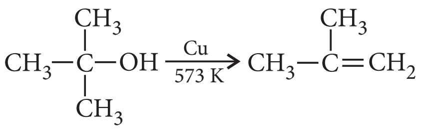
$$RCH_2OH \xrightarrow{[O]} \underset{\text{Aldehyde}}{R-\overset{H}{C}{=}O} \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{R-\overset{OH}{C}{=}O}$$

$$RCH_2OH \xrightarrow{CrO_3\text{ or Cu/573 K}} RCHO$$

$$CH_3CH{=}CHCH_2OH \xrightarrow{PCC} CH_3CH{=}CHCHO$$



$$\underset{Sec\text{-alcohol}}{R-\underset{OH}{CH}-R'} \xrightarrow{CrO_3\text{ or Cu/573 K}} \underset{\text{Ketone}}{R-\underset{O}{\overset{}{\underset{\|}{C}}}-R'}$$



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[573\text{ K}]{Cu} CH_3-\overset{CH_3}{C}{=}CH_2$$

Some commercially important alcohols :

- **Methanol (wood spirit) :** It is produced by catalytic hydrogenation of CO in the presence of ZnO – Cr_2O_3 as catalyst at high temperature and pressure.

$$CO + 2H_2 \xrightarrow[200\text{-}300\text{ atm, }573\text{-}673\text{ K}]{ZnO-Cr_2O_3} CH_3OH$$

  - Methanol is a colourless liquid and is highly poisonous in nature.

- Ingestion of small quantities can cause blindness while large quantities can cause death.
- It is used as a solvent in paints, varnishes and for making formaldehyde.

▶ **Ethanol :** It is commercially manufactured by using fermentation of sugar present in molasses, sugarcane or fruits such as grapes.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

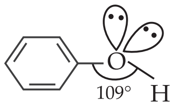
- Ethanol is colourless liquid and is used as a solvent in paint industry and in preparation of a number of carbon compounds.
- Commercial alcohol made unfit for drinking by mixing it with copper sulphate and pyridine is called *denatured alcohol.*

PHENOLS

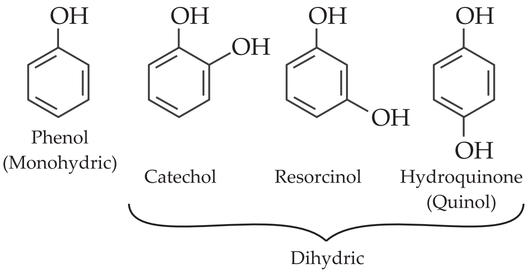
General formula : Phenols are the compounds in which hydroxy (—OH) group is directly linked to aromatic ring having formula C_6H_5OH.

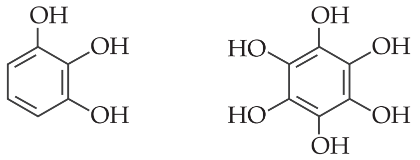
Nomenclature : The simplest hydroxy derivative of benzene is phenol also called *carbolic acid.* It is its common name and also an accepted IUPAC name.

Structure : In phenols, the —OH group is attached to sp^2 hybridised C-atom of an aromatic ring.



Classification : Like alcohols, phenols are also classified as mono and polyhydric phenols.



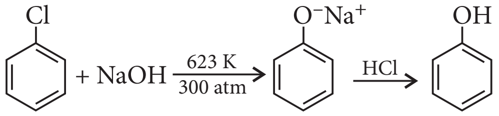


Pyrogallol (Trihydric)

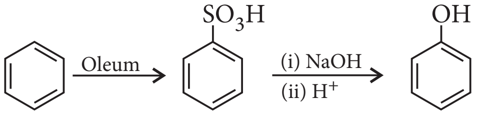
Hexaphenol (Polyhydric)

Preparation :

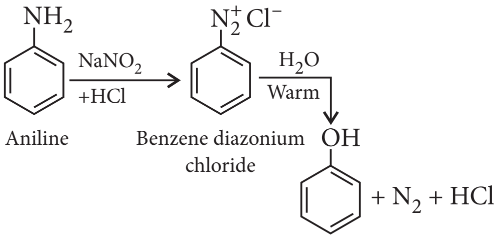
▶ **From haloarenes :**



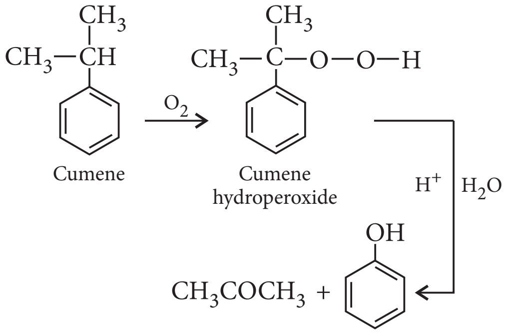
▶ **From benzenesulphonic acid :**



▶ **From diazonium salts :**



▶ **From cumene :**



Physical properties :

▶ **Physical state :** Phenols are colourless crystalline solids or liquids.

▶ **Odour :** They have characteristic phenolic odours.

▶ **Solubility :** Like alcohols, phenols are soluble in water due to the formation of hydrogen bonding with water.

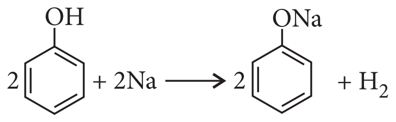
- Phenols are less soluble than alcohols due to large hydrocarbon (benzene ring) part.

- Phenols are soluble in alcohols, ethers and also in NaOH.

- **Boiling points :** Much higher than the corresponding aromatic hydrocarbons and haloarenes due to intermolecular hydrogen bonding.

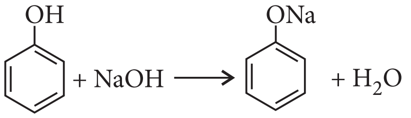
Chemical properties :

- **Acidity of phenols :** Phenols are weakly acidic in nature due to polar O—H bond directly attached to sp^2-hybridised C-atom.
  - They turn blue litmus red and react with alkali metals and alkalies to form their salts.
  - Phenol is weaker acid than carboxylic acid. It does not react with sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$).
  - Phenols are more acidic than alcohols which can be explained on the basis of resonance.
  - Electron withdrawing groups increase the acidic strength of phenols.
  - Electron releasing groups decrease the acidic strength of phenols.
  - **Reaction with metals :**



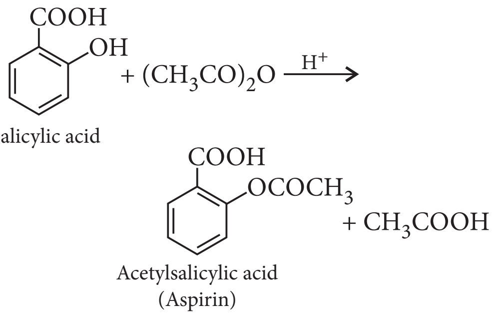
Phenol Sodium phenoxide

In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.



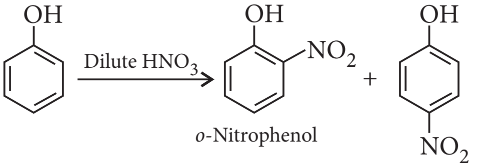
Sodium phenoxide

- **Esterification :**

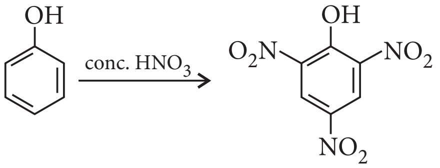


Acetylsalicylic acid (Aspirin)

- **Electrophilic aromatic substitution :**
  - **Nitration :**

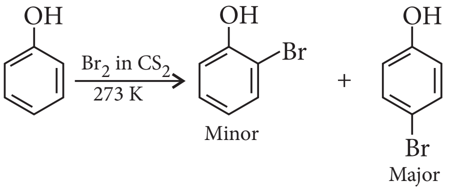


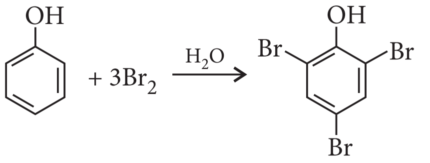
p-Nitrophenol



2,4,6-Trinitrophenol (Picric acid)

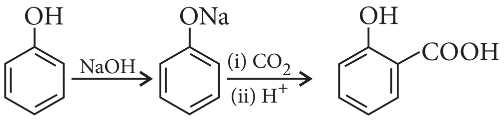
  - **Halogenation :**





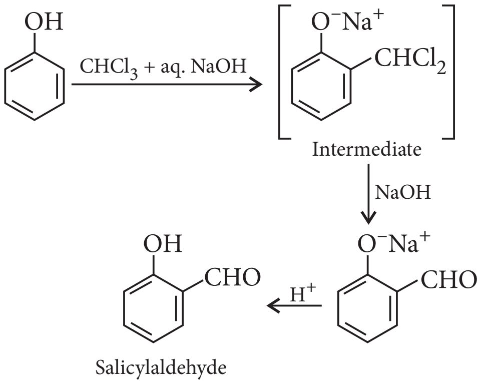
2,4,6-Tribromophenol

- **Kolbe's reaction :**



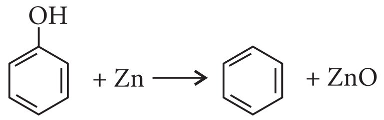
2-Hydroxybenzoic acid (Salicylic acid)

- **Reimer-Tiemann reaction :**

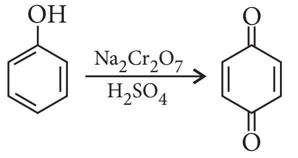


Salicylaldehyde

- **Reaction of phenol with zinc dust :**

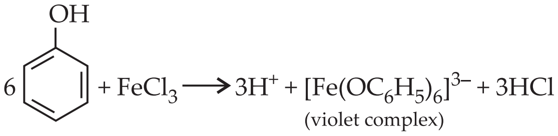


- **Oxidation**



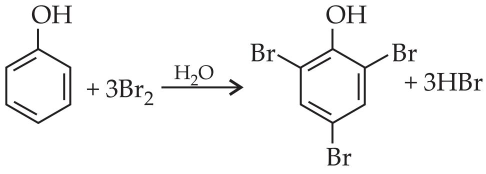
Benzoquinone

- **Test for phenols :**
  - **Ferric chloride test :** Phenol gives violet colour with neutral $FeCl_3$ solution.



(violet complex)

  - **Bromine water test :** Phenol gives white ppt. with Br_2-water due to the formation of 2, 4, 6-tribromophenol.



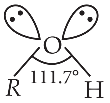
(white ppt.)

ETHERS

General formula : Ethers are the compounds having general formula $C_nH_{2n+2}O$ where n is always greater than 1.

Nomenclature : Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word '*ether*' at the end. If both the alkyl groups are the same, the prefix '*di*' is added before the alkyl group. According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an $-OR$ or $-OAr$ group, where R and Ar represent alkyl and aryl groups, respectively. The larger R group is chosen as the parent hydrocarbon.

Sturcture : In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons on O atom are arranged approximately in a tetrahedral arrangement.



Classification : Ethers can be classified as symmetrical or simple ethers having formula, $R-O-R$ and unsymmetrical or mixed ethers having formula, $R-O-R'$.

Preparation :

- **From alcohols by dehydration :**

$$2ROH \xrightarrow{H_2SO_4,\ 413\ K} ROR$$

- **From alkyl halide :**

$$R-X + RONa \xrightarrow[-NaX]{\Delta} ROR$$

(Williamson synthesis)

  - Williamson synthesis can be used to prepare ethers containing 2° or 3° alkyl groups through S_N2 mechanism. In this case, the alkyl halide must be 1°. In the case of 2° and 3° alkyl halides, elimination takes place. It cannot be used to prepare diaryl ethers.
  - Dehydration of alcohols for the formation of ethers follows the order : 1° > 2° > 3°

Physical properties :

- **Physical state and odour :** Dimethyl ether and ethyl methyl ether are exceptionally gases at room temperature while all other ethers are colourless liquids with characteristic ethereal smell.
- **Solubility :** Ethers are soluble in water to a certain extent due to hydrogen bonding.
  - Solubility decreases with increase in molecular mass.
  - Ethers are fairly soluble in all organic solvents such as alcohol, chloroform, benzene, etc.
- **Boiling points :** Ethers have lower boiling points than isomeric alcohols due to their inability to form hydrogen bonds and get associated.
  - But lower ethers have slightly higher boiling points than n-alkanes of comparable molecular masses due to dipole-dipole interactions.
  - Higher ethers (containing carbon atom more than four) have slightly lower boiling points than n-alkanes of comparable molecular

masses due to weak van der Waals forces of attraction.

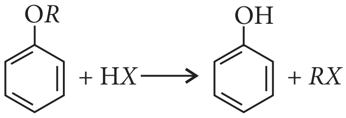
- **Polarity :** Ethers are polar in nature.
- **Density :** Ethers have low density. All ethers are lighter than water.

Chemical properties :

Cleavage of C—O bond in ethers :

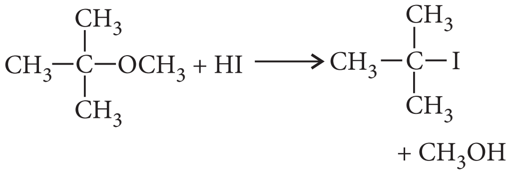
$ROR + HX \longrightarrow RX + ROH$

$ROH + HX \longrightarrow R—X + H_2O$



$ROR' + HX \longrightarrow RX + R'OH$

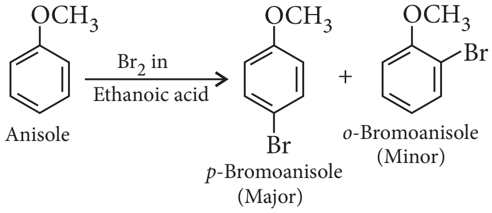
The order of reactivity of hydrogen halides is as follows : HI > HBr > HCl.



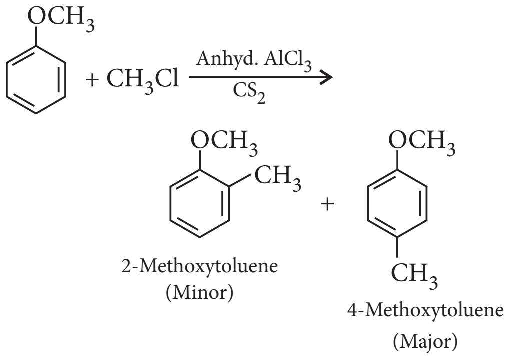
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OCH_3 + HI \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-I + CH_3OH$$

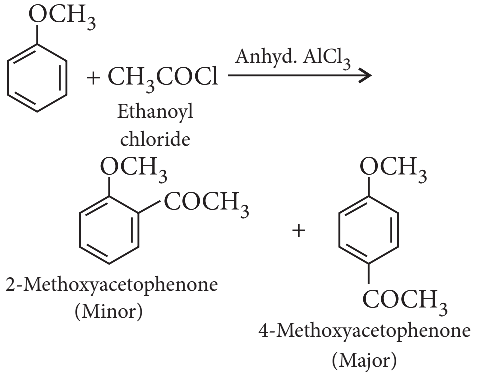
Electrophilic substitution :

- **Halogenation :**

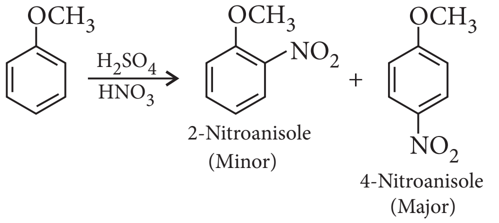


- **Friedel-Crafts reaction :**





- **Nitration :**

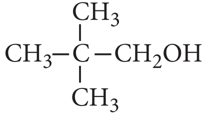


Previous Years' CBSE Board Questions

11.1 Classification

SA II (3 marks)

1. Classify the following as primary, secondary and tertiary alcohols :

(i) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH$

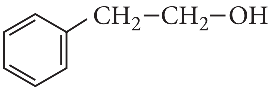
(ii) $H_2C=CH-CH_2OH$

(iii) $CH_3-CH_2-CH_2-OH$ *(AI 2009)*

11.2 Nomenclature

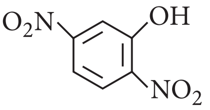
VSA (1 mark)

2. Write the IUPAC name of the given compound.



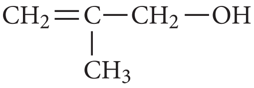
(AI 2016)

3. Write the IUPAC name of the given compound :

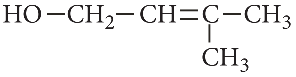


(Delhi 2015)

4. Write the IUPAC name of the given compound :


$CH_2=\underset{CH_3}{C}-CH_2-OH$ *(AI 2015)*

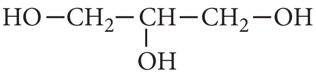
5. Write the IUPAC name of the given compound:


$HO-CH_2-CH=\underset{CH_3}{C}-CH_3$ *(Foreign 2015)*

6. Name the following according to IUPAC system :


$CH_3-\underset{OH}{CH}-CH_2-CH_3$ *(1/2, Delhi 2015C)*

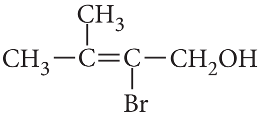
7. Write IUPAC name of the following compound :


$HO-CH_2-\underset{OH}{CH}-CH_2-OH$ *(Foreign 2014)*

8. Draw the structural formula of 2-Methylpropan-2-ol molecule. *(Delhi 2012)*

9. Draw the structure of hex-1-en-3-ol compound. *(Delhi 2012)*

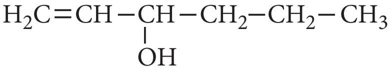
10. Write the IUPAC name of the following :


$CH_3-\overset{CH_3}{C}=\underset{Br}{C}-CH_2OH$ *(AI 2012C)*

11. Give the structure and IUPAC name of the product formed when propanone is reacted with methylmagnesium bromide followed by hydrolysis. *(AI 2012C)*

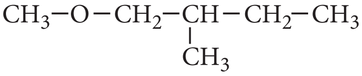
12. Write the structure of the molecule of compound whose IUPAC name is 1-Phenylpropan-2-o1 *(AI 2010)*

13. Give the IUPAC name of the following compound :


$H_2C=CH-\underset{OH}{CH}-CH_2-CH_2-CH_3$ *(AI 2009)*

14. Write the structure of the following compound : 2-Methyl-2-ethoxypentane. *(Delhi 2009C)*

15. Write the IUPAC name of the following compound :


$CH_3-O-CH_2-\underset{CH_3}{CH}-CH_2-CH_3$ *(AI 2008)*

11.3 Structures of Functional Groups

VSA (1 mark)

16. The C—O bond is much shorter in phenol than in ethanol. Give reason. *(Delhi 2012C)*

11.4 Alcohols and Phenols

VSA (1 mark)

17. Write the equation involved in the acetylation of Salicylic acid. *(Delhi 2015)*

18. Give reason for the following :

Phenol is more acidic than ethanol. *(1/3, AI 2015)*

19. Which of the following isomers is more volatile : *o*-nitrophenol or *p*-nitrophenol? *(Delhi 2014)*

20. Write the equation involved in the following reaction :
Reimer –Tiemann reaction *(1/2, AI 2014, 2013)*

21. Write the equation involved in the following reaction :
Kolbe's reaction *(1/2, Delhi 2014C, 2013C)*

22. How is toluene obtained from phenol? *(1/3, Delhi 2013C)*

23. Give a chemical test to distinguish between 2-Pentanol and 3-Pentanol. *(1/2, Delhi 2013C)*

24. Of the two hydroxy organic compounds *R*OH and *R′*OH, the first one is basic and other is acidic in behaviour. How is *R* different from *R′*? *(Delhi 2013C)*

25. How would you obtain ethane-1, 2-diol from ethanol ? *(AI 2013C)*

26. How would you obtain acetophenone from phenol? *(AI 2013C)*

27. *Ortho*-nitrophenol has lower boiling point than *p*-nitrophenol. Why? *(Delhi 2012C)*

28. Give a chemical test to distinguish between Benzoic acid and Phenol. *(Delhi 2012C)*

29. Illustrate the following name reaction
Reimer-Tiemann Reaction. *(Delhi 2012C)*

30. Give a chemical test to distinguish between 2-propanol and 2-methyl-2-propanol. *(Delhi 2012C)*

31. *Ortho*-nitrophenol is more acidic than *ortho*-methoxyphenol. Why? *(1/2, Delhi 2012C)*

32. Explain the following giving one example :
Reimer-Tiemann reaction. *(1/3, Delhi 2011, 2010, AI 2009C)*

33. How would you convert ethanol to ethene? *(AI 2011)*

34. Illustrate the following reaction giving a chemical equation :
Kolbe's reaction *(Delhi 2010)*

35. Give one chemical test to distinguish between the following pairs of compounds.
1-Propanol and 2-Propanol. *(1/2, Delhi 2009C)*

36. Describe the following with an example : Kolbe's reaction *(AI 2009C)*

37. Give reasons for the following :
Propanol has higher boiling point than that of the hydrocarbon butane. *(AI 2009C)*

38. Why do phenols not give the protonation reaction readily? *(1/3, AI 2008)*

39. How would you account for the following :
Phenols are much more acidic than alcohols. *(1/2, Delhi 2007)*

SA I (2 marks)

40. Write the main product(s) in each of the following reactions :

(i) $CH_3{-}CH{=}CH_2 \xrightarrow[\text{(ii) } 3H_2O_2/OH^-]{\text{(i) } B_2H_6}$

(ii) $C_6H_5-OH \xrightarrow[\text{(ii) } CO_2,\ H^+]{\text{(i) aq. NaOH}}$ *(Delhi 2016)*

41. Write the final product(s) in each of the following reactions :

(i) 
$CH_3CH_2-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_3 \xrightarrow{Cu/573\ K}$

(ii) $C_6H_5-OH \xrightarrow[\text{(ii) } H^+]{\text{(i) } CHCl_3 + \text{aq. NaOH}}$

(Delhi 2016)

42. Explain the mechanism of dehydration steps of ethanol :

$$CH_3CH_2OH \xrightarrow[443\ K]{H^+} CH_2{=}CH_2{+}H_2O$$

(Delhi 2015C)

43. How are the following conversions carried out?
(i) Propene to propane-2-ol
(ii) Benzyl chloride to Benzyl alcohol
(2/3, Delhi 2015C)

44. Write the mechanism of acid dehydration of ethanol to yield ethene. *(AI 2015C)*

45. Write the mechanism of the following reaction :

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

(AI 2014, 2/3 Foreign 2014)

46. Name the reagents used in the following reactions :
(i) Bromination of phenol to 2, 4, 6-tribromophenol
(ii) Butan-2-one to Butan-2-o1
(iii) Friedel–Crafts alkylation of anisole
(iv) Oxidation of primary alcohol to carboxylic acid *(Foreign 2014)*

47. Name the different reagents needed to perform the following reactions :
(i) Phenol to Benzene
(ii) Dehydration of propan-2-ol to propene

(iii) Friedel-Crafts alkylation of anisole
(iv) Dehydrogenation of ethanol to ethanal

(Foreign 2014)

48. How are the following conversions carried out?
(i) Propene to Propan-2-ol
(ii) Ethyl chloride to Ethanal *(Delhi 2014C)*

49. Explain the following with an example for each :
(i) Kolbe's reaction
(ii) Reimer-Tiemann reaction *(2/3, AI 2014C)*

50. How will you convert :
(i) Propene to propan-2-ol?
(ii) Phenol to 2,4,6-trinitrophenol?

(Delhi 2013)

51. How will you convert the following :
(i) Propan-2-ol to propanone.
(ii) Phenol to 2,4,6-tribromophenol.

(Delhi 2013)

52. Explain the mechanism of the following reaction :

$$CH_3—CH_2—OH \xrightarrow[443\text{ K}]{H^+} CH_2=CH_2 + H_2O$$

(AI 2013)

53. Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol. *(AI 2012)*

54. Explain the following behaviours :
(i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.
(ii) *Ortho*-nitrophenol is more acidic than *ortho*-methoxyphenol. *(AI 2012)*

55. Give a separate chemical test to distinguish between the following pairs of compounds :
(i) Ethanol and Phenol
(ii) 2-Pentanol and 3-Pentanol *(Delhi 2012C)*

56. How would you obtain the following :
(i) 2-methylpentan-2-ol from 2-methyl-1-pentene
(ii) Acetophenone from phenol *(2/3, AI 2012C)*

57. How would you obtain
(i) Picric acid (2, 4, 6-trinitrophenol) from phenol.
(ii) 2-Methylpropene from 2-methylpropanol?

(Delhi 2011)

58. How would you obtain the following :
(i) Benzoquinone from phenol
(ii) 2-Methylpropan-2-ol from methyl magnesium bromide
(iii) Propan-2-ol from propene? *(AI 2011)*

59. Give the names of the reagents of bringing about the following transformations :
(i) Hexan-1-ol to hexanal
(ii) But-2-ene to ethanol *(Delhi 2011C)*

60. Account for the following :
(i) Propanol has higher boiling point than butane.
(ii) *Ortho*-nitrophenol is more acidic than *ortho*-methoxyphenol. *(2/3, Delhi 2011C)*

61. Account for the following :
(i) The boiling point of ethanol is higher than that of methanol.
(ii) Phenol is a stronger acid than an alcohol.

(Delhi 2011C)

62. Write Reimer–Tiemann reaction giving an example. *(AI 2011C)*

63. How are the following conversions carried out?
(i) Benzyl chloride to benzyl alcohol.
(ii) Methyl magnesium bromide to 2-methylpropan-2-ol. *(Delhi 2010)*

64. Describe the mechanism of hydration of ethene to yield ethanol. *(AI 2010C)*

65. Describe a chemical test each to distinguish between the following pairs :
(i) Ethanol and Phenol
(ii) 1-Propanol and 2-Propanol

(Delhi 2008C, AI 2008)

SA II (3 marks)

66. How do you convert the following?
(i) Phenol to anisole
(ii) Propan-2-ol to 2-methylpropan-2-ol
(iii) Aniline to phenol *(Delhi 2015)*

67. Predict the products of the following reactions :

(i) $CH_3—CH=CH_2 \xrightarrow[\text{(ii) } 3H_2O_2/OH^-]{\text{(i) } B_2H_6} ?$

(ii) $C_6H_5OH \xrightarrow{Br_2(aq)} ?$

(iii) $CH_3CH_2OH \xrightarrow{Cu/573\text{ K}} ?$ *(Foreign 2015)*

68. How are the following conversions carried out?
(i) Benzyl chloride to benzyl alcohol
(ii) Ethyl magnesium chloride to Propan-1-ol
(iii) Propene to Propan-2-ol.
(AI 2015C, 2014C)

69. (a) Write the mechanism of the following reaction :
$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$
(b) Write the equation involved in Reimer–Tiemann reaction. *(Delhi 2014)*

70. (a) Give chemical tests to distinguish between the following pairs of compounds :
(i) Pentan-2-ol and Pentan-3-ol
(ii) Methanol and Phenol
(b) *o*-nitro phenol is more acidic than *o*-methoxy phenol. Explain why.
(AI 2013C)

71. Draw the structure and name of the product formed if the following alcohols are oxidized. Assume that an excess of oxidising agent is used.
(i) $CH_3CH_2CH_2CH_2OH$
(ii) 2-butenol
(iii) 2-methyl-1-propanol *(Delhi 2012)*

72. (a) Describe the mechanism of hydration of ethene to yield ethanol.
(b) Write Kolbe's reaction with an example.
(AI 2011C)

73. Acid catalysed dehydration of *t*-butanol is faster than that of *n*-butanol. Explain. *(AI 2011C)*

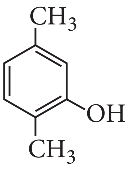
74. How would you convert the following :
(i) Phenol to benzoquinone
(ii) Propanone to 2-methylpropan-2-ol
(iii) Propene to propan-2-o1. *(AI 2010)*

75. (i) Describe the mechanism of acid dehydration of ethanol to yield ethene.
(ii) Describe a chemical test to distinguish between ethanol and phenol.
(Delhi 2010C)

76. Explain the mechanism of the following reactions :
(i) Addition of Grignard's reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis.
(ii) Acid catalysed dehydration of an alcohol forming an alkene.
(iii) Acid catalysed hydration of an alkene forming an alcohol. *(Delhi 2009)*

77. Name the reagents which are used in the following conversions :
(i) A primary alcohol to an aldehyde
(ii) Butan-2-one to butan-2-ol
(iii) Phenol to 2, 4, 6-tribromophenol
(Delhi 2008)

78. (a) Write the IUPAC name of the following :



(b) Give reasons for the following :
(i) Phenol is a stronger acid than alcohol.
(ii) Alcohols are comparatively more soluble in water than the corresponding hydrocarbons. *(AI 2008C)*

11.5 Some Commercially Important Alcohols

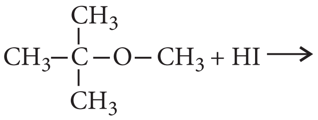
VSA (1 mark)

79. Name a substance that can be used as an antiseptic as well as a disinfectant.
(Delhi 2008)

11.6 Ethers

VSA (1 mark)

80. Write the main product(s) in the following reaction :



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O-CH_3 + HI \longrightarrow$$

(1/3, Delhi 2016, 1/2, AI 2016)

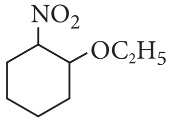
81. How is the following conversion carried out?
Anisole to *p*-bromoanisole *(1/3, Delhi 2015C)*

82. Write the equations involved in the following reaction :
Williamson synthesis
(1/2, AI 2014, 2013, 1/2, Delhi 2014C)

83. Explain the following with an example :
Williamson ether synthesis.
(1/3, AI 2014C, 2009C)

84. Illustrate the following name reaction :
Williamson Synthesis
(1/3, Delhi 2012C, 1/2 Delhi 2010)

85. Write IUPAC name of the following :



(1/3, AI 2012C)

86. Explain the following giving one example :
Friedel Craft's acetylation of anisole.
(1/3, Delhi 2011)

87. Account for the following :
Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. *(1/3, Delhi 2011C, 1/2, Delhi 2008)*

88. Account for the following :
The boiling points of ethers are lower than isomeric alcohols. *(1/3, AI 2011C)*

89. Phenylmethyl ether reacts with HI to give phenol and methyl iodide and not iodobenzene and methyl alcohol. Why? *(Delhi 2010C)*

90. Describe the following :
Unsymmetrical ether *(1/2, AI 2009C)*

91. Why is the preparation of ether by acid dehydration of secondary alcohol not a suitable method? *(AI 2008C)*

92. The boiling points of ethers are much lower than those of the alcohols of comparable molar masses. *(1/3, Delhi 2007)*

SA I (2 marks)

93. Write the mechanism of the following reaction :

$$2CH_3CH_2OH \xrightarrow[413\text{ K}]{\text{Conc. } H_2SO_4} CH_3CH_2-O-CH_2-CH_3$$

(Delhi 2016, 2015, 2013)

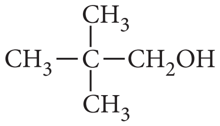
94. Give reasons for the following :
(i) Boiling point of ethanol is higher in comparison to methoxymethane.
(ii) $(CH_3)_3C—O—CH_3$ on reaction with HI gives CH_3OH and $(CH_3)_3C—I$ as the main products and not $(CH_3)_3C—OH$ and CH_3I. *(2/3, AI 2015)*

95. Give mechanism of preparation of ethoxy ethane from ethanol. *(Delhi 2013C)*

96. How is 1-propoxypropane synthesised from propan-1-ol? *(Delhi 2010)*

97. Name the reagents and write the chemical equations for the preparation of the following compounds by Williamson's synthesis :
(i) Ethoxybenzene
(ii) 2-Methyl-2-methoxypropane *(AI 2008)*

Detailed Solutions

1. (i) 
$CH_3-C(CH_3)_2-CH_2OH$

Primary (1°)

(ii) $H_2C{=}CH-CH_2OH$

Primary (1°)

(iii) $CH_3CH_2CH_2OH$

Primary (1°)

2. 2-Phenylethanol

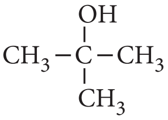
3. 2,5-Dinitrophenol

4. 2-Methylprop-2-en-1-ol

5. 3-methylbut-2-en-1-ol

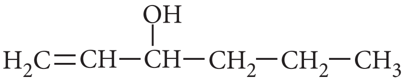
6. Butan-2-ol

7. Propane-1,2,3-triol

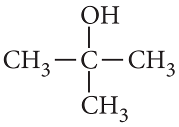
8. 
$CH_3-C(OH)(CH_3)-CH_3$

2-Methylpropan-2-ol

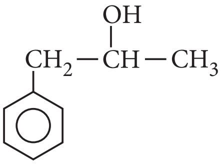
9. Hex-1-en-3-ol


$H_2C{=}CH-CH(OH)-CH_2-CH_2-CH_3$

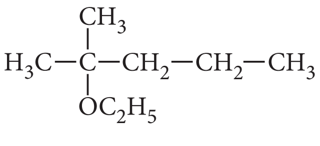
10. 2-Bromo-3-methylbut-2-en-1-ol

11. 
$CH_3-C(OH)(CH_3)-CH_3$

2-Methylpropan-2-ol

12. 

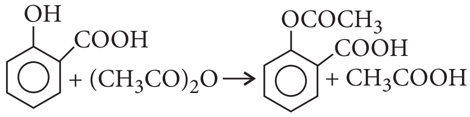
13. Hex-1-en-3-ol

14. 
$H_3C-C(CH_3)(OC_2H_5)-CH_2-CH_2-CH_3$

15. 1-methoxy-2-methylbutane

16. Due to resonance C—O bond acquires some partial double bond character.

So, in phenol C—O bond length is smaller than ethanol.

17. 

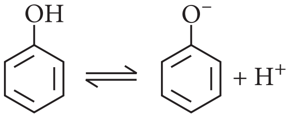
Salicylic acid Aspirin

18. Phenols are more acidic than alcohols. It can be explained on the basis that alcohol on losing H^+ ions form alkoxide ion and phenol forms phenoxide ion.

The greater acidity of phenol is due to the stability of the phenoxide ion which is resonance stabilized as shown below.

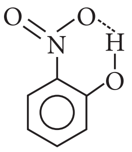
$$R-\ddot{\underset{\cdot\cdot}{O}}-H \rightleftharpoons R-\ddot{\underset{\cdot\cdot}{O}}{:}^- + H^+$$

Alcohol Alkoxide ion

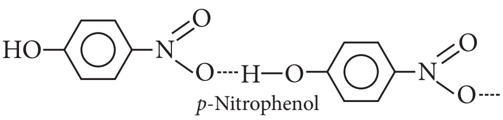


On the other hand, alkoxide ion shows no such resonance stabilisation and is unstable.

19. *o*-Nitrophenol is more steam volatile than *p*-Nitrophenol due to the presence of intramolecular H-bonding. *p*-nitrophenol shows intermolecular H–bonding.



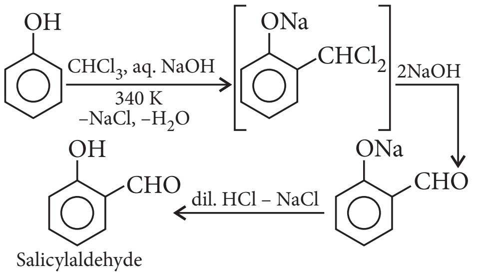
o-Nitrophenol
(intramolecular H-bonding)



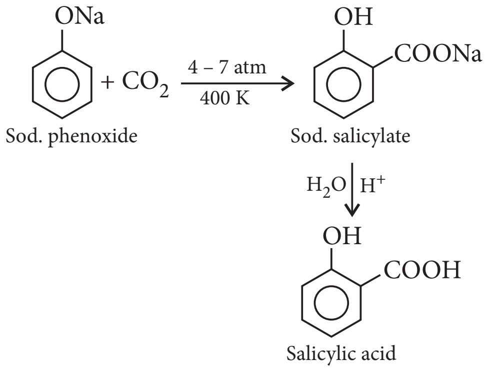
p-Nitrophenol
(intermolecular H-bonding)

That's why *o*-nitrophenol has lower boiling point than *p*-nitrophenol.

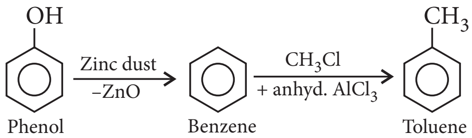
20. Reimer–Tiemann reaction



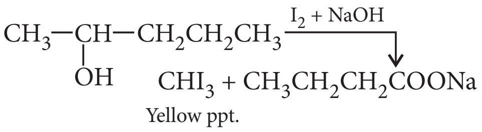
21. Kolbe's reaction : When sodium phenoxide is heated with carbon dioxide under pressure, it gives salicylic acid.



22.



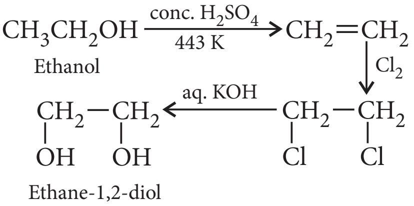
23. On adding I_2 and NaOH, 2-pentanol will give yellow precipitate of iodoform whereas 3-pentanol will not give yellow precipitate.



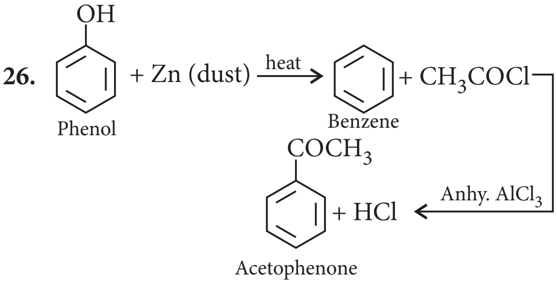
$$CH_3-\underset{OH}{CH}-CH_2CH_2CH_3 \xrightarrow{I_2 + NaOH} \underset{\text{Yellow ppt.}}{CHI_3} + CH_3CH_2CH_2COONa$$

24. *R* is alkyl group and *R′* is aryl group. *R* must be a group having more electron density than H. *i.e.,* having *+I* effect where as *R′* must be having *–I* effect.

25.



26.



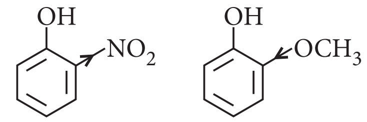
27. *Refer to answer 19.*

28. Benzoic acid gives brisk effervescence of CO_2 on addition of $NaHCO_3$ while phenol does not.

29. *Refer to answer 20.*

30. 2-propanol will give yellow precipitate of iodoform on addition of I_2 and NaOH while 2-methyl-2-propanol will not.

31. As we know that the electron withdrawing groups enhance the acidic character of phenols because they help in the stabilisation of phenoxide ion be dispersing negative charge. Nitro group is an electron withdrawing group whereas methoxy group destabiliser the phenoxide ion by intensifying the negative charge. Thus, *o*-nitrophenol is more acidic than *o*-methoxyphenol.



o-Nitrophenol *o*-Methoxyphenol

32. *Refer to answer 20.*

33. $CH_3CH_2OH \xrightarrow[443\text{ K}]{\text{conc. } H_2SO_4} CH_2{=}CH_2$

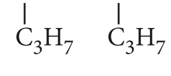
Ethanol Ethene

34. *Refer to answer 21.*

35. On adding I_2 and NaOH 2-Propanol will give yellow ppt. of iodoform, whereas 1-propanol will not give yellow ppt.

36. *Refer to answer 21.*

37. The molecules of butane are held together by weak van der Waals forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.

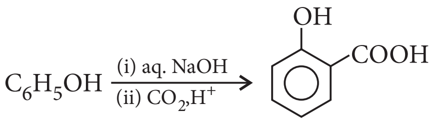


38. Due to electron withdrawing effect of phenyl group the electron density on the oxygen atom of –OH group in phenol is less. Hence, phenols do not undergo protonation.

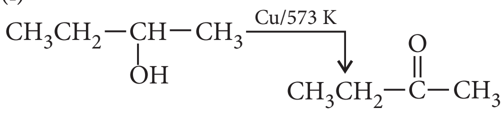
39. *Refer to answer 18.*

40. (i) $$CH_3-CH=CH_2 \xrightarrow[\text{(ii) } 3H_2O_2/OH^-]{\text{(i) } B_2H_6} CH_3CH_2CH_2OH$$

Propanol

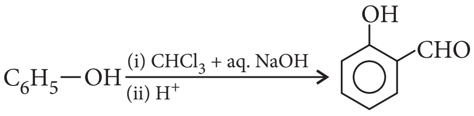
(ii) 

Salicylic acid

41. (i) 

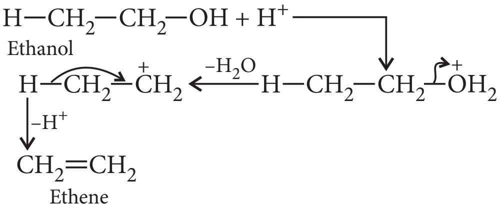
$$CH_3CH_2-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{Cu/573\ K} CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

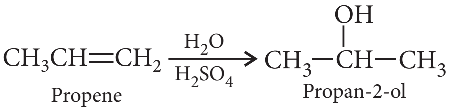
Butan-2-one

(ii) 

Salicylaldehyde

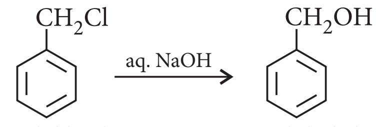
42. Acid catalysed dehydration of alcohols at high temperature takes place with formation of an alkene.



43. (i) 

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

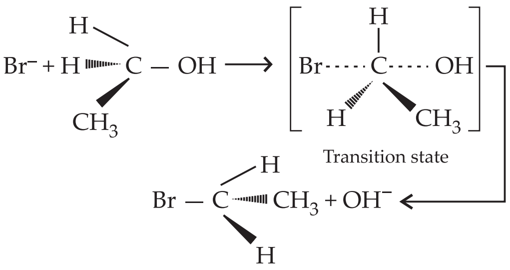
Propene Propan-2-ol

(ii) 

Benzyl chloride Benzyl alcohol

44. *Refer to answer 42.*

45. The reaction proceeds through nucleophilic substitution bimolecular (S_N2) mechanism, as shown below :



Inversion of configuration takes place during the reaction.

46. (i) Bromine water, ($Br_{2(aq)}$)

(ii) Lithium aluminium hydride, ($LiAlH_4$) or H_2/Ni

(iii) Alkyl halide in the presence of anhydrours aluminium chloride, CH_3Cl and $AlCl_3$ (anhy.)

(iv) Acidified potassium permangante, $KMnO_4$, H_3O^+

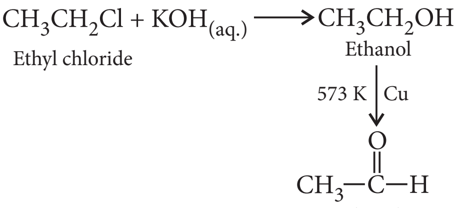
47. (i) Zinc dust

(ii) Concentrated H_2SO_4

(iii) *Refer to answer 46(iii).*

(iv) Cu/573 K

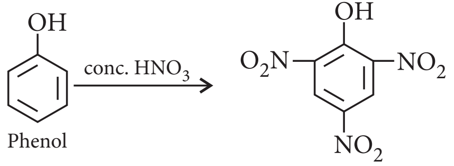
48. (i) *Refer to answer 43(i).*

(ii) 

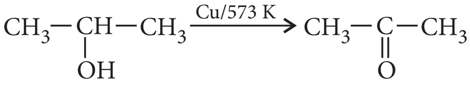
49. (i) *Refer to answer 21.*

(ii) *Refer to answer 20.*

50. (i) *Refer to answer 43(i).*

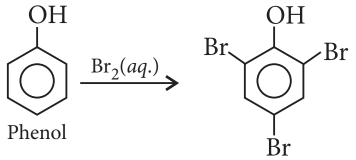
(ii) 

Picric acid (2,4,6-Trinitrophenol)

51. (i) 

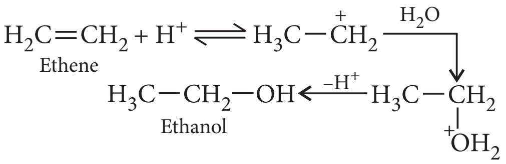
$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{Cu/573\ K} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

Propan-2-ol Propanone

(ii) 

2,4,6-tribromophenol

52. *Refer to answer 42.*

53. 

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + H^+ \rightleftharpoons H_3C-\overset{+}{C}H_2 \xrightarrow{H_2O} H_3C-\underset{\overset{|}{\overset{+}{O}H_2}}{CH_2}$$

$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} \xleftarrow{-H^+} H_3C-\underset{\overset{|}{\overset{+}{O}H_2}}{CH_2}$$

54. (i) The solubility of alcohols in water is due to their ability to form hydrogen bonds with water molecules. Hydrocarbons cannot form such hydrogen bonds, hence they are insoluble in water.

(ii) *Refer to answer 31.*

55. (i) Distinction between ethanol and phenol.

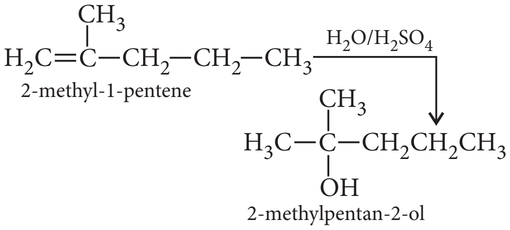
$FeCl_3$ test : Phenol gives a violet colouration with $FeCl_3$ solution while ethanol does not.

$$\underset{\text{Phenol}}{3C_6H_5OH} + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{(C_6H_5O)_3Fe} + 3HCl$$

$$C_2H_5OH + FeCl_3 \longrightarrow \text{No violet colouration.}$$

(ii) *Refer to answer 26.*

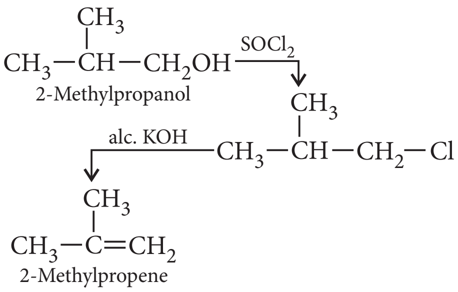
56. (i)



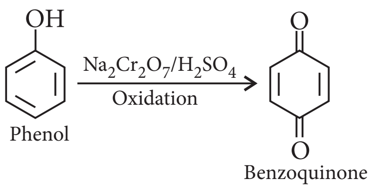
$$\underset{\text{2-methyl-1-pentene}}{H_2C{=}\overset{\overset{CH_3}{|}}{C}-CH_2-CH_2-CH_3} \xrightarrow{H_2O/H_2SO_4} \underset{\text{2-methylpentan-2-ol}}{H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_2CH_3}$$

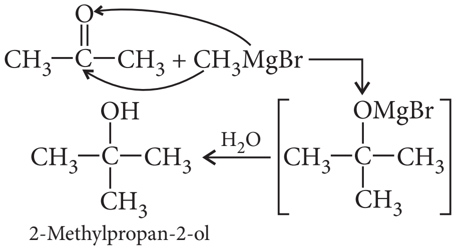
(ii) *Refer to answer 26.*

57. (i) *Refer to answer 51(ii).*

(ii) 

$$\underset{\text{2-Methylpropanol}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2OH} \xrightarrow{SOCl_2} CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-Cl \xrightarrow{\text{alc. KOH}} \underset{\text{2-Methylpropene}}{CH_3-\overset{\overset{CH_3}{|}}{C}{=}CH_2}$$

58. (i) 

(ii) 

$$CH_3-\underset{\overset{\|}{O}}{C}-CH_3 + CH_3MgBr \longrightarrow \left[CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}}-CH_3\right] \xrightarrow{H_2O} \underset{\text{2-Methylpropan-2-ol}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}$$

(iii) *Refer to answer 43(i).*

59. (i) Cu at 573 K

(ii) $$\underset{\text{But-2-ene}}{H_3C-CH{=}CH-CH_3} \xrightarrow{\text{Ozonolysis}}$$

$$2CH_3CHO \xrightarrow{H_2/Ni} \underset{\text{Ethanol}}{2CH_3CH_2OH}$$

60. (i) *Refer to answer 37.*

(ii) *Refer to answer 31.*

61. (i) It is due to higher molecular weight, more surface area, more van der Waal's forces of attraction in C_2H_5OH than CH_3OH.

(ii) *Refer to answer 18.*

62. *Refer to answer 20.*

63. (i) *Refer to answer 43(ii).*

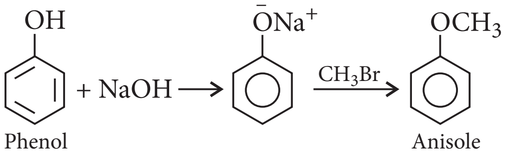
(ii) *Refer to answer 58(i).*

64. *Refer to answer 53.*

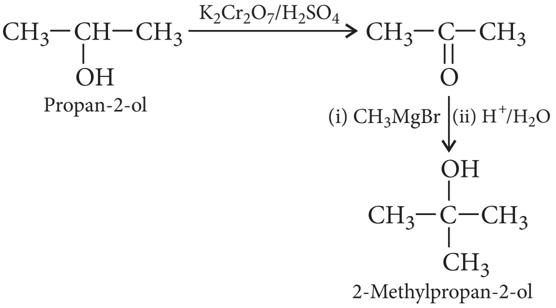
65. (i) *Refer to answer 55(i).*

(ii) *Refer to answer 35.*

66. (i) Phenol to anisole

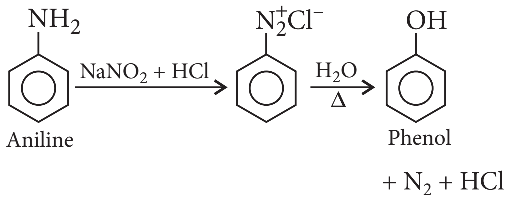


(ii) Propan-2-ol to 2-methylpropan-2-ol



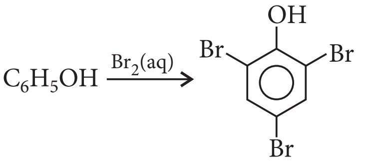
$$\underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{\text{(i) }CH_3MgBr\text{ (ii) }H^+/H_2O} \underset{\text{2-Methylpropan-2-ol}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}$$

(iii) Aniline to phenol



67. (i) $CH_3-CH=CH_2 \xrightarrow[\text{(ii) } 3H_2O_2/OH^-]{\text{(i) } B_2H_6} CH_3CH_2CH_2OH$

(ii) $C_6H_5OH \xrightarrow{Br_2(aq)}$

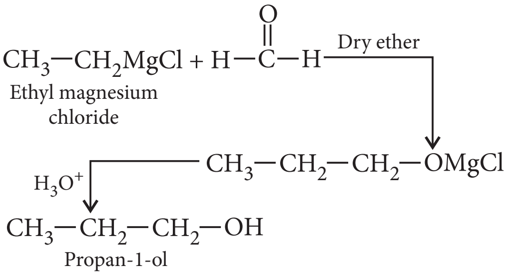


2,4,6-Tribromophenol

(iii) $CH_3CH_2OH \xrightarrow{Cu/573\ K} CH_3CHO$

68. (i) *Refer to answer 43(ii).*

(ii) Ethyl magnesium chloride on addition to formaldehyde followed by hydrolysis gives propan-1-ol.



$$CH_3-CH_2MgCl + H-\overset{\overset{O}{\|}}{C}-H \xrightarrow{\text{Dry ether}} CH_3-CH_2-CH_2-OMgCl \xrightarrow{H_3O^+} CH_3-CH_2-CH_2-OH$$

(iii) *Refer to answer 43(i).*

69. (i) *Refer to answer 46.*

(ii) *Refer to answer 20.*

70. (a) (i) *Refer to answer 23.*

(ii) *Refer to answer 55(i).*

(b) *Refer to answer 31.*

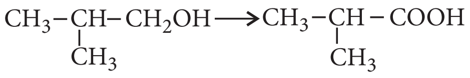
71. (i) $CH_3CH_2CH_2CH_2OH \xrightarrow{\text{Oxidation}} CH_3-CH_2CH_2COOH$

Butanoic acid

(ii) $CH_3-CH=CH-CH_2OH \longrightarrow CH_3CH=CH-COOH$

2-Butenol

But-2-enoic acid



(iii) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2OH \longrightarrow CH_3-\underset{CH_3}{\underset{|}{CH}}-COOH$

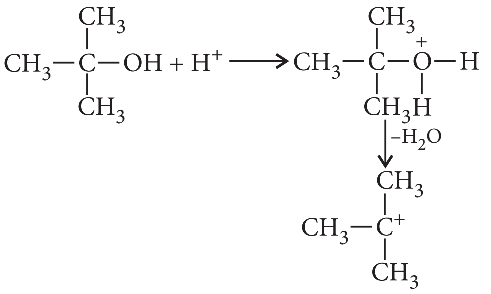
2-methylpropanoic acid

72. (a) *Refer to answer 53.*

(b) *Refer to answer 21.*

73. Acid catalysed dehydration of alcohols follows carbocation mechanism.

Hence, dehydration of *t*-butanol which form 3° carbocation is faster than *n*-butanol which form primary carbocation.



$$CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-OH + H^+ \longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-\underset{H}{\underset{|}{\overset{+}{O}}}-H \xrightarrow{-H_2O} CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C^+}}}$$

3°(more stable)

$$CH_3CH_2CH_2CH_2OH + H^+ \longrightarrow$$

$$CH_3CH_2CH_2CH_2\overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3CH_2CH_2\overset{+}{C}H_2$$

1°(less stable)

74. (i) *Refer to answer 58(i).*

(ii) *Refer to answer 58(ii).*

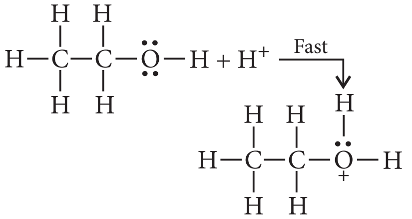
(iii) *Refer to answer 43(i).*

75. (i) Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 453 K.

$$C_2H_5OH \xrightarrow[453\ K]{H_2SO_4} CH_2=CH_2 + H_2O$$

Mechanism : The dehydration of ethanol involves the following steps :

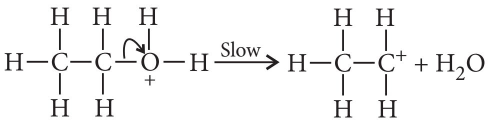
(a) Formation of protonated alcohol.



$$H-\underset{H}{\underset{|}{\overset{\overset{H}{|}}{C}}}-\underset{H}{\underset{|}{\overset{\overset{H}{|}}{C}}}-\ddot{\underset{\cdot\cdot}{O}}-H + H^+ \xrightarrow{\text{Fast}} H-\underset{H}{\underset{|}{\overset{\overset{H}{|}}{C}}}-\underset{H}{\underset{|}{\overset{\overset{H}{|}}{C}}}-\underset{+}{\overset{\overset{H}{|}}{\ddot{O}}}-H$$

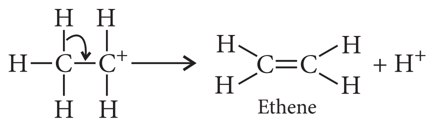
Protonated alcohol

(b) Formation of carbocation.



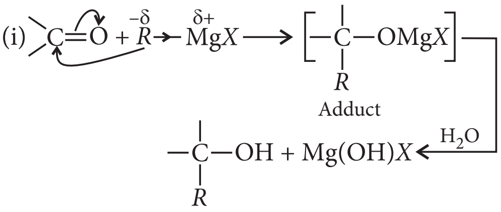
$$H-\underset{H}{\underset{|}{\overset{\overset{H}{|}}{C}}}-\underset{H}{\underset{|}{\overset{\overset{H}{|}}{C}}}-\underset{+}{\overset{\overset{H}{|}}{O}}-H \xrightarrow{\text{Slow}} H-\underset{H}{\underset{|}{\overset{\overset{H}{|}}{C}}}-\underset{H}{\underset{|}{\overset{\overset{H}{|}}{C^+}}} + H_2O$$

(c) Formation of ethene.



(ii) *Refer to answer 55(i).*

76. (i)



(ii) *Refer to answer 42.*

(iii) *Refer to answer 53.*

77. (i) Copper at 573 K

(ii) Sodium borohydride ($NaBH_4$)

(iii) Bromine water ($Br_2(aq)$)

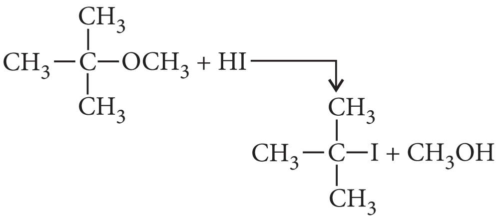
78. (a) 2,5-Dimethylphenol

(b) (i) *Refer to answer 18.*

(ii) *Refer to answer 54(i).*

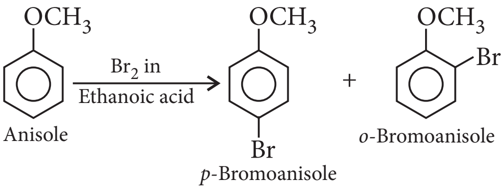
79. **Phenol :** 0.2% solution of phenol is an antiseptic while 2% solution is used as disinfectant.

80.



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OCH_3 + HI \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-I + CH_3OH$$

81.



82. **Williamson ether synthesis :** Alkyl halide when treated with sodium alkoxide gives dialkyl ether.

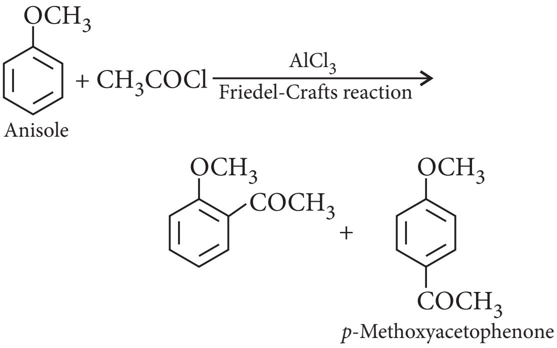
$C_2H_5ONa + C_2H_5Cl \longrightarrow C_2H_5-O-C_2H_5 + NaCl$

83. *Refer to answer 82.*

84. *Refer to answer 82.*

85. 1-Ethoxy-2-nitrocyclohexane.

86. **Reagents :** Acetyl chloride and Lewis acid catalyst.

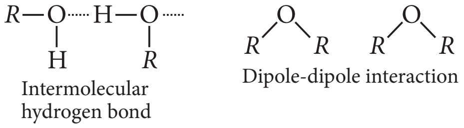


87. Acid dehydration of 2° and 3° alcohols give alkenes rather than ethers.

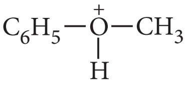
Due to steric hindrance the nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur.

The protonated 2° and 3° alcohols lose water molecules to form stable 2° and 3° carbocations.

88. The boiling points of ethers are much lower than, those of alcohol of comparable molar masses because like alcohols they cannot form intermolecular hydrogen bonds.



89. Protonation of anisole (Phenyl methyl ether) gives methyl phenyl oxonium ion.



$$C_6H_5-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_3$$

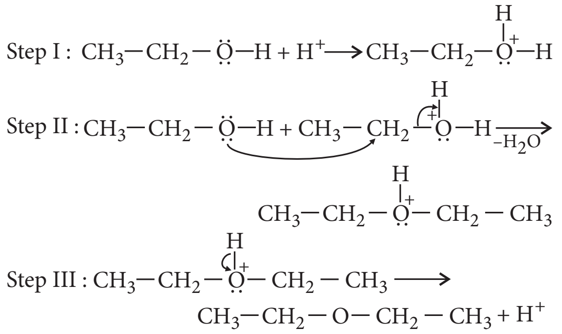
In this ion, the stronger bond is $O-C_6H_5$. Therefore, attack by I^- ion exclusively breaks the weaker $O-CH_3$ bond forming methyl iodide and phenol. The phenol formed does not react further to give aryl halides.

90. **Unsymmetrical ether :** Ethers in which two alkyl groups are different are known as unsymmetrical ether. *e.g.,* $CH_3OCH_2CH_3$ Methoxyethane.

91. *Refer to answer 87.*

92. *Refer to answer 88.*

93. **Mechanism :** The formation of ether is nucleophilic bimolecular reaction.



$$\text{Step I}: CH_3-CH_2-\ddot{O}-H + H^+ \longrightarrow CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-H$$

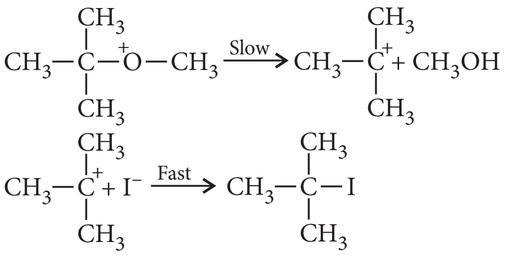
$$\text{Step II}: CH_3-CH_2-\ddot{O}-H + CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-H \xrightarrow[-H_2O]{} CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-CH_2-CH_3$$

$$\text{Step III}: CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-CH_2-CH_3 \longrightarrow CH_3-CH_2-O-CH_2-CH_3 + H^+$$

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

(ii) When one alkyl group is a tertiary group the halide formed is tertiary halide.

In step II the departure of leaving group (CH_3—OH) creates a more stable carbocation (3°) and the reaction follows S_N1 mechanism.



$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{+}{O}-CH_3 \xrightarrow{\text{Slow}} CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C^+}}}} + CH_3OH$$

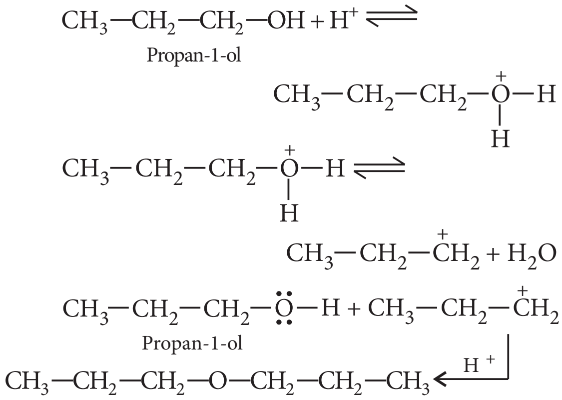
$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C^+}}}} + I^- \xrightarrow{\text{Fast}} CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-I$$

95. *Refer to answer 93.*

96. Propan-1-ol on treatment with conc. H_2SO_4 at 413 K would yield 1-propoxypropane. In this method, the alcohol is continuously added to keep its concentration in excess.

$$2\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-OH} + H_2SO_4 \xrightarrow{413\text{ K}} \underset{\text{1-Propoxypropane}}{CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3}$$

Mechanism :

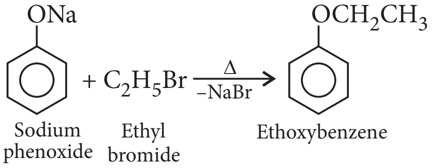


$$\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-OH} + H^+ \rightleftharpoons CH_3-CH_2-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-H$$

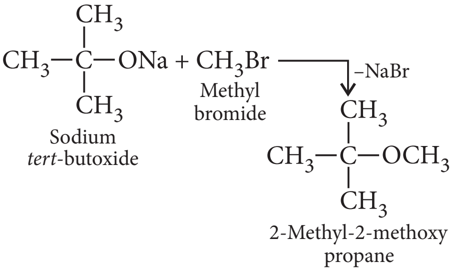
$$CH_3-CH_2-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-H \rightleftharpoons CH_3-CH_2-\overset{+}{C}H_2 + H_2O$$

$$\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H} + CH_3-CH_2-\overset{+}{C}H_2 \xrightarrow{H^+} CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$$

97. (i)



(ii)

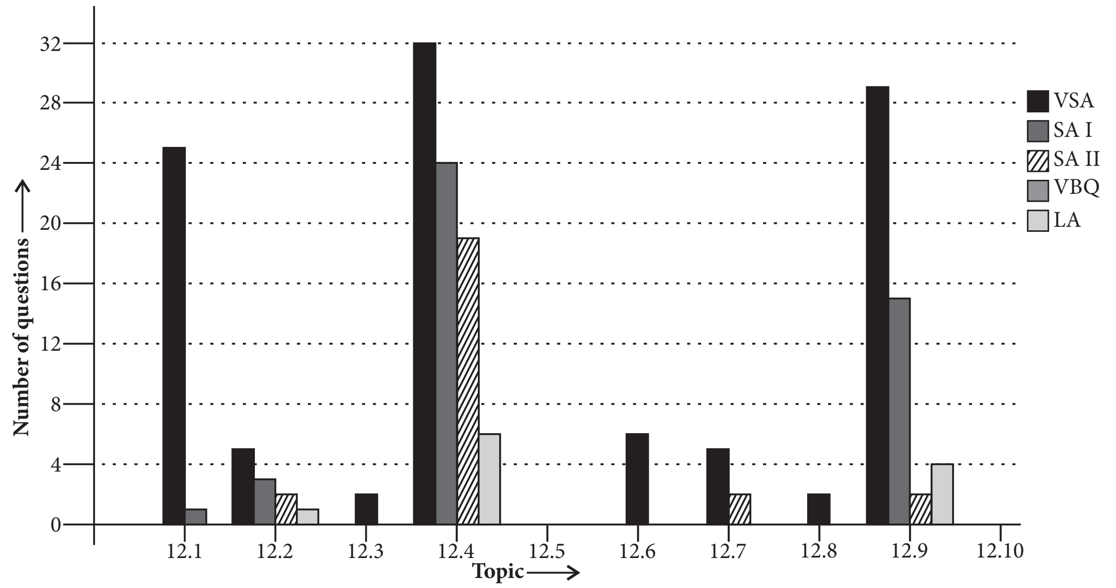


$$\underset{\text{Sodium }tert\text{-butoxide}}{CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-ONa} + \underset{\text{Methyl bromide}}{CH_3Br} \xrightarrow{-NaBr} \underset{\text{2-Methyl-2-methoxy propane}}{CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-OCH_3}$$

12

Aldehydes, Ketones and Carboxylic Acids

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)

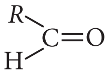


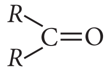
- ⏩ Maximum total weightage is of *Chemical Reactions of Aldehydes and Ketones.*
- ⏩ Maximum VSA type questions were asked from *Chemical Reactions of Aldehydes and Ketones.*
- ⏩ Maximum SA I and SA II type questions were asked from *Chemical Reactions of Aldehydes and Ketones.*

QUICK RECAP

ALDEHYDES AND KETONES

- **General formula :** $C_nH_{2n}O$ having $>C=O$ group.

- **Aldehydes :**  $\overset{R}{\underset{H}{>}}C=O$ where R = H, alkyl or aryl.

- **Ketones :**  $\begin{matrix}R\\R\end{matrix}\!\!>C{=}O$ where R = alkyl or aryl.

Nomenclature : The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending –'*ic*' of acid with aldehyde.

– The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –'*e*' with –'*al*' and –'*one*' respectively.

Structure : The C-atom of carbonyl group is sp^2 hybridised and forms three σ bonds and one π bond with O atom. Carbonyl carbon with three atoms attached to it lie in a same plane with bond angle 120° (trigonal coplanar structure) and π-electron cloud lies above and below of this plane.

Preparation :

- **Oxidation of alcohols :**

$$RCH_2OH + [O] \xrightarrow[H_2SO_4\,(dil.)]{K_2Cr_2O_7\,+} RCHO + H_2O$$

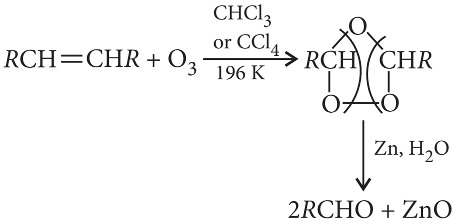
$$R_2CHOH + [O] \xrightarrow[H_2SO_4\,(dil.)]{K_2Cr_2O_7\,+} R-\overset{\overset{\displaystyle O}{\|}}{C}-R + H_2O$$

- **Catalytic dehydrogenation of alcohols :**

$$RCH_2OH \xrightarrow[573\,K]{Cu} RCHO + H_2\uparrow$$

$$R_2CHOH \xrightarrow[573\,K]{Cu} R_2CO + H_2\uparrow$$

- **Reductive ozonolysis of alkenes :**



$$RCH{=}CHR + O_3 \xrightarrow[196\,K]{CHCl_3\text{ or }CCl_4} \text{ozonide} \xrightarrow{Zn,\,H_2O} 2RCHO + ZnO$$

- **Rosenmund reduction :**

$$RCOCl + H_2 \xrightarrow[\text{boiling xylene}]{Pd\text{-}BaSO_4,\,S} RCHO + HCl$$

- **Reduction of nitriles :**

$$RC{\equiv}N \xrightarrow[(ii)\,H_2O]{(i)\,AlH(i\text{-}Bu)_2} RCHO$$

$$RC{\equiv}N \xrightarrow[(ii)\,H_3O^+]{(i)\,R'MgX/\text{dry ether}} RCOR'$$

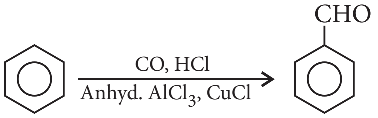
$$RC{\equiv}N \xrightarrow[(ii)\,\text{Ether}\;(iii)\,H_2O]{(i)\,SnCl_2\,+\,HCl} RCHO + NH_4Cl$$

(Stephen reduction)

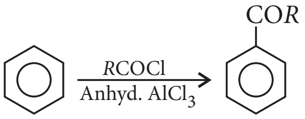
- **From esters :**

$$RCOOR \xrightarrow[(ii)\,H_2O]{(i)\,DIBAL\text{-}H,\,195\,K} RCHO$$

- **Gatterman-Koch reaction :**



- **Friedel-Crafts acylation :**

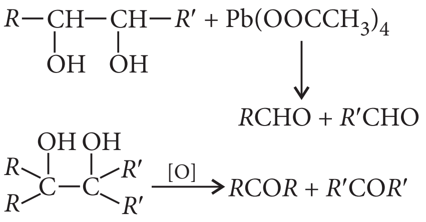


- **From alkynes :**

$$-C{\equiv}C- \xrightarrow[HgSO_4,\,333\,K]{dil.\,H_2SO_4} RCHO \text{ or } RCOR$$

$$-C{\equiv}C- \xrightarrow[H_2O_2/OH^-]{B_2H_6,\,THF} RCHO \text{ or } RCOR$$

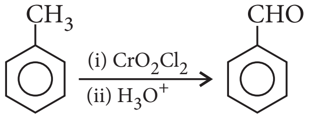
- **Oxidation of 1,2-glycols :**



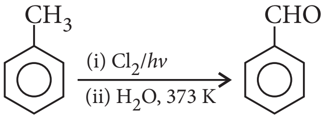
$$R-\underset{OH}{CH}-\underset{OH}{CH}-R' + Pb(OOCCH_3)_4 \longrightarrow RCHO + R'CHO$$

$$R_2\underset{}{\overset{OH}{C}}-\overset{OH}{C}R'_2 \xrightarrow{[O]} RCOR + R'COR'$$

- **Etard reaction :**



- **Side chain chlorination :**



Physical properties :

- **Physical state :** Lower members of aldehydes and ketones (upto C_{10}) are colourless, volatile liquids except formaldehyde which is gas at ordinary temperature.
  - Higher members of aldehydes and ketones are solids with fruity odour.
  - Lower aldehydes have unpleasant odour but ketones possess pleasant smell.
- **Boiling points :** The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses due to weak dipole-dipole interactions.

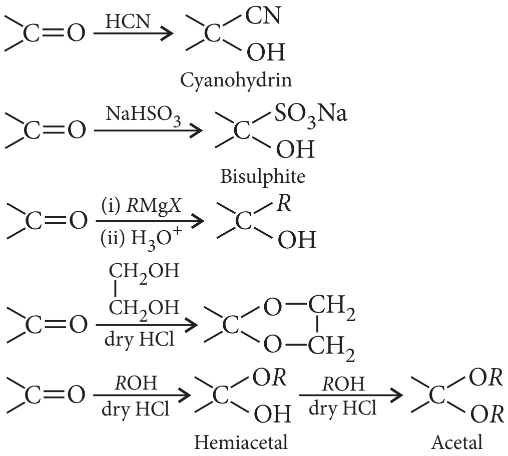
- Their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
- Among isomeric aldehydes and ketones, ketones have slightly higher boiling points due to the presence of two electron releasing alkyl groups which make carbonyl group more polar.

▶ **Solubility :** Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water. However, solubility decreases with increase in molecular weight.

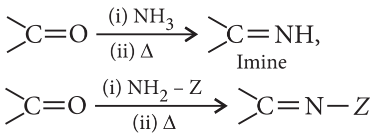
- Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger benzene ring.
- All carbonyl compounds are fairly soluble in organic solvents.

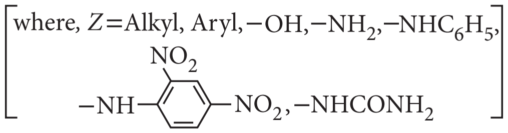
Chemical properties :

▶ **Nucleophilic addition reactions :**

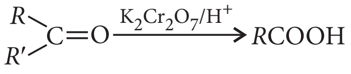


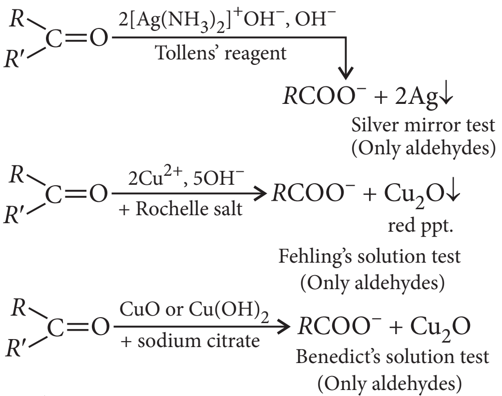
▶ **Nucleophilic addition-elimination reactions :**



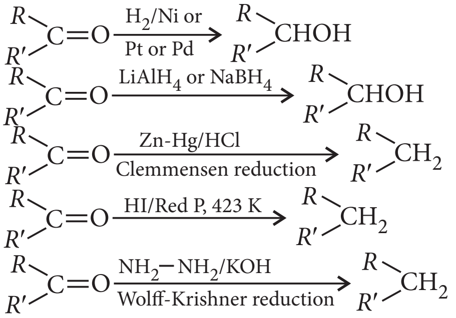


▶ **Oxidation :**





▶ **Reduction :**



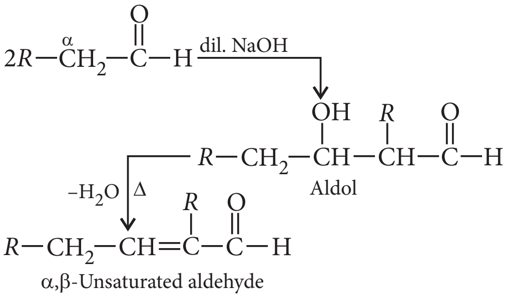
▶ **Haloform reaction :**

$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$

$RCOCH_3 + 3NaOI \longrightarrow RCOONa + \underset{\text{Iodoform (yellow ppt.)}}{CHI_3\downarrow} + 2NaOH$

(Given by compounds having CH_3CO group or $CH_3CH(OH)$ group).

▶ **Aldol condensation :**



(aldehydes and ketones having at least one α-hydrogen)

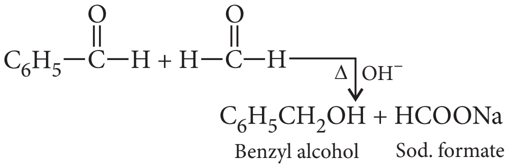
- **Intramolecular aldol condensation :** It takes place in diketones and gives rise to cyclic products.
- **Crossed aldol condensation :** Aldol condensation is carried out between two different aldehydes and/or ketones and if both of them contain α-hydrogen atoms, it gives a mixture of four products.

- **Cannizzaro reaction :**

$$\underset{\text{Formaldehyde}}{HCHO + HCHO} \xrightarrow{\text{conc. KOH}} \underset{\text{Methanol}}{CH_3OH} + \underset{\substack{\text{Potassium}\\ \text{formate}}}{HCOOK}$$

(aldehydes which do not have an α-hydrogen atom)

  - **Crossed Cannizzaro reaction :**



$$C_6H_5-\overset{\overset{O}{\|}}{C}-H + H-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\Delta]{OH^-} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. formate}}{HCOONa}$$

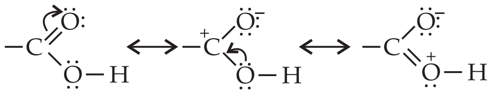
  - **Intramolecular Cannizzaro reaction :** It is given by dialdehydes having no α-hydrogen atoms.

- **Electrophilic substitution reactions :** Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta* directing group.
- **Distinction between aldehydes and ketones :**

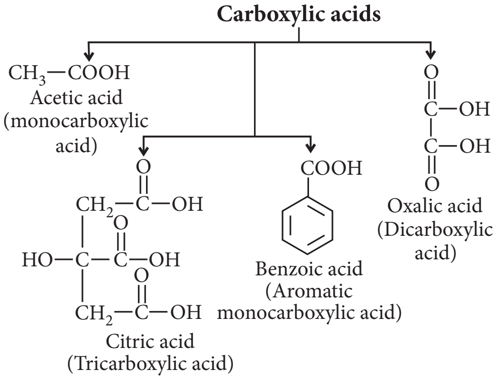
Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Silver mirror	No silver mirror
2,4-Dinitrophenyl-hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.

CARBOXYLIC ACIDS

- **General Formula :** $C_nH_{2n}O_2$ having —COOH group.
  RCOOH where R=H or alkyl or aryl.
- **Nomenclature :** The common names end with the suffix –'*ic acid*' and have been derived from Latin or Greek names of their natural sources.
  - In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending –'*e*' in the name of the corresponding alkane with –'*oic* acid'. In numbering the carbon chain, the carboxylic carbon is numbered one.
- **Structure :** In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.



- **Classification :** They are classified as mono, di, tri and polycarboxylic acids depending upon the number of carboxyl groups present in a molecule.



- Aliphatic monocarboxylic acids and aliphatic esters are known as *functional isomers.* Some higher aliphatic monocarboxylic acids (C_{12}—C_{18}) are known as *fatty acids* because they occur in natural fats as esters of glycerol. *e.g.,* palmitic acid and stearic acid are obtained on hydrolysis of fats.
- **Preparation :**

$$\underset{\substack{\text{Primary}\\ \text{alcohol}}}{RCH_2OH} \xrightarrow[K_2Cr_2O_7 + \text{dil. } H_2SO_4]{\substack{\text{Oxidation, alk. } KMnO_4,\ H_3O^+\\ \text{or } CrO_3\text{–}H_2SO_4}} RCOOH$$

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow[\substack{K_2Cr_2O_7 + \text{dil. } H_2SO_4\\ \text{or Fehling's solution}\\ \text{or Tollens' reagent}}]{\text{Oxidation}} RCOOH$$

$$\underset{\substack{\text{Alkyl}\\ \text{Cyanide}}}{RCN} \xrightarrow[\substack{\text{Mineral acid}\\ HCl,\ H_2SO_4,\text{ etc.}}]{\text{Hydrolysis}} RCOOH$$

$$\begin{tikzcd} \underset{\substack{\text{Alkyl}\\ \text{Cyanide}}}{RCN} \arrow[r, "\text{Hydrolysis}", "\substack{\text{Alkali}\\ NaOH\text{ or }KOH}"'] & RCOONa \arrow[d, "HCl"] \\ & RCOOH \end{tikzcd}$$

$$\underset{\substack{\text{Grignard}\\ \text{reagent}}}{RMgX} \xrightarrow[\text{dry ether}]{CO_2\text{ (dry ice)}} RCOOH$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow[\Delta]{H_3O^+} RCOOH$$

$$\underset{\text{Acyl halide}}{RCOCl} \xrightarrow[\text{or, (i) } OH^-/H_2O \text{ (ii) } H_3O^+]{H_2O} RCOOH$$

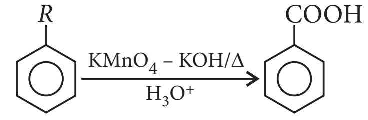
$$\underset{\text{Acid anhydride}}{(RCO)_2O} \xrightarrow{H_2O} RCOOH$$

$$\underset{\text{Ester}}{RCOOR'} \xrightarrow{H_3O^+,\ \Delta} RCOOH$$

$$\underset{\text{Ester}}{RCOOR'} \xrightarrow{NaOH,\ H_3O^+} RCOOH$$

$$\underset{\text{Alkene}}{RCH{=}CHR} \xrightarrow[\Delta,\ H_3O^+]{KMnO_4/OH^-} 2RCOOH$$

$$\underset{\text{Alkyne}}{RC{\equiv}CR} \xrightarrow[\Delta,\ H_3O^+]{KMnO_4/OH^-} RCOOH$$



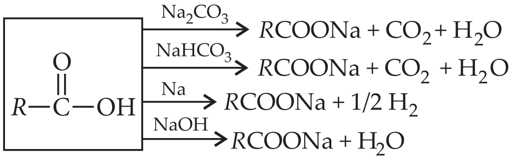
Alkyl benzene

Physical Properties :

- **Physical state :** The lower fatty acids upto C_9 are colourless liquids. The higher ones are colourless waxy solids.
- **Odour :** The first three members have a sharp pungent odour. The middle ones, C_4 to C_9, have an odour of rancid butter. The higher members do not possess any smell.
- **Solubility :** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.
  - The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.
  - Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water.
  - Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.
- **Boiling points :** Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses due to more extensive association of their molecules through intermolecular hydrogen bonding. The H-bonds are not broken completely even in the vapour phase.

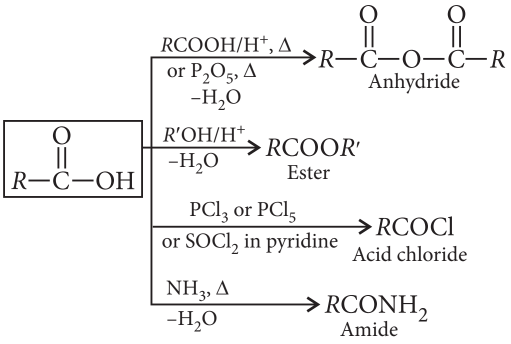
Chemical reactions :

- **Reactions involving cleavage of O—H bond :**



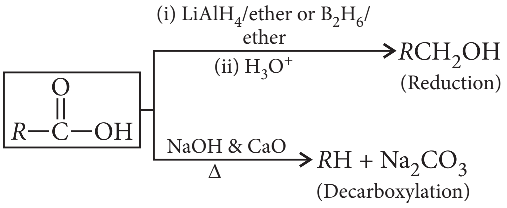
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{Na_2CO_3} RCOONa + CO_2 + H_2O$$
$$\xrightarrow{NaHCO_3} RCOONa + CO_2 + H_2O$$
$$\xrightarrow{Na} RCOONa + 1/2\ H_2$$
$$\xrightarrow{NaOH} RCOONa + H_2O$$

- **Reactions involving cleavage of C—OH bond :**



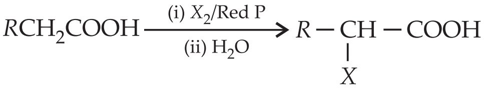
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[\text{or } P_2O_5,\ \Delta \;\; -H_2O]{RCOOH/H^+,\ \Delta} \underset{\text{Anhydride}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R}$$
$$\xrightarrow[-H_2O]{R'OH/H^+} \underset{\text{Ester}}{RCOOR'}$$
$$\xrightarrow[\text{or } SOCl_2 \text{ in pyridine}]{PCl_3 \text{ or } PCl_5} \underset{\text{Acid chloride}}{RCOCl}$$
$$\xrightarrow[-H_2O]{NH_3,\ \Delta} \underset{\text{Amide}}{RCONH_2}$$

- **Reactions involving —COOH group :**



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4/\text{ether or } B_2H_6/\text{ether}} \underset{\text{(Reduction)}}{RCH_2OH}$$
$$\xrightarrow[\Delta]{NaOH\ \&\ CaO} \underset{\text{(Decarboxylation)}}{RH + Na_2CO_3}$$

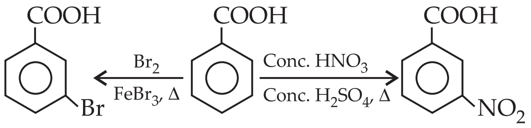
- **Hell-Volhard-Zelinsky reaction :**



$$RCH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red P}} R-\underset{\underset{\displaystyle X}{|}}{CH}-COOH$$

α-Halocarboxylic acid

- **Ring substitution in aromatic acids :** Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a *deactivating* and *meta* directing group.



- **Distinction test between phenol and carboxylic acid :**

Test	Phenol	Carboxylic acid
$NaHCO_3$ test	No reaction	Brisk effervescence of CO_2 gas.
$FeCl_3$ test	Violet colour	Buff coloured ppt.

Previous Years' CBSE Board Questions

12.1 Nomenclature and Structure of Carbonyl Group

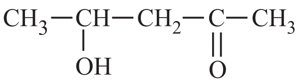
VSA (1 mark)

1. Write the structure of 2-methylbutanal. *(1/5, AI 2015)*

2. Draw the structure of 3-methylpentanal. *(Delhi 2015C)*

3. Write the IUPAC name of the following :
$CH_3—CH_2—CHO$ *(AI 2015C)*

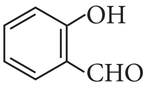
4. Write the IUPAC name of the compound :



$CH_3—\underset{OH}{\underset{|}{C}H}—CH_2—\underset{O}{\underset{||}{C}}—CH_3$ *(Delhi 2014)*

5. Write the structure of 4-chloropentan-2-one. *(AI 2014, 2008, Delhi 2013)*

6. Write the IUPAC name of the following compound :



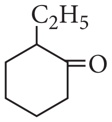
(Foregin 2014)

7. Write the structure of 3-methyl butanal. *(Delhi 2013)*

8. Write the structure of *p*-Methylbenzaldehyde molecule. *(Delhi 2013)*

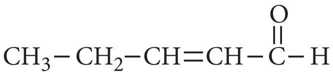
9. Draw the structure of the compound named 4-methylpent-3-en-2-one. *(Delhi 2013C)*

10. Write the IUPAC name of the following :



(AI 2013C)

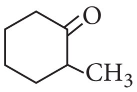
11. Write the IUPAC name of the following :



$CH_3-CH_2-CH=CH-\overset{O}{\overset{||}{C}}-H$ *(AI 2012)*

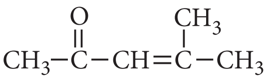
12. Write the IUPAC name of
$Ph—CH=CH—CHO$ *(AI 2012)*

13. Write the IUPAC name of the following :



(AI 2012C)

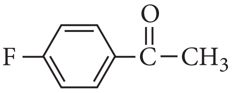
14. Write the IUPAC name of



$CH_3-\overset{O}{\overset{||}{C}}-CH=\overset{CH_3}{\overset{|}{C}}-CH_3$ *(AI 2011C)*

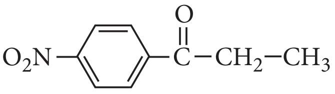
15. Draw the structural formula of 1-phenyl Propan-1-one molecule. *(Delhi 2010)*

16. Write the IUPAC name of the compound :



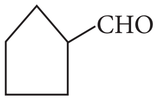
(Delhi 2010C)

17. Write the IUPAC name of the compound :



(Delhi 2010C)

18. Write the IUPAC name of the following compound :

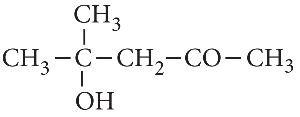


(AI 2010C)

19. Write the structure of 3-oxopentanal. *(Delhi 2009)*

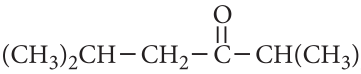
20. Write the structural formula of 1-phenylpentan-1-one. *(AI 2009)*

21. Write the IUPAC name of the following :



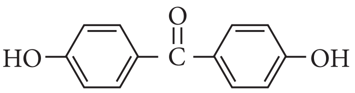
$CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CO-CH_3$ *(Delhi 2009C)*

22. Write the IUPAC name of the following compound



$(CH_3)_2CH-CH_2-\overset{O}{\overset{||}{C}}-CH(CH_3)_2$ *(AI 2009C)*

23. Write the IUPAC name of the following :



(Delhi 2008C)

SA I (2 marks)

24. Draw the structures of the following :
(i) *p*-Methylbenzaldehyde
(ii) 4-Methylpent-3-en-2-one *(2/5, AI 2015C)*

12.2 Preparation of Aldehydes and Ketones

VSA **(1 mark)**

25. Write the product in the following reaction :

$$CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}}$$

(1/5, Delhi 2016)

26. How do you convert the following :
Ethyne to Ethanal *(1/3, Foregin 2015)*

27. How will you obtain the following :
Benzaldehyde from Phenol *(1/5, AI 2013C)*

28. How is following obtained?
Benzaldehyde from toluene. *(1/5, Delhi 2009)*

29. How would you convert :
Ethanol to acetone. *(1/5, AI 2007)*

SA I **(2 marks)**

30. Write the structure of *A* and *B* in the following reaction :

$$CH_3COCl \xrightarrow{H_2,\ Pd-BaSO_4} A \xrightarrow{H_2N-OH} B$$

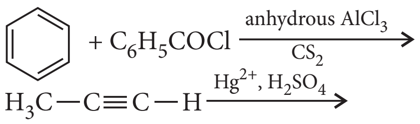
(2/5, AI 2016)

31. Write the equations involved in the following reactions :
(i) Stephen reaction
(ii) Etard reaction *(2/3, Foregin 2015)*

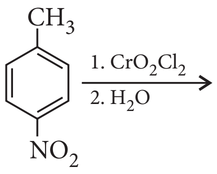
32. An organic compound *A*, having the formula, C_3H_8O, on treatment with copper at 573 K, gives *B*. *B* does not reduce Fehling's solution but gives a yellow precipitate of the compound *C* with I_2/NaOH. Deduce the structure of *A*, *B* and *C*. *(2/5, Delhi 2011C)*

SA II **(3 marks)**

33. Write the structures of the main products of the following reactions :

(i) 

(ii) $H_3C-C\equiv C-H \xrightarrow{Hg^{2+},\ H_2SO_4}$

(iii) 

(Delhi 2012)

34. How will you bring about the following conversions?
(i) Ethanol to acetone
(ii) Benzene to acetophenone
(iii) Benzoic acid to benzaldehyde
(3/5, Delhi 2008)

LA **(5 marks)**

35. Identify *A*, *B*, *C*, *D* and *E* in following sequence of reactions :

$$A \xrightarrow{Cl_2} CHCl_3 \xrightarrow{NaOH} B \xrightarrow{C_6H_5COCl}$$
$$C \xrightarrow{C_6H_6/AlCl_3} D + E$$

(Delhi 2009C)

12.3 Physical Properties

VSA **(1 mark)**

36. Aldehydes and Ketones have lower boiling points than corresponding alcohols. Why?
(AI 2012C)

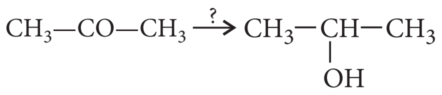
37. How would you account for the following :
The boiling points of aldehydes and ketones are lower than of the corresponding acids.
(1/5, Delhi 2008)

12.4 Chemical Reactions

VSA **(1 mark)**

38. Distinguish between the following :
(i) $C_6H_5-COCH_3$ and C_6H_5-CHO
(1/2, AI 2016, 1/5, AI 2015)

39. Name the reagents used in the following reactions :

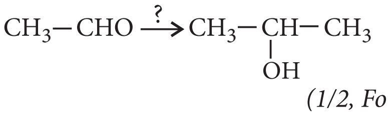
(i) 

$$CH_3-CO-CH_3 \xrightarrow{?} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

(Delhi 2015)

40. Give a simple chemical test to distinguish between the following pair of compounds:
CH_3CH_2CHO and $CH_3CH_2COCH_3$
(1/2 AI 2016, 1/5, AI 2015)

41. Name the reagents used in the following reactions :



$$CH_3-CHO \xrightarrow{?} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

(1/2, Foregin 2015)

42. Draw the structure of the following derivatives :
(i) Propanone oxime
(ii) Semicarbazone of the CH_3CHO
(2/5, AI 2015C)

43. Give chemical tests to distinguish between the following pairs of compunds :
Benzaldehyde and Acetophenone.
(1/5, Delhi 2015C, AI 2012C)

44. Give simple chemical tests to distinguish between the following pairs of compounds :
(i) Benzaldehyde and benzoic acid
(ii) Propanal and propanone.
(1/5, Delhi 2014, AI 2009)

45. Account for the following :
CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. *(Delhi 2014)*

46. Give simple chemical tests to distinguish between the following pair of compounds :
Propanal and Propanone *(1/5, AI 2014)*

47. Give simple chemical tests to distinguish between the following pair of compounds.
Propanal and Butan-2-one *(1/5, Foreign 2014)*

48. Give simple chemical tests to distinguish between the following pair of compounds :
Ethanal and Propanal
(1/5, Delhi 2013, Delhi 2012C, AI 2009)

49. Given reason :
pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compounds. *(1/5, Delhi 2013C)*

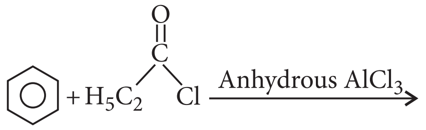
50. Give reason :
Aldehydes are more reactive than ketones towards nucleophilic reagents. *(1/5, AI 2013C)*

51. Arrange the following compounds in an increasing order of their reactivity in nucleophilic addition reactions : ethanal, propanal, propanone, butanone.
(Delhi 2012)

52. Give chemical tests to distinguish between Benzophenone and acetophenone
(1/5, Delhi 2012)

53. Arrange the following compounds in an increasing order of their property as indicated :
Acetaldehyde, acetone, methyl *tert*-butyl ketone (reactivity towards HCN) *(1/5, AI 2012)*

54. Write the structure of the product formed in the following reaction :

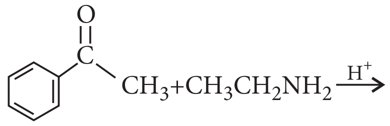


(AI 2012C)

55. Predict the organic product of the following reactions :

(1/2, AI 2011C)

56. Predict the products of the following reactions:



(1/5, AI 2011C)

57. What is Tollens' reagent? Write one usefulness of this reagent. *(AI 2010)*

58. Describe how the following conversions can be brought about :
Cyclohexanol to cyclohexan 1-one
(1/5, AI 2010)

59. Illustrate the following name reaction :
Wolff–Kishner reduction reaction
(1/5, AI 2010)

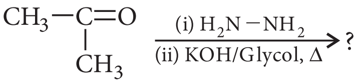
60. Write chemical equations to illustrate the following name bearing reaction :
Cannizzaro's reaction. *(1/5, AI 2009)*

61. State chemical tests to distinguish between the following pairs of compounds :
Propanal and propanone
(1/5, AI 2008, Delhi 2007)

62. Write Cannizzaro reaction giving an example.
(AI 2008C)

SA I (2 marks)

63. Predict the products of the following reactions :

(i) 

$$\underset{\displaystyle CH_3}{CH_3-\overset{|}{C}=O}\ \xrightarrow[\text{(ii) KOH/Glycol, }\Delta]{\text{(i) }H_2N-NH_2}\ ?$$

(ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} ? + ?$

(2/3, Delhi 2015)

64. A compound '*A*' of molecular formula C_2H_3OCl undergoes a series of reactions as shown below. Write the structure of *A*, *B*, *C* and *D* in the following reactions :

$$(C_2H_3OCl)A \xrightarrow{H_2/Pd\text{-}BaSO_4} B \xrightarrow{\text{dil. NaOH}} C \xrightarrow{\text{Heat}} D$$

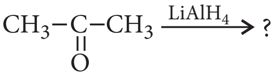
(AI 2015)

65. Describe the following reactions :

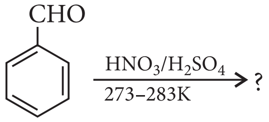
(i) Acetylation

(ii) Aldol condensation *(2/5, Delhi 2015C)*

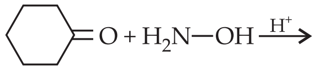
66. Write the main product in the following equations :

(i)


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

(ii)


(2/5, Delhi 2015C)

67. (i)


(ii) $2C_6H_5CHO + \text{conc. NaOH} \longrightarrow$

(2/5, Delhi 2014)

68. Account for the following :

(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.

(ii) There are two $-NH_2$ groups in semicarbazide($H_2NNHCONH_2$). However, only one is involved in the formation of semicarbazone. *(2/5, Foregin 2014)*

69. Write the chemical equation to illustrate each of the following name reactions :

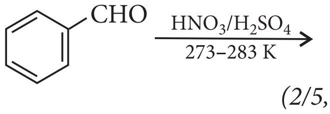
(i) Rosenmund reduction

(ii) Cannizzaro reaction *(2/5, Foregin 2014)*

70. Complete the following reactions :

(i)


$2H-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\text{Conc. KOH}}$

(ii)


(2/5, Delhi 2013)

71. How will you convert the following :

(i) Propanone to Propan-2-ol

(ii) Ethanal to 2-hydroxy propanoic acid

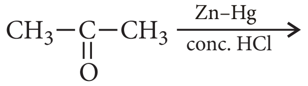
(2/5, AI 2013)

72. Give simple chemical test to distinguish between :

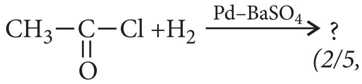
(a) Pentan-2-one and Pentan-3-one.

(b) Ethanal and Propanal *(2/5, AI 2013)*

73. Write the products of the following reactions :

(i)


$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\text{conc. HCl}]{\text{Zn–Hg}}$

(ii)


$CH_3-\underset{\underset{O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd\text{–}BaSO_4} ?$

(2/5, AI 2013)

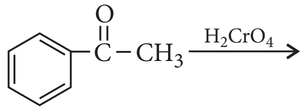
74. Give chemical tests to distinguish between

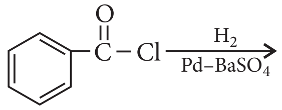
(i) Propanal and propanone

(ii) Benzaldehyde and acetophenone

(2/5, AI 2012)

75. Predict the products of the following reactions :

(i)


(ii)


(2/5, AI 2011C)

76. Explain the mechanism of a nucleophilic attack on the carbonyl group of an aldehyde or a ketone. *(2/5, Delhi 2010)*

77. How will you bring about the following conversions?

(i) Ethanal to but-2-enal

(ii) Propanone to propene *(2/5, Delhi 2010)*

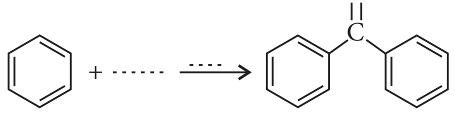
78. Illustrate the following name reactions giving a chemical equations in each case :

(i) Clemmensen reaction

(ii) Cannizzaro's reaction *(AI 2010)*

79. Complete each synthesis by giving the missing material, reagent or products:

(i) $C_6H_5COCl \xrightarrow[Pd\text{–}BaSO_4]{H_2} \cdots\cdots$

(ii)


(2/5, Delhi 2009)

80. How will you bring about the following conversions :

(i) Ethanol to 3-hydroxybutanal

(ii) Benzaldehyde to Benzophenone

(2/5, AI 2009)

81. How would you bring about the following conversions :
(i) Propanone to Propene
(ii) Bromobenzene to 1-phenylethanol
(2/5, AI 2009)

82. How would you account for the following
(i) Aldehydes are more reactive than ketones toward nucleophiles.
(ii) The aldehydes and ketones undergo a number of addition reactions.
(2/5, Delhi 2008)

83. Give chemical tests to distinguish between :
(i) Acetaldehyde and benzaldehyde
(ii) Propanone and propanal. *(2/5, Delhi 2008)*

84. Give a chemical equation for each, illustrate the following processes :
(i) Cannizzaro reaction
(ii) Acetylation *(2/5, AI 2008)*

85. Write the chemical tests to distinguish between the following pairs of compounds :
(i) Acetophenone and Benzophenone
(ii) Ethanal and Propanal *(2/5, AI 2008)*

86. Write one chemical equation for each to illustrate the following reactions :
(i) Rosenmund's reduction
(ii) Cannizzaro reaction *(AI 2007)*

SA II (3 marks)

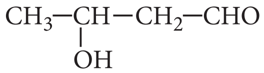
87. (a) Write the chemical equation for the reaction involved in Cannizzaro reaction.
(b) Draw the structure of the semicarbazone of ethanal.
(c) How can you distinguish between propanal and propanone? *(3/5, Delhi 2016)*

88. (a) Write the chemical reaction involved in Wolff-Kishner reduction.
(b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction.

$C_6H_5COCH_3$, CH_3-CHO, CH_3COCH_3

(c) *A* and *B* are two functional isomers of compound C_2H_6O. On heating with NaOH and I_2, isomer *B* forms yellow precipitate of iodoform whereas isomer A does not form any precipitate. Write the formulae of *A* and *B*. *(3/5, AI 2016)*

89. Write the structures of the main products when acetone ($CH_3-CO-CH_3$) reacts with the following reagents :
(i) Zn—Hg/conc. HCl
(ii) $H_2N-NHCONH_2/H^+$
(iii) CH_3MgBr and then H_3O^+ *(3/5, AI 2015)*

90. How will you convert ethanal into the following compounds? Give the chemical equations involved.
(i) CH_3-CH_3
(ii)

$CH_3-\underset{OH}{\underset{|}{C}H}-CH_2-CHO$
(iii) CH_3CH_2OH *(3/5, Delhi 2015C)*

91. Write the chemical equations to illustrate the following name reactions :
(i) Wolff–Kishner reduction
(ii) Aldol condensation
(iii) Cannizzaro reaction *(3/5, Delhi 2014)*

92. Write the products formed when CH_3CHO reacts with the following reagents :
(i) HCN
(ii) H_2N-OH
(iii) CH_3CHO in the presence of dilute NaOH
(3/5, AI 2014)

93. (a) Write the chemical equations to illustrate the following name reactions :
(i) Rosenmund reduction
(ii) Cannizzaro's reaction
(b) Out of $CH_3CH_2-CO-CH_2-CH_3$ and $CH_3CH_2-CH_2-CO-CH_3$, which gives iodoform test? *(3/5, AI 2014)*

94. Write the products formed when ethanal reacts with the following reagents :
(i) CH_3MgBr and then H_3O^+
(ii) Zn-Hg/conc. HCl
(iii) C_6H_5CHO in the presence of dilute NaOH
(3/5, Foregin 2014)

95. How will you bring about the following conversions?
(i) Propanone to propane
(ii) Benzoyl chloride to benzaldehyde
(iii) Ethanal to but-2-enal *(3/5, Delhi 2013)*

96. An organic compound (*A*) which has characteristic odour, on treatment with NaOH forms two compounds (*B*) and (*C*). Compound (*B*) has the molecular formula C_7H_8O which on oxidation with CrO_3 gives back compound (*A*). Compound (*C*) is the sodium salt of the acid. Compound (*C*) when heated with soda lime yields an aromatic hydrocarbon (*D*). Deduce the structures of (*A*), (*B*), (*C*) and (*D*). Write chemical equations for all reactions taking place. *(3/5, AI 2013C, 2012C)*

97. An organic compound with molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1,2-benzenedicarboxylic acid. Identify the compound. *(3/5, AI 2012, 2012C)*

98. An organic compound (*A*) with molecular formula C_8H_8O forms an orange red precipitate with 2, 4-DNP reagent and gives yellow precipitate on heating with I_2 and NaOH. It neither reduces Tollens' reagent nor Fehling's reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (*B*) having molecular formula $C_7H_6O_2$. Identify the compounds (*A*) and (*B*) and explain the reactions involved. *(3/5, Delhi 2012C)*

99. An organic compound with molecular formula $C_5H_{10}O$ does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite and gives a positive iodoform test. On vigorous oxidation, it gives ethanoic acid and propanoic acid. Identify the compound and write all chemical equations for the reactions. *(3/5, AI 2012C)*

100. An organic compound *A* has the molecular formula $C_8H_{16}O_2$. It gets hydrolysed with dilute sulphuric acid and gives a carboxylic acid *B* and an alcohol *C*. Oxidation of *C* with chromic acid also produced *B*. *C* on dehydration reaction gives but-1-ene. Write equations for the reactions involved. *(3/5, AI 2009)*

101. An organic compound contains 69.77% carbon, 11.63% hydrogen and the rest is oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite and gives a positive iodoform test. On vigorous oxidation it gives enthanoic and propanoic acids. Deduce the possible structure of the organic compound. *(3/5, AI 2009, 2008, Delhi 2008)*

LA (5 marks)

102. (a) Give a plausible explanation for each one of the following :

(i) There are two $-NH_2$ groups in semicarbazide. However, only one such group is involved in the formation of semicarbazones

(ii) Cyclohexanone forms cyanohydrins in good yield but 2,4,6-trimethylcyclohexanone does not.

(b) An organic compound with molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1,2-benzene-di-carboxylic acid. Identify the compound. *(Delhi 2012)*

103. (a) Identify *A*, *B* and *C* in the following sequence of reactions :

$$CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } C_2H_5MgCl} A \xrightarrow{\text{conc. } H_2SO_4} B \xrightarrow{\text{HBr + Peroxide}} C$$

(b) Predict the structures of the products formed when benzaldehyde is treated with

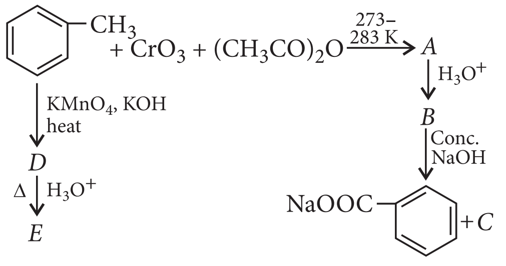
(i) conc. NaOH

(ii) HNO_3/H_2SO_4 (at 273– 383 K)

(Delhi 2011C)

104. A ketone $A(C_4H_8O)$, which undergoes a haloform reaction gives compound *B* on reduction. *B* on heating with sulphuric acid gives a compound C which forms monozonide *D*. *D* on hydrolysis in presence of zinc dust gives only acetaldehyde *E*. Identify *A*, *B*, *C*, *D* and *E*. Write the reactions involved. *(Delhi 2010C)*

105. Identify *A* and *E* in the following series of reactions :



(AI 2010C)

106. (a) Illustrate the following name reactions by giving example :

(i) Cannizzaro's reaction

(ii) Clemmensen reduction

(b) An organic compound A contains 69.77% carbon, 11.63% hydrogen and rest oxygen.

The molecular mass of the compound is 86. It does not reduce Tollens' reagent but form an addition compound with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation it gives enthanoic and propanoic acids. Derive the possible structure of compound *A*. *(Delhi 2009)*

107. An organic compound *A*(C_3H_6O) is resistant to oxidation but forms compound *B*(C_3H_8O) on reduction. *B* reacts with HBr to form the compound *C*. *C* with Mg forms Grignard reagent *D* which reacts with *A* to form a product which on hydrolysis gives *E*. Identify *A* and *E*. *(AI 2008C)*

12.6 Nomenclature and Structure of Carboxyl Group

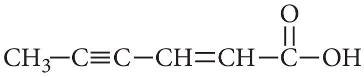
VSA **(1 mark)**

108. Write the IUPAC name of the compound :

$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-COOH$

(Delhi 2014, Delhi 200C)

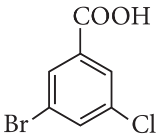
109. Write the IUPAC name of the following :



$CH_3-C\equiv C-CH=CH-\overset{\displaystyle O}{\overset{\|}{C}}-OH$

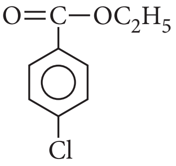
(Delhi 2011C, Delhi 2009)

110. Write the IUPAC name of



(AI 2011C)

111. Write the IUPAC name of the following compound:



(AI 2009)

12.7 Methods of Preparation of Carboxylic Acids

VSA **(1 mark)**

112. Name the reagents used in the following reaction :

$C_6H_5-CH_2-CH_3 \xrightarrow{?} C_6H_5-COO^-K^+$

(1/2, Delhi 2015)

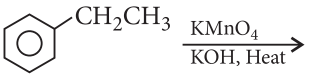
113. How will you convert the following :
Ethanal to 2-hydroxy propanoic acid

(1/5, AI 2013)

114. How will you obtain the following :
Benzoic acid from Aniline

(1/5, AI 2013C)

115. Predict the organic products of the following reaction :



(1/3, AI 2011C)

116. How is the following obtained?
Benzoic acid from ethyl benzene.

(1/5, Delhi 2009)

SA II **(3 marks)**

117. How are the following conversions carried out?
(i) Ethyl cyanide to ethanoic acid.
(ii) Butan-1-ol to butanoic acid.
(iii) Benzoic acid to *m*-bromobenzoic acid.

(Delhi 2012)

118. How are the following conversions carried out :
(i) Ethylcyanide to ethanoic acid
(ii) Butan-1-o1 to butanoic acid
(iii) Methylbenzene to benzoic acid
Write Chemical equations for the involved reactions. *(AI 2010)*

12.8 Physical Properties

VSA **(1 mark)**

119. Arrange the following in the increasing order of their boiling points.
CH_3CHO, CH_3COOH, CH_3CH_2OH

(1/5, AI 2016, 2015)

12.9 Chemical Reactions

VSA **(1 mark)**

120. Write the product in the following reaction :

$CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}}$

(1/5, Delhi 2016)

121. Why carboxylic acid does not give reactions of carbonyl group? *(1/5, AI 2016)*

122. Distinguish between
CH_3COOH and HCOOH *(1/2, AI 2016)*

123. Predict the products of the following reaction :

$CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} ?$ *(1/3, Delhi 2015)*

124. Name the reagent used in the following reaction :

$CH_3—COOH \xrightarrow{?} CH_3—COCl$

(1/2, Foreign 2015)

125. Write the main product in the following equation :

$CH_3—COOH \xrightarrow{PCl_5}$ *(1/5, Delhi 2015C)*

126. Describe the following giving chemical equation :
De-carboxylation reaction

(1/5, Delhi 2015C, 2012, 2008)

127. How will you bring about the following conversion?
Benzoic acid to Benzaldehyde

(1/5, Delhi 2015C)

128. Account for the following :
Carboxylic acids do not give reactions of carbnyl group. *(1/5, AI 2014)*

129. Give simple chemical tests to distinguish between the following pairs of compounds :
Benzoic acid and Phenol

(1/5, AI 2014, Delhi 2013C, 2012, 2012C, 2010, 1/5 AI 2009)

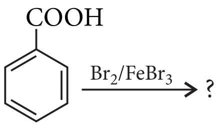
130. Give simple chemical tests to distinguish between the following pairs of compounds:
Benzoic acid and Ethyl benzoate

(1/3, Foregin 2014, 1/5 AI 2009)

131. Write the chemical equation to illustrate the following name reaction :
Hell-Volhard-Zelinsky reaction

(1/5, Foregin 2014, Delhi 2012, AI2010)

132. Write the products of the following reaction :

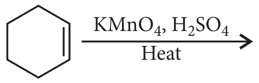


(1/5, AI 2013)

133. Give reasons :
Chloroacetic acid is stronger than acetic acid.

(1/5, Delhi 2013C)

134. Predict the products of the following reaction :



(1/5, AI 2011C)

135. Arrange the following compounds in increasing order of their acid strengths
$(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$ *(Delhi 2008)*

136. How are the following conversions carried out
Acetic acid to methylamine. *(1/5, Delhi 2007)*

137. Write one chemical equation for each to illustrate the following reaction :
Fischer esterification. *(AI 2007)*

138. How would you convert :
Benzoic acid to benzamide. *(1/5, AI 2007)*

SA I (2 marks)

139. (a) Write the product of the following reaction :

$CH_3COOH \xrightarrow{Cl_2/P}$

(b) Give simple chemical tests to distinguish between the following pairs of compounds :
Benzaldehyde and benzoic acid

(2/5, Delhi 2014)

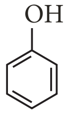
140. Account for the following :

Cl — CH_2COOH is a stronger acid than CH_3COOH. *(2/5, AI 2014)*

141. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Give two reasons. *(2/5, Delhi 2013)*

142. Which acid of each pair shown here would you expect to be stronger?

(i) $F—CH_2—COOH$ or $Cl—CH_2—COOH$

(ii) 

or CH_3COOH *(2/5, AI 2013)*

143. How will you carry out the following conversions?
(i) Acetylene to Acetic acid
(ii) Toluene to *m*-nitrobenzoic acid

(2/5, Delhi 2013C)

144. Give reasons :
(i) Electrophilic substitution in benzoic acid takes place at meta position.
(ii) Carboxylic acids do not give the characteristic reactions of carbonyl group.

(2/5, AI 2013C, Delhi 2012C)

145. Write a suitable chemical equation to complete each of the following transformations :
(i) Butan-1-ol to butanoic acid

(ii) 4-Methylacetophenone to benzene-1,4-dicarboxylic acid *(2/5, AI 2012)*

146. Arrange the following compounds in an increasing order of their property as indicated :

(i) Benzoic acid, 3,4-dinitrobenzoic acid, 4-methoxybenzoic acid (acid strength)

(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$ (acid strength) *(2/5, AI 2012)*

147. Write the mechanism of esterification of carboxylic acids. *(2/5, Delhi 2012C)*

148. Describe how the following conversions can be brought about :

(i) Ethylbenzene to benzoic acid

(ii) Bromobenzene to benzoic acid *(2/5, AI 2010)*

149. Arrange the following compounds in an increasing order of their indicated property :

(i) Benzoic acid, 4-Nitrobenzoic acid, 3, 4-Dinitrobenzoic acid.
4-Methoxybenzoic acid (acid strength)

(ii) $CH_3CH_2CH(Br)COOH$,
$CH_3CH(Br)CH_2COOH$
$(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$
(acid strength) *(2/5, AI 2009)*

150. State reasons for the following :

(i) Monochloroethanoic acid has a higher pK_a value than dichloroethanoic acid.

(ii) Ethanoic acid is a weaker acid than benzoic acid. *(Delhi 2008)*

151. (a) Giving a chemical equation for the following process :
Decarboxylation
(b) State chemical tests to distinguish between the following pairs of compounds :
Phenol and Benzoic acid *(AI 2008)*

152. Give chemical tests to distinguish between the following pairs of compounds :

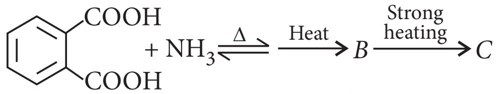
(i) Methyl acetate and ethyl acetate.

(ii) Benzaldehyde and benzoic acid. *(Delhi 2007)*

SA II (3 marks)

153. Two moles of organic compound '*A*' on treatment with a strong base gives two compound '*B*' and '*C*'. Compound '*B*' on dehydrogenation with Cu gives '*A*' while acidification of '*C*' yields carboxylic acid '*D*' with molecular formula of CH_2O_2. Identify the compounds *A*, *B*, *C* and *D* and write all chemical reactions involved. *(3/5, Delhi 2013C)*

154. Identify, *A*, *B* and *C* in the following sequence of reactions :



(3/5, AI 2011C)

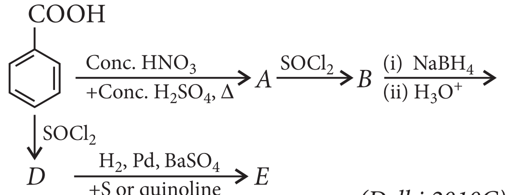
LA (5 marks)

155. Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions :

$$\begin{tikzcd} C_6H_6 \arrow[r, "CH_3COCl", "\text{Anhyd. }AlCl_3"'] & A \arrow[r, "Zn-Hg/conc.HCl"] \arrow[d, "NaOI"] & B \arrow[d, "(ii)\ H_3O^+", "(i)\ KMnO_4-KOH,\ \Delta"'] \\ & D+E & C \end{tikzcd}$$

(Delhi 2016)

156. Identify *A* to *E* in the following reactions :



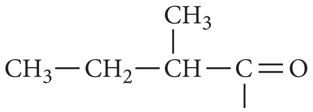
(Delhi 2010C)

157. An organic compound (*A*) on treatment with ethyl alcohol gives a carboxylic acid (*B*) and compound (*C*). Hydrolysis of (*C*) under acidified conditions gives (*B*) and (*D*). Oxidation of (*D*) with $KMnO_4$ also gives (*B*). (*B*) on heating with $Ca(OH)_2$ gives (*E*) having molecular formula C_3H_6O. (E) does not give Tollen's test and does not reduce Fehling's solution but forms a 2, 4-dinitrophenylhydrazone. Identify (*A*), (*B*), (*C*), (*D*) and (*E*). *(AI 2010C)*

158. An organic compound (*A*) on treatment with acetic acid in the presence of sulphuric acid produces an ester (*B*). (*A*) on mild oxidation gives (*C*). (*C*) with 50% KOH followed by acidification with dilute HCl generates (*A*) and (*D*). (*D*) with PCl_5 followed by reaction with ammonia gives (*E*). (*E*) on dehydration produces hydrocyanic acid. Identify the compounds *A*, *B*, *C*, *D* and *E*. *(Delhi 2009C)*

Detailed Solutions

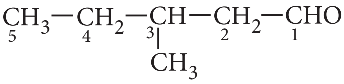
1.



$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle H}{|}}{C}=O$$

2-Methylbutanal

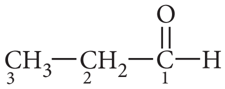
2.



$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{\underset{\displaystyle CH_3}{|}}{\underset{3}{CH}}-\underset{2}{CH_2}-\underset{1}{CHO}$$

3-Methylpentanal

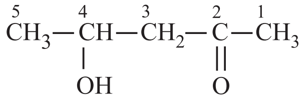
3.



$$\underset{3}{CH_3}-\underset{2}{CH_2}-\underset{1}{\overset{\overset{\displaystyle O}{||}}{C}}-H$$

1-propanal

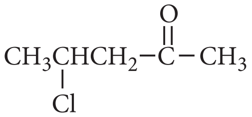
4.



$$\overset{5}{CH_3}-\underset{\underset{\displaystyle OH}{|}}{\overset{4}{CH}}-\overset{3}{CH_2}-\underset{\underset{\displaystyle O}{||}}{\overset{2}{C}}-\overset{1}{CH_3}$$

4-Hydroxypentan-2-one

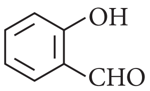
5.



$$CH_3\underset{\underset{\displaystyle Cl}{|}}{C}HCH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$$

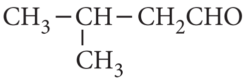
4-Chloropentan-2-one

6.



2-Hydroxybenzaldehyde

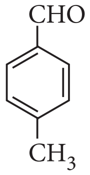
7.



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2CHO$$

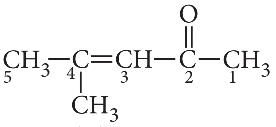
3-methylbutanal

8.



p-methylbenzaldehyde

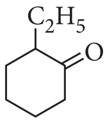
9.



$$\underset{5}{CH_3}-\underset{\underset{\displaystyle CH_3}{|}}{\underset{4}{C}}=\underset{3}{CH}-\underset{2}{\overset{\overset{\displaystyle O}{||}}{C}}-\underset{1}{CH_3}$$

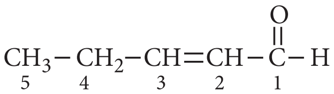
4-methylpent-3-en-2-one

10.



2-Ethylcyclohexanone

11.



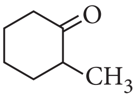
$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{\overset{\overset{\displaystyle O}{||}}{C}}-H$$

Pent-2-enal

12. $Ph-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CHO}$

3-Phenylprop-2-enal

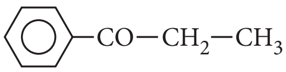
13.



2-methylcyclohexanone

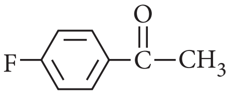
14. *Refer to answer 9.*

15.



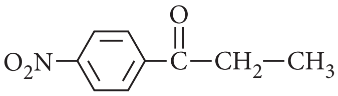
1-phenylpropan-1-one

16.



4-Fluoroacetophenone

17.

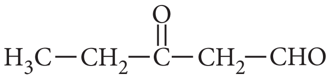


1-(4-nitrophenyl)propan-1-one

18.

Cyclopentanecarbaldehyde

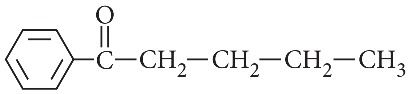
19.



$$H_3C-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH_2-CHO$$

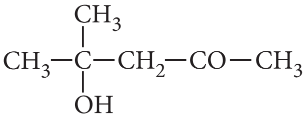
3-oxopentanal

20.



1-phenylpentan-1-one

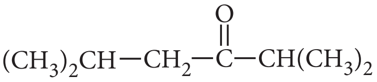
21.



$$CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CO-CH_3$$

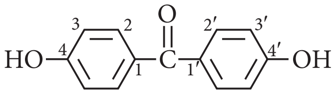
4-Hydroxy-4-Methylpentan-2-one

22.



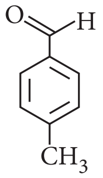
$$(CH_3)_2CH-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH(CH_3)_2$$

2,5-dimethylhexan-3-one

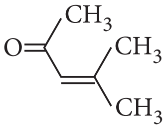
23. 

4,4′-dihydroxybenzophenone

24. (i) *p*-Methylbenzaldehyde :

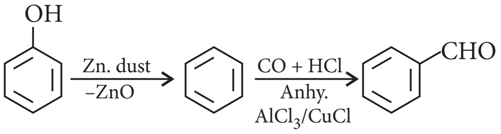


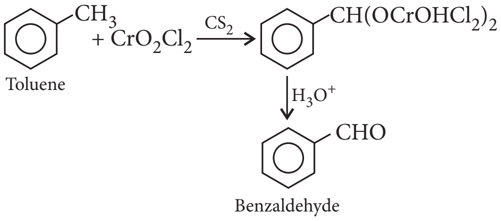
(ii) 4-Methylpent-3-en-2-one :



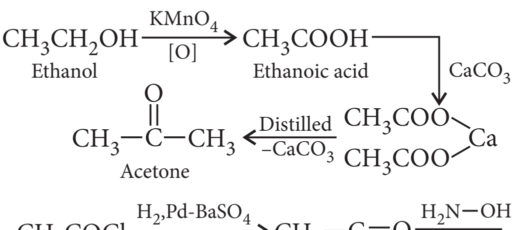
25. $CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} CH_3-CH=CH-CH_2CHO$

26. $\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow[HgSO_4]{\text{dil. } H_2SO_4} \underset{\text{Ethanal}}{CH_3-CHO}$

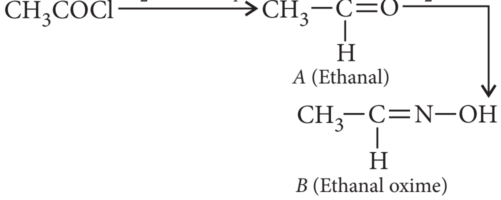
27. 

28. 

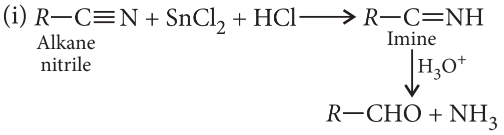
29. Ethanol to acetone :



$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{[O]}]{KMnO_4} \underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{CaCO_3} (CH_3COO)_2Ca \xrightarrow[-CaCO_3]{\text{Distilled}} \underset{\text{Acetone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

30. 

$$CH_3COCl \xrightarrow{H_2,Pd\text{-}BaSO_4} \underset{A\text{ (Ethanal)}}{CH_3-\underset{\underset{\displaystyle H}{|}}{C}=O} \xrightarrow{H_2N-OH} \underset{B\text{ (Ethanal oxime)}}{CH_3-\underset{\underset{\displaystyle H}{|}}{C}=N-OH}$$

31. (i) 

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

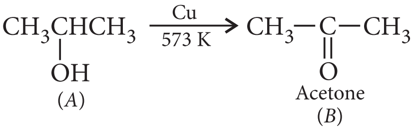
(ii) *Refer to answer 28.*

32. Compound *B* gives positive iodoform test, it means it contains $-COCH_3$ (methyl ketone) group *i.e.*, it is a ketone. Moreover, *B* is obtained by the oxidation of *A*, thus *A* must be a 2° alcohol. (As only 2° alcohol give ketones on oxidation with Cu at 573 K. Hence, the structure of compound *A* is $R\underset{\underset{\displaystyle OH}{|}}{C}HCH_3$

Comparing with the given molecular formula gives $R = CH_3$.

Thus, compound *A* is $CH_3\underset{\underset{\displaystyle OH}{|}}{C}HCH_3$
(Propan-2-ol)

The reaction are as follows :



$$\underset{(A)}{CH_3\underset{\underset{\displaystyle OH}{|}}{C}HCH_3} \xrightarrow[573\text{ K}]{Cu} \underset{\substack{\text{Acetone}\\(B)}}{CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3}$$

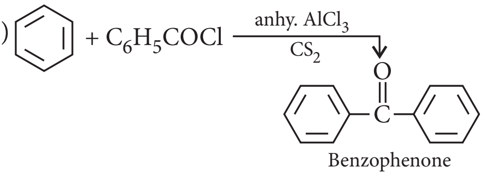
$\text{Acetone} \xrightarrow[\text{solution}]{\text{Fehling}} \text{No reaction}$

$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CH_3COONa + 3NaI + \underset{\substack{\text{Iodoform}\\(C)}}{CHI_3\downarrow} + 3H_2O$$

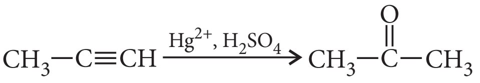
Thus, $A = CH_3CH(OH)CH_3$

$B = CH_3COCH_3$

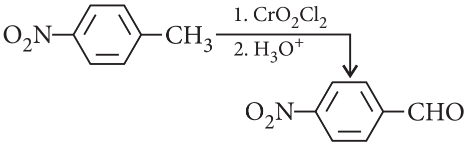
$C = CHI_3$

33. (i) 

Benzophenone

(ii) 

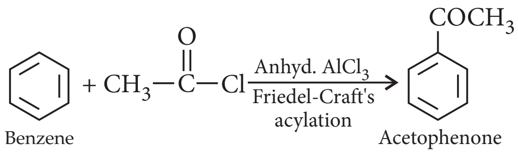
$$CH_3-C\equiv CH \xrightarrow{Hg^{2+}, H_2SO_4} \underset{\text{Propanone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

(iii) 

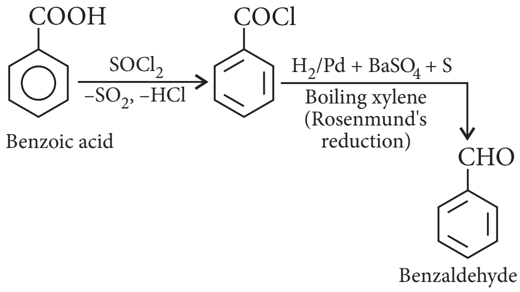
p-Nitrobenzaldehyde

34. (i) *Refer to answer 29.*

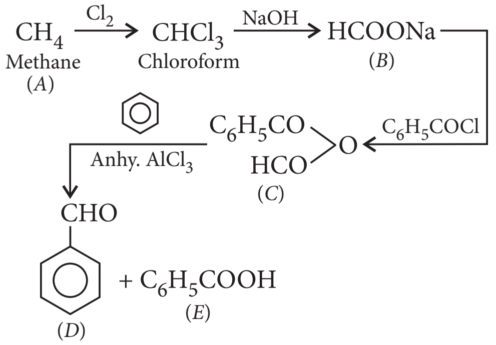
(ii) Benzene to acetophenone.



(iii) Benzoic acid to benzaldehyde.



35.



36. The boiling points of aldehydes and ketones are lower than that of corresponding alcohols and acids due to absence of intermolecular H–bonding in aldehydes and ketones.

37. *Refer to answer 36.*

38. Benzaldehyde and acetophenone can be distinguished by Tollens' test.

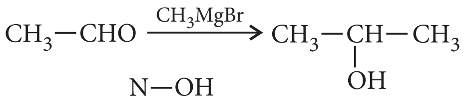
Benzaldehyde will form silver mirror, on treatment with Tollens' reagent whereas acetophenone will not show Tollens' Test.

39. (i) Lithium aluminium hydride ($LiAlH_4$).

40. Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

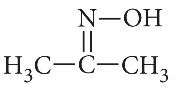
Propanal will form the silver mirror, but propanone does not react.

41.



$$CH_3-CHO \xrightarrow{CH_3MgBr} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

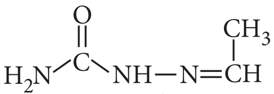
42. (i)



$$H_3C-\overset{\overset{N-OH}{\|}}{C}-CH_3$$

2-propanone oxime

(ii)



Semicarbazone

43. *Refer to answer 38.*

44. (i) Benzaldehyde and benzoic acid can be distinguished by sodium bicarbonate test.

Benzoic acid will give effervescence with $NaHCO_3$ but benzaldehyde will not react.

(ii) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

Propanal will form the silver mirror, but propanone does not react.

45. It is a nucleophilic addition reaction, in which CN^- acts as a nucleophile. CH_3CHO undergoes nucleophilic addition reactions faster than CH_3COCH_3 as in CH_3COCH_3 there are two electron releasing methyl groups attached to the carbonyl carbon that hinders the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group while in CH_3CHO, there is only one methyl group attached to carbonyl carbon.

46. *Refer to answer 45(ii).*

47. Propanal and Butan-2-one can be distinguised by their reactions with tollen's reagent. Propanal will form the silver mirror, but Butan-2-one does not react.

48. Ethanal and propanal can be distinguished by iodoform test.

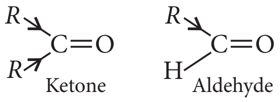
Yellow precipitate of iodoform will be formed from ethanal on heating with iodine and sodium hydroxide solution.

49. In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic medium, OH^- will attack carbonyl group.

Therefore, pH of a reaction should be carefully controlled.

50. Ketones are less reactive than aldehydes towards nucleophilic addition reactions because :

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



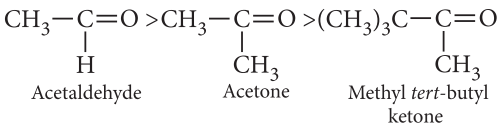
The two bulkier alkyl groups hinder the approach of the nucleophile to the carbonyl carbon. This is called steric factor.

51. Butanone < propanone < propanal < ethanal.

52. Acetophenone and benzophenone can be distinguished by iodoform test.

Acetophenone will give the yellow precipitate of iodoform, but benzophenone will not react.

53.

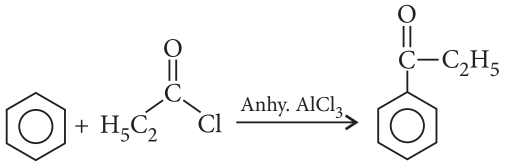


$$\underset{\text{Acetaldehyde}}{CH_3-\underset{\mid}{\overset{}{C}}=O} > \underset{\text{Acetone}}{CH_3-\underset{CH_3}{C}=O} > \underset{\text{Methyl } tert\text{-butyl ketone}}{(CH_3)_3C-\underset{CH_3}{C}=O}$$

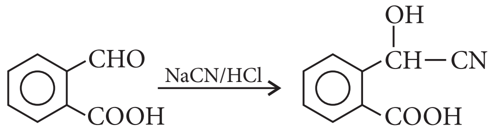
$$CH_3-\underset{H}{C}=O > CH_3-\underset{CH_3}{C}=O > (CH_3)_3C-\underset{CH_3}{C}=O$$

Acetaldehyde Acetone Methyl *tert*-butyl ketone

54.



55.



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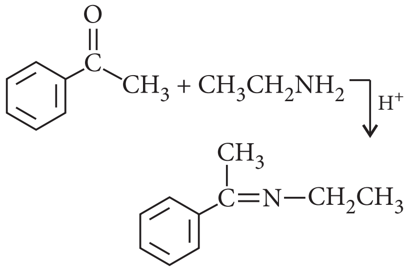
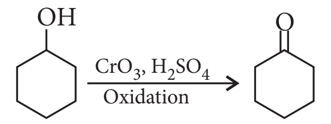


57. Tollens' reagent is an ammoniacal silver nitrate solution.

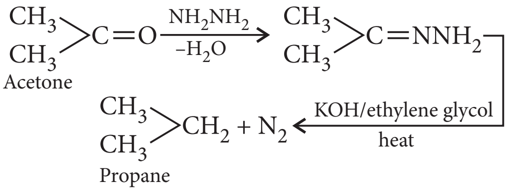
Tollens' reagent is used to test an aldehyde. Both aliphatic and aromatic aldehydes reduce Tollens' reagent and give silver mirror.

58.



Cyclohexanol Cyclohexan-1-one

59. **Wolff-Kishner reduction reaction :** The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with hydrazine followed by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol.



Acetone

Propane

60. **Cannizzaro's reaction :** Aldehydes which do not contain α-H atom undergo disproportionation when heated with concentrated (50 %) NaOH.

$$\underset{\text{Methanal}}{HCHO + HCHO} \xrightarrow{50\%\ NaOH} \underset{\text{Sodium formate}}{HCOONa} + \underset{\text{Methanol}}{CH_3OH}$$

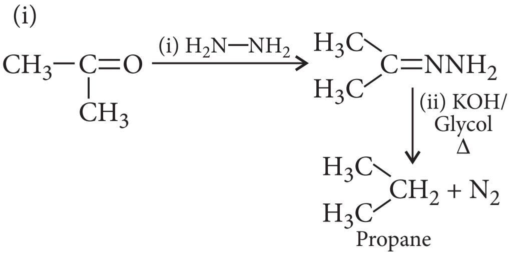
61. Propanal reduces Tollen's reagent into silver mirror while propanone does not gives this test.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]^+} + 2OH^- \longrightarrow$$

$$CH_3CH_2COONH_4 + \underset{\text{Silver mirror}}{2Ag} + H_2O + 2NH_3$$

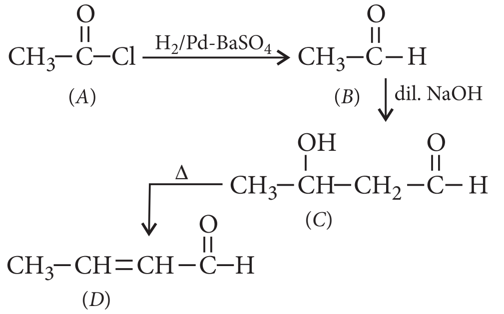
62. *Refer to answer 60.*

63. (i)

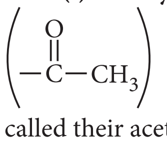


(ii) $C_6H_5—CO—CH_3 \xrightarrow{NaOH/I_2} \underset{\text{Iodoform}}{CHI_3\downarrow} + C_6H_5COONa$

64.

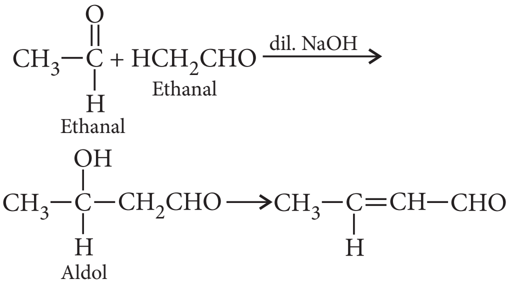


65. **(i)** **Acetylation :** Introduction of acetyl group



$\left(-\overset{O}{\overset{\|}{C}}-CH_3\right)$ in alcohols, phenols or amines is called their acetylation.

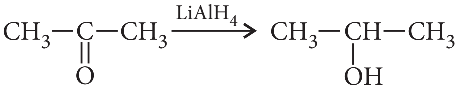
(ii) Aldol condensation : Two molecules of an aldehyde or ketones having at least one α-hydrogen atom condense in the presence of a dilute alkali to give β-hydroxyaldehyde or β-hydroxyketone which upon heating give α,β-unsaturated aldehyde or ketone.



$$\underset{\text{Ethanal}}{CH_3-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}}} + \underset{\text{Ethanal}}{HCH_2CHO} \xrightarrow{\text{dil. NaOH}}$$

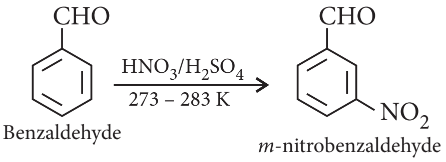
$$\underset{\text{Aldol}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CHO} \longrightarrow CH_3-\underset{\underset{H}{|}}{C}=CH-CHO$$

66. (i)

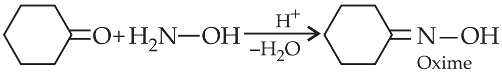


$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

(ii)



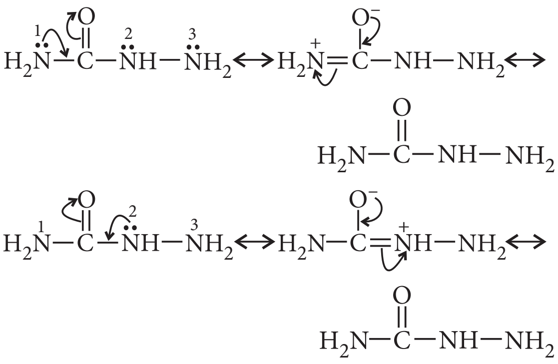
67. (i)



(ii) $2C_6H_5CHO + \text{conc. NaOH} \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$

68. (i) *Refer to answer 45.*

(ii) Semicarbazide has the following resonance structures arising due to the electron withdrawing nature of the O atom.



Lone pairs of N-1 and N-2 are involved in conjugation with $>C=O$ group while that of N-3 is not involved in resonance thus, it is involved in the formation of semicarbazone.

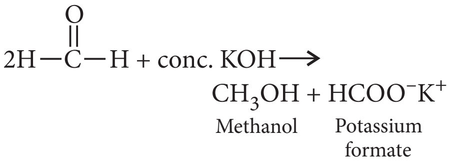
69. (i) **Rosenmund's reaction :**

$$CH_3COCl + H_2 \xrightarrow[\text{Boiling xylene}]{Pd/BaSO_4,\ S} CH_3CHO + HCl$$

Ethanoyl chloride (Acetyl chloride) → Ethanal (Acetaldehyde)

(ii) *Refer to answer 60.*

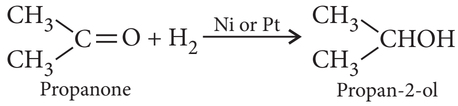
70. (i)



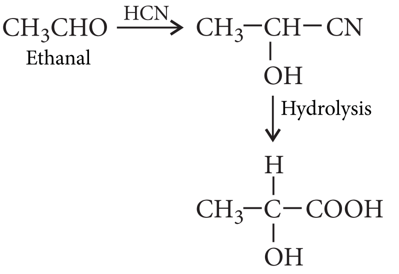
$$2H-\overset{\overset{O}{\|}}{C}-H + \text{conc. KOH} \longrightarrow \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Potassium formate}}{HCOO^-K^+}$$

(ii) *Refer to answer 66(ii).*

71. (i)



(ii)

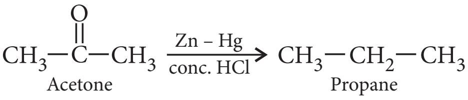


$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{HCN} CH_3-\underset{\underset{OH}{|}}{CH}-CN \xrightarrow{\text{Hydrolysis}} \underset{\text{2-Hydroxypropanoic acid}}{CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-COOH}$$

72.

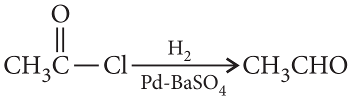
(a) NaOI	$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$ Pentan-3-one ⟶ No reaction	$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_2CH_3$ Pentan-2-one gives iodoform test.
(b) NaOI	CH_3CHO Ethanal gives iodoform test.	$CH_3CH_2CHO \longrightarrow$ Propanal No reaction

73. (i)



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow[\text{conc. HCl}]{Zn-Hg} \underset{\text{Propane}}{CH_3-CH_2-CH_3}$$

(ii)

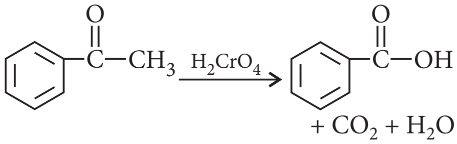


$$CH_3\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[Pd\text{-}BaSO_4]{H_2} CH_3CHO$$

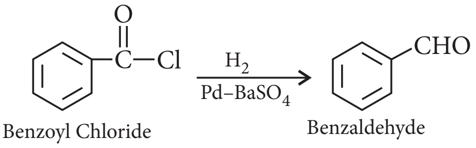
74. (i) *Refer to answer 46.*

(ii) *Refer to answer 38.*

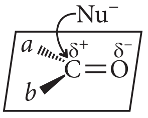
75. (i)



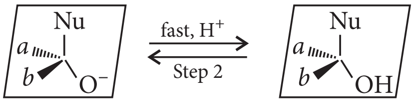
(ii)



76. Mechanism of nucleophilic addition reactions : Nucleophile attacks from the top face :



Planar

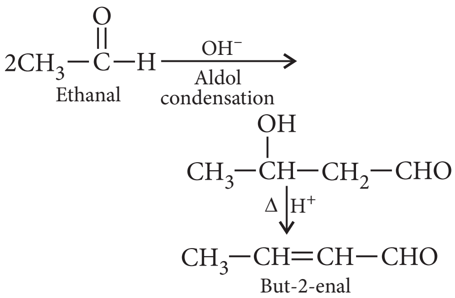


Tetrahedral intermediate Addition product

A nucleophile attacks the electrophilic carbon atom from a direction perpendicular to the plane of sp^2 hybridised orbital of carbonyl carbon. The hybridisation of carbon changes from sp^2 to sp^3 in this process and a tetrahedral alkoxide intermediate is produced.

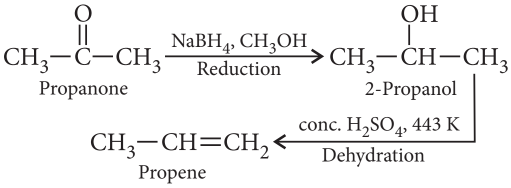
This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of Nu^- and H^+ across the carbon oxygen double bond.

77. (i)



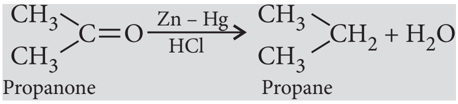
$$\underset{\text{Ethanal}}{2CH_3-\overset{\overset{O}{\|}}{C}-H} \xrightarrow[\text{Aldol condensation}]{OH^-} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[\Delta]{H^+} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$$

(ii) Propanone to propene



$$\underset{\text{Propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow[\text{Reduction}]{NaBH_4,\ CH_3OH} \underset{\text{2-Propanol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_3} \xrightarrow[\text{Dehydration}]{\text{conc. }H_2SO_4,\ 443\text{ K}} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

78. (i) **Clemmensen reduction :** The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid.

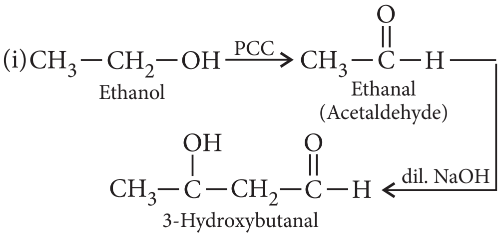


(ii) *Refer to answer 60.*

79. (i) *Refer to answer 75(ii).*

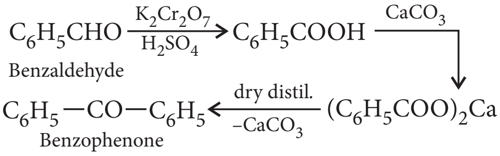
(ii) *Refer to answer 33(i).*

80. (i)



$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow{PCC} \underset{\text{Ethanal (Acetaldehyde)}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \xrightarrow{\text{dil. NaOH}} \underset{\text{3-Hydroxybutanal}}{CH_3-\overset{\overset{OH}{|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-H}$$

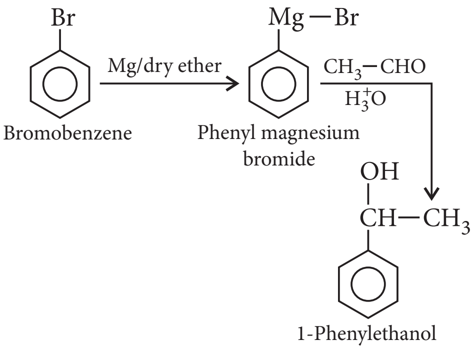
(ii)



$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} C_6H_5COOH \xrightarrow{CaCO_3} (C_6H_5COO)_2Ca \xrightarrow[-CaCO_3]{\text{dry distil.}} \underset{\text{Benzophenone}}{C_6H_5-CO-C_6H_5}$$

81. (i) *Refer to answer 77(ii).*

(ii)



82. (i) *Refer to answer 50.*

(ii) Aldehydes and ketones undergo a number of addition reactions as both possess the carbonyl functional group which reacts with a number of nucleophiles such as HCN, $NaHSO_3$, alcohols, ammonia derivatives and Grignard reagents.

83. (i) Distinction between acetaldehyde and benzaldehyde : Acetaldehyde and benzaldehyde can be distinguish by Fehling solution.

Acetaldehyde gives red coloured precipitate with Fehling solution while benzaldehyde does not.

$$CH_3CHO + \underbrace{2Cu^{2+} + 5\bar{O}H}_{\text{Fehling solution}} \longrightarrow CH_3COO^- + \underset{\text{red ppt.}}{Cu_2O} + 3H_2O$$

(ii) *Refer to answer 46.*

84. (i) *Refer to answer 60.*

(ii) *Refer to answer 65(i).*

85. (i) Refer to answer 52.

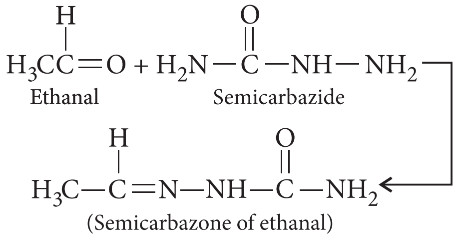
(ii) *Refer to answer 48.*

86. (i) *Refer to answer 69(i).*

(ii) *Refer to answer 60.*

87. (i) *Refer to answer 60.*

(ii)



$$H_3\overset{H}{\overset{|}{C}}C=O + H_2N-\overset{O}{\overset{||}{C}}-NH-NH_2 \longrightarrow H_3C-\overset{H}{\overset{|}{C}}=N-NH-\overset{O}{\overset{||}{C}}-NH_2$$

Ethanal Semicarbazide

(Semicarbazone of ethanal)

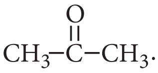
(iii) *Refer to answer 44(ii).*

88. (i) *Refer to answer 59.*

(ii) Increasing order of reactivity towards nucleophilic addition reaction :

$C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$

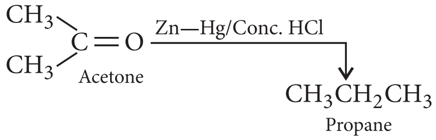
(iii) Formula of compounds A and B = C_3H_6O B forms yellow precipitate of iodoform. Hence, B must contain $—COCH_3$ group. Therefore, compound 'B' must be



$CH_3-\overset{O}{\overset{||}{C}}-CH_3$.

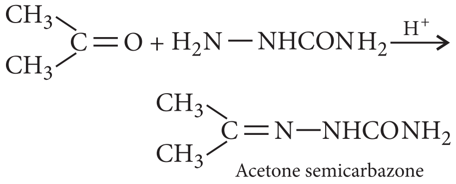
A does not give iodoform test and it is functional isomer of B thus, it may be CH_3CH_2CHO.

89. (i)



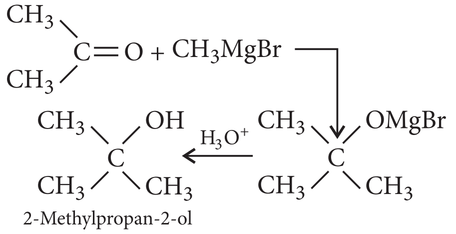
$$\underset{\text{Acetone}}{(CH_3)_2C=O} \xrightarrow{\text{Zn—Hg/Conc. HCl}} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

(ii)



$$(CH_3)_2C=O + H_2N-NHCONH_2 \xrightarrow{H^+} \underset{\text{Acetone semicarbazone}}{(CH_3)_2C=N-NHCONH_2}$$

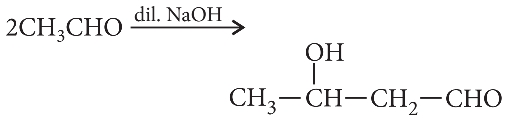
(iii)



$$(CH_3)_2C=O + CH_3MgBr \longrightarrow (CH_3)_3C-OMgBr \xrightarrow{H_3O^+} \underset{\text{2-Methylpropan-2-ol}}{(CH_3)_3C-OH}$$

90. (i) $CH_3CHO \xrightarrow{\text{Zn – Hg/conc. HCl}} CH_3—CH_3$

(ii)



$$2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO$$

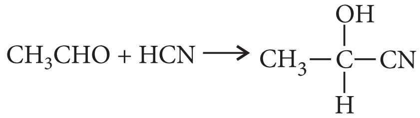
(iii) $CH_3CHO \xrightarrow{H_2/Ni} CH_3—CH_2—OH$

91. (i) *Refer to answer 59.*

(ii) *Refer to answer 65(ii).*

(iii) *Refer to answer 60.*

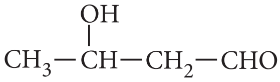
92. (i)



$$CH_3CHO + HCN \longrightarrow CH_3-\overset{OH}{\overset{|}{\underset{H}{\underset{|}{C}}}}-CN$$

(ii) $CH_3CHO + H_2NOH \longrightarrow CH_3—CH=N—OH$

(iii) $2CH_3CHO + \text{dil. NaOH} \longrightarrow$

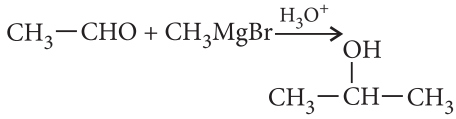


$$CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO$$

93. (a) *Refer to answers 69(i) and 60.*

(b) $CH_3CH_2CH_2—CO—CH_3$ will give iodoform test because it contains acetyl group.

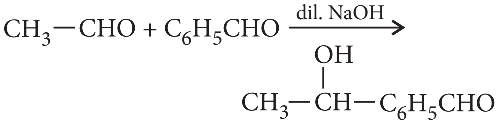
94. (i)



$$CH_3-CHO + CH_3MgBr \xrightarrow{H_3O^+} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3$$

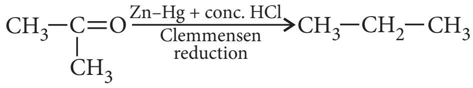
(ii) $CH_3CHO \xrightarrow[\text{Conc. HCl}]{\text{Zn-Hg}} CH_3-CH_3$

(iii)



$$CH_3-CHO + C_6H_5CHO \xrightarrow{\text{dil. NaOH}} CH_3-\overset{OH}{\overset{|}{C}H}-C_6H_5CHO$$

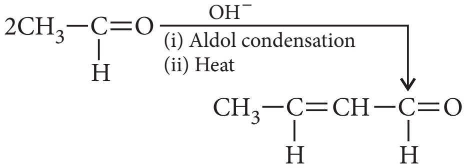
95. (i)



$$CH_3-\underset{CH_3}{\underset{|}{C}}=O \xrightarrow[\text{Clemmensen reduction}]{\text{Zn–Hg + conc. HCl}} CH_3-CH_2-CH_3$$

(ii) *Refer to answer 75(ii).*

(iii)



$$2CH_3-\underset{H}{\underset{|}{C}}=O \xrightarrow[\text{(i) Aldol condensation (ii) Heat}]{OH^-} CH_3-\underset{H}{\underset{|}{C}}=CH-\underset{H}{\underset{|}{C}}=O$$

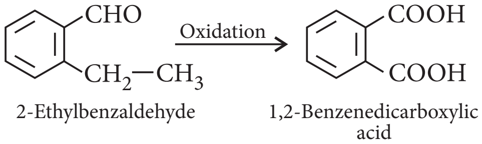
96. Benzaldehyde has a characteristic odour. Reaction of 'A' with NaOH appears to be Cannizzaro reaction which gives 'B' (benzyl alcohol) and 'C' (Sodium salt of benzoic acid). Oxidation of alcohols gives aldehydes. Sodium salt of benzoic acid on heating with soda lime given benzene (D).

$$\underset{'A'}{C_6H_5CHO} \xrightarrow{NaOH} \underset{\substack{'B' \\ (C_7H_8O)}}{C_6H_5CH_2OH} + \underset{\substack{'C' \\ \text{(Sodium salt of} \\ \text{benzoic acid)}}}{C_6H_5COONa}$$

$$\underset{'B'}{C_6H_5CH_2OH} \xrightarrow{CrO_3} \underset{'A'}{C_6H_5CHO}$$

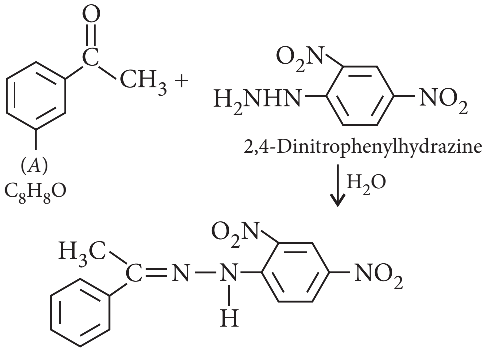
$$\underset{\text{'}C\text{'}}{C_6H_5COONa} \xrightarrow[\Delta]{NaOH/CaO} \underset{\substack{\text{'}D\text{'}\\ \text{(Benzene)}\\ \text{(Aromatic)}}}{C_6H_6} + Na_2CO_3$$

97. The compound forms 2,4-DNP derivative. It shows that it is a carbonyl compound. Further it reduces Tollens' reagent which shows that it contains aldehydic group. It undergoes Cannizzaro reaction indicating that aldehyde group is without any α-hydrogen. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid which shows that there are two carbon residues on benzene ring. Since the molecular formula is $C_9H_{10}O$, it fits into the structure, 2-ethylbenzaldehyde.

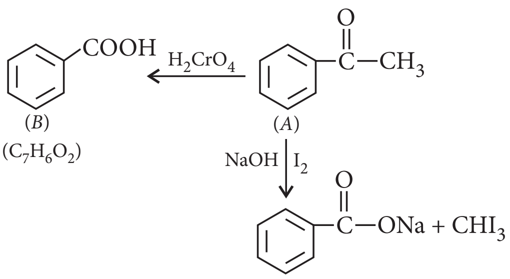


98. (*A*) forms, 2, 4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollen's or Fehling reagent, (*A*) must be a ketone. (*A*) responds to iodoform test.

Compound (*B*), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (*B*) indicates that it should be benzoic acid and compound (*A*) should, therefore, be a mono-substituted aromatic methyl ketone.



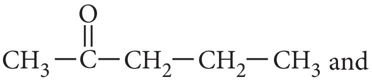
2,4-DNP derivative



99. The given compound does not reduce Tollens' reagent, so it is not an aldehyde but the formation of addition compound with sodium hydrogen sulphite indicates it to be a carbonyl compound. Since this compound gives positive iodoform test, so it should

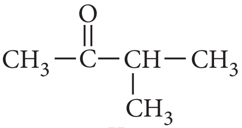
contain  $-\overset{\overset{\Large O}{\|}}{C}-CH_3$ group.

On the basis of this information, two possible structures are written as under :



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3 \text{ and}$$

I

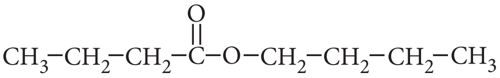


$$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

II

On oxidation, this compound gives ethanoic and propanoic acids which confirm its structure to be I.

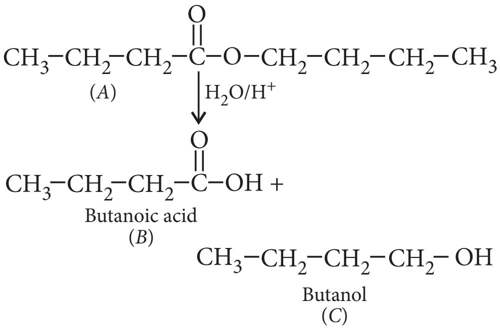
100. Compound '*A*' ($C_8H_{16}O_2$) on hydrolysis gives an acid '*B*' and an alcohol '*C*'. It shows that '*A*' is an ester. Since the oxidation of alcohol '*C*' also gives the acid '*B*' indicates that '*B*' and '*C*' both contain same number of carbon atoms, *i.e,* four carbon atoms each and same arrangement of atoms. Formation of but-1-ene on dehydration of '*C*' indicates it to be butan-1-ol, so the possible structure for '*A*' could be

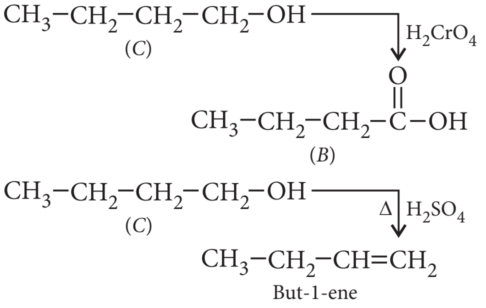


$$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-CH_2-CH_3$$

Butyl butanoate

The various reactions involved are written as follows :





$$\underset{(C)}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow{H_2CrO_4} \underset{(B)}{CH_3-CH_2-CH_2-\overset{\overset{O}{||}}{C}-OH}$$

$$\underset{(C)}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow[\Delta]{H_2SO_4} \underset{\text{But-1-ene}}{CH_3-CH_2-CH=CH_2}$$

101. Calculation of the empirical formula of the compound :

Element	Percentage	Atomic mass	Relative numbers of atoms	Simple molar ratio
C	69.77	12	$\frac{69.77}{12} = 5.814$	5
H	11.63	1	$\frac{11.63}{1} = 11.63$	10
O	18.6	16	$\frac{18.6}{16} = 1.163$	1

So, the empirical formula is $C_5H_{10}O$

Empirical formula mass

$$= (5 \times 12) + (10 \times 1) + (1 \times 16) = 86$$

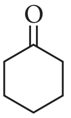
Given that molecular mass of the compound = 86

Hence, the molecular formula of the compound is $C_5H_{10}O$

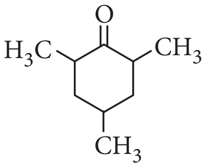
Refer to answer 99.

102. (a) (i) *Refer to answer 68(ii).*

(ii) Formation of cyanohydrin involves the nucleophilic attack of cyanide ions (CN^-) at the carbonyl carbon. In cyclohexanone, reaction proceeds but in 2,4,6-trimethylcyclohexanone, the methyl groups cause steric hindrance and yields are poor.



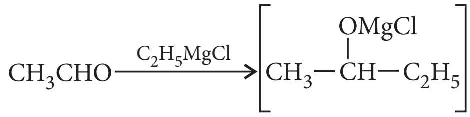
Cyclohexanone

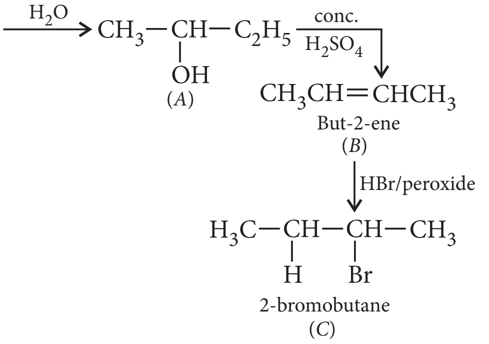


2,4,6-Trimethylcyclohexanone

(b) *Refer to answer 97.*

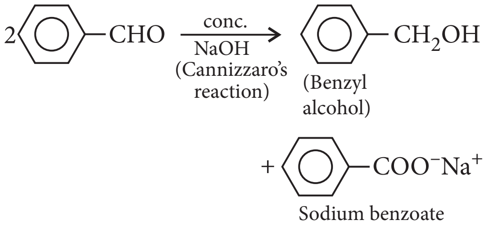
103. (a)





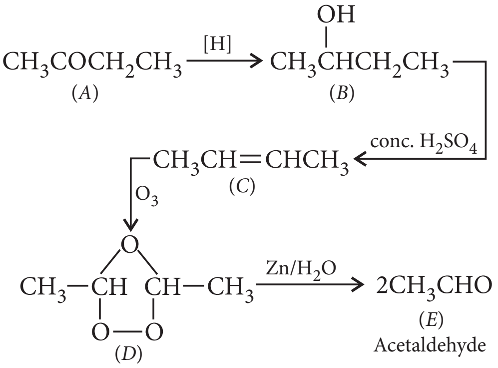
$$CH_3CHO \xrightarrow{C_2H_5MgCl} \left[CH_3-\overset{OMgCl}{\overset{|}{C}H}-C_2H_5\right] \xrightarrow{H_2O} \underset{(A)}{CH_3-\underset{OH}{\underset{|}{C}H}-C_2H_5} \xrightarrow{\text{conc. } H_2SO_4} \underset{\substack{\text{But-2-ene}\\(B)}}{CH_3CH=CHCH_3} \xrightarrow{HBr/\text{peroxide}} \underset{\substack{\text{2-bromobutane}\\(C)}}{H_3C-\underset{H}{\underset{|}{C}H}-\underset{Br}{\underset{|}{C}H}-CH_3}$$

(b) (i)



(ii) *Refer to answer 70(ii).*

104. The equations involved are :

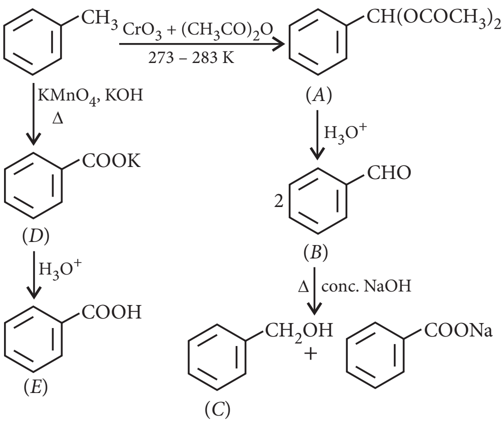


$$\underset{(A)}{CH_3COCH_2CH_3} \xrightarrow{[H]} \underset{(B)}{CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_3} \xrightarrow{\text{conc. } H_2SO_4} \underset{(C)}{CH_3CH=CHCH_3} \xrightarrow{O_3} (D) \xrightarrow{Zn/H_2O} \underset{\substack{(E)\\\text{Acetaldehyde}}}{2CH_3CHO}$$

A gives haloform reaction as :

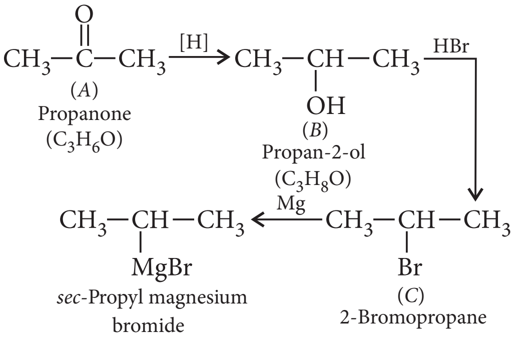
$$CH_3COCH_2CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + C_2H_5COONa + 3NaI + 2H_2O$$

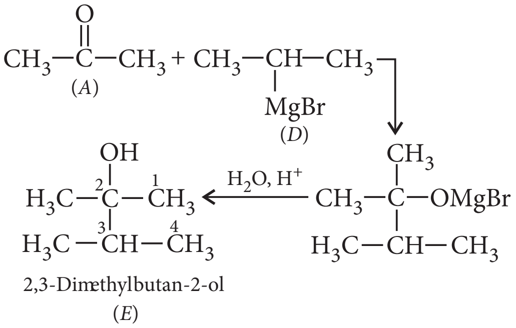
105.



106. (a) (i) *Refer to answer 60.*
(ii) *Refer to answer 78(i).*
(b) *Refer to answer 101.*

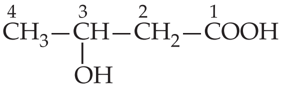
107. Ketones are oxidised under vigrous conditions.





Therefore, (*A*) : Propanone
(*B*) : Propan-2-ol
(*C*) : 2-Bromopropane
(*D*) : *sec*-Propyl magnesium bromide
(*E*) : 2,3-Dimethylbutan-2-ol

108.



$$\overset{4}{C}H_3-\underset{OH}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}OOH$$

3-Hydroxybutan-1-oic acid

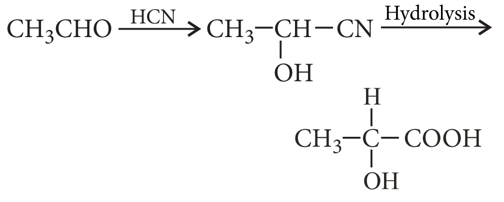
109. Hex-2-en-4yn-oic acid

110. 3-Bromo-5-chloro Benzoic acid

111. Ethyl-4-chlorobenzoate

112. Alkaline potassium permanganate ($KMnO_4$, KOH)

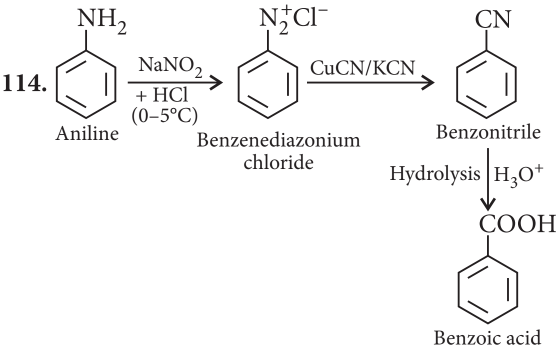
113.



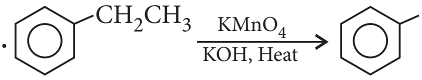
$$CH_3CHO \xrightarrow{HCN} CH_3-\underset{OH}{CH}-CN \xrightarrow{Hydrolysis} CH_3-\underset{OH}{\overset{H}{C}}-COOH$$

2- Hydroxypropanoic acid

114.

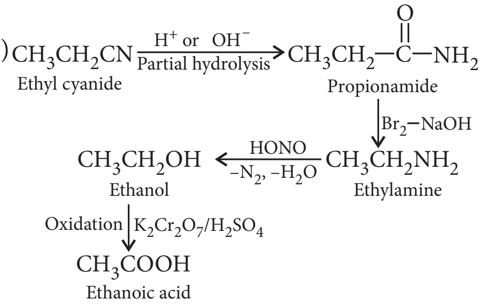


115.

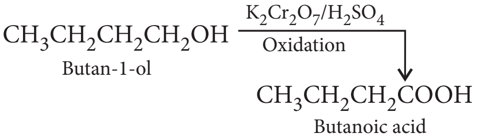


116. *Refer to answer 115.*

117. (i)



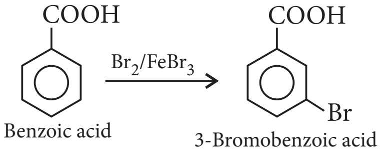
(ii)



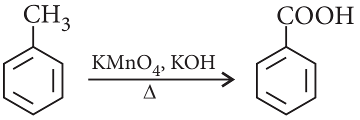
$$CH_3CH_2CH_2CH_2OH \xrightarrow[Oxidation]{K_2Cr_2O_7/H_2SO_4} CH_3CH_2CH_2COOH$$

Butan-1-ol → Butanoic acid

(iii)



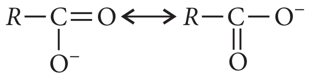
118. (i) *Refer to answer 117(i).*
(ii) *Refer to answer 117(ii).*
(iii)



119. Increasing order of boiling point :
$CH_3-CHO < C_2H_5OH < CH_3-COOH$

120. $CH_3-CH=CH-CH_2CN \xrightarrow[(ii)\ H_2O]{(i)\ DIBAL\text{-}H} CH_3-CH=CH-CH_2CHO$

121. The carbonyl group in —COOH is inert and does not show nucleophilic addition reaction like carbonyl compound. It is due to resonance stabilisation of carboxylate ion :



$$R-\underset{\underset{O^-}{|}}{C}=O \longleftrightarrow R-\underset{\underset{O}{||}}{C}-O^-$$

122. Add Tollens' reagent to formic acid and warm. Silver mirror is formed.

$$\underset{\text{Formic acid}}{HCOOH} + 2[Ag(NH_3)_2]^+ + 2OH^- \xrightarrow{\text{Warm}} \underset{\text{Silver mirror}}{2Ag} + CO_2 + 2NH_3 + 2NH_4OH$$

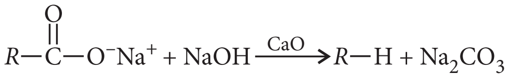
Acetic acid does not give this test.

123. $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$

124. $CH_3-COOH \xrightarrow{PCl_5} CH_3-COCl + POCl_3 + HCl$

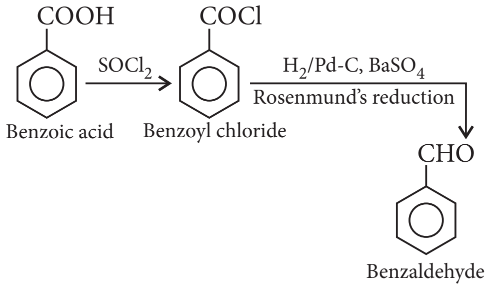
125. *Refer to answer 124.*

126. Decarboxylation : Sodium or potassium salt of carboxylic acids on heating with soda lime (NaOH and CaO), loses a molecule of carbon dioxide and alkanes are obtained as products.



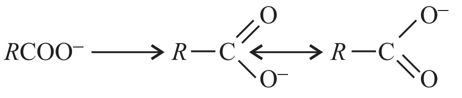
$$R-\overset{\overset{O}{||}}{C}-O^-Na^+ + NaOH \xrightarrow{CaO} R-H + Na_2CO_3$$

127.



128. In carboxylic acid C $=$ O is in resonance and not available for reaction.

$$RCOOH \rightleftharpoons RCOO^- + H^+$$



129. Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ but phenol will not react.

130. Benzoic acid and ethyl benzoate can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$.

131. Hell-Volhard-Zelinsky reaction : Carboxylic acids react with chlorine or bromine in the presence of phosphorous to give compounds in which α-hydrogen atom is replaced by halogen atom.

$$\underset{\text{Acetic acid}}{CH_3COOH} + Cl_2 \xrightarrow{\text{Red P}} \underset{\text{Chloroacetic acid}}{ClCH_2-COOH} + HCl$$

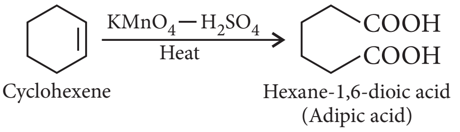
$$ClCH_2-COOH + Cl_2 \xrightarrow{\text{Red P}} \underset{\text{Dichloroacetic acid}}{Cl_2CHCOOH} + HCl$$

$$Cl_2CHCOOH + Cl_2 \xrightarrow{\text{Red P}} \underset{\text{Trichloroacetic acid}}{Cl_3CCOOH} + HCl$$

132. *Refer to answer 117(iii).*

133. Chloroacetic acid has lower pK_a value than acetic acid; 'Cl' in chloroacetic acid shows –I effect, it creates less electron density on oxygen of carboxylic acid. Thus, release of proton becomes easier. In case of acetic acid, the state of affair is just opposite. Hence, chloroacetic acid is stronger than acetic acid.

134.



135. We know that $+I$-effect decreases while $-I$-effect increases the acid strength of carboxylic acids. The overall acid strength increases in the order.

$(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

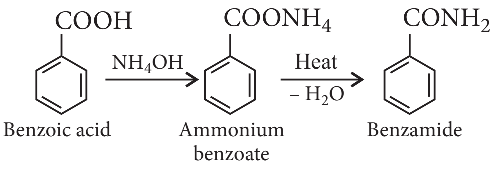
136. Acetic acid to methyl amine :

$$\begin{tikzcd}
\underset{\text{Acetic acid}}{CH_3COOH} \arrow[r, "NH_3"] & CH_3COONH_4 \arrow[d, "\Delta", "H_2O"'] \\
\underset{\text{Methyl amine}}{CH_3NH_2} & CH_3CONH_2 \arrow[l, "NaOBr"']
\end{tikzcd}$$

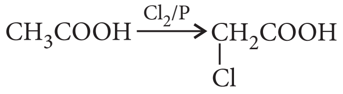
137. Fischer esterification :

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \rightleftharpoons RCOOR' + H_2O$$

138. Benzoic acid to benzamide :



139. (a)

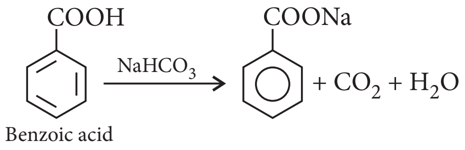


$$CH_3COOH \xrightarrow{Cl_2/P} \underset{\underset{Cl}{|}}{C}H_2COOH$$

(b) Benzaldehyde when treated with ammoniacal silver nitrate gives silver mirror.

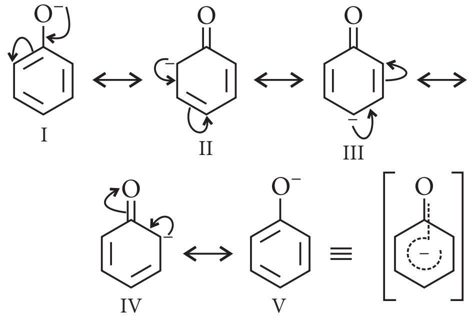
$$C_6H_5CHO + 2[Ag(NH_3)_2]^+ 3OH^- \longrightarrow$$
$$C_6H_5COO^- + \underset{\text{Siliver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

Benzoic acid reacts with sodium bicarbonate to liberate CO_2.

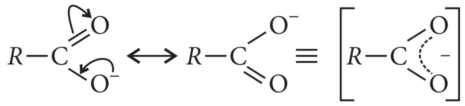


140. *Refer to answer 133.*

141. Phenoxide ion has the following resonating structures :



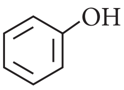
Carboxylate ion has the following resonating structures.



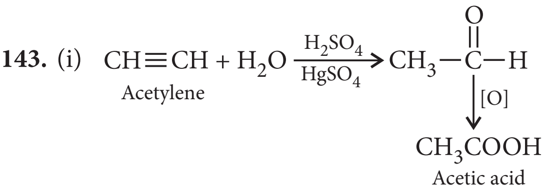
(i) Phenoxide ion is a resonance hybrid of structures I to V, where each structure has a contribution of 20% in the resonance hybrid. On the other hand, each of the two contributing structures of carboxylate ion contribute 50% towards the resonance hybrid. Therefore, the carboxylate ion tends to be more stable than the phenoxide ion and hence has higher acidity.

(ii) The negative charge rests on the electronegative O atom in carboxylate ion. The presence of negative charge on an electronegative atom makes the ion more stable. For the same reason $RCOO^-$ is more stable than the phenoxide ion where the carbon has negative charge on it. For the above two reasons carboxylate ion is more stable and has higher acidity than phenol.

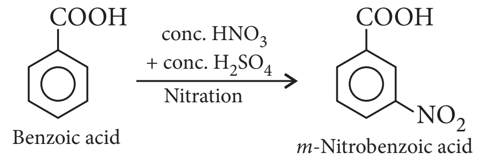
142. (i) F—CH_2COOH > Cl—CH_2COOH.

(ii) CH_3COOH is stronger than 

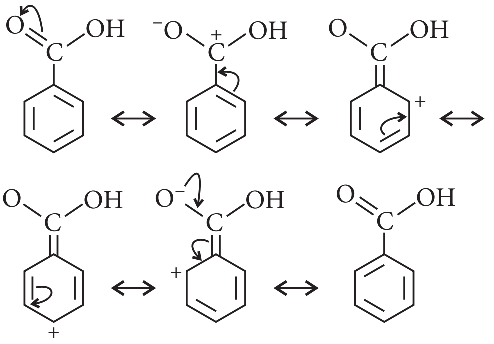
143. (i)



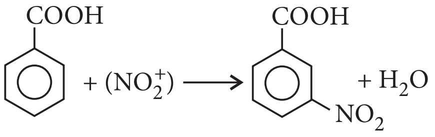
(ii)



144. (i) Electrophilic substitution in benzoic acid takes place at *meta*-position. Due to resonance in benzoic acid, there is high electron density at *meta*-position. Therefore, electrophilic substitution in benzoic acid takes place at *meta*-position.

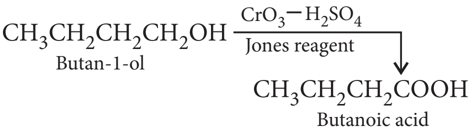


e.g.,

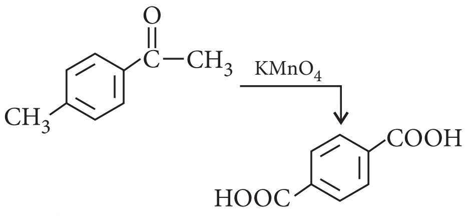


(ii) *Refer to answer 128.*

145. (i)



(ii)



146. (i) The overall acid strength increases in the order.

4-methoxybenzoic acid < benzoic acid < 3,4-dinitrobenzoic acid.

(ii) *Refer to answer 135.*

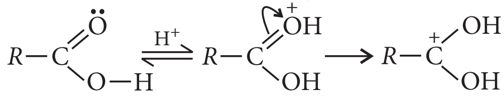
147. Esterification : Carboxylic acids react with alcohols or phenols in the presence of a mineral acid like concentrated H_2SO_4 or HCl gas as catalyst and give ester.

$$R\text{—COOH} + R'\text{OH} \rightleftharpoons R\text{—COO}R' + H_2O$$

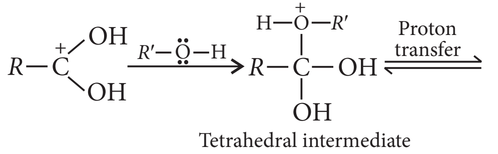
$$e.g., \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + H_2O$$

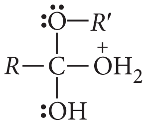
Mechanism of esterification : It is a nucleophilic acyl substitution.

(a) Protonation of carboxyl oxygen :

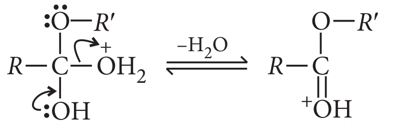


(b) Nucleophilic addition of alcohol :

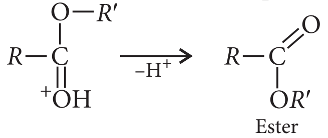




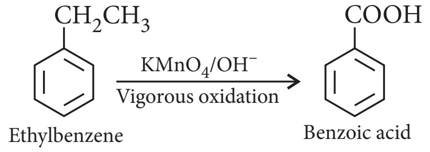
(c) Elimination of water molecule :



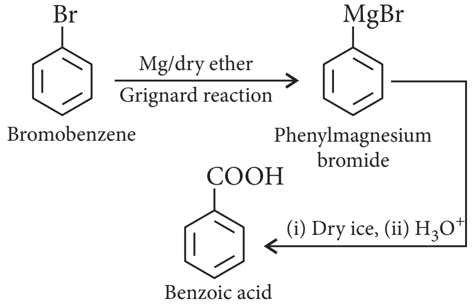
(d) Protonated ester loses a proton to give ester :



148. (i)



(ii)



149. (i) 4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid.

(ii) The overall acidic strength increases in the order :

$(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

150. (i) The strength of an acid is indicated by pK_a value, where, $pK_a = -\log K_a$

Since monochloroethanoic acid is weaker than dichloroethanoic acid so it has lower value of dissociation constant K_a.

Therefore, it has higher value of pK_a.

(ii) The —COOH group in benzoic acid is attached to sp^2 - carbon of the phenyl ring and is more acidic than acetic acid in which —COOH group is attached to sp^3 – carbon atom of CH_3 group.

So, benzoic acid is stronger than acetic or acetic acid is weaker acid than benzoic acid.

151. (i) *Refer to answer 126.*

(ii) *Refer to answer 129.*

152. (i) Ethylacetate is hydrolysed slowly by water to form ethyl alcohol while methyl acetate gives methyl alcohol.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \longrightarrow CH_3COOH + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

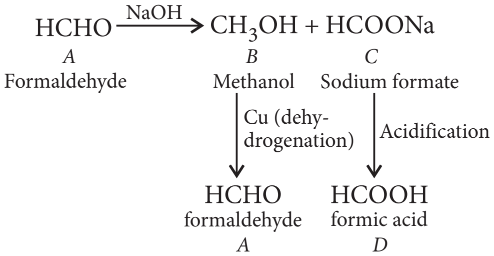
$$\underset{\text{Methyl acetate}}{CH_3COOCH_3} + H_2O \longrightarrow CH_3COOH + \underset{\text{Methyl alcohol}}{CH_3OH}$$

The hydrolysis product of ethyl acetate undergo iodoform test with iodine and alkali.

(ii) *Refer to answer 139(b).*

153. Since the molecular formula of *D* is CH_2O_2, thus, *D* is HCOOH (formic acid). *D* is obtained by the acidification of *C*, so, *C* is sodium formate (HCOONa).

Thus, *A* must be formaldehyde (as it undergoes Cannizzaro reaction with a strong base).



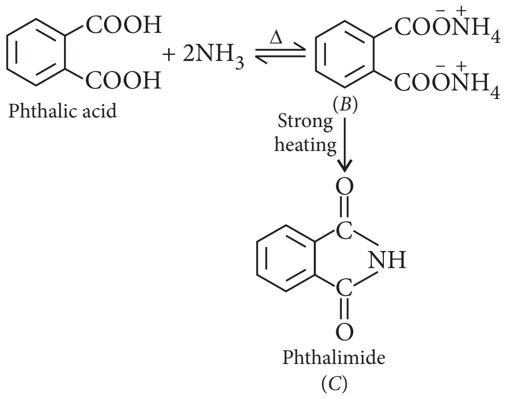
$$\underset{\substack{A\\ \text{Formaldehyde}}}{HCHO} \xrightarrow{NaOH} \underset{\substack{B\\ \text{Methanol}}}{CH_3OH} + \underset{\substack{C\\ \text{Sodium formate}}}{HCOONa}$$

Thus, *A* = Formaldehyde (HCHO)

B = Methanol (CH_3OH)

C = Sodium formate (HCOONa)
D = Formic acid (HCOOH)

154.



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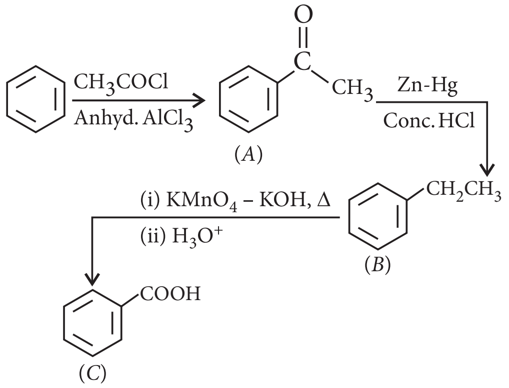

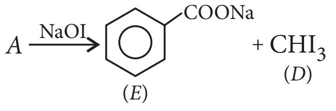

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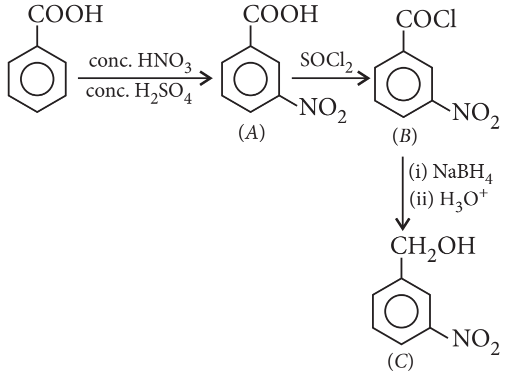
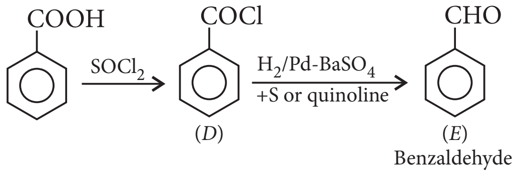
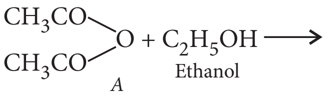




157.



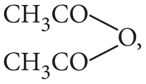
$$\underset{\substack{C\\ \text{Ethyl ethanoate}}}{CH_3COOC_2H_5} + \underset{\substack{B\\ \text{Ethanoic acid}}}{CH_3COOH}$$

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} \underset{B}{CH_3COOH} + \underset{D}{CH_3CH_2OH}$$

$$\begin{tikzcd} \underset{D}{CH_3CH_2OH} \arrow[r, "KMnO_4"] & \underset{B}{CH_3COOH} \arrow[d, "Ca(OH)_2"', "\text{Dry distillation}"] \\ & \underset{E}{CH_3COCH_3} + CaCO_3 \end{tikzcd}$$

E does not give Tollen's reagent test and does not reduce Fehling's solution as it is ketone.

A =



B = CH_3COOH

C = $CH_3COOC_2H_5$, *D* = CH_3CH_2OH

E = CH_3COCH_3

158. $$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\substack{\text{Methyl alcohol}\\ (A)}}{CH_3OH} \xrightarrow{\substack{\text{conc.}\\ H_2SO_4}} \underset{\substack{\text{Methyl acetate}\\ (B)}}{CH_3COOCH_3}$$

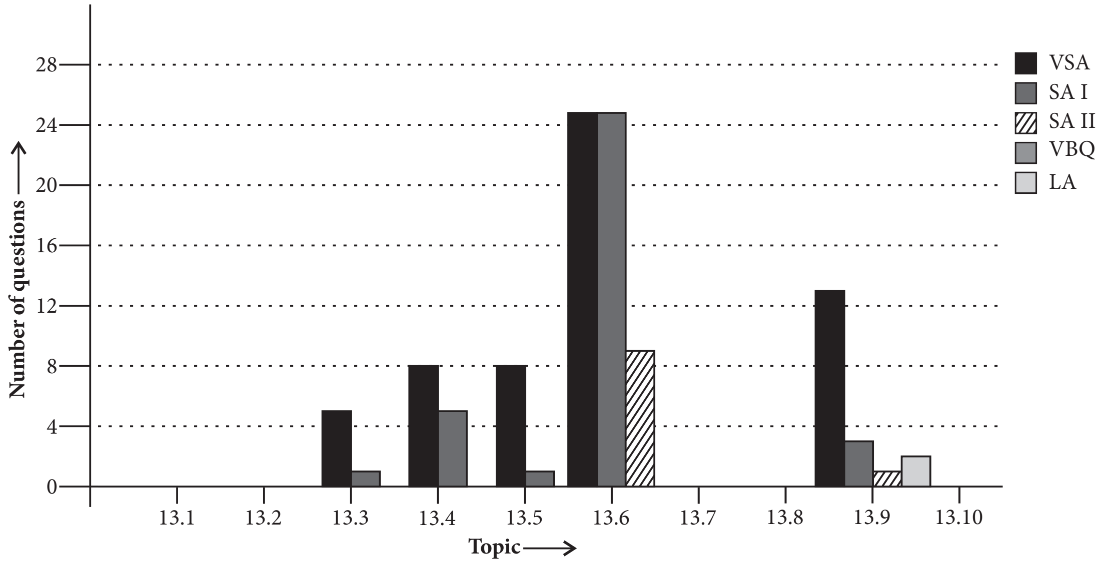
$$\underset{\substack{\text{Methyl alcohol}\\ (A)}}{CH_3OH} \xrightarrow{\text{mild }[O]} \underset{\substack{\text{Formaldehyde}\\ (C)}}{HCHO} \xrightarrow[\text{(ii) HCl}]{\text{(i) 50\% KOH}} \underset{\substack{\text{Methanol}\\ (A)}}{CH_3OH} + \underset{\substack{\text{Methanoic}\\ \text{acid}\\ (D)}}{HCOOH}$$

$$\underset{\substack{\text{Formic acid}\\ (D)}}{HCOOH} \xrightarrow{PCl_5} HCOCl \xrightarrow{NH_3} \underset{\substack{\text{Methanamide}\\ (E)}}{HCONH_2} \xrightarrow[P_2O_5]{\text{dehydration}} \underset{\substack{\text{Hydrocyanic}\\ \text{acid}}}{HCN}$$

Therefore, (*A*) : Methyl alcohol
(*B*) : Methyl acetate
(*C*) : Formaldehyde
(*D*) : Formic acid
(*E*) : Formamide

13 Amines

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



- Maximum total weightage is of *Chemical Reactions of Amines.*
- Maximum VSA type questions were asked from *Chemical Reactions of Amines.*
- Maximum SA I and SA II type questions were asked from *Chemical Reactions of Amines.*

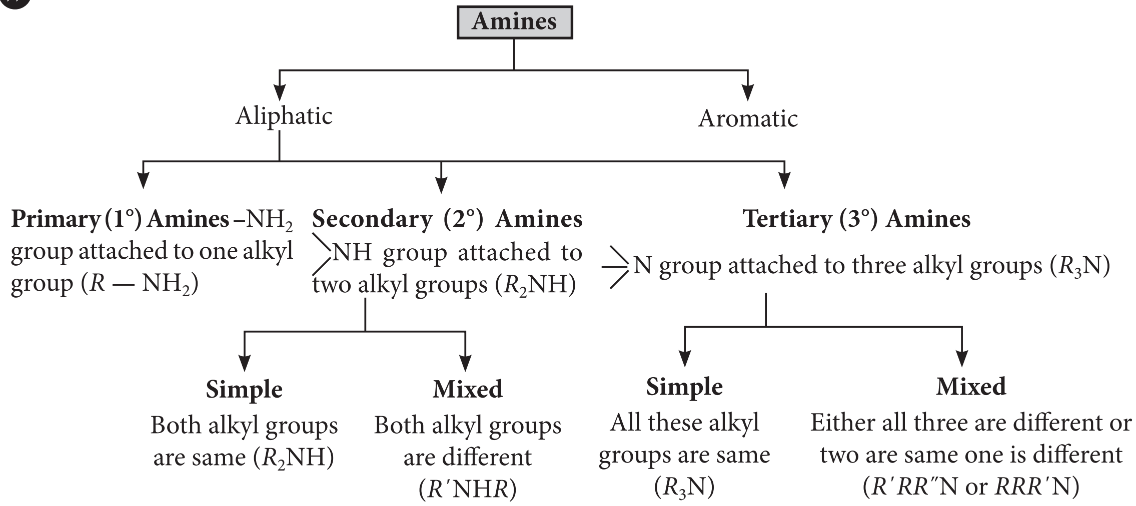
QUICK RECAP

AMINES

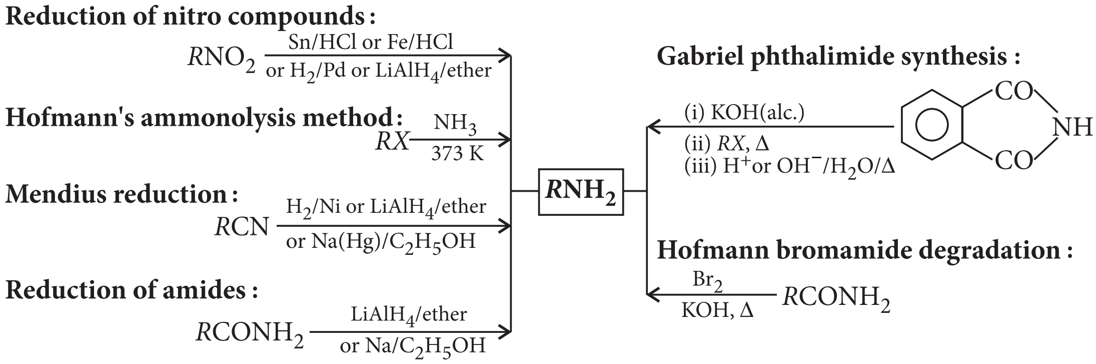
- **Amines :** These are alkyl or aryl derivatives of ammonia and are obtained by replacing one, two or three hydrogen atoms by alkyl/aryl groups.

Nomenclature : In common system, an aliphatic amine is named by prefixing alkyl group to amine, *i.e.*, *alkylamine*. In IUPAC system, amines are named as *alkanamines*. In secondary and tertiary amines, when two or more groups are the same, the prefix *di* or *tri* is appended before the name of alkyl group.

Classification :



Preparation :



- **Limitations of Gabriel phthalimide synthesis :**
  - It is used for the preparation of only 1° amines. *tert*-Butylamine is a 1° amine, but cannot be prepared by this method. In this case, elimination takes place.
  - Aromatic 1° amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.

Structure : Nitrogen orbitals in amines are sp^3 hybridised and the geometry of amines is pyramidal. Due to the presence of unshared pair of electrons, the angle $C-N-E$, (where E is C or H) is less than 109.5°.

Physical properties :

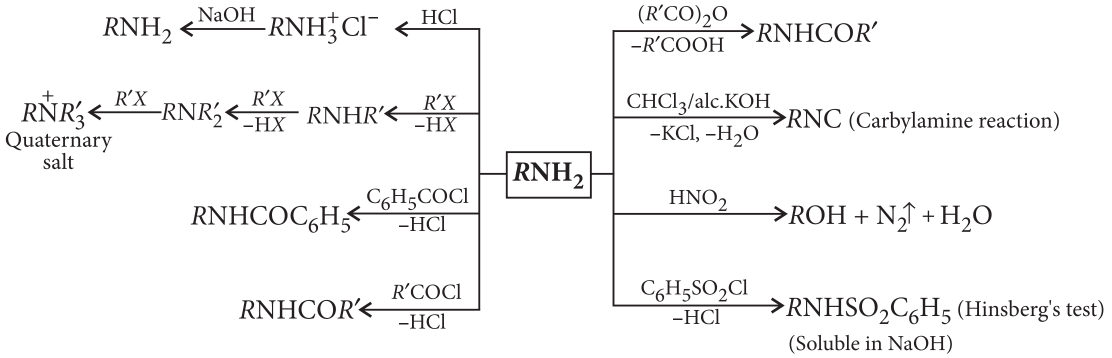
- Lower amines are gases and liquids but higher amines are solids.
- Primary and secondary amines have higher boiling points than other organic compounds due to hydrogen bonding.
- Primary and secondary amines are soluble in water due to hydrogen bonding between –NH_2 and H_2O molecules.

Chemical properties :

- **Basic character of amines :**
  - Amines are basic in nature due to the presence of lone pair of electrons on nitrogen atom.
  - Aliphatic amines are stronger bases than ammonia due to +*I* effect of alkyl groups present in amines.
  - Aromatic amines are weaker bases than ammonia due to –*I* effect of aryl group.
  - Besides inductive effect, there are other effects like steric effect, solvation effect, resonance effect which effect the basic strength of amines.
  - In gaseous phase, the order of basicity of amines is 3° amine > 2° amine > 1° amine > NH_3.
  - In aqueous phase, despite of inductive effect, solvation effect and steric hindrance also play an important role. Thus, the order of basicity of amines is

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ and $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

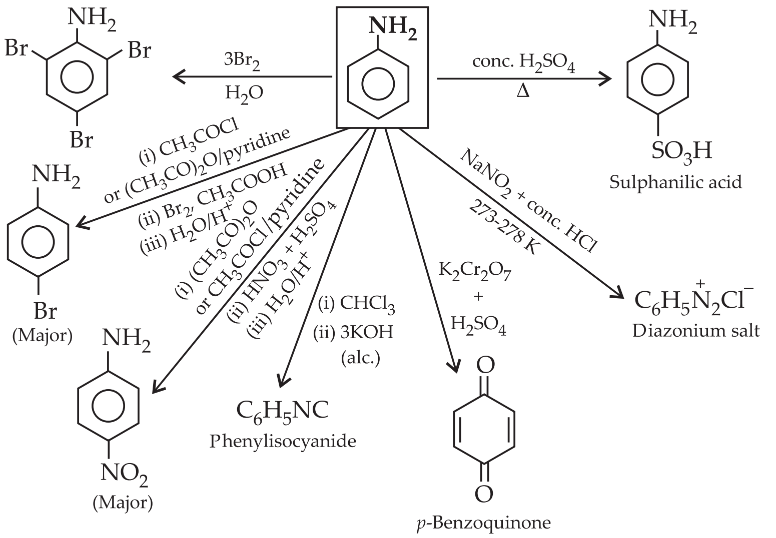
- **Chemical reactions :**



- **Identification of primary, secondary and tertiary amines :**

	Test	Primary amine	Secondary amine	Tertiary amine
1.	Reaction with nitrous acid.	Gives alcohol with effervescence of N_2 gas.	Gives oily nitrosoamine which gives Liebermann's nitrosoamine test.	Forms nitrite in cold which is soluble in water and on heating gives nitrosoamine.
2.	Reaction with benzene sulphonyl chloride (*Hinsberg's reagent*)	Gives *N*-alkylbenzene-sulphonamide which is soluble in alkali.	Gives *N*,*N*-dialkylbenzene sulphonamide which is insoluble in alkali.	No reaction
3.	*Carbylamine test* : Reaction with chloroform and alcoholic KOH	Forms carbylamine or isocyanide (*R*NC) with characteristic unpleasant odour.	No reaction	No reaction
4.	*Hofmann's mustard oil reaction* : Reaction with CS_2 and $HgCl_2$.	Forms *N*-substituted isothiocyante with characteristic unpleasant smell of mustard oil.	No reaction	No reaction

- **Electrophilic substitution reactions of arylamines :** Aniline undergoes electrophilic substitution reactions. —NH_2 group is *ortho* and *para* directing and a powerful activating group.



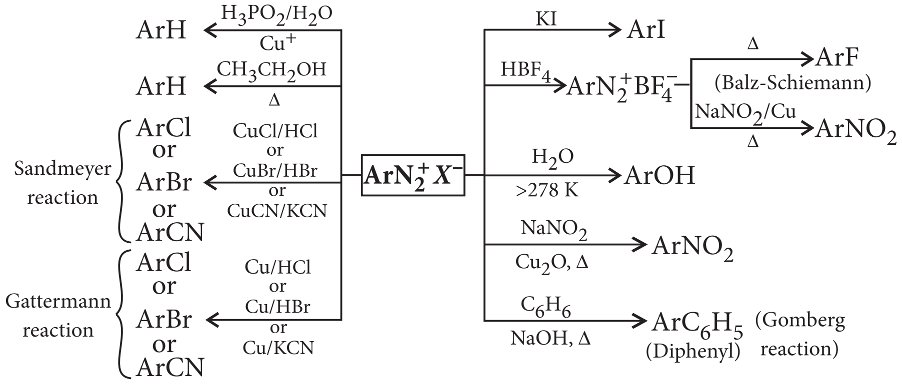
DIAZONIUM SALTS

- **Arenediazonium salts :** They have the general formula $ArN_2{}^+X^-$, Ar stands for the aryl $(-C_6H_5)$ group and X^- is Cl^-, Br^-, NO_3^-, HSO_4^-, BF_4^-.
- **Nomenclature :** They are named by suffixing diazonium to the name of parent hydrocarbon followed by anion.
- **Preparation :** Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid (sodium nitrite and hydrochloric acid) at 0-5 °C.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0-5°\,C} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

- **Stability :** Arenediazonium salts are more stable (for short time) than alkanediazonium salts due to dispersal of positive charge over the benzene ring.
- **Physical properties :** These are generally colourless, crystalline solids, which are soluble in water. They are unstable and explode in dry state.
- **Chemical properties :**

▶ **Reactions involving displacement of nitrogen (diazo group) :**



▶ **Reactions involving retention of diazo group (coupling reactions) :**

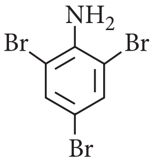
$$ArN{=}NC_6H_4NH_2 \xleftarrow[pH\,=\,4\text{-}5,\ 0\text{-}5°C]{C_6H_5NH_2/H^+} \boxed{ArN_2^+X^-} \xrightarrow[pH\,=\,9\text{-}10,\ 0\text{-}5°C]{C_6H_5OH/OH^-} ArN{=}NC_6H_4OH$$

Previous Years' CBSE Board Questions

13.3 Nomenclature

VSA (1 mark)

1. Write the IUPAC name of the given compound:



(Delhi 2016)

2. Write the structure of *N*-methylethanamine. *(AI 2013)*

3. Write the structure of 2-aminotoluene. *(AI 2013)*

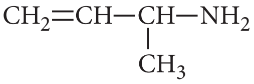
4. Give the IUPAC name of $H_2N-CH_2-CH_2-CH=CH_2$. *(Delhi 2010)*

5. Write the structure for *N*, *N*-ethylmethylamine. *(1/3, Delhi 2010C)*

SA I (2 marks)

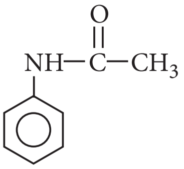
6. Give IUPAC names of the following compounds:

(a)



$CH_2=CH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$

(b)



(Delhi 2012C)

13.4 Preparation of Amines

VSA (1 mark)

7. Write the chemical equation involved in the following reaction:
Hofmann bromamide degradation reaction *(1/2, AI 2016, 2012, Delhi 2008C)*

8. How do you convert the following:
Ethanenitrile to ethanamine *(1/3, AI 2015)*

9. State and illustrate the following:
Gabriel synthesis *(1/2, AI 2013C)*

10. Write chemical equations for the following conversion:
Benzyl chloride to 2-phenylethanamine. *(1/3, Delhi 2012)*

11. Why cannot primary aromatic amines be prepared by Gabriel phthalimide synthesis? *(1/2, AI 2011C)*

12. Write the chemical reaction to illustrate the following:
Ammonolysis *(1/2, Delhi 2009C)*

SA I (2 marks)

13. How will you convert the following:
    (i) Nitrobenzene into aniline
    (ii) Ethanoic acid into methanamine *(2/3, Delhi 2014)*

14. How are the following conversions carried out?
    (i) CH_3CH_2Cl to $CH_3CH_2CH_2NH_2$
    (ii) Benzene to aniline. *(Delhi 2012C)*

15. Illustrate the following reactions giving a chemical equation in each case:
    (i) Gabriel phthalimide synthesis
    (ii) Hofmann's bromamide reaction. *(2/3, Foreign 2011, AI 2008)*

16. How would you achieve the following conversions:
    (i) Nitrobenzene to aniline.
    (ii) An alkyl halide to a quaternary ammonium salt.
    Write the chemical equation with reaction conditions in each case. *(2/3, Delhi 2007)*

13.5 Physical Properties

VSA (1 mark)

17. Give reasons for the following:
Primary amines have higher boiling point than tertiary amines. *(1/3, AI 2016, Delhi 2008C)*

18. Arrange the following in the increasing order of their boiling point:
$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$ *(1/5, Delhi 2015)*

19. Account for the following :
Primary amines (R—NH_2) have higher boiling point than tertiary amines (R_3N). *(1/3, AI 2014)*

20. Out of CH_3NH_2 and $(CH_3)_3N$, which one has higher boiling point? *(Delhi 2014C)*

21. Account for the following :
Ethylamine is soluble in water whereas aniline is not. *(1/3, Delhi 2014C, Delhi 2009C)*

22. Account for the following :
Nitro compounds have higher boiling points than the hydrocarbons having almost the same molecular mass. *(1/3, AI 2007)*

SA I (2 marks)

23. State reasons for the following :
(i) Ethylamine is soluble in water whereas aniline is not soluble in water.
(ii) Primary amines have higher boiling points than tertiary amines. *(2/3, AI 2011)*

13.6 Chemical Reactions (Amines)

VSA (1 mark)

24. Give a simple chemical test to distinguish between the following pair of compounds :
$(CH_3)_2NH$ and $(CH_3)_3N$ *(1/5, Delhi 2015)*

25. Arrange the following in increasing order of basic strength :
Aniline, *p*-nitroaniline, and *p*-toluidine *(AI 2015C)*

26. Arrange the following compounds in increasing order of solubility in water :
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$ *(Delhi 2014, AI 2011C)*

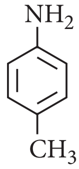
27. How will you convert the following :
Aniline into *N*-phenylethanamide
(Write the chemical equations involved.) *(1/3, Delhi 2014)*

28. Arrange the following in increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$ *(Delhi 2014)*

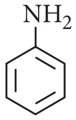
29. Arrange the following in increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$ *(Delhi 2014)*

30. Which of the two is more basic and why?
CH_3NH_2 or NH_3 *(Foreign 2014)*

31. Which of the two is more basic and why?

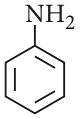


and



(Foreign 2014)

32. Which of the two is more basic and why?

CH_3NH_2 or 

(Foreign 2014)

33. Arrange the following in increasing order of their basic strength in aqueous solution :
CH_3NH_2, $(CH_3)_3N$, $(CH_3)_2NH$ *(Delhi 2013)*

34. Arrange the following in the decreasing order of their basic strength in aqueous solutions :
CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ and NH_3 *(Delhi 2012, AI 2009)*

35. Describe the following giving the relevant chemical equation :
Carbylamine reaction *(1/2, AI 2012, Delhi 2008C)*

36. Complete the following reaction equation :
$C_6H_5NH_2 + Br_{2(aq)} \rightarrow$ *(1/2, AI 2012)*

37. Rearrange the following in an increasing order of their basic strengths :
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_6H_5)_2NH$ and CH_3NH_2 *(AI 2011)*

38. State reasons for the following :
pK_b value for aniline is more than that for ethylamine. *(1/3, AI 2011)*

39. How will you differentiate between aniline and ethylamine? *(AI 2011)*

40. Why is an alkylamine more basic than ammonia? *(Foreign 2011, Delhi 2009)*

41. How will you bring about the following conversion :
Ethanamine to ethanoic acid *(Delhi 2011C)*

42. Assign reason for the following :
The pK_b of aniline is higher than that of methylamine. *(1/2, Delhi 2009C)*

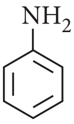
43. Why do amines act as nucleophiles? *(AI 2007)*

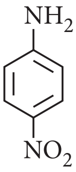
44. Account for the following :
Amines are basic substances while amides are neutral. *(1/3, AI 2007)*

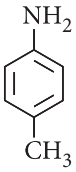
SA I (2 marks)

45. Give reasons for the following :
(i) Aniline does not undergo Friedel-Crafts reaction.
(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. *(2/3, AI 2016, 2014)*

46. Arrange the following in increasing order of their basic strength :
(i) $C_6H_5—NH_2$, $C_6H_5—CH_2—NH_2$, $C_6H_5—NH—CH_3$
(ii)







(AI 2015)

47. How do you convert the following :
(i) $C_6H_5CONH_2$ to $C_6H_5NH_2$
(ii) Aniline to phenol *(2/3, AI 2015)*

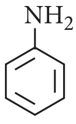
48. Illustrate the following reactions giving suitable example in each case :
(i) Ammonolysis
(ii) Acetylation of amines *(2/5, Foreign 2015)*

49. Give the structures of *A*, *B* and *C* in the following reactions :
(i) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow{H_2O} C$
(ii) $CH_3CN \xrightarrow{H_2O/H^+} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{Br_2 + KOH} C$
(2/3, Delhi, AI 2014)

50. Account for the following :
(i) Aniline does not give Friedel-Crafts reaction.
(ii) pK_b of methylamine is less than that of aniline. *(2/3, Delhi 2014C)*

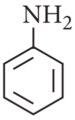
51. (i) Arrange the following compounds in an increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2
(ii) Arrange the following compounds in a decreasing order of pK_b values :
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$ *(Delhi 2014C)*

52. Complete the following reactions :
(i) $CH_3CH_2NH_2 + CHCl_3 + \text{alc. } KOH \longrightarrow$
(ii)



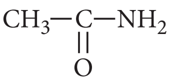
$+ HCl_{(aq)} \longrightarrow$ *(2/3, AI 2013)*

53. Write the main products of the following reactions :
(i)



$\xrightarrow{Br_{2(aq)}} ?$

(ii)



$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—NH_2 \xrightarrow{Br_2 + NaOH} ?$
(2/3, AI 2013)

54. Give chemical tests to distinguish between the following pairs of compounds :
(i) Aniline and ethylamine
(ii) Ethylamine and dimethylamine
(Delhi 2013C)

55. Give reasons :
(i) Aniline is a weaker base than cyclohexyl amine.
(ii) It is difficult to prepare pure amines by ammonolysis of alkyl halides. *(AI 2013C)*

56. Give reasons :
(i) Electrophilic substitution in aromatic amines takes place more readily than benzene.
(ii) CH_3CONH_2 is weaker base than $CH_3CH_2NH_2$. *(AI 2013C)*

57. How would you account for the following :
(i) Aniline is a weaker base than cyclohexylamine.
(ii) Methylamine in aqueous medium gives reddish-brown precipitate with $FeCl_3$.
(AI 2012C)

58. Give the chemical tests to distinguish between the following pairs of compounds :
(i) Ethylamine and aniline
(ii) Aniline and benzylamine *(AI 2010)*

59. Give the chemical tests to distinguish between the following pairs of compounds :
(i) Methylamine and dimethylamine
(ii) Aniline and *N*-methylaniline *(AI 2010)*

60. Write one chemical reaction each to illustrate the following :
(i) Carbylamine reaction
(ii) Acetylation reaction *(2/3, Delhi 2010C)*

61. Account for the following :
(i) pK_b of aniline is more than that of methylamine.
(ii) Aniline does not undergo Friedel-Crafts reaction. *(AI 2010C)*

62. Describe a chemical test each to distinguish between the following :
(i) Ethylamine and aniline
(ii) Methylamine and dimethylamine *(AI 2010C, 2009C)*

63. Assign reason for the following :
(i) Amines are less acidic than alcohols of comparable molecular masses.
(ii) Aliphatic amines are stronger bases than aromatic amines. *(AI 2009C)*

64. (i) Arrange the following in an increasing order of basic strength in water :
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3.
(ii) Arrange the following in increasing order or basic strength in gas phase :
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and CH_3NH_2. *(AI 2008)*

65. Account for the following :
(i) Aniline does not undergo Friedel-Crafts reaction.
(ii) Aliphatic amines are stronger bases than aromatic amines. *(AI 2008C)*

66. Give one chemical test each to distinguish between the following pairs of compounds :
(i) Ethylamine and aniline
(ii) Aniline and *N*-methylaniline *(AI 2008C)*

SA II (3 marks)

67. Write the structures of *A*, *B* and *C* in the following :

(i)
$$\begin{tikzcd} C_6H_5-CONH_2 \arrow[r, "Br_2/aq.\ KOH"] & A \arrow[d, "NaNO_2+HCl", "0\text{-}5^\circ C"'] \\ C & B \arrow[l, "KI"'] \end{tikzcd}$$

(ii)
$$\begin{tikzcd} CH_3-Cl \arrow[r, "KCN"] & A \arrow[r, "LiAlH_4"] & B \arrow[dll, "CHCl_3 + alc.\ KOH", "\Delta"'] \\ C & & \end{tikzcd}$$

(Delhi 2016)

68. Write the structures of main products when aniline reacts with the following reagents :
(i) Br_2 water
(ii) HCl
(iii) $(CH_3CO)_2O$/pyridine *(3/5, Delhi 2015)*

69. Write the chemical equations involved when aniline is treated with the following reagents :
(i) Br_2 water (ii) $CHCl_3$ + KOH
(iii) HCl *(AI 2015)*

70. Write the structures of *A*, *B* and *C* in the following reactions :

(i)
$$\begin{tikzcd} C_6H_5NO_2 \arrow[r, "Sn/HCl"] & A \arrow[r, "NaNO_2 + HCl", "273\ K"'] & B \arrow[d, "H_2O", "\Delta"'] \\ & & C \end{tikzcd}$$

(ii) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

(3/5, Foreign 2015)

71. An aromatic compound '*A*' on treatment with aqueous ammonia and heating forms compound '*B*' which on heating with Br_2 and KOH forms a compound '*C*' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds *A*, *B* and *C*. *(Delhi 2015C)*

72. Give the structures of *A*, *B* and *C* in the following reactions :
(i) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$
(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2 + KOH} B \xrightarrow{CHCl_3 + NaOH} C$
(Delhi 2014)

73. Give the structures of products *A*, *B* and *C* in the following reactions :
(i) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^\circ C]{HNO_2} C$

(ii)
$$\begin{tikzcd} CH_3COOH \arrow[r, "NH_3", "\Delta"'] & A \arrow[r, "NaOH + Br_2"] & B \arrow[d, "CHCl_3 + Alc.\ NaOH"'] \\ & & C \end{tikzcd}$$

(Delhi 2013)

74. Account for the following observations :
(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-Crafts reaction. *(Delhi, AI 2008)*

13.9 Chemical Reactions (Diazonium salts)

VSA (1 mark)

75. Complete the following reaction equation :
$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow ...$
(Delhi 2015C, AI 2013, 2012)

76. The conversion of primary aromatic amines into diazonium salts is known as ___________.
(AI 2014)

77. Complete the following reactions :
$C_6H_5N_2^+Cl^- \xrightarrow[\text{(Room temp.)}]{H_2O}$ *(1/3, AI 2013)*

78. State and illustrate the following :
Coupling reaction *(1/2, AI 2013C, Foreign 2011)*

79. How is the following conversion carried out :
Aniline to *p*-hydroxyazobenzene.
(1/2, Delhi 2012C)

80. How will you bring about the following conversion :
Nitrobenzene to phenol *(1/2, Delhi 2011C)*

81. How will you bring about the following conversion :
Aniline to chlorobenzene
Write the chemical equation involved.
(1/2, Delhi 2011C)

82. How will you bring about the following conversion :
Aniline to benzonitrile. *(Delhi 2011C)*

83. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt. *(Delhi 2008)*

84. How would you achieve the following conversion :
Aniline to benzonitrile.
Write the chemical equation with reaction conditions in each case. *(Delhi 2007)*

SA I (2 marks)

85. Write chemical equations for the following conversions :
(i) Nitrobenzene to benzoic acid.
(ii) Aniline to benzyl alcohol. *(2/3, Delhi 2012)*

86. Illustrate the following with an example of reaction in each case :
(i) Sandmeyer's reaction
(ii) Coupling reaction.
(AI 2012C, Delhi 2011C)

SA II (3 marks)

87. Give the structure of *A*, *B* and *C* in the following reactions :

(i) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(ii)
$$\begin{tikzcd}
C_6H_5NO_2 \arrow[r, "Sn + HCl"] & A \arrow[r, "NaNO_2 + HCl", "273\text{ K}"'] & B \arrow[d, "H_2O/H^+"', "\Delta"] \\
& & C
\end{tikzcd}$$
(Delhi 2013)

LA (5 marks)

88. An aromatic compound '*A*' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions :

$$\begin{tikzcd}
(C_7H_7ON)\,A \arrow[rrd, "Br_2 + KOH"] & & \\
C & B \arrow[l, "CH_3CH_2OH"'] \arrow[d, "KI"] & C_6H_5NH_2 \arrow[l, "NaNO_2 + HCl"', "273\text{ K}"] \arrow[d, "CHCl_3 + NaOH"] \\
& E & D
\end{tikzcd}$$
(Delhi 2015)

89. (i) Write the structures of main products when benzenediazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with the following reagents :
(a) HBF_4/Δ (b) Cu/HBr
(ii) Write the structures of *A*, *B* and *C* in the following reactions :

(a)
$$\begin{tikzcd}
C_6H_5NO_2 \arrow[r, "Sn/HCl"] & A \arrow[r, "NaNO_2 + HCl", "273\text{ K}"'] & B \arrow[d, "H_2O"', "\Delta"] \\
& & C
\end{tikzcd}$$

(b) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\text{ K}]{HNO_2} C$

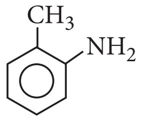
(Foreign 2015)

Detailed Solutions

1. 2, 4, 6-Tribromoaniline

2. $CH_3CH_2NHCH_3$ (*N*-methylethanamine)

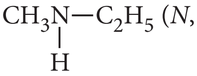
3.



2-Aminotoluene

4. But-3-en-1-amine

5.



$CH_3\underset{\substack{|\\H}}{N}-C_2H_5$ (*N*, *N*-ethylmethylamine)

6. (a) But-3-en-2-amine

(b) *N*-phenylethanamide

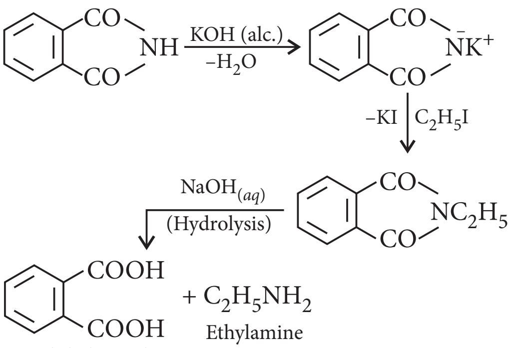
7. $R-CONH_2 + Br_2 + 4NaOH \longrightarrow$
Acid amide

$R-NH_2 + Na_2CO_3 + 2\ NaBr + 2H_2O$
1° amine

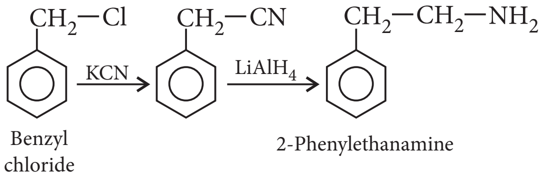
8. $CH_3CN + 4[H] \xrightarrow{Na + C_2H_5OH} CH_3CH_2NH_2$

Ethanenitrile Ethanamine

9. **Gabriel phthalimide synthesis :** In this reaction phthalimide is converted into its potassium salt by treating it with alcoholic potassium hydroxide. Then potassium phthalimide is heated with an alkyl halide to yield an *N*-alkylpthalimide which is hydrolysed to phthalic acid and primary amine by alkaline hydrolysis.

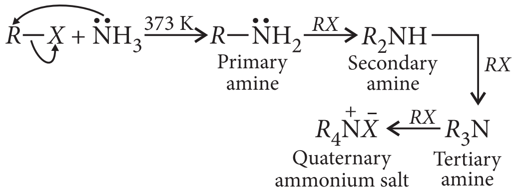


10.

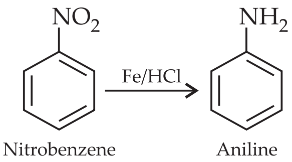


11. Aromatic amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

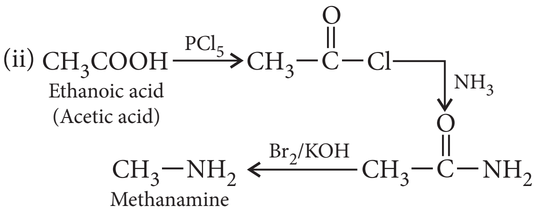
12. Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary, tertiary amines and quaternary ammonium salt.



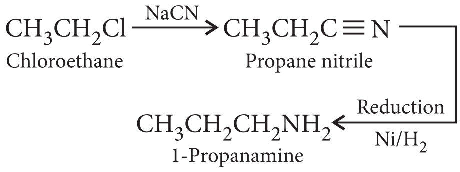
13. (i)



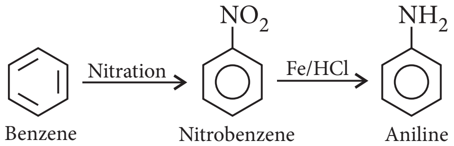
(ii)



14. (i)



(ii)



15. (i) *Refer to answer 9.*

(ii) *Refer to answer 7.*

16. (i) *Refer to answer 13(i).*

(ii) *Refer to answer 12.*

17. Primary amines (R – NH_2) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines (R_3N). So, primary amines boil at a higher temperature than tertiary amines.

18. Increasing order of boiling points :
$(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$
Tertiary amine does not have hydrogen to form hydrogen bonding and hydrogen bonding in alcohol is stronger than that of amines because oxygen is more electronegative than nitrogen.

19. *Refer to answer 17.*

20. *Refer to answer 17.*

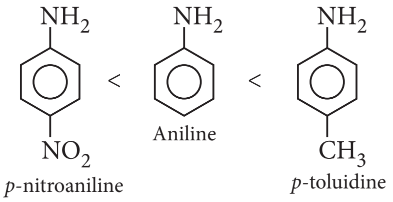
21. Ethylamine is soluble in water due to formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic aryl group the extent of hydrogen bonding decreases considerably and hence aniline is insoluble in water.

22. The nitro compounds are highly polar molecules. Due to this polarity they have strong intermolecular dipole - dipole interactions which causes them to have higher boiling points in comparison to the hydrocarbons having almost same molecular mass.

23. (i) *Refer to answer 21.*
(ii) *Refer to answer 17.*

24. When treated with benzenesulphonyl chloride (Hinsberg's reagent), $(CH_3)_2NH$ forms insoluble *N*, *N*-dialkylbenzene sulphonamide which is insoluble in KOH whereas tertiary amine does not react at all.

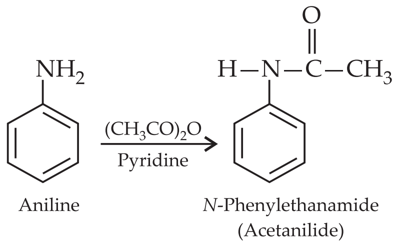
25.



Electron withdrawing group ($-NO_2$) on benzene ring decreases the basicity and electron donating group ($-CH_3$) on benzene ring increases the basicity of compound.

26. $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$
1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

27.



28. $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$
$C_6H_5NH_2$ and $C_6H_5NHCH_3$ are less basic than aliphatic amine $C_6H_5CH_2NH_2$ due to lone pair of nitrogen is in conjugation with benzene ring. But due to $+I$ effect of —CH_3 group in $C_6H_5NHCH_3$, it is more basic than $C_6H_5NH_2$.

29. Increasing order of basic strength in gaseous state is as follows :
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5N(CH_3)_2$
As the number of —CH_3 groups ($+I$ effect) attached to nitrogen increases, its basicity its basicity will increases.

30. Methyl amine is more basic than ammonia because of the presence of electron donating methyl group ($+I$ effect), which increases the electron density on nitrogen atom.

31. $CH_3(C_6H_4)NH_2$ is more basic than $C_6H_5NH_2$ due to electron releasing nature of methyl group which pushes electrons towards nitrogen.

32. CH_3NH_2 is more basic than $C_6H_5NH_2$ because in aniline the lone pair of electrons on nitrogen are involved in resonance.

33. In case of small alkyl groups like CH_3 the order of basicity is secondary amine > primary amine > tertiary amine due to solvation effect and $+I$ effect of —CH_3 group.

	$(CH_3)_2NH$	>	CH_3NH_2	>	$(CH_3)_3N$
pK_b	3.27		3.38		4.22

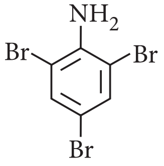
34. $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

35. Carbylamine reaction is the reaction in which 1° amines produce a bad smelling compound when treated with chloroform in the presence of alkali.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow R\text{—}N \overset{\rightarrow}{\equiv} C + 3KCl + 3H_2O$$

It is the test for primary amines.

36. $C_6H_5NH_2 + Br_{2(aq)} \longrightarrow$



$+ 3HBr$

37. $(C_6H_5)_2NH < C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2$

38. In aniline, the lone pair of electrons on N-atom is delocalised over benzene ring due to resonance. As a result, electron density on the nitrogen atom decreases. In contrast, in methylamine, +*I*-effect of CH_3 group increases electron density on the nitrogen atom. Therefore, aniline is a weaker base than methylamine hence, its pK_b value is more than that for methylamine.

39. Aniline being an aromatic primary amine on treatment with $HNO_2[NaNO_2 + HCl\ (dil.)]$ at 273–278 K followed by treatment with an alkaline solution of β-naphthol gives an orange coloured azo dye. Ethylamine does not give this test.

40. Electron density of N-atom increases due to the +*I* effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia.

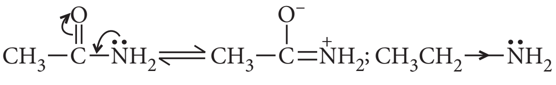
$$\ddot{N}H_3,\quad R \rightarrow \ddot{N}H_2$$

41.
$$CH_3CH_2NH_2 \xrightarrow[\text{(ii) } H_2O,\ 273\text{-}278\ K]{\text{(i) } NaNO_2/HCl} CH_3CH_2OH \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH$$

42. In aniline, the lone pair of electrons of N-atom are delocalised over the benzene ring. As a result, electron density on the nitrogen decreases. In contrast, in $CH_3—NH_2$, +*I* effect of $—CH_3$ group increases the electron density on the N-atom.
Therefore, aniline is a weaker base than methylamine and hence, its pK_b value is higher than that of methylamine.

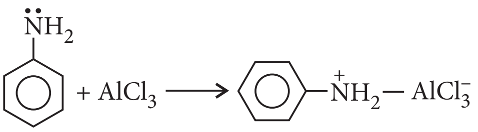
43. Because the electron pair of nitrogen can coordinate with the electron deficient electrophiles.

44. In CH_3CONH_2, the lone pair of electrons on nitrogen atom is involved in resonance with the carbonyl group. So, the electron pair of nitrogen is not easily available for protonation. Hence, CH_3CONH_2 is a weaker base than $CH_3CH_2NH_2$.



$$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 \rightleftharpoons CH_3-\overset{O^-}{\overset{|}{C}}=\overset{+}{N}H_2;\ CH_3CH_2 \rightarrow \ddot{N}H_2$$

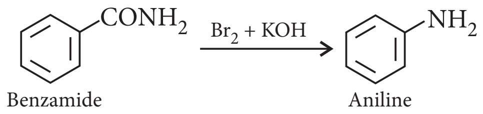
45. (i) In Friedel - Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel - Crafts reaction.



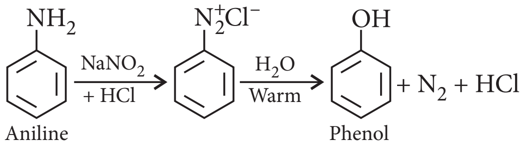
(ii) In aqueous solution 2° amine is more basic than 3° amine due to the combination of inductive effect, solvation effect and steric reasons.

46. (i) *Refer to answer 28.*
(ii) *Refer to answer 25.*

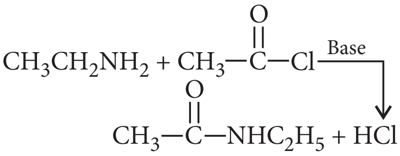
47. (i)



(ii)



48. (i) *Refer to answer 12.*
(ii) Acetylation of amines : The process of introducing an acetyl group $(CH_3-\overset{O}{\overset{\|}{C}}-)$ into a molecule is called acetylation.



$$CH_3CH_2NH_2 + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{Base} CH_3-\overset{O}{\overset{\|}{C}}-NHC_2H_5 + HCl$$

N-ethyl acetamide

49. (i)
$$\begin{tikzcd} C_6H_5NO_2 \arrow[r, "Sn + HCl"] & \underset{A}{C_6H_5NH_2} \arrow[d, "NaNO_2 + HCl", "273\ K"'] \\ \underset{C}{C_6H_5OH} & \underset{B}{C_6H_5N_2^+Cl^-} \arrow[l, "H_2O"'] \end{tikzcd}$$

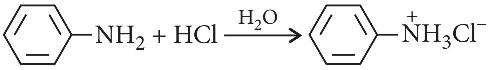
(ii)
$$CH_3CN \xrightarrow{H_2O/H^+} \underset{A}{CH_3COOH} \xrightarrow{NH_3} \underset{B}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{C}{CH_3NH_2}$$

50. (i) *Refer to answer 45(i).*
(ii) *Refer to answer 42.*

51. (i) Increasing order of basic strength is
$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$
(ii) Stronger the base lower will be its pK_b value hence, the decreasing order of pK_b values :
$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

52. (i) $CH_3—CH_2—NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3—CH_2—NC + 3KCl + 3H_2O$

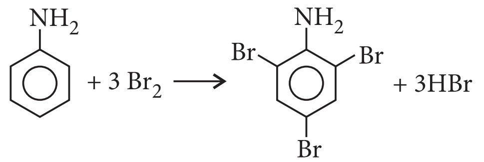
(ii)



53. (i) *Refer to answer 36.*

(ii) $CH_3{-}NH_2$
Methanamine

54. (i) Aniline gives white or brown precipitate with bromine water.

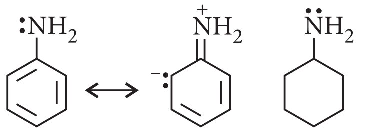


(white ppt.)

Ethylamine does not react with bromine water.

(ii) When heated with an alcoholic solution of KOH and $CHCl_3$, ethylamine gives foul smelling ethyl isocyanide. Dimethylamine does not give this test.

55. (i) Aniline is weaker base than cyclohexylamine because of resonance. Due to electromeric effect, the lone pair on nitrogen is attracted by benzene ring. Hence, donor tendency of $-\ddot{N}H_2$ group decreases. There is no resonance in cyclohexylamine. Electron repelling nature of cyclohexyl group further increases the donor property of NH_2 group. So, cyclohexylamine is a stronger base.

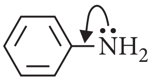


Aniline (Resonance structures)
Cyclohexylamine (No resonance)

(ii) The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which ammonia acts as a nucleophile by donating the electron pair on nitrogen atom to form primary amine as the initial product. Now, the primary amine can act as a nucleophile and combine with alkyl halide (if available) to give secondary amine and the reaction continues in the same way to form tertiary amine and finally quaternary ammonium salt. Thus, a mixture of products is formed and it is not possible to separate individual amines from the mixture.

$$R-X \xrightarrow[-HX]{NH_3} R-NH_2 \xrightarrow[-HX]{R-X} R_2NH \xrightarrow[-HX]{R-X} R_3N \xrightarrow{R-X} R_4N^+X^-$$

56. (i) Benzene ring in aromatic amines is highly activated. Due to the displacement of lone pair of nitrogen towards the ring. It results, increase in the electron density on the ring. This facilitates the electrophilic attack on the ring.



(ii) *Refer to answer 44.*

57. (i) *Refer to answer 55(i).*

(ii) Methylamine forms hydroxide ions when dissolved in water due to the following acid - base equilibrium.

$$CH_3{-}NH_2 + H_2O \rightleftharpoons CH_3{-}\overset{+}{N}H_3 + OH^-$$

These OH^- ions react with Fe^{3+} ions to form ferric hydroxide.

$$2Fe + 6OH^- \longrightarrow 2Fe(OH)_3$$

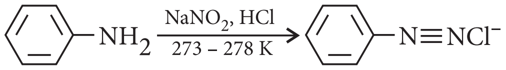
58. (i) *Refer to answer 54 (i).*

(ii) **Aniline and benzylamine :** Benzylamine reacts with nitrous acid to form a diazonium salt which is unstable at low temperature and decomposes with evolution of N_2 gas.

$$\underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} \xrightarrow[HCl]{NaNO_2} \underset{\text{Unstable}}{[C_6H_5CH_2{-}N^+{\equiv}NCl^-]}$$

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + N_2\uparrow + HCl \xleftarrow{H_2O}$$

Aniline reacts with HNO_2 to form benzene diazonium chloride which is stable at 273 - 278 K and hence does not evolve N_2 gas. It forms orange dye with 2-naphthol.



Aniline
Benzenediazonium chloride

59. (i) Methyl amine gives carbylamine test, *i.e.,* on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethyl amine does not give this test.

(ii) Aniline gives carbylamine test, *i.e.,* on treatment with alc. KOH and chloroform followed by heating it gives offensive odour of phenylisocyanide but *N*-methylaniline being secondary amine, does not show this test.

60. (i) *Refer to answer 35.*

(ii) *Refer to answer 48(ii).*

61. (i) *Refer to answer 42(ii).*

(ii) *Refer to answer 45(i).*

62. (i) *Refer to answer 54(i).*
(ii) *Refer to answer 59(i).*

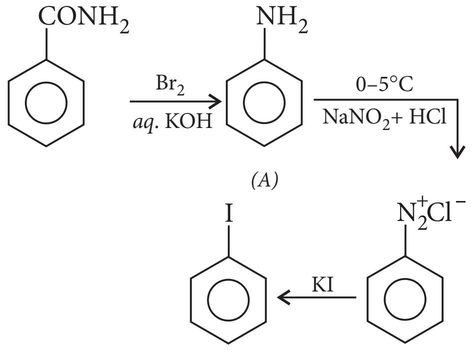
63. (i) Loss of proton from amines gives RNH^- ion whereas loss of proton from alcohol forms alkoxide ion. Since, O is more electronegative than N therefore, RO^- can accommodate the negative charge more easily than RN^-H. Further, O—H bond is more polar than N—H bond. Hence, amines are less acidic than alcohols.
(ii) In aromatic amines, the lone pair of electrons present on nitrogen takes part in resonance and hence, not available for donation. However, in aliphatic amines, the lone pair is available for donation. That's why aliphatic amines are more basic than aromatic amines.

64. (i) The increasing order of basic strength in water of the given amines and ammonia follows the following order :
$C_6H_5NH_2 < NH_3 < (C_2H_5)_3N < (C_2H_5)_2NH$
(ii) The increasing order of basic strength in gas phase of the given amines follows the order :
$CH_3NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$

65. (i) *Refer to answer 45(i).*
(ii) *Refer to answer 63(ii).*

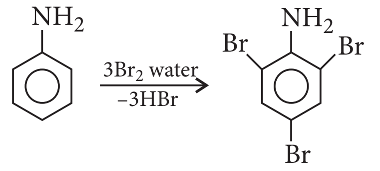
66. (i) *Refer to answer 54(i).*
(ii) *Refer to answer 59(ii).*

67. (i)



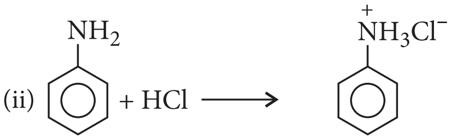
(ii)
$$\begin{tikzcd} CH_3{-}Cl \arrow[r, "KCN"] & \underset{(A)}{CH_3CN} \arrow[r, "LiAlH_4"] & \underset{(B)}{CH_3CH_2NH_2} \arrow[dll, "CHCl_3 + alc.\ KOH", "\Delta"'] \\ \underset{(C)}{CH_3CH_2NC} & & \end{tikzcd}$$

68. (i)



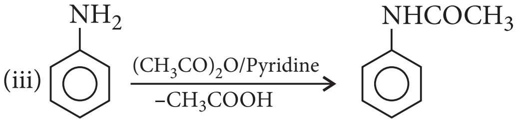
2,4,6-Tribromoaniline

(ii)



Anilinium chloride

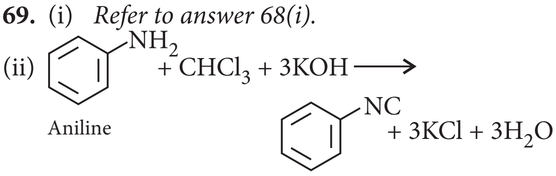
(iii)



Acetanilide

69. (i) *Refer to answer 68(i).*

(ii)



Aniline

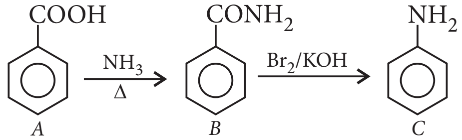
Phenyl isocyanide

(iii) *Refer to answer 68(ii).*

70. (i) *Refer to answer 49(i).*

(ii)
$$\begin{tikzcd} CH_3Cl \arrow[r, "KCN"] & \underset{A}{CH_3CN} \arrow[r, "LiAlH_4"] & \underset{B}{CH_3CH_2NH_2} \arrow[d, "HNO_2"', "273\ K"] \\ & & \underset{C}{CH_3CH_2OH} \end{tikzcd}$$

71. Formula of the compound '*C*' indicates it to be an amine. Since it is obtained by the reaction of Br_2 and KOH with the compound '*B*' so compound '*B*' can be an amide. As '*B*' is obtained from compound '*A*' by reaction with ammonia followed by heating so, compound '*A*' could be an aromatic acid. Formula of compound '*C*' shows it to be aniline, then '*B*' is benzamide and compound '*A*' is benzoic acid. The sequence of reactions can be written as follows :



72. (i)
$$\begin{tikzcd} CH_3Br \arrow[r, "KCN"] & \underset{(A)}{CH_3CN} \arrow[r, "LiAlH_4"] & \underset{(B)}{CH_3CH_2NH_2} \arrow[d, "273\ K"', "HNO_2"] \\ & & \underset{(C)}{CH_3CH_2OH} \end{tikzcd}$$

(ii)
$$\begin{tikzcd} CH_3COOH \arrow[r, "NH_3", "\Delta"'] & \underset{(A)}{CH_3CONH_2} \arrow[d, "Br_2 + KOH"] \\ \underset{(C)}{CH_3NC} & \underset{(B)}{CH_3NH_2} \arrow[l, "CHCl_3 + NaOH"'] \end{tikzcd}$$

73. (i) $A = CH_3CH_2CN$
$B = CH_3CH_2CH_2NH_2$
$C = CH_3CH_2CH_2OH$

(ii) *Refer to answer 72(ii).*

74. (i) *Refer to answer 42.*

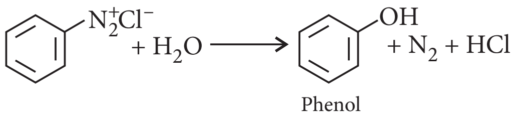
(ii) *Refer to answer 57(ii).*

(iii) *Refer to answer 45(i).*

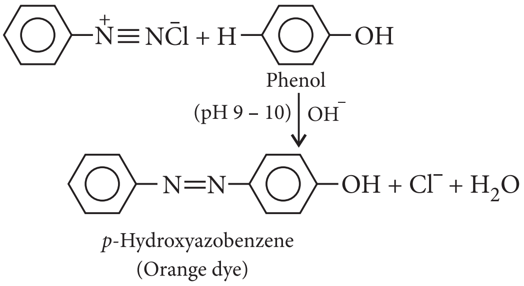
75. $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$

76. Diazotisation reaction.

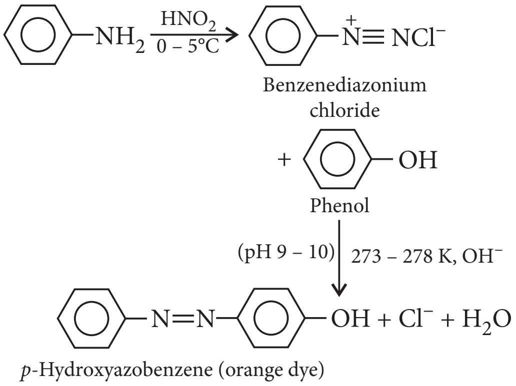
77.



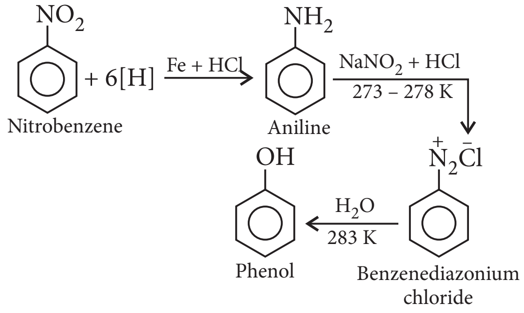
78. Diazonium salts react with aromatic amines in weakly acidic medium and phenols in weakly alkaline medium to form coloured compounds called azo dyes by coupling at *p*-position of amines or phenols.



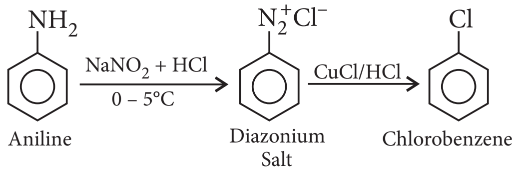
79.



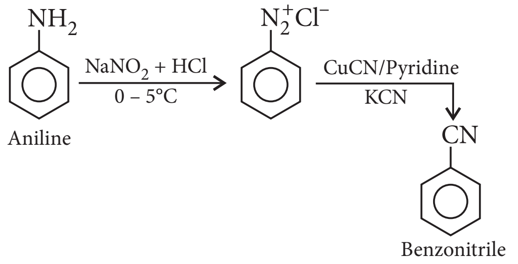
80.



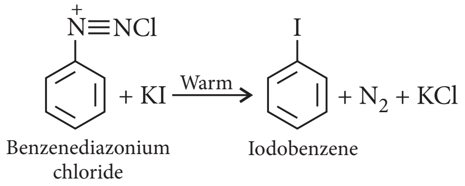
81.



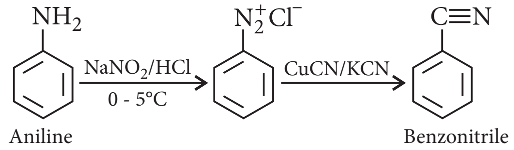
82.



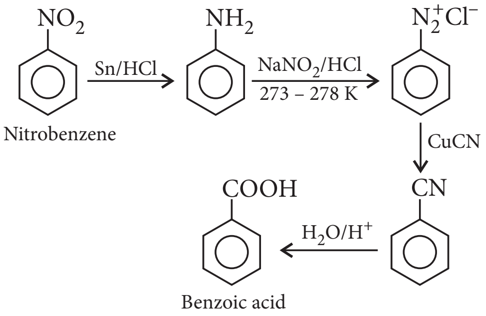
83.



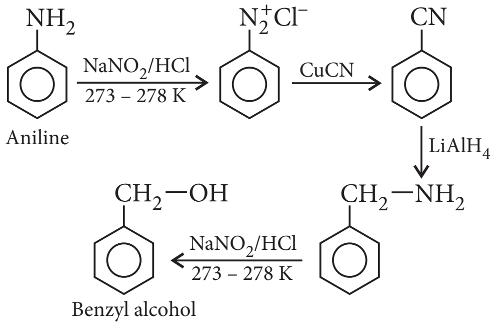
84.



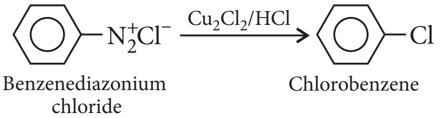
85. (i)



(ii)



86. (i) **Sandmeyer reaction :** By this reaction nulceophiles like Cl⁻, Br⁻, CN⁻ etc. can easily be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of Cu(I) ion.



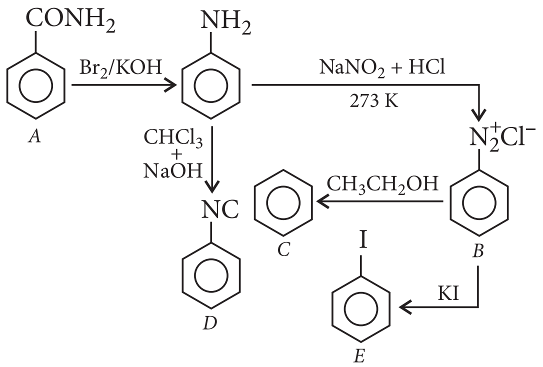
(ii) *Refer to answer 78.*

87. (i)

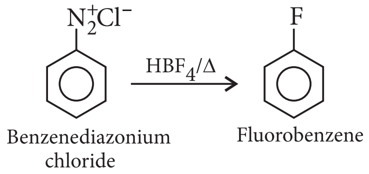
$$\begin{tikzcd} C_6H_5N_2^+Cl^- \arrow[r, "CuCN"] & \underset{(A)}{\underset{\text{Benzonitrile}}{C_6H_5CN}} \arrow[d, "H_2O/H^+"] \\ \underset{(C)}{\underset{\text{Benzamide}}{C_6H_5CONH_2}} & \underset{(B)}{\underset{\text{Benzoic acid}}{C_6H_5COOH}} \arrow[l, "NH_3", "\Delta"'] \end{tikzcd}$$

(ii) *Refer to answer 49(i).*

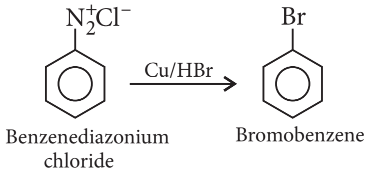
88.



89. (i) (a)



(b)



(ii) (a) *Refer to answer 49(i).*

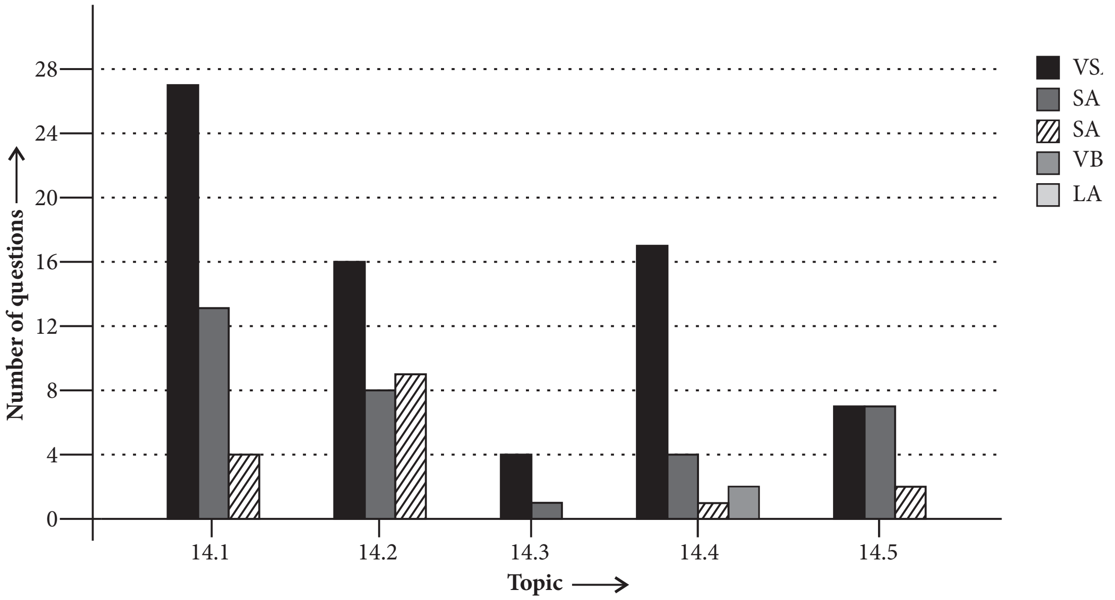
(b) *Refer to answer 70(ii).*

14

Biomolecules

14.1 Carbohydrates
14.2 Proteins
14.3 Enzymes
14.4 Vitamins
14.5 Nucleic Acids

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



- Maximum total weightage is of *Carbohydrates.*
- Maximum VSA type questions were asked from *Carbohydrates.*
- Maximum SA I and SA II type questions were asked from *Carbohydrates and Vitamins respectively.*

QUICK RECAP

CARBOHYDRATES

- **General formula :** $C_x(H_2O)_y$
- **Sugars or Saccharides :** They are optically active polyhydroxyaldehydes or ketones.

Classification :

Carbohydrates are classified as either reducing or non-reducing sugars :

Reducing sugars

- Free aldehydic or ketonic group.
- Reduce Fehling's solution and Tollens' reagent.
- *e.g.*, maltose and lactose.

Non-reducing sugars

- Do not have free aldehydic or ketonic group
- Do not reduce. Fehling's solution and Tollens' reagent.
- *e.g.*, Sucrose.

On the basis of their behaviour towards hydrolysis :

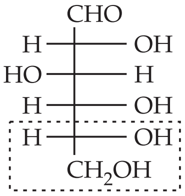
Carbohydrates

Monosaccharides	**Oligosaccharides**	**Polysaccharides**
Cannot be hydrolysed further. $(CH_2O)_n$, where $n = 3\text{-}7$ *e.g.*, glucose, fructose, ribose, etc.	Yield 2-10 monosaccharides on hydrolysis. $(C_6H_{10}O_5)_n$, where $n = 2\text{-}10$ *e.g.*, sucrose, maltose, etc.	Yield large number of monosaccharides on hydrolysis. $(C_6H_{10}O_5)_n$ where $n = 100\text{-}3000$ *e.g.*, starch, cellulose, etc.

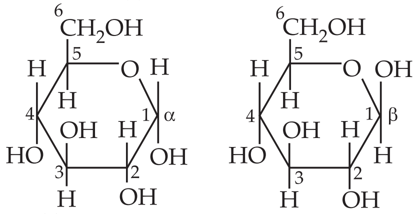
Monosaccharides :

Glucose ($C_6H_{12}O_6$) : An aldohexose as it contains six carbon atoms and aldehydic group.

– **Structure :**



Fischer projection of *D*-(+)-Glucose



α-*D*-(+)-Glucopyranose β-*D*-(+)-Glucopyranose

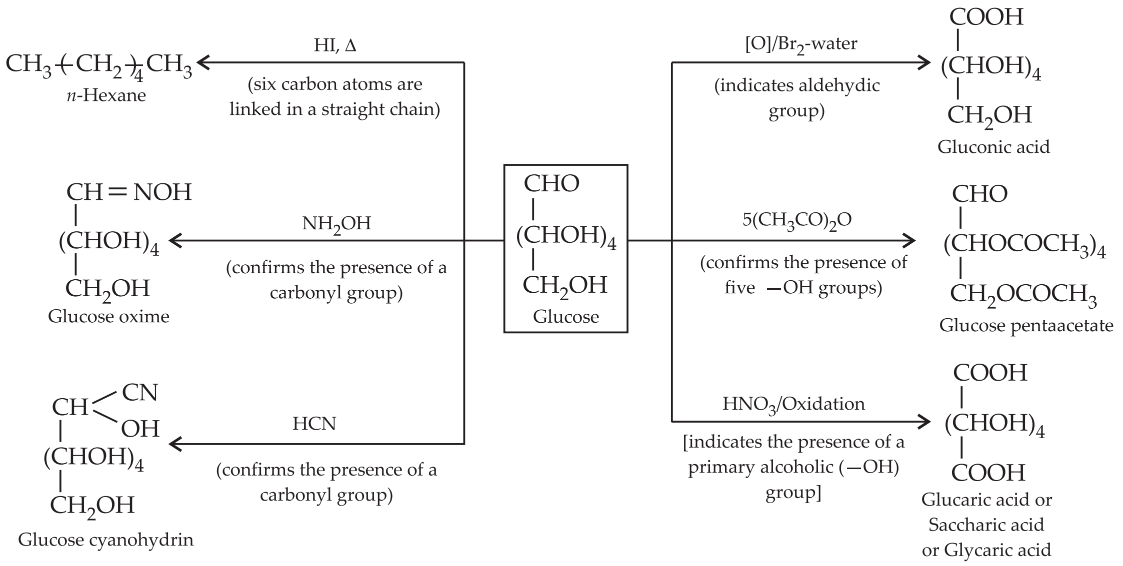
Haworth structures :
(Anomers)

– **Preparation :**

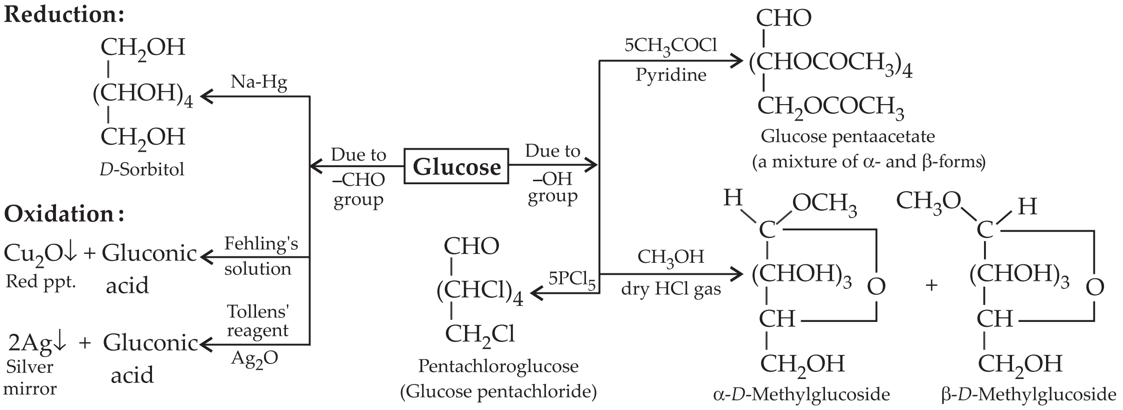
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \text{ (\textit{Laboratory method})}$$

$$\underset{\text{Starch or Cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{393 K, 2-3 atm}]{H^+/\Delta} \underset{\text{Glucose}}{nC_6H_{12}O_6} \text{ (\textit{Commercial method})}$$

– Glucose was assigned open chain structure on the basis of following evidences :

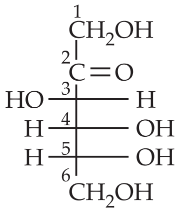


– **Chemical reactions :**

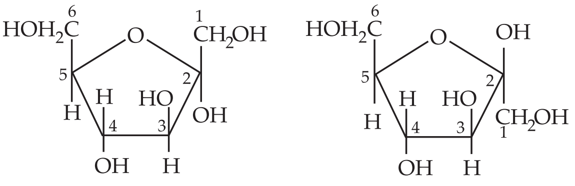


▶ **Fructose ($C_6H_{12}O_6$) :** A ketohexose as it contains six carbon atoms and ketonic group.

– **Structure :**



D-(–)-Fructose



α-D-(–)-Fructofuranose β-D-(–)-Fructofuranose

(Haworth Structures)

- **Mutarotation :** The change in specific rotation of an optically active compound with time to an equilibrium value is called *mutarotation*.

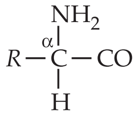
$$\underset{[\alpha]_D = +112^\circ}{\alpha\text{-}D\text{-Glucose}} \rightleftharpoons \underset{[\alpha]_D = +52.7^\circ}{\underset{\text{mixture}}{\text{Equilibrium}}} \rightleftharpoons \underset{[\alpha]_D = +19^\circ}{\beta\text{-}D\text{-Glucose}}$$

Disaccharides and Polysaccharides

Carbohydrate	Hydrolysis products	Linkage	Reducing property
Sucrose (Disaccharide)	α-*D*-Glucose and β-*D*-Fructose	C-1 (Glucose) and C-2(Fructose)	Non-reducing
Maltose (Disaccharide)	α-*D*-Glucose	C-1 (Glucose) and C-4 (glucose)	Reducing
Lactose (Disaccharide)	β-*D*-Galactose and β-*D*-Glucose	C-1 (Galactose) and C-4 (Glucose)	Reducing
Starch (Polysaccharide)	Amylose and amylopectin	Amylose (C-1 and C-4 glycosidic linkage betweeen α-D-Glucose) Amylopectin (C-1 and C-4 linkage between α-D-Glucose and branching occurs by C-1 and C-6 linkage)	Non-reducing
Cellulose (Polysaccharide)	β-*D*-Glucose	C-1(glucose) and C-4(glucose)	Non-reducing
Glycogen (Polysaccharide)	α-*D*-Glucose	C-1 (glucose) and C-4(glucose)	Non-reducing

PROTEINS

Proteins : They are the biomolecules of the living system made up of nitrogenous organic compounds by condensation polymerisation of α-amino acids.

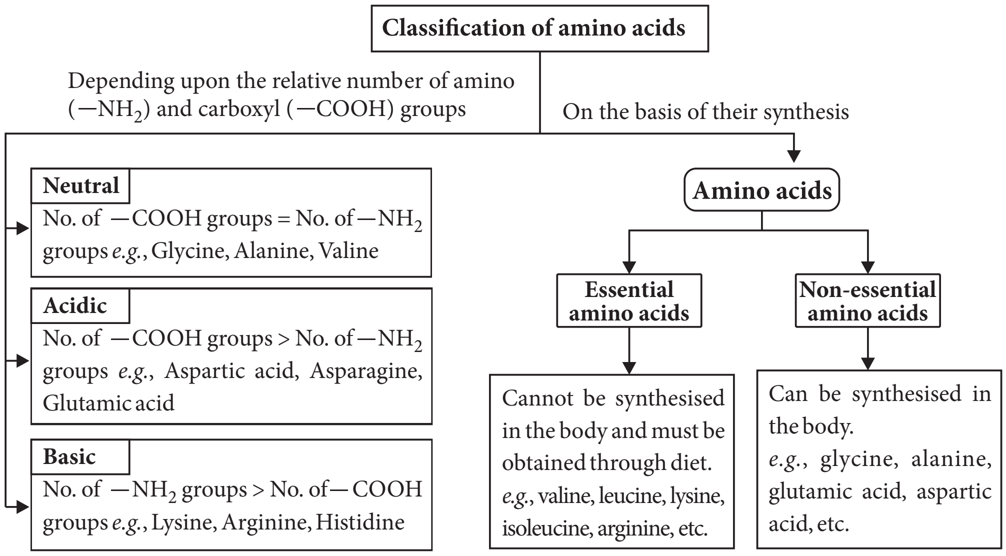


$$R-\overset{\overset{NH_2}{|}}{\underset{\underset{H}{|}}{C}}-COOH$$

(*R* = side chain)

α-Amino acid

Classification of Amino Acids :



Classification of amino acids

Depending upon the relative number of amino (—NH_2) and carboxyl (—COOH) groups

Neutral
No. of —COOH groups = No. of —NH_2 groups *e.g.*, Glycine, Alanine, Valine

Acidic
No. of —COOH groups > No. of —NH_2 groups *e.g.*, Aspartic acid, Asparagine, Glutamic acid

Basic
No. of —NH_2 groups > No. of — COOH groups *e.g.*, Lysine, Arginine, Histidine

On the basis of their synthesis

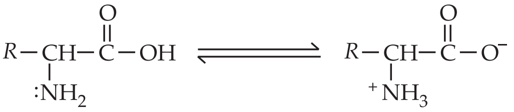
Amino acids

Essential amino acids
Cannot be synthesised in the body and must be obtained through diet. *e.g.*, valine, leucine, lysine, isoleucine, arginine, etc.

Non-essential amino acids
Can be synthesised in the body. *e.g.*, glycine, alanine, glutamic acid, aspartic acid, etc.

Properties :

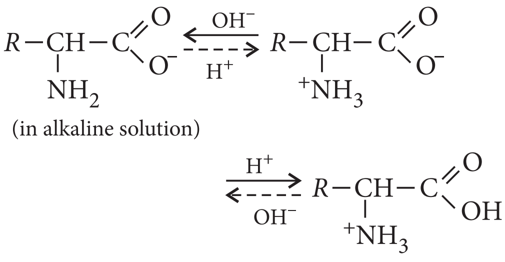
- In aqueous solution, the carboxylic group can lose a proton and amino group can accept a proton giving rise to a dipolar ion known as *zwitter ion*. This is neutral but contains both positive and negative charges.



$$R-\underset{\underset{:NH_2}{|}}{CH}-\overset{\overset{O}{||}}{C}-OH \rightleftharpoons R-\underset{\underset{^+NH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-O^-$$

Zwitter ion

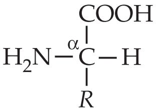
- Since these form salts with acids as well as with bases, their chemical reactions are similar to primary amines and carboxylic acids.



(in alkaline solution)

(in acidic solution)

- **Isoelectric point :** The pH at which dipolar ion (zwitter ion) exists as neutral ion, *i.e.*, +ve and –ve charge is equal and it does not migrate to either electrode, is called *isoelectric point*. The amino acids have least solubility in water at isoelectric point which helps in their separation.
- Except glycine, all other naturally occurring α-amino acids are optically active because they contain chiral, asymmetric carbon atom.
- They exist in both *D*- and *L*-forms. Most naturally occurring α-amino acids have *L*-configuration.

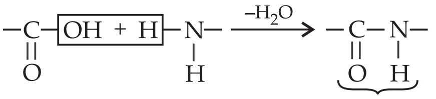


$$H_2N-\overset{\overset{COOH}{|}}{\underset{\underset{R}{|}}{C}}-H$$

L-Amino acid

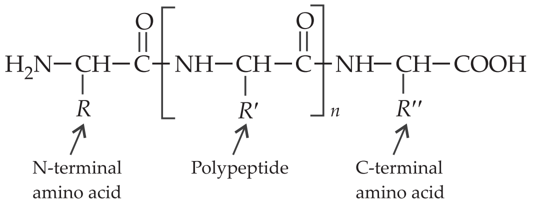
Peptides and their classification :

- **Peptide bond :** The bond formed between two amino acids by the elimination of a water molecule is called a *peptide linkage or bond.*



$$-\underset{\underset{O}{||}}{C}-\boxed{OH + H}-\underset{\underset{H}{|}}{N}- \xrightarrow{-H_2O} \underbrace{-\underset{\underset{O}{||}}{C}-\underset{\underset{H}{|}}{N}-}_{\text{Peptide bond}}$$

- The products formed by the linking of amino acids by peptide linkage are known as *peptides.*
- Peptides are further divided into *di*, *tri*, *tetra* depending upon the number of amino acids combined.
- **Oligopeptide :** It contains anywhere between 2-10 amino acids.
- **Polypeptides :** Structures with more than ten amino acids are known as *polypeptides*.



where R, R', R'' may be same or different.

- A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 u is called a *protein*.

Classification of proteins : On the basis of molecular structure, proteins are classified as :

Fibrous proteins

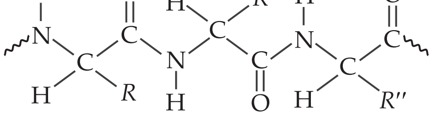
In fibrous proteins, polypeptide chains are parallel and are held together by hydrogen and disulphide bonds. These are insoluble in water, *e.g.*, keratin and myosin.

Globular proteins

Globular proteins results when the polypeptide chains coil around to give three dimensional spherical shape. These are soluble in water, e.g., insulin and albumins.

Structure :

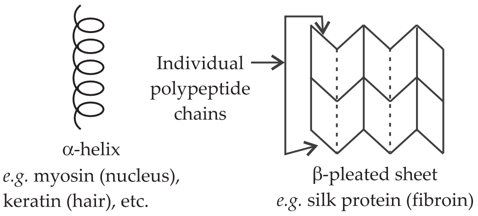
- **Primary structure :** It refers to the number and linear sequence of amino acids held together by peptide bonds.



Primary structure

- **Secondary structure:** It is due to folding or coiling of the peptide chain. It is mainly of two types :
  - α-**helix :** These coils are stabilized by hydrogen bonds between carbonyl oxygen of first amino acid to amide nitrogen of fourth amino acid.

- **β-pleated sheet structure :** β-pleated sheet structure is formed when hydrogen bonds are formed between the carbonyl oxygens and amide hydrogens of two or more adjacent polypeptide chains. The bonding in β-pleated sheet structure is intermolecular H-bonding. The structure is not planar but is slightly pleated. Silk fibroin is rich in β-pleated sheets.



α-helix
e.g. myosin (nucleus), keratin (hair), etc.

β-pleated sheet
e.g. silk protein (fibroin)

- **Tertiary structure :** It represents overall folding of the polypeptide chains, *i.e.*, further folding of the secondary structure and the bonds responsible for such interaction are hydrophobic interactions, hydrogen bonds, ionic interactions, van der Waals' forces and Disulphide bonds.
- **Quaternary structure :** The spatial arrange-ment of the subunits (two or more polypeptide chains) with respect to each other.

Denaturation of proteins :

- When a protein in its native form, is subjected to physical changes like change in temperature or chemical changes like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called *denaturation of protein*.
- The denaturation causes change in secondary and tertiary structures but primary structure remains intact *e.g.*, coagulation of egg white on boiling, curdling of milk, formation of cheese, when an acid is added to milk.

ENZYMES

The enzymes are *biocatalysts* produced by living cells which catalyse biochemical reactions in living organisms. Chemically, enzymes are naturally occurring simple or conjugated proteins. Some enzymes may be non-proteins also.

HORMONES

Hormones : They are the molecules that act as intercellular messangers and are poured directly in the blood stream by endocrine glands.

Types of hormones :

- **Steroids :** Estrogens and androgens
- **Polypeptides :** Insulin and endorphins
- **Amino acid derivatives :** Epinephrine and norepinephrine.

VITAMINS

Vitamins: These are complex organic molecules which cannot be produced by the body and must be supplied in small amounts in diet to carry out essential metabolic reactions which are required for normal growth and maintenance of the body.

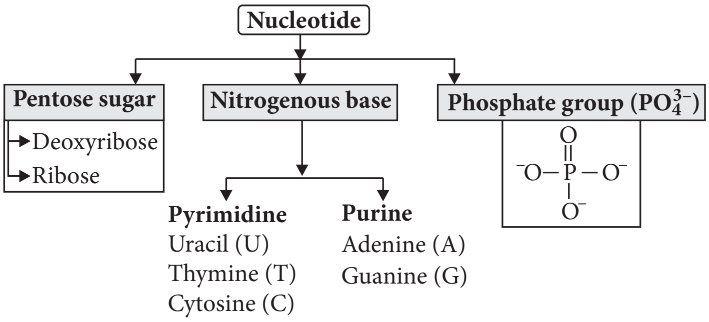
Classification :

- **Water soluble vitamins :** Soluble in water. Must be supplied regularly in diet as they are regularly excreted in urine (except vitamin B_{12}) *e.g.*, Vitamin– B_1, B_2, B_6, B_{12} and C.
- **Fat soluble vitamins:** Soluble in fat and oils. Stored in liver and adipose tissues *e.g.*, Vitamin – A, D, E and K.

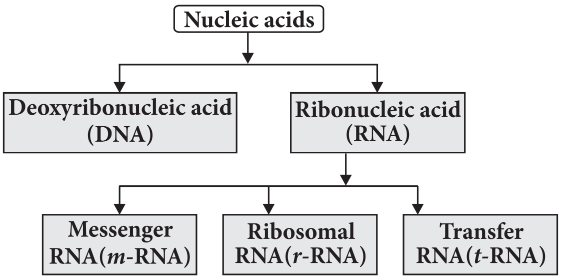
Deficiency of more than one vitamin in the body causes *avitaminosis* while excess intake of vitamins (A and D) may cause *hypervitaminoses.*

NUCLEIC ACIDS

Nucleic acids are the polymers of nucleotides present in nucleus of all living cells and play an important role in transmission of the hereditary characteristics and biosynthesis of proteins.



Types of nucleic acids :



Chargaff's rule : Amount of purine bases is always equal to that of pyrimidine bases. Purine base of one strand of DNA molecule pairs with pyrimidine base of the other strand. Adenine (A) pairs with thymine (T) through two H-bonds ($A = T$) and guanine (G) pairs with cytosine (C) through three H-bonds ($G \equiv C$).

In case of RNA, adenine (A) pairs with uracil (U), ($A = U$).

Replication : It is the process by which a single DNA molecule produces two identical copies of itself.

Protein synthesis : It occurs in two steps :

- **Transcription :** It is the process of synthesis of RNA.
- **Translation :** The synthesis of proteins occur in the cytoplasm of the cell. The *m*-RNA directs protein synthesis with the help of *r*-RNA and *t*-RNA.

Previous Years' CBSE Board Questions

14.1 Carbohydrates

VSA (1 mark)

1. Write the name of two monosaccharides obtained on hydrolysis of lactose sugar. *(Delhi 2016)*

2. Write the structural difference between starch and cellulose. *(AI 2016)*

3. Which one of the following is a disaccharide : Starch, Maltose, Fructose, Glucose? *(Delhi 2015)*

4. Write the product obtained when *D*-glucose reacts with $H_2N—OH$. *(AI 2015)*

5. Which one of the following is a monosaccharide : starch, maltose, fructose, cellulose *(Foregin 2015)*

6. Which of the two components of starch is water soluble? *(Delhi 2014)*

7. Write the product formed on reaction of *D*-glucose with Br_2 water. *(Delhi 2014)*

8. Write the product formed when glucose is treated with HI. *(Delhi 2014)*

9. Define the following term :
Anomers *(AI 2014, Foreign 2014)*

10. Define the following term :
Polysaccharides *(Foreign 2014)*

11. Define the following term :
Invert sugar *(Foreign 2014, Delhi 2010)*

12. What is a glycosidic linkage? *(Delhi 2013, 2009)*

13. Name two components of starch. *(Delhi 2013C)*

14. Write the structure of the product obtained when glucose is oxidised with nitric acid. *(AI 2012)*

15. Write a reaction which shows that all the carbon atoms in glucose are linked in a straight chain. *(AI 2012)*

16. State two functions of carbohydrates. *(AI 2012C)*

17. Explain what is meant by the following : pyranose structure of glucose? *(AI, Foreign 2011)*

18. What is meant by 'reducing sugars'? *(AI 2010)*

19. What are the products of hydrolysis of sucrose? *(AI 2010)*

20. Name of the expected products of hydrolysis of lactose. *(Delhi 2010C, 2009C)*

21. What is the structural feature characterising reducing sugar? *(Delhi 2009C)*

22. Describe the following, giving an example :
Glycosidic linkage *(AI 2008)*

SA I (2 marks)

23. Enumerate the reactions of glucose which cannot be explained by its open chain structures. *(Delhi 2014C, AI 2011C, 2010C, 2009C)*

24. Write any two reactions of glucose which cannot be explained by the open chain structure of glucose molecule. *(Delhi 2012)*

25. Write down the structures and names of the products formed when *D*-glucose is treated with (i) Hydroxylamine (ii) Acetic anhydride. *(AI 2012C)*

26. Write down the structures and names of the products formed when *D*-glucose is treated with
(i) Bromine water
(ii) Hydrogen Iodide (Prolonged heating) *(AI 2012C)*

27. What is essentially the difference between α-form and β-form of glucose? Explain. *(Delhi 2011)*

28. Write such reactions and facts about glucose which can not be explained by open chain structure. *(AI 2011)*

29. Name the products of hydrolysis of (i) sucrose and (ii) lactose. *(AI 2010, 2009)*

30. Name the products of hydrolysis of sucrose. Why is sucrose not a reducing sugar? *(Delhi 2010)*

31. What happens (write chemical equations) when *D*-glucose is treated with the following :
(i) HI
(ii) Bromine water *(AI 2010C)*

32. Answer the following question briefly :
How are carbohydrates classified? *(AI 2007)*

SA II (3 marks)

33. Define the following terms :
(i) Glycosidic linkage
(ii) Invert sugar
(iii) Oligosaccharides *(AI 2014)*

34. What is essentially the difference between α-glucose and β-glucose? What is meant by pyranose structure of glucose?

35. Mention the structural feature characterising reducing sugar. *(Delhi 2011C)*

36. What happens when *D*-glucose is treated with the following reagents :
(i) HI
(ii) Bromine water
(iii) HNO_3 *(AI 2008)*

37. Name the three major classes of carbohydrates & give an example of each of these classes. *(Delhi 2007)*

14.2 Proteins

VSA (1 mark)

38. Give one example each for fibrous protein and globular protein. *(AI 2016, Delhi 2014, AI 2013C)*

39. What is the difference between fibrous protein and globular protein? *(Delhi 2015)*

40. Amino acids show amphoteric behaviour. Why? *(AI 2015)*

41. What is the difference between acidic amino acids and basic amino acids? *(Foreign 2015)*

42. What type of linkage is responsible for the formation of proteins? *(Delhi, Foreign 2014)*

43. Define the following term :
Essential amino acids *(AI 2014)*

44. Define the following term :
Denaturation of proteins *(Foreign 2014)*

45. Define the following term :
Amino acids *(Foreign 2014)*

46. Define a 'Peptide linkage'. *(AI 2014C, 2011, Foreign 2011)*

47. Where does the water present in the egg go after boiling the egg? *(Delhi 2012C)*

48. Explain the following term :
Polypeptides *(Delhi 2010)*

SA I (2 marks)

49. Describe what you understand by primary structure and secondary structure of proteins? *(Delhi 2011)*

50. Explain what is meant by a peptide linkage. *(Delhi 2011)*

51. State what you understand by primary and secondary structure of proteins. *(Foreign 2011)*

52. Define the following terms in relation to proteins :
(i) Peptide bond
(ii) Denaturation of proteins *(Delhi 2008)*

53. Describe the following terms in reference of proteins :
(i) Primary structure
(ii) Denaturation *(AI 2008)*

54. What are essential and non-essential amino acids? Give one example of each type. *(AI 2008C)*

55. Mention the type of linkage responsible for the formation of the following :
(i) Primary structure of proteins
(ii) Cross-linkage of polypeptide chains
(iii) α-helix formation
(iv) β-sheet structure *(AI 2008C)*

56. Answer the following :
(i) What type of linkage is responsible for the primary structure of proteins?
(ii) Name the location where protein synthesis occurs in our body. *(Delhi 2007)*

SA II (3 marks)

57. Define the following terms as related to proteins :
(i) Peptide linkage
(ii) Primary structure
(iii) Denaturation *(AI 2015, 2014)*

58. What are essential and nonessential amino acids? Give two examples of each. *(AI 2014C, Delhi 2012C)*

59. **(a)** Give two differences between globular and fibrous proteins.
(b) What change occurs in the nature of egg protein on boiling? *(Delhi 2013C)*

60. Amino acids may be acidic, alkaline or neutral, How does this happen? What are essential and non-essential amino acids? Name one of each type. *(AI 2010)*

61. Differentiate between fibrous proteins and globular proteins. What is meant by the denaturation of a protein? *(AI 2010)*

62. (a) What type of bonding helps in stabilising of α-helix structure of proteins?
(b) Differentiate between globular and fibrous proteins. *(Delhi 2010C)*

63. What are proteins? State a difference between globular and fibrous proteins. *(AI 2007)*

14.3 Enzymes

VSA (1 mark)

64. Define the following term:
Enzymes *(Foreign 2014, AI 2007)*

65. What are enzymes? *(AI 2014C)*

66. What is meant by biocatalysts? *(Delhi 2012)*

SA I (2 marks)

67. List two characteristic features of enzymes. *(AI 2007)*

14.4 Vitamins

VSA (1 mark)

68. Why Vitamin C cannot be stored in our body? *(Delhi 2016)*

69. Write the name of vitamin whose deficiency causes bone deformities in children. *(Delhi 2015)*

70. Write the name of the vitamin whose deficiency causes bleeding of gums. *(Foreign 2015)*

71. Deficiency of which vitamin causes night-blindness? *(Delhi 2014)*

72. Deficiency of which vitamin causes rickets? *(Delhi 2014)*

73. Deficiency of which vitamin causes scurvy? *(Delhi 2014)*

74. Define the following term:
Vitamins *(Foregin 2014)*

75. Why are vitamin A and vitamin C essential for us? *(Delhi 2014C)*

76. Name the deficiency diseases resulting from lack of Vitamins A and E in the diet. *(Delhi 2013C)*

77. Name one of the water soluble vitamin which is powerful antioxidant. Give its one natural source. *(Delhi 2013C, AI 2012C)*

78. How are hormones and vitamins different in respect of their source and functions? *(AI 2013C)*

79. Name the only vitamin which can be synthesized in our body. Name the disease caused due to the deficiency of this vitamin. *(Delhi 2013C)*

80. Name the deficiency disease resulting from lack of vitamin A in the diet. *(Delhi 2011C)*

81. The deficiency of which vitamin causes the disease, 'pernicious anaemia'? *(AI 2011C)*

82. What are vitamins? Deficiency of which vitamin causes
(i) Pernicious anaemia?
(ii) Convulsions? *(AI 2010C)*

83. Name two water soluble vitamins, their sources and diseases caused due to their deficiency in diet. *(Delhi 2009)*

SA I (2 marks)

84. Name two fat soluble vitamins, their sources and the diseases caused due to their deficiency in diet. *(AI 2009)*

85. How are the vitamins classified? Mention the chief sources of vitamins A and C. *(AI 2008)*

86. B-complex is an often prescribed vitamin. What is complex about it and what is its usefulness? *(AI 2007)*

87. Answer the following questions briefly:
(i) What are the two good sources of vitamin A?
(ii) Why is vitamin C essential to us? Give its important sources. *(AI 2007)*

SA II (3 marks)

88. How are vitamins classified? Name the vitamin responsible for the coagulation of blood. *(Delhi 2015C)*

VBQ (3 marks)

89. After watching a programme on TV about the adverse effects of junk food and soft drinks on the health of school children, Sonali, a student of Class XII, discussed the issue with the school principal. Principal immediately instructed the canteen contractor to replace the fast food with the fibre and vitamins rich food like sprouts, salad, fruits etc. This decision was welcomed by the parents and the students.

After reading the above passage, answer the following questions:

(a) What values are expressed by Sonali and the Principal of the school?

(b) Give two examples of water-soluble vitamins. *(Delhi 2013)*

90. Shanti, a domestic helper of Mrs. Anuradha, fainted while mopping the floor. Mrs. Anuradha immediately took her to the nearby hospital where she was diagnosed to be severely 'anaemic'. The doctor prescribed an iron rich diet and multivitamins supplement to her. Mrs. Anuradha supported her financially to get the medicines. After a month, Shanti was diagnosed to be normal.

After reading the above passage, answer the following questions:

(i) What values are displayed by Mrs. Anuradha?

(ii) Name the vitamin whose dificiency causes 'pernicious anaemia'.

(iii) Give an example of a water soluble vitamin. *(AI 2013)*

14.5 Nucleic Acids

VSA (1 mark)

91. What is difference between a nucleoside and nucleotide? *(Delhi 2016, 2014C)*

92. What type of linkage is present in nucleic acids? *(AI 2016)*

93. Name of the base that is found in nucleotide of RNA only. *(Delhi 2014)*

94. Define the following term:
Nucleoside *(Foregin 2014)*

95. Mention one important function of nucleic acids in our body. *(AI 2013C)*

96. Name of the purines present in DNA. *(AI 2007)*

SA I (2 marks)

97. Write the structural and functional difference between DNA and RNA. *(Delhi 2013C)*

98. Write the main structural difference between DNA and RNA. Of the two bases, thymine and uracil, which one is present in DNA? *(Delhi 2012)*

99. Name the bases present in RNA. Which one of these is not present in DNA? *(Delhi 2011)*

100. Write the main structural difference between DNA and RNA. Of the four bases, name those which are common to both DNA and RNA. *(AI 2011)*

101. Name the four bases present in DNA. Which one of these is not present in RNA? *(AI 2009)*

102. (a) What is the structural difference between a nucleoside and a nucleotide?

(b) The two strands in DNA are not identical but are complementary. Explain. *(Delhi 2009C)*

103. When RNA is hydrolysed, there is no relationship among the quantities of different bases formed. What does this fact suggest about the structure of RNA? *(AI 2008C)*

SA II (3 marks)

104. What are the different types of RNA found in cells of organisms? State the functions of each type. *(Delhi 2012C)*

105. (a) Write the important structural difference between DNA and RNA.

(b) Mention the names of the bases produced on hydrolysis of DNA. *(AI 2009C)*

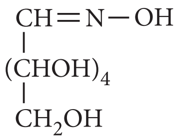
Detailed Solutions

1. Lactose on hydrolysis gives β-*D*-glucose and β-*D*-galactose.

2. The basic structural difference between starch and cellulose is of linkage between the glucose units. In starch, there is α-*D*-glycosidic linkage. Both the components of starch-amylose and amylopectin are polymer of α-*D*-glucose. On the other hand, cellulose is a linear polymer of β-*D*-glucose in which C_1 of one glucose unit is connected to C_4 of the other through β-*D*-glycosidic linkage.

3. Maltose is a disaccharide as it consists of two α-*D*-glucose units.

4. *D*-Glucose reacts with $H_2N{-}OH$ to give glucose oxime.

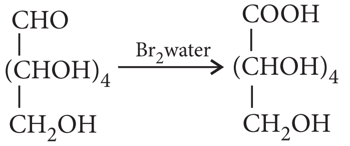


$$\begin{array}{l} CH{=}N{-}OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

5. Fructose is a monosaccharide because it cannot be hydrolysed to simpler polyhydroxy aldehydes or ketones.

6. Amylose is water soluble and amylopectin is insoluble in water.

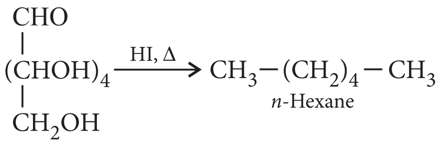
7. *D* - Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with bromine water.



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{Br_2\,water} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

D-Glucose Gluconic acid

8. On prolonged heating with HI, *D*-Glucose forms *n*-hexane.

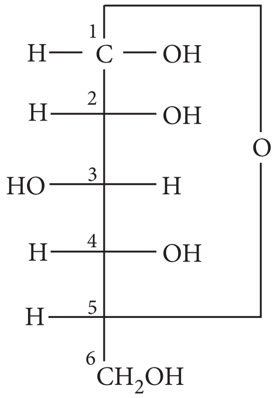


$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{HI,\ \Delta} CH_3{-}(CH_2)_4{-}CH_3$$

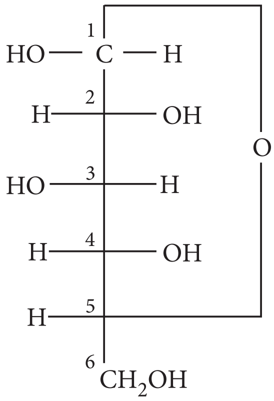
n-Hexane

D-Glucose

9. The pair of stereoisomers which differ only in the configuration of the hydroxyl group at C_1 are called anomers.



α-*D*-(+) Glucose

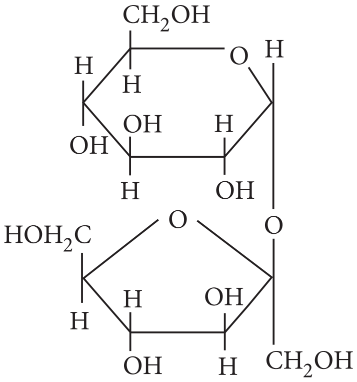


β-*D*-(+) Glucose

10. Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides.

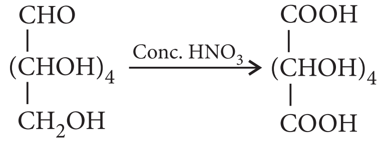
11. An equimolar mixture of glucose and fructose, obtained by hydrolysis of sucrose in presence of an acid or the enzyme invertase is called invert sugar.

12. The two monosaccharides are joined together by an oxide linkage formed by the loss of water molecule. Such linkage is called glycosidic linkage.



13. Amylose and amylopectin are the two components of starch.

14. On oxidation with nitric acid, *D* - glucose yields saccharic acid.



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{Conc.\ HNO_3} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{array}$$

D - Glucose *D* - Saccharic acid

15. Glucose when heated with red P and HI gives *n*-hexane.

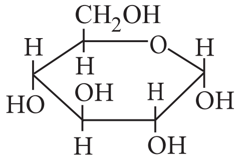
$$C_6H_{12}O_6 \xrightarrow[\Delta]{\text{Red P-HI}} \underset{n\text{-Hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$

It indicates presence of straight chain of six carbon atoms in glucose.

16. (i) Carbohydrates act as storage molecules as starch in plants and glycogen in animals.

(ii) They act as constituent of cell membrane.

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



α-*D*-(+)-Glucopyranose

18. Carbohydrates which reduce Tollen's reagent are reducing sugars. All monosaccharides, aldoses or ketoses are reducing sugars.

19. Glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

20. *Refer to answer 1.*

21. The reducing sugars have free aldehydic or ketonic groups.

22. *Refer to answer 12.*

23. The following reactions of *D*-glucose cannot be explained on the basis of its open chain structure :

(i) *D*-Glucose does not react with sodium bisulphite ($NaHSO_3$).

(ii) It does not give 2, 4-DNP test and Schiff's test.

(iii) The pentaacetate of *D*-glucose does not react with hydroxylamine.

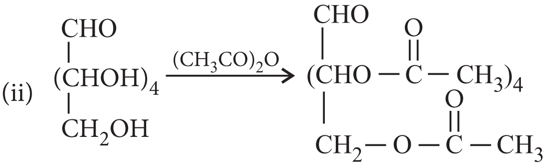
(iv) *D*-Glucose shows the phenomenon of mutarotation, *i.e.*, when its aqueous solution is kept for sometime its optical activity changes.

(v) On reaction with 1 mole of methanol, it yield two monomethyl derivatives which are known as methyl α-*D*-glucoside and methyl-β-*D*-glucoside.

24. *Refer to answer 23.*

25. (i) *Refer to answer 4.*

(ii)



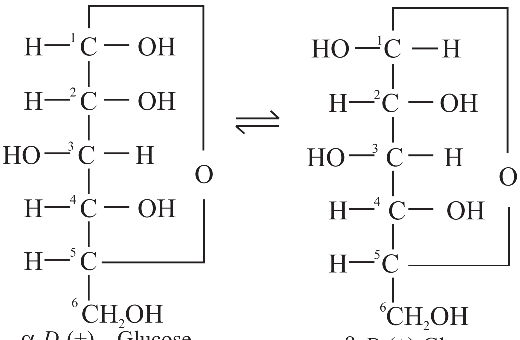
$$\begin{array}{c}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow{(CH_3CO)_2O} \begin{array}{l}CHO\\ |\\ (CHO-\overset{\overset{O}{\|}}{C}-CH_3)_4\\ |\\ CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3\end{array}$$

Glucose pentaacetate

26. (i) *Refer to answer 7.*

(ii) *Refer to answer 8.*

27. In α-*D* Glucose, the –OH group at C1 is towards right whereas in β-glucose, the –OH group at C1 is towards left. Such a pair of stereoisomers which differ in the configuration only at C1 are called anomers.



α-*D*-(+) – Glucose β-*D*-(+)-Glucose

28. *Refer to answer 23.*

29. (i) *Refer to answer 19.*

(ii) *Refer to answer 1.*

30. (i) *Refer to answer 19.*

Sucrose is not a reducing sugar because reducing groups of glucose and fructose are involved in glycosidic bond formation.

31. (i) *Refer to answer 8.*

(ii) *Refer to answer 7.*

32. On the basis of hydrolysis, carbohydrates can be divided in three major classes :

(i) **Monosaccharides :** These cannot be hydrolysed into simpler molecules. These are further classified as aldoses and ketoses.

(ii) **Oligosaccharides :** These are the carbohydrates which on hydrolysis give 2 - 10 monosaccharides. For example, sucrose, lactose, maltose, etc.

(iii) **Polysaccharides :** These are high molecular mass carbohydrates which give many molecules of monosaccharides on hydrolysis. For example starch and cellulose.

33. (i) *Refer to answer 12.*
(ii) *Refer to answer 11*
(iii) *Refer to answer 32 (ii)*

34. *Refer to answers 27 and 17.*

35. Reducing sugar : The sugars which reduce Fehling's solution and Tollen's reagent are called reducing sugars. For example, all monosaccharides containing free $-CHO$ or $-\overset{|}{C}=O$ group are reducing sugars.

36. (i) *Refer to answer 8.*
(ii) *Refer to answer 7.*
(iii) *Refer to answer 14.*

37. *Refer to answer 32.*

38. Globular protein – Insulin
Fibrous protein – Keratin

39. Characteristic differences between globular and fibrous proteins can be given as :

S. No.	Globular proteins	Fibrous proteins
1.	These are cross-linked proteins and are condensation product of acidic and basic amino acids.	These are linear condensation polymer.
2.	These are soluble in water, mineral acids and bases.	These are insoluble in water but soluble in strong acids and bases.
3.	These proteins have three dimensional folded structure. These are stabilised by internal hydrogen bonding. *e.g.*, egg albumin, enzymes.	These are linear polymers held together by intermolecular hydrogen bonds. *e.g.*, hair, silk.

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

41. Acidic amino acids are those which contain more number of carboxyl groups as compared to amino groups whereas basic amino acids are those which contains more number of amino groups than carboxyl groups.

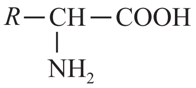
42. Peptide linkage.

43. **Essential amino acids :** Amino acids which cannot be synthesized in the body and must be obtained through diet are known as essential amino acids. *e.g.*, valine, leucine, etc.

44. **Denaturation :** The loss of biological activity of a protein by changing the pH, temperature or by adding some salt due to disruption of the native structure of protein is called denaturation.

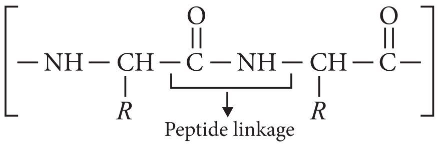
During denaturation secondary and tertiary structure of protein is destroyed but primary structure remains intact.

45. Organic compounds containing both amino (— NH_2) and carboxy (— COOH) functional groups are called amino acids.



$$R-\underset{\substack{|\\ NH_2}}{CH}-COOH$$

46. Proteins are the polymers of α-amino acids linked by amide formation between carboxyl and amino group. This is called peptide linkage or peptide bond *e.g.*,



$$\left[-NH-\underset{\substack{|\\ R}}{CH}-\underbrace{\overset{\substack{O\\ \|}}{C}-NH}_{\text{Peptide linkage}}-\underset{\substack{|\\ R}}{CH}-\overset{\substack{O\\ \|}}{C}-\right]$$

47. An egg contains a soluble globular protein called allumin which is present in the white part. On boiling, denaturation (loss of biological activity) of this protein takes place which results in the formation of insoluble fibrous proteins. The water molecules are utilized in this process.

48. Polypeptides are the macromolecules formed by combination of 10 or more amino acids.

49. **Primary structure :** The specific sequence in which the various amino acids present in a protein are linked to one another is called its primary structure. Any change in the primary structure creates a different protein.

Secondary structure : The conformation of the polypeptide chain is known as secondary structure. The two types of secondary structure are α-helix and β-pleated sheet structure.

In α-helix structure, the polypeptide chain forms all the possible hydrogen bonds by twisting into a right handed screw (helix) with the — NH groups of each amino acid residue hydrogen bonded to the $>C=O$ group of an adjacent turn of the helix. In β-pleated sheet structure, all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds.

50. (i) *Refer to answer 46.*

51. *Refer to answer 49.*

52. (i) *Refer to answer 46.*
(ii) *Refer to answer 44.*

53. (i) *Refer to answer 49.*
(i) *Refer to answer 44.*

54. Amino acids which cannot be synthesised in the body and must be obtained through diet are known as essential amino acids, *e.g.*, valine and leucine. There are ten essential amino acids. Amino acids which can be synthesised in the body are known as non-essential amino acids, *e.g.*, alanine and glutamic acids.

55.

(i)	Primary structure of protein	– Peptide bond (linkage)
(ii)	Cross linkage of polypeptide chain	– Hydrogen bonds, – disulphide linkage, electrostatic force of attraction
(iii)	α-helix formation	– Hydrogen bond
(iv)	β-sheet structure	– Intermolecular hydrogen bonds

56. (i) *Refer to answer 42.*
(ii) Protein synthesis takes place in cytoplasm.

57. (i) *Refer to answer 46.*
(ii) *Refer to answer 49.*
(iii) *Refer to answer 44.*

58. *Refer to answer 54.*

59. (a) *Refer to answer 39.*
(b) Protein is denatured and its biological activity is lost.

60. Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecules.
(a) Equal number of amino and carboxyl groups makes it neutral (b) more number of amino groups than carboxyl groups make it basic and (c) more carboxyl groups as compared to amino groups make it acidic.
Refer to answer 54.

61. *Refer to answers 39 and 44.*

62. (a) Hydrogen bonding
(b) *Refer to answer 39.*

63. Macromolecules formed by the combination of 100-1000 amino acid groups in a proper conformation are called proteins.
Refer to answer 39.

64. Enzymes : Most of the chemical reactions which occur in living systems process at very slow rates under mild condition of temperature and pH. These reactions are catalysed by a group of biomolecules called enzymes.

65. *Refer to answer 64.*

66. Substances which catalyse chemical reactions taking place in living organisms are called biocatalysts. *e.g.*, enzymes

67. (i) Enzymges are highly specific for a particular reaction and for a particular substrate.
(ii) Very small amount of enzyme is required for the process of a reaction.

68. Vitamin C is soluble in water and regularly excreted in urine and hence cannot be stored in body.

69. Vitamin D

70. Vitamin C

71. Vitamin A

72. Vitamin D

73. Vitamin C

74. Organic compounds required in the diet in small amounts to perform specific biological functions for normal maintainance of optimum growth and health of the organism are called vitamins.

75. The deficiency of vitamin A leads to xerophthalmia and night blindness. The deficiency of vitamin C leads to scurvy.

76. Vitamin – A : Night blindness
Vitamin E : Muscular weakness.

77. Vitamin C is water soluble and powerful antioxidant. Natural source of vitamin C is amla.

78.

	Hormones	**Vitamins**
(i)	The biomolecules which transfer information from one group of cell to distant tissue or organ.	These are essential dietary factors required by an organism in minute quantities.
(ii)	They are produced in the body in ductless glands.	They are supplied to the body from the food eaten.

79. Vitamin D
Disease caused due to deficiency of Vitamin D is rickets.

80. *Refer to answer 76.*

81. Vitamin B_{12}

82. *Refer to answer 74.*
(i) *Refer to answer 81.*
(ii) Vitamin B_6

83. Examples of water soluble vitamins :
Vitamin B and vitamin C.

Name of vitamins	**Source**	**Deficiency diseases**
Vitamin B_1	Yeast, milk, green vegetables, cereals etc.	Beri beri
Vitamin C	Citrus fruits, *amla*, and leafy vegetables.	Scurvy (bleeding gums)

84. Examples of fat soluble vitamins are vitamin A and D.

Name of vitamins	**Source**	**Deficiency diseases**
Vitamin A	Fish liver oil, carrots, butter, milk	Night blindness
Vitamin D	Fish and egg yolk	Rickets and osteomalacia

85. Vitamins are classified into two groups depending upon their solubility in water or fat.
(i) Fat soluble vitamins.
(ii) Water soluble vitamins.

Sources of vitamin A : Fish, liver oil, carrots, butter and milk.

Sources of vitamin C : Citrus fruits, amla and green leafy vegetables.

86. B-complex is a group of vitamins which contains vitamins B_1, B_2, B_6, B_{12}, biotin, folic acid, pantothenic acid and nicotinic acid. It is required to release energy from food and to promote healthy skin and muscles. Its deficiency causes beri beri and pernicious anaemia.

87. (i) Milk and butter are two good sources of vitamin A.
(ii) *Refer to answer 84.*

88. *Refer to answer 85.*
Vitamin K is responsible for the coagulation of blood.

89. (a) Awareness and social thinking
(b) Vitamin B complex and vitamin C.

90. (i) Humanitarian (kindness and caring)
(ii) *Refer to answer 81.*
(iii) *Refer to answer 83.*

91. Nucleoside contains pentose sugar, and base whereas nucleotide contains pentose sugar, base as well as phosphate group.
Nucleoside = Base + Sugar
Nucleotide = Base + Sugar + Phosphate.

92. Ester linkage

93. Uracil

94. *Refer to answer 91.*

95. DNA is reserve of genetic information and responsible for heredity transmission.

96. Adenine and guanine

97. **Structural differences between DNA and RNA**
(i) The sugar in DNA is deoxyribose while that in RNA is ribose.
(ii) DNA has a double-stranded helical structure, while RNA has a single-stranded helical structure.

Functional differences between DNA and RNA
(i) DNA is the chemical basis of heredity and is responsible for maintaining the identity of different species.
(ii) RNA molecules are responsible for protein synthesis but the message for the synthesis of a particular protein is present in DNA.

98. *Refer to answer 97.*
In DNA, thymine is present.

99. The bases present in RNA are adenine (A), guanine (G) cytosine (C) and Uracil (U).
Uracil is not present in DNA

100. *Refer to answer 97* (Structural difference).
Common bases in DNA and RNA are adenine, guanine and cytosine.

101. DNA contains four bases viz adenine (A) guanine (G), cytosine (C), and thymine (T). RNA also contains four bases but thymine is not present in RNA.

102. (a) *Refer to answer 91.*
(b) DNA is a double helix in which the two strands of DNA are held by the hydrogen bonds between the bases on the two strands. Thymine (T) pairs with adenine through two hydrogen bonds and cytosine (C) pairs with guanine (G) through three H–bonds. Hence, the two strands of DNA are complementary to each other.

103. When a RNA molecule is hydrolysed then there is no relationship between the quantities of four bases viz. adenine (A), guanine (G), cytosine (C), and uracil (U). This fact suggests that RNA has single stranded structure.

104. RNA are of three types :

(i) **Messenger RNA (*m*-RNA) :** Function as messenger carrying the information in a gene to the protein synthesizing machinery.

Transfer RNA (*t*-RNA) : They transfer the amino acids from cytoplasm to the protein synthesizing machinery.

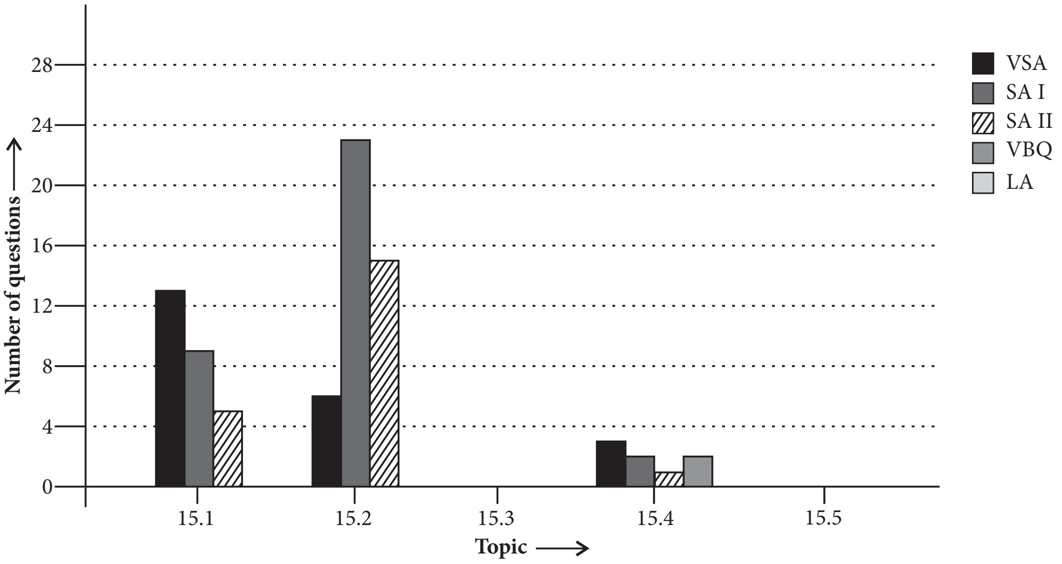
(ii) **Ribosomal RNA (*r*RNA) :** They associates with a set of proteins to form ribosomes. These complex structures, which physically move among an *m*RNA molecule, catalyze the assembly of amino acids into protein chains. They also bind *t*-RNAs and various molecules necessary for protein synthesis.

105. (a) *Refer to answer 97* (Structural difference).
(b) DNA an hydrolysis gives pentose sugar, Phosphoric acid and nitrogen containing heterocyclic bases *viz*. adenine, guanine, cytosine and thymine.

15 Polymers

15.1 Classification of Polymers
15.2 Types of Polymerisation
15.3 Molecular Mass of Polymers
15.4 Biodegradable Polymers
15.5 Polymers of Commercial Importance

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)

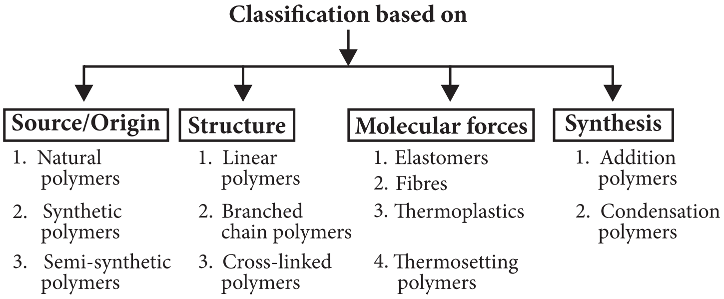


- Maximum total weightage is of *Types of Polymerisation.*
- Maximum VSA type questions were asked from *Classification of Polymers.*
- Maximum SA I and SA II type questions were asked from *Types of Polymerisation.*

QUICK RECAP

- **Polymers :** They are macro-sized, high molecular mass compounds, formed by the combination of a large number of simple molecules or repeating units.
- **Monomers :** These simple molecules or repeating units which combine to give polymers are called *monomers*.
- The process of joining together of a large number of the monomers is termed as *polymerization*.
- A polymer formed from one type of monomers is called *homopolymer*, *e.g.*, polyethene, PVC, polyacrylonitrile, etc.

- A polymer formed from two or more different monomers is called *copolymer e.g.,* Nylon-6,6, polyester, bakelite, etc.
- **Classification of polymers :**



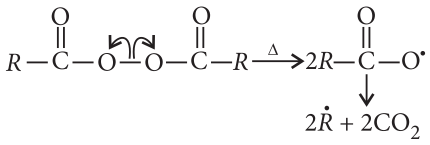
- **Natural polymers :** These are substances of natural origin and are mainly found in plants and animals, *e.g.*, starch, cellulose, proteins, etc.
- **Synthetic polymers :** These polymers are prepared in the laboratories, they are also called *man-made polymers*, *e.g.*, teflon, terylene, synthetic rubber, etc.
- **Semi-synthetic polymers :** They are mostly derived from naturally occurring polymers by chemical modifications, *e.g.*, vulcanised rubber, cellulose nitrate, etc.
- **Linear polymers :** In these polymers monomers are linked together to form linear chains, *e.g.*, polyethene, polyester, nylon, etc.
- **Branched chain polymers :** In these polymers the monomers are joined to form long chains or branches of different lengths, *e.g.*, glycogen, starch, etc.
- **Cross-linked polymers :** In these polymers the monomer units are cross-linked together to form a three-dimensional network polymers, *e.g.*, bakelite, melamine, etc.
- **Elastomers :** These are the polymers having very weak intermolecular forces between the polymer chains. The weak forces permit the polymer to be stretched. Elastomers, thus, possess elastic character, *e.g.*, vulcanised rubber.
- **Fibres :** These are the polymers which have strong intermolecular forces between the chains. These are either hydrogen bonds or dipole-dipole interactions, *e.g.*, Nylon-6,6.

- The number of times a monomer unit is repeated in a polymer, is called its *degree of polymerization*.

- **Thermoplastics :** These are the polymers in which the intermolecular forces of attraction are intermediate between those of elastomers and fibres. These polymers do not have any cross-links between the chains, they can be easily mouled on heating, *i.e.*, thermoplastics soften on heating and become hard on cooling, *e.g.*, polythene, polystyrene, PVC, etc.
- **Thermosetting polymers :** They have extensive cross-links formed between polymer chains on heating. They undergo a permanent change on heating, *e.g.*, bakelite, melamine, etc.
- **Addition polymerization :** A polymer formed by direct addition of repeated monomers without the elimination of by-product molecules is called *addition polymer* and the phenomenon is known as *addition polymerization*, *e.g.*, polythene.
- **Condensation polymerization :** A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, alcohol, etc. is called *condensation polymer* and the phenomenon is known as *condensation polymerization*, *e.g.*, Terylene.

- **Types of polymerisation reactions :**
- **Addition or chain growth polymerisation :** Depending upon the reactive particles formed, it is of three types :
  - **Free radical polymerisation :** It takes place in three steps :

- **Chain initiating step :** This step requires initiators which are free radicals produced on heating *e.g.*, benzoyl peroxide, acetyl peroxide, dioxygen, etc.



$$R-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-R \xrightarrow{\Delta} 2R-\overset{\overset{O}{\|}}{C}-O^{\bullet}$$

$$\downarrow$$

$$2\dot{R} + 2CO_2$$

$$\dot{R} + \dot{C}H_2=CH_2 \rightarrow R-CH_2-\dot{C}H_2$$

- **Chain propagating step :** The free radical thus formed adds to the double bond of the monomer to form larger free readical.

$$R CH_2\dot{C}H_2 \xrightarrow{CH_2=CH_2} R CH_2CH_2CH_2\dot{C}H_2$$

$$\downarrow$$

$$R\!-\!(CH_2-CH_2)_n CH_2-\dot{C}H_2$$

- **Chain terminating step :** The growing free radical chain consumes free radicals either by combination or by disproportionation to get polymer.

- **Combination :**

$$2R\!-\!(CH_2-CH_2)_n CH_2-\dot{C}H_2 \longrightarrow$$

$$R\!-\!(CH_2CH_2)_n CH_2CH_2CH_2CH_2-(CH_2CH_2)_n R$$

- **Disproporation :**

$$2R\!-\!(CH_2-CH_2)_n CH_2-\dot{C}H_2 \longrightarrow$$

$$\underset{\text{Alkene}}{R\!-\!(CH_2-CH_2)_n CH=CH_2}$$

$$+ \underset{\text{Alkane}}{R\!-\!(CH_2-CH_2)_n CH_2-CH_3}$$

  - **Cationic addition polymerisation :** Initiated by the use of strong Lewis acids such as HF, $AlCl_3$, H_2SO_4, etc.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

$$H^+ + CH_2=CH_2 \longrightarrow CH_3-\overset{+}{C}H_2$$

e.g., polyvinyl ether, polyisobutylene, polystyrene, etc.

  - **Anionic addition polymerisation :** Initiated by strong bases such as $NaNH_2$, C_4H_9Li and Grignard reagent, etc.

$$B: + CH_2=CH_2 \longrightarrow \underset{\text{carbanion}}{B-CH_2-CH_2^-}$$

e.g. polyacrylonitrile, polyvinyl chloride and polymethyl methacrylate, etc.

▶ **Condensation or step growth polymerisation :** In this type of polymerisation reactions monomers are bifunctional and form bond with the loss of simple molecule of water, alcohol, ammonia, etc.

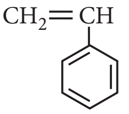
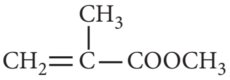
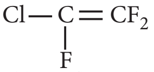
Differences between LDPE and HDPE :

Polyethylene

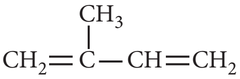
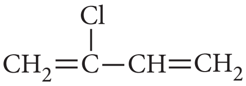
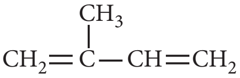
Low density polyethylene (LDPE)	**High density polyethylene (HDPE)**
– Addition or chain growth homopolymer.	– Linear addition or chain growth homopolymer
– By heating ethylene under high pressure (1000-2000 atm) at temperature of 350-570 K in presence of traces of oxygen or peroxide.	– By heating ethylene at 333-343 K and 6-7 atm in presence of Ziegler-Natta catalyst.
– Free radical addition polymerisation.	– Coordination polymerisation
– Highly branched polymer.	– Linear molecules, closely packed.
– Low density (0.92 g/cm^3), low melting point (384 K)	– High density (0.97 g/cm^3), high melting point (403 K).
– Transparent, moderate tensile strength.	– Translucent
– Chemically inert, tough but flexible.	– Chemically inert, quite harder, greater tensile strength.
– Used for packing, insulation and manufacturing squeeze bottles, pipes, toys, etc.	– Used for manufacturing containers, housewares and pipes, etc.

Preparation of some important addition homopolymers :

Polyolefins

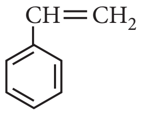
Polymer	Structure of monomers
Polythene	$CH_2=CH_2$ Ethylene
Polypropylene	$CH_3-CH=CH_2$ Propylene
Polytetrafluoroethene (Teflon) (PTFE)	$CF_2=CF_2$ Tetrafluoroethene
Polyacrylonitrile (Orlon) (PAN)	$CH_2=CHCN$ Acrylonitrile (Vinyl cyanide)
Polyvinyl chloride (PVC)	$CH_2=CHCl$ Chloroethene (Vinyl chloride)
Polystyrene (Styron)	
Polymethylmethacrylate (PMMA)	 $CH_2=\overset{\overset{CH_3}{\vert}}{C}-COOCH_3$ Methylmethacrylate
Polymonochlorotrifluoroethylene (PCTFE)	 $Cl-\underset{\underset{F}{\vert}}{C}=CF_2$ Chlorotrifluoroethylene

Polydienes

Polymer	Structure of monomers
Natural rubber (cis-1, 4-polyisoprene)	 $CH_2=\overset{\overset{CH_3}{\vert}}{C}-CH=CH_2$ Isoprene (2-Methyl-1, 3-butadiene)
Neoprene (synthetic rubber)	 $CH_2=\overset{\overset{Cl}{\vert}}{C}-CH=CH_2$ Chloroprene (2-chloro-1, 3-butadiene)
Gutta-percha (*trans*-polyisoprene)	 $CH_2=\overset{\overset{CH_3}{\vert}}{C}-CH=CH_2$ Isoprene (2-Methyl-1, 3-butadiene)

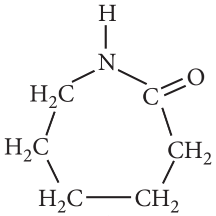
Preparation of some important addition copolymers :

Polydienes

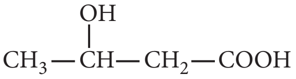
Polymer	Structure of monomers
Buna-S (Styrene Butadiene Rubber) (SBR)	$CH_2=CH-CH=CH_2$ 1,3-Butadiene  Styrene
Buna-N (Nitrile rubber)	$CH_2=CH-CH=CH_2$ 1,3-Butadiene $CH_2=CH-CN$ Acrylonitrile

Preparation of some important condensation homopolymers :

Polyamides

Polymer	Structure of monomers
Nylon-6 (Perlon-L)	 Caprolactam

Polyesters

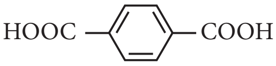
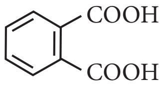
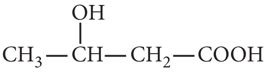
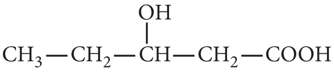
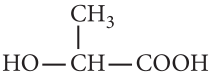
Polymer	Structure of monomers
Polyhydroxy butyrate (PHB)	 $CH_3-\overset{\overset{OH}{\vert}}{CH}-CH_2-COOH$ 3-Hydroxybutanoic acid

Preparation of some important condensation copolymers :

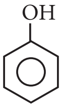
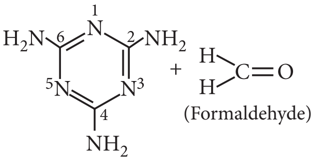
Polyamides

Polymer	Structure of monomers
Nylon-6, 6	$HOOC-(CH_2)_4-COOH$ Adipicocid $H_2N-(CH_2)_6-NH_2$ Hexamethylenediamine
Nylon-6, 10	$HOOC-(CH_2)_8-COOH$ Sebacic acid $H_2N-(CH_2)_6-NH_2$ Hexamethylenediamine
Nylon-2, 6	H_2N-CH_2-COOH Glycine $H_2N-(CH_2)_5-COOH$ 6-Aminohexanoic acid

Polyesters

Polymer	Structure of monomers
Terylene (Dacron)	$HOCH_2-CH_2OH$ Ethylene glycol (Ethane-1,2,-diol)  Terephthalic acid (Benzene-1, 4-dicarboxylic acid)
Glyptal (Alkyd resin)	$HOCH_2-CH_2OH$ Ethylene glycol  Phthalic acid (Benzene-1, 2-dicarboxylic acid)
Poly β-hydroxy butyrate-co-β-hydroxy valerate (PHBV)	 $CH_3-\overset{\overset{OH}{\vert}}{CH}-CH_2-COOH$ 3-Hydroxybutanoic acid  $CH_3-CH_2-\overset{\overset{OH}{\vert}}{CH}-CH_2-COOH$ 3-Hydroxypentanoic acid
Poly (glycolic acid) poly(lactic acid) (Dextron)	$HO-CH_2-COOH$ Glycolic acid  $HO-\overset{\overset{CH_3}{\vert}}{CH}-COOH$ Lactic acid

Formaldehyde resins

Polymer	Structure of monomers
Phenol-formaldehyde resin (Bakelite)	 + HCHO Formaldehyde Phenol
Melamine-formaldehyde resin (Melmac)	 (Formaldehyde) Melamine (2, 4, 6-Triamino-1,3,5-triazine)
Urea-formaldehyde resin	NH_2CONH_2 + HCHO Urea Formaldehyde

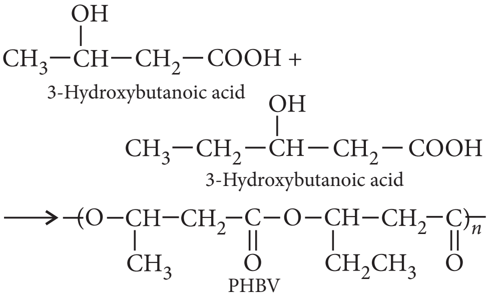
Polysulphide

Polymer	Structure of monomers
Thiokol $-\!\!\left[CH_2CH_2-S-S-S-S\right]\!\!-_n$	$Cl-CH_2CH_2-Cl$ Ethylene dichloride Na_2S_4 Sodium tetrasulphide

- **Differences between natural rubber and vulcanized rubber :**

	Natural rubber	Vulcanized rubber
1.	Natural rubber is soft and sticky.	Vulcanized rubber is hard and non-sticky.
2.	It has low tensile strength.	It has high tensile strength.
3.	It has low elasticity.	It has high elasticity.
4.	It can be used over a wide narrow range of temperature (from 10°C to 60°C).	It can be used over a wide range of temperature (– 40°C to 100°C).
5.	It has low wear and tear resistance.	It has high wear and tear resistance.
6.	It is soluble in solvents like ether, carbon tetrachloride, petrol, etc.	It is insoluble in all the common solvents.

- **Biodegradable polymers :** Aliphatic polyesters are one of the most important class of biodegradable polymers. Some important examples are given below :
- **Poly β-hydroxybutyrate-co-β-hydroxy valerate (PHBV) :** PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.

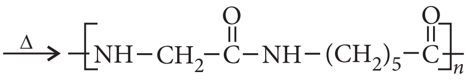


$$\underset{\text{3-Hydroxybutanoic acid}}{CH_3-\overset{\overset{OH}{\vert}}{CH}-CH_2-COOH} + \underset{\text{3-Hydroxybutanoic acid}}{CH_3-CH_2-\overset{\overset{OH}{\vert}}{CH}-CH_2-COOH}$$

$$\longrightarrow \underset{\text{PHBV}}{-\!\!\left(O-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-\underset{\underset{O}{\Vert}}{C}-O-\underset{\underset{CH_2CH_3}{\vert}}{CH}-CH_2-\underset{\underset{O}{\Vert}}{C}\right)\!\!-_n}$$

- **Nylon 2-nylon 6 :** It is an alternating polyamide copolymer of glycine (H_2NCH_2COOH) and amino caproic acid [$H_2N(CH_2)_5COOH$] and is biodegradable.

$$nH_2N-CH_2-COOH + nH_2N-(CH_2)_5-COOH$$



$$\xrightarrow{\Delta} -\!\!\left[NH-CH_2-\overset{\overset{O}{\Vert}}{C}-NH-(CH_2)_5-\overset{\overset{O}{\Vert}}{C}\right]\!\!-_n$$

Nylon 2-nylon 6

Previous Years' CBSE Board Questions

15.1 Classification of Polymers

VSA (1 mark)

1. Arrange the following polymers in the increasing order of their intermolecular forces : Polystyrene, Terylene, Buna-S. *(1/3, Delhi 2016)*

2. Arrange the following polymers in the increasing order of their intermolecular forces : Terylene, Polythene, Neoprene. *(1/3, AI 2016)*

3. Write the name and structure of the monomers of the following polymer :

Buna-S *(1/3, Delhi 2015C, 2013, 2010, 2008)*

4. Which of the following is a natural polymer?
Buna-S, Proteins, PVC *(AI 2014)*

5. Based on molecular forces what type of polymer is neoprene? *(AI 2014)*

6. Which of the following is a fibre?
Nylon, Neoprene, PVC *(AI 2014)*

7. Define the term, 'homopolymerisation' giving an example. *(Delhi 2012)*

8. Explain the following term giving a suitable example :
Elastomers *(1/3, AI 2012)*

9. Write a distinguishing feature between homopolymer and copolymer. *(Delhi 2010C)*

10. Define the term 'polymerisation'. *(AI 2008)*

SA I (2 marks)

11. Define thermoplastic and thermosetting polymers. Give one example of each. *(2/3, AI 2013, 2008)*

12. How are thermosetting polymers different from thermoplastic polymers? *(2/3, Delhi 2013C, 2012C)*

13. Distinguish between homopolymers and copolymers. Give one example of each. *(AI 2013, 2008)*

14. Explain the following terms giving a suitable example for each:
(i) Condensation polymers
(ii) Addition polymers *(AI 2012)*

15. Differentiate between molecular structures and behaviours of thermoplastic and thermosetting polymers. Give one example of each type. *(AI 2009)*

16. What is the difference between elastomers and fibres? Give one example of each. *(2/3, AI 2008C)*

SA II (3 marks)

17. Differentiate between thermoplastic and thermosetting polymers. Give one example of each. *(AI 2012)*

18. What are addition polymers? How are the two types of addition polymers different from each other? Give one example of each type. *(Forign 2011)*

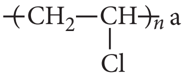
19. Find the main difference between them
(i) Thermoplastic polymers
(ii) Thermosetting polymers *(Delhi 2010)*

20. Differentiate between condensation and addition polymerisations. Give one example each of the resulting polymers. *(AI 2009)*

21. (a) Distinguish between homopolymers and copolymers. Give one example of each.
(b) Is $\left(\!-CH_2-CH(C_6H_5)-\!\right)_n$ a homopolymer or a copolymer? Why? *(Delhi 2008C)*

15.2 Types of Polymerisation

VSA (1 mark)

22. Is  $\left(\!-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-\!\right)_n$ a homopolymer or a copolymer? *(AI 2013)*

23. Name the polymer which is used for making non-stick cooking utensils. *(1/3, Delhi 2013C)*

24. What does the part '6,6' mean in the name nylon-6, 6? *(Delhi 2009)*

25. What does '6,6' indicate in the name nylon-6,6? *(AI 2009)*

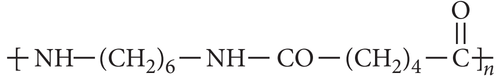
26. What is the primary structural feature necessary for a molecule to make it useful in a condensation polymerisation reaction? *(AI 2009)*

27. What is the difference between the two notations : nylon – 6 and nylon – 6,6 ? *(AI 2008C)*

SA I (2 marks)

28. (i) What is the role of *t*-butyl peroxide in the polymerisation of ethene?

(ii) Identify the monomers in the following polymer :

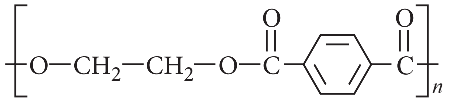


$$\left[NH-(CH_2)_6-NH-CO-(CH_2)_4-\overset{\overset{\displaystyle O}{||}}{C} \right]_n$$

(2/3, Delhi 2016)

29. (i) What is the role of sulphur in the vulcanisation of rubber?

(ii) Identify the monomers in the following polymer :



(2/3, AI 2016)

30. Write the names and structures of the monomers of the following polymers :

(i) Nylon 6, 6 (ii) Neoprene *(2/3, Delhi 2015, 2013)*

31. Write the names and structures of the monomers of the following polymers :

(i) Neoprene (ii) Teflon *(2/3, Delhi 2015C)*

32. Explain the term 'copolymerisation' and give two examples of copolymerization. *(2/3, AI 2015C)*

33. Write the name of monomers used for getting the following polymers :

(i) Bakelite (ii) Neoprene *(AI 2014)*

34. Write the name of monomers used for getting the following polymers :

(i) Terylene (ii) Nylon-6,6 *(AI 2014)*

35. Write the name of monomers used for getting the following polymers :

(i) Teflon (ii) Buna-N *(AI 2014)*

36. Give names of the monomers of the following polymers :

(i) Neoprene (ii) Polystyrene

(iii) Polypropene *(Delhi 2014C)*

37. Write the names and structures of monomers used for getting the following polymers :

(i) Buna-S (ii) Nylon-6,6 *(AI 2014C)*

38. Draw the structure of the monomer for each of the following polymers.

(i) Nylon-6 (ii) Polypropene *(Delhi 2012)*

39. Write down the structure of monomer and one use of the polymer polystyrene. *(2/3, Delhi 2012C)*

40. Mention two important uses of each of the following :

(i) Bakelite (ii) Nylon 6 *(2/3, Delhi 2011)*

41. Write the name and structure of the monomer of each of the following polymers :

(i) Neoprene (ii) Buna-S (iii) Teflon *(2/3, Delhi 2010)*

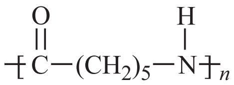
42. Draw the molecular structures of the monomers of

(i) PVC (ii) Teflon *(AI 2010)*

43. Draw the structures of the monomers of the following polymers :

(i) Bakelite (ii) Nylon-6 *(AI 2010)*

44. Write the names of monomers of the following polymers.

(i) 

$$\left[\overset{\overset{\displaystyle O}{||}}{C}-(CH_2)_5-\overset{\overset{\displaystyle H}{|}}{N} \right]_n$$

(b) $\left[CF_2-CF_2 \right]_n$ *(Delhi 2009)*

45. Write the names and structures of the monomers of the following polymers :

(i) Neoprene (ii) Nylon-6 *(2/3, Delhi 2008)*

46. What is step growth polymserisation? Explain the steps involved in this process. *(AI 2008C)*

47. Write the structures of monomers used in the preparation of

(a) Teflon (b) PMMA *(AI 2007)*

48. Draw the structures of the monomer of each of the following polymers.

(i) Polyvinylchloride (PVC)

(ii) Nylon-6. *(Delhi 2007)*

SA II (3 marks)

49. Write the mechanism of free radical polymerisation. *(Delhi 2016)*

50. Write the names and structures of the monomers of the following polymers :
(i) Buna-S (ii) Glyptal
(iii) Polyvinyl chloride *(AI 2015)*

51. Write the names and structures of the monomers of the following polymers :
(i) Terylene (ii) Bakelite
(iii) Buna-S *(Foreign 2015)*

52. Write the name of the monomers of the following polymers :
(i) Polythene (ii) Polyvinyl chloride
(iii) Bakelite *(Delhi 2014C)*

53. Write the names and structures of the monomers of the following polymers :
(i) Bakelite (ii) Nylon-6
(iii) Polythene *(Delhi 2013)*

54. (a) Differentiate between copolymerisation and homopolymerisation. Give one example of each.
(b) What is the role of Benzoyl peroxide in preparation of polythene? *(Delhi 2013C)*

55. Write the monomers of the following polymers and classify them as addition or condensation polymers :
Teflon, Bakelite and Natural rubber *(AI 2013C)*

56. Explain the term co-polymerization and give two examples of copolymers and the reactions for their preparations. *(AI 2012C)*

57. Draw the structure of the monomers of the following polymers :
(i) Polythene (ii) PVC
(iii) Teflon *(AI 2011)*

58. Mention two important uses for each of the following polymers :
(i) Bakelite (ii) Nylon 6,6
(iii) PVC *(Forign 2011)*

59. Distinguish between addition polymers and condensation polymers. Classify the following into addition and condensation polymers :
(i) Polythene (ii) PTFE
(iii) Polybutadiene (iv) Bakelite *(AI 2011C)*

60. Give one example each of
(i) addition polymers,
(ii) condensation polymers,
(iii) copolymers. *(Delhi 2010)*

61. Write the (i) structure and (ii) one use of each of the following polymers :
(a) PVC
(b) Urea-formaldehyde resin
(c) Bakelite *(AI 2010C)*

62. Write the monomers which are used for the synthesis of the following polymers :
(i) Terylene (ii) Polythene
(iii) Bakelite
Indicate the type of polymerisation for each which forms the polymer. *(AI 2009C)*

63. Write chemical equations to form the following:
(i) Nylon-6 (b) Nylon-6,6
(iii) Polythene *(AI 2009C)*

15.4 Biodegradable Polymers

VSA (1 mark)

64. Write the names and structures of the monomer of the following polymer :
PHBV *(1/3, Delhi 2015)*

65. What are biodegradable polymers? Give one example. *(1/3, AI 2013C)*

66. What are biodegradable polymers? *(Delhi 2011)*

SA I (2 marks)

67. What is a biodegradable polymer? Give an example of a biodegradable aliphatic polyester. *(2/3, AI 2013)*

68. What are biodegrable and non-biodegradable polymers? Give one example of each class. *(Delhi 2008)*

SA II (3 marks)

69. What are biodegradable polymers? Give an example of such a polymer and mention its uses. *(Delhi 2009C)*

VBQ (3 marks)

70. After the ban on plastic bags, students of one school decided to make the people aware of the harmful effects of plastic bags on environment and Yamuna River. To make the awareness more impactful, they organized rally by joining hands with other schools and distributed paper bags to vegetable vendors, shopkeepers and departmental stores. All students pledged not to use polythene bags in future to save Yamuna River. After reading the above passage, answer the following questions:

(i) What values are shown by the students?
(ii) What are biodegradable polymers? Give one example.
(iii) Is polythene a condensation or an addition polymer?

(Delhi 2014)

71. After the ban on plastic bags, students on one school decided to create awareness among the people about the harmful effects of plastic bags on the environment and the Yamuna river. To make it more impactful, they organised a rally by joining hands with other schools and distributed paper bags to vegetable vendors, shopkeepers and departmental stores. All students pledged not to use polythene bags in future to save the Yamuna river.

After reading the above passage, answer the following questions :

(i) What values are shown by the students?
(ii) What are biodegradable polymers? Give one example.
(iii) Is polythene a homopolymer or copolymer?

(Foreign 2014)

Detailed Solutions

1. The intermolecular forces are least in case of elastomers like Buna-S while strongest in case of fibres like terylene and in case of thermoplastics like polystrene the intermolecular forces are intermediate in between elastomers and fibres.

Thus, the increasing order of their intermolecular forces is Terylene > Polystyrene > Buna-S

2. Neoprene < Polythene < Terylene.

3. Buna-S :

$$\underset{\text{1,3–Butadiene}}{\mathrm{CH_2{=}CH{-}CH{=}CH_2}} \text{ and } \underset{\text{Styrene}}{\mathrm{C_6H_5CH{=}CH_2}}$$

4. Proteins are natural polymers.

5. Elastomer.

6. Nylon is a fibre.

7. A polymer made by polymerisation of a single monomer is known as homopolymer and the process is known as homopolymerisation For *e.g.*, Polythene made by polymerisation of ethene molecules.

$$\underset{\text{Ethene}}{n\mathrm{CH_2 = CH_2}} \longrightarrow \underset{\text{Polythene}}{-\!\!\left(\mathrm{CH_2{-}CH_2}\right)\!\!-_n}$$

8. Elastomers are the polymers in which polymer chains are held by weakest intermolecular forces.

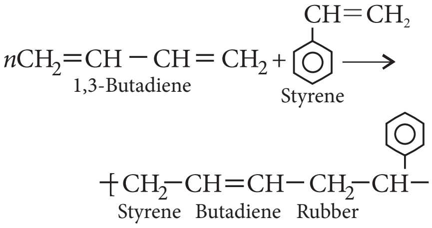
e.g. Buna-S, Buna-N.

9. Homopolymer : A polymer made by polymerisation of a single monomer is known as homopolymer and the reaction is called homopolymerisation.

e.g. Polythene made by ethene molecules.

$$\underset{\text{Ethene}}{n\mathrm{CH_2{=}CH_2}} \rightarrow \underset{\text{Polythene (homopolymer)}}{-\!\!\left(\mathrm{CH_2{-}CH_2}\right)\!\!-_n}$$

Copolymer : A polymer made by polymerisation of two or more different monomers is called copolymer and the reaction is called copolymerisation. When styrene and butadiene are polymerised together, a polymer called styrene-butadiene rubber is formed



10. The process of formation of macromolecules/ polymers from their respective monomeric units, is called polymerisation.

11. Thermoplastics : Thermoplastics are linear or slightly branched polymers which can be repeatedly softened on heating and hardened on cooling and hence can be used again and again without any change in chemical composition and mechanical strength.

Example : Polythene and polystyrene.

Thermosetting Polymers: Thermosetting polymers on heating in a mould get hardened and set and cannot be softned again. This hardening on heating is due to cross-linking between different polymer chains to give a three-dimensional network solid.

Example : Bakelite.

12. *Refer to answer 11.*

13. *Refer to answer 9.*

14. Addition polymers : The polymers formed by the addition reaction of a large number of unsaturated monomers are called addition polymers.

For example : Polythene, polystyrene.

Condensation polymers : The polymers formed by the condensation of two or more bifunctional monomers are called condensation polymers.

For example : Nylon 6,6, Bakelite.

15. *Refer to answer 11.*

16. (i) In elastomers polymer chains are held together by weakest intermolecular forces.

These have elastic properties. e.g. Buna-N, Buna-S.

(ii) In fibres polymer chains are held together by strong intermolecular forces like hydrogen bonding.

These have high tensile strength.

e.g., Terylene, Nylon 6,6, etc.

17. *Refer to answer 11.*

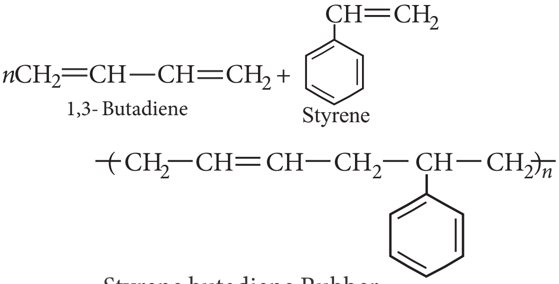
18. Polymers which are formed by the repeated addition reaction of unsaturated monomer molecules are called the addition polymers.

The two types of addition polymers are :

(i) **Homopolymers :** The addition polymers formed by the polymerisation of a single compound are called homopolymers. *e.g.*, polyethene.

$$\underset{\text{Ethene}}{nCH_2{=}CH_2} \longrightarrow \underset{\text{Polyethene}}{-\!\!(CH_2-CH_2)\!\!-_n}$$

(ii) **Copolymers :** The polymers made by addition polymerisation from two different compounds are known as copolymers. *e.g.*, Buna-S.



Styrene butadiene Rubber

19. *Refer to answer 11.*

20. *Refer to answer 14.*

21. (a) *Refer to answer 9.*

(b) It is a homopolymer because it is formed by the repetition of single compound *i.e.*, monomer unit $C_6H_5CH=CH_2$.

22. Homopolymer

23. Teflon $-\!\!(CF_2-CF_2)\!\!-_n$

24. In nylon 6, 6, designation '6, 6' mean that both the monomers hexamethylene diamine and adipic acid contain six carbon atoms each.

25. *Refer to answer 24.*

26. Monomers should possess more than one functional group.

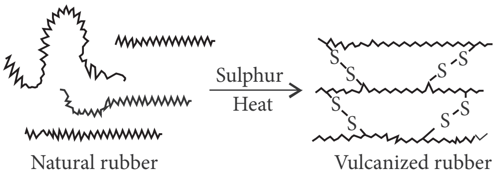
27. Nylon 6 is obtained from the monomer caprolactam which contains 6 carbon atoms. Nylon 6,6 is a condensation polymer of hexamethylene diamine and adipic acid. Both the monomers have 6 carbon atoms each.

28. (i) Polymerisation of ethene requires an initiator to start the polymerisation with free radical mechanism. Thus, peroxide like *t*-butyl peroxide decomposes to give free radical that initiates the reaction.

(ii) Hexamethylene diamine and adipic acid.

29. Vulcanisation is a process of heating natural rubber with sulphur and an appropriate additive to modify its properties.

It gives greater elasticity and ductility. Sulphur forms cross linked network which gives mechanical strength to the rubber.

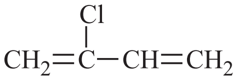


(ii) Terephthalic acid and ethylene glycol.

30. (i) Nylon 6,6 : $\underset{\text{Adipic acid}}{HOOC-\!\!(CH_2)_4-COOH}$ and

$$\underset{\text{Hexamethylene diamine}}{H_2N-\!\!(CH_2)_6\!\!-NH_2}$$

(ii) Neoprene :



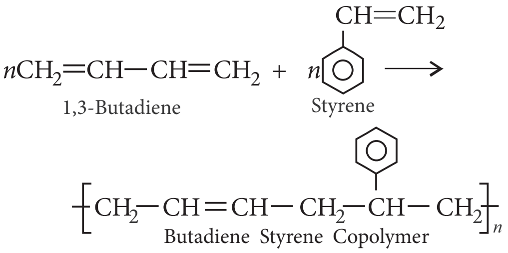
$$\underset{\text{Chloroprene}}{CH_2{=}\overset{\displaystyle Cl}{\overset{|}{C}}-CH{=}CH_2}$$

31. (i) *Refer to answer 30(ii).*

(ii) Teflon : $\underset{\text{Tetrafluroethylene}}{CF_2{=}CF_2}$

32. Copolymerization : When the polymers are synthesised by polymerization of two or more than two different monomers then this process is called as copolymerization. example,

(i) Styrene butadiene rubber (SBR) :



(ii) Buna–N :

$$\underset{\text{1,3-Butadiene}}{nCH_2{=}CH-CH{=}CH_2} + \underset{\text{Acrylonitrile}}{nCH_2{=}CHCN} \rightarrow$$

$$\underset{\text{Buna - N}}{-\!\!(CH_2-CH{=}CH-CH_2-CH_2-\overset{\displaystyle CN}{\overset{|}{CH}})\!\!-_n}$$

33. (i) Bakelite : Formaldehyde (HCHO) and Phenol (C_6H_5OH)

(ii) *Refer to answer 30(ii).*

34. (i) *Refer to answer 29(ii).*

(ii) *Refer to answer 30(i).*

35. (i) *Refer to answer 31(ii).*

(ii) Buna–N : $\underset{\text{1,3–Butadiene}}{CH_2{=}CH-CH{=}CH_2}$ and

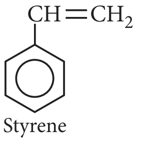
$$\underset{\text{Acrylonitrile}}{CH_2{=}CHCN}$$

36.

Name of polymer	Monomer
Neoprene	Chloroprene
Polystyrene	Styrene
Polypropene	Propene

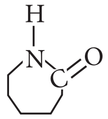
37. (i)Buna–S : $CH_2{=}CH{-}CH{=}CH_2$ and

1,3-Butadiene


Styrene

(ii) *Refer to answer 30(i).*

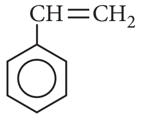
38. (i) Nylon–6 :


Caprolactam

(ii) Polypropene : $CH_3{-}CH{=}CH_2$

Propene

39. Polystyrene :


Styrene

Used to make transparent drinking cups.

40. (i) Bakellite is used for making combs, electrical switches, handles of various utensils and phonograph records.

(ii) Nylon–6 is used for making tyre cords, ropes and fabrics.

41. (i) *Refer to answer 30(ii).*

(ii) *Refer to answer 37(i).*

(iii) *Refer to answer 31(ii).*

42. (i) Structure of monomer PVC : $CH_2{=}CHCl$

Vinyl chloride

(ii) *Refer to answer 31(ii).*

43. (i) *Refer to answer 33(i).*

(ii) *Refer to answer 38(i).*

44. (i) Caprolactam

(ii) Tetrafluoroethene

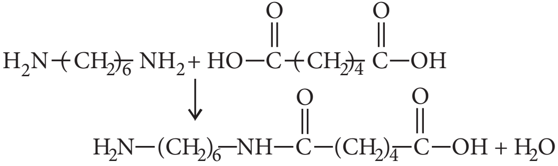
45. (i) *Refer to answer 30(ii).*

(ii) *Refer to answer 38(i).*

46. Step growth polymerisation involves a repetitive condensation reaction between two bi-functional monomers. Each step produces a distinct functionalised species and in independent of each other.

All condensation polymerisation are step growth polymerisation.

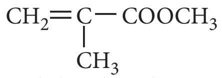
Step : It involves condensation reaction of bifunctional molecules with elimination of smaller molecules like H_2O.



$$H_2N{-}(CH_2)_6{-}NH_2 + HO{-}\overset{\overset{\large O}{\|}}{C}{-}(CH_2)_4{-}\overset{\overset{\large O}{\|}}{C}{-}OH \downarrow H_2N{-}(CH_2)_6{-}NH{-}\overset{\overset{\large O}{\|}}{C}{-}(CH_2)_4{-}\overset{\overset{\large O}{\|}}{C}{-}OH + H_2O$$

47. (i) *Refer to answer 31(ii).*

(ii) PMMA :



$$CH_2{=}\underset{\underset{\large CH_3}{|}}{C}{-}COOCH_3$$

Methyl methacrylate

48. (i) *Refer to answer 42(i).*

(ii) *Refer to answer 38(i).*

49. Chain initiation :

$$\dot{R} + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}\dot{C}H_2$$

Chain propagation :

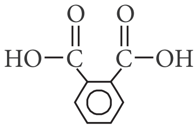
$$R{-}CH_2{-}\dot{C}H_2 + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H_2$$

Chain termination :

$$R{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H_2 + \dot{R} \longrightarrow R{-}(CH_2)_4{-}R$$

50. (i) *Refer to answer 37(i).*

(ii) Glyptal :


and $HO{-}CH_2{-}CH_2{-}OH$

Ethylene glycol

Phthalic acid

(iii) *Refer to answer 42(i).*

51. (i) $HOH_2C{-}CH_2OH$ and

Ethylene glycol


Terephthalic acid

(ii) *Refer to answer 33(i).*

(iii) *Refer to answer 37(i).*

52. (i) Monomer of polythene is ethene.

(ii) Monomer of PVC is vinyl chloride.

(iii) Monomers of Bakelite are formaldehyde and Phenol.

53. (i) *Refer to answer 33(i).*

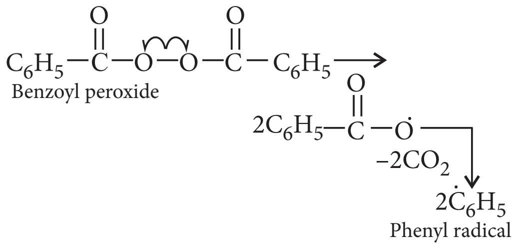
(ii) *Refer to answer 38(i).*

(iii) Polythene : $CH_2{=}CH_2$

Ethene

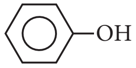
54. (a) *Refer to answer 9.*

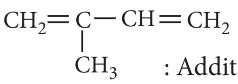
(b) In the preparation of polythene from ethene, benzoyl peroxide acts as an initiator or free radical generator.



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2C_6H_5-\overset{O}{\overset{\|}{C}}-\dot{O} \xrightarrow{-2CO_2} 2\dot{C}_6H_5$$

55. Teflon : $CF_2 = CF_2$: Addition Polymer

Bakelite : HCHO +  : Condensation Polymer

Natural Rubber :  : Addition Polymer.

$$CH_2=\underset{CH_3}{\underset{|}{C}}-CH=CH_2$$

56. *Refer to answer 32.*

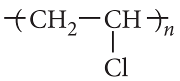
57. (i) *Refer to answer 53(iii).*
(ii) *Refer to answer 42(i).*
(iii) *Refer to answer 31(ii).*

58. (i) Bakelite – (1) In electrical switches
(2) In making handles of various utensils.
(ii) Nylon 6,6 – (1) In Fabrics
(2) In tyre cords
(iii) PVC – (1) In hand bags
(2) In water pipes

59. *Refer to answer 14.*
(i) Polythene – addition polymer
(ii) PTFE – addition polymer
(iii) Polybutadiene – addition polymer
(iv) Bakelite – condensation polymer

60. (i) Addition polymers : Polythene, rubber.
(ii) Condensation polymers : Terylene, Nylon 6,6.
(iii) Copolymers : SBR, Buna-N.

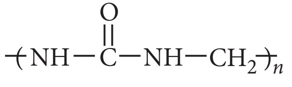
61. (i) PVC

Structure 

$$-\!\!(CH_2-\underset{Cl}{\underset{|}{CH}})_n\!\!-$$

Use in making pipes and raincoats.

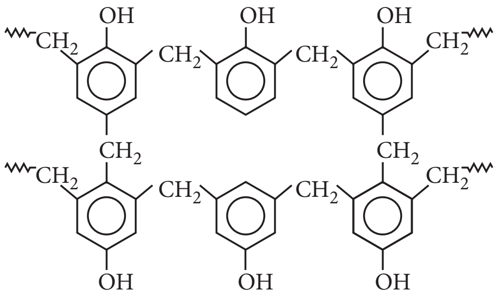
(ii) Urea-formaldehyde resin

structure 

$$-\!\!(NH-\overset{O}{\overset{\|}{C}}-NH-CH_2)_n\!\!-$$

Used in making unbreakable crockery.

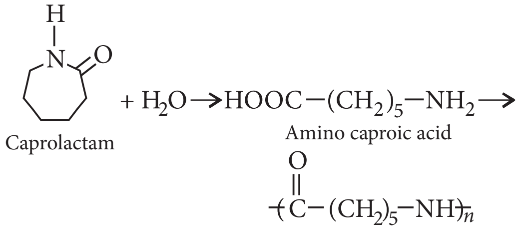
(iii) Bakelite



Used in making electrical switches and handles of utensils.

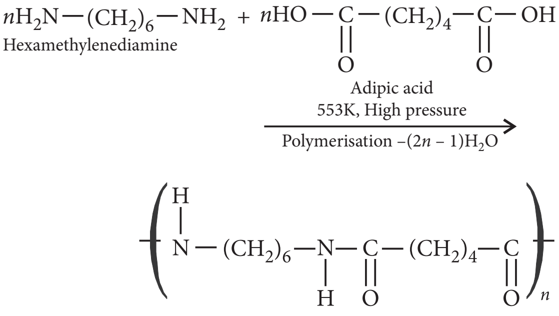
62. (i) *Refer to answer 29(ii).* It is a condensation polymer.
(ii) *Refer to answer 52(i).* It is an addition polymer.
(iii) *Refer to answer 33(i).* It is a condensation polymer.

63. (i) Nylon–6 : It is formed by self condensation of caprolactam in the presence of water.



Nylon 6

(ii) Nylon–6'6



$$nH_2N-(CH_2)_6-NH_2 + nHO-\underset{O}{\underset{\|}{C}}-(CH_2)_4-\underset{O}{\underset{\|}{C}}-OH \xrightarrow[\text{Polymerisation }-(2n-1)H_2O]{553K,\text{ High pressure}} -\!\!\left(\overset{H}{\overset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-(CH_2)_4-\underset{O}{\underset{\|}{C}}\right)_n\!\!-$$

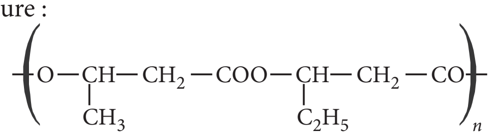
Nylon-6'6

(iii) Polythene

$$nCH_2=CH_2 \xrightarrow[200°C]{O_2} -\!\!(CH_2-CH_2)_n\!\!-$$

64. PHBV – Poly – β – hydroxybutyrate – co – β – hydroxyvalerate

Structure :



$$-\!\!\left(O-\underset{CH_3}{\underset{|}{CH}}-CH_2-COO-\underset{C_2H_5}{\underset{|}{CH}}-CH_2-CO\right)_n\!\!-$$

65. **Biodegradable Polymers :** The natural polymer, which disintegrates by itself or by micro-ogranisms within certain period of time is called biodegradable polymer, *e.g.*, PHBV (poly–β–hydroxybutyrate–co–β–hydroxyvalerate), Nylon 2–nylon 6.

66. *Refer to answer 65.*

67. *Refer to answer 65.*

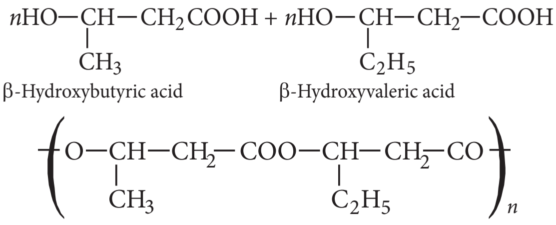
68.

Biodegradable polymer	**Non-biodegradable polymer**
The natural polymer, which disintegrates by itself or by micro-ogranisms within certain period of time is called *biodegradable polymer*, *e.g.*, PHBV (poly–β–hydroxybutyrate–co–β–hydroxyvalerate), Nylon 2–nylon 6.	They generally consist of long chains of carbon and hydrogen atoms. The interatomic bonding of these molecules is very strong, which makes it very difficult for microbes to break the bonds and digest them. Thus a long period of time is required to decompose them. For *e.g.*, Polythene, PTFE etc.

69. *Refer to answer 65.*

PHBV (Poly-β-hydroxybutyrate-co-β-hydroxy valerate) :

It is a co-polymer of β-hydroxybutyric acid and β-hydroxy valeric acid.



$$\underset{\beta\text{-Hydroxybutyric acid}}{n\text{HO}-\underset{\underset{CH_3}{|}}{CH}-CH_2COOH} + \underset{\beta\text{-Hydroxyvaleric acid}}{n\text{HO}-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-COOH}$$

$$\left(-O-\underset{\underset{CH_3}{|}}{CH}-CH_2-COO-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-CO-\right)_n$$

PHBV

Butyric acid provides stiffness and valeric acid imparts flexibility to the polymer.

Uses : In packaging orthopaedic devices and control drug release.

A drug is put in capsules of PHBV, which is degraded in the body and drug is released. PHBV also undergoes bacterial degradation in the environment.

70. (i) Students show awareness and responsibility towards the environment.

(ii) *Refer to answer 65.*

(iii) Polythene is an addition polymer that is formed by addition of ethene molecules.

$$\underset{\text{Ethene}}{n\,CH_2{=}CH_2} \xrightarrow{\text{Polymerisation}} \underset{\text{(Repeating unit)}}{n\left[-CH_2-CH_2-\right]}$$

$$\longrightarrow \underset{\text{Polythene}}{\left[-CH_2-CH_2-\right]_n}$$

71. (i) *Refer to answer 70(i).*

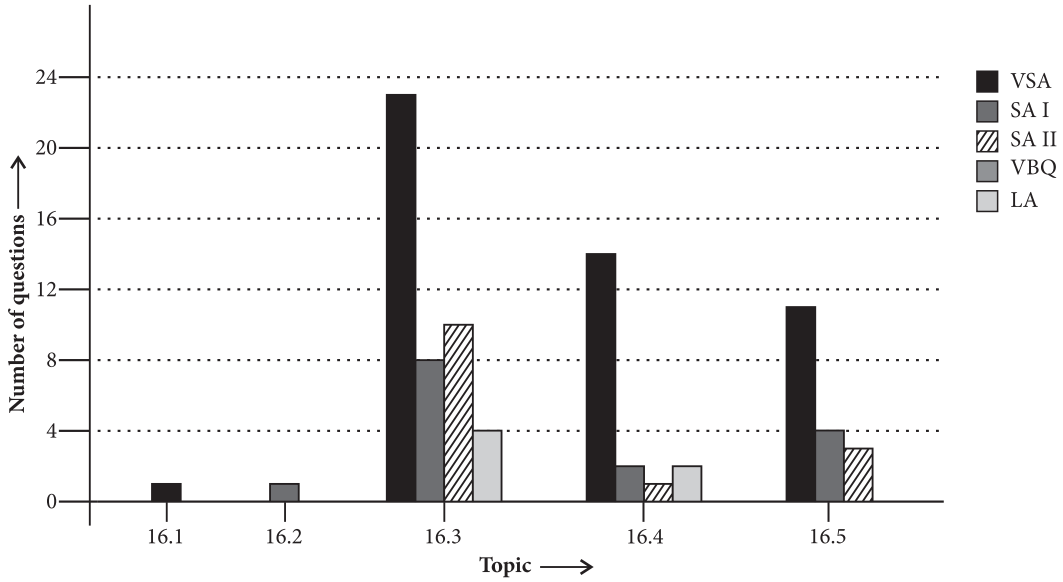
(ii) *Refer to answer 65.*

(iii) Polythene is homopolymer because it is formed by the repeatition of single monomer unit *i.e.*, ethene, $CH_2 = CH_2$.

16 Chemistry in Everyday Life

16.1 Drugs and their Classification
16.2 Drug-Target Interaction
16.3 Therapeutic Action of Different Classes of Drugs
16.4 Chemicals in Food
16.5 Cleansing Agents

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2016-2007)



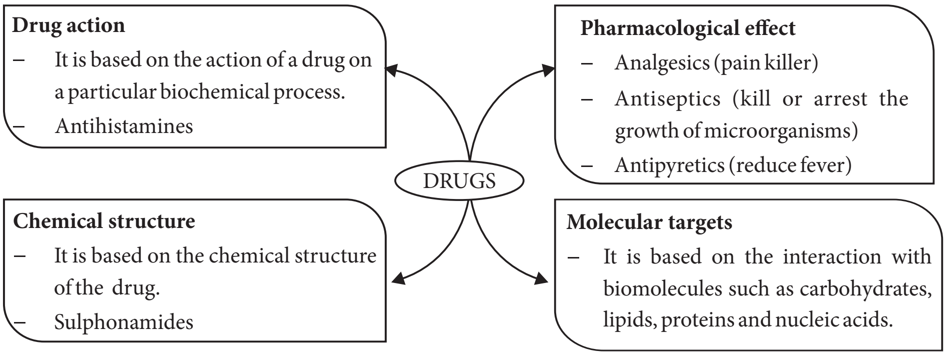
- Maximum total weightage is of *Therapeutic Action of Different Classes of Drugs*.
- Maximum VSA type questions were asked from *Therapeutic Action of Different Classes of Drugs*.
- Maximum SA I and SA II type questions were asked from *Therapeutic Action of Different Classes of Drugs*.

QUICK RECAP

CHEMICALS IN MEDICINES

- **Drugs :** These are the chemicals of low molecular masses (~ 100-500 u) which interact with macromolecular targets and produce a biological response.
- **Medicines :** These are the drugs which are therapeutic and used for diagnosis, prevention and treatment of diseases.
- Use of chemicals for therapeutic effect is called *chemotherapy*.

Classification of drugs : Drugs are classified on the basis of



Drug action
- It is based on the action of a drug on a particular biochemical process.
- Antihistamines

Pharmacological effect
- Analgesics (pain killer)
- Antiseptics (kill or arrest the growth of microorganisms)
- Antipyretics (reduce fever)

DRUGS

Chemical structure
- It is based on the chemical structure of the drug.
- Sulphonamides

Molecular targets
- It is based on the interaction with biomolecules such as carbohydrates, lipids, proteins and nucleic acids.

Drug Target Interaction :

- **Enzymes as drug target :** Drugs inhibit any of the two activities of the enzymes, they can block the binding site of the enzyme and prevent the binding of substrate or they can inhibit the catalytic activity of enzyme.
- **Receptors as drug target :** Proteins which transmit communication to the different parts of the body are called *receptors*. Receptor proteins are embedded in the cell membrane and receptor changes its shape to accommodate a chemical messenger which brings about transfer of message into the cell.
- **Drug interact with receptors in two ways :**
  - Drugs bind to their receptor sites and inhibit its natural function (antagonists). These are useful when blocking of message is required.
  - Some drugs mimic the natural messenger by switching on the receptor (agonists). These are useful when there is lack of natural chemical messenger.

Therapeutic action of different classes of drugs :

- **Antacids :** These are chemicals which neutralise excess acid in the gastric juices and give relief from acid indigestion, acidity, heart burns and gastric ulcers, *e.g.*, magnesium hydroxide, calcium carbonate, etc.
- **Antihistamines :** They diminish or abolish the main action of histamine released in the body and hence, prevent allergic reactions, they are also called *anti-allergic drugs*, *e.g.*, diphenylhydramine (benadryl), pheniramine maleate (avil), etc.
- **Tranquilizers :** These are chemical substances used for the treatment of stress, mild and severe mental diseases. They are neurologically active drugs and are also called *psychotherapeutic drugs, e.g.,* veronal amytal, seconal, equanil, chlordiazepoxide, etc.

  Veronal, amytal and seconal are called barbiturates. Barbiturates are hypnotic, *i.e.,* sleep producing agents.
- **Analgesics :** These are chemical substances which reduce pain. They are classified as :
  - **Non-narcotic analgesics :** Aspirin and paracetamol belong to this class of drugs. They are effective in relieving skeletal pain such as that due to arthritis. They have many other effects such as reducing fever and preventing platelets coagulation. Aspirin finds use in prevention of heart attacks because of its anti blood clotting action.
  - **Narcotic analgesics :** Morphine and many of its homologues, when administered in medicinal doses, relieve pain and produce sleep. In poisonous doses, they cause convulsions and ultimately death. These are mainly used for the relief of post operative pain, cardiac pains and pains of terminal cancer.
- **Antimicrobials :** These are chemical substances used to cure infections due to microorganisms, *e.g.*, sulphadiazine, sulphadoxine, etc. Antibiotics, antiseptics and disinfectants are antimicrobial drugs.

- **Antibiotics :** These are chemical substances produced wholly or partly by chemical synthesis which in low concentration inhibit the growth or destroy microorganisms by intervening in their metabolic processes.
  - The antibiotics may be either *bacteriocidal* (kill the organisms in the body) *e.g.*, penicillin, ofloxacin, etc., or *bacteriostatic* (inhibit the growth of organisms), *e.g.*, erythromycin, chloramphenicol, etc.
  - Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be *broad spectrum antibiotics*, *e.g.*, tetracycline, chloromycetin and chloramphenicol.
  - Those effective mainly against Gram-positive or Gram-negative bacteria are *narrow spectrum antibiotics*, *e.g.*, penicillin-G.
- **Antiseptics :** These are chemicals which either kill or prevent the growth of microorganisms and are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces.
  - Dettol is a commonly used antiseptic and it is a mixture of chloroxylenol and terpineol
  - Bithionol is added to soaps.
  - Tincture of iodine, *i.e.*, 2-3% solution in alcohol-water mixture is applied on wounds.
- **Disinfectants :** These are also used to kill microorganisms, but they are applied to inanimate objects.
  - Some substances can act as antiseptic as well as disinfectant by varying the concentration.
  - 0.2% phenol is an antiseptic, whereas its 1% solution is disinfectant.
  - 0.2-0.4 ppm chlorine in aqueous solution acts as disinfectant.

▶ **Antifertility drugs :** Chemical substances used to prevent conception or fertilization are called *antifertility drugs*. These are essentially a mixture or estrogen and progesterone derivatives which are more potent than the natural hormones, *e.g.*, mifepristone, ormeloxifene, etc.

CHEMICALS IN FOOD

- **Preservatives :** These are the chemical substances which are added to the food materials to prevent their spoilage and to retain their nutritive value for long periods. These preservatives prevent the rancidity of food and inhibit the growth or kill the microorganisms.
- The preservation of food by adding sufficient amount of salt to it is called *salting*. Salt prevents the water from being available for microbial growth.
- The microbial growth in food materials can also be prevented by adding certain chemical substances. The most common preservative used is sodium benzoate (C_6H_5COONa). It is metabolised by conversion to hippuric acid, $C_6H_5CONHCH_2COOH$ which ultimately is excreted through urine.
- Certain food preservatives such as BHA and BHT are used for edible oils, also act as antioxidants.
- **Artificial sweetening agents :** These are chemical compounds which give sweetening effect to the food and enhance its odour and flavour.

Artificial sweetener	Sweetness value in comparision to cane sugar
Aspartame	100
Saccharin	550
Alitame	2000

- **Antioxidants :** These are the chemical substances which prevent oxidation and subsequent spoilage of the food. These act as sacrificial materials, *i.e.*, they are more reactive towards oxygen than the materials they are protecting. They also reduce the rate of involvement of free radicals in the ageing process.

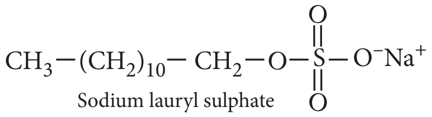
CLEANSING AGENTS

- **Soaps :** These are sodium or potassium salts of long chain fatty acids, *e.g.*, stearic, oleic and palmitic acids. Soaps containing sodium salts are prepared by heating glyceryl ester of fatty acid with aqueous NaOH solution and the reaction is known as *saponification*.

- Only sodium or potassium soaps are soluble in water and are used for cleaning purposes. Generally potassium soaps are soft to the skin than sodium soaps.

- **Detergents :** These are the materials which are used for cleaning purposes. They are also called *soapless soaps*.
  - *Anionic detergents* : Their polar head is negatively charged.

    e.g.,

    $$CH_3-(CH_2)_{10}-CH_2-O-\overset{\overset{\Large O}{||}}{\underset{\underset{\Large O}{||}}{S}}-O^-Na^+$$

    Sodium lauryl sulphate

    Such detergents are used to wash clothes.
  - *Cationic detergents* : Their polar head is positively charged *e.g.*

    $CH_3(CH_2)_{15}-N^+-(CH_3)_3Cl^-$

    trimethylhexadecylammonium chloride

    These are used as fabric softener and hair conditioner.
  - *Non-ionic detergents* : Their polar head is neutral. *e.g.,*

    $CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$

    Polyethyleneglycol stearate

    Such detergents are used in dish washers.

- **Action of soap in hard water :** Hard water contains Ca^{2+} or Mg^{2+} ions which react with sodium or potassium salt of fatty acid (soap) to form calcium or magnesium salt of fatty acids called *scum*.

  $$2C_{17}H_{35}COONa + Ca^{2+} \rightarrow 2Na^+ + \underset{\text{Insoluble soap or scum}}{(C_{17}H_{35}COO)_2Ca}$$

  $$2C_{17}H_{35}COONa + Mg^{2+} \rightarrow 2Na^+ + (C_{17}H_{35}COO)_2Mg$$

- **Advantages of synthetic detergents over soaps :**
  - They can be used in hard water, in acidic medium while soaps get precipitated.
  - They are more soluble in water and thus, form lather more easily.
  - They are stronger cleansing agents than soaps as they decrease the surface tension to greater extent.

Previous Years' CBSE Board Questions

16.1 Drugs and their Classification

VSA (1 mark)

1. Give two examples of macromolecules that are chosen as drug targets. *(1/3, Delhi 2010C)*

16.2 Drug-Target Interaction

SA I (2 marks)

2. Discuss the two ways in which drugs prevent attachment of natural substrate on active site of an enzyme. *(Delhi 2008C)*

16.3 Therapeutic Action of Different Classes of Drugs

VSA (1 mark)

3. What is the following? Give one example.
   Antibiotics *(1/3, Delhi 2014)*
4. What are antiseptics? Give one example. *(1/3, AI 2014, Foreign 2011, 1/3, Delhi 2009, Delhi 2008C)*
5. Which class of drugs is used in sleeping pills? *(1/3, Delhi 2013)*
6. What are limited spectrum antibiotics ? Give one example. *(1/3, Delhi 2013C)*
7. What is the following substance? Give one example?
   Tranquillizers *(1/3, AI 2012, 2010C)*
8. What is the cause of a feeling of depression in human beings? Name a drug which can be useful in treating this depression. *(AI 2012)*
9. Differentiate between disinfectants and antiseptics. *(AI 2012, 2010C, Delhi 2010, 2009,)*
10. Determine the following giving one example:
    Antacids *(1/3, Delhi 2011, 2009)*
11. What is meant by a 'broad spectrum antibiotic'? *(Foreign 2011, Delhi 2008C)*
12. Name the main constituents of dettol. *(Delhi 2010)*
13. Explain the following type of substance with one suitable example.
    Analgesics. *(1/3, Delhi 2009)*
14. Describe the following substance with one suitable example :
    Disinfectants *(1/3, AI 2009)*
15. Define the following term :
    Narcotic drugs *(AI 2009C)*
16. Name a substance that can be used as an antiseptic as well as a disinfectant. *(Delhi 2008)*

SA I (2 marks)

17. (i) Define Antihistamine with an example.
    (ii) Which one of the following drugs is an antibiotic?
    Morphine, Equanil, Chloramphenicol, Aspirin. *(2/3, Foreign 2014)*
18. Explain the following terms with a suitable example for each :
    (i) Disinfectants
    (ii) Antacids *(2/3, Delhi 2014C)*
19. (i) What class of drug is ranitidine?
    (ii) Which of the following is an antiseptic?
    0.2% phenol, 1% phenol *(2/3, AI 2013)*
20. How do antiseptics differ from disinfactants? Give one example of each. (Give two differences). *(2/3, Delhi 2012C)*
21. What are the following substances ? Give one example of each :
    (i) Broad Spectrum antibiotics
    (ii) Narcotic analgesics *(2/3, AI 2012C)*
22. Explain the following terms with one suitable example for each :
    (i) Enzymes
    (ii) Analgesics *(2/3, Delhi 2011)*
23. Answer the following questions :
    (i) What are the main constituents of dettol?
    (ii) How do antiseptics differ from disinfectants? *(2/3, Delhi 2011)*

24. Explain the following terms with one suitable example in each case.
(i) Enzymes
(ii) Antifertility drugs *(2/3, Delhi 2010)*

SA II (3 marks)

25. Answer the following questions :
(i) Why should medicines not be taken without consulting a doctor?
(ii) What is meant by 'broad spectrum antibiotics'?
(iii) What are the main constituents of Dettol? *(Delhi 2014)*

26. (i) How do antiseptics differ from disinfectants? Give one example of each.
(ii) What are the tranquilizers ? Give one example. *(AI 2013C)*

27. What are the following substances ? Give one example of each :
(i) Antihistamines
(ii) Tranquilizers
(iii) Broad spectrum antibiotics *(AI 2012C)*

28. What are the following substances ? Give one example of each :
(i) Analgesics
(ii) Antibiotics
(iii) Tranquilizers *(AI 2012C)*

29. Mention the action of the following on the human body in bringing relief from a disease:
(i) Brompheniramine
(ii) Aspirin
(iii) Equanil *(Delhi 2011)*

30. What are analgesic medicines ? How are they classified and when are they commonly recommended for use ? *(Delhi 2010)*

31. What is meant by the term, 'broad-spectrum antibiotics' ? Name a broad-spectrum antibiotic and state two diseases for which it is prescribed. *(AI 2009)*

32. Mention one use each of the following drugs:
(i) Ranitidine
(ii) Paracetamol
(iii) Tincture of iodine. *(AI 2008, 2007)*

33. (i) What are antihistamines and how do they act ?
(ii) Mention the name of a substance which can be used both as an antiseptic as well as a disinfectant. *(Delhi 2008C)*

VBQ (4 marks)

34. Due to hectic and busy schedule, Mr. Angad made his life full of tensions and anxiety. He started taking sleeping pills to overcome the depression without consulting the doctor. Mr. Deepak, a close friend of Mr. Angad, advised him to stop taking sleeping pills and suggested to changes his lifestyle by doing Yoga, meditation and some physical exercise. Mr. Angad followed his friend's advice and after few days he started feeling better.

After reading the above passage, answer the following :
(i) What are the values (at least two) displayed by Mr. Deepak?
(ii) Why is it not advisable to take sleeping pills without consulting doctor?
(iii) What are the tanquilizers? Give two examples. *(Delhi 2016)*

35. Due to hectic and busy schedule, Mr. Singh started taking junk food in the lunch break and slowly became habitual of eating food irregularly to excel in his field. One day during meeting he felt severe chest pain and fell down. Mr. Khanna, a close friend of Mr. Singh took him to doctor immediately. The doctor diagnosed that Mr. Singh was suffering from acidity and prescribed some medicines. Mr. Khanna advised him to eat home made food and change his lifestyle by doing yoga, meditation and some physical exercise. Mr. Singh followed his friend's advice and after few days he started feeling good:

After reading the above passage, answer the following :
(i) What are the values (at least two) displayed by Mr. Khanna?
(ii) What are antacids? Give one example.
(iii) Would it be advisable to take antacids for a long period of time? Give reason. *(AI 2016)*

36. Mr. Roy, the principal of one reputed school organized a seminar in which he invited parents and principals to discuss the serious issue of diabetes and depression in students. They all resolved this issue by strictly banning the junk food in schools and to introduce healthy snacks and drinks like soup, lassi, milk etc. in school canteens. They also decided to make compulsory half an hour physical activities for the students in the morning assembly daily. After six months, Mr. Roy conducted the health survey in most of the schools and discovered a tremendous improvement in the health of students.

After reading the above passage, answer the following:

(i) What are the values (at least two) displayed by Mr. Roy?
(ii) As a student, how can you spread awareness about this issue?
(iii) What are the tranquilizers? Give an example.
(iv) Why is use of aspartame limited to cold foods and drinks? *(Delhi 2015)*

37. Seeing the growing cases of diabetes and depression among young children, Mr. Lugani, the principal of one reputed school organized a seminar in which he invited parents and principals. They all resolved this issue by strictly banning junk food in schools and introducing healthy snacks and drinks like soup, lassi, milk, etc. in school canteens. They also decided to make compulsory half an hour of daily physical activities for the students in the morning assembly. After six months, Mr. Lugani conducted the health survey in most of the schools and discovered a tremendous improvement in the health of the students.

After reading the above passage, answer the following questions :

(i) What are the values (at least two) displayed by Mr. Lugani?
(ii) As a student, how can you spread awareness about this issue?
(iii) What are antidepressant drugs? Give an example.
(iv) Name the sweetening agent used in the preparation of sweets for a diabetic patient. *(AI 2015)*

16.4 Chemicals in Food

VSA (1 mark)

38. Why is use of aspartame limited to cold foods and soft drinks? *(1/3, Delhi 2014, 2011, 1/3, Foreign 2014)*

39. Name sweetening agent used in the preparation of sweets for a diabetic patient. *(1/3, Delhi 2014)*

40. What are the following substance? Give one example?
Food preservatives *(1/3, Delhi 2014, 2012, 2011, 2010, 2009)*

41. Which one of the following is a food preservative?
Equanil, Morphine, Sodium benzoate. *(1/3, Delhi 2013)*

42. Why do we require artificial sweetening agents? *(Delhi 2013C)*

43. Explain the following terms with one suitable example.
A sweetening agent for diabetic patients *(1/3, Delhi 2011)*

44. What are the following substance ? Give one example?
Sweetening agents *(1/3, AI 2009)*

45. Define the following term :
Alitame *(1/3, AI 2009C)*

SA I (2 marks)

46. What are the following? Give one example.
(i) Sweetening agents
(ii) Food preservatives *(2/3, Delhi 2014C)*

47. What are the food preservatives? Name two such substances. *(AI 2012)*

SA II (3 marks)

48. What are the artificial sweetening agents? Give two examples. Name the sweetening agent used in the preparation of sweets for a diabetic patient. *(AI 2009C)*

VBQ (4 marks)

49. Neeraj went to the departmental store to purchase groceries. On one of the shelves he noticed sugar-free tablets. He decided to buy them for his grandfather who was a diabetic. There were three types of sugar-free tablets. He decided to buy sucralose which was good for his grandfather's health.

(i) Name another sugar-free tablet which Neeraj did not purchase.

(ii) Was it right to purchase such medicines without doctor's prescription?
(iii) What quality of Neeraj is reflected above?
(Delhi 2015C)

50. On the occasion of World Health Day, Dr. Satpal organized a 'health camp' for the poor farmers living in a nearby village. After check-up, he was shocked to see that most of the farmers suffered from cancer due to regular exposure to pesticides and many were diabetic. They distributed free medicines to them. Dr. Satpal immediately reported the matter to the National Human Rights Commission (NHRC). On the suggestions of NHRC, the government decided to provide medical care, financial assistance, setting up of super-speciality hospitals for treatment and prevention of the deadly disease in the affected villages all over India.
(i) Write the values shown by
(a) Dr. Satpal (b) NHRC.
(ii) What type of analgesics are chiefly used for the relief of pains of terminal cancer?
(iii) Give an example of artificial sweetener that could have been recommended to diabetic patients. *(3 Marks) (AI 2014)*

16.5 Cleansing Agents

VSA (1 mark)

51. If water contains dissolved Ca^{2+} ions, out of soaps and synthetic detergents, which will you use for cleaning clothes? *(1/3, AI 2013)*

52. What are the following substance? Give one example?
Synthetic detergents
(1/3, Delhi 2012C, 2011)

53. Why do soaps not work in hard water ?
(1/3, Delhi 2012C, 2011)

54. Explain the following terms with one suitable example?
Cationic detergents *(1/3, Delhi 2010, 2009)*

55. Explain the following term with one example?
Detergents *(1/3, AI 2010)*

56. How are synthetic detergents better than soaps? *(1/3, AI 2010)*

57. What are the following substance ? Give one example.
Nonionic detergents *(1/3, Delhi 2009)*

58. Define the following term :
Saponification *(1/3, AI 2009C)*

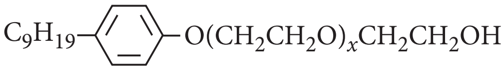
SA I (2 marks)

59. Explain the following terms with suitable examples :
(a) Cationic detergents
(b) Anionic detergents *(Delhi 2013C)*

60. State the reason in each of the following cases:
(i) Soaps do not work well in hard water.
(ii) Synthetic detergents are better than soaps.
(Foreign 2011)

61. Explain the following terms :
(i) Cationic detergents
(ii) Anionic detergents
(iii) Neutral detergents *(Delhi 2010C)*

62. Label the hydrophilic and hydrophobic parts in the following molecule of a non-ionic detergent:



Identify the functional groups(s) present in the molecule. *(Delhi 2010C)*

SA II (3 marks)

63. (i) What are disinfectants? Give an example.
(ii) What are anionic detergents? Give an example. *(Delhi 2014)*

64. What are biodegradable and non-biodegradable detergents ? Give one example of each.
(Delhi 2011C)

65. What are anionic detergents ? How are they prepared ? Write their two main uses.
(Delhi 2009C)

Detailed Solutions

1. Drugs interact with macro molecules like carbohydrates, proteins, nucleic acids and lipids present in the cell.

2. Drugs compete with the natural substrate for their attachment on the active sites of enzymes. Such drugs are called competitive inhibitors.
Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is called allosteric site. This binding of inhibitor at allosteric site changes the shape of the active site in such a way that substrate can not recognise it. If the bond formed between an enzyme and an inhibitor is a strong covalent bond and cannot be broken easily, then the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesize the new enzyme.

3. Antibiotics are chemical substances (prepared wholly or partially by chemical synthesis) which in low concentration either kill or inhibit the growth of microorganisms by intervening in their metabolic processes. E.g.,
Dysidazirine - Toxic towards cancer cells.

4. **Antiseptics :** These are the chemical substances used to prevent the growth of microorganisms or to kill them and are safe to be applied on living tissues. These are applied to wounds and cuts. For examples (i) iodoform (ii) tincture of iodine.

5. Tranquilizers are used in sleeping pills.

6. Antibiotics which are effective against *a* single organism or disease are called limited spectrum antibiotics. For *e.g.*, Dysidazirine which is toxic towards certain strains of cancer cells.

7. **Tranquilizers :** Those medicines which act on central nervous system and help in reducing anxiety and relieve tension on the nerves are called tranquilizers. For example, valium.

8. Low level of noradrenaline is the cause of depression of human being.
Equanil is used for treatment.

9. *Refer to answer 4.*

Disinfectants : These are chemical substances used to kill micro-organisms in inanimate materials and are not safe to be applied to the living tissues. Examples
(i) 1% solution of phenol.
(ii) Solution of *o*-, *m*- and *p*-methylphenols (cresols) in soapy water is called lysol and is used as a disinfectant.

10. **Antacids :** These are the chemical substances which neutralize the excess acid and raise the pH to an appropriate level in the stomach. *e.g.* Sodium hydrogen carbonate or a mixture of aluminium and magnesium hydroxide are some common antacids.

11. The antibiotic which is effective against a wide range of Gram positive and Gram negative bacteria is known as broad spectrum antibiotic. For example, chloramphenicol.

12. Chloroxylenol and terpineol.

13. Analgesics are drugs that reduce pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system.
Example : Aspirin, Paracetamol, Morphine etc.

14. Disinfectants are chemicals which either kill or prevent the growth of microorganisms but not safe for living tissues. They are applied on floors, drainage system etc. For *e.g.,* 1% of phenol, low concentration of SO_2 etc.

15. Narcotic analgesics are pain killers and induce sleep. If taken in high amount they produce coma, convulsions and ultimately, death for *e.g.* Morphine.

16. Phenol : 0.2% solution of phenol acts as an antiseptic whereas 1% solution acts as a disinfectant.

17. (i) The drugs which prevents the interaction of histamine with the receptors where histamine exerts its effect are called antihistamines. E.g. Synthetic drug brompheniramine (Dimetapp) and terfenadine (Seldane) acts as antihistamines.
(ii) Chloramphenicol is an antibiotic.

18. (i) *Refer to answer 14.*
(ii) *Refer to answer 10.*

19. (i) It is an antacid as it helps in removing acidity of stomach.
(ii) *Refer to answer 16.*

20. *Refer to answer 9.*

Difference : 1. Antiseptics are applied to the living tissues and disinfectants are applied to inanimate objects.
2. Some substance can act as an antiseptics at low concentration and as disinfectant at high concentration.

21. (i) *Refer to answer 11.*
(ii) *Refer to answer 15.*

22. (i) Proteins which play an important role of biological catalyst in the body are called enzymes. For *e.g.*, Invertase, Maltase etc.
(ii) *Refer to answer 13.*

23. (i) *Refer to answer 12*
(ii) *Refer to answer 9.*

24. (i) *Refer to answer 22(i).*
(ii) Drugs which are used to control birth rate are called antifertility drugs. *e.g.,* Norethindrone, novestrol.

25. (i) We should not take medicine without consulting doctor because we don't know about that particular medicine that what would be its reaction and sideffect. May be a single medicine can cause death. It could be harmful for our life. So, don't take medicine without consulting of doctor.
(ii) *Refer to answer 11.*
(iii) *Refer to answer12.*

26. (i) *Refer to answer 9.*
(ii) *Refer to answer 7.*

27. (i) *Refer to answer 17(i).*
(ii) *Refer to answer 7.*
(iii) *Refer to answer 11.*

28. (i) *Refer to answer 13.*
(ii) *Refer to answer 3.*
(iii) *Refer to answer 7.*

29. (i) Brompheniramine acts as antihistamine (antiallergic). It interferes with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.
(ii) Aspirin acts as an analgesic, *i.e.*, used to reduce pain and antipyretic, *i.e.*, brings down the body temperature. Aspirin inhibits the synthesis of compounds which stimulate inflammation in the tissue and cause pain.
(iii) Equanil is used for controlling depression and hypertension.

30. Analgesic medicines : The chemical substances which are used to relieve pain without causing impairment of consciousness are called analgesic medicines.
There are two types of analgesic medicines.
(i) **Non narcotic drugs :** These are effective in relieving skeletal pain, preventing heart attack and viral inflammation etc. For *e.g.*, Aspirin and paracetamol.
(ii) **Narcotic drugs :** These are recommended for the relief in postoperative pain, cardiac pain, pains of terminal cancer, and child birth. These are morphine derivatives and habit forming.

31. *Refer to answer 11.*

Chloramphenicol is a antibiotic and prescribed for typhoid, meningitis and pneumonia etc.

32. (i) Ranitidine is used as an antacid
(ii) Paracetamol is used to bring down the body temperature during high fever.
(iii) Tincture of iodine is used as an antiseptic. It is 2-3% solution of iodine in alcohol and water.

33. (i) *Refer to answer 17(i).*
(ii) *Refer to answer 16.*

34. (i) (a) Mr. Deepak is very much concerned about the healthy life and he knows the benefits of doing yoga, meditation and physical exercise.
(b) Mr. Deepak is very good friend and helped Mr. Angad to come out from tensions and anxiety.
(ii) It is not advisable to take sleeping pills without consulting doctor because if they have taken in doses higher than recommended, may produce harmful effects and act as poison and cause even death.
(iii) Drugs which are used for the treatment of stress fatigue, mild and severe mental disease anxiety, irritability are called tranquilizers.
e.g., Equanil, chlordiazepoxide.

35. (i) Mr. Khanna is concerned and caring to his friend. He believes in living healthy life by doing yoga, meditation, physical exercise etc.
(ii) The substances which neutralize the excess acid and raise the pH to an appropriate level in stomach are called antacides *e.g.,* Ranitidine.
(iii) No, it is not advisable to take antacides for a long period because they make the stomach alkaline and trigger the production of even more acid. Hence, causes more acidity. Moreover, it causes esophageal cancer.

36. (i) Mr. Roy displayed responsibility and concern towards the health needs of students.
(ii) Awareness regarding diabetes and depression can be spread by conducting workshops for students, teachers as well as parents, by health camps, seminars and through school magazines.
(iii) *Refer to answer 7.*
(iv) Use of aspartame is limited to cold food and drinks because it is unstable at cooking temperature.

37. (i) Two values displayed by Mr. Lugani are
(a) He showed concern about the health of students and banned junk food.
(b) He took the responsibility of improving the health of students and introduced half an hour compulsory physical activity in the morning assembly.
(ii) Awareness about this issue can be spread by organizing awareness camps in our society, using social media etc.
(iii) Chemicals used for the treatment of depression are called antidepressant drugs or tranquillizers. *e.g.*, phenelzine
(iv) Saccharin is the sweetener used in the preparation of sweets for a diabetic person.

38. *Refer to answer 36 (iv).*

39. *Refer to answer 37(iv).*

40. Chemicals which prevent the spoilage of food due to microbial growth are called food preservatives. Table salt, sugar, vegetable oils are some commonly used food preservatives.

41. Sodium benzoate-food preservative. Morphine-narcoti-analgesic equanil-tranquilizer.

42. Artificial sweetening agents are required by diabetic persons and people who need to control intake of calories.

43. Sweetening agents : The substances which provide sweetness to the food without increasing the calories to the body are known as artificial sweetening agents. Saccharin and aspartame are artificial sweetening agents.

44. *Refer to answer 43.*

45. Alitame : Alitame is more stable than aspartame. It is very high potency sweetener. Its sweetness is difficult to control hence its use is limited.
It is 2000 times as sweet as cane sugar.

46. (i) *Refer to answer 43.*
(ii) *Refer to answer 40.*

47. *Refer to answer 40.*

48. The chemicals that give sweetness to the food but do not add any calorie to our body are called artificial sweetening agents.
e.g., saccharine, aspartame.
Any artificial sweetening agent like aspartame, alitame, etc., can be added to the food consumed by diabetic patient.

49. (i) Alitame and aspartame
(ii) Yes, sucralose can be purchased without doctor's consultation because Sucralose pass through the human body unmetabolised without producing any calories.
(iii) General awareness and responsibility knowledge of chemical.

50. (i) (a) Dr. Satpal showed that a doctor should be sympathetic to the health needs of the society.
(b) NHRC showed that government should provide medical care and financial assistance to rural population of India.
(ii) Narcotic analgesics are chiefly used for the relief of pain of terminal cancer.
(iii) Saccharin is an artificial sweetener which could be recommended to diabetic patients.

51. As the water contains dissolved Ca^{2+} ions, therefore it is hard water. Hence, synthetic detergents are preferred over the soaps for cleaning the clothes because calcium salts of detergents are soluble in water while calcium salts of soaps are insoluble. As a result, lot of soap is wasted.

52. Synthetic detergents : These are cleansing agents which have all the properties of soaps but actually do not contain any soap. These can be used both in soft and hard water. *e.g.,* sodium *p*-dodecylbenzene-sulphonate.

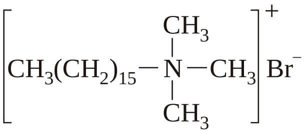
53. Soap has a hydrophobic part (hydrocarbon) that attracts dirt, grease oil, etc. whereas hydrophilic part (— COONa) attracts water that take oil, dirt and grease. Soaps do not work well with hard water because Mg^{2+} and Ca^{2+} ions of hard water react with soap to form magnesium and calcium salts of fatty acids which are insoluble in water and form scum.

$$\underset{\text{Soap}}{2C_{17}H_{35}COONa} + CaCl_2 \rightarrow 2NaCl + \underset{\text{Insoluble calcium stearate (soap)}}{(C_{14}H_{35}COO)_2Ca}$$

54. Cationic detergents : Detergents in which large part of molecules is cation are called cationic detergents.

These are quaternary ammonium salts.

e.g. Cetyltrimethyl ammonium bromide



$$\left[CH_3(CH_2)_{15}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3\right]^+ Br^-$$

55. Chemical substances which improve cleansing property of water and helps in removal of dirt from skin, fabric or other materials are called detergents. *e.g.*, sodium dodecyl benzenes sulphonate (SDS).

56. Synthetic detergents are better than soaps because they form foam even in hard water whereas soaps do not. Some of the detergents give foam even in ice cold water.

57. Non-ionic detergents some detergents like esters of high molecular mass, formed by reaction between polyethylene glycol and stearic acid, are called non-ionic detergents. These detergents do not contain any ion in their constitution *e.g.*,

$CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$

58. Saponification : Soaps containing sodium salts are formed by heating fat with aqueous sodium hydroxide solution. This reaction is known as saponification.

59. (i) *Refer to answer 54.*

(ii) **Anionic detergent :** A detergent whose large part of the molecule is anion is called anionic detergent.

These are sodium salts of sulphonated long chain alcohols or hydrocarbons.

e.g. Sodium laurylsulphate

$CH_3-(CH_2)_{10}CH_2OSO_3^-Na^+$

60. (i) *Refer to answer 53.*

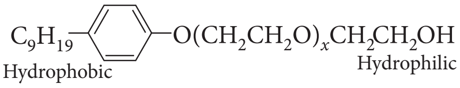
(ii) *Refer to answer 56.*

61. (i) *Refer to answer 54.*

(ii) *Refer to answer 59 (b)*

(iii) *Refer to answer 57.*

62.



Functional groups : (i) —OH (hydroxy)

(ii) –O– (oxy)

63. (i) *Refer to answer 14.*

(ii) *Refer to answer 59(b).*

64. Biodegradable detergents : Detergents having straight chain hydrocarbons are easily decomposed by micro organisms. These are called biodegradable detergents.

Example : Sodium 4- (1, 3, 5, 7 - Tetramethyloctyl) benzene sulphonate.

Non-biodegradable detergents : Detergents having highly branched hydrocarbon chains are not degraded by bacteria easily. These are called non-biodegradable detergents.

Example : Trimethyl stearyl ammonium chloride.

65. *Refer to answer 59(b).*

Preparation : Alkyl hydrogen sulphate formed by treating long chain alcohols with concentrated sulphuric acid are neutralised with alkali to form anionic detergents.

$$CH_3(CH_2)_{10}CH_2OH \xrightarrow{H_2SO_4} \underset{\text{Alkyl hydrogen sulphate}}{CH_3(CH_2)_{10}CH_2OSO_3H}$$

$$\xrightarrow{NaOH_{(aq)}} \underset{\text{Anionic detergents}}{CH_3(CH_2)_{10}CH_2OSO_3^-Na^+}$$

Uses : These are mostly used (i) for household work (ii) in toothpaste.

Value Based Questions

1. Ekta and Akanksha went to the market for shopping. They were looking for a fancy lamp in a shop. Shopkeeper showed them two types of lamps. One was electric rechargeable lamp and the other one was solar lamp. Ekta wanted to buy electric rechargeable lamp but Akanksha advised her to go for solar lamp.

(i) What are the values shown by Akanksha by giving preference to solar lamp?
(ii) What is the main component of a solar cell?
(iii) What is the role of semiconductor in solar cell?
(iv) How is it beneficial to us?

2. Ms. Vandana a social worker, always tells people in the village not to cook food in open *kadahi*. She insists on using pressure cooker or covered pans for cooking as it will preserve the nutritional value of the food and cook food faster.

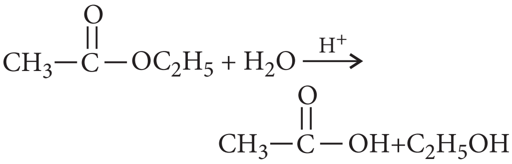
(i) What values are displayed by Ms. Vandana?
(ii) What is the reason for fast cooking in pressure cooker?
(iii) What is molal elevation constant?
(iv) How is it related to elevation in boiling point?

3. Prem and his father went to a shop to purchase a battery for their invertor. The shopkeeper showed them two types of batteries, one with lead plates and the other with cadmium plates. The battery with cadmium plates was more expensive than the lead battery. Prem's father wanted to purchase lead battery as it was cheaper but Prem suggested to buy battery with cadmium plates.

After reading the above passage answer the following questions :

(i) Why would Prem suggest to buy the expensive cadmium plate battery. Give two reasons.
(ii) What are the values shown by Prem?
(iii) Name the species reduced at cathode in lead storage batteries.

4. Udit, a student of class XII was performing an experiment to study the kinetics of acid hydrolysis of ester by titration method using 0.1 N NaOH. He recorded his observations in the table given below as instructed by his teacher.



$$CH_3-\overset{\overset{O}{||}}{C}-OC_2H_5 + H_2O \xrightarrow{H^+} CH_3-\overset{\overset{O}{||}}{C}-OH + C_2H_5OH$$

Time (min)	Volume of 0.1 N NaOH (mL)
0.00	5
10.00	20
1.00 h (complete)	45

(i) Mention the values displayed by Udit.
(ii) What is the order of reaction?
(iii) Why did the volume of 0.1 N NaOH increase, as reaction proceeded?
(iv) What is the role of H^+ ion in the reaction?

5. Sunaina noticed that many people of her colony are suffering from nausea, headache, vomiting, etc. She analysed the situation and came to the conclusion that her locality is near the industrial area due to which air and water around get contaminated. She suggested them to wear gas masks and use alum to purify water.

(i) What values are shown by Sunaina?
(ii) What is the purpose of wearing gas mask?
(iii) How can the industrial pollution be reduced?
(iv) How can water be purified by alum?

6. Mayank got the job in a production unit of metallurgical industry that produces different metals from their ores. On his first day, he got confused about choosing the correct reducing agent. His senior, Ashok advised him to go through Ellingham diagram.

(i) What is an Ellingham diagram?
(ii) How Ellingham diagram is helpful in extraction of metal?
(iii) What are the two values shown by Ashok?

7. In an adventurous sport, four teams have to cross a river. Team leader of one team carries a container having calcium carbide and calcium phosphide. He told his team members that in any emergency situation, pierce the bottom of container and throw into the river. This creates instantaneous fire and others will know that we need their help.

(i) What values are displayed by the team leader?
(ii) Which substance causes the instantaneous fire?
(iii) Write the chemistry behind the fire.
(iv) Write the chemical reaction for laboratory production of substance that causes instantaneous fire.

8. Kamal got a job as a junior scientist in a textile factory just after passing M.Sc. in Chemistry. He came to know that factory is using Cl_2 based bleaching agent for bleaching of textiles. He suggested his seniors to use potassium permanganate instead of chlorine for bleaching purposes.

Now answer the following questions :
(i) Which property of $KMnO_4$ makes it a bleaching agent?
(ii) Write reduction half reaction of $KMnO_4$ in acidic medium.
(iii) Why is $KMnO_4$ better bleaching agent than chlorine?
(iv) What value is associated with the suggestion of Kamal?

9. During an experiment in a chemistry laboratory, Aakash consumed lead acetate. He was vomitting too much. His friends wanted to take him to the doctor immediately. But their teacher gave him a solution to take and after some time he was normal.

Answer the following questions based on the above passage.
(i) Name the solution given by the teacher.
(ii) How this solution works ?
(iii) Is there any side effect of the solution ingested?
(iv) What are the values shown by the teacher?

10. Carbon tetrachloride (CCl_4) is widely used as a cleaning fluid in industry, as a degreasing agent and a spot remover at home and as a fire extinguisher. An NGO is demanding complete ban on the use of CCl_4.

Now answer the following questions :
(i) Write the structure and IUPAC name of carbon tetrachloride.
(ii) Why is the NGO demanding for ban on the use of this chemical? Give two reasons.
(iii) What value is associated with this demand of NGO?

11. To refrain people from drinking alcohol, the production of alcohol is Government controlled and a heavy excise duty is levied on the sale of alcoholic beverages. However, to supply cheaper alcohol to industries where it is used in large quantities, it is denatured.
(i) What are the values displayed by the Government?
(ii) Should production of alcohol be completely banned? Give two reasons.
(iii) Why alcohol is denatured?
(iv) How can we spread awareness to stop addiction to alcohol?

12. During the chemistry practical in laboratory, Piyush removed labels from the bottles of acetaldehyde and acetone to irritate lab assistants. His classmate, Abhishek who noticed his act told him that he should not play with the chemicals like this as it could be dangerous for us.
(i) What values are shown by Abhishek?
(ii) How can these chemicals be distinguished for correct labelling?
(iii) Name two methods which are commonly used to convert $\rangle C{=}O$ group present in acetaldehyde and acetone into a $\rangle CH_2$ group.
(iv) Write two uses of acetone.

13. Hansa, a class XII student, was discussing diazonium salts. She emphasized that although azo dyes are excellent for dyeing fabric but the food coloured with azo dyes is harmful particularly for young children and asthma patients. Therefore, she stressed that only natural dyes should be used for colouring food.

After reading the above passage, answer the following questions :
(i) What are azo dyes? Give one example.
(ii) Name an azo dye which has been used as a food colour in the past but has now been banned?
(iii) Name a few natural food dyes.
(iv) What values are expressed by Hansa.

14. Sushant had been complaining about stomach ache every now and then. His teacher called the parents and asked them to stop giving him junk food and include fibre and vitamin rich food like sprouts, fruits, whole wheat bread and green leafy vegetables in his diet plan.

(i) What values are expressed by the teacher?
(ii) Give two examples of water soluble vitamins.
(iii) What is the importance of fibre rich food?
(iv) Why do children need a protein rich diet?

15. Riya wanted to buy some crockery for her kitchen. The shopkeeper showed two varieties of crockeries. Some were made of porcelain and others were made of melamine. Both were colourful and decorative. Shopkeeper told her that melamine made articles are lighter and durable than porcelain but Riya being a chemistry teacher decides to buy porcelain made crockeries.

Now answer the following questions :
(i) What is melamine?
(ii) Name one more polymer which is used to make unbreakable cups.
(iii) Why Riya buys porcelain made crockeries than that of melamine?
(iv) What are the values associated with this decision?

16. Mr. Praveen have too much responsibilities of his office which made his life full of tension and anxiety. This made his nights sleepless due to which he started taking sleeping pills. One day, he discussed all this with his friend, who is a doctor by profession. His friend advised him not to take sleeping pills but prescribed him some mild tranquillisers and asked him to change his lifestyle by doing yoga, meditation and some physical exercises. After a few days, he started feeling better.

After reading the above passage, answer the following :
(i) What values are expressed by the doctor?
(ii) What is the main ingredient of sleeping pills and how does it work?
(iii) Name two mild tranquillisers.

Detailed Solutions

1. (i) By giving preference to eco-friendly solar cell. Akanksha showed her awareness and concern towards the environment.

(ii) The main component used in solar cell is a semiconductor.

(iii) When sunlight falls on semiconductor then the energy is used for movement of electrons and holes which generates electric current.

(iv) Solar cells are used to convert solar energy into electric energy. It helps us in saving non-renewable sources of energy and utilizing the renewable source of energy.

2. (i) Ms. Vandana showed social values of saving energy and fuel as well as concern towards the health of villagers.

(ii) In pressure cooker, pressure is high and water boils at higher temperature. Hence, more heat is available for cooking the material.

(iii) Molal elevation constant may be defined as the elevation in boiling point when molality of the solution is unity.

(iv) $\Delta T_b = K_b \times m$

3. (i) (a) Lead battery will result into harmful effects on human beings as well as on the environment because it causes environmental pollution.

(b) Battery with cadmium plates will have sustained long term benefits regarding health and money.

(ii) Knowledge is useful only when put to practice. Awareness of less usage of lead batteries to keep ourselves and the environment healthy are the values shown by Prem.

(iii) PbO_2 is reduced to Pb^{2+} at cathode.

4. (i) The values displayed by Udit are :
   (a) Keen observation
   (b) Discipline and critical thinking.

(ii) It is a pseudo first order reaction. As water is present in large excess, its concentration will remain almost constant during the reaction. Therefore, the rate of reaction will depend only on the concentration of the reactant present in smaller amount *i.e.*, ester.

$$\text{Rate} = k[CH_3COOC_2H_5]$$

(iii) The volume of 0.1 N NaOH increased, as reaction proceeded due to the formation of CH_3COOH. Volume of NaOH consumed depends on both the acetic acid produced during the reaction and the acid present originally as catalyst as it is an acid-catalysed reaction. During the reaction, as the amount of acetic acid produced increased, the volume of NaOH used also increased.

(iv) H^+ ion acts as a catalyst in the reaction.

5. (i) Caring nature and social responsibility.

(ii) Gas masks contain charcoal which is a good adsorbent and therefore adsorbs many poisonous gases.

(iii) The nuisance of smoke in big industrial cities can be avoided by the use of Cottrell precipitator which allows smoke and many poisonous gases to get precipitated before coming out through the chimneys.

(iv) The precipitation of colloidal impurities present in water can be done by adding certain electrolytes like alum, etc. Impurities get coagulated and settle down and pure water can be decanted off.

6. (i) The graphical representation of Gibbs energy ($\Delta_f G°$) *vs* absolute temperature for formation of oxides of elements is known as Ellingham diagram.

(ii) Ellingham diagram shows that reduction of the oxide of the elements in upper line is feasible by the elements represented in the lower line. Reduction is easier if the difference is large.

(iii) (a) Hand holding and concern for juniors
   (b) Scientific knowledge and responsibility

7. (i) Team leader showed responsibility and alertness.

(ii) Phosphine, frequently contains traces of highly inflammable diphosphine P_2H_4 which catches fire spontaneously.

(iii) Calcium phosphide (Ca_3P_2) reacts with water to give PH_3 which catches fire instantaneously. Also, calcium carbide (CaC_2) on reaction with water produces acetylene which burns strongly to produce a signal.

(iv) $P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{Phosphine}}{PH_3} + 3NaH_2PO_2$

8. (i) Oxidising property of $KMnO_4$ makes it a bleaching agent.

(ii) Reduction half reaction of $KMnO_4$ in acidic medium :

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O, E^\circ = +1.52\text{ V}$

(iii) Chlorine may form some harmful compounds during bleaching of textiles. These compounds may cause water pollution whereas the bleaching by $KMnO_4$ is harmless.

(iv) By suggesting that industries should use chemicals which are less toxic to environment, Kamal showed the social values of awareness and concern towards the environment.

9. (i) Teacher gave him the solution of $[Ca(EDTA)]^{2-}$

(ii) On consumption of $[Ca(EDTA)]^{2-}$,

Pb^{2+} (poison) is replaced by Ca^{2+} ions.

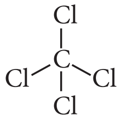
$Pb^{2+} + [Ca(EDTA)]^{2-} \longrightarrow [Pb(EDTA)]^{2-} + Ca^{2+}$

K_f (formation constant) of $[Pb(EDTA)^{2-}$ is 1×10^{18} and is much higher than that of $[Ca(EDTA)]^{2-}$ thus, this exchange reaction takes place to the completion and Pb^{2+} is removed completely.

(iii) Lead complex $[Pb(EDTA)]^{2-}$ is excreted by the body and Ca^{2+} remains in the body as nutrient. Hence, there are no side effects of this solution.

(iv) Scientific knowledge, care and concern for the students and alertness are the values shown by the teacher.

10. (i) Structure :



CCl_4

Hybridisation= sp^3

Structure = Tetrahedral

IUPAC name : Tetrachloromethane

(ii) There are evidences that exposure to carbon tetrachloride causes cancer in humans and many other fatal diseases. Carbon tetrachloride released in air rises to the atmosphere and depletes ozone layer. This depletion increases human exposure to ultraviolet rays leading to skin cancer and disruption of immune system.

(iii) Judicious use of chemicals to save atmosphere and human health.

11. (i) The Government is concerned about the well being of people and takes responsibility for the same.

(ii) No, production of alcohol should not be banned as :

(a) It is an important solvent for paints, lacquers, dyes, perfumes etc.

(b) It is used as an antiseptic and disinfectant and can also be used in the manufacture of important chemicals such as ether, chloroform etc.

(iii) Industrial alcohol is cheaper and to prevent workers from drinking this alcohol, it is denatured and hence rendered unfit for drinking.

(iv) We can spread awareness by

(a) showing programmes like skits, dramas, plays etc. to alcoholics, which will highlight the bad effects of alcohol.

(b) slogan writing at public places.

12. (i) Abhishek showed his concern and responsible nature by emphasizing that one should not play with chemicals in the laboratory.

(ii) Acetaldehyde reduces Tollens' reagent to silver mirror but acetone does not.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + CH_3COO^- + 2H_2O$$

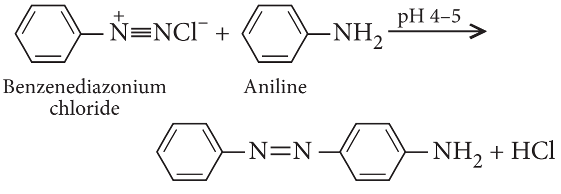
$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{\text{Tollens' reagent}} \text{No reaction}$$

(iii) Clemmensen reduction and Wolff–Kishner reduction.

(iv) (a) Acetone is used as a solvent in industries.

(b) Acetone is used in the preparation of a number of chemicals such as chloroform ketene, acetic anhydride etc.

13. (i) Dyes containing – N = N – as the functional group are called azo dyes. For example, aniline yellow obtained by coupling benzenediazonium chloride with aniline.



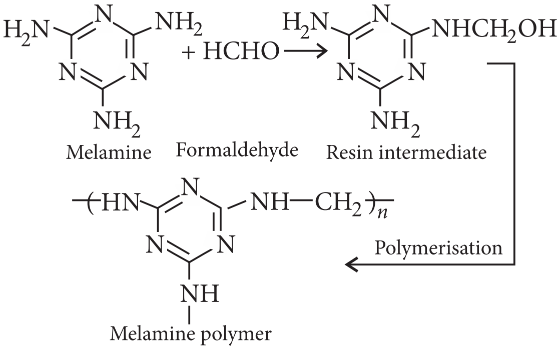
(ii) An example of synthetic azo dye which has been used to colour food is tetrazine which is suspected to be a cancer agent.

(iii) The natural food dyes are : turmeric, caramel, carotene, saffron, etc.

(iv) Hansa has displayed values about healthcare by emphasizing the use of natural dyes only.

14. (i) Teacher has expressed her responsibility and concern about the health of children.
(ii) Vitamin B complex and vitamin C.
(iii) Fibre rich food prevents constipation which is responsible for many other problems.
(iv) Children require protein rich diet to build muscles for the growth.

15. (i) Melamine polymer is a condensation polymer of melamine and formaldehyde.



(ii) Urea formaldehyde resin, polymer of urea and formaldehyde is also used for making unbreakable cups.

$$\left[NH-CO-NH-CH_2 \right]_n$$

Urea formaldehyde resin

(iii) Melamine is non-biodegradable polymer. Its accumulation will cause environmental problems. Porcelain is degradable and causes no problem of waste disposal.
(iv) Environmental protection must be kept in mind during the use of household articles.

16. (i) The doctor expressed concern about the healthcare of his friend and made him aware of the harmful effects of sleeping pills, overdoses of which act as poison and may even cause death.
(ii) The main ingredient of most of the sleeping pills is barbiturates. These chemicals make you breathe slowly and less deeply. That can be dangerous for people who have asthma or some other heart problems.
(iii) Chlordiazepoxide and meprobamate are mild tranquillizers.

CBSE Sample Paper

Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Name the non stoichiometric point defect responsible for colour in alkali metal halides.

2. What is shape selective catalysis?

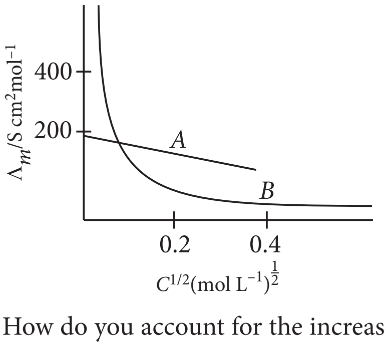
3. Amongst the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields a single monochloride.

4. Give the IUPAC name and structure of the amine obtained when 3-chlorobutanamide undergoes Hoffmann–bromamide reaction.

5. How many ions are produced from the complex, $[Co(NH_3)_6]Cl_2$ in solution?

6. Will the elevation in boiling point be same if 0.1 mol of sodium chloride or 0.1 mol of sugar is dissolved in 1L of water? Explain.

7. The following curve is obtained when molar conductivity (Λ_m) is plotted against the square root of concentration, $C^{1/2}$ for two electrolytes A and B



(a) How do you account for the increase in the molar conductivity of the electrolyte A on dilution.

(b) As seen from the graph, the value of limiting molar conductivity (Λ°_m) for electrolyte B cannot be obtained graphically. How can this value be obtained?

8. Name the following :

(a) A transition metal which does not exhibit variation in oxidation state in its compounds.

(b) A compound where the transition metal is in the +7 oxidation state.

(c) A member of the lanthanoid series which is well known to exhibit +4 oxidation state.

(d) Ore used in the preparation of potassium dichromate.

9. Arrange the following in order of property indicated for each set :

(a) F_2, Cl_2, Br_2, I_2 – increasing bond dissociation enthalpy

(b) PH_3, AsH_3, BiH_3, SbH_3, NH_3 – increasing base strength

10. (a) Predict the major product of acid catalysed dehydration of 1-Methylcyclohexanol.

(b) You are given benzene, conc.H_2SO_4, NaOH and dil.HCl. Write the preparation of phenol using these reagents.

OR

Draw the structures of any two isomeric alcohols (other than 1° alcohols) having molecular formula $C_5H_{12}O$ and give their IUPAC names.

11. An element occurs in the *bcc* structure with cell edge of 288 pm. The density of the element is 7.2 g cm^{-3}. How many atoms of the element does 208 g of the element contain?

12. Calculate the boiling point of a 1 M aqueous solution (density 1.04 g mL^{-1}) of potassium chloride (K_b for water = 0.52 K kg mol^{-1}, Atomic masses : K = 39 u, Cl = 35.5 u. Assume, potassium chloride is completely dissociated in solution.

13. A galvanic cell consists of a metallic zinc plate immersed in 0.1 M $Zn(NO_3)_2$ solution and metallic plate of lead in 0.02 M $Pb(NO_3)_2$ solution. Calculate the emf of the cell. Write the chemical equaiton for the electrode reactions and represent the cell.

(Given : $E^\circ_{Zn^{2+}/Zn} = -0.76V$; $E^\circ_{Pb^{2+}/Pb} = -0.13V$)

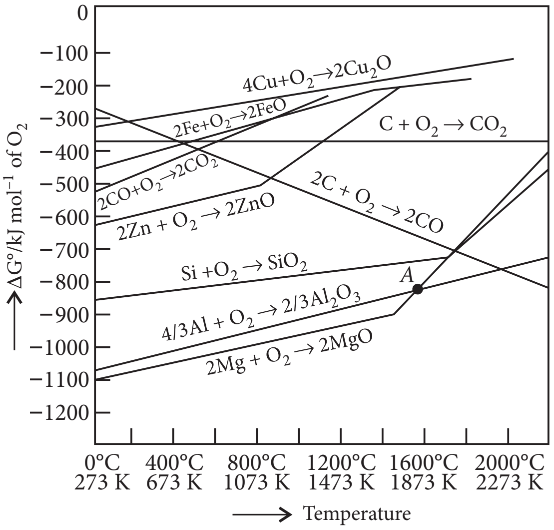
14. Answer the following questions :

(a) What happens when a freshly precipitated $Fe(OH)_3$ is shaken with a little amount of dilute solution of $FeCl_3$?

(b) Why are lyophilic colloidal sols more stable than lyophobic colloidal sols ?

(c) What form Freundlich adsorption equation will take at high pressure ?

15. What chemical principle is involved in choosing a reducing agent for getting the metal from its oxide ore? Consider the metal oxides, Al_2O_3 and FeO and justify the choice of reducing agent in each case.



OR

Account for the following facts :

(a) The reduction of a metal oxide is easier if the metal formed is in the liquid state at the temperature of reduction.

(b) Limestone is used in the manufacture of pig iron from haematite.

(c) Pine oil is used in the froth floatation process used to concentrate sulphide ores.

16. (i) For M^{2+}/M and M^{3+}/M^{2+} systems, E° values for some metals are as follows :

$Cr^{2+}/Cr = -0.9$ V $Cr^{3+}/Cr^{2+} = -0.4$ V
$Mn^{2+}/Mn = -1.2$ V $Mn^{3+}/Mn^{2+} = +1.5$ V
$Fe^{2+}/Fe = -0.4$ V $Fe^{3+}/Fe^{2+} = +0.8$ V

Use this data to comment upon

(a) The stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+}

(b) The ease with which iron can be oxidised as compared to the similar process for either Cr or Mn metals.

(ii) What can be inferred from the magnetic moment of the complex $K_4[Mn(CN)_6]$ Magnetic moment : 2.2 BM?

17. (i) Describe the type of hybridisation for the complex ion $[Fe(H_2O)_6]^{2+}$.

(ii) Write the IUPAC name of the ionisation isomer of the coordination compound $[Co(NH_3)_5Br]SO_4$. Give one chemical test to distinguish between the two compounds.

18. (a) Explain why the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(b) An optically active compound having molecular formula $C_7H_{15}Br$ reacts with aqueous KOH to give a racemic mixture of products. Write the mechanism involved in this reaction.

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

(a) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{HNO_2;\ 273K} B \xrightarrow{C_6H_5OH;\ 273K} C$

(b) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3,\Delta} C$

20. (a) A non reducing disaccharide '*A*' on hydrolysis with dilute acid gives an equimolar mixture of *D*-(+)-glucose and *D*-(–)-Fructose.

$$\underset{[\alpha]_D=+66.5^\circ}{A + H_2O} \xrightarrow{HCl} \underset{+52.5^\circ}{C_6H_{12}O_6} + \underset{-92.4^\circ}{C_6H_{12}O_6}$$

Identify *A*. What is the mixture of *D*-(+)-glucose and *D*-(–)-fructose known as? Name the linkage that holds the two units in the disaccharide.

(b) α-amino acids have relatively higher melting points than the corresponding halo acids. Explain.

21. (a) Pick out the odd one from among the following on the basis of their medicinal properties mentioning the reasion : Luminal, Seconal, Phenacetin, Equanil.

(b) Give an example of a substance that can act as a disinfectant as well as antiseptic depending upon its concentration. (Specifiy concentration)

(c) Name any two macromolecules chosen as drug targets.

22. The following is not an appropriate reaction for the preparation of *tert*-butyl ethyl ether :

$C_2H_5ONa + (CH_3)_3C—Cl \rightarrow (CH_3)_3C—OC_2H_5$

(i) What would be the major product of the given reaction?

(ii) Write a suitable reaction for the preparation of *tert*-butyl ethyl ether, specifying the names of reagents used.

Justify your answer in both cases.

23. Study the given passage carefully and answer the questions that follow :

Shalini studied a chapter on polymers in school and came across the following paragraph :

The durability, strength, low cost, water and chemicals resistance and light weight are advantages of plastic bags.

Shalini is confused as she has been reading in the newspaper about the ban on the usage of plastic substances.

She further finds that despite the durability, the use of these materials has presented mankind with serious waste disposal problem as these materials do not disintegrate by themselves. In view of this, certain polymers are being developed which are broken down rapidly by microorganisms. Shalini feels relaxed that such kinds of biomaterials are being developed.

(a) Name the class of these useful polymers which do not harm the environment.

(b) Give any one example of these polymers and name its monomers.

(c) Comment on the qualities of Shalini.

24. (a) Give a plausible explanation for each one of the following :

(i) Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol.

(ii) There are two $–NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

(b) Carry out the following conversions in not more than two steps :

(i) Phenyl magnesium bromide to benzoic acid.

(ii) Acetaldehyde to but-2-enal.

(iii) Benzene to *m*-nitroacetophenone

OR

(a) Give a simple chemical test to distinguish between the pair of organic compounds : Ethanal and Propanal

(b) Name and complete the following chemical reaction :

$RCH_2COOH \xrightarrow{(i) X_2/\text{red P} (ii) H_2O}$

(c) Draw the structures of the following derivatives :

(i) The 2,4-Dintitrophenylhydrazone of benzaldehyde

(ii) Acetaldehydedimethyl acetal

(iii) Cyclopropanone oxime

25. (a) Write the rate law for a first order reaction. Justify the statement that half life for a first order reaction is independent of the initial concentration of the reactant.

(b) For a first order reaction, show that the time required for 99% completion of a first order reaction is twice the time required for the completion of 90%.

OR

(a) For the reaction $A \rightarrow B$, the rate of reaction becomes twenty seven times when the concentration of A is increased three times. What is the order of the reaction?

(b) The activation energy of a reaction is 75.2 kJ mol^{-1} in the absence of a catalyst and it lowers to 50.14 kJ mol^{-1} with a catalyst. How many times will the rate of reaction grow in the presence of a catalyst if the reaction proceeds at 25°C?

26. (a) Write balanced chemical equations for the following :

- (i) Complete hydrolysis of XeF_6.
- (ii) Disproportionation reaction of orthophosphorus acid.

(b) Draw the structure of a noble gas species which is isostructural with BrO_3^-.

(c) Considering the parameters such as bond dissociation enthalpy, electron gain entalpy and hydration enthalpy, compare the oxidising power of F_2 and Cl_2.

(d) Why is $K_{a_2} << K_{a_1}$ for H_2SO_4 in water?

OR

Explain the following :

(a) Hydrogen fluoride is a weaker acid than hydrogen chloride in aqueous solution.

(b) PCl_5 is ionic in nature in the solid state.

(c) SF_6 is inert towards hydrolysis.

(d) H_3PO_3 is diprotic.

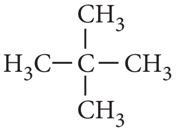
(e) Out of noble gases only Xenon is known to form established chemical compounds.

Detailed Solutions

1. Metal excess or anionic vacancies or *F*-centres [1]

2. Catalysis which depends on the shape and size of the reactants and the products and to those of the pores and cavities of catalyst. [1]

3. Neopentane or 2,2-Dimethylpropane



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$ [1]

4. 2-Chloropropanamine : $CH_3CH(Cl)CH_2NH_2$ [½,½]

5. Three ions : $[Co(NH_3)_6]^{2+}$ and $2Cl^-$ [1]

6. No, the elevation in boiling point is not the same. Elevation in boiling point is a colligative property which depends on the number of particles. NaCl is an ionic compound which dissociates in solution to give more number of particles whereas sugar is made up of molecules and thus does not dissociate. [½, 1½]

7. (a) As seen from the graph, electrolyte *A* is a strong electrolyte which is completely ionised in solution. With dilution, the ions are far apart from each other and hence the molar conductivity increases. [1]

(b) To determine the value of limiting molar conductivity for electrolyte *B*, indirect method based upon Kohlrausch's law of independent migration of ions is used. [1]

8. (a) Scandium (Sc) [½]

(b) $KMnO_4$ [½]

(c) Cerium (Ce) [½]

(d) Chromite ore [½]

9. (a) $I_2 < F_2 < Br_2 < Cl_2$ [1]

(b) $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$ [1]

10. (a) 1-Methylcyclohexene [1]

(b) $C_6H_6 \xrightarrow{Conc.H_2SO_4,\Delta} C_6H_5SO_3H \xrightarrow{NaOH,fuse,575K} C_6H_5ONa \xrightarrow{dil.HCl} C_6H_5OH$ [1]

OR

(i) $CH_3–CH_2–CH_2–CH(OH)–CH_3$: Pentan-2-ol [½+½]

(ii) $CH_3–CH_2–CH(OH)–CH_2–CH_3$: Pentan-3-ol [½+½]

11. For the *bcc* structure, $Z = 2$

Density, $\rho = \dfrac{Z \times M}{a^3 \times N_A}$ [½]

$7.2\ g\ cm^{-3} = \dfrac{2 \times M}{(288 \times 10^{-10}\ cm)^3 \times (6.022 \times 10^{23})mol^{-1}}$ [½]

Or $M = 51.8\ g\ mol^{-1}$ [½]

By mole concept,

51.8 g of the element contains 6.022×10^{23} atoms [½]

208 g of the element will contain

$= \dfrac{6.022 \times 10^{23} \times 208}{51.8}$ atoms [½]

$= 24.17 \times 10^{23}$ atoms. [½]

12. Molar mass of KCl = 39 + 35.5 = 74.5 g mol^{-1}

As KCl dissociates completely, number of ions produced are 2.

Therefore, van't Hoff factor, $i = 2$ [½]

Mass of KCl solution = 1000 × 1.04 = 1040 g

Mass of solvent = 1040 – 74.5 = 965.5 g = 0.9655 kg

Molality of the solution :

$\dfrac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}} = \dfrac{1\,\text{mole}}{0.9655\,\text{kg}} = 1.0357\,\text{m}$ [½]

$\Delta T_b = i \times K_b \times m$ [½]

$= 2 \times 0.52 \times 1.0357 = 1.078°C$ [½]

Therefore, boiling point of solution

$= 100 + 1.078 = 101.078°C$ [1]

13. Anode reaction : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ [½]

Cathode reaction : $Pb^{2+}_{(aq)} + 2e^- \longrightarrow Pb_{(s)}$ [½]

Cell representation : $Zn_{(s)}|Zn^{2+}_{(aq)}||Pb^{2+}_{(aq)}|Pb_{(s)}$ [½]

According to Nernst equation :

$E_{cell} = E°_{cell} - \dfrac{0.059}{n}\log\dfrac{[Zn^{2+}]}{[Pb^{2+}]}$ [½]

$E_{cell} = [-0.13-(-0.76)] - \dfrac{0.059}{2}\log\dfrac{0.1}{0.02}$ [½]

$= 0.63 - 0.0295 \times \log 5$

$= 0.63 - 0.0295 \times 0.6989$

$= 0.63 - 0.0206 = 0.6094$ V [½]

14. (a) A reddish brown positively charged colloidal sol is obtained. [1]

(b) Stability of lyophilic sols is due to :

(i) same charge on all the colloidal particles.

(ii) solvation of the colloidal particles. [½+½]

(c) At high pressures, amount of gas adsorbed (x/m) becomes independent of pressure (p).

$$\frac{x}{m} = k \times p^0$$ [1]

15. The feasibility of thermal reduction can be predicted on the basis of Ellingham diagram. Metals for which the standard free energy of formation ($\Delta_f G°$) is more negative can reduce those metals for which $\Delta_f G°$ is less negative. At a given temperature, any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram. [1]

(a) Below the temperature approx 1623 K, corresponding to the point of intersection of Al_2O_3 and MgO curves, Mg can reduce alumina. [1]

(b) At temperatures between 673 K and 1073 K, the CO , CO_2 line lies below Fe, FeO line, thus CO can reduce FeO to Fe.

At temperatures above this temperature, coke will reduce FeO and itself get oxidised to CO. [1]

OR

(a) Entropy is higher when a metal is in the liquid state than when it is in the solid state. Thus, $T\Delta S°$ increases, thus, $\Delta G°$ becomes more negative and the reduction becomes easier. ($\Delta G° = \Delta H° - T\Delta S°$) [1]

(b) Limestone provides the flux (CaO) which combines with the impurities (SiO_2) to form slag ($CaSiO_3$). Thus, it helps in the removal of impurities. [1]

(c) Pine oil (collector) enhances the non wettability of the ore particles, which become lighter and hence rise to the surface along with the froth. [1]

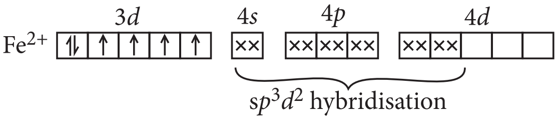
16. (i)(a) Cr^{3+}/Cr^{2+} has a negative reduction potential. Hence, Cr^{3+} cannot be reduced to Cr^{2+}. Cr^{3+} is most stable. Mn^{3+}/Mn^{2+} have large positive $E°$ values. Hence, Mn^{3+} can be easily reduced to Mn^{2+}. Thus, Mn^{3+} is least stable. Fe^{3+}/Fe^{2+} couple has a positive $E°$ value but smaller than Mn^{3+}/Mn^{2+}. Thus, the stability of Fe^{3+} is more than Mn^{3+} but less stable than Cr^{3+}. [1]

(b) If we compare the reduction potential values, Mn^{2+}/Mn has the most negative value *i.e.*, its oxidation potential value is most positive. Thus, it is most easily oxidised. Thus, the decreasing order for their ease of oxidation is Mn > Cr > Fe. [1]

(ii) $K_4[Mn(CN)_6]$

Mn is in +2 oxidation state. Magnetic moment 1.4 indicates that it has one unpaired electron and hence forms inner orbital or low spin complex. In presence of CN^- (a strong ligand), hybridisation involved is d^2sp^3 (octahedral complex). [1]

17. (i) Fe exists as Fe^{2+}. There are 4 unpaired electrons.

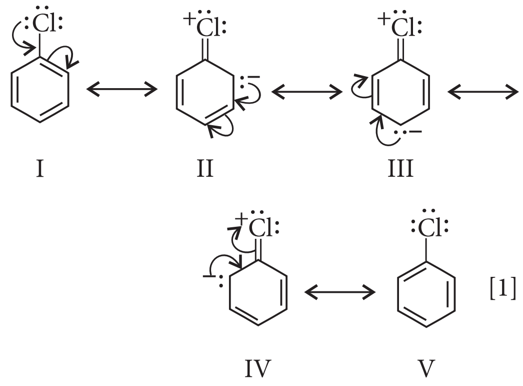


Water is a weak ligand. Thus, the hybridation involved is sp^3d^2. It is an octahedral outer orbital complex. [1]

(ii) The ionisation isomer is $[Co(NH_3)_5SO_4]Br$. The IUPAC name is Pentaamminesulphatocobalt(III) bromide. [1]

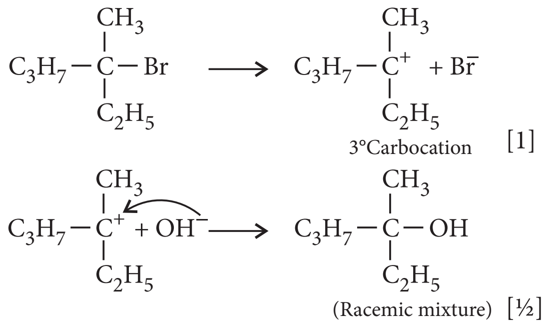
The isomer $[Co(NH_3)_5Br]SO_4$ gives a white precipitate of $BaSO_4$ with $BaCl_2$ solution whereas the isomer $[Co(NH_3)_5SO_4]Br$ does not form this precipitate. [1]

18. (a) Due to greater *s*-character, a sp^2 hybrid carbon is more electronegative than a sp^3 hybrid carbon. Therefore, the sp^2 hybrid carbon of C-Cl bond in chlorobenzene has less tendency to release electrons to Cl than a sp^3 hybrid carbon of cyclohexyl chloride.



[1]

(b) Since the alkyl halide reacts with KOH to form a racemic mixture, it must be a 3° alkyl halide and the reaction will follow S_N1 mechanism. [½]



$C_3H_7-\overset{CH_3}{\underset{C_2H_5}{C}}-Br \longrightarrow C_3H_7-\overset{CH_3}{\underset{C_2H_5}{C^+}} + Br^-$

3°Carbocation [1]

$C_3H_7-\overset{CH_3}{\underset{C_2H_5}{C^+}} + OH^- \longrightarrow C_3H_7-\overset{CH_3}{\underset{C_2H_5}{C}}-OH$

(Racemic mixture) [½]

19. (a) *A* – $C_6H_5NH_2$ *B* – $C_6H_5N_2^+Cl^-$
C – $C_6H_5 - N_2 - C_6H_4 - OH$ [½+½+½]

(b) *A* – C_6H_5CN *B* – C_6H_5COOH
C – $C_6H_5CONH_2$ [½+½+½]

20. (a) *A*–Sucrose ($C_{12}H_{22}O_{11}$) [½]

The mixture of *D*-(+)-glucose and *D*-(–)-fructose is known as invert sugar. [½]

The linkage which holds the two monosaccharide units through oxygen atom is called glycosidic linkage. [1]

(b) The amino acids exist as dipolar zwitter ion. Due to this dipolar salt like character they have strong dipole attractions. Thus, their melting points are higher than the corresponding haloacids which do not exist as zwitter ions. [1]

21. (a) Phenacetin is an antipyretic, while the rest are tranquilizers. [½+½]

(b) 0.2% solution of phenol acts as antiseptic whereas 1% solution of phenol acts as disinfectant. [1]

(c) Carbohydrates and proteins [½+½]

22. (i) Since the alkyl halide is a 3° halide and C_2H_5ONa is strong base, therefore, elimination occurs preferably. The product obtained is 2-methylprop-1-ene. $CH_3C(CH_3){=}CH_2$ [1]

(ii) To prepare *tert*-butyl ethyl ether, the alkyl halide should be 1° *i.e.*, chloroethane and the nucleophile should be sodium *tert*-butoxide because the 3° nucleophile is able to attack 1° alkyl halide. [½+½]

$(CH_3)_3CO^-Na^+ + CH_3CH_2Cl \rightarrow (CH_3)_3COCH_2CH_3$ [1]

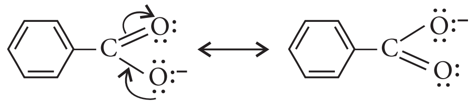
23. (a) The class of polymers is biodegradable polymers. [1]

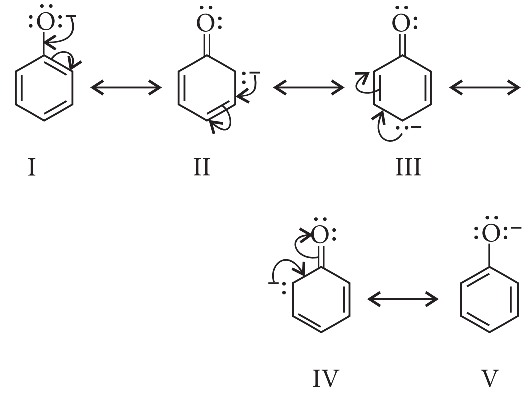
(b) One example of biodegradable polymers is PHBV (poly-β-hydroxybutyrate-co-β-hydroxyvalerate). [1]

The names of its monomers are : 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. [1]

(c) Care for environment, concern for the health of the people. [½+½]

24. (a)(i)





In case of phenoxide ion, strucutres (II-IV) carry a negative charge on the less electronegatice carbon atom.

In structure I and V, the negative charge on the oxygen atom remains localized while the electrons of the benzene rign only are delocalized.

While the negative charge on the carboxylate ion is delocalized over two oxygen atoms and in structure III and VII, the negative charge on the oxygen atom remians localized while the electrons of the benzene ring only are delocalized.

Thus, carboxylic acids are stronger acids than phenols. [1]

(ii) Semicarbazide has two $-NH_2$ groups. One of them, which is directly attached to C=O is involved in resonance. Thus, electron density on this group decreases and it does not act as a nucleophile. In contrast, the lone pair of electrons on the other $-NH_2$ group is available for nucleophilic attack. [1]

(b) (i) $PhMgBr + O{=}C{=}O \rightarrow PhCOOMgBr \xrightarrow{H_2O} PhCOOH$ [1]

(ii) $2CH_3CHO \xrightarrow{OH^-} CH_3CH(OH)-CH_2CHO \xrightarrow{heat} CH_3CH{=}CH-CHO$ [1]

(iii) $C_6H_6 \xrightarrow[\text{or } CH_3COCl/AlCl_3]{(CH_3CO)_2O\text{ , anh.}AlCl_3} PhCOCH_3$

$\xrightarrow{\text{conc.}H_2SO_4+\text{conc.}HNO_3} m\text{ - }NO_2C_6H_4COCH_3$ [1]

OR

(a) Ethanal and propanal can be distinghished by iodofrom test.

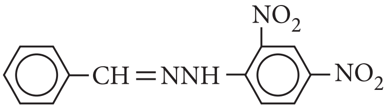
Ethanal gives a yellow precipitate of iodoform with an alkaline solution of NaOH. Propanal does not give this test.

$CH_3CHO + 4NaOH + 3I_2 \rightarrow CHI_3 + HCOONa + 3H_2O + 3NaI$ [1]

(b) $RCH_2COOH \xrightarrow[\text{(ii)}H_2O]{\text{(i)}X_2\text{, red P}} RCH(X)COOH$ [½]

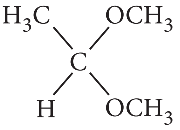
The name of the reaction is Hell-Vohlard-Zelinsky reaction. [½]

(c) (i)



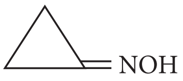
[1]

(ii)



[1]

(iii)



[1]

25. (a) For a first order reaction

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

$[R]$ = conc. after time t [1]

When half of the reaction is completed, $[R] = [R]_0/2$. Representing, the time taken for half of the reaction to be completed, by $t_{½}$, equation becomes :

$$k = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]_0/2} \quad [½]$$

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

$$t_{1/2} = \frac{2.303}{k}\times 0.3010$$

$$t_{1/2} = \frac{0.693}{k} \quad [½]$$

The above equation shows that half life first order reaction is independent of the initial concentration of the reactant.

(b) For a first order reaction,

$$t = \frac{2.303}{k}\log\frac{a}{a-x} \quad [1]$$

$$t_{99\%} = \frac{2.303}{k}\log\frac{a}{a-0.99a} \quad [½]$$

$$t_{90\%} = \frac{2.303}{k}\log\frac{a}{a-0.90a} \quad [½]$$

$$\frac{t_{99\%}}{t_{90\%}} = \left(\frac{2\times 2.303}{k}\right) / \frac{2.303}{k} = 2$$

$t_{99\%} = 2 \times t_{90\%}$ [1]

OR

(a) $r = k[A]^n$

When concentration is increased three times, $[A] = 3a$ [½]

$27r = k(3A)^n$

$\frac{27r}{r} = \frac{k(3A)^n}{kA^n}$ or $27 = 3^n$ or $3^3 = 3^n$ [½]

$n = 3$ [1]

(b) According to Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303RT}$$

For uncatalysed reaction

(i) $\log k_1 = \log A - \frac{E_{a_{(1)}}}{2.303RT}$ [½]

For catalysed reaction

(ii) $\log k_2 = \log A - \frac{E_{a_{(2)}}}{2.303RT}$ [½]

A is equal for both the reactions.

Subtracting equation(i) from equation(ii)

$$\log\frac{k_2}{k_1} = \frac{E_{a_{(1)}} - E_{a_{(2)}}}{2.303RT}$$

$$\log\frac{k_2}{k_1} = \frac{(75.2-50.14)\times 10^3\,\text{J mol}^{-1}}{2.303\times 8.314\,\text{JK}^{-1}\text{mol}^{-1}\times 298\text{ K}} \quad [1]$$

$$\log\frac{k_2}{k_1} = 4.39$$

$$\frac{k_2}{k_1} = \text{anti}\log 4.39$$

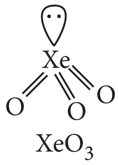
$$= 2.45 \times 10^4$$

Rate of reaction increases by 2.45×10^4 times. [1]

26. (a)(i) $XeF_{6(s)} + 3H_2O_{(l)} \rightarrow XeO_{3(s)} + 6HF_{(aq)}$ [1]

(ii) $4H_3PO_3 \xrightarrow{\text{heat}} PH_3 + 3H_3PO_4$ [1]

(b) XeO_3 is isostructural with BrO_3^- (pyramidal structure).



Pyramidal

[1]

(c) The bond dissociation enthalpy of F—F bond is lower than that of Cl—Cl bond and hydration enthalpy of F^- ion is much higher than that of Cl^- ion.

These two factors more than compensate the less negative electron gain enthalpy of F_2. Thus, F_2 is a stronger oxidizing agent than Cl_2. [1]

(d) H_2SO_4 ionises in two stages and hence has two dissociation constants.

$K_{a_2} << K_{a_1}$.

This is because the negatively charged HSO_4^- ion has much less tendency to donate a proton to H_2O as compared to neutral H_2SO_4. [1]

OR

(a) Due to stronger H-F bond than HCl bond, HF ionises less readily than HCl in aqueous solution to give H^+ ions. Therefore, HF is a weaker acid than HCl. [1]

(b) In solid state, PCl_5 consists of ions $[PCl_4]^+[PCl_6]^-$. On melting, these ions becomes free to move and hence conducts electricity in the molten state. [1]

(c) In SF_6, S is sterically protected by six F atoms and hence does not allow H_2O molecules to attack the S molecule. Also, F does not have *d*-orbitals to accept the electrons donated by H_2O molecules. [1]

(d) In the structure of H_3PO_3, it contains only two ionisable H-atoms which are present as –OH groups thus, it behaves as a dibasic acid. [1]

(e) Except radon which is radiocative, Xenon has least ionisation energy among noble gases and hence it forms chemical compounds particularly with O_2 and F_2. [1]

Practice Paper -1 (Solved)

Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. An organic compound C_8H_{18} on chlorination gives a single monochloride. Write the structure of the hydrocarbon.

2. Pure silicon is an insulator then, how does it behave as a semiconductor on heating?

3. Explain why the bond angle $(C-O-C)$ in ether is slightly greater than the tetrahedral angle (109.5°28')?

4. Which of the following electrolyte is most effective for the coagulation of $Fe(OH)_3$ sol and why?
Na_3PO_4, Na_2SO_4, NaCl

5. Comment on how sulphuric acid is a dibasic acid.

6. The partial pressure of ethane over a saturated solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what would be the partial pressure of the gas?

7. How will you bring about the following conversions?
(i) Propanone to propene
(ii) Benzoic acid to *m*-nitrobenzyl alcohol

8. Explain the following observations :
(i) Many of the transition elements are known to form interstitial compounds.
(ii) There is a general increase in density from titanium ($Z = 22$) to copper ($Z = 29$).

9. For the cell $Zn|Zn^{2+}_{(aq)} \,||\, Cu^{2+}_{(aq)}|Cu$, derive the relation between E°_{cell} and K_c at 298 K.

10. Write the formulae of the following complexes :
(i) Triamminetriaquachromium(III) chloride
(ii) *Tris*(ethane-1, 2-diammine)cobalt(III) sulphate
(iii) Diamminesilver(I) dicyanoargentate(I)
(iv) Mercury(I)tetrathiocyanatocobaltate(III)

OR

The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion.

11. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallises in cubic lattice. If the density is 2 g/cc, then find the radius (in pm) of metal atom.
(Given, $N_A = 6 \times 10^{23}$).

12. Write the chemical equations for synthesis of following polymers :
(i) Teflon (ii) PVC (iii) Glyptal

13. (i) What is meant by van't Hoff factor?
(ii) The osmotic pressure of a 0.0103 molar solution of an electrolyte is found to be 0.70 atm at 27°C. Calculate the van't Hoff factor.
($R = 0.082$ L atm mol^{-1} K^{-1}).
What conclusion do you draw about the molecular state of the solute in the solution?

14. How can reducing and non-reducing sugars be distinguished? Mention the structural feature characterising reducing sugars.

15. Calculate the standard cell potential of the given galvanic cell in which the following reaction takes place :
$2Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Cd_{(s)}$
Given : $E^\circ_{Cr^{3+}/Cr} = -0.74$ V, $E^\circ_{Cd^{2+}/Cd} = -0.40$ V
Also, calculate $\Delta_r G^\circ$ and equilibrium constant of the reaction.

OR

Calculate the standard cell potential, $\Delta_r G^\circ$ and equilibrium constant for the reaction :

$\mathrm{Fe}^{2+}_{(aq)} + \mathrm{Ag}^{+}_{(aq)} \rightarrow \mathrm{Fe}^{3+}_{(aq)} + \mathrm{Ag}_{(s)}$

Given : $E^\circ_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}} = -0.77\ \mathrm{V}, E^\circ_{\mathrm{Ag}^{+}/\mathrm{Ag}} = 0.80\ \mathrm{V}$

16. Give explanation for the following statements :

(i) Chloroacetic acid has lower pK_a value than acetic acid.

(ii) Carboxylic acids have higher boiling points than alcohols of comparable molecular masses.

(iii) Sodium bisulphite is used for the purification of aldehydes and ketones.

17. Explain what happens when

(i) ethanol vapours are passed over alumina at 600 K.

(ii) excess of ethanol is heated with conc. H_2SO_4 at 413 K.

(iii) phenol is treated with acetyl chloride.

18. Explain the following phenomenon giving reasons :

(i) Rate of physical adsorption decreases with rise of temperature.

(ii) Brownian movement

(iii) Colloidal particles scatter light.

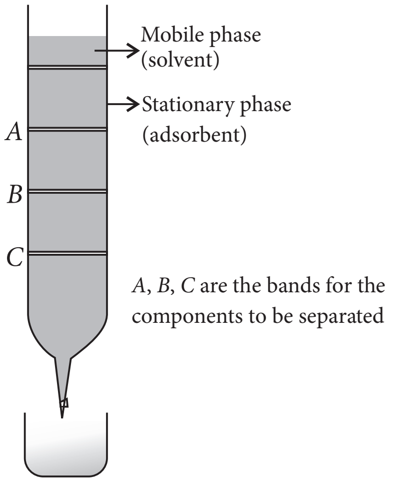
19. Give reasons for the following statements :

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

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

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

20. Consider the following chromatogram of column chromatography :



Answer the following questions :

(i) Which substance can act as stationary phase?

(ii) Which of the three components A, B and C is eluted first of all?

(iii) What is the principle of this technique?

21. Write short notes on :

(i) Ionisation isomerism

(ii) Linkage isomerism

(iii) Coordination isomerism.

22. Account for the following statements :

(i) Cerium (atomic number = 58) forms tetrapositive ion, Ce^{4+} in aqueous solution.

(ii) The second and third members in each group of transition element have similar atomic radii.

(iii) Write the structures of

(a) MnO_4^- (b) CrO_5

23. A local resident, Shyam observed that some people wash clothes in the Ganga river everyday and some people wash their cars, scooters, rickshaw etc. too. At the same time, local residents consumed the same water. Shyam held a resident's meeting to educate people to stop polluting the river water. During the meeting a local resident, Vidhu resisted this by arguing that running water of river which is in huge amount does not get polluted by washing clothes and vehicles.

(i) How does river water get polluted by washing clothes and vehicles using detergents?

(ii) What values are displayed by Shyam?

(iii) How many categories of detergents are there?

24. (i) The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is a first order reaction.

(a) After 50 seconds at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.

(b) Calculate the pressure of Cl_2O_7 after 100 sec of decomposition at this temperature.

(ii) One-fourth of a first order reaction is completed in 32 minutes. What is the half-life period of this reaction?

OR

Explain the following statements :

(i) Average rate of reaction does not give the true picture of the reaction rate.

(ii) A lump of coal burns at a moderate rate in air while coal dust burns explosively.

(iii) It takes more time to boil an egg or cook rice at higher altitudes.

(iv) Hydrogen and oxygen do not react at room temperature.

(v) How is rate constant related to concentration of the reactants?

25. (i) Arrange the following in decreasing order of property indicated :

(a) H_2O, H_2S, H_2Se, H_2Te (Boiling point)

(b) NH_3, PH_3, AsH_3, SbH_3 (Base strength)

(ii) Account for the following observations :

(a) The +5 oxidation state of phosphorus is stable but not for bismuth.

(b) Nitrogen forms a number of oxides while fewer number of oxides are possible for other elements of the group.

(c) Hydrogen fluoride has higher boiling point than hydrogen chloride.

OR

(i) Account for the following statements :

(a) Decomposition of O_3 molecule is a spontaneous process.

(b) SF_6 is inert towards hydrolysis.

(c) H_2S is less acidic than H_2Te.

(d) SO_2 is an air pollutant.

(ii) What happens when white phosphorus is heated with conc. NaOH solution in an inert gas atmosphere?

26. (i) An organic compound *(A)* with molecular formula $C_9H_{13}N$ dissolves in dil. HCl and releases N_2 with nitrous acid giving an optically active alcohol *(B)*. The alcohol *(B)* on oxidation gives dicarboxylic acid which on heating forms an anhydride. Identify the compounds *(A)* and *(B)*.

(ii) Give plausible explanations for the following :

(a) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.

(b) Tertiary amines do not undergo acylation reaction.

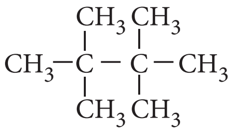
OR

(i) An aromatic compound, C_7H_8 *(A)* on nitration gives *(B)* as a major product which on reduction with Sn/HCl gives *(C)*. The compound *(C)* on treatment with $NaNO_2$/HCl at 273 K following by subsequent treatment with CuCl/HCl gives *(D)*. When *(D)* is oxidised, it forms *ortho*-substituted monocarboxylic acid with the formula $C_7H_5O_2Cl$. Predict the structures of *(A)*, *(B)*, *(C)* and *(D)*.

(ii) Outline the steps for the conversion of methylcyanide to methylamine.

Detailed Solutions

1. As C_8H_{18} on chlorination gives a single mono-chloride therefore, all the hydrogen atoms in it are equivalent. The possible structure of the hydrocarbon is



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

2. On heating some covalent bonds among silicon atoms break and electrons become free to move under applied field hence, silicon behaves like a semiconductor at high temperature.

3. There are two lone pairs on oxygen which cause lone pair-bond pair repulsions and hence, bond angle (C—O—C) should decrease and have value less than 109°28’ but steric hindrance of bulky alkyl groups causes increase in bond angle from 109.5°28’ to 111.7°.

4. $Fe(OH)_3$ is a positively charged sol hence, the anion having maximum charge will be more effective in coagulation. Therefore, Na_3PO_4 having PO_4^{3-} ion (charge = –3) will be most effective.

5. H_2SO_4 forms two series of salts, *i.e.*, both the hydrogen atoms are replaceable.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-}$$

$$H_2SO_4 + NaOH \rightarrow \underset{\text{Sodium hydrogen sulphate (Acid salt)}}{NaHSO_4} + H_2O$$

$$H_2SO_4 + 2NaOH \rightarrow \underset{\text{Sodium sulphate (Normal salt)}}{Na_2SO_4} + 2H_2O$$

6. According to Henry's law, $m = K_H \times p$

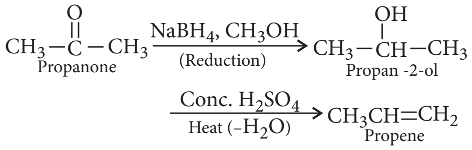
Case I: 6.56×10^{-3} g $= K_H \times 1$ bar

or, $K_H = 6.56 \times 10^{-3}$ g bar^{-1}

Case II : 5.00×10^{-2} g $= (6.56 \times 10^{-3}$ g bar$^{-1}) \times p$

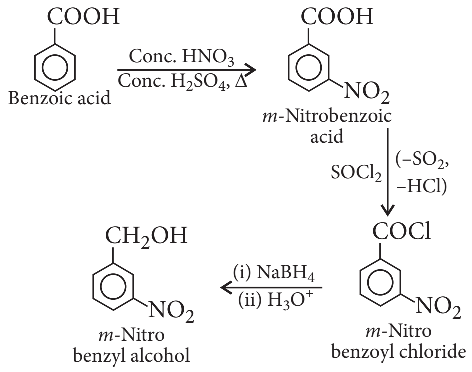
$$\text{or} \quad p = \frac{5.00\times10^{-2}\,\text{g}}{6.56\times10^{-3}\,\text{g bar}^{-1}} = 7.62 \text{ bar}$$

7. (i)



$$\underset{\text{Propanone}}{CH_3-\overset{\overset{\large O}{||}}{C}-CH_3} \xrightarrow[\text{(Reduction)}]{NaBH_4,\ CH_3OH} \underset{\text{Propan -2-ol}}{CH_3-\overset{\overset{\large OH}{|}}{CH}-CH_3} \xrightarrow[\text{Heat }(-H_2O)]{\text{Conc. }H_2SO_4} \underset{\text{Propene}}{CH_3CH{=}CH_2}$$

(ii)



8. (i) In the crystal lattice, transition elements have interstitial vacant spaces into which small sized non-metal atoms such as H, B, C, or N are trapped. These compounds are known as interstitial compounds. These are non-stoichiometric, neither typically ionic nor covalent, *e.g.*, TiC, Mn_4N, Fe_3H, etc.

(ii) As we move from left to right along a transition series (from Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Therefore, atomic volume decreases with increase in atomic mass and hence, density increases.

9. In this cell, electrons will flow from Zn electrode to Cu electrode.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + Cu_{(s)}$$

Apply the law of mass action,

$$K_c = \frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad (\because [Cu_{(s)} = [Zn_{(s)}] = 1)$$

According to Nernst equation for cell potential,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium E_{cell} is zero.

$$\therefore E^\circ_{\text{cell}} = \frac{2.303RT}{nF}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{2.303RT}{nF}\log K_c$$

$$\text{or} \quad \log K_c = \frac{n\times96500}{2.303\times8.314\times298}\,E^\circ_{\text{cell}}$$

$$\log K_c = \frac{n}{0.059}\,E^\circ_{\text{cell}}$$

$$E^\circ_{\text{cell}} = \frac{0.059}{n}\log K_c \quad \text{or } E^\circ_{\text{cell}} = \frac{0.059}{2}K_c$$

$[\because n = 2$ for Zn^{2+} and Cu^{2+} cell$]$

10. (i) $[Cr(NH_3)_3(H_2O)_3]Cl_3$

(ii) $[Co(en)_3]_2(SO_4)_3$

(iii) $[Ag(NH_3)_2][Ag(CN)_2]$

(iv) $Hg[Co(SCN)_4]$

OR

Oxidation number of Mn in the complex = +2

Mn(25) : [Ar] $3d^5 4s^2$

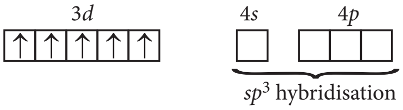
Mn^{2+} : [Ar] $3d^5$

$[Ar]\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

Magnetic moment (spin only) of five unpaired electrons in Mn^{2+} is

$$\sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.91 \text{ BM}$$

This is equal to the experimental value given (5.90 BM). Since all the *d*-orbitals are half-filled hence, the only possible geometry is tetrahedral with sp^3 hybridisation.



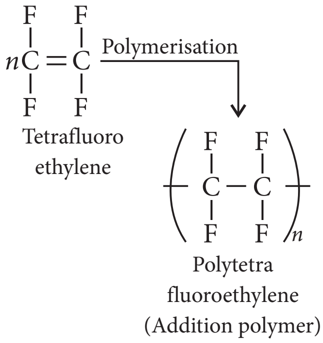
11. $$\rho = \frac{Z\times M}{a^3\times N_A} \text{ or } Z = \frac{\rho\times a^3\times N_A}{M}$$

$$= \frac{(2\text{ g cm}^{-3})(5\times10^{-8}\text{ cm})^3(6\times10^{23}\text{ mol}^{-1})}{75\text{ g mol}^{-1}} = 2$$

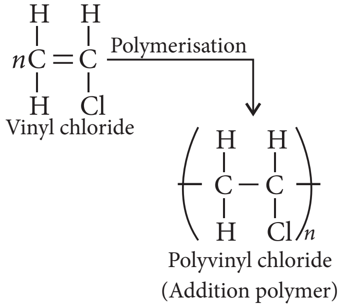
For a metal with $Z = 2$ means that it has body centred cubic *(bcc)* structure. For *bcc* structure,

$$\text{Atomic radius } (r) = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 5\ \text{Å} = 2.165\ \text{Å} = 216.5\ \text{pm}$$

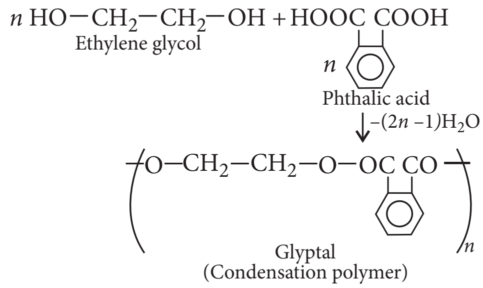
12. (i) Tetrafluoroethylene is the monomer that undergoes addition polymerisation to form telflon or polytetrafluoroethylene.



(ii) Vinyl chloride is the monomer that undergoes addition polymerisation of form polyvinyl chloride (PVC).



(iii) Phthalic acid and ethylene glycol are the monomers that undergo condensation polymerisation to form glyptal.



13. (i) van't Hoff factor *(i)* is the ratio of normal molecular mass to observed molecular mass or the ratio of observed colligative property to normal colligative property.

When $i > 1$, there is dissociation of solute in the solution.

When $i < 1$, there is association of solute in the solution.

When $i = 1$, there is no association or dissociation of solute in the solution.

(ii) $\pi = iCRT$

or, $0.70 = i \times 0.0103 \times 0.082 \times (27 + 273)$

or, $i = \dfrac{0.70}{0.0103 \times 0.082 \times 300} = 2.76$

Since i is >1 this shows that solute molecules are dissociated in the solution.

14. Reducing sugars are those carbohydrates which can reduce reagents like Tollens' reagent (ammoniacal $AgNO_3$), Benedict's solution and Fehling's solution whereas, non-reducing sugars cannot reduce these reagents.

All monosaccharides whether aldoses or ketoses are reducing sugars.

The characteristic structural feature of reducing sugars is that they must have aldehydic group ($-CHO$) or ketonic group ($>C=O$) in the hemiacetal or hemiketal form.

15. $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= -0.40\ V - (-0.74\ V) = +0.34\ V$

$\Delta_r G^\circ = -nFE^\circ_{cell}$

$= -6 \times 96500\ C\ mol^{-1} \times 0.34\ V$

$= -196860\ C\ V\ mol^{-1} = -196860\ J\ mol^{-1}$

$\Delta_r G^\circ = -2.303\ RT \log K_c$

$-196860 = -2.303 \times 8.314 \times 298 \log K_c$

or $\log K_c = 34.5014$

$K_c = \text{Antilog } 34.5014 = 3.172 \times 10^{34}$

OR

$E^\circ_{cell} = +0.80\ V - 0.77\ V = +0.03\ V$

$\Delta_r G^\circ = -nFE^\circ_{cell}$

$= -(1) \times (96500\ C\ mol^{-1}) \times (0.03\ V)$

$= -2895\ C\ V\ mol^{-1} = -2895\ J\ mol^{-1}$

$\Delta_r G^\circ = -2.303\ RT \log K_c$

$-2895 = -2.303 \times 8.314 \times 298 \times \log K_c$

or $\log K_c = 0.5074$

or $K_c = \text{Antilog } (0.5074) = 3.22$

16. (i) 'Cl' in chloroacetic acid shows $-I$ effect which creates less electron density on oxygen of carboxylic acid. Thus, release of proton becomes easier. In case of acetic acid, $+I$ effect of $-CH_3$ group makes the release of proton difficult. Hence, chloroacetic acid is stronger acid than acetic acid. Thus, chloroacetic acid has lower pK_a value than that of acetic acid.

(ii) Carboxylic acids and alcohols both undergo hydrogen bonding among their molecules. Hydrogen bonding among acid molecules is far stronger than among alcohol molecules. Hence, carboxylic acids have higher boiling points than alcohols.

Strong hydrogen bonding among carboxylic acid molecules (Dimer formation).

(iii) Sodium bisulphite reacts with aldehydes and ketones to form insoluble, crystalline addition products. These products can be easily separated in pure state. These products can be decomposed by dilute mineral acid or alkali to give back original aldehyde or ketone.

Hence, it can be used for purification of aldehydes and ketones.

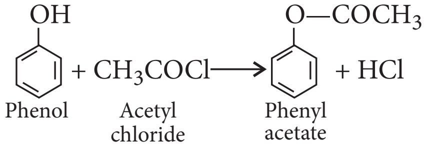
17. (i) Dehydration will take place and ethene will be formed.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[600\text{ K}]{Al_2O_3} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

(ii) Diethylether is formed.

$$2C_2H_5OH \xrightarrow[413\text{ K}]{\text{Conc. }H_2SO_4} \underset{\text{Ethoxyethane}}{C_2H_5OC_2H_5} + H_2O$$

(iii) Phenylethanoate is formed.



18. (i) Physical adsorption is an exothermic process and the equilibrium is represented as

Gas (Adsorbate) + Solid (Adsorbent) ⇌ Gas adsorbed on Solid + Heat

As the temperature is increased, equilibrium shifts in the backward direction, *i.e.*, adsorption decreases (Le Chatelier's principle).

(ii) Brownian movement is due to bombardment of colloidal particles by the molecules of the dispersion medium with unequal forces from different directions. As a result, there is a resultant force acting on them causing the particles to move in zig-zag directions.

(iii) Scattering of light by colloidal particles or Tyndall effect is observed when the diameter of the dispersed particles is not much smaller as compared to the wavelength of the light. So, colloidal particles can scatter light as they have desirable particle size of 10 Å – 10,000 Å.

19. (i) The rate of S_N2 reaction depends on the tendency of leaving group to leave and the tendency of attacking nucleophile to attack. Iodide is a better leaving group because of its larger size than bromide therefore, ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.

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

(iii) Due to delocalisation of lone pair of electrons of the X atom over the benzene ring, C—X bond in halobenzene acquires some double bond character while in $CH_3—X$, C—X bond is a pure single bond. Therefore, C—X bond in halobenzene is shorter than in $CH_3—X$.

20. (i) Silica gel and alumina can act as stationary phase.

(ii) Component C is weakly adsorbed component thus, travels faster than A and B components with mobile phase and hence, eluted first.

(iii) Different components of the mixture are adsorbed at different rates on the surface of adsorbent. Thus, in mobile phase each component move on stationary phase to different levels and get separated.

21. (i) Ionisation isomerism : When two complexes have same molecular formula but give different ions in solution, they are said to be ionisation isomers and the phenomenon is known as ionisation isomerism. This isomerism arises due to the exchange of ions between coordination sphere and ionisation sphere. For example,

$[Co(NH_3)_5Br]SO_4$ and
Pentaamminebromidocobalt(III) Sulphate
$[Co(NH_3)_5SO_4]Br$
Pentaamminesulphatocobalt(III) bromide

(ii) Linkage isomerism : When any monodentate ligand in a complex has more than one donor atoms, it may be bonded to metal ion through either of the atoms and gives different isomers. For example, ligand SCN^- may be bonded to the metal either through sulphur or through nitrogen to give two different isomers.

$[Co(NH_3)_5SCN]Cl_2$ and $[Co(NH_3)_5NCS]Cl_2$
Pentaamminethiocyanato cobalt(III) chloride   Pentaammineisothiocyanato cobalt(III) chloride

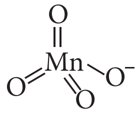
(iii) Coordination isomerism : This type of isomerism arises when both positive and negative ions of a compound are complex ions. There may be an exchange of ligand molecules between the two coordination spheres of two ions to give two coordination isomers.

$[Cu(NH_3)_4]\,[PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
Tetraamminecopper(II) tetrachloridoplatinate(II)   Tetraammineplatinum(II) tetrachloridocuprate(II)

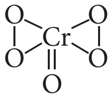
22. (i) The electronic configuration of Ce ($Z = 58$) is $_{58}Ce = [Xe]\ 4f^1 5d^1 6s^2$
Cerium can lose four electrons ($4f^1 5d^1 6s^2$) in aqueous solution to acquire stable configuration of rare gas xenon. Due to small size and high charge, Ce^{4+} ion has high hydration energy

(ii) The second and third members in each group of transition elements have very similar atomic radii due to lanthanoid contraction which arises due to poor shielding effect of *f*-electrons.

(iii) (a)



(b)



23. (i) Detergents get accumulated in the river water causing foaming in river and thus, water gets polluted and becomes unfit for drinking.

(ii) Leadership, awareness and concern for people and environment, are the values displayed by Shyam.

(iii) Detergents are mainly classified into three categories :
(a) Anionic detergents, which are sodium salts of sulphonated long chain alcohols or hydrocarbons.
(b) Cationic detergents, which are quarternary ammonium salts of acetates, chlorides or bromides as anions.
(c) Non-ionic detergents which do not contain any ion in their constitution.

24 (i) $a \propto P_0$ and $(a - x) \propto P_t$

Hence, $k = \dfrac{2.303}{t}\log\dfrac{P_0}{P_t}$ (P_t = pressure of Cl_2O_7 at time t)

(a) $t = 50$ s, $P_0 = 0.062$ atm, $P_t = 0.044$ atm

$$k = \frac{2.303}{50\text{ s}}\log\frac{0.062\text{ atm}}{0.044\text{ atm}} = 6.86 \times 10^{-3}\text{ s}^{-1}$$

(b) $t = 100$ s, $P_t = ?$, $k = 6.86 \times 10^{-3}\text{ s}^{-1}$

$$6.86 \times 10^{-3}\text{ s}^{-1} = \frac{2.303}{100\text{s}}\log\frac{0.062\text{ atm}}{P_t}$$

$$\log\frac{0.062}{P_t} = 0.2979$$

$$\Rightarrow \frac{0.062}{P_t} = \text{Antilog } 0.2979 = 1.986$$

or $P_t = 0.0312$ atm

(ii) $$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{32\text{ min}}\log\frac{a}{a - a/4}$$

$$= \frac{2.303}{32}\log\frac{4}{3}\text{ min}^{-1} = 0.009\text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.009} = 77\text{ min}$$

OR

(i) Average rate of reaction is obtained by dividing the change in concentration of a particular species by the time interval. As the concentration changes are not uniform, the average rate does not give a true picture of the reaction rate.

(ii) Coal dust has greater surface area than a lump of coal. Thus, coal dust has greater ease of coming in contact with air and therefore burns explosively.

(iii) Water boils at temperature lower than 100°C due to low atmospheric pressure at higher altitudes. Thus, when eggs or rice are boiled in water at higher altitudes, the water boils earlier *i.e.,* at lower temperature. Hence, to cook the food completely the food should be heated for more time.

(iv) At room temperature, there is no reaction between hydrogen and oxygen as the activation energy of the reaction is very high. They require very high temperature to react which can be produced generally by electric spark or explosion.

(v) Consider the reaction

$A + B \rightarrow C$

Then, according to rate law,

Rate = $k\ [A]^x[B]^y$

where k = rate constant

$[A]$ and $[B]$ are concentrations of A and B and x and y are the order of the reaction w.r.t. A and B respectively.

Now, as the concentration of A and B changes, the rate of reaction changes such that rate constant remains unchanged. Thus, rate constant of a reaction does not depend on the concentration of the reactants.

25. (i) (a) $H_2O > H_2Te > H_2Se > H_2S$

Because the boiling points of hydride increase with the increase in molecular mass of the elements. H_2O has exceptionally high boiling point because of intermolecular hydrogen bonding.

(b) $NH_3 > PH_3 > AsH_3 > SbH_3$

With the increase in size of the metal, the electron density of the lone pair gets diffused over a large region and ability to donate lone pair gets reduced hence, basic character decreases.

(ii) (a) In bismuth, due to inert pair effect only $6p^3$ electrons are used, thus Bi^{3+} is formed and Bi^{5+} does not exist (except in BiF_5). However, in phosphorus, $3s^2$ and $3p^3$ electrons can take part in bonding thus, P^{5+} can exist.

(b) Nitrogen has a strong tendency to form $p\pi$-$p\pi$ multiple bonds between N and O atoms and thus, it forms number of oxides which have no P, As, Sb or Bi analogues as these elements of group 15 do not have tendency to form $p\pi$-$p\pi$ multiple bonds.

(c) In hydrogen fluoride, strong intermolecular hydrogen bonding is present, due to small size and high electronegativity of fluorine and hence, HF is a liquid having higher boiling point than HCl which is a gas due to the absence of hydrogen bonding.

OR

(i) (a) For spontaneity of a reaction, ΔG must be negative. Decomposition of O_3 is an exothermic process (ΔH = –ve) and occurs with increase in entropy (ΔS = +ve). These two effects reinforce each other which results in large negative Gibbs energy change according to the relation,

$\Delta G = \Delta H - T\Delta S$

Thus, its decomposition is a spontaneous reaction.

(b) In SF_6, S is surrounded by 6 F^- octahedrally. Therefore, attack of water molecule on S is sterically hindered. Hence, it is an inert substance.

(c) In a group, on moving down the group there is decrease in E–H bond dissociation enthalpy which increases acidic character. Thus, H_2S is less acidic than H_2Te.

(d) SO_2 is water soluble therefore, it dissolves in rain water causing acid rain. Moreover, when released in air, it leads to several diseases like eye irritation, redness in eyes, asthma, bronchitis, etc. Thus, it is considered as an air pollutant.

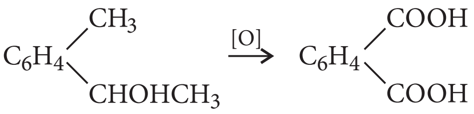
(ii) When white phosphorus is heated with conc. NaOH solution in an inert gas atmosphere, phosphine gas is produced.

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{Phosphine}}{PH_3} + 3NaH_2PO_2$$

26. (i) (a) Since (A) releases N_2 with nitrous acid, it must be a primary amine.

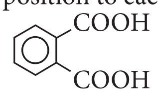
$$\underset{A}{C_9H_{11}NH_2} \xrightarrow{HNO_2} \underset{B}{C_9H_{11}OH} + N_2$$

(b) The alcohol *(B)* is optically active, therefore, it should contain a chiral carbon atom. Keeping in view, the molecular formula of *(A)* and *(B)* as well as the fact that *(B)* on oxidation gives a dicarboxylic acid, *i.e.,* has two side chains on the benzene ring, the compound *(B)* can be

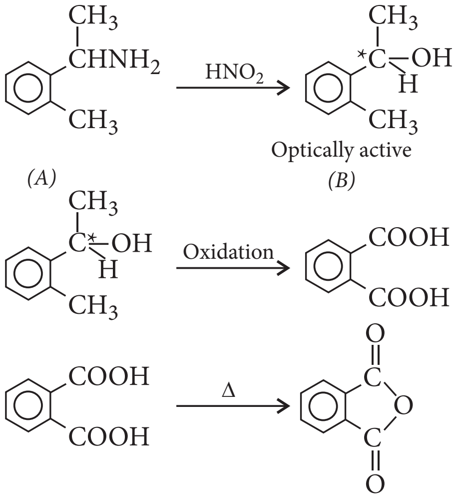


(B) (Dicarboxylic acid)

(c) Since the dicarboxylic acid on heating forms an anhydride, the two side chains as well as the two –COOH groups are at *ortho*-position to each other, *i.e.,*



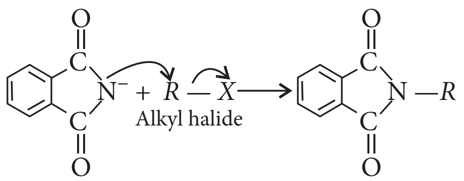
The reactions can be explained as follows :



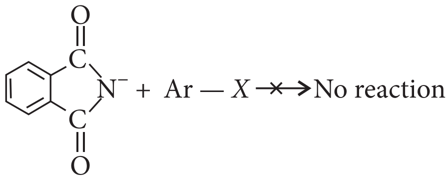
(A) Optically active *(B)*

Phthalic acid Phthalic anhydride

(ii) (a) Gabriel phthalimide reaction involves the nucleophilic attack of the phthalimide anion on organic halogen compound.



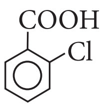
Due to resonance in aryl halides, there is some double bond character in Ar – *X* because of which it is difficult to break. Therefore, aryl halides do not undergo nucleophilic substitution reactions easily and aromatic primary amines cannot be prepared by Gabriel synthesis.



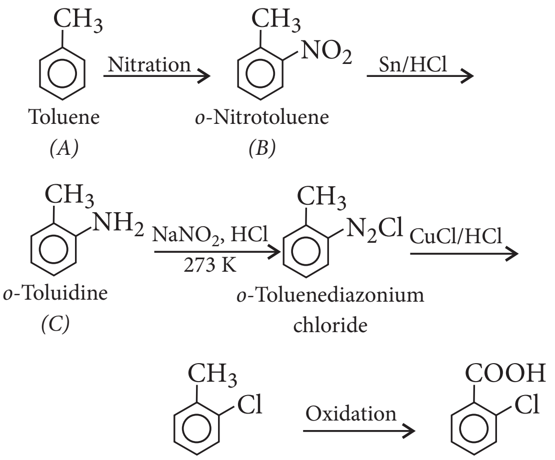
(b) Tertiary amines do not undergo acylation reaction because they do not have hydrogen attached to nitrogen.

OR

(i) The final product is an *ortho*-substituted monocarboxylic acid. Therefore, it is monocarboxylic aromatic acid with chloro group at the *ortho*-position. Therefore, it is



Thus, the sequence of the reactions can be visualised as follows :

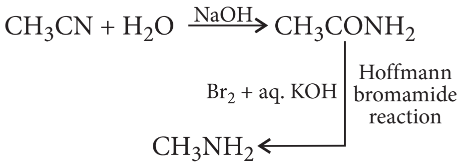


Toluene *(A)* *o*-Nitrotoluene *(B)*

o-Toluidine *(C)* *o*-Toluenediazonium chloride

o-Chlorotoluene *(D)* *o*-Chlorobenzoic acid

(ii)



$$CH_3CN + H_2O \xrightarrow{NaOH} CH_3CONH_2 \xrightarrow[\text{Br}_2 + \text{aq. KOH}]{\text{Hoffmann bromamide reaction}} CH_3NH_2$$

Practice Paper -2 (Solved)

Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

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

2. For the reaction, $X_2 + 2Y_2 \rightarrow 2XY_2$, write the rate equation in terms of the rate of disappearance of Y_2.

3. Pick out the odd one amongst the following on the basis of their medicinal properties mentioning the reason.
Chloroxylenol, phenol, chloramphenicol, bithional.

4. Aniline is a weaker base than cyclohexylamine. Why?

5. Account for the following : *o*-nitrophenol has lower boiling point than *p*-nitrophenol.

6. A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

7. Rate constant of the first order reaction is 6.93×10^{-3} s^{-1}. Calculate
(i) half-life.
(ii) time of 75% completion of reaction.

8. (i) Give the electronic configuration of the *d*-orbitals of Ti in $[Ti(H_2O)_6]^{3+}$ ion in an octahedral crystal field.
(ii) Why is the given complex coloured? Explain on the basis of distribution of electrons in the *d*-orbitals.

9. Predict the products of electrolysis obtained at the electrodes in each case when the electrodes used are of platinum :
(i) An aqueous solution of $AgNO_3$.
(ii) An aqueous solution of H_2SO_4.

10. Explain how vacancies are introduced in an ionic solid when a cation of higher valency is added as an impurity in it.

OR

Ionic solids, which have anionic vacancies due to metal-excess defect, develop colour. Explain with the help of a suitable example.

11. Give reasons for the following :
(i) Addition of Cl_2 to KI solution gives it a brown colour, but excess of Cl_2 turns it colourless.
(ii) Phosphinic acid behaves as a monoprotic acid.
(iii) White phosphorus is much more reactive than red phosphorus.

12. (i) A given ore is a mixed sulphide of lead and zinc (PbS-ZnS). Suggest a method to separate the mixture.
(ii) Write the chemical reactions involved in the extraction of gold by cyanide process.

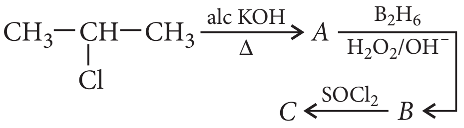
13. Explain the following terms with a suitable example in each case :
(i) Shape-selective catalysis
(ii) Dialysis
(iii) Multimolecular colloids

14. (i) Give the IUPAC name of $[PtCl(NH_2CH_3)(NH_3)_2]Cl$.
(ii) Compare the magnetic behaviour of the complex entities $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{3-}$. [Fe = 26].

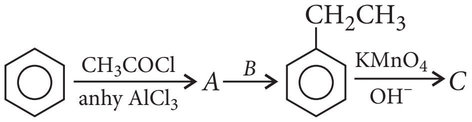
15. A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential ($E^\circ_{Zn^{2+}/Zn} = -0.76$ V)

16. Write the structures of *A*, *B* and *C* in the following reactions.

(i)



(ii)



17. Write structures and names of the monomers of the following polymers :

(i) Nylon 6,6
(ii) Nylon 6
(iii) Urea formaldehyde resin

OR

(i) How will you differentiate between low density and high density polythenes?
(ii) Arrange the following polymers in order of increasing intermolecular forces :
Bakelite, Nylon 6,6, Polythene, Neoprene.

18. State Henry's law for solubility of a gas in a liquid and give its important applications.

19. Give plausible explanation for each of the following :

(i) There are two —NH_2 groups in semicarbazide. However, only one is involved in the formation of semicarbazone.
(ii) Give the mechanism of esterification of carboxylic acids.

20. (i) What is the structural difference between a nucleoside and a nucleotide?
(ii) "The two strands of DNA are not identical but are complementary." Explain.
(iii) Differentiate between fibrous and globular proteins.

21. Mention the action of the following on the human body in bringing relief from a disease.

(i) Brompheniramine
(ii) Aspirin
(iii) Equanil

22. Outline the principles of refining of metals by the following methods :

(i) Zone refining
(ii) van Arkel method
(iii) Liquation method

23. Dr. Rachna – a dietician conducted a seminar for the students of class XII. She emphasized the importance of balanced diet for good health. She also discussed with students that under special conditions like for pregnant women, growing children and HIV/AIDS patients or heart patients, protein rich diet is recommended.

(i) What values are displayed by Dr. Rachna?
(ii) Why do HIV/AIDS or heart patients need a protein rich diet?
(iii) Name some rich sources of proteins.
(iv) What are the chief components of a balanced diet?

24. (i) Give one chemical test to distinguish between the following pairs of compounds:
(a) Methylamine and dimethylamine
(b) Ethanal and propanal
(c) Benzoic acid and ethyl benzoate
(ii) How will you bring about the following conversions in not more than two steps?
(a) Benzene to *m*-nitroacetophenone
(b) 2-Methylpropanol to 2-methylpropene

OR

(i) An organic compound (*A*) [molecular formula $C_8H_{16}O_2$] was hydrolysed with dilute sulphuric acid to give a carboxylic acid (*B*) and an alcohol (*C*). Oxidation of (*C*) with chromic acid produced (*B*). (*C*) on dehydration gives but-1-ene. Write equations for the reactions involved.
(ii) Write the equations involved in the following reactions :
(a) Kolbe's reaction
(b) Cannizzaro reaction

25. (i) Why is freezing point depression of 0.1 M sodium chloride solution nearly twice that of 0.1 M glucose solution?
(ii) At 300 K, 36 g of glucose present per litre in its solution has an osmotic pressure of 4.98 bar. If osmotic pressure of solution is 1.52

bar at the same temperature, what would be its concentration?

(iii) Osmotic pressure is more useful to calculate molecular mass than other colligative properties. Why?

OR

(i) 15 g of an unknown molecular mass substance was dissolved in 450 g of water. The resulting solution freezes at – 0.34°C. What is the molar mass of the substance? (K_f for water = 1.86 K kg mol^{-1})

(ii) Non-ideal solutions exhibit either positive or negative deviations from Raoult's law. What are these deviations and why are they caused? Explain with one example for each type.

26. Assign reason for the following :

(i) The enthalpies of atomisation of transition elements are high.

(ii) The transition metals and many of their compounds act as good catalyst.

(iii) Actinoid contraction is greater from element to element than the lanthanoid contraction.

(iv) The $E°$ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.

(v) Scandium (Z = 21) does not exhibit variable oxidation states and yet it is regarded as transition element.

OR

(i) Write the steps involved in the preparation of

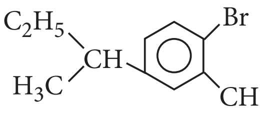
(a) $K_2Cr_2O_7$ from Na_2CrO_4

(b) $KMnO_4$ from K_2MnO_4.

(ii) What is meant by lanthanoid contraction? What effect does it have on the chemistry of the elements which follow lanthanoid contraction?

Detailed Solutions

1.



2. Rate of reaction = $-\frac{1}{2}\frac{d[Y_2]}{dt}$

3. Chloramphenicol is an antibiotic while all the remaining are antiseptics.

4. In aniline there is delocalisation of lone pair of electrons of N atom in benzene ring therefore it is less basic than cyclohexylamine.

5. *o*-Nitrophenol has intramolecular H-bonding which is weaker than intermolecular H-bonding present in *p*-nitrophenol.

6. No. of atoms in the close packing = 0.5 mol = $0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$

No. of octahedral voids = 1 × No. of atoms in the packing = 3.011×10^{23}

No. of tetrahedral voids = 2 × No. of atoms in the packing = $2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$

Total no. of voids $= 3.011 \times 10^{23} + 6.022 \times 10^{23}$

$= 9.033 \times 10^{23}$

7. (i) For first order reaction,

$$\text{half-life} = \frac{0.693}{k} = \frac{0.693}{6.93\times10^{-3}\,s^{-1}} = 100\ s$$

(ii) For first order reaction, half-life is related to time of 75% completion of reaction by

t_{75} = 2 × half-life = 2 × 100 = 200 s

8. (i) In $[Ti(H_2O)_6]^{3+}$ ion, Ti is in +3 oxidation state. The electronic configuration of Ti^{3+} ion is $3d^1$. In an octahedral field, it is $t_{2g}^1e_g^0$.

(ii) Due to *d*-*d* transition, the electron present in t_{2g} absorbs green and yellow radiation of white light for excitation to e_g. The complementary colour is purple.

9. (i) $AgNO_{3(aq)} \longrightarrow Ag^+_{(aq)} + NO^-_{3(aq)}$

$H_2O_{(l)} \longrightarrow H^+_{(aq)} + OH^-_{(aq)}$

At cathode: $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$

At anode: $2OH^-_{(aq)} \longrightarrow O_2 + 2H^+_{(aq)} + 4e^-$

Or $2H_2O_{(l)} \longrightarrow O_2 + 4H^+_{(aq)} + 4e^-$

(ii) $H_2SO_{4(aq)} \longrightarrow 2H^+_{(aq)} + SO^{2-}_{4(aq)}$

$H_2O_{(l)} \longrightarrow H^+_{(aq)} + OH^-_{(aq)}$

At cathode: $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

At anode: $2OH^-_{(aq)} \longrightarrow O_2 + 2H^+_{(aq)} + 4e^-$

Or $2H_2O_{(l)} \longrightarrow O_2 + 4H^+_{(aq)} + 4e^-$

10. When a cation of higher valency is added as an impurity in the ionic solid, some of the sites of the original cations are occupied by the cations of higher valency. Each cation of higher valency replaces two or more original cations and occupies the site of one original cation and the other site(s) remains vacant.

Cationic vacancies produced = Number of cations of higher valency × Difference in valencies of the original cation and cation of higher valency

OR

In ionic solids with anionic vacancies due to metal-excess defect, when the metal atoms deposit on the surface, they diffuse into the crystal and after ionization, the metal ion occupies cationic vacancy while electron occupies anionic vacancy. These electrons get excited to higher energy levels by absorption of suitable wavelengths from the visible white light and, therefore appear coloured.

Example : Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{Heat}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

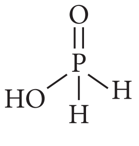
The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites. These electrons absorb visible light and impart yellow colour to zinc oxide.

11. (i) Chlorine being stronger oxidising agent than iodine displaces iodine from KI which brings brown colour to the solution. In excess of chlorine, the liberated iodine is further oxidised to iodic acid and solution becomes colourless.

$Cl_2 + 2KI \longrightarrow 2KCl + \underset{\text{(Brown)}}{I_2}$;

$I_2 + 5Cl_2 + 6H_2O \longrightarrow \underset{\text{(Colourless)}}{2HIO_3 + 10HCl}$

(ii) Phosphinic acid has only one replaceable hydrogen atom.



(iii) White P_4 is monomeric whereas red phosphorus is polymeric. White P_4 has less bond dissociation energy than red P_4.

12. (i) PbS and ZnS both form froth with pine oil on bubbling air inside the mixture. In such case NaCN is used as a depressant.

Before froth floatation process is used, NaCN is mixed (as a depressant) which forms a complex with ZnS.

$ZnS + 4NaCN \longrightarrow Na_2[Zn(CN)_4] + Na_2S$

PbS remains insoluble and is separated. $CuSO_4$ is then added to activate depressed ZnS and air is blown when ZnS floats. This method is called differential floatation.

(ii) **Step I :**

$$4Au_{(s)} + 8CN^-_{(aq)} + O_{2(g)} + 2H_2O_{(aq)} \longrightarrow 4[Au(CN)_2]^-_{(aq)} + 4OH^-_{(aq)}$$

Step II : $2[Au(CN)_2]^-_{(aq)} + Zn_{(s)} \longrightarrow 2Au_{(s)} + [Zn(CN)_4]^{2-}_{(aq)}$

13. (i) Shape-selective catalysis : The catalytic reaction which depends upon the pore size of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis. Zeolites are good shape-selective catalysts because of their honey comb-like structures.

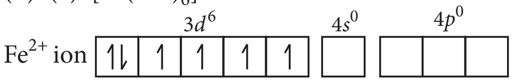
(ii) Dialysis : The process of separating a crystalloid from a colloid by filteration or diffusion through a membrane is called dialysis. The apparatus employed to affect such a separation is known as dialyser.

Purification of blood in the artificial kidney machine.

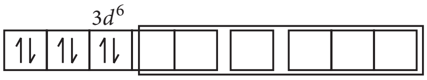
(ii) Multimolecular colloids : A large number of atoms or smaller molecules of a substance on dissolution aggregate together to form species having size (diameter < 1 nm) in the colloidal range (1–1000 nm). Such species are known as multimolecular colloids. For example, a sulphur sol consists of particles containing a thousand or more of S_8 sulphur molecules.

14. (i) Diamminechlorido(methylamine) platinum(II) chloride

(ii) (a) $[Fe(CN)_6]^{4-}$ ion

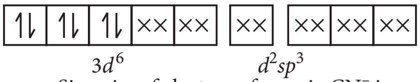


Fe^{2+} ion hybridised (under the influence of strong field ligand).



Six empty d^2sp^3 hybrid orbitals

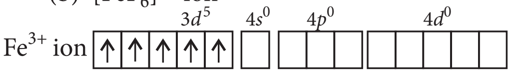
$[Fe(CN)_6]^{4-}$ ion formation :



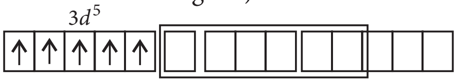
Six pairs of electrons from six CN^- ions.

Since the complex ion does not contain any unpaired electron, so it is diamagnetic.

(b) $[FeF_6]^{3-}$ ion

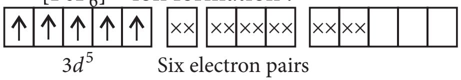


Fe^{3+} ion hybridised (under the influence of weak field ligand).



Six empty sp^3d^2 hybrid orbitals

$[FeF_6]^{3-}$ ion formation :



Six electron pairs from six F^- ions

As the complex ion contains five unpaired electrons, it is highly paramagnetic in nature.

$$\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.9 \text{ BM}$$

15. The electrode reaction written as reduction reaction is $Zn^{2+} + 2e^- \longrightarrow Zn (n = 2)$

Applying Nernst equation, we get

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{0.0591}{2}\log\frac{1}{[Zn^{2+}]}$$

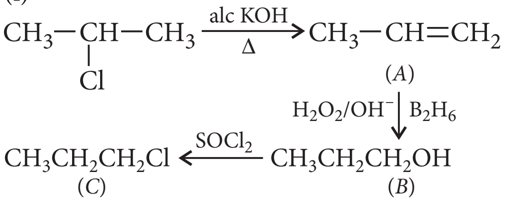
As 0.1 M $ZnSO_4$ solution is 95% dissociated, this means that in the solution,

$$[Zn^{2+}] = \frac{95}{100} \times 0.1 \text{ M} = 0.095 \text{ M}$$

$$\therefore \quad E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2}\log\frac{1}{0.095}$$

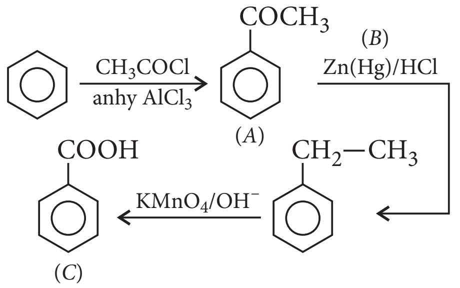
$$= -0.76 - 0.02955 (\log 1000 - \log 95)$$
$$= -0.76 - 0.02955 (3 - 1.9777)$$
$$= -0.76 - 0.03021 = -0.79021 \text{ V}$$

16. (i)



$$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\Delta]{\text{alc KOH}} \underset{(A)}{CH_3-CH=CH_2} \xrightarrow{B_2H_6,\ H_2O_2/OH^-} \underset{(B)}{CH_3CH_2CH_2OH} \xrightarrow{SOCl_2} \underset{(C)}{CH_3CH_2CH_2Cl}$$

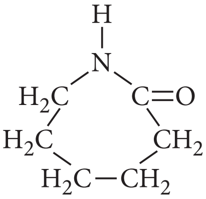
(ii)



17. (i) $HOOC(CH_2)_4COOH$ and $NH_2(CH_2)_6NH_2$

Adipic acid　　Hexamethylene diamine

(ii)



Caprolactam

(iii) NH_2CONH_2 and $HCHO$

Urea　　Formaldehyde

OR

(i)

Low density polythene	High density polythene
1. It is tough but flexible.	It is tougher and harder.
2. Highly branched structure so, it has low density.	It is linearly arranged and has a high density due to close packing.

(ii) Neoprene < Polythene < Nylon 6,6 < Bakelite

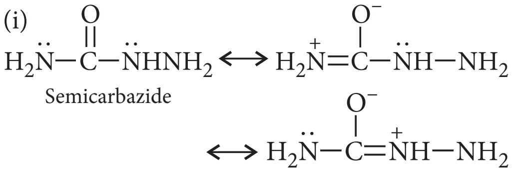
18. Henry's law : Mole fraction of a gas in the solution is proportional to the partial pressure of the gas over the solution.

Applications of Henry's law :

(i) Soft drinks and soda water bottles are sealed under high pressure to increase the solubility of CO_2.

(ii) The tanks used by scuba divers [persons swimming under water use underwater breathing apparatus known as scuba] are filled with air diluted with helium.

19. (i)

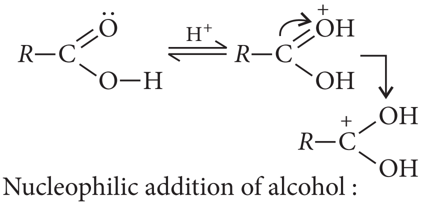


$$\underset{\text{Semicarbazide}}{H_2\ddot{N}-\overset{\overset{O}{\|}}{C}-\ddot{N}HNH_2} \longleftrightarrow H_2\overset{+}{N}=\overset{\overset{O^-}{|}}{C}-\ddot{N}H-NH_2 \longleftrightarrow H_2\ddot{N}-\overset{\overset{O^-}{|}}{C}=\overset{+}{N}H-NH_2$$

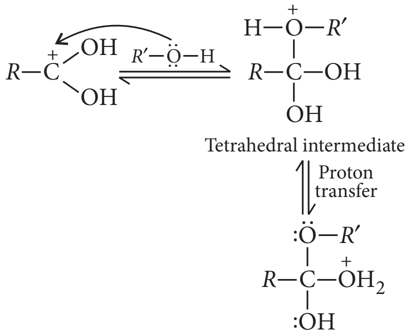
As electron density on one —NH_2 group decreases due to resonance it does not act as a nucleophile while the lone pair of electrons on the other NH_2 group (*i.e.*, attached to NH) is not involved in resonance and hence is available for nucleophilic attack on the C=O group of aldehydes and ketones.

(ii) Mechanism of esterification : It is a nucleophilic acyl substitution.

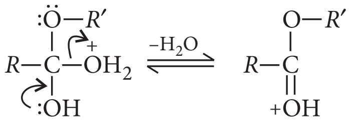
(a) Protonation of carboxyl oxygen:



(b) Nucleophilic addition of alcohol :

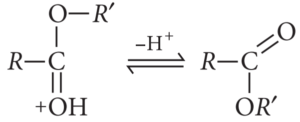


(c) Elimination of water molecule :



Protonated ester

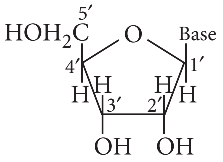
(d) Protonated ester loses a proton to give ester :



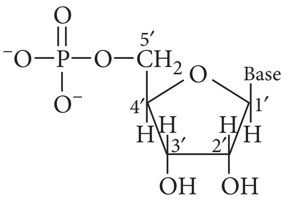
Ester

20. (i) A unit formed by attachment of a base to C-1′ position of sugar is known as nucleoside.

When nucleoside is linked to phosphoric acid at C-5′ position of sugar moiety, resulting species is called nucleotide.



Nucleoside



Nucleotide

(ii) James Watson and Francis Crick gave a double strand helix structure for DNA. Two nucleic acid chains are bonded to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine (A=T) whereas cytosine forms hydrogen bonds with guanine (C≡G).

(iii)

Fibrous protein	Globular protein
Elongated, insoluble in water because of hydrophobic *R* group *e.g.* keratin, collagen	Spherical, water soluble because of hydrophilic amino acids with polar *R* group *e.g.* enzymes, antibodies and haemoglobin

21.

S. No.	Drug	Effect
(i)	Brompheniramine	Antiallergic, it inferes with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.
(ii)	Aspirin	Pain reliever and antipyretic
(iii)	Equanil	For controlling depression and hypertension

22. (i) Zone refining : The method is based on the difference in solubility of impurities in molten and solid state of the metal.

(ii) van Arkel method : In this method, impure metal is converted to a volatile compound while the impurities are not affected. The volatile compound is then decomposed to get pure metal.

(iii) Liquation method : This process is based on the difference in fusibility of metal and impurities. Impure metal is gently heated on the sloping hearth of a furnace. The metal melts and flows down leaving behind the impurities on the hearth.

23. (i) Dr. Rachna, showed concern towards the health needs of students.

(ii) Protein rich diet helps to strengthen the immune system of HIV/AIDS patients and helps to reduce blood pressure as well as cholesterol of heart patients.

(iii) Eggs, sprouts, beans, lentils are rich sources of proteins.

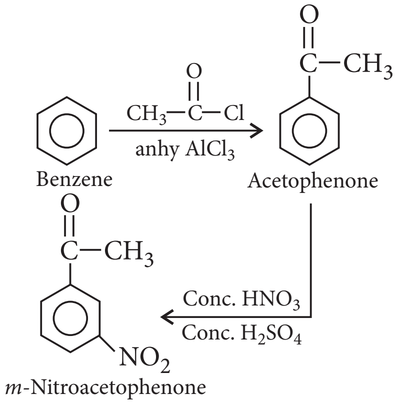
(iv) Carbohydrates, fats and proteins are basic components of a balanced diet.

24. (i) (a) Methylamine and dimethylamine can be distinguished by carbylamine test. Methylamine, a primary amine, gives offensive smell on heating with chloroform and alcoholic solution of KOH whereas dimethylamine does not react.

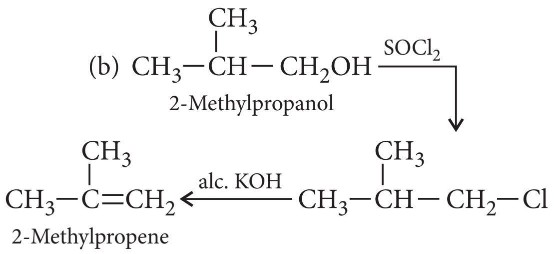
(b) Ethanal and propanal can be distinguished by iodoform test. Yellow precipitate of iodoform will be formed from ethanal on heating with iodine and sodium hydroxide solution whereas propanal does not give iodoform test.

(c) Benzoic acid and ethyl benzoate can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ whereas ethyl benzoate does not react.

(ii) (a)



(b)



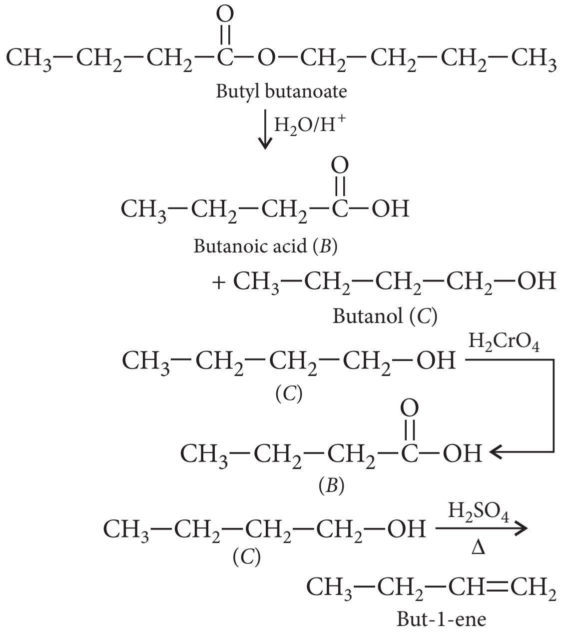
$$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2OH \xrightarrow{SOCl_2} CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-Cl \xrightarrow{\text{alc. KOH}} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$$

2-Methylpropanol

2-Methylpropene

OR

(i) Compound '*A*' ($C_8H_{16}O_2$) on hydrolysis gives an acid '*B*' and an alcohol '*C*'. It shows that '*A*' is an ester. Since the oxidation of alcohol '*C*' also gives the acid '*B*' indicates that '*B*' and '*C*' both contain same number of carbon atoms, *i.e.*, four carbon atoms each and same arrangement of atoms. Formation of but-1-ene on dehydration of '*C*' indicates it to be butan-1-ol, so the possible ester (*A*) could be butyl butanoate.



$$CH_3-CH_2-CH_2-\overset{O}{\overset{||}{C}}-O-CH_2-CH_2-CH_2-CH_3$$

Butyl butanoate

$$\downarrow H_2O/H^+$$

$$CH_3-CH_2-CH_2-\overset{O}{\overset{||}{C}}-OH$$

Butanoic acid (*B*)

$$+\ CH_3-CH_2-CH_2-CH_2-OH$$

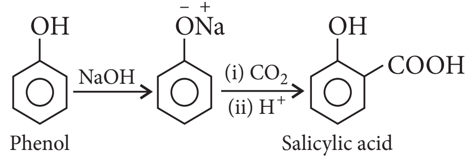
Butanol (*C*)

$$\underset{(C)}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow{H_2CrO_4} \underset{(B)}{CH_3-CH_2-CH_2-\overset{O}{\overset{||}{C}}-OH}$$

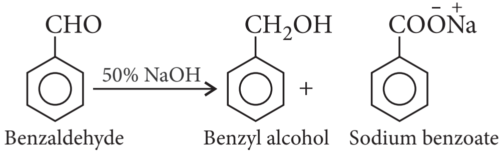
$$\underset{(C)}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow[\Delta]{H_2SO_4} CH_3-CH_2-CH=CH_2$$

But-1-ene

(ii) (a) Kolbe's reaction :



(b) Cannizzaro reaction :



25. (i) Sodium chloride being a strong electrolyte completely dissociates in the solution while glucose does not dissociate. The number of particles in sodium chloride solution becomes double than that of glucose solution. Hence freezing point depression of sodium chloride is nearly twice that of glucose solution of same molarity, because it is a colligative property.

(ii) $\pi = CRT$

R and T are same in both cases hence

$$\frac{\pi_1}{\pi_2} = \frac{C_1}{C_2} \text{ or, } C_2 = \frac{\pi_2 C_1}{\pi_1}$$

Molarity of first solution

$$C_1 = \frac{36}{180} = 0.2 \text{ mol L}^{-1}$$

$$C_2 = \frac{\pi_2 C_1}{\pi_1} = \frac{1.52 \times 0.2}{4.98} = 0.0610 \text{ M}$$

(iii) Magnitude of osmotic pressure is large even for very dilute solutions and it can be measured at room temperature hence it is more useful for the calculation of molecular mass.

OR

(i) Given: $w_2 = 15$ g, $w_1 = 450$ g

$K_f = 1.86$ K kg mol^{-1}, $M_2 = ?$

$\Delta T_f = 0 - (-0.34) = 0.34°\text{C}$ or 0.34 K

Now, $\Delta T_f = K_f \cdot m$

$$\Rightarrow \Delta T_f = K_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$\Rightarrow M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1}$$

$$\Rightarrow M_2 = \frac{1.86 \times 15 \times 1000}{0.34 \times 450}$$

$M_2 = 182.35$ g mol^{-1}

(ii) When the vapour pressure of a non-ideal solution is either higher or lower than that predicted by Raoult's law, the solution exhibits deviation.

These deviations are caused because of unequal intermolecular attractive forces between solute-solvent molecules and solute-solute or solvent-solvent molecules.

Examples of positive deviations : Mixture of ethanol and acetone, carbon disulphide and acetone.

Examples of negative deviations: Chloroform and acetone, nitric acid and water.

26. (i) As transition metals have a large number of unpaired electrons in the d-orbitals of their atoms they have strong interatomic attractions or metallic bonds. Hence they have high enthalpy of atomization.

(ii) Many transition metals and their compounds act as catalysts. The catalytic activity is due to their ability to exhibit multiple oxidation states. For example, V_2O_5 in Contact process and finely divided iron in Haber process.

(iii) The actinoid contraction is more than lanthanoid contraction due to poor shielding by 5f-electrons than by 4f-electrons.

(iv) Much larger third ionisation energy of Mn(where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance.

(v) Scandium ($Z = 21$) has incompletely filled 3d-orbitals in the ground state (3d^1). Hence it is considered as a transition element.

OR

(i) (a)

$$\underset{\text{Sod. chromate}}{2Na_2CrO_4} + H_2SO_4 \longrightarrow \underset{\text{Sod. dichromate}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\text{Pot. dichromate}}{K_2Cr_2O_7} + 2NaCl$$

(b) The potassium manganate is oxidised to potassium permanganate by oxidation with chlorine.

$$2K_2MnO_{4(aq)} + Cl_{2(g)} \rightarrow 2KMnO_{4(aq)} + 2KCl_{(g)}$$

(ii) Lanthanoid contraction : The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction.

It is caused due to imperfect shielding of nuclear charge by 4f-electrons.

Lanthanum (La) has the largest ionic radius while lutetium (Lu) has the smallest among the 4f-series elements.

Consequences of lanthanoid contraction :

(a) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.

(b) Atomic and ionic sizes of 4d transition series elements and 5d series elements are similar. *e.g.* Atomic radii of zirconium(Zr) is same as that of hafnium(Hf).

Practice Paper -3 (Unsolved)

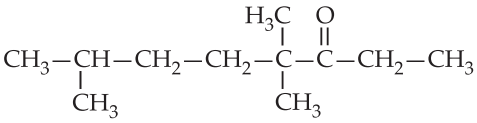
Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Why is hydrogen sulphide, with greater molar mass, a gas, while water a liquid at room temperature?

2. Give the IUPAC name of the following compound:



$$CH_3-\underset{CH_3}{CH}-CH_2-CH_2-\overset{H_3C}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

3. For the reaction $A \longrightarrow B$, rate becomes eight times when the concentration of A is doubled. What is the order of the reaction?

4. What is the cause of Brownian movement observed in colloidal solution?

5. Write the reaction that indicates the presence of a primary alcoholic group in glucose.

6. Draw the structure of xenon oxyfluoride molecule which is isoelectronic with IF_5.

7. What is the shape of the complex used as an antitumour agent in treatment of cancer?

OR

What are chelates? Giving one example write the importance of chelate.

8. Dipole moment of phenol is smaller than that of methanol. Why?

9. (a) Write nernst equation to calculate the cell potential of the given cell:

$$Mg_{(s)} \mid Mg^{2+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag_{(s)}$$

(b) Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

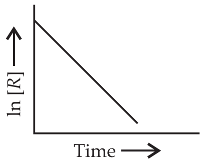
10. Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of the reaction.

OR

Show that in a first order reaction, time required for 99% completion is twice the time required for the completion of 90% reaction.

11. Do the following conversions:
(i) Bromomethane to propanone
(ii) 1-Bromopropane to 2-bromopropane

12. For a chemical reaction, a graph is shown below:



(i) What is the order of the reaction?
(ii) What is the unit of rate constant k for the reaction?

13. Explain why $[Fe(H_2O)_6]^{3+}$ has magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM.

14. Give reason for the following:
(i) Aniline is a weaker base than cyclohexylamine.
(ii) Ammonolysis of alkyl halide does not give a corresponding amine in pure state.

15. Write the following reactions:
(i) Carbylamine reaction
(ii) Coupling reaction

16. If NaCl is doped with 10^{-3} mol % of $SrCl_2$, what is the concentration of cation vacancies?

17. In the button cell widely used in watches, the following reaction takes place:

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$$

Determine $E°$ and $\Delta G°$ for the reaction.

Given: $E°_{Ag^+/Ag} = 0.80$ V, $E°_{Zn^{2+}/Zn} = -0.76$ V

18. Explain what is observed:

(i) when a beam of light is passed through a colloidal solution.

(ii) an electrolyte is added to hydrated ferric oxide sol.

(iii) electric current is passed through a colloidal solution.

19. (a) Name the element that is purified by

(i) zone refining process

(ii) van Arkel method.

(b) The value of $\Delta_f G°$ for formation of Cr_2O_3 is – 540 kJ mol^{-1} and that of Al_2O_3 is – 827 kJ mol^{-1}. Is the reduction of Cr_2O_3 possible with aluminium?

OR

(a) What is the role of depressant in froth floatation process? Give one example.

(b) Describe the principle involved in Mond process for refining of nickel.

20. (a) Draw the structures of the following molecules:

(i) $H_2S_2O_8$ (ii) IF_7

(b) Unlike phosphorus, nitrogen shows little tendency for catenation. Why?

(c) What happens when orthophosphorous acid is heated?

21. (a) Of the two bases named below, which one is present in RNA and which one is present in DNA?

(i) Thymine (ii) Uracil

(b) The deficiency of which vitamin causes the following diseases?

(i) Pernicious anaemia

(ii) Xerophthalmia

(c) Give one structural difference between amylose and amylopectin.

22. (a) Write the reaction of preparation of melamine-formaldehyde resin.

(b) How is dacron obtained from ethylene glycol and terephthalic acid?

(c) Write the formulae of the monomers of

(i) Natural rubber (ii) Nylon 6.

23. Gaurav took his father to doctor for routine check-up. He told his doctor about the symptoms like increase in appetite, excessive thirst, frequent urination, feeling fatigued, high depression. After examine, doctor advised him to add artifical sweeteners in tea or coffee.

(i) From which disease, Gaurav's father was suffering? What values are shown by Gaurav?

(ii) Name two artificial sweeteners that Gaurav's father must use instead of using sugar.

24. (a) State Raoult's law for solutions of volatile liquids. Explain the meaning of positive and negative deviations from Raoult's law. Also give examples.

(b) Vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg respectively. Calculate the vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of CH_2Cl_2 at 298 K.

OR

(a) Define the term osmotic pressure. Describe how the molecular mass of a substance can be determined by a method based on measurement of osmotic pressure.

(b) At 300 K, 36 g of glucose $C_6H_{12}O_6$ present per litre in its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of another solution is 1.52 bar at the same temperature, calculate the concentration of the other solution.

25. **(a)** Answer the following questions with reasons.

(i) Which element of the first transition series has highest second ionisation enthalpy?

(ii) Which element of the first transition series has highest third ionisation enthalpy?

(iii) Which element of the first transition series has lowest enthalpy of atomisation?

(b) Complete the following reactions:

(i) $SO_2 + Cr_2O_7^{2-} + H^+ \longrightarrow$

(ii) $S_2O_3^{2-} + MnO_4^- + H_2O \longrightarrow$

OR

(a) When a chromite ore (*A*) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (*B*) is obtained. After treatment of this yellow solution with sulphuric acid, compound (*C*) can be crystallised from the solution. When compound (*C*) is treated with KCl, orange crystals of compound (*D*) crystallise out. Identify *A* to *D* and also write the reactions involved.

(b) Write the structures of

(i) dichromate ion

(ii) manganate ion.

26. (a) (i) Carboxylic acid is a stronger acid than phenol. Why?

(ii) Arrange the following compounds in decreasing order of their acidic strength:

C_6H_5COOH, CH_3COOH, HCOOH

(b) An organic compound (*A*) having molecular formula ($C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give two compounds (*B*) and (*C*). Oxidation of (*C*) with chromic acid produced (*B*). (*C*) on dehydration gives but-1-ene. Write equations for the reactions involved.

OR

(a) How will you prepare the following compounds starting with benzene:

(i) Benzaldehyde (ii) Acetophenone?

(b) Write the following conversions in not more than two steps:

(i) Benzaldehdye to α-hydroxyphenylacetic acid

(ii) Bromobenzene to 1-phenylethanol

(iii) Benzaldehyde to benzophenone

Hints & Solutions

1. Intermolecular H-bonding

2. 4, 4, 7-Trimethyloctan-3-one

3. It is a third order reaction.

6. $XeOF_4$ is isoelectronic with IF_5 and has square pyramidal structure.

9. (a) $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{2.303\,RT}{nF}\log\dfrac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$

(b) $E_{H^+/H_2} = -\,0.591$ V

10. $\Rightarrow \dfrac{t_{99.9\%}}{t_{1/2}} = \dfrac{6.909}{k} \times \dfrac{k}{0.693} \simeq 10$

OR

$\dfrac{t_{99\%}}{t_{90\%}} = \dfrac{4.606}{k} \times \dfrac{k}{2.303} = 2 \Rightarrow t_{99\%} = 2t_{90\%}$

12. (i) The graph shows it is a first order reaction.

(ii) Unit of rate constant *k*, for a first order reaction is s^{-1}.

13. Fe (26) : [Ar] $3d^6\,4s^2$

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

In $[Fe(H_2O)_6]^{3+}$

Magnetic moment of five unpaired electrons

$= \sqrt{n(n+2)}$ BM $= \sqrt{35} = 5.92$ BM

In $[Fe(CN)_6]^{3-}$

Manetic moment of one unpaired electron

$= \sqrt{n(n+2)} = \sqrt{3} = 1.74$ BM

14. (i) In case of aniline, the lone pair of electrons on the nitrogen atom is delocalized over the benzene ring.

(ii) $\underset{1^\circ}{RNH_2} \xrightarrow{RX} \underset{2^\circ}{R_2NH} \xrightarrow{RX} \underset{3^\circ}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$

This mixture is difficult to separate.

16. The concentration of cation vacancies is 6.023×10^{18}.

17. $E^\circ_{\text{cell}} = E^\circ_{\text{Zn/Zn}^{2+}} + E^\circ_{\text{Ag}^+/\text{Ag}}$

$= 0.76 + 0.80 = 1.56 \text{ V}$

$\Delta G^\circ_{\text{cell}} = -nFE^\circ_{\text{cell}}$

$= -301.08 \text{ kJ mol}^{-1}$

19. (a) (i) Germanium (ii) Zirconium

(b) $\frac{4}{3}\text{Al}_{(s)} + \frac{2}{3}\text{Cr}_2\text{O}_{3(s)} \longrightarrow \frac{2}{3}\text{Al}_2\text{O}_{3(s)} + \frac{4}{3}\text{Cr}_{(s)}$

$\Delta_r G^\circ = -287 \text{ kJ mol}^{-1}$

As $\Delta_r G^\circ$ of the reaction is –ve, reduction of Cr_2O_3 is possible with aluminium.

OR

(a) In froth floatation process, the role of the depressant is to prevent one type of sulphide ore particles from forming the froth with air bubbles.

(b) $\text{Ni} + 4\text{CO} \xrightarrow{330\text{ - }350\text{ K}} \text{Ni(CO)}_4$

$\text{Ni(CO)}_4 \xrightarrow{450\text{ - }470\text{ K}} \text{Ni} + 4\text{CO}$

20. (c) $$\underset{\substack{\text{Orthophosphorous}\\ \text{acid}}}{4\text{H}_3\overset{+3}{\text{P}}\text{O}_3} \xrightarrow{\text{Heat}} \underset{\text{Phosphine}}{\overset{-3}{\text{P}}\text{H}_3} + \underset{\substack{\text{Orthophosphoric}\\ \text{acid}}}{\text{H}_3\overset{+5}{\text{P}}\text{O}_4}$$

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

(b) $x_{\text{CH}_2\text{Cl}_2} = \frac{0.47}{0.683} = 0.688$

$p_{\text{total}} = p_1^\circ + (p_2^\circ - p_1^\circ)\, x_2$

$= 200 + (415 - 200) \times 0.688$

$= 200 + 147.9 = 347.9 \text{ mm Hg}$

OR

(b) $M' = 0.2 \times \frac{1.52}{4.98} = 0.061 \text{ M}$

25. (b) (i) $3\text{SO}_2 + \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ \longrightarrow 3\text{SO}_4^{2-} + 2\text{Cr}^{3+} + \text{H}_2\text{O}$

(ii) $3\text{S}_2\text{O}_3^{2-} + 8\text{MnO}_4^- + \text{H}_2\text{O} \longrightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^-$

OR

(a) $A = \text{FeCr}_2\text{O}_4$, $B = \text{Na}_2\text{CrO}_4$,
$C = \text{Na}_2\text{Cr}_2\text{O}_7.2\text{H}_2\text{O}$, $D = \text{K}_2\text{Cr}_2\text{O}_7$

$$\underset{(A)}{4\text{FeCr}_2\text{O}_4} + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow \underset{(B)}{8\text{Na}_2\text{CrO}_4} + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$$

$$\underset{(B)}{2\text{Na}_2\text{CrO}_4} + \text{H}_2\text{SO}_4 \longrightarrow \underset{(C)}{\text{Na}_2\text{Cr}_2\text{O}_7} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$

$$\underset{(C)}{\text{Na}_2\text{Cr}_2\text{O}_7} + 2\text{KCl} \longrightarrow \underset{(D)}{\text{K}_2\text{Cr}_2\text{O}_7} + 2\text{NaCl}$$

Practice Paper -4 (Unsolved)

Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. What is activation energy?

2. Write the name of enzyme, which converts starch into maltose.

3. Give an example of compounds in which nitrogen exhibits oxidation states of −3 and +3.

4. Name the reagents used in the following reactions :
(i) Oxidation of primary alcohol to carboxylic acid.
(ii) Benzyl alcohol to benzoic acid.

5. Name one disease caused by the deficiency of
(i) Vitamin E (ii) Vitamin D

6. Which of the following compounds has a lone pair of electrons at the central atom?
$H_2S_2O_3$, $H_2S_2O_7$, H_2SO_3, H_2SO_4

7. Give an example of Hell-Volhard-Zelinsky reaction.

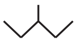
8. Draw the structure of optical isomers of $[Cr(C_2O_4)_3]^{3-}$.

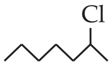
9. Define the following terms with suitable examples.
(i) Primitive unit cell (ii) Ferromagnetism

OR

Write any two differences between *n*-type and *p*-type semiconductors.

10. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

(i)  and 

(ii)  and 

11. For the complex $[Fe(en)_2Cl_2]Cl$, identify the following :
(i) Type of hybridisation and geometry.
(ii) IUPAC name of the complex.

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

13. Write the structure and IUPAC name of DDT.

14. The following initial rate data were obtained at 300 K for the reaction $2P + Q \longrightarrow R + S$.

	[*P*]/mol L^{-1}	**[*Q*]/mol L^{-1}**	**Rate/mol L^{-1} s^{-1}**
I.	0.2	0.1	6.0×10^{-2}
II.	0.4	0.1	2.4×10^{-1}
III.	0.2	0.2	1.2×10^{-1}

(a) Deduce the rate law.
(b) If the half-life of a reaction is inversely proportional to initial concentration of the reactant then what is the order of reaction?

15. Write the chemical reactions of the following :
(i) Coupling reaction
(ii) Hoffmann bromamide reaction.

16. Explain the following terms :
(i) Micelles (ii) Dialysis
(iii) Hardy-Schulze rule.

OR

Explain the following observations :

(i) A beam of light passing through a colloidal solution is visible.

(ii) Passing an electric current through a colloidal solution removes colloidal particles from it.

(iii) Ferric hydroxide solution coagulates on addition of a solution of potassium sulphate.

17. Complete the following chemical reactions :

(i) $F_2 + H_2O \longrightarrow$

(ii) $Ca_3P_2 + H_2O \longrightarrow$

(iii) $XeF_4 + H_2O \longrightarrow$

18. (a) What is the role of depressant in the froth floatation process?

(b) Out of C and CO which is a better reducing agent for FeO ?

(i) In the lower part of blast furnace (higher temperature).

(ii) In the upper part of blast furnace (lower temperature).

19. The reaction occurs in galvanic cell is

$$Zn_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$$

Give the answers of the following :

(i) Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode.

20. How are the following conversions carried out?

(i) Propene → propan-2-ol.

(ii) Benzyl chloride → benzyl alcohol.

(iii) Ethyl magnesium chloride → propan-1-ol.

21. Draw the structure of the following species :

(i) $XeOF_4$ (ii) $H_2S_2O_7$

(iii) $H_4P_2O_7$

22. Answer the following questions.

(i) What are biodegradable polymers?

(ii) Identify the aliphatic biodegradable polyester which is used in packaging and orthopaedic devices. Write its full form.

(iii) Write the name and structure of the monomer of nylon 6.

23. Sarika's mother, a diabetic patient, wished to have homemade sweets. Sarika went to a nearby supermarket to buy artificial sweeteners to make sweets. She noticed there were two brands of sweeteners, one containing aspartame and the other containing sucrolose. Sarika choose the brand having sucrolose.

After reading the above passage, answer the following questions.

(a) Why did Sarika choose this brand?

(b) How is 'sucrolose' different from 'sucrose'?

24. (a) Define:

(i) Mole fraction (ii) Molality

How are these two related?

(b) What is the value of van't Hoff factor for a solute which undergo dimerisation upto 40%?

OR

(a) State the following :

(i) Henry's law about partial pressure of a gas in a mixture.

(ii) Raoult's law in its general form in reference to solutions.

(b) A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming the gene fragment is a non-electrolyte, determine its molar mass.

25. (a) Write chemical equations for the following reactions :

(i) Oxidation of nitrite ion by MnO_4^- in acidic medium.

(ii) Acidification of potassium chromate solution.

(iii) Disproportionation of manganese (VI) in acidic solution.

(b) Explain the following observations :

(i) Transition elements generally form coloured compounds.

(ii) Zinc is not regarded as a transition element.

OR

(a) Account for the following:

(i) Europium (II) is more stable than cerium (II)

(ii) Transition metals have high enthalpies of atomization.

(iii) Actinoid ions are generally coloured.

(b) Write the steps involved in the preparation of

(i) $K_2Cr_2O_7$ from Na_2CrO_4

(ii) $KMnO_4$ from K_2MnO_4.

26. (a) A compound *P* on oxidation gives $Q(C_2H_4O_2)$. *P* reacts with dil. NaOH and on subsequent heating forms *R*. *R* on catalytic hydrogenation gives *S*. Identify *P*, *Q*, *R*, *S* and write down the reactions involved.

(b) Write chemical equations to carry out the following conversions:

(i) Benzene to benzyl alcohol.

(ii) Propane nitrile to 1-phenyl propanone.

OR

(a) Two moles of organic compound '*W*' on treatment with a strong base give two compounds '*X*' and '*Y*'. Compound '*X*' on dehydrogenation with Cu gives '*W*' while acidification of '*Y*' yields carboxylic acid '*Z*' having molecular formula of CH_2O_2. Identify the compounds *W*, *X*, *Y* and *Z*.

(b) Explain why :

(i) The aldol and ketol readily lose water molecules to give α, β-unsaturated carbonyl compounds ?

(ii) Benzaldehyde is less reactive than acetalde-hyde towards nucleophilic substitution reaction?

Hints & Solutions

2. Diastase.

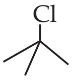
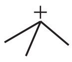
3.

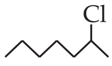
Oxidation state	–3	+3
Compound	NH_3	N_2O_3

4. (i) Potassium dichromate in presence of dilute sulphuric acid.

(ii) Potassium permanganate in alkaline medium.

10. Reactivity towards S_N1 reaction :

(i)  will react faster since  is more stable than 2° carbocation.

(ii)  reactsfasterbecause2°carbocation is more stable than 1° carbocation.

11. (i) Hybridisation d^2sp^3 ; geometry-octahedral

(iii) Dichlorido *bis*-(ethane-1,2-diamine) iron (III) chloride.

12. Using formula, $Z = \dfrac{d \times N_A \times a^3}{M}$

$$Z = \frac{2.7\times10^3\ \text{kg m}^{-3}\times6.022\times10^{23}\times(4.05\times10^{-10}\ \text{m})^3}{2.7\times10^{-2}\ \text{kg mol}^{-1}}$$

$\therefore Z = 4$

Hence, unit cell is cubic close pack (*fcc*).

13. IUPAC name : 1, 1, 1-Trichloro-2,2-di (4-chlorophenyl) ethane

14. (a) Let the rate law for the reaction be

Rate = $k[P]^x[Q]^y$.

Then, $\dfrac{r_2}{r_1} = \dfrac{2.4\times10^{-1}}{6.0\times10^{-2}} = \dfrac{k[0.4]^x\times[0.1]^y}{k[0.2]^x\times[0.1]^y}$

$4 = 2^x \Rightarrow x = 2$

Again, $\dfrac{r_3}{r_1} = \dfrac{1.2\times10^{-1}}{6\times10^{-2}} = \dfrac{k[0.2]^x\times[0.2]^y}{k[0.2]^x\times[0.1]^y}$

or, $2 = 2^y \Rightarrow y = 1$.

Hence, the rate law = $k[P]^2[Q]^1$.

17. (i) $2F_{2(g)} + 2H_2O_{(l)} \longrightarrow 4H^+_{(aq)} + 4F^-_{(aq)} + O_{2(g)}$

(ii) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

(iii) $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

23. Cell can be represented as

$Zn|Zn^{2+}_{(aq)}||Ag^+_{(aq)}|Ag$

(i) The zinc electrode is negatively charged (anode) and would act as the sink for electrons lost by atoms.

(ii) Current is carried by the wire connecting two electrodes. Current flows from cathode (Ag) to anode (Zn) in the external circuit.

(iii) The reactions occurring at the two electrodes are :

At zinc electrode (anode) : $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

At silver electrode (cathode) : $2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(s)}$

24. (a) Relation between *m* and *X*

$$X_1 = \frac{n_1}{n_1 + n_2}, X_2 = \frac{n_2}{n_1 + n_2} \begin{cases} n_1 = \text{No. of moles of solute} \\ n_2 = \text{No. of moles of solvent} \end{cases}$$

$$\frac{X_1}{X_2} = \frac{n_1}{n_2} = \frac{\text{Moles of solute}}{\text{Moles of solvent}} = \frac{w_1}{m_1} \times \frac{m_2}{w_2}$$

OR

$$\frac{X_1 \times 1000}{X_2 \times m_2} = \frac{w_1 \times 1000}{m_1 \times w_2}$$

$$\therefore \quad \frac{X_1 \times 1000}{(1 - X_1)m_2} = \text{Molality}$$

(b) Using formula $\alpha = \dfrac{i - 1}{n - 1}$

or $0.4 = \dfrac{i - 1}{0.5 - 1}$ or $0.4 = \dfrac{i - 1}{-0.5}$

or $i = 1 - 0.2 = 0.8$.

OR

(b) $M_B = \dfrac{W_B \times R \times T}{\pi \times V}$

We get,

$$M_B = \frac{8.95 \times 10^{-3}\,\text{g} \times 0.0821\,\text{L atm K}^{-1}\,\text{mol}^{-1} \times 298\,\text{K}}{\frac{0.335}{760}\,\text{atm} \times 35 \times 10^{-3}\,\text{L}}$$

$M_B = 14193.29\ \text{g mol}^{-1}$

25. (a)

(i) $5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$

(ii) $2K_2CrO_4 + 2H^+ \longrightarrow K_2Cr_2O_7 + 2K^+ + H_2O$

(iii) $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

Practice Paper -5 (Unsolved)

Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Iodine forms I_3^- but F_2 does not form F_3^- ions. Why?

2. What is meant by inversion of sugar?

3. Why is sulphuric acid not used during the reaction of alcohols with KI?

4. For the reaction $A + 2B \longrightarrow AB_2$, the rate constant is 1.26×10^{-3} L mol^{-1}s^{-1}. What is the order of the reaction?

5. Name the ionisation isomer of $[Cr(H_2O)_5Br]SO_4$.

6. Arrange the following carbonyl compounds in increasing order of their reactivity in nucleophilic addition reaction.
Benzaldehyde, *p*-tolualdehyde, *p*-nitrobenzaldehyde, acetophenone.

7. What happens when an electric field is applied to a colloidal dispersion?

OR

Do the vital functions of body such as digestion get affected during fever? Explain your answer.

8. Alcohols are comparatively more soluble in water than the hydrocarbons of comparable molecular mass? Explain this fact.

9. State reasons for the following :
(i) Rusting of iron is said to be an electrochemical phenomenon.
(ii) For a weak electrolyte, its molar conductance in dilute solution increases sharply as its concentration in solution is decreased.

10. (a) Why does chlorine water lose its yellow colour on standing?
(b) What happens when Cl_2 reacts with cold dilute sodium hydroxide? Write equation only.

11. Account for the following :
(i) CH_3CONH_2 is a weaker base than $CH_3CH_2NH_2$.
(ii) ROH is a stronger acid than RNH_2.

12. While preparing monobromoaniline why is aniline acetylated before reacting it with bromine? Explain.

13. (a) Express the relationship between the rate of production of iodine and the rate of disappearance of hydrogen iodide in the following reaction :

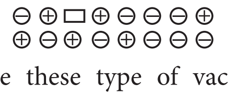
$$2HI \longrightarrow H_2 + I_2$$

(b) The rate of formation of a dimer in a second order dimerisation reaction is 9.1×10^{-6} mol L^{-1}s^{-1} at 0.01 mol L^{-1} monomer concentration. Calculate the rate constant.

14. Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.
(i) What is the length of the side of the unit cell?
(ii) How many unit cells are there in 1.00 cm^3 of aluminium?

OR

Examine the illustrations of a portion of a defective crystal given below and answer the following questions.



(i) What are these type of vacancy defects called?
(ii) How is the density of a crystal affected by these defects?

(iii) Name one ionic compound which can show this type of defect in crystalline state.

(iv) How is the stoichiometry of the compound affected?

15. What is an adsorption isotherm ? Describe Freundlich adsorption isotherm.

16. Account for the following :

(i) Bond dissociation energy of F_2 is less than that of Cl_2.

(ii) Both NO and ClO_2 are odd electron species but NO dimerises while ClO_2 does not.

(iii) Bleaching of flowers by chlorine is permanent while that by sulphur dioxide is temporary.

17. Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides, though polar, are immiscible with water ?

(iii) Grignard reagents should be prepared under anhydrous conditions?

18. Write the names and molecular structures of the monomers of the following polymers. Give one use of each specifying the property responsible for this use.

(i) Glyptal (ii) Nylon-6,

(iii) Neoprene

19. Give reasons for the following :

(i) Amino acids have relatively higher melting point as compared to corresponding halo acids.

(ii) Amino acids are amphoteric in nature.

(iii) On electrolysis in acidic solution amino acids migrate towards cathode while in alkaline solution these migrate towards anode.

20. Show how will you synthesize

(i) 1-phenylethanol from a suitable alkene

(ii) Cyclohexylmethanol using an alkyl halide by S_N2 reaction.

(iii) Pentan-1-ol using a suitable alkyl halide

OR

Give equations of the following reactions :

(i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.

(ii) Bromine in CS_2 with phenol

(iii) Treating phenol with chloroform in presence of aqueous NaOH.

21. **(a)** How is leaching carried out in case of low grade copper ores ?

(b) The value of $\Delta_f G°$ for formation of Cr_2O_3 is -540 kJ mol^{-1} and that of Al_2O_3 is -827 kJ mol^{-1}. Is the reduction of Cr_2O_3 possible with aluminium?

22. Describe the following with suitable examples :

(i) Tranquilizers (ii) Antifertility drugs

(iii) Antihistamines

23. Suresh, a chemistry student of class XII is suffering from fever. His mother consulted the doctor and took a medicine from store as prescribed by doctor. She added boiled water and cold water to the medicine and shook the content properly as per the instructions given on the bottle of medicine. His mother said that why they do not prepare this medicine so that it can be consumed as such. Suresh then explained to his mother why this medicine is available in this form.

(i) Why the medicine is available in this form?

(ii) Why it is instructed to shake the content well after addition of water in medicine?

(iii) What are the values shown by Suresh?

(iv) What is the name of process done by his mother to prepare medicine?

24. **(a)** Henry's law constant for CO_2 in water is 1.67×10^8 pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

(b) The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.

OR

(a) 0.5 g KCl was dissolved in 100 g of water and the solution originally at 20°C, froze at – 0.24°C. Calculate the percentage ionisation of salt. K_f per 1000 g water = 1.86 K.

(b) What role does the molecular interaction play in solution of alcohol and water?

25. Give plausible explanation for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6-trimethylcyclohexanone does not.

(ii) There are two $—NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazone.

(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester formed should be removed as soon as it is formed.

OR

An organic compound (*A*) molecular formula $C_8H_{16}O_2$ was hydrolysed with dilute sulphuric acid to a carboxylic acid (*B*) and an alcohol (*C*). Oxidation of (*C*) with chromic acid produced (*B*),(*C*) on dehydration gives but-1-ene. Write equations for the reactions involved.

26. **(a)** The electronic configurations of two members of the lanthanoid series are as follows:

$4f^1 5d^1 6s^2$ and $4f^7 5d^0 6s^2$

What are their atomic numbers ? Predict the oxidation states exhibited by these elements in their compounds.

(b) Assign reasons for each of the following statements :

(i) The largest number of oxidation states are exhibited by the elements in the middle of the first row of the transition elements.

(ii) The atomic radii decreases in size with the increasing atomic number in the lanthanoid series.

OR

(a) Explain giving reasons :

(i) Transition elements and their compounds exhibit paramagnetic behaviour.

(ii) Transition elements and their compounds are found to be good catalysts.

(iii) Enthalpies of atomization of the transition elements are high.

(b) Compare the chemistry of actinoids with that of the lanthanoid in reference to

(i) Atomic and ionic sizes.

(ii) Oxidation states.

Hints & Solutions

4. The unit of rate constant is L mol^{-1} s^{-1} or $(mol\ L^{-1})^{-1}\ s^{-1}$. Equate this with general expression of $(mol\ L^{-1})^{1-n}\ s^{-1}$.

$(mol\ L^{-1})^{-1}\ s^{-1} = (mol\ L^{-1})^{1-n}\ s^{-1}$

$\therefore \quad -1 = 1 - n$ or $n = 2$

The order of reaction = 2

5. The ionisation isomer of $[Cr(H_2O)_5Br]SO_4$ is $[Cr(H_2O)_5SO_4]Br$.

6. The correct order is

Acetophenone < p-Tolualdehyde
< Benzaldehyde < p-Nitrobenzaldehyde

8. Alcohols are relatively more soluble in water than the corresponding hydrocarbons because alcohol molecules can form hydrogen bonds with water.

10. (a) $Cl_2 + H_2O \longrightarrow 2HCl + [O]$

(b) $\underset{\text{(Cold and dilute)}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$

13. (a) Rate of production of iodine

$= \frac{1}{2} \times$ Rate of disappearance of HI

$$\frac{d[I_2]}{dt} = \frac{1}{2} \times \left(\frac{-d[HI]}{dt}\right)$$

(b) $k = 9.1 \times 10^{-2}\ L\ mol^{-1}\ s^{-1}$

14. (i) Cubic close-packed structure is having face centred cubic structure.

Thus, for *fcc*, $a = 2\sqrt{2} \cdot r$

or $a = 2 \times 1.414 \times 125$ pm = 354 pm

(ii) Volume of unit cell, $a^3 = (354 \times 10^{-10}\ cm)^3$

$= 44.36 \times 10^{-24}\ cm^3$

Number of unit cells in 1.00 cm^3 $= \frac{1}{44.36 \times 10^{-24}}$

$= 2.25 \times 10^{22}$

24. (a) Mass of CO_2 = Moles of CO_2 × Mol. mass of CO_2

$= 42.14 \times 10^{-3} \times 44 = 1.854$ g

OR

(a) $M_B = \frac{K_f \cdot W_B \cdot 1000}{\Delta T_f \cdot W_A} = \frac{1.86 \times 0.5 \times 1000}{0.24 \times 100} = 38.75$

Now, normal molecular mass of KCl

= 39 + 35.5 = 74.5

So, $i = \frac{\text{Observed moles of solute}}{\text{Normal moles of solute}} = \frac{1+\alpha}{1}$

$\therefore \quad \frac{1+\alpha}{1} = 1.92$ or $1 + \alpha = 1.92$

or $\alpha = 0.92$

$\therefore$ Percentage ionisation = 92 %

Practice Paper -6 (Unsolved)

Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Why is enthalpy of chemisorption higher than that of physisorption ?

2. Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic numbers?

3. How does the conductivity of a semiconductor change if its temperature is raised ?

4. What is de-icing agent? How does it work ?

5. Why electrolysis of aqueous solution of NaBr and NaI gives Br_2 and I_2 respectively while that of NaF gives O_2 instead of F_2 ?

6. For the reaction $A \rightarrow B$, the rate of reaction becomes twenty seven times when the concentration of A is increased three times. What is the order of the reaction ?

OR

Define the term activation energy why different reaction proceed at different speeds?

7. Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction ?

8. The value of $\Delta_f G^\circ$ for the formation of Cr_2O_3 is $-540\ \text{kJ mol}^{-1}$ and that of Al_2O_3 is $-827\ \text{kJ mol}^{-1}$. Is the reduction of Cr_2O_3 possible with Al?

9. (a) $K_2[PtCl_6]$ is a well known compound whereas the corresponding Ni compound is not known. State reason for it.
(b) Mercury is normally not considered a transition metal. State reason.

10. Deduce the (a) shape and (b) magnetic behaviour of $[Co(NH_3)_5NO_2]^{2+}$.

11. Explain why :
(a) Alkyl halides although polar and immiscible in water.
(b) Iodoform is formed by reaction of acetone with hypoiodite ion and not iodide ion.

12. How would you account for the following :
(i) Phenols are much more acidic than alcohols.
(ii) The boiling points of ethers are much lower than those of the alcohols of comparable molecular masses.

13. How will you bring about the following conversion :
(a) Benzene – Ethyl benzene
(b) Ethanal – But-2-en-oic acid

14. On electrolysis in acidic solution amino acids migrate towards cathode, while in alkaline solution these migrate towards anode. Comment.

15. Tabulate the differences between chain growth polymerisation and step-growth polymerisation.

16. Account for the following :
(a) SO_2 is a gas while SeO_2 is a solid.
(b) Ammonia acts as a Lewis base.

OR

Write the conditions to maximise the yield of H_2SO_4 by contact process.

17. Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.

18. Explain the following observation :
(i) Finely divided substance is more effective as an adsorbent.

(ii) Rate of physical adsorption decreases with rise of temperature.

(iii) Physical adsorption is multilayered while chemical adsorption is monolayered.

19. Give plausible explanation for each of the following.

(i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6-trimethylcyclohexanone does not

(ii) There are two–NH_2 groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of a acid catalyst, the water or the ester should be removed as soon as it is formed.

20. (a) Di-tert-butyl ether cannot be prepared by Williamson's synthesis. Explain.

(b) Alcohols donot react with NaBr but when H_2SO_4 is added they form alkyl bromides. Explain.

(c) Sodium metal can be used for drying diethylether and benzene but not for ethanol. Explain.

21. Zinc granules are added in excess to a 500 mL of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potentials of $Zn^{2+} \mid Zn$ and $Ni^{2+} \mid Ni$ are – 0.75 V and – 0.24 V respectively, find out the concentration of Ni^{2+} in solution at equilibrium.

22. At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C.

23. Kavita noticed that she has put on a lot of weight. She immediately switched over to artificial sweeteners to reduce her sugar intake. Her friend Amrita, a class XII student suggested that instead of artificial sweeteners, she should control her weight by taking less sugar in diet, morning walk and daily exercise.

(i) What values are displayed by Amrita?

(ii) What are the consequences of using artificial sweeteners?

(iii) Name an artificial sweetener which is stable at cooking temperature.

(iv) Why artificial sweeteners are recommended for diabetic patients?

24. (i) (a) Does the hydrolysis of XeF_6 lead to a redox reaction?

(b) Draw the structure of $XeOF_4$.

(c) Complete and balance the following equation : $XeF_4 + H_2O \longrightarrow$

(ii) Account for the following :

(a) H_2S has lower boiling point than H_2O.

(b) Reducing character decreases from SO_2 to TeO_2.

OR

(i) How would you account for the following?

(a) Fluorine atom is more electronegative than iodine atom, yet HF is weaker acid than HI.

(b) Cl has more electron gain enthalpy than F.

(ii) Give the structure of PCl_5 in

(a) the vapour phase (b) the solid state.

(iii) Why does a nitric acid bottle appear yellow?

25. (i) Why is camphor preferred as a solvent in determination of depression in freezing point (ΔT_f)?

(ii) Aquatic species are more comfortable in cold water rather than in warm water. Why?

(iii) The vapour pressures of pure liquids *A* and *B* are 450 and 700 mm Hg at 350 K respectively. Find out the composition of the liquid mixture, if total vapour pressure is 600 mm Hg. Also, find the composition of the vapour phase.

OR

(i) When kept in water, raisins swell in size. Name and explain the phenomenon involved with the help of a diagram. Give three applications of the phenomenon.

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

26. (i) Give one chemical test to distinguish between the following pairs of compounds :

(a) Methylamine and dimethylamine

(b) Secondary and tertiary amines

(ii) Write the chemical reaction stating the reaction conditions required for each of the following conversions :

(a) Methyl bromide to ethylamine
(b) Aniline to phenol
(c) *p*-Toluidine to 2-bromo-4-methylaniline

OR

(i) Write the chemical reaction stating the reaction conditions required for each of the following conversions :
(a) Aniline to chlorobenzene
(b) Acetaldehyde to ethylamine

(ii) Give one chemical test to distinguish between the following pairs of compounds:
(a) Ethylamine and aniline
(b) Aniline and benzylamine
(c) Aniline and *N*-methylaniline

Hints & Solutions

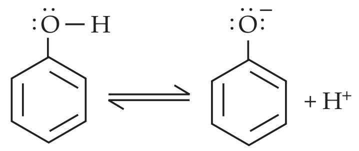
1. Since the force of attraction between adsorbate and adsorbent is more in chemisorption as compared to physisorption, so the heat evolved is more, hence, enthalpy is higher.

4. Common salt is called de-icing agent.

10. The d^2sp^3 hybridisation of Co^{3+} gives the complex ion octahedral shape and it is diamagnetic as all the electrons are paired.

11. (a) All the alkyl halides are unable to form hydrogen bond with water or to break the already present hydrogen bond in water.
(b) Hypoiodite ion can act as an oxidising agent while iodide ion does not.

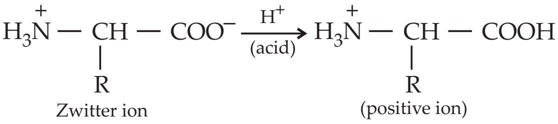
12. (i)



$$R-\ddot{O}-H \rightleftharpoons \underset{\text{Alkoxide ion}}{R-\ddot{O}{:}^{-}} + H^+$$

(ii) Ethers have low polarity and as a result do not show any association by intermolecular hydrogen bonding.

14. In acidic solution, the carboxylate anion accepts a proton and gets converted into carboxylic group resulting in the formation of a positive ion.



$$\underset{\text{Zwitter ion}}{H_3\overset{+}{N}-\underset{\displaystyle R}{\underset{|}{CH}}-COO^-} \xrightarrow[\text{(acid)}]{H^+} \underset{\text{(positive ion)}}{H_3\overset{+}{N}-\underset{\displaystyle R}{\underset{|}{CH}}-COOH}$$

18. (i) The extent of adsorption increases with the increase of surface area of the adsorbent. (ii) Gas (adsorbate) + Solid (adsorbent)

$$\underset{\text{Evaporation}}{\overset{\text{Condensation}}{\rightleftharpoons}} \text{Gas adsorbed on solid + Heat}$$

21. $$\text{Conc. of } Ni^{2+} = \frac{1}{K_c} = \frac{1}{1.941\times10^{17}}$$
$$= 5.15 \times 18^{-12}$$

22. Applying Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$
$$k_2 = 35.38 \times 1.925 \times 10^{-3}\ \text{min}^{-1}$$
$$= 6.81 \times 10^{-2}\ \text{min}^{-1}$$

For 75% decomposition, x = 75% of a = 0.75 a

$$t = \frac{2.303}{k}\log\frac{a}{a-x} = \frac{2.303}{6.81\times10^{-2}\ \text{min}^{-1}} \times \log\frac{a}{a-0.75a}$$
$$= \frac{2.303}{6.81\times10^{-2}\ \text{min}^{-1}}\log\frac{1}{0.25}\ \text{min} = 20.36\ \text{min}.$$

25. (iii) Given, $p_A^\circ = 450$ mm, $p_B^\circ = 700$ mm, $P_{\text{total}} = 600$ mm

According to Raoult's law, $p_A = x_A \times p_A^\circ$

$$p_B = x_B \times p_B^\circ = (1-x_A)\,p_B^\circ$$
$$P_{\text{total}} = p_A + p_B = x_A p_A^\circ + (1-x_A)p_B^\circ$$
$$= p_B^\circ + (p_A^\circ - p_B^\circ)x_A$$

On substituting the values, we get

$$600 = 700 + (450 - 700)x_A$$

or $$250x_A = 100$$

or $$x_A = \frac{100}{250} = 0.40$$

Thus, composition of the liquid mixture will be

mole fraction of $A(x_A) = 0.40$,
mole fraction of $B(x_B) = 1 - 0.40 = 0.60$

$\therefore$ $p_A = x_A \times p_A^\circ = 0.40 \times 450\ \text{mm} = 180\ \text{mm}$
$p_B = x_B \times p_B^\circ = 0.60 \times 700\ \text{mm} = 420\ \text{mm}$

Thus, mole fraction of A in vapour phase

$$= \frac{p_A}{p_A + p_B} = \frac{180}{180+420} = 0.30$$

Mole fraction of B in vapour phase = 1 – 0.30
= 0.70

Practice Paper -7 (Unsolved)

Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. What positions do the anions occupy in a zinc blende type structure ?

2. What is the molality of acetic acid solution containing 6 g of acetic acid in 100 g water ?

3. Give two examples of heterogeneous catalytic reactions.

4. NaCN acts as depressant in preventing ZnS from forming the froth. Explain.

5. What are ambidient nucleophiles ? Explain with an example.

6. Write the net reaction for the formation of the aldol and dehydration products obtained from phenyl acetaldehyde.

7. Bond angle in PH_4^+ is higher than in PH_3. Why ?

8. Nitrogen exists as diatomic molecule and phosphorus as P_4. Why ?

9. Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. $K_f = 3.9$ K kg mol^{-1}.

OR

Henry's law constant for the molality of methane in benzene at 298 K is 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

10. The value of ΔG_f° for formation of Cr_2O_3 is –540 kJ/mol and that of Al_2O_3 is – 872 kJ/mol. Is the reduction of Cr_2O_3 possible with Al ?

11. Convert
(i) Diethyl ether into ethylene
(ii) Anisole into toluene

12. Account for the following :
(i) Aniline is a weaker base than cyclohexyl amine.
(ii) $C_2H_5NH_2$ is soluble in water, whereas $C_6H_5NH_2$ is insoluble.

13. What is a peptide bond ? Illustrate its formation with an example.

14. On electrolysis in acidic solution amino acids migrate towards cathode, while in alkaline solution these migrate towards anode. Why ?

OR

Why do monoamino monocarboxylic acids have two p*K* values ?

15. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallises in cubic lattice. If the density is 2 g/cm^3 then find the radius of metal atom ($N_A = 6.022 \times 10^{23}$).

16. A first order reaction is half complete in 40 min at 27°C and 80% complete in 20 min at 47°C. Calculate its energy of activation.

17. (i) Explain coagulating power.
(ii) What are protective colloids ?
(iii) What are emulsions ? How are they classified ?

18. Give the molecular shapes of XeF_2, XeF_4 and XeF_6.

OR

Arrange the following in the order of property indicated for each set :
(i) F_2, Cl_2, Br_2, I_2 → increasing bond dissociation enthalpy.
(ii) HF, HCl, HBr, HI → increasing acid strength
(iii) NH_3, PH_3, AsH_3, SbH_3, BiH_3 → increasing base strength.

19. Account for the following :
(i) SF_6 is known but SCl_6 does not exist.
(ii) CF_4 and SF_4 are not isostructural.
(iii) Noble gases have very low boiling points. Why ?

20. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene.

(i) 1-Bromo-1-methylcyclohexane
(ii) 2-Chloro-2-methylbutane
(iii) 2, 2, 3-Trimethyl-3-bromopentane

21. Write the names and molecular structures of the monomers of the following polymers. Give one use of each specifying the property responsible for this use.

(i) Glyptal (ii) Nylon-6
(iii) Neoprene

22. Describe the following with suitable examples :

(i) Tranquilizers (ii) Antifertility drugs.
(iii) Antihistamines

23. Dr. S.P. Rahman, a professor of Medical Science, organised a seminar on cancer. The following paragraph highlights the important message given by him :

"Cancer is not a communicable disease and it occurs due to unlimited growth of body cells leading to tumours. We should shake hands, eat together with the people suffering from cancer. These activities will boost up the confidence in them for living."

(i) Mention the values reflected by the message given by Dr. Rahman.
(ii) Write the name of coordination compound used for the treatment of cancer and give its structure.
(iii) Give the uses of two other coordination compounds in medicinal chemistry.

24. (i) A cell is prepared by dipping a copper rod in 0.01 M copper sulphate solution, and zinc rod in 0.02 M $ZnSO_4$ solution. The standard reduction potentials of copper and zinc are +0.34 V and –0.76 V respectively.

(a) What will be the cell reaction ?
(b) How will the cell be represented ?
(c) What will be the emf of the cell ?

(ii) The standard cell potential for Daniell cell is +1.10 V. Calculate the standard Gibb's energy for the reaction

OR

(i) The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

(ii) From the following molar conductivities at infinite dilution calculate λ_m° for NH_4OH

Λ_m for $Ba(OH)_2 = 457.6\ \Omega^{-1}\ cm^2\ mol^{-1}$
Λ_m for $BaCl_2 = 240.6\ \Omega^{-1}\ cm^2\ mol^{-1}$
Λ_m for $NH_4Cl = 129.8\ \Omega^{-1}\ cm^2\ mol^{-1}$

25. (i) A black solid (A) on fusion with potassium hydroxide and oxygen gives a green colour solution (B). (B) disproportionates in acidic medium to give back (A) and a pink colour solution of (C). What are A, B and C ? Write all the chemical equations involved.

(ii) Complete and balance the following equations :

(a) $MnO_4^{-} + S_2O_3^{2-} + H_2O \rightarrow$
(b) $Cr_2O_7^{2-} + Sn^{2+} + H^{+} \rightarrow$

OR

(i) Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents. Why ?
(ii) Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state ?
(iii) Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only ?
(iv) Explain why Cu^{+} ion is not stable in aqueous solution ?
(v) Why are interstitial compounds well known for transition metals ?

26. **(i)** Give simple chemical tests to distinguish between the following pairs of compounds :

(a) Acetophenone and Benzophenone
(b) Benzoic acid and Ethyl benzoate

(ii) Describe the following :

(a) Cannizzaro reaction
(b) Cross aldol condensation
(c) Decarboxylation

OR

An organic compound 'A' on treatment with ethyl alcohol gives carboxylic acid 'B' and compound 'C'. Hydrolysis of 'C' under acidic conditions gives 'B' and 'D'. Oxidation of 'D' with $KMnO_4$ also gives 'B'. 'B' on heating with $Ca(OH)_2$ gives 'E' with molecular formula C_3H_6O. 'E' does not give Tollen's test or reduce Fehling solution but forms 2,4-dinitrophenyl hydrazone. Identify A, B, C, D and E.

Hints & Solutions

1. Anions in zinc blende type structure occupy fcc positions.

2. 1 molal.

4. $ZnS + 4NaCN \longrightarrow \underset{\text{Sodium tetracyanozincate(II)}}{Na_2[Zn(CN)_4]} + Na_2S$

8. Nitrogen because of its small size and high electronegativity forms $p\pi$-$p\pi$ multiple bonds. Phosphorus due to its larger size and lower electronegativity usually does not form $p\pi$-$p\pi$ multiple bonds with itself.

9. $$W_B = \frac{\Delta T_f \times M_B \times W_A}{K_f \times 1000} = \frac{1.5 \times 176 \times 75}{3.9 \times 1000} = 5.08 \text{ g}$$

OR

Applying Henry's law

$$p = k_H x$$

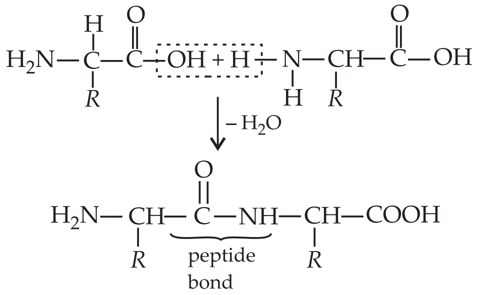
$$\therefore \quad x = \frac{p}{k_H} = \frac{760 \text{ mm}}{4.27 \times 10^5 \text{ mm}} = 1.78 \times 10^{-3}$$

10. $$2Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3; \quad \Delta G_f^\circ = -827 \text{ kJ/mol}$$

$$2Cr + \frac{3}{2}O_2 \longrightarrow Cr_2O_3; \quad \Delta G_f^\circ = -540 \text{ kJ/mol}$$

$$\therefore \quad Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr;$$
$$\Delta G = -827 - (-540) = -287 \text{ kJ/mol}$$

13.



$$H_2N-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH + H-\underset{H}{N}-\underset{R}{CH}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{-H_2O} H_2N-\underset{R}{CH}-\underbrace{\overset{O}{\overset{\|}{C}}-NH}_{\text{peptide bond}}-\underset{R}{CH}-COOH$$

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

As the metal ($z = 2$) has bcc structure

$$\therefore \quad r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 5 = \frac{1.732 \times 5}{4} = 2.165 \text{ Å}$$

16. $$E_a = \frac{2.303\,RT_1T_2}{(T_2 - T_1)} \log\left(\frac{k_2}{k_1}\right) = 61.292 \text{ kJ/mol.}$$

18. XeF_2 is linear in shape with Xe in sp^3d hybridised state.

XeF_4 is square planar with Xe in sp^3d^2 hybridised state.

XeF_6 has distorted octahedral structure.

OR

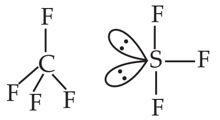
(i) $I_2 < Br_2 < F_2 < Cl_2$.

(ii) $HF < HCl < HBr < HI$

(iii) $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

19. (i) SCl_6 does not exist due to large size of chlorine atom.

(ii) CF_4 is tetrahedral in shape because carbon is sp^3 hybridised while S in SF_4 is sp^3d hybridised (as S has two lone pairs) and has a distorted trigonal bipyramidal shape.



(iii) Noble gases being monoatomic have no interatomic forces.

24. **(i)** $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

(b) The cell can be represented as

$Zn_{(s)}|Zn^{2+}_{(aq)}\,(0.02 \text{ M})\|Cu^{2+}_{(aq)}\,(0.01 \text{ M})|Cu_{(s)}$

(c) $$E = E^\circ - \frac{0.059}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = +1.091 \text{ V}$$

(ii) $\Delta_r G^\circ = -nFE^\circ = -212300 \text{ J}$

OR

(i) $$\text{Conductivity} = \kappa = \frac{1}{\rho} = \left(\frac{1}{87.135}\right) \text{S cm}^{-1}$$

$$= 0.01148 \text{ S cm}^{-1}$$

Molar conductivity,

$$\Lambda_m = \frac{\kappa \times 1000}{c} = \frac{0.01148 \times 1000}{0.05}$$
$$= 229.6 \text{ S cm}^2 \text{ mol}^{-1}$$

(ii) $\Lambda_m^\circ(NH_4OH) = 238.3\ \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

25. **(i)** $A \rightarrow MnO_2 \quad B \rightarrow K_2MnO_4$
$C \rightarrow MnO_4^-$

The chemical equations involved are :

$$\underset{(A)}{MnO_2} + 2\,KOH + \frac{1}{2}O_2 \longrightarrow \underset{(B)}{K_2MnO_4} + H_2O$$

$$3\,\underset{(B)}{MnO_4^{2-}} + 4H^+ \longrightarrow \underset{(A)}{MnO_2} + 2\underset{(C)}{MnO_4^-} + 2H_2O$$

(ii) **(a)** $$2MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 2MnO_2 + 3SO_4^{2-} + 2OH^- + 3S$$

(b) $$Cr_2O_7^{2-} + 3\,Sn^{2+} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 3\,Sn^{4+} + 7\,H_2O$$

Practice Paper -8 (Unsolved)

Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Why are powdered substances more effective adsorbents than their crystalline forms?

2. Arrange the following alkyl halides in the order of increasing dipole moment.
$CH_3—F$, $CH_3—Cl$, $CH_3—Br$, $CH_3—I$

3. Trimethylamine and *n*-propylamine have the same molecular weight but the former boils at lower temperature than the latter. Give reason.

4. Why is Frenkel defect not found in pure alkali metal halides?

5. Why outer octahedral complexes are called high spin complexes?

6. 4% NaOH solution (mass/volume) and 6% urea solution (mass/volume) are equimolar but not isotonic. Why?

7. The $E°$ values corresponding to the following two reduction electrode processes are :
$Cu^+/Cu = +\ 0.52$ V
$Cu^{2+}/Cu^+ = +\ 0.16$ V
Formulate the galvanic cell for their combination. What will be the standard cell potential for it? Calculate $\Delta_r G°$ for the cell reaction.

8. (i) In the transition series, starting from lanthanum ($_{57}La$), the next element hafnium ($_{72}Hf$) has an atomic number of 72. Why do we observe this jump in atomic number?
(ii) Ce(IV) is a good analytical reagent. Why?

9. Give reason for the following :
(i) Ferric iodide is very unstable but ferric chloride is stable.
(ii) ClF_3 molecule has a T-shaped structure and not a trigonal planar one.

10. How can propan-2-one be converted into *tert*-butyl alcohol?

OR

What happens when
(i) ethyl alcohol reacts with red P and Br_2?
(ii) ethanol is heated with conc. H_2SO_4 at 443 K?

11. (i) Explain why does conductivity of germanium crystals increase on doping with gallium.
(ii) Why does table salt, NaCl, sometimes appear yellow in colour?

12. (i) Heptane and octane form ideal solution. At 373 K, the vapour pressure of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35.0 g of octane?
(ii) Give an example of a material used for making semipermeable membrane for carrying out reverse osmosis.

13. Write the overall reaction that occurs during the use of nickel-cadmium cell. Is it a primary or a secondary cell? Mention its one merit over the lead storage cell.

14. (i) What is meant by van't Hoff factor?
(ii) The osmotic pressure of a 0.0103 molar solution of an electrolyte is found to be 0.70 atm at 27°C. Calculate the van't Hoff factor. ($R = 0.082$ L atm K^{-1} mol^{-1})
What conclusion do you draw about the molecular state of the solute in the solution?

15. Explain the following :

(i) CO_2 is a better reducing agent below 710 K whereas CO is a better reducing agent above 710 K.

(ii) Silica is added to the sulphide ore of copper in the reverberatory furnace.

(iii) Vapour phase refining method is used for the purification of Ti.

OR

(i) Indicate the principle behind the method used for the refining of zinc.

(ii) How is cast iron different from pig iron?

(iii) Which form of the iron is the purest form of commercial iron?

16. (i) What type of battery is mercury cell? Why is it more advantageous than dry cell?

(ii) Electrolysis of aqueous $CuCl_2$ solution liberates Cl_2 at anode not O_2. Why?

17. Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value for the following : $[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{4-}$

18. Compound (*A*) with molecular formula C_4H_9Br is treated with aqueous KOH solution. The rate of this reaction depends upon the concentration of the compound '*A*' only. When another optically active isomer '*B*' of this compound was treated with aqueous KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.

(i) Write down the structural formula of both compounds '*A*' and '*B*'.

(ii) Out of these two compounds, which one will be converted to the product with inverted configuration.

19. Accomplish the following conversions :

(i) Aniline to 2,4,6-tribromofluorobenzene

(ii) Benzamide to toluene

20. (i) Mention the type of linkage responsible for the formation of the following :

(a) Primary structure of protein

(b) Cross linkage of polypeptide chains

(c) α-helix formation

(d) β-sheet structure

(ii) What is meant by reducing sugars?

21. Explain each of the following terms with one suitable example.

(i) A sweetening agent for diabetic patients

(ii) Enzymes

(iii) Analgesics

22. (i) Write the name of the reagents and equations in the conversion of

(a) phenol to salicylaldehyde

(b) anisole to *p*-methoxyacetophenone.

(ii) Ethers are soluble in water. Why?

23. Seema went to market to buy vegetables. The vendor put the vegetables in the polythene bag but Seema refused to take polythene bag and told the vendor to put the things in the cloth bag which she was carrying with her.

(i) What values are shown by Seema?

(ii) Why did Seema carry cloth bag with her instead of taking polythene bag from vendor?

(iii) What are the bad effects of non-biodegradable polymers?

24. Compound '*A*' ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yields two compounds '*B*' and '*C*'. The compound '*B*' on oxidation gives '*D*' which on treatment with aqueous alkali and subsequent heating furnishes '*E*'. The later on catalytic hydrogenation gives '*C*'. The compound '*D*' on further oxidation gives CH_3COOH. Deduce the structures of *A*, *B*, *C*, *D* and *E*.

OR

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

(a) Propanoyl chloride and propanoic acid

(b) Benzaldehyde and acetophenone

(ii) How would you account for the following?

(a) Aldehydes are more reactive than ketones towards nucleophiles.

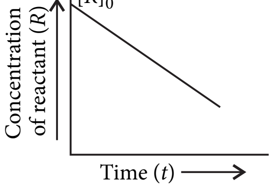
(b) The boiling points of aldehydes and ketones are lower than the corresponding acids.

(c) The aldehydes and ketones undergo a number of addition reactions.

25. (i) The graph for the reaction,

$R \longrightarrow P$

is represented by



(a) Predict the order of the reaction in this case.

(b) What does the slope of the graph represent?

(ii) The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume :

$$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$

Experiment	**Time/s**	**Total pressure/ atm**
1	0	0.4
2	100	0.7

Calculate the rate constant.

[Given : log 4 = 0.6021, log 2 = 0.3010]

OR

(i) The thermal decomposition of HCO_2H is a first order reaction with a rate constant of $2.4 \times 10^{-3}\ s^{-1}$ at a certain temperature. Calculate how long will it take for three-fourth of initial quantity of HCO_2H to decompose?

(Given : log 4 = 0.6021)

(ii) The decomposition of a compound is found to follow a first order rate law. If it takes 15 minutes for 20 percent of original material to react, calculate

(a) the specific rate constant

(b) the time at which 10 percent of the original material remains unreacted

(c) the time it takes for the next 20 percent of the reactant left after the first 15 minutes.

26. (i) Why do noble gases form compounds with fluorine and oxygen only?

(ii) Why HF is stored in wax coated glass bottles?

(iii) SF_6 is not easily hydrolysed though thermodynamically it should be. Why?

(iv) Structures of xenon fluorides cannot be explained by valence bond approach. Explain?

(v) Draw the structure of H_2SO_5.

OR

(i) Explain the Ostwald's process for the manufacture of nitric acid.

(ii) Write the balanced reactions when nitric acid reacts with

(a) I_2 (b) C

(c) S_8 (d) P_4

(iii) Give any two uses of HNO_3.

Hints & Solutions

1. Powdered substances have large surface area which increases the extent of adsorption than their crystalline forms.

2. Increasing order of dipole moment :

$CH_3—I < CH_3—Br < CH_3—F < CH_3—Cl$

5. Pairing does not occur in outer octahedral complexes, hence, they have unpaired electrons and show large values of magnetic moments.

7. At cathode : $Cu^+ + e^- \longrightarrow Cu \quad E° = +0.52\ V$

At anode : $Cu^+ \longrightarrow Cu^{2+} + e^- \quad E° = +0.16\ V$

Cell reaction : $2Cu^+ \longrightarrow Cu + Cu^{2+}$

Cell representation is

$Cu^+ \mid Cu^{2+} \parallel Cu^+ \mid Cu$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.52 - 0.16 = 0.36\ V$$

$$\Delta_r G° = -nE°F = -1 \times 0.36 \times 96500$$
$$= -34740\ J\ mol^{-1}$$

12. (i)

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

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

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

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

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

13. Reaction during discharging,

At anode : $Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^-$

At cathode :

$NiO_{2(s)} + 2H_2O_{(l)} + 2e^- \rightarrow Ni(OH)_{2(s)} + 2OH^-_{(aq)}$

$$Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(s)}$$

When charging takes place, reactions are reversed.

14. (ii) $\pi = iCRT$

or, $0.70 = i \times 0.0103 \times 0.082 \times (27 + 273)$

or, $i = \dfrac{0.70}{0.0103 \times 0.082 \times 300} = 2.76$

Since $i > 1$, solute molecules are dissociated in the solution.

15. (i) According to Ellingham diagram, at temperature below 710 K,

ΔG°(C, CO2) < ΔG°(C, CO) hence CO2 is better reducing agent.

At temperature above 710 K,

ΔG°(C, CO2) > ΔG°(C, CO) hence CO is better reducing agent.

(ii) $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

$FeO + SiO_2 \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$

(iii) $\underset{\text{Impure}}{Ti} + 2I_2 \longrightarrow TiI_4,\ TiI_4 \xrightarrow{1800\text{ K}} \underset{\text{Pure}}{Ti} + 2I_2$

16. (ii) $CuCl_2 \longrightarrow Cu^{2+} + 2Cl^-$

At cathode, $Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$

At anode, two reactions are possible

$2Cl^- \longrightarrow Cl_{2(g)} + 2e^-;\ E° = 1.36\text{ V}$

$H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-;$

$E° = 1.23\text{ V}$

17. $[FeF_6]^{3-}$: Number of unpaired electrons = 5

Magnetic moment = $\sqrt{5(5+2)} = 5.92$ B.M.

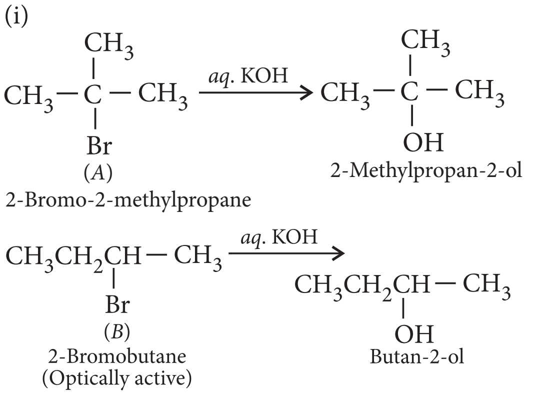
$[Fe(H_2O)_6]^{2+}$: Number of unpaired electrons = 4

Magnetic moment = $\sqrt{4(4+2)} = 4.9$ B.M.

$[Fe(CN)_6]^{4-}$:

Diamagnetic and its magnetic moment is zero.

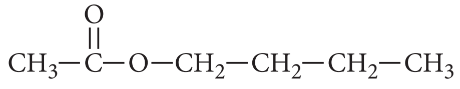
18. (i)



(*A*) 2-Bromo-2-methylpropane → 2-Methylpropan-2-ol

(*B*) 2-Bromobutane (Optically active) → Butan-2-ol

24. (*A*)



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-CH_2-CH_3$

(*B*) CH_3CH_2OH

(*C*) $CH_3CH_2CH_2CH_2OH$

(*D*) CH_3CHO

(*E*) $CH_3-CH=CH-CHO$

25. (i) (a) The reaction is of zero order.

(b) Slope of the straight line graph gives rate constant.

$$-k = \frac{d[R]}{dt}$$

According to first order kinetic equation,

$$k = \frac{2.303}{t}\log\left(\frac{p_{SO_2Cl_2\,(\text{initial})}}{p_{SO_2Cl_2\,(\text{after reaction})}}\right)$$

$$= \frac{2.303}{100}\log\left(\frac{0.4}{0.1}\right) = 1.38 \times 10^{-2}\ s^{-1}$$

OR

(i) For a first order reaction,

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

$t = 577.7\ s \approx 578\ s$

(ii) (a) For a first order reaction,

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

$k = 0.015\ \text{min}^{-1}$

(b) When $[R]_t = 0.1\,[R]_0$, $t = ?$

$$k = \frac{2.303}{t_1}\log\frac{[R]_0}{0.1\,[R]_0} = \frac{2.303}{t_1}\log 10$$

$t_1 = 153.53$ min

∴ After 153.53 min, 10% of the original material remains unreacted.

(c) Also,

$$k = \frac{2.303}{t_2}\log\frac{0.8\,[R]_0}{0.64\,[R]_0} = \frac{2.303}{t_2}\log\frac{10}{8}$$

$t_2 = 15$ min

26. (i) $4NH_{3(g)} + 5O_{2(g)} \xrightarrow[500\text{K, 9bar}]{\text{Pt}} 4NO_{(g)} + 6H_2O_{(g)}$

$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$

$3NO_{2(g)} + H_2O_{(l)} \longrightarrow 2HNO_{3(aq)} + NO_{(g)}$

(ii) (a) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(b) $C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2$

(c) $S_8 + 48HNO_{3(\text{conc.})} \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$

(d) $P_4 + 20HNO_{3(\text{conc.})} \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

Practice Paper-9 (Unsolved)

Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. What is the order of the reaction whose *k* value is 2.3×10^{-5} L mol^{-1} s^{-1}?

2. Write one condition for a colloidal solution to show Tyndall effect.

3. Draw the structure of
(i) Red phosphorus
(ii) Orthophosphoric acid

4. Write the IUPAC name of $[Co(NH_3)_4(H_2O)_2]Cl_3$.

5. Write the structure of 4-tertbutyl-3-iodoheptane.

6. Out of aldehydes and ketones which one is more reactive towards nucleophilic addition reaction?

7. Ethers are soluble in water. Why?

OR

Write an equation of a chemical reaction which shows that phenol is acidic.

8. Draw the Zwitter ionic structure of amino acid.

9. Write two differences between Frenkel and Schottky defects.

10. Calculate packing efficiency of BCC unit cell.

11. A first order reaction has rate constant 1.15×10^{-3} s^{-1}. How long will 5 g of this reactant take to reduce to 3.0 g ?

12. Explain the principle involved in the contact process for the manufacture of H_2SO_4. Give necessary equations.

13. Explain the following :
(i) Spectrochemical series
(ii) Crystal field splitting energy.

OR

(i) $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic. Explain.
(ii) What are ambidentate ligands? Give example.

14. Explain the following with suitable equation.
(i) Hoffmann bromamide reaction
(ii) Gabriel phthalimide synthesis

15. The electrical resistance of a column of diameter 1 cm and length 50 cm containing 0.05 mol NaOH solution is 5.5×10^3 Ohms. Calculate.
(i) Resistivity
(ii) Conductivity
(iii) Molar conductance.

16. Explain the following
(i) Ellingham diagram
(ii) Leaching
(iii) Use of cryolite in the extraction of aluminium.

17. Give reasons for the following
(i) Molecular nitrogen is chemically inert.
(ii) BiH_3 is the strongest reducing agent among the hydrides of group-15 elements.
(iii) NH_3 acts as a Lewis base.

18. (i) Arrange the following in order of increasing boiling point.
1-chloropropane, isopropyl chloride
1-chlorobutane, isobutyl chloride.
(ii) Dipole moment of chlorobenzene is lower than that of cyclohexyl chloride. Why?
(iii) What do you mean by the term chirality?

19. (a) Write the mechanism of hydration of ethene to give ethanol.

(b) Write the chemical equation for the reaction of HI with methoxy benzene.

20. What happens when
- (i) Glucose is treated with red P and HI.
- (ii) Protein undergoes denaturation.
- (iii) DNA undergoes complete hydrolysis.

21. Write the structures of monomers of the following polymers.
- (i) Bakelite
- (ii) Teflon
- (iii) Buna-N

22. Explain the following with one suitable example of each
- (i) Tranquillizers
- (ii) Analgesics
- (iii) Antacids

23. Suresh, a chemistry student of class XII is suffering from fever. His mother consulted the doctor and took a medicine from store as prescribed by doctor. She added boiled water and cold water to the medicine and shook the content properly as per the instructions given on the bottle of medicine. His mother said that why they do not prepare this medicine so that it can be consumed as such. Suresh then explained to his mother why this medicine is available in this form.
- (i) Why the medicine is available in this form?
- (ii) Why it is instructed to shake the content well after addition of water in medicine?
- (iii) What are the values shown by Suresh?
- (iv) What is the name of process done by his mother to prepare medicine?

24. (i) Mention one important application of Henry's law.

(ii) Calculate depression in freezing point when 1.225 g of chlorobutanoic acid is added to 250 g of water. Given Ka = 1.4×10^{-3}, $K_f = 1.86\ K\ \text{kg mol}^{-1}$.

(iii) Osmotic pressure is more useful to calculate molecular mass than other colligative properties. Why?

OR

(i) Explain with suitable examples in each case why the molar masses of some substances determined with the help of colligative properties are
- (a) higher
- (b) lower than the actual values.

(ii) Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

25. Name the lanthanoid element which shows well known + 4 oxidation state.
- (ii) Why are Mn^{2+} compounds more stable than Fe^{2+} towards their oxidation to +3 state?
- (iii) What are the different oxidation states shown by actinoids?
- (iv) Write the electronic configuration of Lu^{3+}.
- (v) Write the formula of the π compound formed by combination of lanthanoids with carbon.

OR

- (i) Explain the preparation of potassium dichromate from chromite ore.
- (ii) What is the effect of pH on dichromate ion?
- (iii) Draw the structure of
  - (a) Dichromate ion
  - (b) Manganate ion
- (iv) Which of the following ions are coloured?
  (a) Cu^+ (b) Co^{2+} (c) Sc^{3+}

26. Explain :
- (i) Out of the two-NH_2 groups in semicarbazide only one involves in the formation of semicarbazone.
- (ii) During ester formation water formed should be removed quickly.
- (iii) Even though phenoxide ion has more resonating structures than carboxylate ion, carboxylic acids are more acidic than phenol.
- (iv) α-hydrogens in aldehydes and ketones are acidic.
- (v) Benzaldehyde does not give Fehling test.

OR

(a) How will you distinguish between
- (i) Benzoic acid and ethanoic acid
- (ii) Propanone and propanal?

(b) Complete the following :

(i) $CH_3-C\equiv CH \xrightarrow[H_2O]{Hg^{2+}\ H_2SO_4}$

(ii) Phthalic acid $\xrightarrow[\Delta]{NH_3}$

(iii) Cyclopentanone $+ H_2N-OH \xrightarrow{H^+}$

Hints & Solutions

1. 2

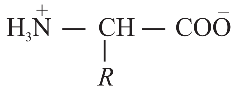
2. Diameter of the dispersed particles is not much smaller than the wavelength of light used.

4. Tetraamminediaquacobalt(III) chloride.

6. Aldehydes are more reactive than ketones.

7. Ethers can form intermolecular hydrogen bond with water, hence are soluble in water.

8.



$$H_3\overset{+}{N} - \underset{\displaystyle R}{\underset{|}{CH}} - CO\overset{-}{O}$$

Zwitter ionic structure of α - amino acid

10. Packing efficiency (PE)

$$= \frac{\text{Volume of lattice point}}{\text{Volume of unit cell}} = \frac{Z \times \frac{4}{3}\pi r^3}{a^3}$$

$$PE = \frac{\sqrt{3}\,\pi}{8} = \frac{1.72 \times 3.14}{8} = 0.68$$

11. Using formula $k = \frac{2.303}{t} \log_{10} \frac{[R]_0}{[R]}$

$$1.15 \times 10^{-3}\ s^{-1} = \frac{2.303}{t} \log_{10} \frac{5}{3}$$

$$1.15 \times 10^{-3}\ s^{-1} = \frac{2.303}{t} \left[0.699 - 0.477\right]$$

or, $t = 444.57$s

15. Cross sectional area = πr^2

$$\text{cell const.} G^* = \frac{l}{a} = \frac{50\ \text{cm}}{0.785\ \text{cm}^2} = 63.69\ \text{cm}^{-1}$$

(i) Resistivity. $\rho = \frac{R}{G^*}$

$= 86.35$ cm

(ii) Conductivity $\kappa = \frac{1}{\rho}$

$= 0.01158\ \text{ohm}^{-1}\ \text{cm}^{-1}$

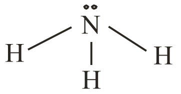
(iii) $\Lambda_m = \frac{\kappa \times 10^{-3}}{M}$

or $\Lambda_m = 2.31 \times 10^{-4}\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

17. (i) Molecular nitrogen is inert due to very high bond dissociation enthalpy (94.4 kJ mol^{-1}) of $N{\equiv}N$.

(ii) BiH_3 is the strongest reducing agent amongst the hydrides of group-15 elements because of its very low bond dissociation enthalpy.

(iii) Due to the presence of a lone pair of electrons on the nitrogen atom ammonia molecule behaves as Lewis base.



24. (i) Soft drink and soda water are filled under high pressure.

Molality of solution $m = \frac{W_2 \times 1000}{M_2 \times W_1}$

$m = 0.04$

Degree of dissociation $\alpha = \sqrt{\frac{K_a}{C}}$

$$\alpha = \frac{i-1}{n-1} \Rightarrow 0.18 = \frac{i-1}{2-1}$$

or $0.18 = i - 1$ or $i = 1.18$

Using $\Delta T_f = iK_f m$

$= 1.18 \times 1.86\ \text{K kg mol}^{-1} \times 0.04$

$= 0.0878$ °C .

Practice Paper -10 (Unsolved)

Time Allowed : 3 hours **Maximum Marks : 70**

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. What are micelles? Give an example of a micellar system.

2. Write the chemical formula for pentammine-chloroplatium (IV) chloride.

3. With the help of chemical equations, show how you will convert 1-propanol to 2-bromopropane in two steps.

4. Arrange the following compounds in increasing order of their boiling points.

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

5. How can a carboxylic acid be converted to an amine having one carbon atom less than the carboxylic acid used?

6. What is the name given to the linkage which holds together two monosaccharide units in a polysaccharide?

7. Write the monomers used for the synthesis of Buna-S?

8. Which of the following do you expect to be coloured and why? Cr^{+}, Cu^{+}.

OR

What is actinoid contraction? How is it different from lanthanoid contraction.

9. Write the relationship between the nearest-neighbour distance (*d*) and the edge (*a*) of a unit cell of a cubic crystal.

10. Give one example of triphenylmethane dyes.

11. The resistance of 0.01 N NaCl solution at 25°C is 200 ohms. Cell constant of the conductivity cell is unity. Calculate the equivalent conductance of the solution.

12. In the compound *AX*, the radius of A^+ ion is 95 pm and that of ion is 181 pm. Predict the crystal structure of *AX* and write the co-ordination numbers of each of the ions.

13. (a) Identify *A, B, C, D* in this reaction.

$$C_2H_4 \xrightarrow{HI} A \xrightarrow{Mg/ether} B \xrightarrow{H_2O} C + D$$

(b) How can you prepare ethyl amine from methyl iodide?

(c) Explain why chloroform is stored in dark-brown coloured bottles?

14. If ΔT is the depression in freezing point of a solvent and *m* is the number of moles of solute per kg of solvent, what is the relationship between ΔT and *m*?

15. (a) Complete the equation :–

(i) $CH_3 - CH_2 - I \xrightarrow[\text{ethyl alcohol}]{\text{Zn - Cu couple}}$

(ii) $C_2H_5 - OH + SOCl_2 \rightarrow$

(b) What happens when ethyl iodide is treated with an etheral solution of magnesium?

16. Give some examples showing chelation by

(a) *en*-a bidentate ligand,
(b) *dien*-a terdentate and
(c) *trien*-a tetradentate ligand.

OR

(i) What will be the correct order for the wavelength of absorption in the visible region for the following :

$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

(ii) $[Ni(H_2O)_6]^{2+}$ is green and becomes violet when ethane 1, 2-diamine is added to it.

17. What are elastomers? Give an example of a natural elastomer.

18. Distinguish physisorption from chemisorption.

19. What happens when

(a) Ethylene is treated with dilute alkaline potassium permanganate solution.

(b) Phenol is treated with sodium hydroxide.

(c) Cyclohexanol is treated with conc. H_2SO_4 at 443 K?

20. How does an isocyanide react with an electrophile and a nucleophile at the same isocyanide carbon? Give an example.

21. (a) Name two metals, which can occur in nature in their native state.

(b) Froth floatation process is generally used for the metallurgy of __________ (oxide ore, sulphide ore, chloride ore).

(c) What is Goldschmidt's aluminothermic process?

(d) What do you mean by autoreduction in metallurgy?

22. What are acid dyes? Give the preparation of orange-I dye?

23. Rohan had been complaining about stomach ache every now and then. His teacher called the parents and asked them to stop giving him junk food and include fibre and vitamin rich food like sprouts, fruits, whole wheat bread and green leafy vegetables in his diet plan.

(i) What values are expressed by the teacher?

(ii) Give two examples of water soluble vitamins.

(iii) What is the importance of fibre rich food?

(iv) Why do children need a protein rich diet?

24. (i) In a reaction between *A* and *B*, the initial rate of reaction was measured for different initial concentration of *A* and *B* as given below :

A/mol L^{-1}	0.20	0.20	0.40
B/mol L^{-1}	0.30	0.10	0.05
r_0/mol L^{-1}s^{-1}	5.07×10^{-5}	5.07×10^{-5}	7.16×10^{-5}

What is the order of reaction with respect to *A* and *B*?

(ii) A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction.

OR

(i) During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1 μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically?

(ii) The decomposition of a hydrocarbon follows the equation

$k = (4.5 \times 10^{11} s^{-1}) e^{-28000 K/T}$. Calculate E_a.

25. **(i)** Free energies of formation ($\Delta_f G$) of $MgO_{(s)}$ and $CO_{(g)}$ at 1273 K and 2273 K are given below :

$\Delta_f G(MgO)_{(s)} = -941$ kJ mol^{-1} at 1273 K

$\Delta_f G(MgO)_{(s)} = -314$ kJ mol^{-1} at 2273 K

$\Delta_f G(CO)_{(g)} = -439$ kJ mol^{-1} at 1273 K

$\Delta_f G(CO)_{(g)} = -628$ kJ mol^{-1} at 2273 K

On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for $MgO_{(s)}$.

(ii) Name an ore having two different metal ions.

(iii) Why zinc and not copper is used for the recovery of Ag from $[Ag(CN)_2]^-$?

OR

(i) Name the metals which are associated with the following terms in their extraction from their ores :

(a) Bessemer's converter (b) Blast furnace

(c) Alumino thermic process

(d) Magnetic separation

(ii) What criterion is followed for the selection of the stationary phase in chromatography?

(iii) Explain the method used for the purification of germanium.

26. Compound '*A*' ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yields two compounds '*B*' and '*C*'. The compound '*B*' on oxidation gives '*D*' which on treatment with aqueous alkali and subsequent heating furnishes '*E*'. The latter on catalytic hydrogenation gives '*C*'. The compound '*D*' on further oxidation gives CH_3COOH. Deduce the structures of *A*, *B*, *C*, *D* and *E*.

OR

(i) What happens when

(a) malonic acid is heated with urea in presence of $POCl_3$

(b) ethanal reacts with air in presence of cobalt acetate?

(ii) Illustrate the following name reactions :

(a) Cross aldol condensation

(b) Hell–Volhard–Zelinsky reaction

Hints & Solutions

2. $[PtCl(NH_3)_5]Cl_4$

4. Increasing order of their boiling points may be as under.

$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

5. By Hofmann Bromamide reaction :

$RCOOH + NH_3 \rightarrow RCONH_2$

$RCONH_2 + 4NaOH + Br_2 \rightarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O$

6. Glycosidic linkage

7. Monomers used for the synthesis of Buna-S is butadiene and styrene.

8. Transition metal ions exhibit colour which have partially filled *d*-orbitals.

9. Simple cubic : $d = a$

Body centered : $d = \frac{\sqrt{3}}{2}a$

Face centered : $d = \frac{a}{\sqrt{2}}$

10. Malachite green is an example of triphenylmethane dye.

11. First calculate k

$$k = \frac{\text{Cell constant}}{R} = \frac{1\text{ cm}^{-1}}{200\text{ ohms}}$$

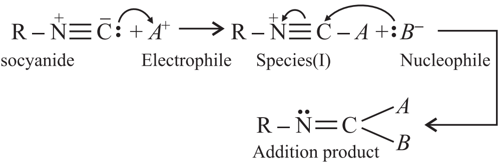
Now equivalent conductivity,

$$\lambda_{eq} = \frac{k}{C_{eq}} = \frac{1\text{ cm}^{-1}}{200\text{ ohms} \times 0.01\text{ eq} \times (1000\text{ cm}^3)^{-1}}$$

$$= \frac{1 \times 1000}{200 \times 0.01}\text{ ohm}^{-1}\text{ cm}^2\text{eq}^{-1} = 500\text{ ohm}^{-1}\text{ cm}^2\text{ eq}^{-1}$$

12. First calculate : $\frac{r^+}{r^-} = \frac{95\text{ pm}}{181\text{ pm}} = 0.525$

20.



24. **(i)** Let the rate law be $r_0 = [A]^m[B]^n$

$(r_0)_1 = 5.07 \times 10^{-5} = (0.20)^m(0.30)^n$ ...(i)

$(r_0)_2 = 5.07 \times 10^{-5} = (0.20)^m(0.10)^n$ ...(ii)

$(r_0)_3 = 7.16 \times 10^{-5} = (0.40)^m(0.05)^n$ ...(iii)

Dividing equation (i) by equation (ii),

$$\frac{(r_0)_1}{(r_0)_2} = \frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{(0.20)^m(0.30)^n}{(0.20)^m(0.10)^n}$$

$1 = 3^n$ or $3^0 = 3^n \Rightarrow n = 0$

Dividing equation (iii) by equation (ii),

$$\frac{(r_0)_3}{(r_0)_2} = \frac{7.16 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{(0.40)^m(0.05)^n}{(0.20)^m(0.10)^n}$$

$1.412 = 2^m$ or $2^{1/2} = 2^m \Rightarrow m = \frac{1}{2}$ or $m = 0.5$

Thus order of reaction w.r.t. $A = 0.5$, order of reaction *w.r.t.* $B = 0$

(ii) As $t_{75\%} = 2t_{50\%}$, this shows that $t_{1/2}$ is independent of initial concentration. Hence, it is a first order reaction.

25. **(i)** $MgO_{(s)} + C_{(s)} \rightarrow Mg_{(s)} + CO_{(g)}$;

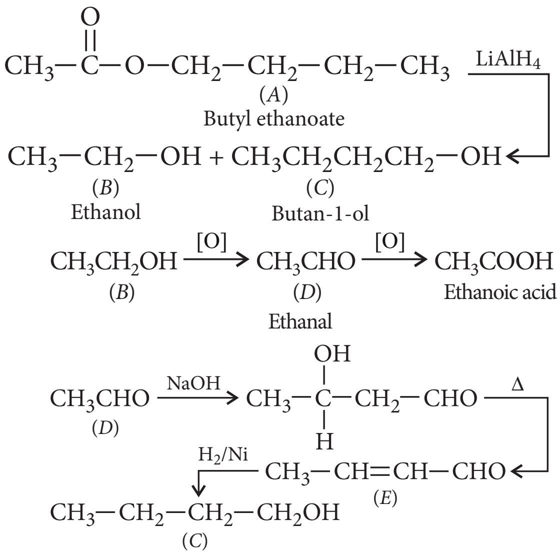
$\Delta_rG = -628 - (-314) = -314$ kJ

As Δ_rG for the reaction is –ve, the reaction is feasible. Therefore, $C_{(s)}$ will reduce MgO to Mg.

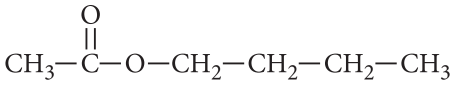
(ii) Dolomite, is $MgCO_3 \cdot CaCO_3$.

(iii) $E°$ of Zn ($E^\circ_{Zn^{2+}/Zn} = -0.76$) is lower than that of copper ($E^\circ_{Cu^{2+}/Cu} = +0.34$), therefore, Zn is a stronger reducing agent than Cu. Thus, zinc reduces $[Ag(CN)_2]^-$ to metallic Ag.

26.



Hence (A)



$$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-O-CH_2-CH_2-CH_2-CH_3$$

(B) CH_3CH_2OH

(C) $CH_3CH_2CH_2CH_2OH$

(D) CH_3CHO

(E) $CH_3-CH{=}CH-CHO$