

केंद्रीय विद्यालय संगठन क्षेत्रीय कार्यालय रायपुर  
Kendriya Vidyalaya Sangathan Regional Office Raipur



**Class - XII**  
**Multiple Choice Question Bank**  
**[MCQ ] Term – I & Term-II**

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CHEMISTRY [ 043 ]  
Based on Latest CBSE Exam Pattern  
for the Session 2021-22

# केंद्रीय विद्यालय संगठन क्षेत्रीय कार्यालय रायपुर

Kendriya Vidyalaya Sangathan Regional Office Raipur

## MESSAGE FROM DUPUTY COMMISSIONER



It is a matter of great pleasure for me to publish study material for different subjects of classes X and XII for Raipur Region. Getting acquainted and familiarized with the recent changes in curriculum and assessment process made by CBSE vide Circular No. 51 and 53 issued in the month of July 2021 will help students to prepare themselves better for the examination. Sound and deeper knowledge of the Units and Chapters is must for grasping the concepts, understanding the questions. Study materials help in making suitable and effective notes for quick revision just before the examination.

Due to the unprecedented circumstances of COVID-19 pandemic the students and the teachers are getting very limited opportunity to interact face to face in the classes. In such a situation the supervised and especially prepared value points will help the students to develop their understanding and analytical skills together. The students will be benefitted immensely after going through the question bank and practice papers. The study materials will build a special bond and act as connecting link between the teachers and the students as both can undertake a guided and experiential learning simultaneously. It will help the students develop the habit of exploring and analyzing the **Creative & Critical Thinking Skills**. The new concepts introduced in the question pattern related to case study, reasoning and ascertain will empower the students to take independent decision on different situational problems. The different study materials are designed in such a manner to help the students in their self-learning pace. It emphasizes the great pedagogical dictum that '*everything can be learnt but nothing can be taught*'. The self-motivated learning as well as supervised classes will together help them achieve the new academic heights.

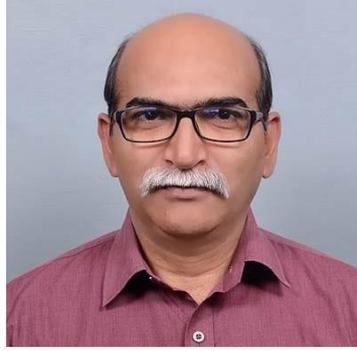
I would like to extend my sincere gratitude to all the principals and the teachers who have relentlessly striven for completion of the project of preparing study materials for all the subjects. Their enormous contribution in making this project successful is praiseworthy.

Happy learning and best of luck!

Vinod Kumar  
(Deputy Commissioner)

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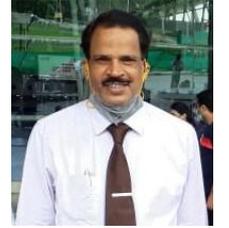
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# **CHEMISTRY**

## **CLASS XII**

### **INDEX – TERM I**

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# SYLLABUS 2021-22

## CHEMISTRY

### CLASS - XII

#### SYLLABUS FOR SESSION 2021-22 CLASS XII Term-I

S.No	UNIT	Periods	MARKS
1	Solid State	8	10
2	Solutions	8	
3	p-Block Elements	7	10
4	Haloalkanes and Haloarenes	9	15
5	Alcohols, Phenols and Ethers	9	
6	Biomolecules	8	
	TOTAL	49	35

#### **Unit I : The Solid states 8 periods**

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

#### **Unit II: Solutions 8 Periods**

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

#### **Unit VII:p-Block Elements 7 Periods**

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

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

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

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

#### **Unit X: Haloalkanes and Haloarenes. 9 Periods**

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

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

**Unit XI: Alcohols, Phenols and Ethers 9 Periods**

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

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

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

**Unit XIV: Biomolecules 8 Periods**

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

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

Nucleic Acids: DNA and RNA.

**SYLLABUS FOR SESSION 2021-22 CLASS XII Term-II**

S.No	UNIT	No. of Periods	MARKS
1	Electrochemistry	7	13
2	Chemical Kinetics	5	
3	Surface Chemistry	5	
4	d-and f-Block Elements	7	9
5	Coordination Compounds	8	
6	Aldehydes, Ketones and Carboxylic Acids	10	13
7	Amines	7	
	TOTAL	49	35

**Unit III: Electrochemistry 7 Periods**

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

**Unit IV: Chemical Kinetics 5 Periods**

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

**Unit V: Surface Chemistry 5 Periods**

Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, colloidal state: distinction between true solutions, colloids and suspension;

lyophilic, lyophobic, multi-molecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation.

#### **Unit VIII: d and f Block Elements 7 Periods**

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

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

#### **Unit IX: Coordination Compounds 8 Periods**

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

#### **Unit XII: Aldehydes, Ketones and Carboxylic Acids 10 Periods**

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

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

#### **Unit XIII: Amines 7 Periods**

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

# TERM - I

## 1. The Solid State

MCQs

[1 Mark each]

- Which of the following is not true about the ionic solids?
  - Bigger ions form the close packed structure.
  - Smaller ions occupy either the tetrahedral or the octahedral voids depending upon their size.
  - Occupation of all the voids is not necessary.
  - The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions occupying the voids.
- Solid A is very hard electrical insulator in solid as well as in molten state and melts at an extremely high temperature. What type of solid is it?
  - Ionic solid
  - Molecular solid
  - Covalent solid
  - Metallic solid
- Which of the following is a network solid?
  - SO<sub>2</sub> (solid)
  - I<sub>2</sub>
  - Diamond
  - H<sub>2</sub>O (ice)
- Graphite cannot be classified as \_\_\_\_\_.
  - Conducting solid
  - Network solid
  - Covalent solid
  - Ionic solid
- Which of the following statements is not true about amorphous solids?
  - On heating they may become crystalline at certain temperature.
  - They may become crystalline on keeping for long time.
  - Amorphous solids can be moulded by heating.
  - They are anisotropic in nature.
- Which of the following is an amorphous solid?
  - Graphite (G)
  - Quartz glass (SiO<sub>2</sub>)
  - Chrome alum
  - Silicon carbide (SiC)
- The sharp melting point of crystalline solids is due to \_\_\_\_\_.
  - a regular arrangement of constituent particles observed over a short distance in the crystal lattice.
  - a regular arrangement of constituent particles observed over a long distance in the crystal lattice.
  - same arrangement of constituent particles in different directions.
  - different arrangements of constituent particles in different directions.
- Which of the following conditions favours the existence of a substance in the solid state?
  - High temperature
  - Low temperature
  - High thermal energy
  - Weak cohesive forces
- A compound is formed by two elements M and N. The element N forms ccp lattice and atoms of M occupy two atoms an Mercury 1/3rd of tetrahedral voids. What is the formula of the compound?
  - MN<sub>2</sub>
  - M<sub>2</sub>N<sub>3</sub>
  - M<sub>3</sub>N<sub>2</sub>
  - M<sub>2</sub>N<sub>2</sub>
- Silver crystallises in f.c.c. Lattice. It edge length of the unit cells is  $4.07 \times 10^{-8}$  cm density and ism  $10.5 \text{ g cm}^{-3}$ . Calculate the atomic mass of silver.
  - 144 g/mol
  - 125 g/mol
  - 106.6 g/mol
  - 213 g/mol
- The correct order of the packing efficiency in different types of unit cells is \_\_\_\_\_.
  - $fcc < bcc < \text{simple cubic}$
  - $fcc > bcc > \text{simple cubic}$
  - $fcc < bcc > \text{simple cubic}$
  - $bcc < fcc = \text{simple cubic}$
- The total number of tetrahedral voids in the face centred unit cell is \_\_\_\_\_.
  - 6
  - 8
  - 10
  - 12

13. The lattice site in a pure crystal cannot be occupied by \_\_\_\_\_.

- (A) Molecule      (B) Ion      (C) Electron      (D) Atom

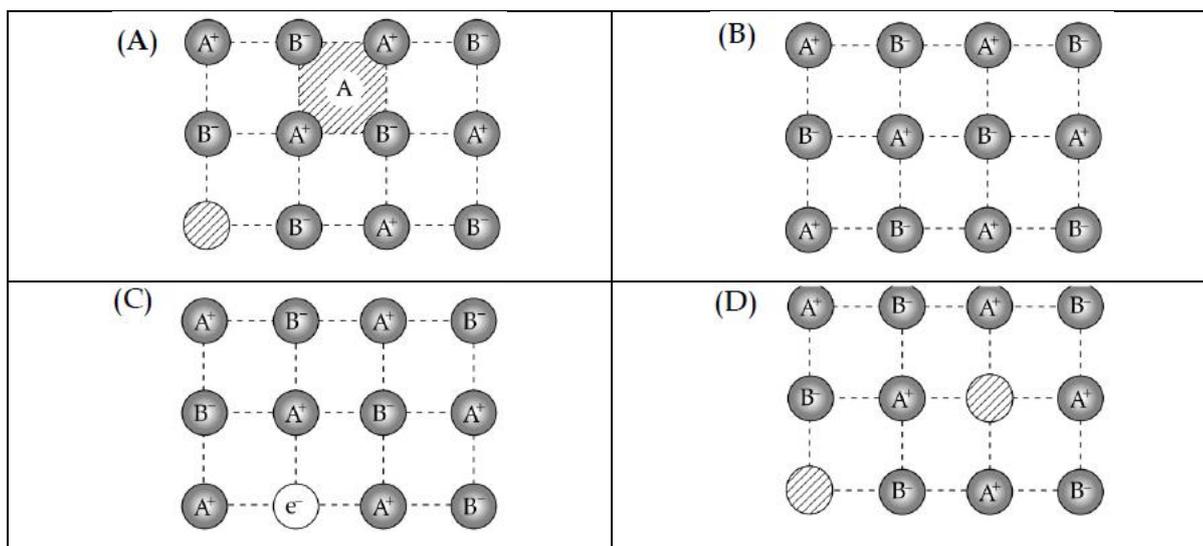
14. Which of the following statements is not true about the hexagonal close packing?

- (A) The coordination number is 12.  
 (B) It has 74% packing efficiency.  
 (C) Tetrahedral voids of the second layer are covered by the spheres of the third layer.  
 (D) In this arrangement spheres of the fourth layer are exactly aligned with those of the first layer.

15. What is the coordination number in a square close packed structure in two dimensions?

- (A) 2      (B) 3      (C) 4      (D) 6

16. The crystal showing defect is:



17. Which stoichiometric defect does not change the density of the crystal?

- (A) Frenkel defect      (B) Schottky defect      (C) Interstitial defect      (D) F-centres

18. Which of the following Defects is also known as dislocation defect?

- (A) Frenkel defect      (B) Schottky defect  
 (C) Non-stoichiometric defect      (D) Simple interstitial defect

19. Interstitial compounds are formed when small atoms are dropped under the curved lattice of metals. Whether the following is not the characteristics property of interstitial compounds?

- (A) They have high melting points in to pure metals      (B) They are very hard  
 (C) They retain metallic Conductivity      (D) They are chemically very reactive

20. Which of the following is true about the value of refractive index of quartz glass?

- (A) Same in all directions      (B) Different in different directions  
 (C) Cannot be measured      (D) Always zero

Assertion - Reason Type Questions – [1Mark each]

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

[A] – Assertion & reason both statements are correct and reason is the correct explanation of assertion.

[B] – Assertion & reason both are the correct statements but reason is not the correct explanation

of the assertion.

[C] – Assertion is correct statement and assertion is incorrect statement.

[D] – Assertion is incorrect statement and reason is correct statement

1. Assertion (A): Most of the solids possess high melting point.

Reason (R): They have strong intermolecular forces of attraction.

2. Assertion (A): Amorphous solids possess a long range order in the arrangement of their particles.

Reason (R): The formation of amorphous solids involves very rapid cooling.

3. Assertion (A): Crystalline solids are anisotropic in nature.

Reason (R): Some of their physical properties show same electrical and optical properties in different directions in the same crystal.

4. Assertion (A): The packing efficiency of simple cubic lattice is 52.4%.

Reason (R): The number of atoms per unit cell is 2.

5. Assertion (A): Schottky defect arises when a non-ionic solid is heated.

Reason (R): It happens because some of the lattice sites are vacant in the crystal.

6. Assertion: Diamond and graphite do not have the same crystal structure.

Reason: Diamond is crystalline while graphite is amorphous.

7. Assertion:  $\text{Na}^+$  and  $\text{Al}^{3+}$  are isoelectronic but the magnitude of ionic radius of  $\text{Al}^{3+}$  is less than that of  $\text{Na}^+$ .

Reason: The magnitude of an effective nuclear charge on the outer shell electrons in  $\text{Al}^{3+}$  is greater than that of  $\text{Na}^+$ .

8. Assertion: White ZnO becomes yellow upon heating.

Reason: On heating ZnO loses oxygen and free electrons go into excited state and upon returning imparts yellow radiation.

9. Assertion: The packing efficiency is maximum for the *fcc* structure.

Reason: The coordination number is 12 in *fcc* structures.

10. Assertion: In caesium chloride crystal,  $\text{Cs}^+$  ion is present on the centre of cube of the unit cell.

Reason: For N-atoms adopting *fcc* arrangement, there are 2N tetrahedral voids.

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

All real structures are three-dimensional structures. They can be obtained by stacking two dimensional layers one above the other while placing the second square close packed layer above the first we follow the same rule that was followed when one row was placed adjacent to the other. The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically. A metallic element crystallises into a lattice having an ABC ABC pattern and packing of spheres leaves out voids in the lattice.

1.1 What type of structure is formed by this arrangement?

- (A) ccp      (B) hcp      (C) ccp/fcc      (D) none of the above

1.2 Name the non-stoichiometric point defect responsible for colour in alkali metal halides.

- (A) Frenkel defect      (B) Interstitial defect      (C) Schottky defect      (D) F-centres

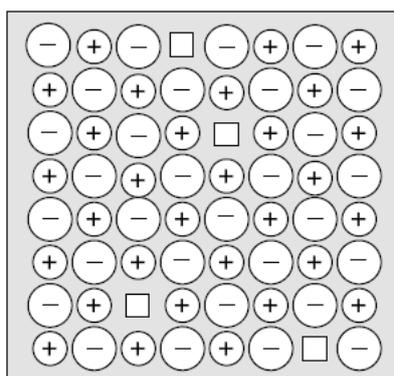
1.3 What is the total volume of atoms in a face centred cubic unit cell of a metal? ( $r$  is atomic radius).

- (A)  $16/3 \pi r^3$       (B)  $\pi r^3$       (C)  $24/3 \pi r^3$       (D)  $12/3 \pi r^3$

1.4 Which of the following statements not true for the amorphous and crystalline solids?

- (A) Amorphous solids are isotropic and crystalline solids are anisotropic.  
 (B) Amorphous solids are short range order and crystalline solids are long range order.  
 (C) Amorphous solids melt at characteristic temperature while crystalline solids melt over a range of temperature.  
 (D) Amorphous solids have irregular shape and crystalline solids have a geometrical shape.

2. Study the diagram given below and answer the following questions: [Assertion-Reason Type Questions]



2.1 Assertion (A): The diagram shows Schottky defect.

Reason (R): Schottky defect occurs in ionic solids.

2.2 Assertion (A): LiCl Crystal is pink.

Reason (R): Pink colour of LiCl crystal is due to excess Lithium.

2.3 Assertion (A): The crystal lattice density increases due to the defect shown in the diagram.

Reason (R): Tetrahedral voids are surrounded by 4 constituent particles.

2.4 Assertion (A): AgCl shows Frenkel defect while NaCl does not.

Reason (R): Frenkel defect is shown when anionic vacancies are occupied by unpaired electrons.

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

In an ideal crystal, there must be regular repeating arrangement of the constituting particles and its entropy must be zero at absolute zero temperature. However, it is impossible to obtain an ideal crystal and it suffers from certain defects called imperfections. In pure crystal, these defects arises either due to disorder or dislocation of the constituting particles from the normal positions or due to the movement of the particles even at absolute zero temperature. Such defects increase with rise in temperature. In addition

to these certain defects arise due to the presence of some impurities. Such defects not only modify the existing properties of the crystalline solids but also impart certain new characteristics to them.

Answer the following MCQs by choosing the most appropriate options:

3.1 AgCl is crystallized from molten AgCl containing a little CdCl<sub>2</sub>. The solid obtained will have

- (a) cationic vacancies equal to number of Cd<sup>2+</sup> ions incorporated.  
(b) cationic vacancies equal to double the number of Cd<sup>2+</sup> ions.  
(c) anionic vacancies.                      (d) neither cationic nor anionic vacancies.

3.2 Lattice defect per 10<sup>15</sup> NaCl is 1. What is the number of lattice defects in a mole of NaCl?

- (a)  $6.02 \times 10^{23}$                       (b)  $6.02 \times 10^8$                       (c)  $10^{14}$                       (d) None of these

3.3 The ionic substances in which the cation and anion are of almost similar size shows

- (a) non-stoichiometric defect                      (b) Schottky defect  
(c) Frenkel defect                      (d) all of these

3.4 Which of the following gives both Frenkel and Schottky defect?

- (a) AgCl                      (b) CsCl                      (c) KCl                      (d) AgBr

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

The transition metals when exposed to oxygen at low and intermediate temperatures form thin, protective oxide films of up to some thousands of Angstroms in thickness. Transition metal oxides lie between the extremes of ionic and covalent binary compounds formed by elements from the left or right side of the periodic table. They range from metallic to semiconducting and deviate by both large and small degrees from stoichiometry. Since d electron bonding levels are involved, the cations exist in various valence states and hence give rise to a large number of oxides. The crystal structures are often classified by considering a cubic or hexagonal close-packed lattice of one set of ions with the other set of ions filling the octahedral or tetrahedral interstices. The actual oxide structures, however, generally show departures from such regular arrays due in part to distortions caused by packing of ions of different size and to ligand field effects. These distortions depend not only on the number of d-electrons but also on the valence and the position of the transition metal in a period or group.

(source: Smeltzer, W. W., & Young, D. J. (1975). *Oxidation properties of transition metals. Progress in Solid State Chemistry, 10, 17-54.*)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

- A. Assertion and reason both are correct statements and reason is correct explanation for assertion.  
B. Assertion and reason both are correct statements but reason is not correct explanation for assertion.  
C. Assertion is correct statement but reason is wrong statement.  
D. Assertion is wrong statement but reason is correct statement.

4.1 Assertion: Cations of transition elements occur in various valence states

Reason: Large number of oxides of transition elements are possible.

4.2 Assertion: Crystal structure of oxides of transition metals often show defects.

Reason: Ligand field effect cause distortions in crystal structures.

4.3 Assertion : Transition metals form protective oxide films.

Reason: Oxides of transition metals are always stoichiometric.

4.4 Assertion: CrO crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by chromium ions.

Reason: Transition metal oxide may be hexagonal close-packed lattice of oxide ions with metal ions filling the octahedral voids.

#### ANSWERS-MCQs

1. (B) 2. (C) 3. (C) 4. (D) 5. (D) 6. (B) 7. (B) 8. (B) 9. (B) 10. (C) 11. (B) 12. (B)  
13. (C) 14. (D) 15. (C) 16. (A) 17. (A) 18. (A) 19. (D) 20. (D)

#### ASSERTION- REASON

1. (A) 2. (D) 3. (C) 4. (C) 5. (D) 6. (C) 7. (A) 8. (A) 9. (B) 10. (B)

#### CASE BASED Q

1.1 (C) 1.2 (D) 1.3 (A) 1.4 (C) 2.1 (B) 2.2 (A) 2.3 (D) 2.4 (B)  
3.1 (A) 3.2 (B) 3.3 (B) 3.4 (D)  
4.1 (B), 4.2 (A), 4.3 (C), 4.4 (D)

## UNIT 2. SOLUTIONS

- **Q.1 to Q.11 are Multiple Choice Questions**
- **Q.12 to Q.16 are Assertion and Reasoning type questions**
- **Q.17 to Q.20 are CCT based questions**

### MULTIPLE CHOICE QUESTIONS

Q1. Acetone and carbon disulphide form binary liquid solution showing positive deviation from Raoult's law. The normal boiling point ( $T_b$ ) of pure acetone is less than that of pure  $CS_2$ . Pick out the incorrect statement among the following-

- (a) Boiling temperature of the mixture is always less than the boiling temperature of acetone
- (b) Boiling temperature of Azeotropic mixture is always less than the boiling temperature of acetone
- (c) When a small amount of  $CS_2$  (less volatile component) is added to an excess of acetone boiling point of the resulting mixture increases

(d) A mixture of  $\text{CS}_2$  and  $\text{CH}_3\text{COCH}_3$  can be completely separated by simple fractional distillation

Q2. An antifreeze solution is prepared from 222.6 g of ethylene glycol  $\text{C}_2\text{H}_4(\text{OH})_2$  and 200 g of water. Calculate the molality of the solution. If the density of this solution be  $1.072 \text{ gmL}^{-1}$ , what will be the molarity of the solution?

- (a) 7.20 M                      (b) 12.03 M                      (c) 9.11 M                      (d) 6 M

Q3. When mercuric iodide is added to the aqueous solution of potassium iodide, the:

- (a) Freezing point is raised                      (b) Freezing point does not change  
(c) Freezing point is lowered                      (d) Boiling point does not change

Q4. The molal elevation constant depends upon

- (a) nature of solute.                      (b) nature of the solvent.  
(c) vapour pressure of the solution.                      (d) enthalpy change.

Q5. The osmotic pressure of a solution is directly proportional to

- (a) the molecular concentration of the solute  
(b) the absolute temperature at a given concentration  
(c) the lowering of vapour pressure                      (d) all the above.

Q6. Which of the following aqueous solutions containing 10 g of solute in each case, has highest m.p.?

- (a) NaCl solution                      (b) KCl solution                      (c) sugar solution                      (d) glucose solution

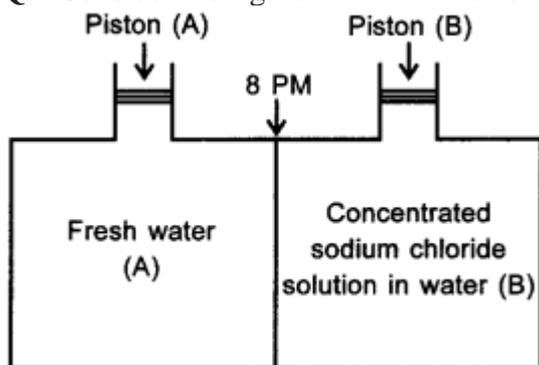
Q7. Equimolar solutions in the same solvent have-

- (a) Same boiling point but different freezing point  
(b) Same freezing point, but different boiling point  
(c) Same boiling and same freezing point  
(d) Different boiling and different freezing points

Q8. The average osmotic pressure of human blood is 7.8 bar at  $37^\circ\text{C}$ . What is the concentration of an aqueous solution of NaCl that could be used in blood stream?

- (a)  $0.15 \text{ mol L}^{-1}$                       (b)  $0.30 \text{ mol L}^{-1}$                       (c)  $0.60 \text{ mol L}^{-1}$                       (d)  $0.45 \text{ mol L}^{-1}$

Q9. Consider the figure and mark the correct option.



- (a) water will move from side (A) to side (B) if a pressure lower than osmotic pressure is applied on piston (B).  
(b) water will move from side (B) to side (A) if a pressure greater than osmotic , pressure is applied on piston (B).  
(c) water will move from side (B) to side (A) if a pressure equal to osmotic pressure is applied on piston (B).  
(d) water will move from side (A) to side (B) if pressure equal to osmotic pressure is applied on piston (A).

Q10. Which of the following is incorrect for an ideal solution?

- (a)  $\Delta H_{\text{mix}} = 0$       (b)  $\Delta V_{\text{mix}} = 0$       (c)  $\Delta P = P_{\text{obs}} - P_{\text{calculated}} = 0$       (d)  $\Delta G_{\text{mix}} = 0$

**Q11.** Low concentration of oxygen in the blood and tissues of people living at high altitude is due to-

- (a) low temperature      (b) low atmospheric pressure  
(c) high atmospheric pressure      (d) both low temperature and high atmospheric pressure

### ANSWERS OF MCQ

[1-d; 2-c; 3-a; 4-b; 5-d; 6-c; 7-c; 8-a; 9-b; 10-d; 11-b]

### ASSERTION- REASON TYPE QUESTIONS

**DIRECTION: Mark the option which is most suitable:**

- A. If both Assertion and Reason are correct and reason is the correct explanation of Assertion .  
B. If both Assertion and Reason are correct and reason is not correct explanation of Assertion  
C. If Assertion is correct but Reason is incorrect.  
D. If Assertion is incorrect and Reason is correct.

**Q12: Assertion:** An aqueous solution of NaCl freezes below 273 K.

**Reason:** Vapour pressure of the solution is less than that of the pure solvent.

Answer- A

**Q13: Assertion:** Isotonic solutions do not show any osmosis when placed side by side.

**Reason:** Isotonic solutions have same solute concentration.

Answer-C

**Q14: Assertion:** Molarity of the solution changes with temperature.

**Reason:** Molarity is a colligative property.

Answer-C

**Q15: Assertion:** Cooking time is reduced in pressure cooker.

**Reason:** Boiling point of water inside the pressure cooker is lowered.

Answer-C

**Q16: Assertion:** 1 M glucose will have a higher boiling point than 2 M glucose

**Reason:** Elevation in boiling point is a colligative property which depends upon the number of particles of solute in the solution

Answer-D

### COMPREHENSION BASED QUESTIONS

**Q17.** The properties of the solutions which depend only on the number of solute particles but not on the nature of the solute are called colligative properties. Relative lowering in vapour pressure is also an example of colligative properties. For an experiment, sugar solution is prepared for which lowering in vapour pressure was found to be 0.061 mm of Hg.(vapour pressure of water at 20°C is 17.5 mm of Hg).

**Answer the following MCQs by choosing the most appropriate options:**

(i) Relative lowering of vapour pressure for the given solution is-

- (a) 0.00348      (b) 0.061      (c) 0.122      (d) 1.75

**Ans. (a) 0.00348**

Vapour pressure of water ( $P_A^0$ ) = 17.5 mm of Hg  
 Lowering of vapour pressure ( $P_A^0 - P_A$ ) = 0.061 mm of Hg  
 Relative lowering of vapour pressure =  $\frac{(P_A^0 - P_A)}{P_A^0}$

= **0.00348**

(ii) The vapour pressure (mm of Hg) of Solution will be

- (a) 17.5                      (b) 0.61                      (c) 17.439                      (d) 0.00348

**Ans. (c) 17.439**

Vapour pressure of solvent – lowering in vapour pressure  
 = 17.5 – 0.061 = **17.439 mm of Hg**

(iii) Mole fraction of sugar in the solution is

- (a) 0.00348                      (b) 0.9965                      (c) 0.061                      (d) 1.75

**Ans. (a) 0.00348**

$$X_B = \frac{(P_A^0 - P_A)}{P_A^0}$$

$$X_B = 0.00348$$

(iv) If weight of sugar taken is 5 g in 108 g of water then molar mass of sugar will be

- (a) 358                      (b) 120                      (c) 240                      (d) 400

**Ans. (c) 240**

$$M_B = \frac{(P_A^0 - P_A)}{P_A^0}$$

$$M_B = 5g, M_A = 18g, w_A = 108g$$

$$\therefore M_B = 5 \times 18/108 \times 0.00348$$

$$M_B = 240$$

(v) The vapour pressure (mm of Hg) of water at 293 K when 25 g of glucose is dissolved in 450 g of water is

- (a) 17.2                      (b) 17.4                      (c) 17.120                      (d) 17.02

**Ans. (b) 17.4**

$$\frac{(P_A^0 - P_A)}{P_A^0} = X_B = \frac{W_B \times M_A}{W_A \times M_B}$$

$$P_A = 17.40 \text{ mm of Hg}$$

**Q18.** The solubility of gases increases with increase of pressure. William Henry made a systematic investigation of the solubility of a gas in a liquid. According to Henry's law "the mass of a gas dissolved per unit volume of the solvent at constant temperature is directly proportional to the pressure of the gas in equilibrium with the solution". Dalton during the same period also concluded independently that the solubility of a gas in a liquid solution depends upon the partial pressure of the gas. If we use the mole fraction of gas in the solution as a measure of its solubility, then Henry's law can be modified as "the partial pressure of the gas in the vapour phase is directly proportional to the mole fraction of the gas in the solution".

**Answer the following MCQs by choosing the most appropriate options:**

(i) Henry's law constant for the solubility of methane in benzene at 298 K is  $4.27 \times 10^5$  mm Hg. The solubility of methane in benzene at 298 K under 760 mm Hg is

- (a)  $4.27 \times 10^{-5}$       (b)  $1.78 \times 10^{-3}$       (c)  $4.27 \times 10^{-3}$       (d)  $1.78 \times 10^{-3}$

Ans. (b)  $1.78 \times 10^{-3}$

$$K_H = 4.27 \times 10^5 \text{ mm Hg}, p = 760 \text{ mm Hg}$$

According to Henry's law,  $p = K_H \times X_{CH_4}$

$$\therefore X_{CH_4} = p / K_H = 760 / 4.27 \times 10^5 = 1.78 \times 10^{-3}$$

(ii) The partial pressure of ethane over a saturated solution containing  $6.56 \times 10^{-2}$  g of ethane is 1 bar. If the solution contains  $5.00 \times 10^{-2}$  g of ethane then what will be the partial pressure (in bar) of the gas?

- (a) 0.762      (b) 1.312      (c) 3.81      (d) 5.0

Ans. (a) 0.762

According to Henry's law,  $m = K_H \times p$

$$6.56 \times 10^{-2} = K_H \times 1$$

$$K_H = 6.56 \times 10^{-2}$$

For another case,  $5 \times 10^{-2} = 6.56 \times 10^{-2} \times p$

$$\therefore p = 5 \times 10^{-2} / 6.56 \times 10^{-2} = 0.762 \text{ bar}$$

(iii)  $K_H$  (K bar) values for Ar(g), CO<sub>2</sub>(g), HCHO(g) and CH<sub>4</sub>(g) are 40.39, 1.67,  $1.83 \times 10^{-5}$  and 0.413 respectively. Arrange these gases in the order of their increasing solubility.

- (a) HCHO < CH<sub>4</sub> < CO<sub>2</sub> < Ar      (b) HCHO < CO<sub>2</sub> < CH<sub>4</sub> < Ar  
(c) Ar < CO<sub>2</sub> < CH<sub>4</sub> < HCHO      (d) Ar < CH<sub>4</sub> < CO<sub>2</sub> < HCHO

Ans. (c) Ar < CO<sub>2</sub> < CH<sub>4</sub> < HCHO

Higher the value of  $K_H$  at a given pressure, the lower is the solubility of the gas.

(iv) When a gas is bubbled through water at 298 K, a very dilute solution of the gas is obtained. Henry's law constant for the gas at 298 K is 150 K bar. If the gas exerts a partial pressure of 2 bar, the number of millimoles of the gas dissolved in 1 L of water is

- (a) 0.55      (b) 0.87      (c) 0.37      (d) 0.66

Ans. (c) 0.37

The mol fraction of the gas in solution

$$X_g = p / K_H = 2 / 150 \times 10^{-3}$$

If  $n$  is the number of moles of gas in a solution 1L of water containing 55.5 mol then

$$X_g = n / (n + 55.5) \quad \text{or} \quad n / 55.5 = 2 / 150 \times 10^{-3} \quad (\text{as } n \text{ is very small, } n + 55.5 = 55.5)$$

$$n = 55.5 / 150 \times 10^{-3}$$

$$n = 0.37 \text{ millimoles}$$

**Q19.** The properties of dilute or ideal solutions which depend only upon the concentration of the solute in the solution and no other characteristics are known as colligative properties. There are in all four such properties i.e. relative lowering in vapour pressure, osmotic pressure, elevation in boiling point temperature and depression in freezing point temperature. All of them help in calculating the observed molar mass of the solute which is inversely proportional to the colligative property involved. Out of these, osmotic pressure may be regarded as the best for the determination of molecular mass of the solute. According to Van't Hoff theory of dilute solution,  $\pi = CRT$ , where ' $\pi$ ' is the osmotic pressure while ' $C$ ' is the molar concentration of the solution.

(i) When liquids A and B are mixed, hydrogen bonding occurs. The solutions will show:

- a) Positive deviation from Raoult's law      b) Negative deviation from Raoult's law  
c) No deviation from Raoult's law      d) Slightly increase in volume

Ans: (b)

(ii) The azeotropic mixture of water and HCl boils at  $108.5^{\circ}\text{C}$  when the mixture is distilled. It is possible to obtain:

- a) Pure HCl
- b) Pure water
- c) Pure water as well as pure HCl
- d) Neither HCl nor water in their pure states.

Ans: (d)

(iii) On freezing an aqueous solution of sugar, the solid which starts separating out is:

- a. Sugar
- b. Ice
- c. Solution with the same composition
- d. Solution with different composition

Ans: (b)

(iv) The value of osmotic pressure does not depend upon:

- a) Concentration of the solution
- b) Temperature of the solution
- c) Number of the particles of the solute present
- d) Structure of the solute particles

Ans: (d)

(v) Effect of adding a non-volatile solute to a solvent is :

- a) to lower the vapour pressure
- b) to increase the freezing point
- c) to decrease the boiling point
- d) to decrease the osmotic pressure

Ans: (a)

**Q20.** Boiling point or freezing point of liquid solution would be affected by the dissolved solids in the liquid phase. A soluble solid in solution has the effect of raising its boiling point and depressing its freezing point. The addition of non-volatile substances to a solvent decreases the vapor pressure and the added solute particles affect the formation of pure solvent crystals. According to many researches the decrease in freezing point directly correlated to the concentration of solutes dissolved in the solvent. This phenomenon is expressed as freezing point depression and it is useful for several applications such as freeze concentration of liquid food and to find the molar mass of an unknown solute in the solution. Freeze concentration is a high quality liquid food concentration method where water is removed by forming ice crystals. This is done by cooling the liquid food below the freezing point of the solution. The freezing point depression is referred as a colligative property and it is proportional to the molar concentration of the solution (m), along with vapor pressure lowering, boiling point elevation, and osmotic pressure. These are physical characteristics of solutions that depend only on the identity of the solvent and the concentration of the solute. The characters are not depending on the solute's identity. (Source: Jayawardena, J. A. E. C., Vanniarachchi, M. P. G., & Wansapala, M. A. J. (2017). *Freezing point depression of different Sucrose solutions and coconut water.*)

**Answer the following MCQs by choosing the most appropriate options:**

(i) When a non volatile solid is added to pure water it will-

- (a) boil above  $100^{\circ}\text{C}$  and freeze above  $0^{\circ}\text{C}$ .
- (b) b) boil below  $100^{\circ}\text{C}$  and freeze above  $0^{\circ}\text{C}$ .
- (c) boil above  $100^{\circ}\text{C}$  and freeze below  $0^{\circ}\text{C}$ .
- (d) boil below  $100^{\circ}\text{C}$  and freeze below  $0^{\circ}\text{C}$ .

Ans. (c)

(ii) Colligative properties are

- (a) dependent only on the concentration of the solute and independent of the solvent's and solute's identity.
- (b) dependent only on the identity of the solute and the concentration of the solute and independent of the solvent's identity.
- (c) dependent on the identity of the solvent and solute and thus on the concentration of the solute.
- (d) dependent only on the identity of the solvent and the concentration of the solute and independent of the solute's identity.

Ans. (d)

(iii) Assume three samples of juices A, B and C have glucose as the only sugar present in them. The concentration of sample A, B and C are 0.1 M, 0.5 M and 0.2 M respectively. Freezing point will be highest for the fruit juice

(a) A                      (b) B                      (c) C                      (d) all have same freezing point

Ans. (a)

(iv) Identify which of the following is a colligative property?

(a) Freezing point      (b) Boiling point      (c) Osmotic pressure      (d) All of the above

Ans. (c)

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## **7 - p- BLOCK ELEMENTS**

### **SECTION –A CASE STUDY BASED QUESTIONS – 1**

Molecular Nitrogen N<sub>2</sub> comprises about 78% by volume of Earth's atmosphere. It occurs as Sodium nitrate, NaNO<sub>3</sub>(chile saltpeter) & Potassium nitrate, KNO<sub>3</sub>(Indian saltpeter) in earth's crust. Since nitrate are very soluble in water so these are not wide spread in the earth's crust. Nitrogen is also an important constituent of amino acids, protein & nucleic acids in plants & animals.

Nitrogen shows anomalous behavior from rest of the elements due to following reasons;

Smaller size, high ionization enthalpy, high electronegativity & absence of d-orbital. It has unique ability to form p-p multiple bonds with itself & with small size atoms like C & O as they have small size & high electronegativity. Heavier elements of this group do not form p-p bonds as their atomic orbitals are so large & diffuse that they can't have effective overlapping.

Thus Nitrogen exists as diatomic molecules (N<sub>2</sub>) with a triple bond. Consequently, its bond enthalpy (941.4 KJ mol<sup>-1</sup>) is very high. P, As & Sb form only single bonds as P-P, As-As & Sb-Sb. Due to much bond enthalpy N is much less reactive than P.

Single N-N bond is weaker than single P-P bond due to high interelectronic repulsion of the non bonding electrons, owing to small bond length. As a result, the catenation tendency is weaker in nitrogen. Hence nitrogen exists as gas while phosphorus exists as solid.

Nitrogen can't form d-d bond due to absence of d- orbitals so it can't expand its covalency beyond four as heavier members can.

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

1.1 Among group 15 elements which exists as gas at room temperature

- a) Arsenic    b) Bismuth    c) Nitrogen    d) Phosphorous

1.2 The stability of +5 oxidation state decreases and that of +3 state increases down the group in group 15 elements due to

- a) inert pair effect                      b) decrease in ionisation enthalpy  
c) increase in size                        d) shielding effect

1.3 Nitrogen is restricted to a maximum covalency of 4 because of

- a) absence of d-orbitals                      b) presence of d-orbitals  
c) absence of s and p-orbitals              d) none of the above

1.4 Extra pure  $N_2$  can be obtained by heating

- a)  $NH_3$  with  $CuO$     b)  $NH_4NO_3$                       c)  $(NH_4)_2Cr_2O_7$                       d)  $Ba(N_3)_2$

1.5 Catenation tendency is weaker in nitrogen, because of

- a) single N–N bond is weaker                      b) single N–N bond is stronger  
c) ability to form pi bonds by N atoms              d) none of the above

### CASE BASE STUDY QUESTION -2

Group 16 elements are called chalcogens i.e., ore forming elements (oxygen, sulphur, selenium etc.) because most of the ores are oxides and sulphides. Oxygen is gas where as other elements of group 16 are solids. Oxygen shows anomalous behaviour. Oxygen is diatomic where as sulphur exists as  $S_8$  which has crown shaped structure. It shows allotropy. Sulphur is present in onion and garlic that is why they have pungent smell. Sulphur is used for manufacture of sulphuric acid which is called 'King of chemicals', used in fertilizer, detergents, dyes and drugs.

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

2.1 Group 16 elements are also known as

- a) Noble elements    b) Halogens                      c) Pnictogens                      d) Chalcogens

2.2 Acidic character of hydrides of group 16 elements is in the order

- a)  $H_2O < H_2S < H_2Se < H_2Te$                       b)  $H_2S < H_2Se < H_2Te < H_2O$   
c)  $H_2O < H_2Se < H_2Te < H_2S$                       d)  $H_2O < H_2S < H_2Te < H_2Se$

2.3 Hybridisation of S in  $SF_4$  and geometry of  $SF_4$  are respectively

- a)  $sp^3d$ , trigonal pyramidal                      b)  $sp^3d$ , see saw  
c)  $sp^3$ , tetrahedral                                      d)  $dsp^2$ , square planar

2.4 Which is not an acidic oxide?

- a)  $CO_2$                       b)  $SO_2$                       c)  $Na_2O$                       d)  $Cl_2O_7$

2.5 Which is not correct about allotropes of sulphur

- a) The stable form at room temperature is rhombic sulphur  
b) Monoclinic sulphur is stable above 369 K and transforms into rhombic sulphur below it  
c) At 369 K both the forms are stable  
d) Monoclinic sulphur is soluble in  $CS_2$  while rhombic sulphur not

### CASE BASED STUDY QUESTIONS -3

Group 18 elements are called noble gases and not inert gases because compounds of Kr, Xe and Rn have been prepared. Their general electronic configuration is  $ns^2 np^6$  except He ( $1s^2$ ). They have highest ionisation enthalpy and positive electron gain enthalpy due to stable electronic configuration. Helium is found in sun and stars. Noble gases have low boiling points due to weak van der Waals' forces of attraction. Xenon forms  $XeF_2$ ,  $XeF_4$ ,  $XeF_6$ ,  $XeOF_4$ ,  $XeO_3$ ,  $XeO_2F_2$ , their structures can be drawn on bases of VSEPR theory. Helium is mixed with oxygen by deep sea divers to avoid pain. Neon is used in coloured advertising lights. Argon is used in bulbs as inert gas. Kr and Xe are used in high efficiency lamps, head light of cars. Radon is radioactive formed by  $\alpha$ -decay of Radium  $^{226}_{88}Ra$  Argon is most abundant (0.9%) noble gas in atmosphere.

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

3.1 What are the elements in group 18 (the far right) of the periodic table called?

- a) Alkali metals      b) Alkaline earth metals      c) Halogens      d) Noble gases

3.2 Out of (i)  $XeO_3$  (ii)  $XeOF_4$  and (iii)  $XeF_6$ , the molecules having the same number of lone pairs on Xe are -

- a) (i) and (ii) only      b) (i) and (iii) only      c) (ii) and (iii) only      d) (i), (ii) and (iii)

3.3 Which one has linear shape?

- a)  $XeF_2$       b)  $XeF_4$       c)  $XeF_6$       d)  $XeO_3$

3.4 Which of the outer electronic configuration represent Argon?

- a)  $ns^2 np^4$       b)  $ns^2 np^3$       c)  $ns^2 np^6$       d)  $ns^1 np^6$

3.5 Which of the following statement is false?

- a) Radon is obtained from the decay of radium      b) Helium is an inert gas  
c) Xenon is the most reactive among the rare gases  
d) The most abundant rare gas found in the atmosphere is helium

## SECTION: B      ASSERTION REASON QUESTIONS

### INSTRUCTIONS:

- a) Assertion and reason both are correct statements and reason is correct explanation for assertion.  
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.  
c) Assertion is correct statement but reason is wrong statement.  
d) Assertion is wrong statement but reason is correct statement.

1. Assertion:-Nitrogen is restricted to a maximum covalency of 4.

Reason:-Nitrogen exists as a diatomic molecule ( $N_2$ ) with a triple bond.

2. Assertion:-The stability of hydrides decreases from  $NH_3$  to  $BiH_3$ .

Reason:-There is a decrease in bond dissociation enthalpy of bond E-H from  $NH_3$  to  $BiH_3$ . (E=Element of group 15)

3. Assertion : -The bond between F-F is weaker than between Cl-Cl.

Reason:- Atomic size of F is smaller than that of Cl.

4. Assertion:-  $H_2O$  is the only hydrides of the Chalcogens which is liquid.

Reason :- In ice each O atom is surrounded by 4H-atom.

5. Assertion :- Nitrogen has higher ionisation enthalpy than that of oxygen.

Reason :- Nitrogen has smaller atomic size than that of Oxygen.

6. Assertion :- Interhalogen compounds are more reactive than halogen.

Reason :- They all undergo hydrolysis giving halide, cation derived from the smaller halogen & anion derived from larger halogen.

7. Assertion :- Solubility of noble gases in water decreases with increasing size of the noble gases.

Reason :- Solubility of noble gases in water is due to dipole- dipole interaction.

8. Assertion :- O<sub>3</sub> acts as a powerful oxidising agent.

Reason :- O<sub>3</sub> oxidises lead sulphide to lead sulphate & iodide ions to iodine

9. Assertion :- Water has high melting point.

Reason :- Water molecules are associated with hydrogen bonding

10. Assertion:- Ammonia gas is highly soluble in water.

Reason:- Its aqueous solution is weakly acidic.

### SECTION – C MULTIPLE CHOICE QUESTIONS

1. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to

- a) Increase in number of shells      b) increase in valence electrons  
c) increase in ionisation enthalpy      d) the presence of completely filled d and/or f orbitals

2. The ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. Which is the most suitable reason?

- a) more effective nuclear charge      b) presence of stable half-filled electronic configuration  
c) smaller size      d) high electronegativity

3. Which one is not correct statement?

- a) Nitrogen does not form pentahalide due to non-availability of the d orbitals in its valence shell  
b) Pentahalides are more covalent than trihalides.  
c) In case of nitrogen, only NF<sub>3</sub> is known to be stable  
d) Trihalides except BiF<sub>3</sub> are predominantly ionic in nature

4. On a large-scale nitric acid is prepared mainly by

- a) Haber's process      b) Ostwald's process      c) Contact Process      d) Deacon's process

5. Brown Ring Test is used to identify the

- a) chloride ion      b) nitrite ion      c) nitride ion      d) nitrate ion

6. Which is incorrect statement.

- a) Oxygen is the most abundant of all the elements on earth  
b) Organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool contain sulphur  
c) Selenium and tellurium are found as metal selenides and tellurides in sulphide ores  
d) Livermorium is a natural radioactive element

7. Which is the correct statement?

- a) valence shell electronic configuration of group 16 elements is ns<sup>1</sup>np<sup>4</sup>  
b) the elements of group 16 have lower ionisation enthalpy values compared to those of Group 15 in the corresponding periods  
c) Oxygen atom has more negative electron gain enthalpy than sulphur

d) oxygen has the highest electronegativity value amongst the elements

8. Stability of hydrides of group 16 elements

- a) increases down the group                      b) decreases down the group  
c) all hydrides are equally stable              d) none of the above

9. SO<sub>2</sub> is -----and TeO<sub>2</sub> is ----- agent

- a) reducing, an oxidising              b) an oxidising, reducing  
c) reducing, reducing                      d) an oxidising, an oxidising

10. which is not the property of dioxygen gas

- a) Dioxygen is a colourless and odourless gas.  
b) Dioxygen is paramagnetic  
c) Dioxygen is diamagnetic  
d) dioxygen is soluble in water which support aquatic life

11. Which statement correct about halogens?

- a) They are all diatomic and form univalent ions  
b) They are all capable of exhibiting several oxidation states  
c) They are all diatomic and form diatomic ions  
d) They are all reducing agents

12. Hypochlorous acid and perchloric acid are, respectively:

- a) HOCl and HClO<sub>4</sub>                      b) HOCl and HClO<sub>3</sub>  
c) HClO<sub>2</sub> and HClO<sub>3</sub>                      d) HClO<sub>2</sub> and HClO<sub>4</sub>

13. Identify the correct order of acidic strength for H-X

- a) HCl>HBr>HI              b) HCl>HI>HBr              c) HI>HCl>HBr              d) HI>HBr>HCl

14. In the periodic table of the elements, the phrase “middle row anomaly” refers to

- a) Middle elements of periodic table are transition metals  
b) Middle element of each group is unstable  
c) the relative instability of bromine oxides compared to the other halogen oxides  
d) The higher oxides of halogens tend to be more stable than the lower ones

15. Chlorine water on standing loses its yellow colour due to the formation of

- a) Cl and HOCl              b) HCl and HOCl              c) HOCl and HOCl<sub>2</sub>              d) HCl and HOCl<sub>2</sub>

16. Why is Helium used in divers' tank but not hydrogen gas?

- a) Helium is lighter than hydrogen              b) Helium is inert to any chemical reactions  
c) Helium is cheaper                              d) Helium is easy to get from market

16. The idea that promoted to Bartlett to prepare first ever compound of Noble gases was

- a) Low bond dissociation enthalpy of F-F bond in F<sub>2</sub>              b) High bond enthalpy of Xe-F bond  
c) Ionization enthalpies of O<sub>2</sub> and Xe are almost same              d) None of the above

17. When Xe reacts with Fluorine in 1:5 ratio at 873 K it forms

- a) XeF<sub>2</sub>              b) XeF<sub>4</sub>              c) XeF<sub>6</sub>              d) XeOF<sub>4</sub>

18. The lowest boiling point of helium is due to its

- a) Inertness                                      b) Gaseous nature  
c) Weak van der Waals force between atoms              d) electronic configuration

19. Which of the following statement is false?



- a) contains asymmetric carbon atoms                      b) is non-polar  
c) is non-superimposable on its mirror image                      d) is superimposable on its mirror image

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

The replacement of hydrogen atom in a hydrocarbon, aliphatic or aromatic results in the formation of haloalkanes and haloarenes respectively. Haloalkanes contain halogen atom attached to  $sp^3$  hybridised carbon atom of an alkyl group whereas haloarenes contain halogen atom attached to  $sp^2$  hybridised carbon atom of an aryl group. Haloalkanes and haloarenes may be classified on the basis of number of halogen atoms in their structures as mono, di or poly halogen compounds and also on the basis of the state of hybridisation of carbon atom to which the halogen atom is bonded.

**(i) Which of the following halide is 2°?**

- (a) Isopropyl chloride                      (b) Isobutyl chloride  
(c) *n*-propyl chloride                      (d) *n*-butyl chloride

**(ii) Which of the following is a Gem-dibromide is :**

- (a)  $CH_3CH(Br)CH_2(Br)$                       (b)  $CH_3CBr_2CH_3$   
(c)  $CH_2(Br)CH_2CH_2$                       (d)  $CH_2BrCH_2Br$

**(iii) IUPAC name of  $(CH_3)_3CCl$  is:**

- (a) 3-Chlorobutane                      (b) 2-Chloro-2-methylpropane  
(c) *t*-butyl chloride                      (d) *n*-butyl chloride

**(iv) Which of the following is a primary halide?**

- (a) Isopropyl iodide                      (b) Secondary butyl iodide  
(c) Tertiarybutyl bromide                      (d) Neohexyl chloride

**(v) Which one of the following is not an allylic halide?**

- (a) 4-Bromopent-2-ene                      (b) 3-Bromo-2-methylbut-1-ene  
(c) 1-Bromobut-2-ene                      (d) 4-Bromobut-1-ene

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

Alkyl halides are prepared by the free radical halogenation of alkanes, addition of halogen acids to alkenes, replacement of -OH group of alcohols with halogens using phosphorus halides, thionyl chloride or halogen acids. Aryl halides are prepared by electrophilic substitution to arene. Fluorine and iodides are best prepared by halogen exchange method. These compounds find wide applications in industry as well as in day-to-day life. These compounds are generally used as solvents and as starting material for the synthesis of a large number of organic compounds.

**(i) The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with**

- (a)  $PCl_5$                       (b) dry HCl in the presence of anhydrous  $ZnCl_2$   
(c)  $SOCl_2$  in presence of pyridine                      (d) None of these

**(ii) The catalyst used in the preparation of an alkyl chloride by the action of dry HCl on an alcohol is**

- (a) anhydrous  $AlCl_3$                       (b)  $FeCl_3$                       (c) anhydrous  $ZnCl_2$                       (d) Cu

**(iii) An alkyl halide reacts with metallic sodium in dry ether. The reaction is known as :**

- (a) Frankland's reaction                      (b) Sandmeyer's reaction  
 (c) Wurtz reaction                              (d) Kolbe's reaction

**(iv) Fluorobenzene (C<sub>6</sub>H<sub>5</sub>F) can be synthesized in the laboratory**

- (a) by direct fluorination of benzene with F<sub>2</sub> gas  
 (b) by reacting bromobenzene with NaF solution  
 (c) by heating phenol with HF and KF  
 (d) from aniline by diazotisation followed by heating the diazonium salt with HBF<sub>4</sub>

**(v) When 2-bromobutane reacts with alcoholic KOH, the reaction is called**

- (a) halogenation                              (b) chlorination  
 (c) hydrogenation                            (d) dehydrohalogenation

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

The polarity of carbon-halogen bond of alkyl halides is responsible for their Nucleophilic **substitution, elimination** and their reaction with metal atoms to form organ **metallic compounds**. Nucleophilic substitution reactions are categorized into **S<sub>N</sub>1** and **S<sub>N</sub>2** on the basis of their kinetic properties. **Chirality** has a profound role in understanding the reaction mechanisms of S<sub>N</sub>1 and S<sub>N</sub>2 reactions. S<sub>N</sub>2 reactions of chiral alkyl halides are characterized by the inversion of configuration while S<sub>N</sub>1 reactions are characterized by racemisation.

**ASSERTION -REASON TYPE**

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

- (a) Both assertion and reason are true and reason is the correct explanation of assertion.  
 (b) Both assertion and reason are true but reason is not the correct explanation of assertion.  
 (c) Assertion is true but reason is false.  
 (d) Assertion is false but reason is true

**(i) Assertion :** S<sub>N</sub>2 reactions do not proceed with retention of configuration.

**Reason :** S<sub>N</sub>2 reactions proceed in a single step.

**(ii) Assertion :** Tertiary alkyl halides show high reactivity in S<sub>N</sub>1 reaction.

**Reason :** Tertiary carbocation has more stability.

**(iii) Assertion:**  $\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{\text{Cl}_2, 773 \text{ K}} \text{Cl} - \text{CH}_2 - \text{CH} = \text{CH}_2 + \text{HCl}$

**Reason :** At high temperature, Cl<sub>2</sub> dissociates into chlorine free radicals which bring about allylic substitution.

**(iv) Assertion :** Nucleophilic substitution reaction in an optically active alkyl halide gives a mixture of enantiomers.

**Reason :** Reaction occurs by S<sub>N</sub>1 mechanism.

**(v) Assertion :** Primary allylic halides show higher reactivity in S<sub>N</sub>1 reactions than other primary alkyl halides.

**Reason :** Intermediate carbocation is stabilized by resonance.

**5. When Benzene diazonium chloride is treated with cuprous chloride in HCl, Chlorobenzene is formed, This reaction is known as –**

- a) Etard Reaction                              b) Perkin's Reaction  
 c) Gattermann's Reaction                    d) Sand Meyer's Reaction

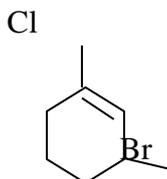
6. Which is the most reactive towards SN1 reaction –

- a)  $C_6H_5CH_2Cl$                       b)  $C_6H_5CH(C_6H_5)Br$   
c)  $C_6H_5CH(CH_3)Br$                 d)  $C_6H_5C(CH_3)(C_6H_5)Br$

7. The reaction  $R-Br + NaCN \rightarrow R-CN + NaBr$  is an example of –

- (a) Elimination Reaction                (b) Nucleophilic Substitution  
(c) Electrophilic Substitution        (d) Oxidation Reduction.

8. The IUPAC name of the compound shown below is –



- a) 2-Bromo-6-Chlorocyclohex-1-ene    b) 6-Bromo-2-Chlorocyclohexene  
c) 3-Bromo-1-Chlorocyclohexene        d) 1-Bromo-1-Chlorocyclohexene

9. The reaction  $(CH_3)_2CHCl + NaI \rightarrow (CH_3)_2CHI + NaCl$  is known as –

- a) Finkelstein's reaction                b) Stephen's reaction  
c) Kolbe's reaction                        d) Wurtz reaction

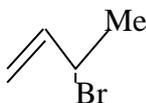
10. The Addition of HBr to 2-Pentene gives –

- a) 2-Bromopentane only.                b) 3-Bromopentane only.  
c) 2-Bromopentane and 3-Bromopentane    d) 1-Bromopentane and 3-Bromopentane

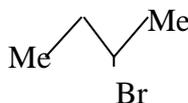
11. Consider the following bromides –



(i)



(ii)



(iii)

The correct form of SN1 reactivity is

- a) I > II > III    b) II > III > I    c) II > I > III    d) III > II > I

12. Which of the following is an example of vic-dihalide?

- (a) Dichloromethane                      (b) 1,2-dichloroethane  
(c) Ethylidene chloride                  (d) Allyl chloride

13. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of  $AlCl_3$ . Which of the following species attacks the benzene ring in this reaction?

- (a)  $Cl^+$                 (b)  $Cl^-$                 (c)  $AlCl_3$                 (d)  $[AlCl_4]^-$

14. Molecules whose mirror image is non-superimposable over them are known as chiral. Which of the following molecules is chiral in nature?

- (a) 2-Bromobutane                        (b) 1-Bromobutane  
(c) 2-Bromopropane                        (d) 2-Bromopropan-2-ol

15. Which is the correct increasing order of boiling points of the following compounds?  
1-Iodobutane, 1-Bromobutane, 1-Chlorobutane, Butane
- (a) Butane < 1-Chlorobutane < 1-Bromobutane < 1-Iodobutane  
 (b) 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane < Butane  
 (c) Butane < 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane  
 (d) Butane < 1-Chlorobutane < 1-Iodobutane < 1-Bromobutane
16. The order of reactivity of following alcohols with halogen acids is:-
- (A)  $\text{CH}_3\text{CH}_2\text{—CH}_2\text{—OH}$   
 (B)  $\text{CH}_3\text{CH}_2\text{—}\underset{\text{CH}_3}{\text{CH}}\text{—OH}$   
 (C)  $\text{CH}_3\text{CH}_2\text{—}\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}\text{—OH}$
- (a) (A) > (B) > (C)                      (b) (C) > (B) > (A)  
 (c) (B) > (A) > (C)                      (d) (A) > (C) > (B)
17. Which of the following will have the maximum dipole moment?  
 (a)  $\text{CH}_3\text{F}$                       (b)  $\text{CH}_3\text{Cl}$                       (c)  $\text{CH}_3\text{Br}$                       (d)  $\text{CH}_3\text{I}$
18. A Grignard reagent may be made by reacting magnesium with  
 a) Methyl amine                      b) Diethyl ether                      c) Ethyl iodide                      d) Ethyl alcohol
19. Aryl halides can not be prepared by the reaction of arylalcohols with  $\text{PCl}_3$ ,  $\text{PCl}_5$  or  $\text{SOCl}_2$  because :
- (a) phenols are highly stable compounds.  
 (b) carbon-oxygen bond in phenols has a partial double bond character.  
 (c) carbon-oxygen bond is highly polar  
 (d) all of these
20. Benzene reacts with  $\text{CH}_3\text{Cl}$  in the presence of anhydrous  $\text{AlCl}_3$  to form :  
 (a) chlorobenzene                      (b) benzylchloride                      (c) xylene                      (d) toluene

### SOLUTIONS

1. (i) (c) Allylic chlorides are most reactive.  
 (ii) c  
 (iii) d  
 (iv) (a) Larger the number of alkyl groups at alpha-carbon atom, more is the steric hindrance and hence lesser the reactivity towards  $\text{SN}_2$  mechanism (v) (a)
2. (i) (a) ,    (ii) (b),                      (iii) (b),                      (iv) (d) ,                      (v) (d)
3. (i) (c) ,    (ii) (c),                      (iii) (c),                      (iv) (d) ,                      (v) (d)
4. (i) (b) ,    (ii) (a),                      (iii) (a),                      (iv) (a) ,                      (v) (a)
5. (d) 6. (d) 7. (b) 8. (c) 9. (a) 10. (c) 11. (b) 12. (b) 13. (a) 14. (a) 15. (a) 16. (b)

17. (b) 18. (c) 19. (b), 20.(d)

## 11. ALCOHOL PHENOL and ETHER

**Case study based (CCT-1):** An organic compound A having molecular formula  $C_6H_6O$  turn blue litmus solution into red but does not react with sodium bicarbonate, but when treated with bromine water then form a white ppt of compound B. when compound A react with chloroform in presence of aqueous caustic soda solution at 340K then form two compound C and D. When compound A treated with caustic soda then form compound E compound E when treated with methyl halide then form compound F.

Question 1. Read the above passage carefully and answer the following questions:

Question (i). The name of compound is:

- (a) 2-methyl propene-2-ol                      (b) 2-methyl phenol  
(c) 2,4,6-tribromophenol                      (d) Butane 1-ol

Question (ii). Which are isomers of each other

- (a) A and C                      (b) B and C                      (c) C and D                      (d) D and E

Question(iii). The IUPAC name of compound F is

- (a) Anisole                      (b) Methoxybenzene  
(c) Salicylaldehyde                      (d) 2-methyl propene-2-ol

Question (iv). When compound E treated with ethyl iodide then ..... form.

- (a) Ehoxybenzene                      (b) Ethoxy hexane  
(c) Propoxypropane                      (d) Benzaldehyde

Question (v). On oxidation with sodium dichromate and conc  $H_2SO_4$  phenol gives

- (a) Benzaldehyde                      (b) p-Benzoquinone  
(c) o-Benzoquinone                      (d) m-benzoquinone

### Case study based (CCT-2):

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

Phenol contains -OH group directly attached to carbon atoms of an aromatic system  $C_6H_5OH$  in phenol the group is attached to  $sp^2$  hybridised carbon of aromatic ring.

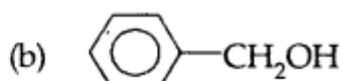
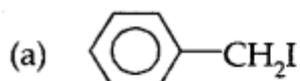
The carbon oxygen bond length is 1:36 pm in phenol is slightly less than that in in methanol this is due to first point partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring s point  $sp^3$  hybridised state of carbon to which oxygen is attached it can be prepared by various means or methods. Some important methods are alkali fusion of sulphonates, hydrolysis of diazonium salts decarboxylation of salicylic acid and from Grignard reagent, it is prepared from Dow's process and from cumene.

Aerial oxidation of human produce cumene peroxide which on hydrolysis produce phenol and acetone.

**INSTRUCTIONS:** In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Both assertion and reason are true and the reason is the correct explanation of assertion.  
(b) Both assertion and reason are true but the reason is not the correct explanation





### MULTIPLE CHOISE QUESTIONS

Question 4. Which of the following alcohols gives 2-butenc on dehydration by conc.  $H_2SO_4$ ?

- (a) 2-methyl propene-2-ol (b) 2-methyl 1 -propanol  
(c) Butane-2-ol (d) Butane 1-ol

Question 5. One mole of ethyl acetate on treatment with an excess of  $LiAlH_4$  in dry ether and subsequent acidification produces

- (a) 1 mole acetic acid + 1 mole ethyl alcohol  
(b) 1 mole ethyl alcohol + 1 mole methyl alcohol  
(c) 2 moles of ethyl alcohol (d) 1 mole of 2-butanol

Question 6. Which of the following reagents cannot, be used to oxidise primary alcohols to aldehydes?

- (a)  $CrO_3$  in anhydrous medium (b)  $KMnO_4$  in acidic medium  
(c) Pyridinium chlorochromate (d) Heat in the presence of Cu at 573 K

Question 7. 1-Phenylethanol can be prepared by the reaction of benzaldehyde with

- (a) methyl bromide (b) ethyl iodide and magnesium  
(c) methyl iodide and magnesium (d) methyl bromide and aluminium bromide

Question 8. Which of the following alcohols will give the most stable carbocation during dehydration?

- (a) 2-methyl-1-propanol (b) 2-methyl-2-propanol  
(c) 1-Butanol (d) 2-Butanol

Question 9. A compound X with the molecular formula  $C_2H_8O$  can be oxidised to another compound Y whose molecular formulae is  $C_3H_6O_2$ . The compound X may be

- (a)  $CH_3CH_2OCH_3$  (b)  $CH_3CH_2CHO$   
(c)  $CH_3CH_2CH_2OH$  (d)  $CH_3CHOHCH_3$

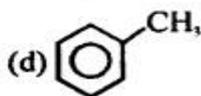
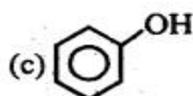
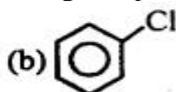
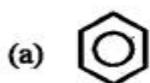
Question 10. Order of esterification of alcohols are

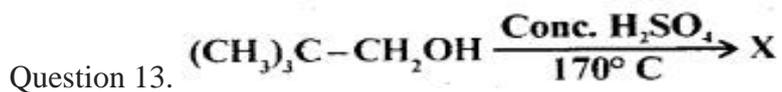
- (a)  $3^\circ > 1^\circ > 2^\circ$  (b)  $2^\circ > 3^\circ > 1^\circ$   
(c)  $1^\circ > 2^\circ > 3^\circ$  (d) None of these

Question 11. What happens when tertiary butyl alcohol is passed over heated copper at  $300^\circ C$ ?

- (a) Secondary butyl alcohol is formed (b) 2-methylpropene is formed  
(c) 1-butene is formed (d) Butanol is formed

Question 12. Which of the following compounds will be most easily attacked by an electrophile?





In the reaction, X is

- (a)  $(\text{CH}_3)_2\text{C} = \text{CHCH}_3$   
 (b)  $\text{CH}_3\text{C} = \text{CH}$   
 (c)  $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$   
 (d)  $\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\text{C}} = \text{CH}_2$

Question 14. What would be the reactant and reagent used to obtain 2, 4-dimethyl pentan-3-ol?

- (a) Propanal and propyl magnesium bromide  
 (b) 3-methylbutanal and 2-methyl magnesium iodide  
 (c) 2-dimethylpropanone and methyl magnesium iodide  
 (d) 2-methylpropanal and isopropyl magnesium iodide

Question 15. The decreasing order of boiling point of the following alcohols is

- (a) 3-methylbutan-2-ol > 2-methylbutan-2-ol > pentan-1-ol  
 (b) Pentan-1-ol > 3-methylbutan-2-ol > 2-methylbutan-2-ol  
 (c) 2-methylbutan-2-ol > 3-methylbutan-2-ol > pentan-1-ol  
 (d) 2-methylbutan-2-ol > pentan-1-ol > 3-methylbutan-2-ol

Question 16. Acid catalysed dehydration of t-butanol is faster than that of n-butanol because

- (a) tertiary carbocation is more stable than primary carbocation  
 (b) primary carbocation is more stable than tertiary carbocation  
 (c) t-butanol has a higher boiling point  
 (d) rearrangement takes place during dehydration of t-butanol

Question 17. An unknown alcohol is treated with "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism?

- (a) Tertiary alcohol by  $\text{S}_{\text{N}}^2$   
 (b) Secondary alcohol by  $\text{S}_{\text{N}}^1$   
 (c) Tertiary alcohol by  $\text{S}_{\text{N}}^1$   
 (d) Secondary alcohol by  $\text{S}_{\text{N}}^2$

Question 18. An alcohol X when treated with hot conc.  $\text{H}_2\text{SO}_4$  gave an alkene Y with formula  $\text{C}_4\text{H}_8$ . This alkene on ozonolysis gives single product with molecular formula  $\text{C}_2\text{H}_4\text{O}$ . The alcohol is

- (a) butan-1-ol, (b) butan-2-ol  
 (c) 2-methylpropan-1-ol (d) 2,2-dimethylbutan-1-ol

Question 19. Which of the following alcohols reacts most readily with Lucas reagent?

- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$   
 (b)  $\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_3$   
 (c)  $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} - \text{OH}$   
 (d)  $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2\text{OH}$

- Question 20. Propanone on reaction with alkyl magnesium bromide followed by hydrolysis will produce
- (a) primary alcohol (b) secondary alcohol  
(c) tertiary alcohol (d) carboxylic acid

### Assertion and Reasoning

**INSTRUCTIONS:** In the following questions (from 21 to 30) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Both assertion and reason are true and the reason is the correct explanation of assertion.  
(b) Both assertion and reason are true but the reason is not the correct explanation of assertion.  
(c) Assertion is true but reason is false.  
(d) Assertion is false but reason is true.

21.**Assertion:** Addition reaction of water to but-1-ene in acidic medium yields butan-2-ol  
**Reason:** Addition of water in acidic medium proceeds through the formation of primary carbocation.

22.**Assertion:** p-nitrophenol is more acidic than phenol.  
**Reason:** Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

23.**Assertion:** IUPAC name of the compound is 2-Ethoxy-2-methylethane.  
**Reason:** In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by -OR or -OAr group [where R = alkyl group and Ar = aryl group]

24.**Assertion:** Bond angle in ethers is slightly less than the tetrahedral angle.  
**Reason:** There is a repulsion between the two bulky (-R) groups.

25.**Assertion:** Boiling points of alcohols are greater than ethers of same molar mass.  
**Reason:** Ethers can form intermolecular hydrogen-bonding with each other.

26.**Assertion:** Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.  
**Reason:** Lewis acid polarises the bromine molecule.

27.**Assertion:** o-Nitrophenol is less soluble in water than the m- and p-isomers.  
**Reason:** m- and p- Nitrophenols exist as associated molecules.

28.**Assertion:** Ethanol is a weaker acid than phenol.  
**Reason:** Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.

29.**Assertion:** Phenol forms 2,4,6-tribromophenol on treatment with Br<sub>2</sub> in carbon disulphide at 273K.  
**Reason:** Bromine and carbon disulphide both are nonpolar.

30.**Assertion:** Phenols give o- and p-nitrophenol on nitration with conc. HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> mixture.  
**Reason:** —OH group in phenol is o-, p- directing.

### Answers:

Question 1 Case study based (CCT-1):

(i) (c) 2,4,6-tribromophenol, (ii) (c) C and D, (iii) (b) Methoxybenzene, (iv) (a) Ehoxybenzene (v) (b) p-Benzoquinone

Question 2 **Case study based (CCT-2):** (i) b, (ii) a, (iii) b (iv) b (v) a

Question 3 **Case study based (CCT-3):**

(i) (d) Di tert. butyl ether, (ii) (c) 3-Methoxy-1-propene,  
(iii) (a) conc.H<sub>2</sub>SO<sub>4</sub> at 413K (iv) (b) Basic (v) (a) benzyl Iodide

### MULTIPLE CHOISE QUESTIONS

4. (c) Butane-2-ol, 5. (c) 2 moles of ethyl alcohol, 6. (b) KMnO<sub>4</sub> in acidic medium 7. (c) methyl iodide and magnesium (Grignard reagent's), 8. (b) 2-methyl-2-propanol,  
9. (c) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH, 10. (c) 1° > 2° > 3° 11. (b) 2-methylpropene is formed,  
12. (c) phenol, 13. (a) (CH<sub>3</sub>)<sub>2</sub>C = CHCH<sub>3</sub>, 14. (d) 2-methylpropanal and isopropyl magnesium iodide 15. (b) Pentan-1-ol > 3-methylbutan-2-ol > 2-methylbutan-2-ol,  
16. (a) tertiary carbocation is more stable than primary carbocation,  
17. (c) Tertiary alcohol by S<sub>N</sub><sup>1</sup> 18. (b) butan-2-ol, 19. (c) tert. Butyl alcohol,  
20. (c) tertiary alcohol, 21. (b) 22. (a) 23. (d) 24. (d)  
25. (a) 26. (d) 27. (b) 28. (c) 29. (d) 30. (d)

## 14. BIOMOLECULES

## MCQs-

- The functional group which is found in amino acid is-  
(a) -COOH                      (b) -NH<sub>2</sub>                      (c) -CH<sub>3</sub>                      (d) both (a) and (b)
- Which base is present in RNA but not in DNA?  
(a) Uracil                      (b) Cytosine                      (c) Guanine                      (d) Thymine
- The anomeric carbon in D(+) glucose is –  
(a) C-1 carbon                      (b) C-2 carbon                      (c) C-5 carbon                      (d) C-6 carbon
- Each polypeptide in protein has amino acids linked with each other in a specific sequence. This sequence of amino acids is said to be-  
(a) primary structure of proteins.                      (b) secondary structure of proteins.  
(c) tertiary structure of proteins.                      (d) quaternary structure of proteins.
- Which statement is incorrect about peptide bond?  
(a) C-N bond length in proteins is longer than usual bond length of C-N bond.  
(b) Spectroscopic analysis shows planar structure of -CO-NH- group  
(c) C-N bond length in proteins is smaller than usual bond length of C-N bond  
(d) None of the above
- The reason for double helical structure of DNA is operation of-  
(a) electrostatic attractions                      (b) dipole-dipole interaction  
(c) van der Waal's forces                      (d) hydrogen bonding
- Which of the following factors is not responsible for the denaturation of proteins?  
(a) Heat                      (b) Charge                      (c) PH change                      (d) Organic solvents
- Fructose contains functional group-  
(a) Aldehyde                      (b) Ketone                      (c) Carboxylic acid                      (d) primary amine
- The letter 'D' in carbohydrates signifies-  
(a) dextrorotatory                      (b) configuration                      (c) diamagnetic nature                      (d) mode of synthesis
- RNA and DNA are chiral molecules. Their chirality is due to :  
(a) Chiral bases                      (b) Chiral phosphate ester units  
(c) D-sugar component                      (d) L-sugar component.

**Ans- 1 (d) 2 (a) 3 (a) 4 (a) 5 (a) 6 (d) 7 (b) 8 (b) 9(b) 10 (c)**

## ASSERTION & REASON TYPE QUESTIONS

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- Assertion and reason both are correct statements and reason is correct explanation for assertion.
- Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- Assertion is correct statement but reason is wrong statement.
- Assertion is wrong statement but reason is correct statement.

11. Assertion: D (+) -Glucose is dextrorotatory in nature.  
Reason: D represents its dextrorotary nature.

12. Assertion: The bond between adenine and thymine is stronger than the bond between Cytocine and

guanine. .

Reason: Cytosine and guanine have a triple hydrogen bond while adenine and thymine have a double hydrogen bond

13. Assertion: Glycine must be taken through diet.

Reason: It is essential amino acid.

14. Assertion: The two strands of DNA are complementary to each other.

Reason: The hydrogen bonds are formed between specific pairs of bases.

15. Assertion: Amino acids in protein remain intact even when it is denatured.

Reason: The primary structure of protein is broken to give individual aminoacids on denaturation.

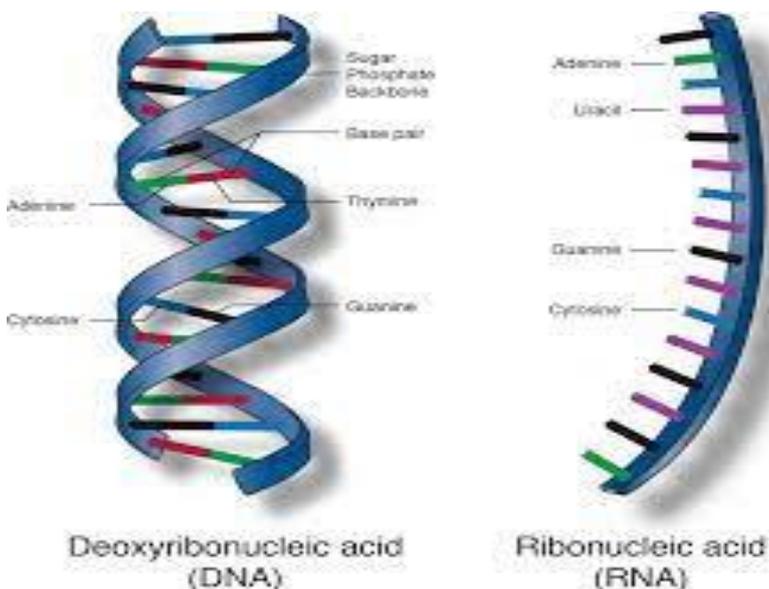
16. Assertion: Glycine is not optically active.

Reason: There is no asymmetrical carbon in glycine to make it chiral.

**Answers: 11 ( C ) 12 ( D ) 13 ( D ) 14 ( A ) 15 ( C ) 16 ( A )**

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

Nucleic acids are macromolecules that store genetic information and enable protein production. Nucleic acids include DNA and RNA . These molecules are composed of long strands of nucleotides ,Nucleotides are composed of a nitrogenous base,a five-carbon sugar, and a phosphate group.



(1) Nucleotides are joined together by:

- i. Glycosidic linkage (b) Phosphodiester linkage\*  
(a) Hydrogen bonds (d) Weak intermolecular forces

(2) Which of the following bases pairs with guanine?

- (i) Adenine (b) Guanine (c) Cytosine (d) Thymine

(3) The nitrogenous base is linked to the ribose or deoxyribose sugar via a

- (a) Glycosidic bond (b) Amide bond (c) Hydrogen bond (d) Phosphodiester bond

(a) In double helix of DNA, the two DNA strands show which type of characteristics?

- (a) Coiled around a common axis (b) Coiled around each other  
(c) Coiled differently (d) Coiled over protein sheath

Answers-1(b) 2(c) 3(a) 4(a)

## II. Read the passage given below and answer the following questions:

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 structures remain intact. Examples of denaturation of protein are coagulation of egg white on boiling, curdling of milk, formation of cheese when an acid is added to milk.

Choose the most appropriate answer:

i) Mark the wrong statement about denaturation of proteins.

- a) The primary structure of the protein does not change
- b) Globular proteins are converted into fibrous proteins.
- c) Fibrous proteins are converted into globular proteins.
- d) The biological activity of the protein is destroyed

ii) Which structure(s) of proteins remains(s) intact during denaturation process ?

- (a) Both secondary and tertiary structures
- (b) **Primary** structure only
- (c) Secondary structure only
- (d) Tertiary structure only

iii)  **$\alpha$ -helix** and  **$\beta$ -pleated** structures of proteins are classified as

- (a) primary structure
- (b) secondary structure
- (c) tertiary structure
- (d) quaternary structure.

(iv) Secondary structure of protein refers to

- a ) mainly denatured proteins and structure of prosthetic groups
- b ) three-dimensional structure, especially the bend between amino acid residues that are distant from each other in the polypeptide chain
- c ) linear sequence of amino acid residues in the polypeptide chain
- d ) regular folding patterns of continuous portions of the polypeptide chain.

Ans II. (i)(c)                      (ii) (b)                      (iii) (b)                      (iv) (d)

## III. Read the passage given below and answer the following questions :

The sequence of bases along the DNA and RNA chain establishes its **primary** structure which controls the specific properties of the nucleic acid. An RNA molecule is usually a single chain of **ribose-containing** nucleotide. On the basis of X-ray analysis of DNA, J.D., Watson and F.H.C. CRYST (shared noble prize in 1962) proposed a three dimensional secondary structure for DNA. DNA molecule is a long and highly complex, spirally twisted, double **helix**, ladder like structure. The two polynucleotide chains or strands are linked up by hydrogen bonding between the nitrogenous base molecules of their nucleotide monomers. Adenine (purine) always links with **thymine** (pyrimidine) with the help of two hydrogen bonds and **guanine** (purine) with cytosine (pyrimidine) with the **help** of three hydrogen bonds. **Hence**, the two strands extend in opposite directions, i.e., are

antiparallel and complimentary.

**In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.**

- a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- c) Assertion is correct statement but reason is wrong statement
- d) Assertion is wrong statement but reason is correct statement.

i) Assertion - DNA molecules and RNA molecules are found in the nucleus of a cell.

Reason : There are two types of nitrogenous bases, purines and pyrimidines. Adenine (A) and guanine (G) are substituted purines; cytosine (C), thymine (T) and uracil (U) are substituted pyrimidines.

ii) Assertion .- In both DNA and RNA, heterocyclic base and phosphate ester linkages are at C- 1' and C-5' respectively of the sugar molecule.

Reason : Nucleotides and nucleosides mainly differ from each other in presence of phosphate units.

iii) Assertion .- The backbone of RNA molecule is a linear chain consisting of an alternating units of heterocyclic base, D-ribose and a phosphate.

Reason : The segment of RNA which acts as the instruction manual for the synthesis of protein is ribose.

iv) Assertion.- In DNA, the complementary bases are, adenine and guanine; thymine and cytosine.

Reason : The phenomenon of mutation is chemical change in DNA molecule.

**Ans III.    i)(d)    ii) (b)    iii) (c)    iv) (d).**

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

Proteins are high molecular mass complex biomolecules of amino acid. The important proteins required for our body are enzymes, hormones, antibodies, transport proteins, structural proteins, contractile proteins etc. Except for glycine, all  $\alpha$ -amino acids have chiral carbon atom and most of them have L-configuration. The amino acids exist as dipolar ion called zwitter ion, in which a proton goes from the carboxyl group to the amino group. A large number of amino acids are joined by peptide bonds forming polypeptides. The peptides having very large molecular mass (more than 10,000) are called proteins. The structure of proteins is described as primary structure giving sequence of linking of amino acids; secondary structure giving manner in which polypeptide chains are arranged and folded; tertiary structure giving folding, coiling or bonding polypeptide chains producing three dimensional structures and quaternary structure giving arrangement of sub-units in an aggregate protein molecule.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- c) Assertion is correct statement but reason is wrong statement.
- d) Assertion is wrong statement but reason is correct statement.

i) **Assertion** .- All amino acids are optically active.

**Reason** : Amino acids contain asymmetric carbon atoms

ii) **Assertion** .- In  $\alpha$ -helix structure, intramolecular H-bonding takes place whereas in  $\beta$ -pleated structure, intermolecular H-bonding takes place.

**Reason** : An egg contains a soluble globular protein called albumin which is present in the white part.

iii) **Assertion** .- Secondary structure of protein refers to regular folding patterns of continuous portions of the polypeptide chain

**Reason** : Out of 20 amino acids, only 12 amino acids can be synthesized by human body.

iv) **Assertion** .- The helical structure of protein is stabilized by intramolecular hydrogen bond between —NH and carbonyl oxygen.

**Reason** : Sanger's reagent is used for the identification of N-terminal amino acid of peptide chain.

**Ans IV.**    i) (d)    ii) (b)    iii) (c)    iv) (b).

# TERM - II

### 3. ELECTROCHEMISTRY

#### GIST: -

1. Electrochemistry is the branch of chemistry which deals with the relationship between electrical energy and chemical energy and inter-conversion of one form into another.
2. An electrochemical cell consists of two metallic electrodes dipped in electrolytic solutions. The cells are of two types:  
(a) Electrolytic cells (b) Galvanic cells
3. A galvanic cell consists of two half cells. Each half cell contains an electrolytic solution and a metallic electrode. The electrode at which- oxidation takes place is called an anode and the electrode at which reduction takes place is called the cathode. The half-cells are separated from each other by means of a salt bridge.
4. The passage of current from one electrode to the other indicates the existence of potential difference between them. This difference of potential which causes current to flow from the electrode of higher negative potential is called the electromotive force (emf).
5. Functions of salt bridge: completes the circuit & maintains electrical neutrality of the cell
6. The potential of SHE is assigned an arbitrary value of zero.  $E^\circ = 0 \text{ V}$ . It is used as a reference electrode for measuring the standard electrode potentials. .
7. When the elements are arranged in order of their standard electrode potentials, a series known as electrochemical series is obtained.
8. Standard emf of a cell,

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

9. Relation between Gibb's free energy &  $E^\circ_{\text{cell}}$

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

If  $E^\circ_{\text{cell}}$  is positive,  $\Delta G^\circ$  would be negative and reaction would be spontaneous.

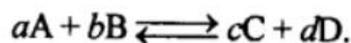
If  $E^\circ_{\text{cell}}$  is negative,  $\Delta G^\circ$  would be positive and the reaction would be non-spontaneous.

10. A species with higher standard reduction potential has greater tendency to accept electrons to undergo reduction or vice versa.
11. **The potential of an electrode** in contact with its ions in solution varies with the concentration of the ion. Thus, for a redox reaction.



$$\text{Nernst equation is } E = E^\circ_{M^{n+}/M} + \frac{RT}{nF} \ln [M^{n+}]$$

12. For an electrochemical cell for which the overall reaction is :



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\text{At 298 K, } \frac{2.303RT}{nF} = \frac{0.0591}{n}$$

Then equation becomes

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

13. The equilibrium constant,  $K_c$  is related to  $E_{\text{cell}}^{\circ}$

$$E_{\text{cell}}^{\circ} = \frac{2.303RT}{nF} \log K_c = \frac{0.0591}{n} \log K_c \text{ at 298 K.}$$

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} = -2.303 RT \log K_c$$

14. Resistance is the measure of obstruction to the flow of current.

$$R \propto \frac{l}{A} \Rightarrow R = \rho \frac{l}{A} \quad (\text{where } \rho = \text{specific resistance or resistivity. Unit of R is ohm}).$$

15. **Resistivity** is defined as the resistance of a conductor of 1cm length and having an area of cross-

section equal to  $1\text{cm}^2$ .  $\rho = \frac{RA}{l}$  (unit of resistivity is ohm-cm)

16. Conductance is reciprocal of resistance,  $G = 1/R$

Unit of conductance is ohm<sup>-1</sup> or mho or Siemen(S).

17. Specific conductance  $\kappa$  (*kappa*) is reciprocal of specific resistance

$$\kappa = G \times G^* \Rightarrow \kappa = \frac{1}{R} \times \frac{l}{A} \text{ or } \kappa = l/\rho$$

18. **Molar conductance** ( $\Lambda_m$ ) is defined as the conductance of the volume of solution which contains one mole of the solute and is placed between two parallel electrodes which are one centimetre apart and having sufficient area to hold the whole of the solution.

Unit of molar conductance is  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  or  $\text{S cm}^2 \text{mol}^{-1}$

$$\lambda_m = \kappa/C \quad \text{where C = concentration of solution in moles per litre (or Molarity)}$$

$$\lambda_m \Rightarrow \frac{\kappa \times 1000}{M} \quad (\text{if } \kappa = \text{Scm}^{-1})$$

$$\lambda_m \Rightarrow \frac{\kappa}{M \times 1000} \quad (\text{if } \kappa = \text{Sm}^{-1})$$

19. Effect of Dilution on Molar conductance: The value of molar conductance increases with dilution and finally attains a maximum value at infinite dilution. ( $\lambda_m^{\circ}$ )

20. **Variation of molar conductance with concentration:**

(a) Strong electrolytes:

**conductance at infinite dilution ( $\Lambda_m^\infty$ )**

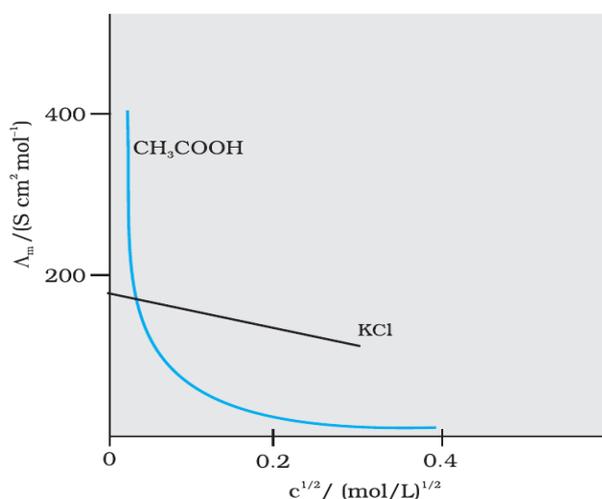
$$\Lambda_m = \Lambda_m^\infty \text{ when } C \rightarrow 0$$

The variation of  $\Lambda_m$  with concentration is given by

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{C} \text{ where } b = \text{constant}$$

(b) Weak electrolytes:

The variation of  $\Lambda_m$  with  $\sqrt{C}$  is very large and so much so that we cannot obtain molar conductance at infinite dilution ( $\Lambda_m^\infty$ ) by extrapolation of the  $\Lambda_m$  Vs.  $\sqrt{C}$  plots.



21. Kohlrausch's Law - "the limiting molar conductivity of an electrolyte can be expressed as the sum of the contributions of the cation and the anion of the electrolyte."

$$\Lambda^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

22. Faraday's laws of electrolysis:

(a) First law: The amount of a substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.

$$Q \propto I \times t$$

$$m = ZIt$$

$I$  = current in amperes

$t$  = time in seconds, and

$Z$  = constant called electrochemical equivalent.

where  $m$  = mass of substance deposited or liberated.

$Z$  = constant called electrochemical equivalent

(b) Second law: When the same quantity of electricity is passed through solutions of different electrolytes,

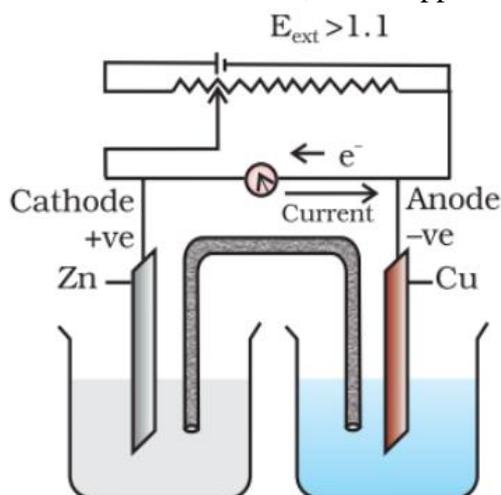
the weight of different substances deposited or liberated at the respective electrodes are proportional to their chemical equivalent weights.

23.. The charge on one mole of electrons is approximately equal to 96500 coulombs. This quantity of electricity is called Faraday constant (F).

SECTION -A (VSA- 1 marks) Part-I

Choose the correct option:

1. Looking at the setup of an electrochemical cell, what happens when  $E_{ext} > 1.1$  V



- a. Zn dissolves at anode & copper deposits at cathode
- b. Current travels from Cu to Zn
- c. Zinc deposits at anode and copper dissolves at cathode.
- d. No current is obtained

2. Limiting molar conductivity of  $\text{NH}_4\text{OH}$  is equal to -:

- a.  $\Lambda^{\circ}\text{mNH}_4\text{Cl} + \Lambda^{\circ}\text{mNaCl} + \Lambda^{\circ}\text{mNaOH}$
- b.  $\Lambda^{\circ}\text{mNaOH} + \Lambda^{\circ}\text{mNaCl} - \Lambda^{\circ}\text{mNH}_4\text{Cl}$
- c.  $\Lambda^{\circ}\text{mNaOH} - \Lambda^{\circ}\text{mNH}_4\text{Cl} - \Lambda^{\circ}\text{mHCl}$
- d.  $\Lambda^{\circ}\text{mNH}_4\text{Cl} + \Lambda^{\circ}\text{mNaOH} - \Lambda^{\circ}\text{mNaCl}$

3. How is electrical conductance of a conductor related with length and area of cross-section of the conductor?

- a.  $G = l \cdot a \cdot k^{-1}$
- b.  $G = k \cdot l \cdot a^{-1}$
- c.  $G = k \cdot a \cdot l^{-1}$
- d.  $G = k \cdot l \cdot a^{-2}$

4. The potential of a hydrogen electrode at  $\text{pH} = 10$  is

- a. 0.591 V
- b. 0.00V
- c. -0.591 V
- d. -0.059 V

5. Which cell will measure standard electrode potential of copper electrode?

- a.  $\text{Pt (s)} | \text{H}_2 (\text{g}, 0.1 \text{ bar}) | \text{H}^+ (\text{aq.}, 1 \text{ M}) || \text{Cu}^{2+} (\text{aq.}, 1 \text{ M}) | \text{Cu}$
- b.  $\text{Pt (s)} | \text{H}_2 (\text{g}, 1 \text{ bar}) | \text{H}^+ (\text{aq.}, 1 \text{ M}) || \text{Cu}^{2+} (\text{aq.}, 2 \text{ M}) | \text{Cu}$
- c.  $\text{Pt (s)} | \text{H}_2 (\text{g}, 1 \text{ bar}) | \text{H}^+ (\text{aq.}, 1 \text{ M}) || \text{Cu}^{2+} (\text{aq.}, 1 \text{ M}) | \text{Cu}$
- d.  $\text{Pt (s)} | \text{H}_2 (\text{g}, 1 \text{ bar}) | \text{H}^+ (\text{aq.}, 0.1 \text{ M}) || \text{Cu}^{2+} (\text{aq.}, 1 \text{ M}) | \text{Cu}$

6. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called \_\_\_\_\_.
- a. Cell potential      b. Electromotive Force      c. Potential difference      d. Cell voltage

### Section A ( VSA ) Part II

#### Assertion- Reason Based question

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (A) Both assertion and reason are true and the reason is the correct explanation of assertion.  
 (B) Both assertion and reason are true and the reason is not the correct explanation of assertion.  
 (C) Assertion is true but the reason is false.  
 (D) Assertion is false but the reason is true.

7. Assertion:  $E^{\circ}$  cell should have a positive value for the cell to function.  
 Reason:  $E_{\text{cathode}} < E_{\text{anode}}$

8. Assertion : Conductivity of all electrolytes decreases on dilution.  
 Reason : On dilution number of ions per unit volume decreases.

9. Assertion :  $\Lambda^{\circ}$  m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.  
 Reason : For weak electrolytes degree of dissociation increases with dilution of solution.

10. Assertion: For measuring resistance of an ionic solution an AC source is used.  
 Reason: Concentration of ionic solution will change if DC source is used.

### ANSWERS: VSA PART 1 & II

1. c    2. d    3. b    4. c    5. c    6. b    7.C    8.A    9.A    10.A

### SA Type I Questions (2 Marks)

- The conductivity of metals decreases while that of electrolytes increases with increase in temperature. Why?
- The conductivity of an aqueous solution of NaCl in a cell is  $92 \Omega^{-1} \text{ cm}^{-1}$  the resistance offered by this cell is  $247.8 \Omega$  . Calculate the cell constant?
- How many electrons flow when a current of 5 amps is passed through a solution for 193 sec. Given  $F = 96500 \text{ C}$ .  $N_0 = 6.002 \times 10^{23} \text{ mol}^{-1}$ ?
- There are two possible reactions for cathode in the electrolysis of aqueous
 
$$\text{ZnCl}_2 : \text{Zn}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s}) \quad E^{\circ} = -0.76\text{v}$$

$$2\text{H}_2\text{O} (\text{l}) + 2\text{e}^- \rightarrow \text{H}_2 (\text{g}) + 2\text{OH}^- (\text{aq}) \quad E^{\circ} = -0.83\text{v}$$

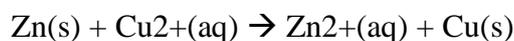
Which one will take place ? Why

5. Calculate pH of following half-cell.

Pt, H<sub>2</sub> / H<sub>2</sub>SO<sub>4</sub>, if its electrode potential is 0.03V.

### SA Type II Questions (3 Marks)

1. (a) Calculate G° for the reaction



Given: E° for Zn<sup>2+</sup>/Zn = -0.76V and E° for Cu<sup>2+</sup>/Cu = +0.34 V

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1} \quad F = 96500 \text{ mol}^{-1}$$

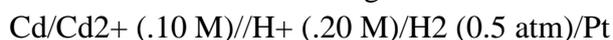
2. Out of the following pairs, predict with reason which pair will allow greater conduction of electricity:

(i) Silver wire at 30°C or silver wire at 60°C.

(ii) 0.1 M CH<sub>3</sub>COOH solution or 1 M CH<sub>3</sub>COOH solution.

(iii) KCl solution at 20°C or KCl solution at 50°C.

3. Calculate emf of the following cell



[Given E° for Cd<sup>2+</sup>/Cd = -0.403V]

4. The molar conductivity of 0.025 mol L<sup>-1</sup> methanoic acid is 46.1 S cm<sup>2</sup> mol<sup>-1</sup>. Calculate its degree of dissociation and dissociation constant Given λ°(H<sup>+</sup>)=349.6 S cm<sup>2</sup> mol<sup>-1</sup> and λ°(HCOO<sup>-</sup>) = 54.6 S cm<sup>2</sup> mol<sup>-1</sup>

5. Consider the reaction: Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> + 14H<sup>+</sup> + 6e<sup>-</sup> → 2Cr<sup>3+</sup> + 7H<sub>2</sub>O What is the quantity of electricity in coulombs needed to reduce 1 mol of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ?

### LA Type Questions – 5 Marks

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

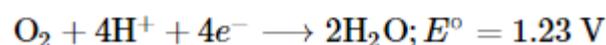
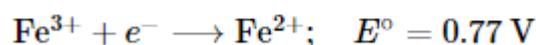
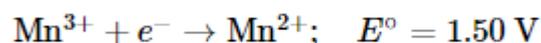
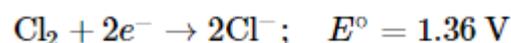
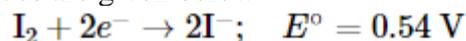
Standard electrode potentials are used for various processes:

(i) It is used to measure relative strengths of various oxidants and reductants.

(ii) It is used to calculate standard cell potential.

(iii) It is used to predict possible reactions.

A set of half-reactions (in acidic medium) along with their standard reduction potential, E° (in volt) values are given below –



Choose the most appropriate answer:

(i) Which of the following statements is correct?

- (a)  $\text{Cl}^-$  is oxidised by  $\text{O}_2$                       (b)  $\text{Fe}^{2+}$  is oxidised by iodine  
 (c)  $\text{I}^-$  is oxidised by chlorine.                (d)  $\text{Mn}^{2+}$  is oxidised by chlorine

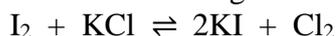
(ii)  $\text{Mn}^{3+}$  is not stable in acidic medium, while  $\text{Fe}^{3+}$  is stable because

- (a)  $\text{O}_2$  oxidises  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$   
 (b)  $\text{O}_2$  oxidises both  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$   
 (c)  $\text{Fe}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$   
 (d)  $\text{Mn}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$

(iii) The strongest reducing agent in the aqueous solution is

- (a)  $\text{I}^-$             (b)  $\text{Cl}^-$             (c)  $\text{Mn}^{2+}$             (d)  $\text{Fe}^{2+}$

(iv) The emf for the following reaction is –



- (a) -0.82 V            (b) +0.82 V            (c) -0.73 V            (d) +0.73 V

(v) The potential of an electrode changes with change in

- (a) concentration of ions in solution                      (b) position of electrodes  
 (c) voltage of the cell    (d) all of these

**Answers**    i) d    ii) c    iii) c    iv) a    v) d

2. Molar conductivity of solution is the conductance of solution containing one mole of electrolyte, kept between two electrodes having unit length between them and large cross-sectional area, so as to contain the electrolyte. In other words, molar conductivity is the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross-section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. It is denoted by  $\lambda_m$ .

Choose the most appropriate answer:

(i) The mathematical expression for molar conductivity is.

- (a)  $k_a = \frac{c\alpha^2}{1-\alpha}$             (b)  $\Lambda_m = \frac{k}{C}$             (c)  $k = \frac{G^*}{R}$             (d)  $\Lambda_m = \alpha \Lambda_m^\circ$

(ii) The units of molar conductivity  $\lambda_m$  is

- (a)  $\text{Scm}^2\text{mol}^{-1}$             (b)  $\text{Scm}^{-1}$             (c)  $\text{Smolcm}^{-2}$             (d)  $\text{cm}^{-1}$

(iii) Solutions of two electrolytes 'A' and 'B' are diluted. The  $\lambda_m$  of 'B' increases 1.5 times while that of A increases 25 times. Which of the two is a strong electrolyte?

- (a) electrolyte A            (b) electrolyte B            (c) electrolyte A & B            (d) None of these

(iv) Molar conductivity of ionic solution depends on \_\_\_\_\_.

- (a) pressure    (b) distance between electrodes  
 (c) concentration of electrolytes in solution            (d) surface area of electrodes

(v) The cell constant of a conductivity cell \_\_\_\_\_.

- (a) changes with change of electrolyte.  
 (b) changes with change of concentration of electrolyte.

(c) changes with temperature of electrolyte. (d) remains constant for a cell.

Answers: i) b ii) a iii) b iv) c v) d

### ANSWERS : SA 2 MARKS

1. With increase in temperature, the K.E. of metal cation increases and obstructs the free flow of electrons decreasing the conducts of metal while in case of electrolytes, increased temperature increases the mobility of ions this increases the conductance of ions.

2. Specific conductivity = Cell constant/ Resistance  
Cell constant = conductivity  $\times$  Resistance  
=  $92 \Omega^{-1} \text{ cm}^{-1} \times 247.8 \Omega$   
=  $22797.6 \Omega^{-1}$

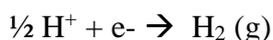
3.  $Q = It = 5 \times 193 = 965 \text{ C}$

$96500 \text{ C} = 1 \text{ mol of electrons} = 6.022 \times 10^{23} \text{ mol}^{-1}$

$965 \text{ C} = 6.022 \times 10^{23} \times 965/96500$   
=  $6.022 \times 10^{21}$  electrons.

4.  $\text{Zn}^{2+}$  is reduced to Zn preferentially at cathode because  $\text{Zn}^{2+}$  has higher reduction potential (-0.76V) than  $\text{H}_2\text{O}$  (-0.83V)

5.  $\text{pH} = -\log [\text{H}^+]$



$$E_{\text{cell}} = E_{\text{cell}}^0 - 0.059/n \log 1/[\text{H}^+]$$

$$0.03 = 0 - 0.059/1 \log 1/[\text{H}^+]$$

$$\text{pH} = 5.07\text{V}$$

### ANSWERS SA 3 MARKS-

1.

$$\begin{aligned} \text{(a) } E^{\circ} \text{ cell} &= E_{\text{Cu}^{+2}/\text{Cu}}^{\circ} - E_{\text{Zn}^{+2}/\text{Zn}}^{\circ} \\ &= 0.34 - (-0.76) \\ &= 1.10 \text{ V} \end{aligned}$$

$$\begin{aligned} \Delta G^{\circ} &= -nFE^{\circ} \\ &= -2 \times 1.10 \times 96500 \\ &= -212300 \text{ J/mol or } -212.3 \text{ kJ/mol} \end{aligned}$$

2. (i) Silver wire at  $30^{\circ}\text{C}$  because as temperature decreases, resistance decreases so conduction increases.

(ii)  $0.1 \text{ M CH}_3\text{COOH}$ , because on dilution degree of ionization increases hence conduction increases.

(iii)  $\text{KCl}$  solution at  $50^{\circ}\text{C}$ , because at high temperature mobility of ions increases and hence conductance increases.

3.  $E_{\text{cell}} = E^{\circ} \text{cell} - 0.0591/n \log [\text{Cd}^{2+}]/ [\text{H}^+]^2$

$$E^{\circ} \text{cell} = 0 - (-.403\text{V}) = 0.403\text{V}$$

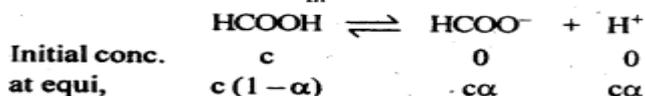
$$= 0.0403 - 0.0591/2 \text{ Log } (0.10) \times 0.5/(0.2)^2 = 0.400\text{V}$$

4.

$$\begin{aligned}\Lambda_m^\circ(\text{HCOOH}) &= \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{HCOO}^-) \\ &= 349.6 + 54.6 \\ &= 404.2 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\Lambda_m^C = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\therefore \alpha = \frac{\Lambda_m^C}{\Lambda_m^\circ} = \frac{46.1}{404.2} = 0.114$$



$$\begin{aligned}\therefore K_a &= \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \\ &= \frac{0.025 \times (0.114)^2}{1-0.114} = 3.67 \times 10^{-4}\end{aligned}$$

5.

From the reaction, 1 mol of  $\text{Cr}_2\text{O}_7^{2-}$  require 6F  
 $= 6 \times 96500 = 579000 \text{ C}$

$\therefore 579000 \text{ C}$  of electricity are required for  
 reduction of  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$

## 4. CHEMICAL KINETICS

IMPORTANT POINTS :

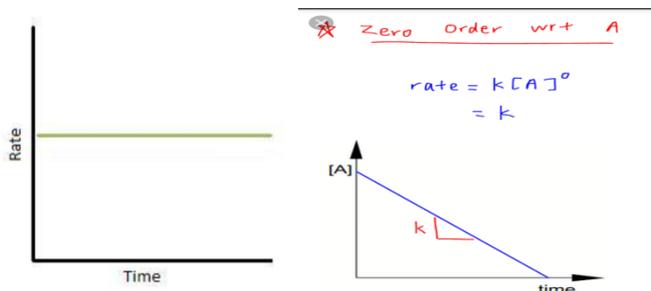
No	CONCEPT	DETAILS (THEORY & FORMULA)
	Rate of Reaction	Change of concentration of reactants & products per unit time. Rate = decrease in conc of reactant/time taken OR Rate = increase in conc of product/time interval Unit = $\text{mol L}^{-1} \text{ s}^{-1}$
	Expression or reaction rate	Consider a reaction, $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ $R = -\Delta[\text{N}_2]/\Delta t = -1/3\Delta[\text{H}_2]/\Delta t = 1/2\Delta[\text{NH}_3]/\Delta t$ Rate of disappearance of $\text{N}_2$ & $\text{H}_2 = -\Delta[\text{N}_2]/\Delta t = -\Delta[\text{H}_2]/\Delta t$ Rate of appearance of ammonia = $\Delta[\text{NH}_3]/\Delta t$ Rate of disappearance of $\text{N}_2$ = rate of reaction Rate of disappearance of $\text{H}_2$ = 3 x rate of reaction & Rate of formation of $\text{NH}_3$ = 2 x rate of reaction
	Factors	Reaction rate increases with increase in concentration of reactants, temperature

affecting reaction rate	& catalyst. A catalyst decreases the activation energy and promotes more reactants to cross energy barrier.
Order of reaction (n)	Sum of no of power of concentration terms of reactants in rate law. It is an experimental quantity, can be zero or fractional value.
Molecularity of reaction (m)	The number of molecules which simultaneously collide to form products in elementary reaction. It is a theoretical value & can't be zero or fractional.
Integrated rate equation	For zero order reaction = $k = [A]_0 - [A] / t$ For first order = $k = (2.303/t) \log [A]_0 / [A]$
Unit of rate constant	for any order = $\text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$ (where n is the order of reaction)
Half -life of a reaction	Time in which half of the reaction is completed or half of the reactant is consumed. For zero order $t_{1/2} = [R]_0 / 2k$ , for first order $t_{1/2} = 0.693/k$
Pseudo 1 <sup>st</sup> order reaction	The bimolecular reaction in which one of the reactants is taken in excess so that the reaction follows 1 <sup>st</sup> order kinetics.

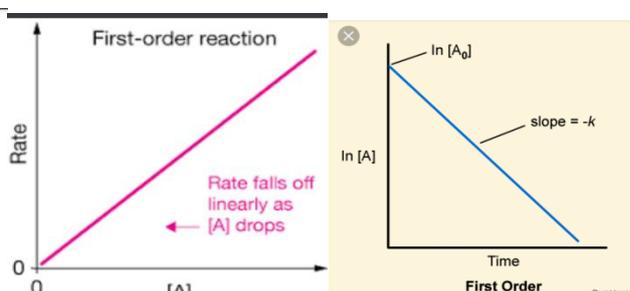
S.No.	order of reaction	molecularity of reaction
1	It is sum of the powers of the concentration of the reactants in the rate law expression	The number of reacting species taking part in an elementary reaction, which must collide to give products is called molecularity of a reaction.
2	Order of a reaction is an experimental quantity.	It is theoretical value.
3	It can be zero and even a fraction.	It cannot be zero or fractional.
4	Order is applicable to elementary as well as complex reactions.	Molecularity is applicable only for elementary reactions.

## GRAPHICAL REPRESENTATIONS OF ZERO & FIRST ORDER REACTION

### ZERO ORDER REACTION



### FIRST ORDER REACTION



### MCQs

- A reaction is first order with respect to reactant A. What will be the initial rate, if concentration of reactant is reduced by half?
  - Halved
  - doubled
  - tripled
  - not changed
- What is the ratio of the rate of decomposition of  $\text{N}_2\text{O}_5$  to the rate of formation of  $\text{NO}_2$ ?
 
$$2\text{N}_2\text{O}_5(\text{g}) \text{-----} > 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$$
  - 1:4
  - 2:1
  - 4:1
  - 1:2

3. In the first order reaction, the concentration of the reactant is reduced to  $1/4^{\text{th}}$  in 60 minutes. What will be its half-life?  
 (a) 120 min (b) 40 min (c) 30 min (d) 25 min
4. Which of the following reaction ends in infinite time?  
 (a) Zero order (b) First order (c) Second order (d) Third order
5. The rate constant of a zero order reaction is-  
 (a) Directly proportional to initial concentration (b) Doesn't depend on concentration  
 (c) Inversely proportional to initial concentration (d) Can't say
6. The first order reaction takes 80 minutes to complete 99.9%. What will be its half-life?  
 (a) 8 min (b) 16 min (c) 24 min (d) 32 min
7. A catalyst increases the reaction rate by:  
 (a) decreasing enthalpy (b) increasing internal energy  
 (c) decreasing activation enthalpy (d) increasing activation enthalpy
8. Chemical kinetics is the study to find out:  
 (a) The feasibility of a chemical reaction (b) Speed of a reaction  
 (c) Extent to which a reaction will proceed (d) All of the above
9. The rate of a reaction:  
 (a) Increases as the reaction proceeds (b) Decreases as the reaction proceeds  
 (c) Remains the same as the reaction proceeds (d) May increase or decrease as the reaction proceeds
10. Which of the following influences the reaction rate performed in a solution?  
 (a) Temperature (b) Activation energy (c) Catalyst (d) All of the above

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ANSWERS – 1.(a) 2.(d), 3.(c), 4.(b), 5.(a), 6.(a), 7.(c), 8.(d), 9.(d), 10.(d)

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### ASSERTION- REASON TYPE QUESTIONS

Read the statements given as assertion & reason both and choose the correct option as (A)/(B)/(C)/(D) as per the following instructions.

Choose (A) – if both assertion & reason are correct statements and reason is the correct explanation of assertion.

Choose (B) - if both assertion & reason are correct statements and reason is not the correct explanation of assertion.

Choose (C) – if assertion is the correct statement & reason is incorrect statement.

Choose (D) – if assertion is incorrect statement and reason is the correct statement.

(4) ASSERTION – Order of reaction can be zero or fractional.

REASON – Order of a reaction cannot be determined from a balanced chemical reaction.

(5) ASSERTION – Order and molecularity of a reaction is always same.

REASON – Order is determined experimentally whereas molecularity by a balanced elementary reaction.

(6) ASSERTION – Rate constant of a zero order reaction has the same unit as the rate of a reaction.

REASON – Rate constant of a zero order reaction does not depend upon the concentration of the reactant.

(7) ASSERTION – In a first order reaction, the concentration of the reactant is doubled, its half-life is also doubled.

REASON – Half-life of a reaction does not depend upon initial concentration of the reactant in a first order reaction.

(8) ASSERTION – Average rate and instantaneous rate of a reaction has the same unit.

REASON – Average rate becomes instantaneous rate when time interval is too small.

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ANSWERS – 1- (B), 2-(D), 3-(A), 4-(D), 5- (B)

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## CASE STUDY QUESTION

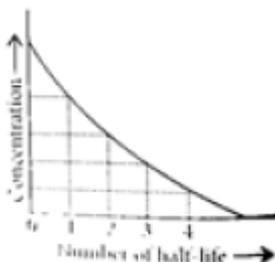
1. The half-life of a reaction is the time required for the concentration of reactant to decrease by half,

i.e.,  $[A]_t = [A]/2$

For first order reaction,

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

This means  $t_{1/2}$  is independent of initial concentration. Figure shows that typical variation of concentration of reactant exhibiting first order kinetics. It may be noted that though the major portion of the first order kinetics may be over in a finite time, but the reaction will never cease, as the concentration of reactant will be zero only at infinite time.



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

(i) A first order reaction has a rate constant  $k=3.01 \times 10^{-3} /s$ . How long it will take to decompose half of the reactants

- (a) 2.303 s      (b) 23.03 s      (c) 230.23 s      (d) 2303 s

(ii) The rate constant for a first order reaction is  $7.0 \times 10^{-4} s^{-1}$ . If initial concentration of reactant is 0.080 M, what is the half-life of reaction?

- (a) 990 s   (b) 79.2 s      (c) 12375 s      (d)  $10.10 \times 10^{-4} s$

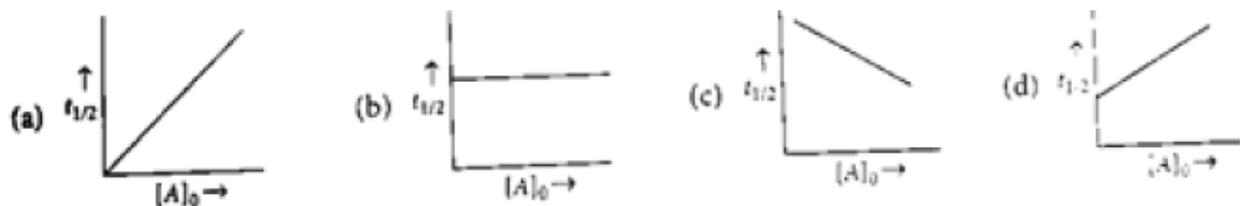
(iii) For the half-life period of a first order reaction, which one of the following statements is generally false?

- a) It is independent of initial concentration.      b) It is independent of temperature.  
c) It decreases with the introduction of a catalyst.      d) None of these.

(iv) The rate of a first order reaction is  $0.04 \text{ mol L}^{-1} \text{ s}^{-1}$  at 10 minutes and  $0.03 \text{ mol L}^{-1} \text{ s}^{-1}$  at 20 minutes after initiation. The half life of the reaction is

- a) 4.408 min      b) 44.086 min      c) 24.06 min      d) 2.408 min

(v) The plot of  $t_{1/2}$  vs initial concentration  $[A]_0$  for a first order reaction is given by



**Answers:**      (i) c      (ii) a      (iii) c      (iv) c      (v) b

**2. Chemical kinetics:** The branch of physical chemistry that is concerned with understanding the rates of chemical reactions. It is to be contrasted with thermodynamics which deals with the direction in which a process occurs but in itself tells nothing about its rate. Thermodynamics is time's arrow while chemical kinetics is time's clock. Chemical kinetics relates to many aspects of cosmology, geology, biology, engineering and even psychology and thus has far-reaching implications. The principles of chemical kinetics applied to purely physical processes as well as to chemical reactions.

The rate of a chemical reaction is defined in terms of the rates with which the products are formed and the reactants (the reacting substances) are consumed. For chemical systems, it is usual to deal with the concentrations of substances, which is defined as the amount of substances per unit volume. The rate can then be defined as the concentration of a substance that is consumed or produced in unit time. Sometimes it is more convenient to express rates as number of molecules formed or consumed in unit time.

READ THE STATEMENTS GIVEN AS ASSERTION & REASON BOTH AND CHOOSE THE CORRECT OPTION AS (A)/(B)/(C)/(D) AS PER THE FOLLOWING INSTRUCTIONS.

Choose (A) – if both assertion & reason are correct statements and reason is the correct explanation of assertion.

Choose (B) - if both assertion & reason are correct statements and reason is not the correct explanation of assertion.

Choose (C) – if assertion is the correct statement & reason is incorrect statement.

Choose (D) – if assertion is incorrect statement and reason is the correct statement.

1. Assertion: All collisions of reactant molecules do not lead to product formation.

Reason: Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

2. Assertion: The enthalpy of reaction remains constant in the presence of a catalyst

Reason: A catalyst lowers down the activation energy but the difference in energy of reactant and product remains same.

3. Assertion: The rate of reaction is the rate of change of concentration of a reactant or product.

Reason: The rate of reaction remains constant during the course of a reaction.

4. Assertion: Instantaneous rate is used to predict the rate of reaction at a particular moment.

Reason: Average rate is constant for the time interval for which it is calculated.

**Answers**      1. A      2. A      3. C      4. B

### VERY SHORT ANSWER TYPE QUESTIONS (1 MARK)

a) What is the effect of adding a catalyst on :

- (c) Activation energy ( $E_a$ ) and      (b) Gibbs energy ( $\Delta G$ ) of a reaction.

- Ans – (a)  $E_a$  decreases (b) Gibbs energy doesn't change.
- b) What is the order of reaction whose rate constant has the same unit as the rate of reaction?  
Ans – Zero order reaction
- c) What is the overall order of reaction which has the rate expression  $r = k [A]^2[B]^0$ ?  
Ans –  $2 + 0 = 2^{\text{nd}}$  order reaction
- d) Unit of 1<sup>st</sup> order reaction and pseudo 1<sup>st</sup> order reaction is same. This statement is true or not.  
Ans – True
- e) If a 1<sup>st</sup> order reaction takes 90 minutes for 75% completion. What will be its half-life?  
Ans - 45 minutes.
- f) A reaction is 2<sup>nd</sup> order in A. How is the rate affected if the concentration of A is doubled?  
Ans – rate of reaction becomes quadruples.
- g) How is the rate constant affected when temperature is raised by 10<sup>0</sup>C?  
Ans – Generally the rate constant becomes doubled.
- h) Define the term instantaneous rate of reaction.  
Ans – The change in conc of either reactants or products when time interval is taken as zero.
- i) How the half-life of a reaction varies with change in initial concentration of a reactant?  
Ans –  $t_{1/2} \propto [R]^{1-n}$ , where n is the order of reaction.
- j) What is the unit of rate constant of a 3/2 order reaction?  
Ans –  $\text{mol}^{-1/2} \text{L}^{1/2} \text{s}^{-1}$

### SHORT ANSWER TYPE QUESTIONS (2/3 MARK)

- a) In a reaction  $2A \rightarrow B$ , the concentration of A decreases from 0.5 M to 0.4 M in 10 minutes. Calculate the rate during this time interval.  
Ans – rate =  $-1/2 \Delta[A]/\Delta t$ , =  $- [0.40-0.50]/10$ , =  $0.01 \text{ mol l}^{-1} \text{ s}^{-1}$
- b) The rate constant of a first order reaction is  $60 \text{ S}^{-1}$ . How much time it will take to reduce the concentration of the reactant to  $1/10^{\text{th}}$  of its initial value?  
Ans –  $t = 2.303/k \log [R]_0/[R]$ , =  $2.303/60 \log 10$ , =  $3.8 \times 10^{-2}$  seconds.
- c) A 1<sup>st</sup> order reaction has the rate constant  $k = 5.5 \times 10^{-12} \text{ S}^{-1}$ . Find its half-life.  
Ans –  $t_{1/2} = 0.693/k$ , =  $0.693/ 5.5 \times 10^{-12}$ , =  $1.3 \times 10^{-11}$  sec.
- d) Show that a 1<sup>st</sup> order reaction takes 10 times more time to complete 99.9% reaction than its half-life.  
Ans –  $t_{1/2} = 0.693/k$   
Find  $t_{99.9} = 2.303/k \log 100/0.1$ , =  $2.303/k.3\log 10$ , =  $6.909/k$   
Compare  $t_{1/2}$  &  $t_{99.9}$  we get  $t_{99.9} = t_{1/2} \times 10$

e) The decomposition of  $\text{NH}_3$  on Pt surface is a zero order reaction. What are the rate of formations of  $\text{N}_2$  &  $\text{H}_2$  if  $k = 2.5 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$ .

Ans – rate of formation of  $\text{N}_2 = 2.5 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$  &  
rate of formation of  $\text{H}_2 = 7.5 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$

f) A 1<sup>st</sup> order reaction is 40% complete in 50 minutes. Calculate the value of rate constant. At what time will the reaction be 80% completed?

Ans – find  $k$  by taking values  $a = 100$  &  $a-x = 60$  i.e.  $= 0.01028 \text{ min}^{-1}$  and then using this value of  $k$ , find the time when the reaction will complete 80%, i.e.  $= 156.52 \text{ min}$ .

### 5 MARKS QUESTION

1. (a) The half-life for radioactive decay of  $^{14}\text{C}$  is 5730 years. An archaeological artifact containing wood had only 80% of the  $^{14}\text{C}$  found in a living tree. Estimate the age of the sample.

(b) A reaction is first order in A and second order in B.

Write the differential rate equation.

How is the rate affected on increasing the concentration of B three times?

How is the rate affected when the concentrations of both A and B are doubled?

Ans. (a) Given  $t_{1/2} = 5730$  years,  $[\text{R}]_0 = 100$ ,  $[\text{R}] = 80$

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

$$t = (2.303/K) \log[\text{R}]_0 / [\text{R}] = (2.303/1.21 \times 10^{-4}) \log 100/80 = (1.9033 \times 10^4)(\log 100 - \log 80)$$

$$= 1.9033 \times 10^{-4} (2 - 1.9031) = 1.9033 \times 10^{-4} (0.0969) = 1845 \text{ year}$$

(b) (i) Rate =  $K[\text{A}]^1 [\text{B}]^2$

(ii) Rate =  $K[\text{A}]^1 [3\text{B}]^2 = 9K[\text{A}]^1 [\text{B}]^2$  hence, it becomes 9 times.

(iii) Rate =  $K[2\text{A}]^1 [2\text{B}]^2 = 8K[\text{A}]^1 [\text{B}]^2$  hence, it becomes 8 times.

2. In a reaction between A and B, the initial rate of reaction ( $r_0$ ) was measured for different initial concentrations of A and B as given below:

A / mol L <sup>-1</sup>	0.20	0.20	0.40
B / mol L <sup>-1</sup>	0.30	0.10	0.05
$r_0$ / mol L <sup>-1</sup> s <sup>-1</sup>	$5.07 \times 10^{-5}$	$5.07 \times 10^{-5}$	$1.43 \times 10^{-4}$

What is the order of the reaction with respect to A and B?

<p><b>Ans.</b> Let the order of the reaction with respect to A be <math>x</math> and with respect to B be <math>y</math>.</p> <p>Therefore, <math>r_0 = k[A]^x[B]^y</math></p> <p><math>5.07 \times 10^{-5} = k[0.20]^x[0.30]^y</math> .....(i)</p> <p><math>5.07 \times 10^{-5} = k[0.20]^x[0.10]^y</math> .....(ii)</p> <p><math>1.43 \times 10^{-4} = k[0.40]^x[0.05]^y</math> .....(iii)</p> <p>Dividing equation (i) by (ii), we obtain</p> $\frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{k[0.20]^x[0.30]^y}{k[0.20]^x[0.10]^y}$ $1 = \frac{[0.30]^y}{[0.10]^y}$ $\left(\frac{0.30}{0.10}\right)^0 = \left(\frac{0.30}{0.10}\right)^y$ <p><math>y = 0</math></p> <p>Continue in next column</p>	<p>Dividing equation (iii) by (ii), we obtain</p> $\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{k[0.40]^x[0.05]^y}{k[0.20]^x[0.30]^y}$ $\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{[0.40]^x}{[0.20]^x} \left[ \begin{array}{l} \text{Since } y = 0, \\ [0.05]^y = [0.30]^y = 1 \end{array} \right]$ $2.821 = 2^x$ <p><math>\log 2.821 = x \log 2</math> (Taking log on both sides)</p> $x = \frac{\log 2.821}{\log 2}$ <p><math>= 1.496</math>  <math>= 1.5</math> (approximately)</p> <p>Hence, the order of the reaction with respect to A is 1.5 and with respect to B is zero.</p>
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## 5. SURFACE CHEMISTRY

### IMPORTANT POINTS TO REMEMBER-

- (iii) The branch of chemistry deals with the surface phenomenon is called surface chemistry.
- (iv) Adsorption – The accumulation of species at the surface rather than in bulk of an adsorbent is called adsorption.
- (v) Desorption – Removal of adsorbed particles from the surface of an adsorbent is called desorption. It is essential so that the new reactant molecules can adsorb & reaction is going on.
- (vi) Sorption – Adsorption & absorption both take place simultaneously.
- (vii) Types of adsorption –
  - Physical adsorption – weak van-der Waal force involved, reversible, decreases with increase of temperature, enthalpy of adsorption is low.
  - Chemical adsorption – strong chemical bond involved, irreversible, first increases with increase of temperature and then decreases, enthalpy of adsorption is high.
- (viii) Adsorption isotherm – The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by a graph, called adsorption isotherm.
- (ix) Factors affecting adsorption:
  - (a) Increase with increase in surface area.
  - (b) Low temp is favorable for physical adsorption & high temp for chemical adsorption
  - (c) Increases with increase of pressure.
  - (d) Easily liquefiable gases are readily adsorbed.
- (x) Colloid – a heterogeneous system in which a substance is dispersed (1-1000nm size) in another substance called dispersion medium.
- (xi) Dialysis – process to remove the unwanted substances from a colloidal system using a membrane.
- (xii) Electro dialysis – when dialysis takes place in electrical field to remove ionic impurities.
- (xiii) Brownian movement- Zig-zag motion of colloidal particles is called Brownian movement.
- (xiv) Tyndall effect – scattering of beam of light by the colloidal particles is called Tyndall effect so that the path of the light becomes visible.

(xv) Electrophoresis – the movement of colloidal particles when an electric field is applied because the colloidal particles have charge.

(xvi) Peptization – converting a freshly prepared precipitate into a colloidal solution using a suitable electrolyte called peptizing agent, is called peptization.

(xvii) Coagulation – process of setting colloidal particles using various methods (heating, shaking or an electrolyte is added) is called coagulation. The electrolyte used for the coagulation a colloid is called coagulating agent.

(xviii) Hardy Schulz rule – the coagulating or flocculating power of an ion is directly proportional to the charge on the ion. More charge – more coagulating power.

$\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$  - for coagulating negatively charged colloids.

$\text{Cl}^- < \text{SO}_4^{2-} < \text{PO}_4^{3-}$  for coagulating positively charged colloids.

(xix) A potential develops between fixed layer and diffused layer in a colloidal system is called ZETA potential.

### **1. VERY SHORT ANSWERS TYPE QUESTIONS (1 mark each)**

i) What are the appropriate conditions favorable for physical adsorption?

Ans- Low T, high P & greater surface area.

ii) What happens when a freshly prepared precipitate of  $\text{Fe}(\text{OH})_3$  is treated with  $\text{FeCl}_3$  solution in water?

Ans- Peptization takes place.

iii) In chemisorption, enthalpy of adsorption is high. Give reason.

Ans- Due to chemical bond formation between adsorbent & adsorbate.

iv) What is the charge on AgI colloidal sol formed when  $\text{AgNO}_3$  is added to excess of KI?

Ans- Negative charge  $\text{AgI/I}^-$

v) What are the main reasons for the stability of colloidal sol?

Ans- Charge on colloidal particles and Brownian movement.

vi) Write the dispersed phase and dispersion medium of milk.

Ans – Both are liquids. (Milk is a type of emulsion)

vii) Write one similarity in between Physisorption & Chemisorption.

Ans - Both are exothermic processes and surface phenomenon.

viii) What is protective colloid?

Ans – Lyophilic colloids which protect the lyophobic colloids from coagulation are called protective colloids.

ix) What is coagulation?

Ans – Precipitation of colloidal particles is called coagulation. It is the reverse process of peptization.

x) Colloids can exhibit Tyndall effect. Why?

Ans – Sufficient size of colloids can scatter the beam of light.

### **2. SHORT ANSWERS TYPE QUESTIONS (2 marks each)**

(a) Compare lyophilic and lyophobic sols. (any two points)

Ans – Lyophilic sols form easily and more stable whereas lyophobic sols form with mechanical or chemical efforts and less stable.

(b) Explain the effect of temperature on physical and chemical adsorption.

Ans – Physical adsorption decreases with increase of temperature whereas chemical adsorption first increases and then decreases with temperature.

(c) Why is adsorption always exothermic?

Ans - because the force of attraction (physical or chemical) increases when particles of a dispersed phase are adsorbed on the surface of dispersion medium and we know that whenever force of attraction increases the certain amount of energy is released.

(d) How is Multimolecular and associated colloids different?

Ans – Multimolecular colloids means the aggregation of molecules whereas associated colloids means the aggregation of ions, act as colloids. Ex Sulphur sol is the example of Multimolecular colloids and micelle is the example of associated colloids.

(e) What is meant by adsorption isotherm? Write equations for the adsorption of gases on solid surface and adsorption from solutions.

Ans – Adsorption isotherm is the graphical representation to show effect of pressure or concentration of a solution on rate of adsorption at constant temperature.

$x/m = k \cdot p^{1/n}$  (for gas) &  $x/m = k \cdot C^{1/n}$  (for solution)

### **3. SHORT ANSWERS TYPE QUESTIONS (3 marks each)**

1. List any three point of difference between Physical & Chemical adsorption.

REFER NCERT TEXT BOOK PAGE 124 TABLE 5.1

2. Give reason –

- Finally divided substance is more effective as an adsorbent.
- Physical adsorption is reversible whereas chemical adsorption is irreversible.
- Lyophilic sols protect lyophobic sols from coagulation.

Ans - (a) Increase of surface area.

(b) Physical adsorption is caused by weak van der Waals forces whereas chemical adsorption is caused by formation of bonds.

(c) By forming a protective layer around the lyophobic sol particles.

3. What happens when-?

- A beam of light is passed through a colloidal sol.
- An electrolyte NaCl is added to hydrated ferric oxide sol.
- Electric current is passed through a colloidal sol.

Ans – (a) Path of light becomes visible due to Tyndall effect.

(b) Coagulation of sol takes place.

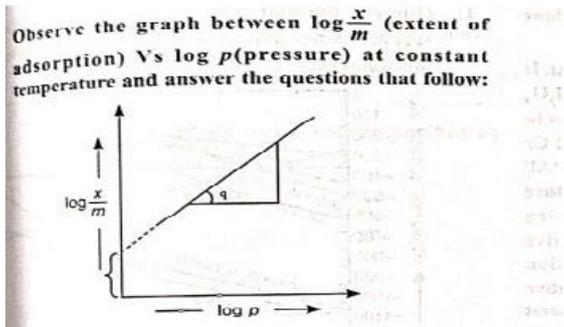
(c) Colloidal particles having charge so they move towards opposite charged electrode.

### **4. CASE STUDY BASED QUESTION (5 MARKS EACH)**

1. Read the passage carefully and observe the graph then give the answers of questions (a) to (e).

The **Freundlich equation** or **Freundlich adsorption isotherm**, an adsorption isotherm, is an empirical relationship between the quantity of a gas adsorbed into a solid surface and the gas pressure. The same relationship is also applicable for the concentration of a solute adsorbed onto the surface of a solid and the concentration of the solute in the liquid phase. In 1909, Herbert Freundlich gave an expression

representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with gas pressure.<sup>[1]</sup> This equation is known as Freundlich adsorption isotherm or Freundlich adsorption equation. As this relationship is entirely empirical, in the case where adsorption behavior can be properly fit by isotherms with a theoretical basis, it is usually appropriate to use such isotherms instead (see for example the Langmuir and BET adsorption theories). The Freundlich equation is also derived (non-empirically) by attributing the change in the equilibrium constant of the binding process to the heterogeneity of the surface and the variation in the heat of adsorption.<sup>[2]</sup>



- What value is shown by  $x/m$  in the graph?
- What is the slope of this graph? What is the range of slope?
- What does the intercept of line represent?
- Write the logarithmic representation of this graph.
- What modification is made during adsorption from a solution by a solid adsorbent?

Ans – (a) rate of adsorption

(b)  $1/n$  and its value is ranging between 0-1

(c)  $\log k$  where  $k$  is a constant and its value depends upon nature of adsorbate & adsorbent.

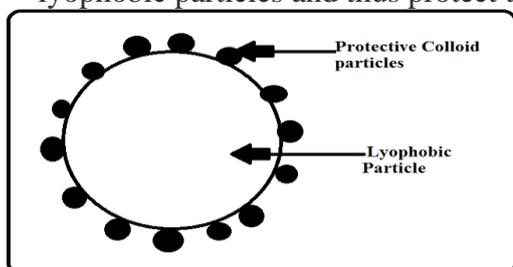
d)  $\log x/m = \log k + 1/n \log p$

e) Concentration is taken into consideration in place of pressure.

## 2. READ THE PASSAGE BELOW AND GIVE THE ANSWERS OF QUESTIONS FOLLOWED.

We should know that a protective colloid is a lyophilic colloid that when present in small quantities keeps lyophobic colloids from precipitating under the coagulating action of electrolytes. We should know that lyophilic sols are more stable than lyophobic sols. It is due to the fact that lyophilic colloids are extensively solvated that means colloidal particles are covered by a sheath of the liquid in which they are dispersed.

It is interesting to know that lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect the latter from electrolytes.



Lyophilic colloids used for this purpose are called protective colloids. Some examples of protective colloids that we should remember are mentioned below along with their gold number. Knowledge of the gold number is important.

We should know that Gold Number is the number of milligrams of a protective colloid which prevents the coagulation of 10 ml of a standard hydro gold sol, on coagulation changes from red to blue, which is prevented by a protective colloid. Coagulation of gold sol is indicated by colour change from red to blue/purple when particle size just increases.

We should know that more is the gold number; less is the protective power of the lyophilic colloid since it means that the amount required is more. The amount is taken in terms of weight in milligrams.

Starch (gold no. =25), Gum Arabic (gold no. =0.15), Egg albumin (gold no. =0.08)

Gelatin (gold no.=0.005)

- (a) If water is a dispersion medium then the sols are called ----- & -----.
- (b) Which one from the given is the best protective colloid?
- (c) How is the protective power of a lyophilic colloid related with the Gold Number?
- (d) Lyophobic sols are more stable and therefore no protection is required at all. This statement is TRUE or FALSE.
- (e) How does an electrolyte coagulate the lyophobic sols?

Ans – (a) Hydrophilic & Hydrophobic

(b) Gelatin

(c) Less Gold Number, more protective power.

(d) FALSE

(e) Oppositely charged ion of the electrolyte neutralizes the charge of sol particles and coagulate.

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## 8. The d & f Block Elements

### SUMMARY

The d-block of the periodic table contains the elements of the groups 3-12 in which the d-orbitals are progressively filled. There are mainly three series of the elements, 3d-series (Sc to Zn) 4d-series (Y to Cd) and 5d-series (La to Hg omitting Ce to Lu). The fourth 6d-series which begins with Ac is still incomplete. The two series of the inner-transition metals, (4f and 5f) are known as lanthanoids and actinoids respectively.

### CASE-BASED/PASSAGE-BASED INTEGRATED QUESTIONS

Read the given passage and answer the questions that follow:

(I) The d-block of the periodic table contains the elements of the groups 3 to 12 and are known as transition elements. In general, the electronic configuration of these elements is  $(n-1)d^{1-10}ns^{1-2}$ . The d-orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals i.e., 3d, 4d and 5d series. However, Zn, Cd and Hg are not regarded as transition elements. Transition elements exhibit certain characteristic properties like variable oxidation states, complex formation, formation of coloured ions, alloys, catalytic activity etc. Transition metals are hard (except Zn, Cd and Hg) and have a high melting point.

(a) Why are Zn, Cd and Hg non-transition elements?

Ans. It is because neither they nor their ions have incompletely filled d-orbitals.

(b) Which transition metal of 3d series does not show variable oxidation state?

Ans. Scandium (Sc) and Zinc (Zn).

(c) Why do transition metals and their compounds show catalytic activity?

Ans. It is because they show variable oxidation state, can form intermediate complexes and have large surface area for adsorption of gases.

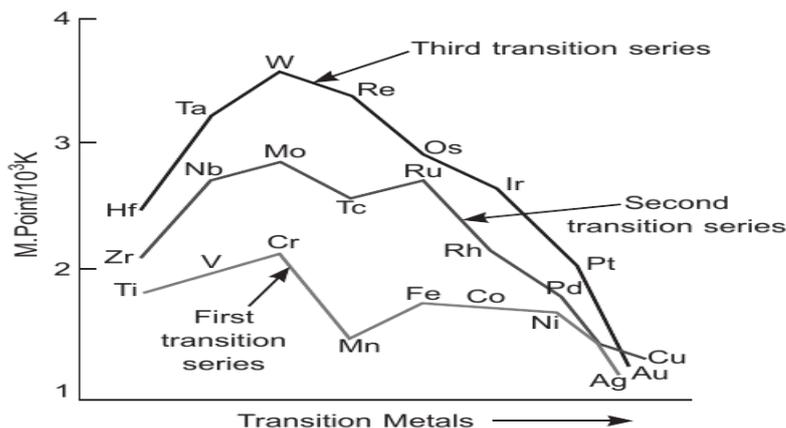
(d) Why are melting points of transition metals high?

Ans. It is due to strong inter atomic forces of attraction due to presence of unpaired electrons.

(e) Why is  $Cu^{2+}$  ion coloured while  $Zn^{2+}$  ion is colourless?

Ans. It is because  $Cu^{2+}$  has one unpaired electron and undergoes d-d transition by absorbing light from visible region and radiate blue colour, whereas  $Zn^{2+}$  is colourless due to absence of unpaired

(II) Observe the graph of transition metal and their melting points and answer the questions based on weak metallic bond which is due to absence of the graph and related concepts.



(a) Why does W (tungsten) has highest melting colourless in aqueous solution?

Ans. It is due to presence of unpaired electrons and there is more frequent metal-metal bonding in 5d series than 3d and 4d series.

(b) Which element in 3d series has lowest enthalpy of atomization and why?

Ans. Zinc has lowest enthalpy of atomization due to weak metallic bond which is due to absence of unpaired electrons.

(c) Why is mercury liquid?

Ans. It is due to larger size, absence of unpaired electron and weak inter atomic attraction and weaker metallic bond.

(d) Why are transition metals less electro positive?

Ans. It is due to smaller atomic size and higher ionization enthalpies.

(e) How does density vary from left to right in 3dseries and why?

Ans. Density goes on increasing from Sc to Cu because atomic mass increases more than atomic volume.

**(III) Observe the table given below belonging to 3d series, their first, second, third ionization enthalpy and  $E^\circ M^{2+}/M$  and  $E^\circ M^{3+}/M^{2+}$  and answer the questions that follow based on table and related concepts.**

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I <sup>st</sup> ionisation enthalpy	631	656	650	652	717	762	758	736	745	905 kJ ml <sup>-1</sup>
II <sup>nd</sup> ionisation enthalpy	1245	1320	1376	1635	1513	1564	1648	1757	1962	1736
III <sup>rd</sup> ionisation enthalpy	2451	2721	2874	2995	3258	2964	3238	3401	3561	3839
$E^\circ_{M^{2+}/M}$ in volts	-	-1.63V	-1.18V	-0.91V	-1.18V	-0.44V	-0.28V	-0.25V	+0.34V	-0.76V
$E^\circ_{M^{3+}/M^{2+}}$ in volts	-	-0.37V	-0.26V	-0.41V	+1.57V	+0.77V	+1.97V	-	-	-

(a) Why does zinc have highest first ionization enthalpy?

Ans. It is because Zn has completely filled '4s' orbital which is stable.

(b) Why is 3<sup>rd</sup> ionization enthalpy of Mn high?

Ans. It is because after losing 2 electrons, it becomes 3d<sup>5</sup> which is more stable.

(c) Why is  $\text{Cr}^{3+}$  more stable than  $\text{Cr}^{2+}$ ?

Ans. It is because  $\text{Cr}^{3+}(t_{2g}^3)$  half-filled orbitals are more stable than  $\text{Cr}^{2+}(3d^4)$ .

(d) Why is  $E^\circ \text{Mn}^{2+}/\text{Mn} = -1.18\text{V}$ ?

Ans. It is due to low enthalpy of atomization, sublimation enthalpy, ionization enthalpy.

(e) Why is  $E^\circ \text{Cu}^{2+}/\text{Cu} = +0.34\text{V}$ ?

Ans. It is due to high ionization enthalpy and low hydration enthalpy.

(f) Why is  $\text{Fe}^{3+}$  more stable than  $\text{Fe}^{2+}$ ?

Ans.  $\text{Fe}^{3+}(3d^5)$  is half filled which is more stable than  $\text{Fe}^{2+}(3d^6)$ .

(g) Why is  $\text{Mn}^{3+}$  good oxidizing agent and  $E^\circ \text{Mn}^{3+}/\text{Mn}^{2+} = 1.57\text{V}$ ?

Ans It is because it can gain one electron easily to form  $\text{Mn}^{2+}(3d^5)$  which is more stable that is why  $E^\circ \text{Mn}^{3+}/\text{Mn}^{2+} = 1.57\text{V}$

### Multiple Choice Questions-

1. Which of the following statement about transition element is not correct?

- (a) They show variable oxidation states.
- (b) They exhibit diamagnetic and paramagnetic properties.
- (c) All ions are coloured
- (d) They exhibit catalytic property.

Ans – (c)

2.The magnetic moment is associated with its spin angular momentum and orbital angular momentum.

Spin only magnetic moment value of  $\text{Cr}^{3+}$  ion is

- (a) 2.87 B.M.
- (b) 3.87 B.M.
- (c) 3.47 B.M
- (d) 3.57 B.M

Ans – (b)

3. Manganese exhibits maximum oxidation state in:

- (a)  $\text{K}_2\text{MnO}_4$
- (b)  $\text{KMnO}_4$
- (c)  $\text{MnO}_2$
- (d)  $\text{Mn}_3\text{O}_4$

Ans – (b)

4.Electronic configuration of a transition element X in +3 oxidation state is  $[\text{Ar}]3d^5$ . What is its atomic number?

- (a) 25
  - (b) 26
  - (c) 27
  - (d) 24
- Ans – (b)

5.Metallic radii of some transition elements are given below. Which of these elements will have highest density?

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

(a) Fe      (b) Ni      (c) Co      (d) Cu      Ans – (d)

### ASSERTION -REASONING QUESTIONS

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

(B) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(C) Assertion is correct, but reason is wrong statement.

(D) Assertion is wrong, but reason is correct statement.

1. Assertion: Manganese has an exceptionally low melting point in 3d series.

Reason: Manganese has weak metallic bonds due to electronic repulsion. Ans (C)

2. Assertion: Scandium does not show variable oxidation state.

Reason: Scandium has only one electron in the 3d orbital. Ans (B)

3. Assertion:  $\text{Fe}^{2+}$  readily oxidizes to  $\text{Fe}^{3+}$  in solution.

Reason:  $\text{Fe}^{3+}$  has a stable  $d^5$  configuration. Ans (A)

4. Assertion: Zirconium and Hafnium have similar properties.

Reason: Zirconium and Hafnium lie in the same group of the periodic table. Ans (B)

5. Assertion: Highest oxidation states of d-block metals are usually seen in oxides and oxo anions.

Reason: Oxygen is capable of forming  $p\pi - d\pi$  bonds with transition metals. Ans (A)

6. Assertion: Zn, Cd and Hg cannot be regarded as transition elements.

Reason: These elements do not belong to d-block of the periodic table. Ans (C)

7. Assertion: Misch metal is a pyrophoric alloy.

Reason: Misch metal is prepared from lanthanoids. Ans (B)

8. Assertion: Transition metals show very low degree of para magnetism.

Reason: Transition metal atoms have large number of unpaired electrons. Ans (D)

9. Assertion: Potassium permanganate is a good oxidizing agent in acidic medium.

Reason: Permanganate readily reduces to manganese dioxide in acidic medium. Ans(C)

10. Assertion: Transition metals have high enthalpy of atomization.

Reason: d-block elements have strong metallic bonds. Ans (A)

### ONE MARK QUESTION

1. Zinc, cadmium and mercury are not considered as transition metals. Why?

Ans. Zinc, cadmium and mercury have fully filled  $d^{10}$  configuration. Therefore, they are not considered as transition metal.

2. Write the general configuration of d- block elements.

Ans. General electronic configuration of d- block elements is  $(n-1)d^{1-10} ns^{1-2}$ .

3. Transition metals generally form coloured ions. Why?

Ans. Due to presence of unpaired electron, crystal field splitting & d-d transition.

4. Which of the following will be coloured?

$\text{Sc}^{3+}$ ,  $\text{V}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Ni}^{2+}$ .

Ans Coloured ions will be those which have unpaired electrons

**Sc<sup>3+</sup>** Colourless

**V<sup>2+</sup>** Coloured

**Mn<sup>2+</sup>** Coloured

**Cu<sup>+</sup>** Colourless

**Ni<sup>2+</sup>** Coloured

5. Give an explanation for the catalytic properties shown by transition metals.

Ans. Because of multiple oxidation state / ability to form complex / having large surface area.

6. Why transition metals form large number of interstitial compounds?

Ans. Because small non-metallic atoms (H, B, C, N etc) are able to fit in the interstitial sites of transition metal lattice to form interstitial compounds.

7. Why do transition elements shows variable oxidation states?

Ans –Due to participation of (n-1) d and ns electron in bond formation.

8. Name a transition element which does not exhibit variable oxidation states.

Ans- Scandium.

9. Which of the 3d series of the transition metals exhibits the largest number of oxidation states and Why?

Ans – In 3d series Mn shows the highest oxidation state of +7 as it has maximum no. of unpaired e- .

10. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

Ans – Oxygen and fluorine have small size and high electro negativity. Hence, they can oxidize the metal to the highest oxidation state.

### TWO MARKS QUESTION

1.  $\text{Cu}^+$  is not stable in aqueous solution. Why?

Ans- Many Cu(I) compounds are unstable in aqueous solution and undergo disproportionate.



The stability of  $\text{Cu}^{2+}$  rather than  $\text{Cu}^+$  is due to more –ve hydration enthalpy of  $\text{Cu}^{2+}$  than  $\text{Cu}^+$  which is much more and compensate for the II ionization enthalpy.

2. Which is the stronger reducing agent  $\text{Cr}^{2+}$  or  $\text{Fe}^{2+}$  and why?

Ans  $\text{Cr}^{2+}$  is the stronger reducing agent because in case of  $\text{Cr}^{2+}$  to  $\text{Cr}^{3+}$  change in configuration is from  $d^4$  to  $d^3$  and in  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  the change is from  $d^6$  to  $d^5$ . In medium like water  $d^3$  is more stable as compared to  $d^5$  due to half- filled  $t_{2g}$  configuration.

3.  $\text{Co}^{2+}$  is stable in aqueous solution but in the presence of complexing agent, it is easily oxidized. Why?

Ans-In the presence of complexing agent, oxidation state of Co changes from +2 to +3 due to CFSE which is more and compensate the  $\Delta_i H_3$ .

4.  $E^0$  for  $\text{Mn}^{3+}/\text{Mn}^{2+}$  is more positive than for  $\text{Fe}^{3+}/\text{Fe}^{2+}$ . Why?

Ans.  $\text{Mn}^{3+}$  has the configuration  $3d^4$  while that of  $\text{Mn}^{2+}$  is  $3d^5$ . So  $\text{Mn}^{3+}$  easily undergo reduction to  $\text{Mn}^{2+}$  having stable  $3d^5$  configuration resulting in higher value of standard reduction potential.

$\text{Fe}^{3+}$  is more stable than  $\text{Fe}^{2+}$  because of having  $3d^5$  configuration and reduction to  $\text{Fe}^{2+}$  will not be easy resulting in the decreased value of  $E^0$ .

5. The highest oxidation state is exhibited in oxo-anions of a transition metal and not in metal fluorides. Suggest a reason.

Ans. The ability of oxygen to stabilize these high oxidation states exceeds that of fluorine due to ability of oxygen to form multiple bonds to metals Thus the highest Mn fluoride is  $\text{MnF}_4$  whereas the highest oxide is  $\text{Mn}_2\text{O}_7$ .

6.  $\text{Ce}^{4+}$  is a good oxidizing agent and  $\text{Eu}^{2+}$  is a good reducing agent. Why?

Ans. The most stable oxidation state in lanthanoids is +3 and all lanthanoids try to attain it.

Thus,  $\text{Ce}^{4+}$  will easily accept an electron i.e. get reduced thus behaving like a good oxidizing agent. The opposite applies to  $\text{Eu}^{2+}$  which loses an electron to attain +3 oxidation state behaving as a good reducing agent.

7. Explain 'Misch metal' and write its use.

Ans. It is an alloy of 95% Lanthanoid and 5% iron and traces of S, C, Ca and Al. Used in lighter flint, bullet tips etc.

8. What is the General electronic configuration and common oxidation state of Lanthanoids?

Ans. General electronic configuration =  $4f^{1-14} 5d^{0-1} 6s^2$  and common oxidation state +3.

### THREE MARKS QUESTION

1. Explain Lanthanoid contraction, its cause & consequence?

Ans. Lanthanoid contraction – The cumulative effect of the regular decrease in size or radii of Lanthanoid with increase in atomic number is called Lanthanoid contraction.

Causes – The shape of f orbitals is diffused. They have poor shielding effect due to which the effective nuclear charge increases with increase in atomic number. This causes a decrease in atomic radii

Consequences – Due to Lanthanoid contraction-

- Radii of the members of the third transition series is similar to those of second transition series.
- It becomes difficult to separate Lanthanoids.

2. Answer the following questions -

1. Why does copper not replace hydrogen from acids?

Ans. The unique behavior of Cu, having a positive  $E^0 = +0.34\text{V}$  accounts for its inability to liberate from acids.

2. Why  $E^0$  values for Mn, Ni and Zn are more negative than expected?

Ans. The stability of the half-filled d sub-shell in  $\text{Mn}^{2+}$  and the completely

filled  $d^{10}$  configuration in  $Zn^{2+}$  are related to their  $E^\circ$  values, whereas for Ni is related to the highest negative H.

3. Why first ionisation enthalpy of Cr is lower than that of Zn?

Ans. The value of first ionisation enthalpy of Cr is lower because of the absence of any change in the  $d$  configuration and the value for Zn is higher because it represents an ionisation from the  $4s$  level.

### FIVE MARKS QUESTIONS

1. Give reasons-

- (i) Transition metals have high melting points.
- (ii) Second and third transition series have similar radii.
- (iii) Second ionization is difficult from Cu and Cr whereas it is easy for Zn.
- (iv) Most of the transition elements are paramagnetic.
- (v) The  $d^1$  configuration is very unstable in ions. Why?

Ans (i) In transition metals besides  $ns$  electrons,  $(n-1) d$  electrons can also participate in bonding making stronger metallic bonds. This increases their melting points.

(ii) Due to Lanthanoid contraction, there is a decrease in size of  $5d$  series. This makes their sizes same as sizes of elements of  $4d$  series.

(iii) In Cr the electronic configuration is  $3d^5 4s^1$  and for Cu, it is  $3d^{10} 4s^1$ . In these after first ionization, which removes the electron from  $4s$ , second ionization requires disturbance in half filled or fully filled configuration which requires high enthalpy whereas the configuration of Zn is  $3d^{10} 4s^2$ . Here after second ionization, the configuration of Zn is completely filled. Therefore, second ionization is easier for Zn but difficult for Cr and Cu.

(iv) Para magnetism in transition elements arises due to presence of one or more unpaired electrons in atomic orbitals.

(v) The ions with  $d^1$  configuration have the tendency to lose the only electron present in  $d$ -subshell to acquire stable  $d^0$  configuration.

2. Mention the type of compounds formed when small atoms like H, C and N get trapped inside the crystal lattice of transition metals. Also give physical and chemical characteristics of these compounds.

Ans. Interstitial compounds are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non-stoichiometric and are neither typically ionic nor covalent. The principal physical and chemical characteristics of these compounds are as follows:

- (i) They have high melting points, higher than those of pure metals.
- (ii) They are very hard, some borides approach diamond in hardness.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert.

## **9. Coordination Compounds**

### **SUMMARY**

**Coordination compounds:** are those addition molecular compounds which retain their identity in solid state as well as in dissolved state. In these compounds the central metal atom or ion is linked by ions or molecules with coordinate bonds.  $K_4[Fe(CN)_6]$

**Double Salts:** These are the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution. e.g.,

Mohr's salt:  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  get dissociated into  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ions.

### **IMPORTANT TERMS:**

**1. Complex ion or Coordination Entity:** It is an electrically charged species in which central metal atom is surrounded by number of ions or neutral molecules.

(i) Cationic complex entity It is the complex ion which carries positive charge.

e.g.,  $[\text{Pt}(\text{NH}_3)_4]^{2+}$

(ii) Anionic complex entity It is the complex ion which carries negative charge.

e.g.,  $[\text{Fe}(\text{CN})_6]^{4-}$

**2. Central Atom or Ion :** The atom or ion to which a fixed number of ions or groups are bonded. It is also referred as Lewis acid. e.g., in  $[\text{NiCl}_2(\text{H}_2\text{O})_4]$ . Ni is central metal atom.

**3. Ligands :** Ligands is electron donating species (ions or molecules) bonded to the Central atom .These may be charged or neutral.

#### **Ligands are of the following types:**

(i) Unidentate It is a ligand, which has one donor atom. e.g.,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ .

(ii) Bidentate It is the ligand. which have two donor sites.  $\text{C}_2\text{O}_4^{2-}$

(iii) Polydentate It is the ligand, which have several donor sites.

e.g.,  $[\text{EDTA}]^{4-}$  is hexadentate ligand.

(iv) Ambidentate ligands- These are the monodentate ligands which can ligate through two different sites, e.g.  $\text{NO}_2^-$ ,  $\text{SCN}^-$ , etc.

(v) Chelating ligands- Di or polydentate ligands cause cyclisation around the metal atom

which are known as chelates, such ligands Uses two or more donor atoms to bind a single metal ion and are known as chelating ligands.

**4. Coordination Number:** It is defined as the number of coordinate bonds formed by central metal atom, with the ligands.

**5. Coordination Sphere:** The central ion and the ligands attached to it are enclosed in square bracket which is known as coordination sphere.

### **Colour in Coordination Compounds**

• In complex compounds d-orbitals split in two sets  $t_{2g}$  and  $e_g$ . These have different energies. The difference in energies lies in visible region and electron jump from ground state  $t_{2g}$  level to higher state  $e_g$  level. This is known as d-d transition and it is responsible for colour of coordination compounds.

• d-d transition takes place in  $d_1$  to  $d_9$  ions, so the ions having  $d_1$  to  $d_9$  configuration are coloured. On the other hand, the ions  $d_0$  and  $d_{10}$  configuration do not show d-d transition.

### **CASE-BASED/PASSAGE-BASED INTEGRATED QUESTIONS**

**I Read the given passage and answer the questions that follow:**

Complex compounds play an important role in our daily life. Werner's theory of complex compounds says every metal atom or ion has primary valency (oxidation state) which is satisfied by negatively charged ions which are ionisable whereas secondary valency (coordination number) is non-ionisable, satisfied by ligands (+ve / -ve/ neutral) but having lone pair. Primary valency is non-directional, secondary valency

is directional. Complex compounds are name according to IUPAC system. Valence bond theory helps in determining shapes of complexes based on hybridization, magnetic properties, outer or inner orbital complex. EDTA is used to treat lead poisoning, cis-platin as anticancer agents. Vitamin B<sub>12</sub> is complex of cobalt. Hemoglobin, oxygen carrier is complex of Fe<sup>2+</sup> and chlorophyll essential for photosynthesis is complex of Mg<sup>2+</sup>.

**Questions:**

(a) What is the oxidation state of Ni in [Ni(CO)<sub>4</sub>]?  
 Ans. Zero

(b) One mole of CrCl<sub>3</sub> · 6H<sub>2</sub>O reacts with excess of AgNO<sub>3</sub> to yield 2 mole of AgCl.  
 Write formula of complex. Write IUPAC name also.

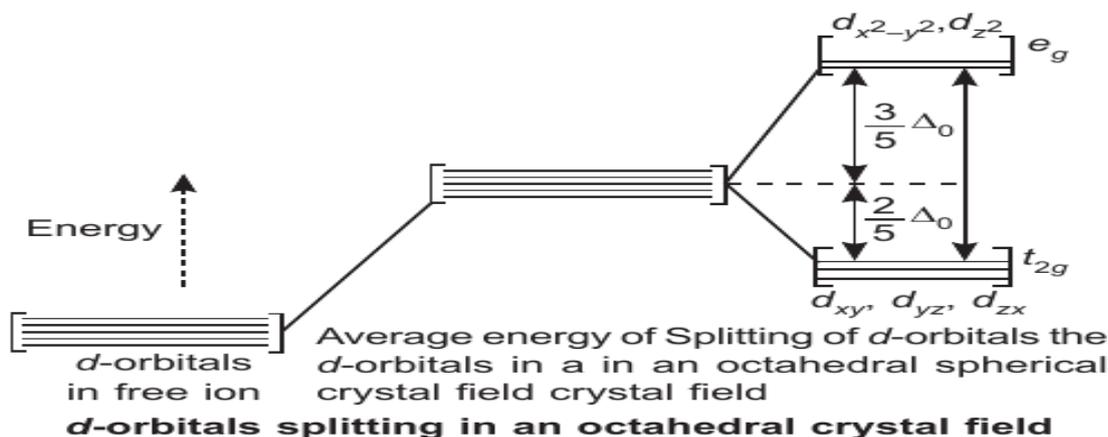
Ans. [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub> · H<sub>2</sub>O, Penta aqua chloride chromium (III) chloride

(c) Name the hexadentate ligand used for treatment of lead poisoning.  
 Ans. EDTA<sup>4-</sup> (ethylene diamine tetra acetate)

(d) What is hybridization of [CoF<sub>6</sub>]<sup>3-</sup>? [Co = 27] . Give its shape and magnetic properties. Ans. sp<sup>3</sup>d<sup>2</sup>, octahedral, paramagnetic. It is outer orbital complex.

(e) Out [Fe(CO)<sub>5</sub>], [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup>, [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, [Fe(CN)<sub>6</sub>]<sup>3-</sup> which is most stable?  
 Ans. [Fe(CO)<sub>5</sub>] is most stable because CO is strongest ligand.

**II Observe the diagram of splitting of d-orbitals in octahedral field and answer the questions based on the diagrams and related studied concepts.**



(a) What is crystal field splitting energy?

Ans : The energy difference between the two sets of d-orbitals is called crystal field splitting energy denoted by  $\Delta_0$

(b) Why  $dx^2-y^2$  ,  $dz^2$  have higher energy than  $dxy$ ,  $dyz$ ,  $dzx$  orbitals in octahedral crystal field?

Ans. The orbitals  $dx^2y^2$ ,  $dz^2$  lying in the direction of ligands, will experience greater repulsion and their

energies will be raised relative to their positions in symmetrical field as compared to orbitals  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  lying in between the axis away from the approach of ligand.

(c) What is relationship between (CFSE)  $\Delta_0$  and strength of ligand?

Ans. Greater the (CFSE)  $\Delta_0$ , more will be strength of ligand.

(d) What is electronic configuration of  $d^5$  ion if  $\Delta_0 < P$ ?

Ans.  $t_{2g}^3 e_g^2$

(e) What is spectrochemical series?

Ans. The series in which ligands are arranged in increasing order of magnitude of crystal field splitting energy ( $\Delta_0$ ) is called spectrochemical series.

### Assertion(A) and Reason Type Questions

In the following questions, a statement of Assertion(A) followed by a statement of Reason (R) is given. Choose the correct option out of the following choices.

- (a) Assertion(A) and Reason both are true, Reason is the correct explanation of Assertion (A).
- (b) Assertion(A) and Reason both are true but Reason is not the correct explanation of Assertion (A).
- (c) Assertion(A) is true, Reason is false.
- (d) Assertion(A) is false, Reason is true.

1. Assertion(A) (A): Toxic metal ions are removed by the chelating ligands.

Reason (R): Chelate complexes tend to be more stable.

Ans: (A)

2. Assertion(A) (A):  $(Fe(CN)_6)^{3-}$  ion shows magnetic moment corresponding to two unpaired electrons.

Reason (R): Because it has  $d^2sp^3$  type hybridization.

Ans: (D)

3. Assertion(A)(A) :  $[Co(NH_3)Br]SO_4$  gives white precipitate with barium chloride.

Reason(R): The complex dissociates in the solution to give  $Br^-$  and  $SO_4^{2-}$ .

Ans (C)

4. Assertion(A)(A) : Low spin tetrahedral complexes are not formed.

Reason(R): For tetrahedral complexes, CFSE is lower than pairing energy.

Ans : (A)

5. Assertion(A)(A): According to crystal field theory during complex formation, the d orbitals split and form two sets of orbitals  $t_{2g}$  and  $e_g$ .

Reason(R) Splitting of d – orbitals occurs only in case of strong field ligands.

Ans :(C)

6. Assertion(A)(A):  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  is  $\text{sp}^3\text{d}^2$  hybridized and paramagnetic complex ion.

Reason(R) : It has four unpaired electrons.

Ans: (A)

7. Assertion(A) :  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar.

Reason(R): It has no unpaired electrons.

Ans: (B)

8. Assertion(A) : Oxalate ion is a bidentate ligand.

Reason(R): Oxalate ion has two donor atoms .

Ans: (A)

9. Assertion(A) :  $[\text{Ni}(\text{CO})_4]$  has square planar geometry while  $[\text{Ni}(\text{CN})_4]^{4-}$  has tetrahedral geometry Reason(R):

Geometry of any complex depends upon the nature of ligands attached. Ans: (D)

10. Assertion(A) :  $[\text{FeF}_6]^{3-}$  is a low spin complex.

Reason(R): Low spin complexes have lesser number of unpaired electrons.

Ans: (D)

### MULTIPLE CHOICE QUESTIONS

1. When 0.1 mol  $\text{COCl}_2(\text{NH}_3)_5$  is treated with excess of  $\text{AgNO}_3$  ; 0.2 mol of  $\text{AgCl}$  are obtained. The conductivity of solution will correspond to-

(a) 1 : 3 electrolyte

(b) 1 : 2 electrolyte

(c) 1 : 1 electrolyte

(d) 3 : 1 electrolyte

Ans : (b)

2. The correct IUPAC name of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  is

(a) Diammine dichloride platinum (II)

(b) Diammine dichloride platinum (IV)

(c) Diammine dichloride platinum (0)

(d) Dimmine dichloride platinum (IV) Ans : (a)

3. This stabilisation of coordination compounds due to chelation is called the chelate effect.

Which of the following is the most stable complex species?

(a)  $[\text{Fe}(\text{CO})_5]$

(b)  $[\text{Fe}(\text{CN})_6]^{3-}$

(c)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3+}$

(d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

Ans : (c)

4. Indicate the complex ion which shows geometrical isomerism.

(a)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$

(b)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]$

(c)  $[\text{Pt}(\text{NH}_3)_6]^{3+}$

(d)  $[\text{Co}(\text{CN})_5(\text{NC})]^{3-}$

Ans : (c)

5. Which of the following is a complex of metal other than transition metal?

(a) Haemoglobin

(b) Chlorophyll

(c) Ferrocene

(d) Vitamin B<sub>12</sub>

Ans : (b)

6. Which of the following is not a double salt but a coordinate compound?

(a)  $\text{KCl.MgCl}_2.6\text{H}_2\text{O}$

(b)  $\text{FeSO}_4.(\text{NH}_4)_2\text{SO}_4.6\text{H}_2\text{O}$

(c)  $\text{K}_2\text{SO}_4.\text{Al}_2(\text{SO}_4)_3.24\text{H}_2\text{O}$

(d)  $4\text{KCN.Fe}(\text{CN})_2$

Ans : (d)

7. The donor atoms in ethylene diamine tetra acetate ion is

(a) two N and two O

(b) two N and four O

(c) four N and two O

(d) three N and three O

Ans : (b)

8. The complex ion  $[\text{Cu}(\text{NH}_3)_4]^{+2}$  is-
- (a) tetrahedral and paramagnetic      (b) tetrahedral and diamagnetic  
 (c) square planar and paramagnetic      (d) square planar and diamagnetic      **Ans : (c)**
9. The hybrid state of Co in high spin complex,  $\text{K}_3[\text{CoF}_6]$  is
- (a)  $\text{sp}^3 \text{d}^2$       (b)  $\text{sp}^3$   
 (c)  $\text{d}^2 \text{sp}^3$       (d)  $\text{sp}^3 \text{d}$       **Ans : (a)**
10. In an octahedral crystal field, the  $t_{2g}$  orbital are
- (a) raised in energy by  $0.4 \Delta_o$       (b) lowered in energy by  $0.4 \Delta_o$   
 (c) raised in energy by  $0.6 \Delta_o$       (d) lowered in energy by  $0.6 \Delta_o$       **Ans : (b)**
11. If  $\Delta_o < P$ , then the correct electronic configuration for  $\text{d}^4$  system will be
- (a)  $t_{2g}^4 e_g^0$       (b)  $t_{2g}^3 e_g^1$   
 (c)  $t_{2g}^0 e_g^4$       (d)  $t_{2g}^2 e_g^2$       **Ans : (b)**
12. The tetrahedral complexes are generally high spin. This is because
- (a)  $\Delta_t < P$       (b)  $\Delta_t > P$   
 (c)  $\Delta_t = P$       (d) none of these      **Ans : (a)**
13. The primary and secondary valency of copper in the complex  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  are
- (a) 2, 4      (b) 4, 2  
 (c) 0, 4      (d) 1, 4      **Ans : (a)**
14. The hybridization state of the Cu in the compound  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  is
- (a)  $\text{sp}^3$       (b)  $\text{sp}^2 \text{d}$   
 (c)  $\text{sp}^3 \text{d}^2$       (d)  $\text{dsp}^2$       **Ans : (d)**
15. Which of the following statement is correct?
- (a)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is diamagnetic while  $[\text{Fe}(\text{CN})_6]^{4-}$  is paramagnetic  
 (b)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is paramagnetic while  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic  
 (c) both are paramagnetic  
 (d) both are diamagnetic      **Ans : (b)**

### Topic:- Nomenclature of coordination compounds

1. What IUPAC names of following complexes?

- |  |  |
|--|--|
| 1. $[\text{Co}(\text{NH}_3)_6]^{3+}$                 | 2. $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$          |
| 3. $[\text{Ni}(\text{CN})_4]^{2-}$                   | 4. $[\text{Pt}(\text{NH}_3)_4 \text{Cl}_2]^{2+}$       |
| 5. $[\text{NiCl}_4]^{2-}$                            | 6. $[\text{Co}(\text{NH}_3)_5 \text{ONO}]^{2+}$        |
| 7. $[\text{Co}(\text{NH}_3)_5 \text{Cl}]\text{Cl}_2$ | 8. $[\text{Cr}(\text{CN})(\text{H}_2\text{O})_5]^{2+}$ |
| 9. $[\text{Co}(\text{NO}_2)_6]^{3-}$                 | 10. $[\text{Co}(\text{en})_3]\text{Cl}_3$              |

Ans 1. Hexamminecobalt (III) ion

Ans 2. Trioxalatoferrate (III) ion

Ans 3. Tetracyanonickelate (II) ion

Ans 4. Tetraamminedichloridoplatinum (IV) ion

Ans 5. Tetrachloridonickelate (II) ion

Ans 6. Pentamminenitrito –O-cobalt (III) ion

Ans 7. Pentamminechlorido cobalt (III) Chloride

Ans 8. Pentaquacyanido chromium (III) ion

Ans 9. Hexanitrito –N-cobaltate (III) ion

Ans 10. Tris (ethylenediamine) Cobalt (III) Chloride

## 2. Write formula for the following compounds.

1. Hexammineplatinum (VI) Chloride

2. Potassium hexacyanoferrate (III) ion

3. diamminedichloridoplatinum (III) ion

4. Tetramminedichloridocobalt (III) ion

5. Annine chlorobis (elhylenediamine) cobalt (III) ion.

6. Hexaamminechromium (III) hexacyanocobaltate (III)

7. Pentramminenitro –N- Cobalt (III) Chloride.

8. Pentramminebromidoocobalt (III) sulphate

9. triamminediaquachlorocobalt (III) Chloride

10. Tetramminedichloridooplatinum (IV) Bromide

Ans1.  $[\text{Pt}(\text{NH}_3)_6] \text{Cl}_6$

Ans2.  $\text{K}_3 [\text{Fe}(\text{CN})_6]$

Ans3.  $[\text{Pt}(\text{Cl}_2)(\text{NH}_3)_2]^+$

Ans4.  $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2]^+$

Ans5.  $[\text{Co} \text{Cl}(\text{en})_2(\text{NH}_3)]^{2+}$

Ans6.  $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$

Ans7.  $[\text{Co}(\text{NH}_3)_5 \text{NO}_2] \text{Cl}_2$

Ans8.  $[\text{Co}(\text{NH}_3)_5 \text{Br}] \text{SO}_4$

Ans9.  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2 \text{Cl}] \text{Cl}_2$

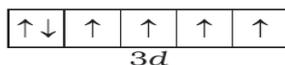
Ans10.  $[\text{Pt} \text{Cl}_2(\text{NH}_3)_4] \text{Br}_2$

## TWO MARKS QUESTION

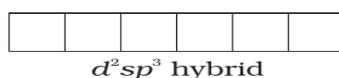
1. Explain that the complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is diamagnetic on the basis of valence bond theory.

Ans. In  $[\text{Co}(\text{NH}_3)_6]^{3+}$  as all the electrons are paired so it is diamagnetic

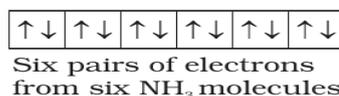
Orbitals of  $\text{Co}^{3+}$  ion



$d^2sp^3$  hybridised orbitals of  $\text{Co}^{3+}$



$[\text{Co}(\text{NH}_3)_6]^{3+}$   
(inner orbital or low spin complex)



2. What are homoleptic and heteroleptic complex explain with suitable example?

Ans. Complexes in which the Central metal ion is bonded to only one kind of donor atom or group.

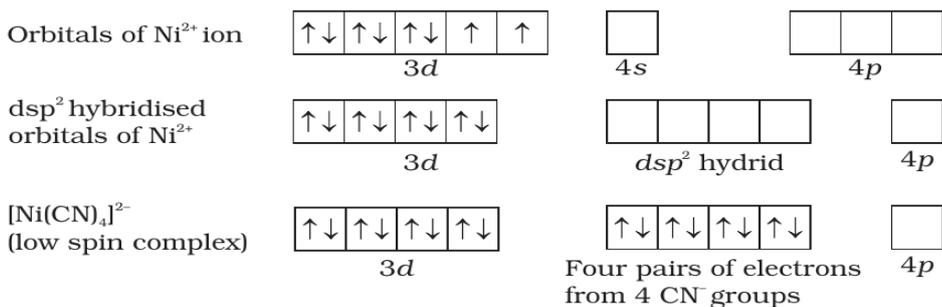
Example-  $\text{Co}(\text{NH}_3)_6^{3+}$  only ammonia is the ligand.

Complexes in which the Central metal ion is bound to more than one kind of donor group.

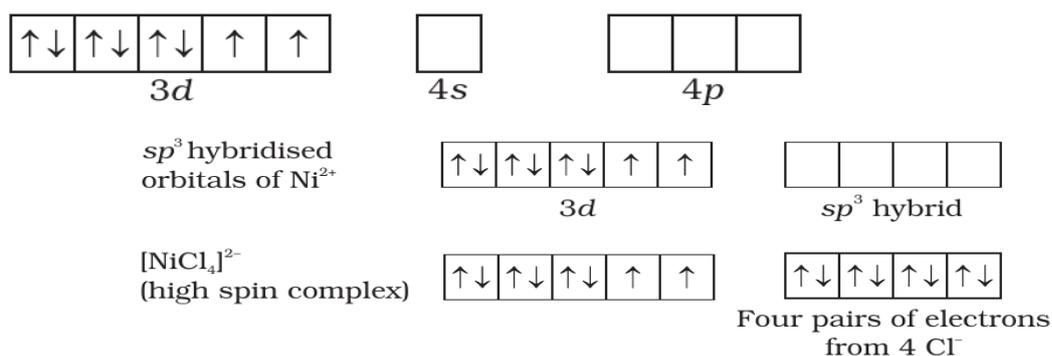
Example-  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

3.  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar whereas  $[\text{NiCl}_4]^{2-}$  is tetrahedral . Explain.

Ans. In  $[\text{Ni}(\text{CN})_4]^{2-}$  hybridization is  $dsp^2$  so square planar geometry



In  $[\text{NiCl}_4]^{2-}$  hybridisation is  $sp^3$  so tetrahedral geometry



4. State crystal field theory.

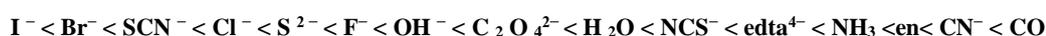
Ans According to crystal field theory- (a). The metal ligand bond is ionic.

(b). Ligands are point charges in case of anions or dipoles in case of neutral molecules

(c). When the asymmetrical negative field of ligands surrounds the metal atom or ion, the degeneracy of its d- orbitals is lifted and they split into two sets.

(d). The pattern of splitting depends on the nature of crystal field.

(e). In general ligands can be arranged in a series in the order of increasing field strength called **spectrochemical series-**



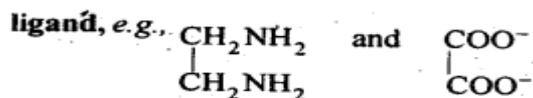
5. Why are complexes coloured? When is a coordination compound colourless?

Ans. The colour of complexes is due to d – d transitions of unpaired electron in d-orbitals  
The complexes will be colourless if the configuration of metal ion or atom is  $d^{10}$  or  $d^0$

6. What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

Ans. A molecule or an ion which has only one donor atom to form one coordinate bond with the central metal atom is called unidentate ligand, e.g.,  $\text{Cl}^-$  and  $\text{NH}_3$ .

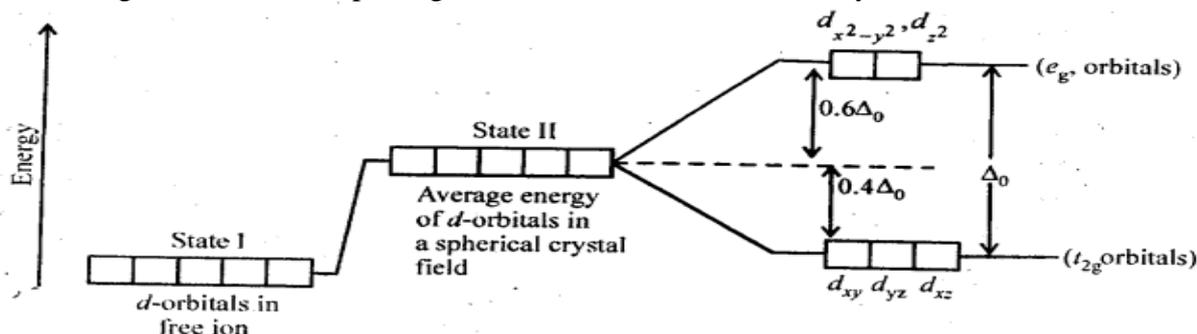
A molecule or ion which contains two donor atoms and hence forms two coordinate bonds with the central metal atom is called didentate



A molecule or an ion which contains two donor atoms but only one of them forms a coordinate bond at a time with the central metal atom is called

**ambidentate ligand, e.g.,**  $\text{:CN}^-$  or  $\text{NC}^-$  and  $\text{NO}_2^-$   
or  $\text{ONO}^-$

7 Draw figure to show the splitting of d orbitals in an octahedral crystal field.



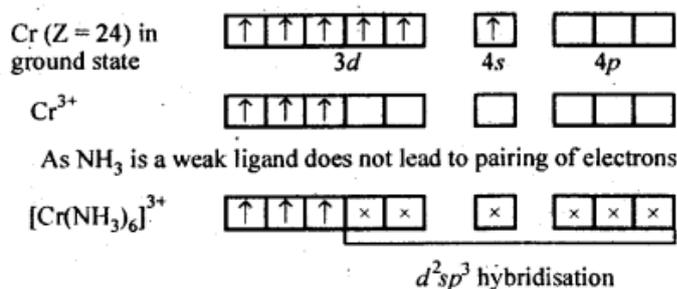
### THREE MARKS QUESTION

1. What is crystal field splitting energy? How does the magnitude of  $\Delta_0$  decide the actual configuration of d orbitals in a coordination entity?

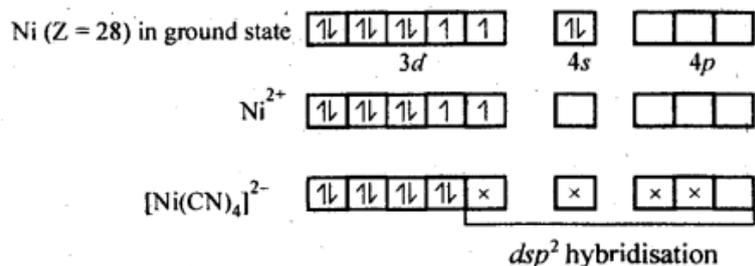
Ans- When the ligands approach a transition metal ion, the d-orbitals split into two sets, one with lower energy and the other with higher energy. The difference of energy between the two sets of orbitals is called crystal field splitting energy ( $\Delta_0$  for octahedral field). If  $\Delta_0 < P$  (pairing energy), the fourth electron enters one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3e_g^1$ , thus forming high spin complexes. Such ligands for which  $\Delta_0 < P$  are called weak field ligands. If  $\Delta_0 > P$ , the fourth electron pairs up in one of the  $t_{2g}$  orbitals giving the configuration  $t_{2g}^4e_g^1$  thereby forming low spin complexes. Such ligands for which  $\Delta_0 > P$  are called strong field ligands.

2.  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  is paramagnetic while  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic. Explain why?

The presence of three unpaired electrons in  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  explains its paramagnetic character.



$[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic, since there is no unpaired electrons.



Pairing of electrons occurs due to strong CN<sup>-</sup> ligand

Ans-

3. A solution of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is green but a solution of  $[\text{Ni}(\text{CN})_4]^{2-}$  is colourless. Explain.

Ans- In  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , Ni is in + 2 oxidation state and having 3d<sup>8</sup> electronic configuration, in which there are two unpaired electrons which do not pair in the presence of the weak H<sub>2</sub>O ligand. Hence, it is coloured. The d-d transition absorbs red light and the complementary light emitted is green.

In  $[\text{Ni}(\text{CN})_4]^{2-}$  Ni is also in + 2 oxidation state and having 3d<sup>8</sup> electronic configuration. But in presence of strong ligand CN<sup>-</sup> the two unpaired electrons in the 3d orbitals pair up. Thus, there is no unpaired electron present. Hence, it is colourless.

4.  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  are of different colours in dilute solutions. Why?

Ans- In both the complexes, Fe is in + 2 oxidation state with d<sup>6</sup> configuration. This means that it has four unpaired electrons. Both CN<sup>-</sup> ion and H<sub>2</sub>O molecules which act as ligands occupy different relative positions in the spectrochemical series. They differ in crystal field splitting energy ( $\Delta_0$ ). Quite obviously, they absorb radiations corresponding to different wavelengths/frequencies from the visible region of light. (VIBGYOR) and the transmitted colours are also different. This means that the complexes have different colours in solutions.

5. Explain the following:

(i) The coordination-complexes are known for transition elements only.

(ii) Nickel (II) does not form low spin octahedral complexes.

(iii)  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  are of different colours in dilute solutions.

**Answer:**

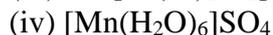
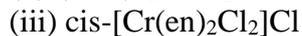
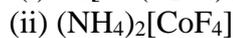
(i) Transition metals have vacant d-orbitals which accept lone pair from ligands to form a bond and give pair of electron to molecular orbital of ligand forming d π - p π -bond.

(ii) Ni<sup>2+</sup> has unpaired electrons, therefore, forms high spin complex as pairing of electrons does not take place because after pairing only one d-orbital will be left which cannot be used in octahedral complex.

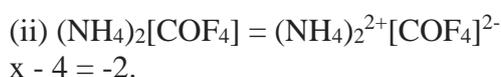
(iii) They absorb different wavelengths from visible light, undergo d-d transitions and radiate complementary colour.  $\text{CN}^-$  is stronger ligand than  $\text{H}_2\text{O}$ .

### FIVE MARKS QUESTION

1. Give the oxidation state, d orbital occupation and coordination number of the central metal ion in the following complexes:



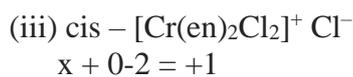
**Ans:** (i)  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \Rightarrow [\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ .  $x + 3(-2) = -3$ . Oxidation state,  $x = +3$   
Coordination number is also 6 as  $\text{C}_2\text{O}_4^{2-}$  is didentate.  
 $\text{Co}^{+3}$  is a case in which all electrons are paired



Oxidation state,  $x = +2$

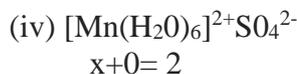
Coordination number = 4.

$\text{Co}^{2+}$  is a  $d^5$  case, paramagnetic



Oxidation state,  $x = +3$

Coordination number is 6 as 'en' is didentate.  $\text{Cr}^{3+}$  is a cfi case, paramagnetic.



•. Oxidation state,  $x = +2$

Coordination number is 6.

$\text{Mn}^{+2}$  is a  $d^5$  case, paramagnetic

2. Discuss briefly giving an example in each case the role of coordination compounds in:

(i) biological systems

(ii) medicinal chemistry

(iii) analytical chemistry

(iv) extraction/metallurgy of metals

**Ans:** (i) 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 acts as oxygen carrier is a coordination compound of iron. Vitamin  $\text{B}_{12}$ , cyanocobalamin, the anti-pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).

(ii) 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 systems. Thus, excess of copper and iron are removed by the chelating ligands D-penicillamine and desferrioxime B via the formation of coordination compounds.

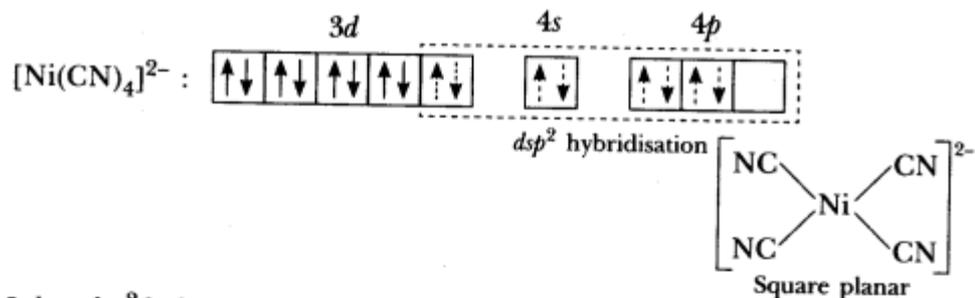
EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: ds-platin and related compounds.

(iii) 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),  $\alpha$ -nitroso- $\beta$ -naphthol, cupron, etc.

(iv) Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity  $[\text{Au}(\text{CN})_2]^-$  in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc.

3. Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units:

(i)  $[\text{Ni}(\text{CN})_4]^{2-}$  (ii)  $[\text{NiCl}_4]^{2-}$  (iii)  $[\text{CoF}_6]^{3-}$  [At. nos. : Ni = 28; Co = 27]



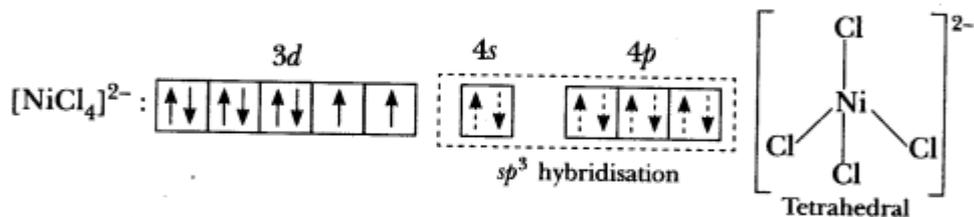
It has  $dsp^2$  hybridisation, square planar shape and diamagnetic in nature.

(ii) In  $[\text{NiCl}_4]^{2-}$ ,

Electronic configuration of Ni(28) :  $[\text{Ar}]4s^23d^8$

Electronic configuration of  $\text{Ni}^{2+}$  :  $[\text{Ar}]4s^03d^8$

$\text{Cl}^-$  is a weak field ligand, cannot cause pairing of electrons.



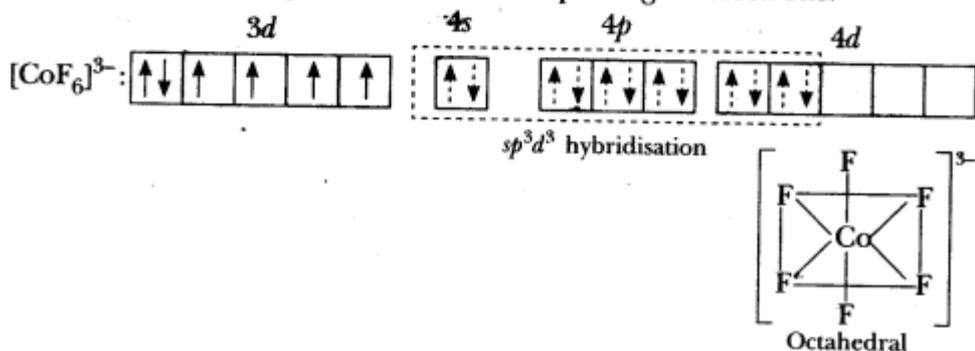
It has  $sp^3$  hybridisation, tetrahedral shape and paramagnetic in nature.

(iii) In  $[\text{CoF}_6]^{3-}$ ,

Electronic configuration of Co(27) :  $[\text{Ar}]4s^23d^7$

Electronic configuration of  $\text{Co}^{3+}$  :  $[\text{Ar}]4s^03d^6$

$\text{F}^-$  is a weak field ligand, cannot cause pairing of electrons.



It has  $sp^3d^2$  hybridisation, octahedral shape and paramagnetic in nature.

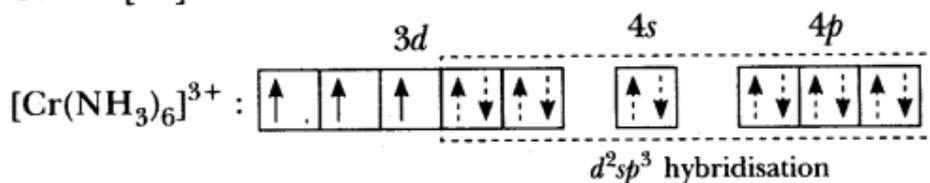
Answer (i) \_

3. Compare the following complexes with respect to their molecular shape and magnetic behaviour :



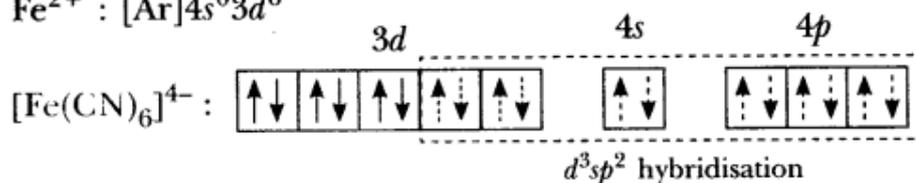
(At. No. : Cr = 24, Fe = 26, Ni = 28)

- (i) In  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
 $\text{Cr}(24) : [\text{Ar}]4s^13d^5$   
 $\text{Cr}^{3+} : [\text{Ar}]4s^03d^3$



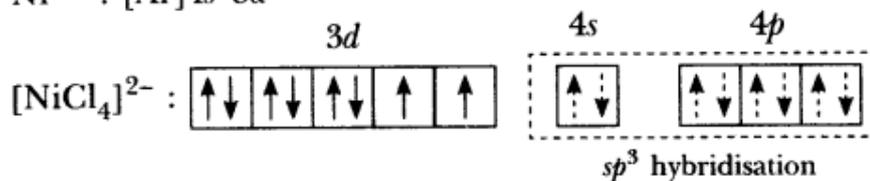
It has  $d^2sp^3$  hybridisation, octahedral shape, paramagnetic in nature.

- (ii) In  $[\text{Fe}(\text{CN})_6]^{4-}$   
 $\text{Fe}(26) : [\text{Ar}]4s^23d^6$   
 $\text{Fe}^{2+} : [\text{Ar}]4s^03d^6$



It has  $d^3sp^2$  hybridisation, octahedral shape, diamagnetic in nature.

- (iii) In  $[\text{NiCl}_4]^{2-}$   
 $\text{Ni}(28) : [\text{Ar}]4s^23d^8$   
 $\text{Ni}^{2+} : [\text{Ar}]4s^03d^8$



It has  $sp^3$  hybridisation, tetrahedral shape, paramagnetic in nature.

Ans-

## 12. ALDEHYDES, KETONES & CARBOXYLIC ACIDS

### SHORT ANSWERS TYPES QUESTION (1 MARKS)

A. Name the  $\text{CH}_3\text{COCH}_2\text{COCH}_3$  according to IUPAC system .

Ans:- Pentan-2,4-dione

B. Write the structures of Hex-2-en-4-ynoic acid?

Ans:-  $\text{CH}_2\text{C}\equiv\text{CCH}=\text{CHCOOH}$ .

C. What happens when – Formaldehyde reacts with conc. KOH?

Ans:- Cannizzaro reaction.

D. During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as fast as it is formed.

Ans.- The formation of ester from carboxylic acid & alcohol is reversible reaction. So to obtain ester in better yield water has to be removed faster to shift equilibrium forward.

E. It is necessary to control the pH during the reaction of aldehydes and ketones with ammonia derivatives. Ans.- Carboxylic acids do not give the characteristic reactions of carbonyl group.

Ans.- Carbonyl carbon of carboxylic group is less electrophilic than carbonyl carbon in aldehyde & ketones & hence nucleophilic addition reaction of aldehyde & ketones does not take place with carboxylic acids.

F. Chloroacetic acid is stronger than acetic acid.

Ans.- Presence of Cl as an electron withdrawing group, increases the acidic strength of acid.

G. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses.

Ans.- Due to excessive hydrogen bonding in carboxylic acids with water than aldehydes, ketones & even alcohols with comparable molar mass.

H. The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.

Ans.- Due to more hydrogen bonding in aldehydes & ketones with water molecules than that of hydrocarbon & ethers

I. Carboxylic acids are more acidic than phenols.

Ans.- Due to more stability of carboxylate ion formed by acids than that of phenoxide ions formed after release of  $\text{H}^+$  ion.

J. Aldehydes (ethanal) are more reactive than ketones (acetone) towards nucleophilic addition reaction.

Ans.- In ketones steric hindrance is more due to presence of bulky alkyl groups but in aldehydes steric hindrance (crowding) is less & nucleophilic attack is easy.

### SHORT ANSWERS TYPES QUESTION (2 MARKS)

1. Give one chemical test to distinguish between (a) Pentan-2-one and Pentan-3-one (b) Benzaldehyde and Acetophenone.

2. Explain why

a) Aldehydes are more reactive than ketones towards nucleophilic addition reaction.

b) Chloroacetic acid is stronger than acetic acid.

3. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

- (i) Ethanal, Propanal, Propanone, Butanone.  
(ii) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.

4. Arrange the following compounds in increasing order of their (acid strength)

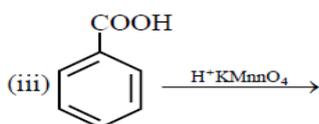
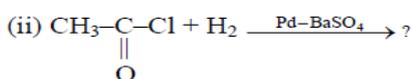
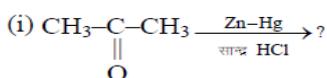
- (a)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$ ,  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$ ,  $(\text{CH}_3)_2\text{CHCOOH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$   
(b) Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

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

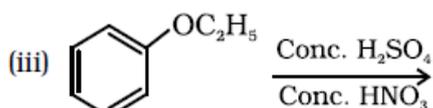
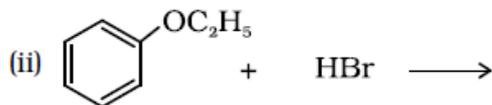
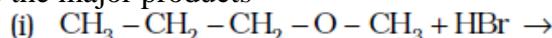
- (i) Propanal and Propanone (ii) Acetophenone and Benzophenone

### LONG ANSWERS TYPES QUESTIONS (3 MARKS)

(a) Complete the reaction



(b) Write the major products



(c) An organic compound A with molecular formula  $\text{C}_8\text{H}_{16}\text{O}_2$  was hydrolysed with 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.

(d) Carry out the following conversions

- (a) Propanone to Propene (b) Benzoic acid to Benzaldehyde  
(c) Ethanol to 3-Hydroxybutanal

### LONG ANSWERS TYPES QUESTIONS (5 MARKS)

1. Aldehydes and ketones are distinguished by using

- (a) Tollen's reagent (b) Lucas reagent (c) Borsche reagent (d) all of these

2. Carbonyl compounds undergo nucleophilic addition because of

- (a) More stable anion with negative charge on oxygen and less stable carbocation  
(b) Electromeric effect  
(c) Electronegativity difference of carbon and oxygen atoms  
(d) None of these

3. Clemmensen reduction is carried with  
 (a)  $\text{LiAlH}_4$  in ether (b)  $\text{Zn-Hg}$  and  $\text{HCl}$   
 (c)  $\text{H}_2$  in the presence of  $\text{Pd}$  (d)  $\text{NH}_2\text{NH}_2/\text{glycol}$  and  $\text{KOH}$
4. The addition of  $\text{HCN}$  to carbonyl compounds is an example of  
 (a) Electrophilic addition (b) Nucleophilic addition  
 (c) Nucleophilic substitution (d) Electrophilic substitution
5. Cyanohydrin of which of the following will yield lactic acid?  
 (a)  $\text{HCHO}$  (b)  $\text{CH}_3\text{COCH}_3$  (c)  $\text{CH}_3\text{CH}_2\text{CHO}$  (d)  $\text{CH}_3\text{CHO}$
6. If formaldehyde and  $\text{KOH}$  are heated, then we get  
 (a) Methyl alcohol (b) Acetylene (c) Methane (d) Ethyl formate
7. Which of the following will not give iodoform test?  
 (a) Ethanol (b) Ethanal (c) Pentan-3-one (d) Pentan-2-one
8. Oxidation of toluene to benzaldehyde by the use of chromyl chloride is called  
 (a) Wurtz reaction (b) Fittig reaction (c) Etard's reaction (d) Rosenmund's reaction

Answers = 1. (a) 2. (a) 3. (b) 4. (b) 5. (d) 6. (a) 7. (c) 8. (c)

### Assertion and Reason

In the following question two statements (Assertion) A and Reason (R) are given Mark.

- (a) if A and R both are correct and R is the correct explanation of A;  
 (b) if A and R both are correct but R is not the correct explanation of A;  
 (c) A is true but R is false;  
 (d) A is false but R is true,  
 (e) A and R both are false.
1. (A) : Resonance energy of carboxylate ion is much greater than that of undissociated carboxylic acid.  
 (R) : Carboxylate ion is a resonance hybrid of equivalent resonating structures.
2. (A) : Claisen Condensation involves the self condensation of ester molecules having  $\alpha$  hydrogen.  
 (R) : Claisen condensation occurs in the presence of a strong base such as sodium ethoxide.
3. (A) : Ethyl acetoacetate gives reddish violet colour on treatment with ferric chloride  
 (R) : It exists predominantly in the keto form.
4. (A) :  $\text{CH}_3\text{COOH}$  but not  $\text{HCOOH}$  can be halogenated in presence of red P and  $\text{Cl}_2$ .  
 (R) : Both formic acid and  $\text{CH}_3\text{COOH}$  are highly soluble in water.
5. (A) : In sodium formate, both the C – O bonds have same value  $1.27 \text{ \AA}$ .  
 (R) : Same bond length is due to the phenomenon of resonance.
6. (A) : Formic acid gives rise to nucleophilic addition reactions.  
 (R) : Carbon oxygen bond length in formic acid are  $1.23 \text{ \AA}$  and  $1.36 \text{ \AA}$ .
7. (A) : Nitration of benzoic acid gives m-nitrobenzoic acid.  
 (R) : Carboxyl group increases the electron density at the meta position.
8. (A) : m-Chlorobenzoic acid is a stronger acid than p-chlorobenzoic acid.  
 (R) : In m-chlorobenzoic acid stronger  $-I$  effect Cl operate but in p-chlorobenzoic acid only  $+R$  effect of Cl operates.

9. (A) : Both formic acid and oxalic acid decolourize  $\text{KMnO}_4$  solution.

(R) : Both are easily oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

10. (A) :  $\text{RCOCl}$ ,  $(\text{RCO})_2\text{O}$  and  $\text{RCOOR}'$  all react with Grignard reagents to form 3° alcohols.

(R) :  $\text{RCOCl}$  reacts with  $\text{R}_2\text{Cd}$  to form ketones but  $(\text{RCO})_2\text{O}$  and  $\text{RCOOR}'$  do not react at all.

11. (A) : p-Hydroxybenzoic acid has lower boiling point than o-hydroxybenzoic acid.

(R) : o-Hydroxybenzoic acid has intramolecular hydrogen bonding.

12. (A) : Acetamide reacts with  $\text{Br}_2$  in presence of methanolic  $\text{CH}_3\text{ONa}$  to form methyl N-methylcarbamate.

(R) : Methyl isocyanate is formed as an intermediate which reacts with methanol to form methyl N-methylcarbamate.

13. (A) : Acid catalysed hydrolysis of ester is reversible on the other hand base catalysed hydrolysis is irreversible.

(R) : In acid catalysed ester hydrolysis carboxylic acid is formed on which nucleophile attack of alcohol is possible while in base catalysed ester hydrolysis carboxylate anion is formed on which nucleophilic attack is not possible.

14. (A) : In aldol condensation the final product is always  $\alpha$ ,  $\beta$ -unsaturated carbonyl compound.

(R) :  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds are stabilized due to conjugation.

15. (A) : Although ketones do not reduce Tollen's reagent and Fehling's solution but  $\alpha$ -hydroxyketones give positive test.

(R) : Secondary alcoholic group of  $\alpha$ -hydroxy ketones gets oxidized to ketonic group.

Answers =

1. (a) 2. (b) 3. (b) 4. (b) 5. (a) 6. (d) 7. (c) 8. (a) 9. (a) 10. (b) 11. (d)

12. (a) 13. (a) 14. (a) 15. (a)

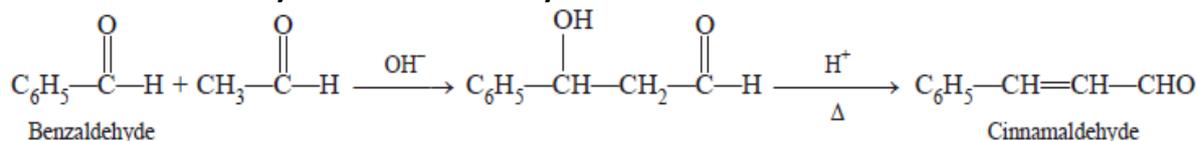
## CASE-BASED/PASSAGE-BASED INTEGRATED QUESTIONS

Read the given passage and answer the questions that follow.

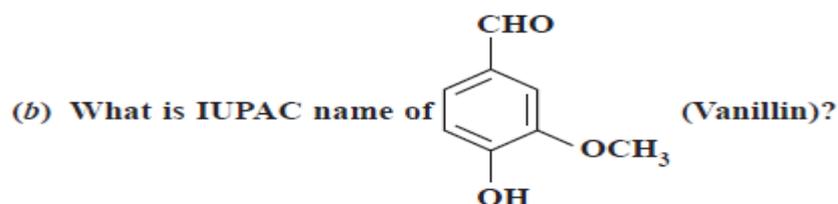
Aldehydes, Ketones, Carboxylic acids and their derivatives are collectively called carboxyl compounds which are widely spread both in plants and animal kingdom. They play an important role in biological processes. They are responsible for fragrance and flavour of naturally occurring compounds *e.g.*, Vanilline (from vanilla beans), salicylaldehyde (from meadowsweet), cinnamaldehyde (from cinnamon) and isoamyl acetate (from banana) have pleasant flavour.

Acetone and acetic acid are widely used as solvents. Various carboxylic acids are used to prepare drugs (Analgesics, antipyretics etc.).

1. Convert benzaldehyde to Cinnamaldehyde?

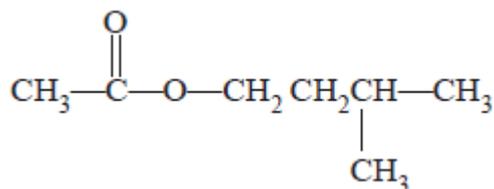


Ans:-



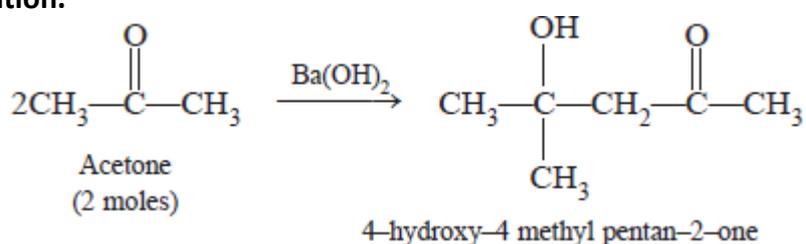
Ans :- 4-hydroxy-3-methoxy benzaldehyde

(c) Write the structural formula of Isoamyl acetate.



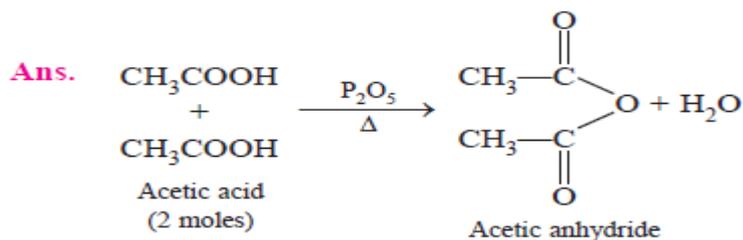
Ans:-

(d) What happens when 2 moles of acetone are condensed in presence of  $\text{Ba}(\text{OH})_2$ ? Write chemical equation.



Ans:-

(e) What happens when acetic acid is heated with  $\text{P}_2\text{O}_5$ ?



Acetic anhydride is formed.

## 13. AMINES

### MULTIPLE CHOICE QUESTIONS

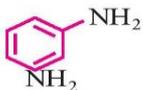
1. In the nitration of benzene using a mixture of Conc  $\text{H}_2\text{SO}_4$  and conc.  $\text{HNO}_3$  the species which initiates the reaction is:

- (a)  $\text{NO}_2$  (b)  $\text{NO}^+$   
(c)  $\text{NO}_2^+$  (d)  $\text{NO}_2^-$

2. The correct IUPAC name of  $\text{CH}_2 = \text{CH}-\text{CH}_2\text{NHCH}_3$  is:

- (a) Allylmethyl amine (b) 2-amino-4-pentene  
(c) 4-aminopent-1-ene (d) N-methylprop-2-en-amine

3. Which is the weakest base:

- (a)  (b)   
(c)  (d)  $\text{CH}_3\text{NH}_2$

4. The correct order of basic strength for the following compounds is:

- (i)  (ii)  (iii) 

- (a)  $\text{ii} < \text{iii} < \text{i}$  (b)  $\text{iii} < \text{i} < \text{ii}$   
(c)  $\text{iii} < \text{ii} < \text{i}$  (d)  $\text{ii} < \text{i} < \text{iii}$

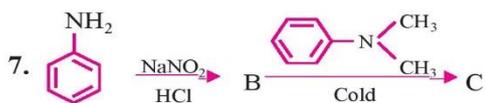
5. Methylamine reacts with  $\text{HNO}_2$  to form

- (a)  $\text{CH}_3-\text{O}-\text{N}=\text{O}$  (b)  $\text{CH}_3\text{OCH}_3$   
(c)  $\text{CH}_3\text{OH}$  (d)  $\text{CH}_3\text{CHO}$

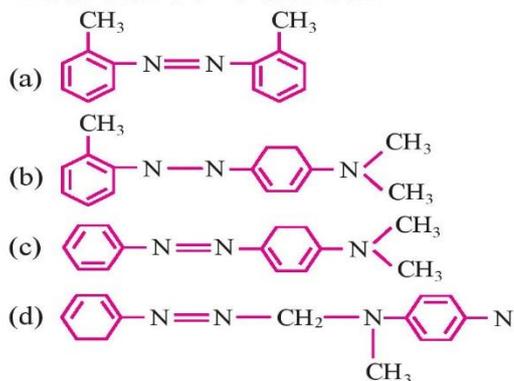
6.  $\text{CH}_3\text{CH}_2\text{COOH}$

The structure of 'c' would be

- (a)  $\text{CH}_3\text{CH}_2\text{CONH}_2$  (b)  $\text{CH}_3\text{CH}_2\text{NHCH}_3$   
(c)  $\text{CH}_3\text{CH}_2\text{NH}_2$  (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$



The structure of 'c' would be



8. Which of the following statement about primary amine is false:

- Aryl amines react with nitrous acid to produce phenol
- Alkylamines are stronger base than ammonia
- Alkyl amines are stronger base than aryl amines
- Alkyl amines react with nitrous acid to produce alcohol

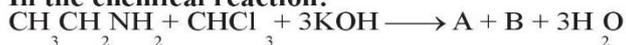
9. Which of the following is most stable diazoniom salt?

- $\text{CH}_3\text{CH}_2\text{NH}_2^+ \text{X}^-$
- $\text{C}_6\text{H}_5\text{NH}_2^+ \text{X}^-$
- $\text{CH}_3\text{CH}_2\text{N}_2^+ \text{X}^-$
- $\text{C}_6\text{H}_5\text{CH}_2\text{N}_2^+ \text{X}^-$

10. Method by which aniline can not be prepared is:

- reduction of nitrobenzene with  $\text{H}_2/\text{Pd}$  in ethanol.
- potassium salt of phthalimide treated with chlorobenzene
- hydrolysis of phenyl isocyanide with acidic solution
- degradation of benzamide with bromine in alkaline medium solution.

11. In the chemical reaction:



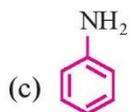
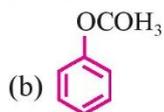
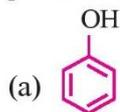
The compound A and B are respectively:

- $\text{CH}_3\text{CH}_2\text{CONH}_2$  and  $3\text{KCl}$
- $\text{CH}_3\text{CH}_2\text{NC}$  and  $\text{K}_2\text{CO}_3$
- $\text{CH}_3\text{CH}_2\text{NC}$  and  $3\text{KCl}$
- $\text{CH}_3\text{CH}_2\text{CNB}$  and  $3\text{KCl}$

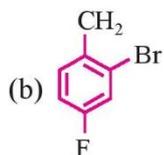
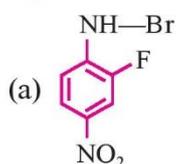
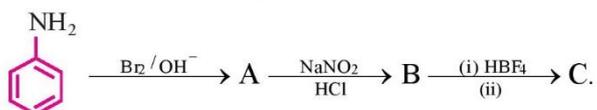
12. Considering the basic strength of amines in aqueous solution which one has the smallest  $\text{p}K_b$  value?

- $(\text{CH}_3)_2\text{NH}$
- $\text{C}_6\text{H}_5\text{NH}_2$
- $\text{CH}_3\text{NH}_2$
- $(\text{CH}_3)_3\text{N}$

13. Which of the following compound will give significant amount of meta product during mono-nitration reaction?

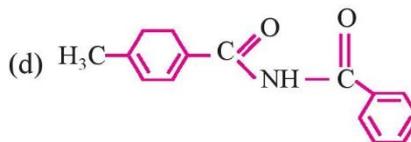
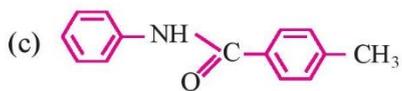
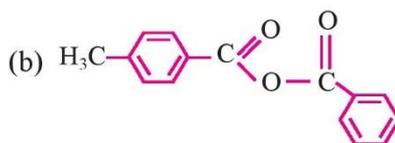


14. The final product (c) in the following sequence of reaction is:



15. In the reaction  $\xrightarrow[\text{(ii) } \text{C}_6\text{H}_5\text{COCl}]{\text{(i) NaOH, Br}_2}$  A

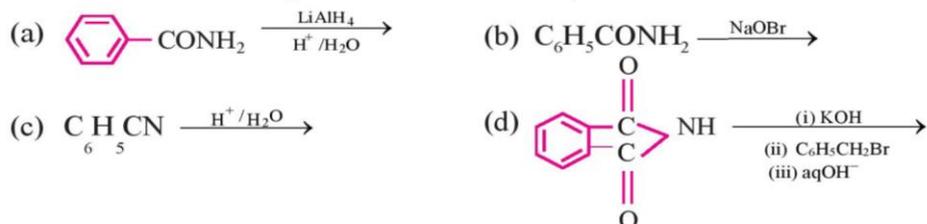
The structure of product A is:



16. A positive carbylamine test is given by

- (a) N,N-Dimethylaniline (b) 2, 4-Dimethylaniline  
 (c) N-Methyl-o-methylaniline (d) *p*-methylbenzylamine

17. Which of the following reactions form benzylamine:



18. Which reagent among the following can affect the conversion?



- (a)  $\text{H}_2$ , Pt (b) Ammoniacal  $\text{AgNO}_3$   
 (c)  $\text{LiAlH}_4$  (d)  $\text{NaBH}_4$

19. In which of the following amines, the first has lower  $\text{p}K_b$  value than the second

- (a) aniline, *m*-nitroaniline (b) *m*-Toluidine, *p*-toluidine  
 (c) aniline, *p*-chloroaniline (d) aniline, *p*-aminophenol

20. Bromobenzene can be prepared from benzene diazonium chloride. When it is treated with

- (a)  $\text{Cu/HBr}$  (b)  $\text{Br}_2$ ;  $\text{HBr}$   
 (c)  $\text{CuBr/HBr}$  (d)  $\text{Br}_2$ ,  $\text{CCl}_4$

### Assertion Reason Type Questions

The question given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.

- (a) Assertion and reason both are CORRECT and reason is the CORRECT explanation of the assertion.  
 (b) Assertion and reason both are wrong statements.  
 (c) Assertion is correct statement but reason is wrong statement.  
 (d) Assertion is wrong statement but reason is correct statement.  
 (e) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

### Assertion and Reasoning

21. **Assertion :** *n*-Propylamine has higher boiling point than trimethylamine.

**Reason :** Among *n*-propylamine molecules, there is hydrogen bonding but there is not hydrogen bonding in trimethylamine.

22. **Assertion :** Aniline does not undergo Friedel Crafts reaction.

**Reason :** Friedel Crafts reaction is an electrophilic substitution reaction.

**23. Match column I and column II**

**Column-I**

(A) Ammolysis

(B) Gabriel phthalimide

(C) Hoffmann bromide amide degradation

(D) Carbylamine reaction

(a) A-s, B-r, C-p, D-q

(c) A-r, B-s, C-p, D-q

**Column-II**

(p) Amine with lesser no. of carbon atom

(q) Detection of primary amine

(r) Reaction of pthalimide with KOH and R-X

(s) Reaction of alkyl halides with NH<sub>3</sub>

(b) A-p, B-q, C-r, D-s

(d) A-s, B-r, C-q, D-p

**24. Match column I and column II**

**Column-I**

(A) Benzene sulphonyl chloride

(B) Sulphanilic acid

(C) Alkyl diazonium salts

(D) Aryl diazonion salts

(a) A-p, B-q, C-s, D-r

(c) A-q, B-p, C-r, D-s

**Column-II**

(p) zwitter ion

(q) Hinsberg reagent

(r) Dyes

(s) Conversion to alcohols

(b) A-q, B-p, C-s, D-r

(d) A-s, B-r, C-q, D-p

**25. The no. of amines having pkb less than C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> among the following.**

P-CH<sub>3</sub>-C<sub>5</sub>H<sub>4</sub>NH<sub>2</sub>, O-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>NH<sub>4</sub>, m-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>, p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, p-ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>

0	1	2	3	4	5	6	7	8	9
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**ANSWERS**

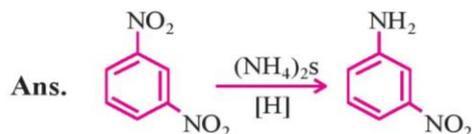
1. (c) 2. (d) 3. (a) 4. (d) 5. (c) 6. (c) 7. (c) 8. (a) 9. (b) 10. (b)  
 11. (c) 12. (a) 13. (c) 14. (d) 15. (a) 16. (b, d) 17. (a, d)  
 18. (a, c) 19. (a, c) 20. (a, c) 21. (a) 22. (b)  
 23. (a) 24. (b) 25. 7

**VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)**

**Q. 1. Write IUPAC name of CH<sub>3</sub>NC.**

**Ans.** Methane carbylamine.

**Q. 2. Convert m-dinitrobenzene to m-nitro aniline.**



**Q. 3. Draw structure of TNT, an explosive.**



**Q. 4. Write IUPAC name of**  $\text{CH}_3 - \text{N} - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{CH}_2 - \text{CH}_3$

Ans. 3-Methyl-N,N-dimethyl pentanamine

**Q. 5. Give one use of quaternary ammonium salts.**

Ans. It is used as detergents, e.g.,  $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]^+\text{Cl}^-$ .

**Q. 6. What is Hinsberg's reagent ?**

Ans. Benzene sulphonyl chloride, 

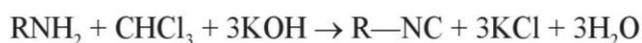
**Q. 7. Why aniline dissolves in HCl ?**

Ans.  $\text{C}_6\text{H}_5\text{NH}_2 + \text{HCl} \rightarrow [\text{C}_6\text{H}_5\text{NH}_3]^+\text{Cl}^-$ .

It dissolves due to its basic nature.

**Q. 8. How will you test the presence of primary amine ?**

Ans. By carbyl amine test.



**Q. 9. What is vapour phase nitration ?**

Ans.  $\text{CH}_4 + \text{HNO}_3 \xrightarrow{623 \text{ K}} \text{CH}_3\text{NO}_2$

(High temperature and nitration in vapour phase only)

**Q. 10. Write one use of dopamine and atropine alkaloid.**

Ans. Dopamine : Neurotransmitter

Atropine alkaloid : 0.5-1.0% solution ophthalmic examination.

**Q. 11. Direct nitration of aniline is not carried out. Explain.**

Ans.  $(\text{H}_2\text{SO}_4 + \text{HNO}_3)$  easily oxidized aniline into tarry complex product due to high  $e^-$  density on the benzene ring of aniline.

Q. 12. Among the compounds as following which will react with  $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$  to give product containing  $> \text{C} = \text{N} - ?$

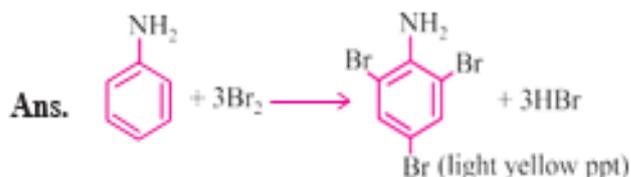
- (i)  $\text{C}_6\text{H}_5\text{NH}_2$  (ii)  $(\text{CH}_3)_3\text{N}$   
 (iii)  $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_5$  (iv)  $\text{C}_6\text{H}_5\text{NHNH}_2$

Ans.  $\text{C}_6\text{H}_5\text{NH}_2$  and  $\text{C}_6\text{H}_5\text{NHNH}_2$ .

Q. 13. How will you give expression for  $K_b$  to indicate its basic strength ?

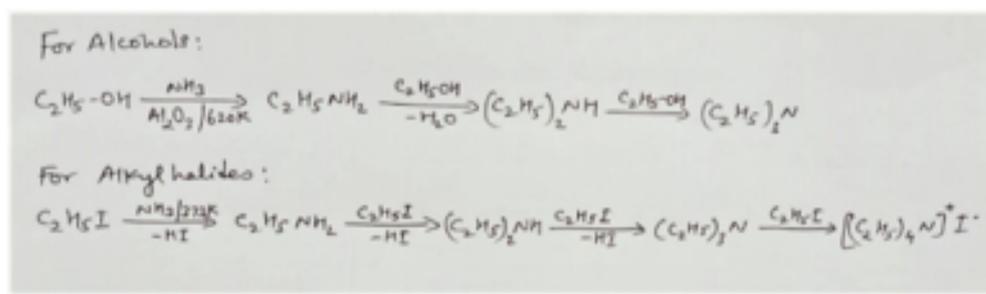
Ans  $K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{R} - \text{NH}_2]}$

Q. 14. What happens when aniline is treated with bromine ?

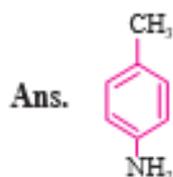


Q. 15. Write a chemical equation to illustrate the ammonolysis.

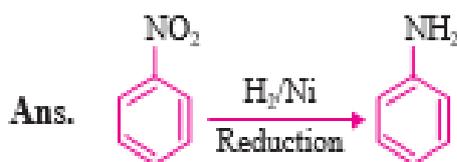
Ans.



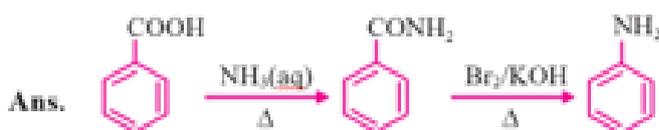
Q. 16. Write the structure of p-toluidine.



Q. 17. Prepare/convert nitrobenzene into aniline.



Q. 18. Convert  $C_6H_5COOH$  to  $C_6H_5NH_2$ .



Q. 19. Write isomerism exhibited by different amines.

Ans. Chain, position, metamerism, functional.

Q. 20. Arrange the following compounds in increasing order of solubility in water:



Ans.  $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

### SHORT ANSWER TYPE QUESTIONS (2 Marks)

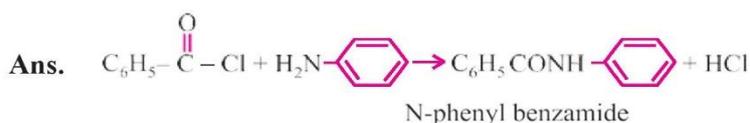
Q. 1. Complete the following acid-base reactions and name the products :



Ans. (i)  $CH_3CH_2CH_2NH_3^+Cl^-$  (n-propyl ammonium chloride)



**Q. 2. Write chemical reaction of  $C_6H_5NH_2 + C_6H_5COCl$  and name product obtained.**



**Q. 3. How will you convert :**

(i) 3-methylaniline  $\rightarrow$  3-nitrotoluene

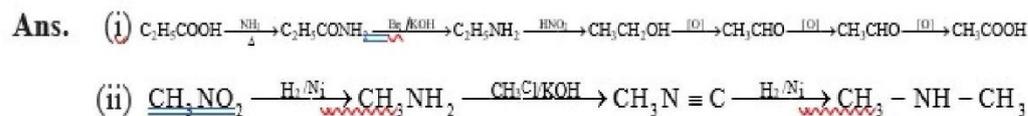
(ii) Aniline  $\rightarrow$  1, 3, 5-tribromobenzene



**Q. 4. How will you convert :**

(i) Propanoic acid  $\rightarrow$  Ethanoic acid

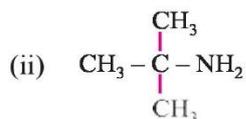
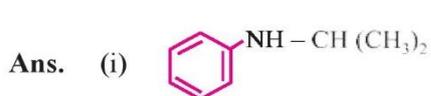
(ii) Nitromethane  $\rightarrow$  Dimethylamine



**Q. 5. Draw the structures of the following compounds :**

(i) N-isopropylaniline

(ii) t-butylamine



**Q. 6. Why  $C_6H_5N^+(CH_3)_3OH^-$  a stronger base than  $NH_4OH$  ?**

**Ans.** Due to - I effect of phenyl group, it decreases  $e^-$  density on nitrogen atom but no such group in  $NH_4OH$ .

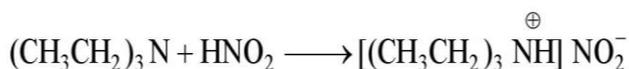
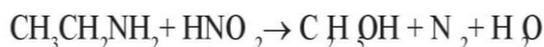
**Q. 7. Explain  $K_b$  order :  $Et_2NH > Et_3N > EtNH_2$  in aqueous solution.**

**Ans.** Basicity of amines in aqueous solution depends upon :

- (i) + I effect of an alkyl group.
- (ii) Extent of hydrogen bonding with  $H_2O$ .
- (iii) Steric effects of alkyl groups.

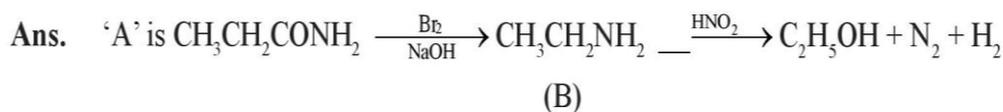
**Q. 8. Distinguish between  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  amines by  $HNO_2$  acid test.**

**Ans.**  $1^\circ$  gives  $N_2$  gas.  $2^\circ$  gives yellow oily compound.  $3^\circ$  form water soluble salts.



Soluble in water

**Q. 9. A compound 'A' having molecular formula  $C_3H_7ON$  reacts with  $Br_2$  in presence of  $NaOH$  to give compound 'B'. This compound 'B' reacts with  $HNO_2$  to form alcohol and  $N_2$  gas. Identify compound 'A' and 'B' and write the reaction involved.**

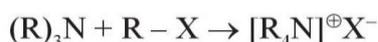
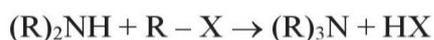
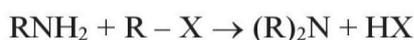
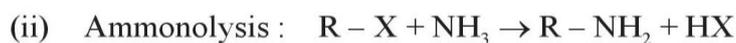




**Q. 13. Write short notes on :**

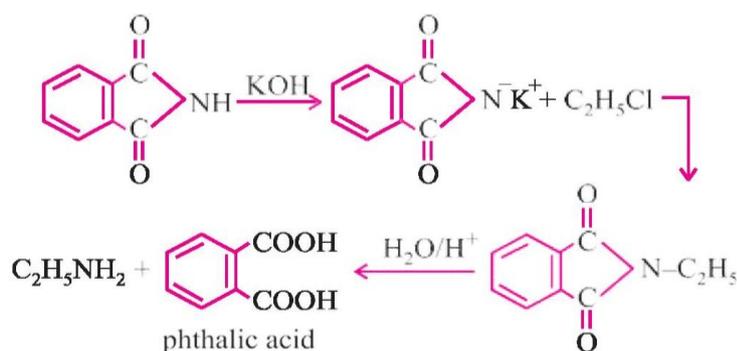
(i) **Coupling reaction**

(ii) **Ammonolysis**



**Q. 14. Prepare pure sample of 1° amine from 1° alkyl halide.**

**Ans. By Gabriel Phthalimide Reaction**



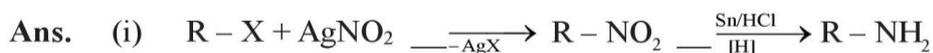
### ANSWER-II TYPE QUESTIONS (3 Marks)

**Q. 1. What happens when :**

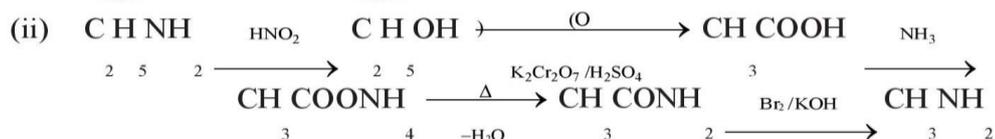
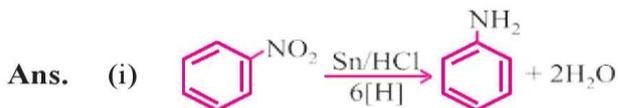
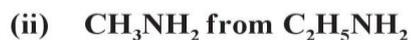
(i) An alkyl halide reacts with  $AgNO_2$  and product is reduced.

(ii) An alkyl halide is treated with  $AgCN$  and product is hydrolysed.

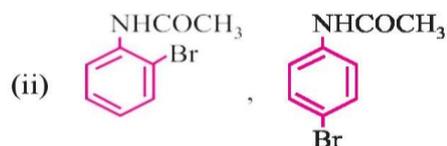
(iii) Methyl magnesium is treated with cyanogens chloride.



Q. 2. How would you prepare :



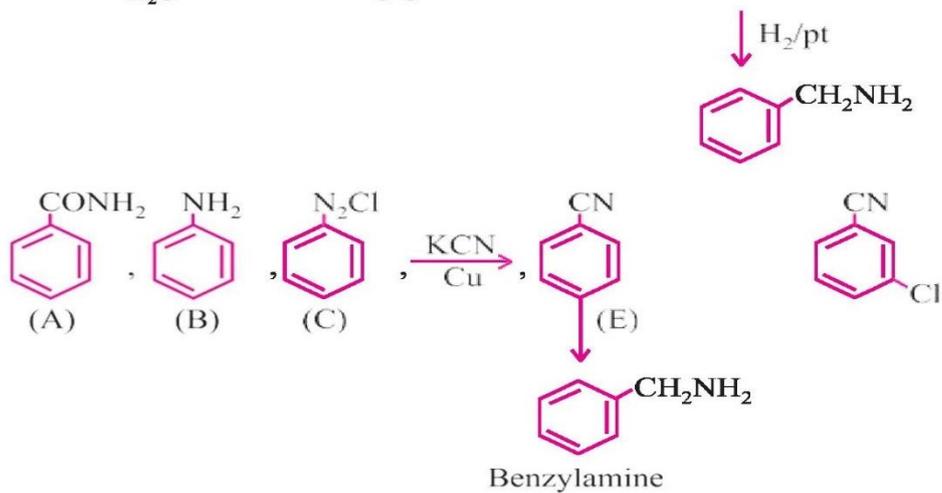
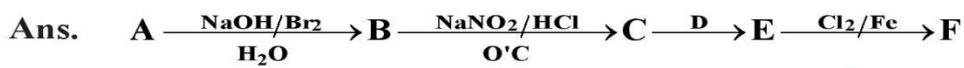
Q. 3. Write the structure of the products in each case :



Q. 4. Write the structures of A, B and C in following



**Q. 5. Write the structure of reagents/organic compounds 'A' to 'F' :**



## LONG ANSWER TYPE QUESTIONS (5 Marks)

**Q. 1. Arrange the following :**

(i) In decreasing order of  $pK_b$  values :

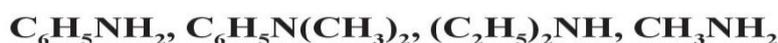


(ii) In increasing order of basic strength :

(a) Aniline, p-nitroaniline and p-toluidine



(iii) In decreasing order of basic strength :



(iv) Decreasing order of basic strength in gas phase :



(v) Increasing order of boiling point :



**Ans.** (i)  $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(ii) (a) p-nitroaniline < aniline < p-toluidine



(iii)  $(C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$

(iv)  $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(v)  $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

**Q. 2 Write short note on the following :**

(i) Carbylamine reaction

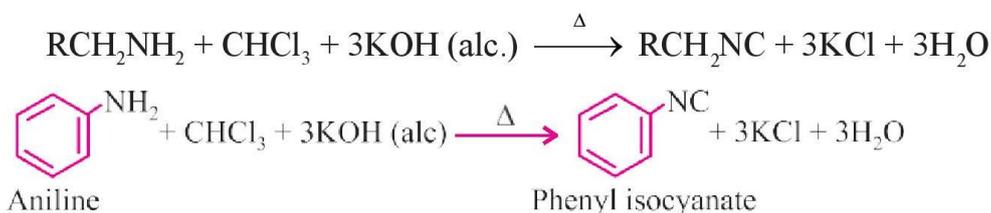
(ii) Diazotization

(iii) Hoffmann's bromide reaction

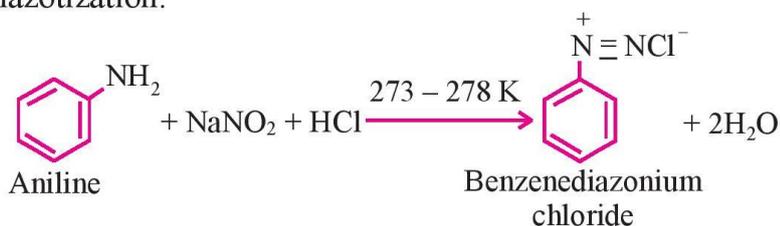
(iv) Coupling reaction

(v) Ammonolysis

**Ans. (i) Carbylamine reaction :** When primary amine (aromatic or aliphatic) warmed with chloroform and alc. KOH, isocyanides are formed which can be identified by their offensive smell. This test is used to identify the presence of primary amine or chloroform.



**(b) Diazotization :** When primary aromatic amine is treated with  $\text{NaNO}_2$  and  $\text{HCl}$  at 273-278 K, diazonium salt is obtained. This reaction is known as diazotization.



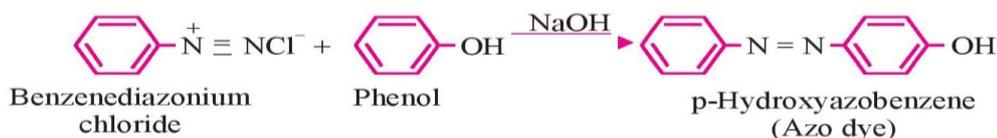
Benzenediazonium chloride is a very important synthetic compound, which can be changed into haloarenes, phenol, cyanobenzene, benzene etc.

- (c) **Hoffmann's bromide reaction** : When any primary amide (aliphatic or aromatic) is treated with bromine and alkali, it gives the amine with one less carbon atom.

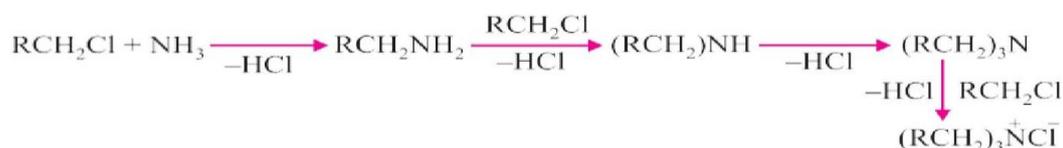


This reaction is used to reduce one carbon atom from a compound.

- (d) **Coupling reaction** : When benzenediazonium chloride is treated with phenols or aromatic amines, azo dyes are produced in which diazo ( $-\text{N}=\text{N}-$ ) group is retained. Coupling reactions generally take place at p-position of phenol or aromatic amines.

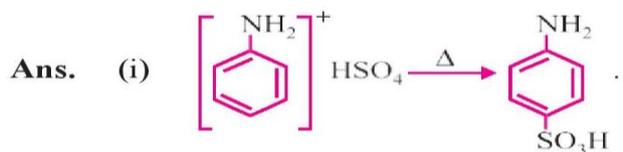


- (e) **Ammonolysis** : Reaction of alkyl halides with ammonia is known as ammonolysis. Ammonolysis generally gives the mixture of 1°, 2°, 3° amines and quaternary ammonium salt.

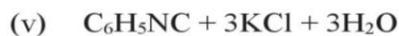


**Q. 3. Complete the following reactions :**

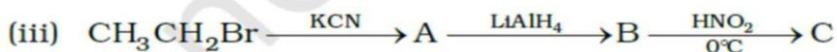
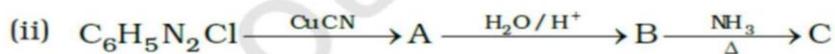
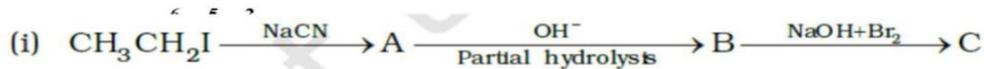
- (i)  $\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{SO}_4(\text{conc.}) \rightarrow$   
 (ii)  $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow$   
 (iii)  $\text{C}_6\text{H}_5\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow$   
 (iv)  $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow$   
 (v)  $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH}(\text{alc.}) \rightarrow$



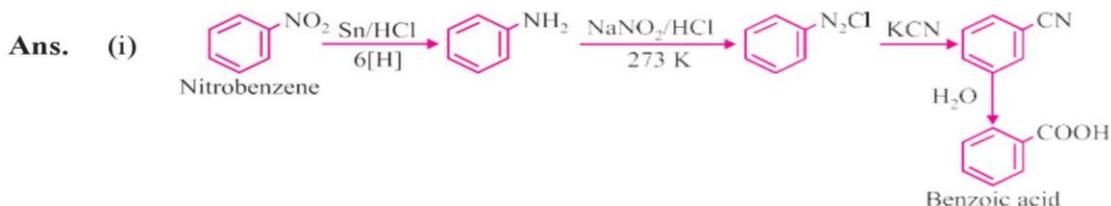
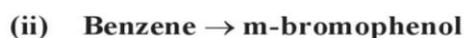
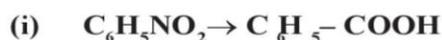
- (ii)  $\text{C}_6\text{H}_6 + \text{N}_2 + \text{HCl} + \text{CH}_3\text{CHO}$   
 (iii)  $\text{C}_6\text{H}_5\text{NHCOCH}_3 + \text{CH}_3\text{COOH}$

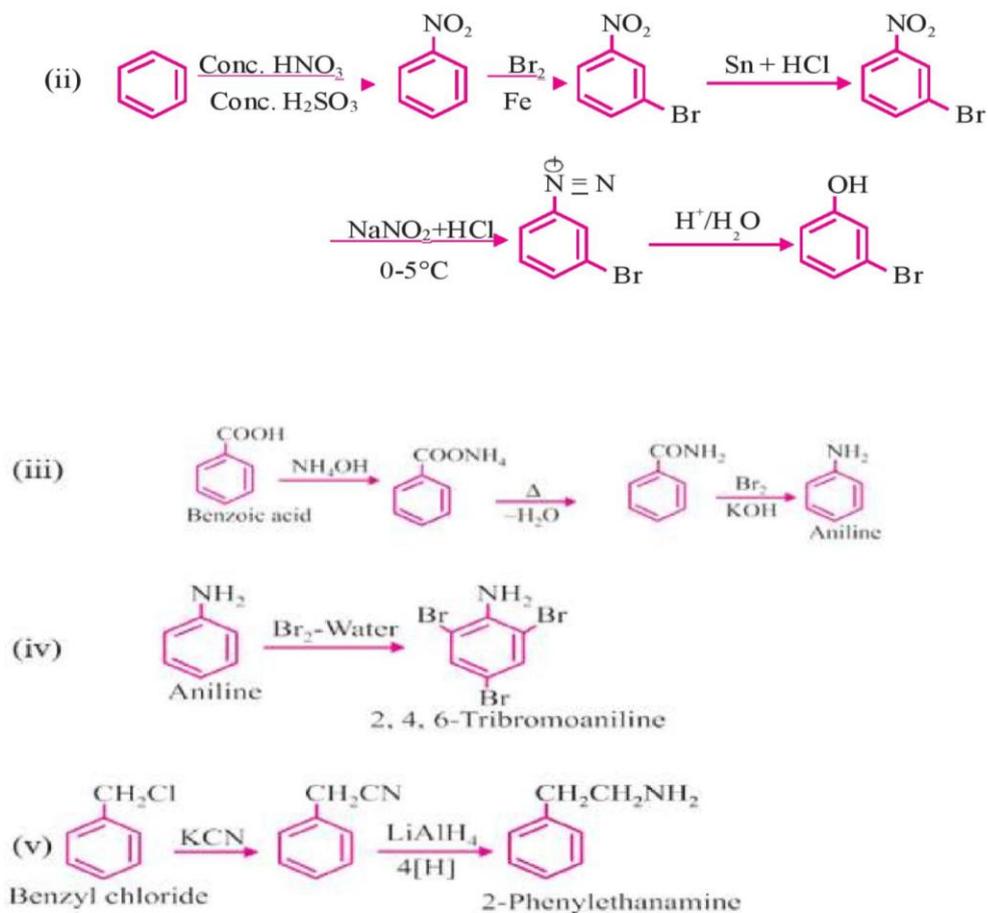


**Q. 4. Write A, B and C in the given reactions :**



**Q. 5. Accomplish the following conversions :**





Q. 6. Given reasons: (i) Acetylation of aniline reduces its activation effect.

(ii)  $\text{CH}_3\text{NH}_2$  is more basic than  $\text{C}_6\text{H}_5\text{NH}_2$

(iii) Although  $-\text{NH}_2$  group is o/p directing, yet aniline on nitration gives a significant amount of m-nitroaniline

Ans. (i) Due to the resonance, the electron pair of nitrogen atom gets delocalised towards carbonyl group/resonating structures.

(ii) Because of +I effect in methylamine electron density at nitrogen increases whereas in aniline resonance takes place and electron density on nitrogen decreases / resonating structures.

(iii) Due to protonation of aniline / formation of anilinium ion