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UNIT - 1

THE SOLID STATE

QUESTIONS

VSA QUESTIONS (1 MARK)

1. What are Bravais lattices?
2. Why are amorphous solids isotropic in nature?
3. Why glass is regarded as an amorphous solid?
4. Define the term 'crystal lattice.'
5. Name the crystal system for which all four types of unit cells are possible.
[Ans. Orthorhombic]
6. What is the total number of atoms per unit cell in a fcc crystal structure?
[Ans. 4]
7. What difference in behaviour between the glass and sodium chloride would you expect to observe, if you break off a piece of either cube?
8. Define the term voids.
9. What type of stoichiometric defect is shown by (i) ZnS and (ii) CsCl?
[Hint. : (i) Frenkel defect (ii) Schottky defect]
- *10. If the formula of a compound is A_2B , which sites would be occupied by A ions?
[Hint. : Number of A atoms is double to B, so it occupied tetrahedral void]
11. What is the coordination number for
(a) an octahedral void

(b) a tetrahedral void.

[Hint. : (a) 6; (b) 4]

*12. How many octahedral voids are there in 1 mole of a compound having cubic closed packed structure? [Ans. : 1 mole]

13. Arrange simple cubic, bcc and fcc lattice in decreasing order of the fraction of the unoccupied space.

[Hint. : fcc < bcc < simple cubic]

14. How much space is empty in a hexagonal closed packed solid?

15. An element crystallises separately both in hcp and ccp structure. Will the two structures have the same density? Justify your answer.

[Hint : Both crystal structures have same density because the percentage of occupied space is same.]

*16. Write dimensions and bond angles of match-box type of unit cells.

[Hint : Orthorhombic crystal system].

*17. Calculate the number of atoms in a cubic unit cell having one atom on each corner and two atoms on each body diagonal.

[Hint : No. of atoms = $8 \times 1/8 + 4 \times 2 = 9$]

18. In NaCl crystal, Cl^- ions form the cubic close packing. What sites are occupied by Na^+ ions.

19. In Corundum, O^{2-} ions form hcp and Al^{3+} occupy two third of octahedral voids. Determine the formula of corundum. [Ans. : Al_2O_3]

20. Why is Frenkel defect not found in pure alkali metal halides?

21. Which point defect is observed in a crystal when a vacancy is created by an atom missing from a lattice site.

22. Define the term 'doping'.

23. Why does conductivity of Silicon increase with the rise in temperature.

24. Name the crystal defect which lowers the density of an ionic crystal.

[Ans. : Schottky defect]

25. What makes the crystal of *KCl* sometimes appear violet?
[Hint : F-Centre]
26. Which Point defect in ionic crystal does not alter the density of the relevant solid?
27. Name one solid in which both Frenkel and Schottky defects occur.
28. Which type of defects are known as thermodynamic defects?
[Ans. : Stoichiometric defects]
29. In a p-type semiconductor the current is said to move through holes. Explain.
30. Solid A is very hard, electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it?
[Hint : Covalent solid]

SA (I) TYPE QUESTIONS (2 MARKS)

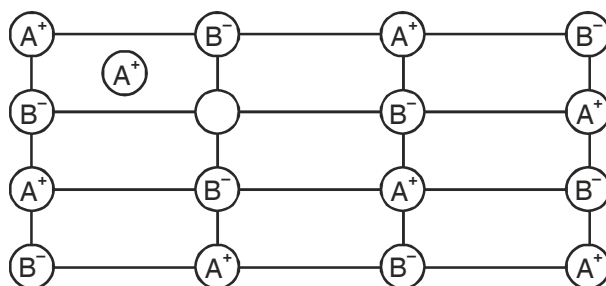
- List four distinctions between crystalline and amorphous solids with one example of each.
- Give suitable reason for the following—
 - Ionic solids are hard and brittle.
 - Copper is malleable and ductile.
- Define F-centre. Mention its two consequences.
- What is packing efficiency. Calculate the packing efficiency in body-centered cubic crystal.
- Explain :
 - List two differences between metallic and ionic crystals.
 - Sodium chloride is hard but sodium metal is soft.
- Account for the following :
 - Glass objects from ancient civilizations are found to become milky in appearance.

- (b) Window glass panes of old buildings are thicker at the bottom than at the top.
7. Why is graphite soft lubricant and good conductor of electricity?
8. What do you understand by the following types of stacking sequences :
- (a) AB AB (b) A B CABC
- What kind of lattices do these sequences lead to?
9. Derive the formula for the density of a crystal whose length of the edge of the unit cell is known?
- $$\left[\text{*Hint : } d = \frac{ZM}{a^3 \times N_A} \right]$$
10. Explain how much portion of an atom located at (a) corner (b) body centre (c) face-centre and (d) edge centre of a cubic unit cell, is part of its neighbouring unit cells.
- *11. In a fcc arrangement of A and B atoms. A are present at the corners of the unit cell and B are present at the face centres. If one atom of A is missing from its position at the corners, what is the formula of the compound? [Ans. : A₇B₂₄]
- *12. A compound made up of elements 'A' and 'B' crystallises in a cubic close packed structure. Atom A are present on the corners as well as face centres, whereas atoms B are present on the edge-centres as well as body centre. What is the formula of the compound? [Ans. A₄B₄ or AB]
13. Explain the terms :
- (a) Intrinsic semiconductor
- (b) Extrinsic semiconductor.
14. Explain how vacancies are introduced in a solid NaCl crystal when divalent cations are added to it.
15. What is meant by non-stoichiometric defect? Ionic solids which have anionic vacancies due to metal excess defect develop colour. Explain with the help of suitable example.
16. Define the term '**point defects**' Mention the main difference between stoichiometric and non-stoichiometric point defects.

SA(II) TYPE QUESTIONS (3 MARKS)

- Write the relationship between atomic radius (r) and edge length (a) of cubic unit cell for
 - Simple cubic unit cell
 - Body-centred cubic unit cell
 - Face-centred cubic unit cell

[Hint : (a) $a = 2r$ (b) $a = \frac{4}{\sqrt{3}} r$ (c) $a = 2\sqrt{2} r$]
- What is a semiconductor? Describe the two main types of semiconductors when it is doped with
 - group 13 element,
 - group 15 element.
- Explain the following with one examples each :
 - Ferrimagnetism
 - Antiferromagnetism
 - 13-15 compounds
- *4. Examine the defective crystal lattice given below and answer the following questions :



- Name the defect present in ionic solid.
- Out of AgCl and NaCl, which is most likely to show this type of defect and why?
- Why this defect is also known as dislocation defect?

NUMERICALS

1. Sodium crystallises in a bcc unit cell. What is the approximate number of unit cells in 4.6 g of sodium? Given that the atomic mass of sodium is 23 g mol⁻¹.
[Ans. : 6.022×10^{22}]
- *2. In a crystalline solid anions 'C' are arranged in cubic close packing, cations 'A' occupy 50% of tetrahedral voids and cations 'B' occupy 50% of octahedral voids. What is the formula of the solid?
[Ans. : A₂BC₂]
- *3. Magnetite, a magnetic oxide of iron used on recording tapes, crystallises with iron atoms occupying $\frac{1}{8}$ of the tetrahedral holes and $\frac{1}{2}$ of the octahedral holes in a closed packed array of oxides ions. What is the formula of magnetite?
[Ans. : Fe₃O₄]
4. A metal crystallises into two cubic lattices fcc and bcc, whose edge length are 3.5Å and 3.0Å respectively. Calculate the ratio of the densities of fcc and bcc lattices.
[Ans. : 1.26]
5. An element of atomic mass 98.5 g mol⁻¹ occurs in fcc structure. If its unit cell edge length is 500 pm and its density is 5.22 g cm⁻³. Calculate the value of Avogadro constant.
[Ans. : 6.03×10^{23} mol⁻¹]
6. An element crystallises in a cubic close packed structure having a fcc unit cell of an edge 200 pm. Calculate the density if 200 g of this element contain 24×10^{23} atoms.
[Ans. : 41.6 g cm⁻³]
7. A fcc unit cell containing atoms of element (molar mass 60.4 g mol⁻¹) has cell edge 4×10^{-8} cm. Calculate the density of unit cell.
[Ans. : 6.23 g/cm³]
- *8. The metal calcium (atomic mass = 40 gm mol⁻¹) crystallises in a fcc unit cell with a = 0.556 nm. Calculate the density of the metal if (i) It contains 0.2% Frenkel defect. (ii) It contains 0.1% schottky defect.
[Ans. : (i) 1.5463 g/cm³; (ii) 1.5448g/cm³]

[Hint : (i) $d = \frac{ZM}{a^3 \times N_A}$ (ii) $Z = \left[4 - \frac{4 \times 0.1}{100} \right] = 3.996$]
9. Analysis shows that a metal oxide has a empirical formula M_{0.96}O. Calculate the percentage of M²⁺ and M³⁺ ions in this crystal.
[Ans. : M²⁺ = 91.7%, M³⁺ = 8.3%]

10. AgCl is doped with 10^{-2} mol% of CdCl_2 , find the concentration of cation vacancies. [Ans. : 6.02×10^{19} mol]

11. A metallic element has a body centered cubic lattice. Edge length of unit cell is 2.88×10^{-8} cm. The density of the metal is 7.20 g cm^{-3} . Calculate

(a) The volume of unit cell.

(b) Mass of unit cell.

(c) Number of atoms in 100 g of metal.

[Ans. : (a) $2.39 \times 10^{-23} \text{ cm}^3$ (b) 1.72×10^{-22} g, (c) 1.162×10^{24} atoms]

12. Molybdenum has atomic mass 96 g mol^{-1} with density 10.3 g/cm^3 . The edge length of unit cell is 314 pm. Determine lattice structure whether simple cubic, bcc or fcc.

(Given $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$)

[Ans. : $Z = 2$, bcc type]

*13. The density of copper metal is 8.95 g cm^{-3} . If the radius of copper atom is 127 pm, is the copper unit cell a simple cubic, a body-centred cubic or a face centred cubic structure?

(Given at. mass of Cu = 63.54 g mol^{-1} and $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)

[Ans. : $Z = 4$ fcc type]

[Hint : $d = \frac{ZM}{a^3 \times N_A}$ calculate Z/a^3 by putting the values given in the question.

Calculate P.E. by $\frac{Z \times 4/3 \pi r^3}{a^3} \times 100$ using value of Z/a^3 , 74% results the fcc unit cells].

14. The well known mineral fluorite is chemically calcium fluoride. It is known that in one unit cell of this mineral there are 4 Ca^{2+} ions and 8 F^- ions and that Ca^{2+} ions are arranged in a fcc lattice. The F^- ions fill all the tetrahedral holes in the fcc lattice of Ca^{2+} ions. The edge of the unit cell is 5.46×10^{-8} cm in length. The density of the solid is 3.18 g cm^{-3} use this information to calculate Avogadro's number (Molar mass of $\text{CaF}_2 = 78.08 \text{ g mol}^{-1}$)

[Ans. : $6.02 \times 10^{23} \text{ mol}^{-1}$]

UNIT - 2

SOLUTIONS

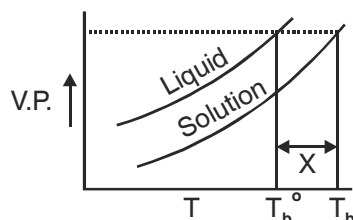
QUESTIONS

VSA TYPE QUESTIONS (1 MARK)

1. Give an example of 'liquid in solid' type solution.
2. Which type of solid solution will result by mixing two solid components with large difference in the sizes of their molecules?
3. What is meant by semimolar and decimolar solutions? [Ans. : $\frac{M}{2}$, $\frac{M}{10}$]
4. What will be the mole fraction of water in C_2H_5OH solution containing equal number of moles of water and C_2H_5OH ? [Ans. : 0.5]
5. Which of the following is a dimensionless quantity : molarity, molality or mole fraction? [Ans. : mole fraction]
6. 10 gm glucose is dissolved in 400 gm. of solution. Calculate percentage concentration of the solution. [Ans. : 2.5% w/w]
7. Gases tend to be less soluble in liquids as the temperature is raised. Why?
8. State the conditions which must be satisfied if an ideal solution is to be formed.
9. A mixture of chlorobenzene and bromobenzene forms nearly ideal solution but a mixture of chloroform and acetone does not. Why?
10. How is the concentration of a solute present in trace amount in a solution expressed?
- *11. Which aqueous solution has higher concentration 1 molar or 1 molal solution of the same solute? Give reason. [Ans. : 1M aqueous solution]

- *12. N_2 and O_2 gases have K_H values 76.48 Kbar and 34.86 kbar respectively at 293 K temperature. Which one of these will have more solubility in water?
- *13. Under what condition molality and molarity of a solution are identical. Explain with suitable reason.
- *14. Addition of HgI_2 to KI (aq.) shows decrease in vapour pressure. Why?
15. What will happen to the boiling point of the solution on mixing two miscible liquids showing negative deviation from Raoult's law.
16. Liquid 'Y' has higher Vapour pressure than liquid 'X', which of them will have higher boiling point?
17. When 50 mL of ethanol and 50 mL of water are mixed, predict whether the volume of the solution is equal to, greater than or less than 100 mL. Justify.
18. Which type of deviation is shown by the solution formed by mixing cyclohexane and ethanol?
19. A and B liquids on mixing produce a warm solution. Which type of deviation from Raoult's law is there?
20. Define cryoscopic constant (molal freezing point depression constant.)
21. Mention the unit of ebullioscopic constant (molal boiling point elevation constant.)
22. If k_f for water is $1.86 \text{ K kg mol}^{-1}$. What is the freezing point of 0.1 molal solution of a substance which undergoes no dissociation or association of solute.
 [Hint : $\Delta T_f = iK_f \cdot m$]
23. Name the component that separate first when salt solution is frozen.
24. What is reverse osmosis? Give one large scale use of it.
- *25. What is the maximum value of Van't Hoff factor (i) for $Na_2SO_4 \cdot 10H_2O$?
 [Ans. : $i = 3$]
26. What is the value of Van't Hoff factor (i) if solute molecules undergo dimerisation.
 [Ans. : $i = 0.5$]
27. Under what conditions is Van't Hoff factor less than one?
 [Ans. : Association]

- *28. The Phase Diagram for pure solvent and the solution containing non-volatile solute are recorded below. The quantity indicated by 'X' in the figure is known as : [Ans. : ΔT_b]



- *29. AgNO_3 on reaction with NaCl in aqueous solution gives white precipitate. If the two solutions are separated by a semi-permeable membrane will there be appearance of a white ppt. in the side 'X' due to osmosis?

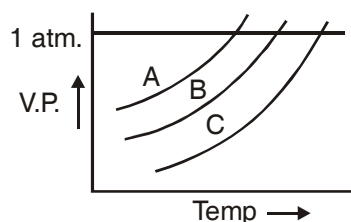
0.1 M AgNO_3 X	S P M	0.01 M NaCl Y
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[Ans. : No ppt, because only solvent particles moves through SPM]

SA (I) - TYPE QUESTIONS (2 MARKS)

1. Explain the following :
 - (a) Solubility of a solid in a liquid involves dynamic equilibrium.
 - (b) Ionic compounds are soluble in water but are insoluble in non-polar solvents.
2. Give two examples each of a solution :
 - (a) showing positive deviation from Raoult's Law.
 - (b) showing negative deviation from Raoult's Law.
3. Draw Vapour pressure vs composition (in terms of mole fraction) diagram for an ideal solution.
4. Define azeotropes with one example of each type.
5. Draw the total vapour pressure Vs. mol fraction diagram for a binary solution exhibiting non-ideal behaviour with negative deviation.

6. The vapour pressure curve for three solutions having the same non-volatile solute in the same solvent are shown. The curves are parallel to each other and do not intersect. What is the correct order of the concentrations of the solutions. [Hint. : A < B < C]



7. Show that the relative lowering of vapour pressure of a solvent is a colligative property.
8. Benzene and toluene form a nearly ideal solution. At a certain temperature, calculate the vapour pressure of solution containing equal moles of the two substances.
[Given : $P^{\circ}_{\text{Benzene}} = 150 \text{ mm of Hg}$, $P^{\circ}_{\text{Toluene}} = 55 \text{ mm of Hg}$]
9. What is meant by abnormal molecular mass? Illustrate it with suitable examples.
- *10. When 1 mole of NaCl is added to 1 litre water the boiling point increases. When 1 mole of CH_3OH is added to 1 litre water, the boiling point decreases. Suggest reason.
11. Can we separate water completely from HNO_3 solution by Vapourisation? Justify your answer.
- *12. 1 gram each of two solutes 'A' and 'B' (molar mass of A > molar mass of B) are dissolved separately in 100 g each of the same solvent. Which solute will show greater elevation in boiling point and Why?

SA (II) TYPE QUESTIONS (3 MARKS)

1. (a) State Henry's Law.
(b) If O_2 is bubbled through water at 393 K how many millimoles of O_2 gas would be dissolved in 1L of water? Assume that O_2 exerts a pressure of 0.95 bar.
(Given K_H for $\text{O}_2 = 46.82 \text{ bar at } 393\text{K}$).

2. Given reason for the following :-
- (a) Aquatic species are more comfortable in cold waters than in warm waters.
 - (b) To avoid bends scuba divers use air diluted with helium.
 - (c) Cold drinks bottles are sealed under high pressure.
3. Why should a solution of a non-volatile solute boil at a higher temperature? Explain with the help of a diagram. Derive the relationship between molar mass and elevation in boiling point.
4. Account for the following :-
- (a) CaCl_2 is used to clear snow from roads in hill stations.
 - (b) Ethylene glycol is used as antifreeze solution in radiators of vehicles in cold countries.
 - (c) The freezing point depression of 0.01 m NaCl is nearly twice that of 0.01 m glucose solution.
5. Why do colligative properties of solution of a given concentration are found to give abnormal molecular weight of solute. Explain with the help of suitable examples.
6. Give reasons for the following :-
- (a) RBC swell up and finally burst when placed in 0.1% NaCl solution.
 - (b) When fruits and vegetables that have been dried are placed in water, they slowly swell and return to original form.
 - (c) A person suffering from high blood pressure is advised to take less amount of table salt.
- *7. Glycerine, ethylene glycol and methanol sell at the same price per Kg. Which would be cheaper for preparing an antifreeze solution for the radiator of an automobile? **[Ans. : Methanol]**
- *8. Determine the correct order of the property mentioned against them :
- (a) 10% glucose (p_1), 10% urea (p_2), 10% sucrose (p_3)
[Osmotic pressure]

- (b) 0.1 m NaCl, 0.1 m urea, 0.1 m MgCl₂ [Elevation in b.pt.]
(c) 0.1 m CaCl₂, 0.1 m sucrose, 0.1 m NaCl [Depression in f.pt.]

LONG ANSWER TYPE QUESTIONS (5 MARKS)

1. (a) What are ideal solutions? Write two examples.
(b) Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0g of polymer of mol. mass 185000 in 450 ml of water at 37°C.
2. (a) Describe a method of determining molar mass of a non-volatile solute from vapour pressure lowering.
(b) How much urea (mol. mass 60 g mol⁻¹) must be dissolved in 50 g of water so that the vapour pressure at the room temperature is reduced by 25%? Also calculate the molality of the solution obtained.
[Ans. : 55.55 g and 18.5 m]
3. (a) Why is the freezing point depression considered as a colligative property?
(b) The cryoscopic constant of water is 1.86 K kg mol⁻¹. Comment on this statement.
(c) Calculate the amount of ice that will separate out on cooling solution containing 50 g of ethylene glycol in 200 g H₂O to -9.3°C. (K_f for water = 1.86 K kg mol⁻¹) [Ans. : 38.71g]
4. (a) Define osmotic pressure.
(b) Why osmotic pressure is preferred over other colligative properties for the determination of molecular masses of macromolecules?
(c) What is the molar concentration of particles in human blood if the osmotic pressure is 7.2 atm at normal body temperature of 37°C?
[Ans. : 0.283 M]

NUMERICAL PROBLEMS

1. Calculate the mass percentage of benzene (C₆H₆) and carbon tetrachloride (CCl₄), if 22 g of benzene is dissolved in 122g of carbon tetrachloride.
[Ans. : C₆H₆ = 15.3%, CCl₄ = 84.7%]

2. Calculate the molarity of a solution prepared by mixing 500 ml of 2.5 M urea solution and 500 mL of 2M urea solution. [Ans. : 2.25 m]

$$\left[\text{Hint : } M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2} \right]$$

3. The mole fraction of CH_3OH in an aqueous solution is 0.02 and density of solution 0.994 g cm^{-3} . Determine the molality and molarity.

[Ans. : 1.13m, 1.08m]

4. 200 mL of calcium chloride solution contains 3.011×10^{22} Cl^- ions. Calculate the molarity of the solution. Assume that calcium chloride is completely ionized. [Ans. : 0.125 M]

5. 6×10^{-3} g oxygen is dissolved per kg of sea water. Calculate the ppm of oxygen in sea water. [Ans. : 6 ppm]

6. The solubility of oxygen in water is $1.35 \times 10^{-3} \text{ mol L}^{-1}$ at 20°C and 1 atm pressure. Calculate the concentration of oxygen at 20°C and 0.2 atm pressure. [Ans. : $2.7 \times 10^{-4} \text{ mol L}^{-1}$]

7. Two liquids X and Y on mixing form an ideal solution. The vapour pressure of the solution containing 2 mol of X and 1 mol of Y is 550 mm Hg. But when 4 mol of X and 1 mole of Y are mixed, the vapour pressure of solution thus formed is 560 mm Hg. What will be the vapour pressure of pure X and pure Y at this temperature?

[Ans. : X = 600 mm Hg; Y = 400 mm Hg]

8. An aqueous solution containing 3.12 g of barium chloride in 250 g of water is found to be boil at 100.0832°C . Calculate the degree of dissociation of barium chloride.

[Given molar mass $\text{BaCl}_2 = 208 \text{ g mol}^{-1}$, K_b for water = 0.52 K/m]

[Ans. : 83.3%]

9. The degree of dissociation of $\text{Ca}(\text{NO}_3)_2$ in a dilute aqueous solution, containing 7.0 g of salt per 100 g of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution. [Ans. : 745.3 mm of Hg]

10. 2g of $\text{C}_6\text{H}_5\text{COOH}$ dissolved in 25g of benzene shows depression in freezing point equal to 1.62K. Molar freezing point depression constant for benzene is $4.9 \text{ K kg mol}^{-1}$. What is the percentage association of acid if it forms a dimer in solution? [Ans. : 99.2%]

11. Calculate the amount of NaCl which must be added to one kg of water so that the freezing point is depressed by 3K. Given $K_f = 1.86 \text{ K kg mol}^{-1}$, Atomic mass : Na = 23, Cl = 35.5). **[Ans. : 0.81 mol NaCl]**
12. Three molecules of a solute, A associate in benzene to form species A_3 . Calculate the freezing point of 0.25 molal solution. The degree of association of solute A is found to be 0.8. The freezing point of benzene is 5.5°C and its K_f value is 5.13 K/m . **[Ans. : 4.9°C]**
13. A 5% solution of sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is isotonic with 0.877% solution of urea. Calculate the molecular mass of urea. **[Ans. : 59.99 g mol^{-1}]**
14. Osmotic pressure of a 0.0103 molar solution of an electrolyte was found to be 0.75 atm at 27°C . Calculate Van't Hoff factor. **[Ans. : $i = 3$]**
- *15. The maximum allowable level of nitrates in drinking water as set by U.S. is 45 mg nitrate ions/ dm^3 . Express this level in ppm? **[Ans. : 45 ppm]**
16. 75.2 g of Phenol ($\text{C}_6\text{H}_5\text{OH}$) is dissolved in 1 kg solvent of $K_f = 14 \text{ K m}^{-1}$, if the depression in freezing point is 7 K, then find the % of Phenol that dimerises. **[Ans. : 75%]**
- *17. An aqueous solution of glucose boils at 100.01°C . The molal boiling point elevation constant for water is $0.5 \text{ K kg mol}^{-1}$. What is the number of glucose molecules in the solution containing 100 g of water. **[Ans. : 1.2×10^{21} molecules]**
18. A bottle of commercial H_2SO_4 [density = 1.787 g/mL] is labelled as 86% by mass.
- What is the molarity of the acid?
 - What volume of the acid has to be used to make 1 litre 0.2 M H_2SO_4 ?
 - What is the molality of the acid?
- [Ans. : 15.7 M, 12.74 mL, 62.86 m]**
19. A solution containing 30g of non-volatile solute exactly in 90g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate :
- molar mass of the solute
 - Vapour pressure of water at 298 K. **[Ans. : 34 g mol^{-1} , 3.4 kPa]**

20. The vapour pressure of pure liquids A and B are 450 and 750 mm Hg respectively, at 350K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase. [**Ans.** : $X_A = 0.4$, $X_B = 0.6$, $Y_A = 0.3$, $Y_B = 0.7$]
21. An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute? [**Ans.** : 41.35 g mol⁻¹]

UNIT - 3

ELECTRO CHEMISTRY

QUESTIONS

VSA TYPE QUESTIONS (1 MARK)

1. What is a galvanic cell?
2. Give the cell representation for Daniell Cell.
3. Mention the purpose of salt-bridge placed between two half-cells of a galvanic cell?
4. Give the condition for Daniell Cell in which there is no flow of electrons or current or we can conclude that there is no chemical reaction.
5. How is electrode potential different from cell potential?
6. Can you store zinc sulphate solution in a copper container? Give suitable reason.
7. How does electrochemical series help us in predicting whether a redox reactions is feasible in a given direction or not?
8. Write Nernst equation for the electrode reaction. $M^{n+}_{(aq)} + ne^{-} \longrightarrow M_{(s)}$ at 298 K and 1 atm. pressure.
9. As per electrochemical series and on the basis of E° values, identify the following :
 - (a) Gas which has highest tendency for reduction.
 - (b) Weakest oxidising ion.
10. List the two factors that influence the value of cell potential of a galvanic cell.

11. How is equilibrium constant of a reaction related to standard cell potential?
12. Write the relation between E°_{cell} and equilibrium constant (K) of cell reaction.
13. Define cell constant. Mention the SI unit of cell constant.
14. How does specific conductance conductivity of electrolic solution. Vary with temperature?
15. What is the SI unit of (i) Conductance; (ii) Conductivity.
16. Represent a concentration cell with a suitable example.
17. State one difference between a primary battery and secondary battery.
- *18. Galvanized iron does not corrode even if the coating of zinc is broken. Explain why?
(Given : $E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$; $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$]
19. Write unit of Faraday constant.
- *20. Write the name of a chemical substance which is used to prevent corrosion.
[Ans. : Bisphenol]
21. Show is the direction of flow of electrons in the following cell :
$$\text{Zn (s) | Zn}^{2+} \text{ (aq) || Ag}^{+} \text{ (aq) | Ag}$$
22. Rusting of iron becomes quicker in saline water. Explain.
- *23. Two metals A and B have reduction potential values of -0.25V and 0.80V respectively. Which of these will liberate hydrogen gas from dilute H_2SO_4 ?
24. Express the relation between conductivity and molar conductivity.
25. Name the cell which was used in Apollo space programme.
26. How many Faradays are required to oxidize 1 mole of H_2O to O_2 .
[Ans. : 2F]

SI (I) TYPE QUESTIONS (2 MARKS)

1. List two points of difference between metallic conductance and electrolytic conductance.

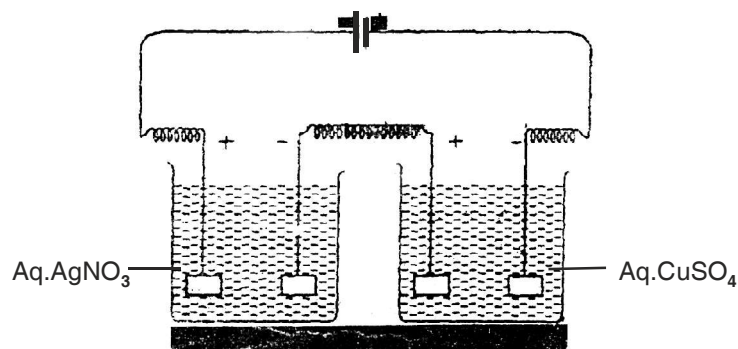
2. List two points of difference between electrochemical cell and electrolytic cell.
3. List four factors which affect the conductivity of ionic solutions.
4. A conventional method of representing a Daniel cell is $Zn(s) | Zn^{2+}(1M) || Cu^{2+}(1M) | Cu(s)$.
 - (i) Draw a diagram of the cell and mark anode and cathode as current is drawn from the cell.
 - (ii) Write the reactions taking place at the cathode and the anode during the operation of Daniel cell.
- *5. Suggest a method to determine the Λ_m° value of water.
6. Write the cell reaction which occur in the lead storage battery (a) when the battery is in use (b) when the battery is on charging.
7. Why absolute value of electrode potential cannot be determined?
8. Account for the fact that when chlorine is passed through a fluoride solution, no reaction takes place. (Given $E_{F_2/2F^-}^\circ = 2.87V$; $E_{Cl_2/2Cl^-}^\circ = 1.36V$).
9. Copper does not dissolve in HCl (aq) but dissolves in HNO_3 (aq) producing Cu^{2+} ions. Explain the difference in behaviour.

[Given $E_{Cu^{2+}/Cu}^\circ = 0.34V$; $E_{Cl_2/2Cl^-}^\circ = 1.36V$ and $NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O$, $E_{NO_3^-/NO}^\circ = 0.97V$].
10. Explain the following observations :
 - (a) The product of electrolysis of molten NaCl are sodium metal and chlorine gas.
 - (b) The product of electrolysis of aqueous sodium chloride solution are NaOH, Cl_2 and H_2 .
11. What are fuel cells? Describe the principle and overall reaction involved in the working of hydrogen–oxygen fuel cell.
12. Explain the meaning of the terms
 - (a) Ionic mobility.
 - (b) Overvoltage.

*13. Some standard reduction potential are as given below :

Half Cell	E° Value
F_2/F^-	2.9V
Ag^+/Ag	0.8V
Cu^+/Cu	0.5V
Fe^{2+}/Fe	-0.4V
Na^+/Na	-2.7V
K^+/K	-2.9V

- (a) Arrange oxidising agents in order of increasing strength.
- (b) Which of these oxidising agents will oxidise Cu to Cu^+ under standard conditions?
14. Account for the following observations :
- (a) In a dry cell, the build up of ammonia around the carbon cathode should disrupt the electric current, but in practice this does not happen.
- (b) Ordinary dry cells are not rechargeable.
- *15. The following figure shows two electrolytic cells connected in series.

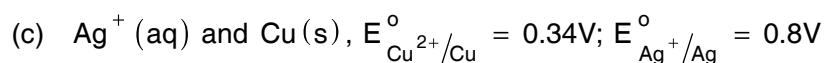
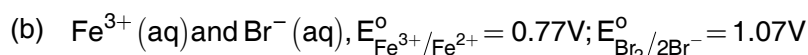
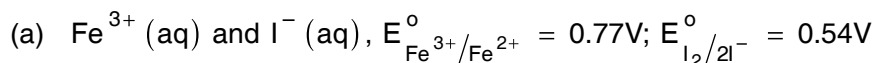


- (a) How much electricity is required for the reduction of 1 mole of Ag^+ ions to Ag?
- (b) If three faradays of electricity is passed through these cells, what is the ratio of cation [Ag^+ and Cu^{2+}] deposited on cathodes?

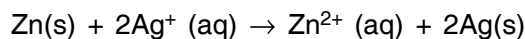
[Ans. : (a) 1F, (b) 2:1]

SA (II) TYPE QUESTIONS (3 MARKS)

1. Using the standard electrode potential, predict the reaction, if any that occurs between the following :-



2. State the relationship amongst cell constant of a cell, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solute related to conductivity of its solution?
3. Describe the composition of anode and cathode in a mercury cell. Write the electrode reactions for this cell. Why it provides constant voltage throughout its life?
4. Give reasons for :
- (a) For a weak electrolyte, its molar conductivity of dilute solution increases sharply as the concentration of solution is decreased.
- (b) Molar conductivity of a strong electrolyte like KCl decrease slightly while increasing concentration?
- (c) It is not easy to determine Λ_m° of a weak electrolyte by extrapolation of \sqrt{c} vs Λ_m curves?
5. (a) Write the mechanism of the corrosion of metals.
(b) How is underground iron pipe is protected from corrosion?
6. Formulate the galvanic cell in which the following reaction takes place :



State

- (a) Which one of its electrodes is negatively charged?
- (b) The reaction taking place at each of its electrode.
- (c) The direction of current within this cell.

*7. The standard reduction potentials are as given below :-

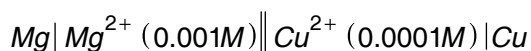
Half Cell	E° Value
Zn (OH) ₂ /Zn	- 1.245 V
Mg (OH) ₂ /Mg	- 2.690 V
Fe (OH) ₂ /Fe	- 0.877 V
Fe (OH) ₃ /Fe	- 2.30 V

Under standard conditions :

- Which is the strongest reducing agent?
- Which reducing agent could reduce Zn(OH)₂ to Zn?
- Which reducing agent could reduce Fe(OH)₂ to Fe?

LONG ANSWER TYPE QUESTIONS (5 MARKS)

- Explain with example the terms weak and strong electrolytes.
 - Calculate the *emf* of the cell



Given $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$; $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = - 2.375\text{V}$.

[Ans. : 2.651 V]

- Explain Kohlrausch's law of independent migration of ions. Mention two applications of this law.
 - The conductivity of 0.001M CH₃COOH is $4.95 \times 10^{-5} \text{ Scm}^{-1}$. Calculate its dissociation constant. Given for acetic acid Λ°_m is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$.
[Ans. : $\alpha = 0.126$]
- Define molar conductivity. Draw the plots showing the variation of molar conductivity for strong and weak electrolysis with square root of concentration.
 - Resistance of a solution (A) is 50 ohm and that of solution (B) is 100 ohm, both solution being taken in the same conductivity cell, if equal volumes of solutions (A) and (B) are mixed, what will be the

resistance of the mixture, using the same cell? Assume that there is no increase in the degree of dissociation of (A) and (B) on mixing. **[Ans. : 66.66 ohm]**

[Hint. : k = Conductivity, y = Cell constant]

$$k_1 = \frac{1}{50} y, k_2 = \frac{1}{100} y : \text{Specific conductance of mixture}$$

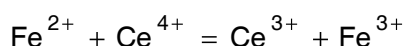
$$= \frac{k_1 + k_2}{2}$$

$$\frac{k_1 + k_2}{2} = \frac{1}{R} \times y, \frac{1}{2} \left[\frac{y}{50} + \frac{y}{100} \right] = \frac{1}{R} \times y \Rightarrow R = 66.66 \text{ ohm}$$

4. (a) State Faraday's first and second laws of electrolysis.
 (b) Silver is deposited on a metallic vessel of surface area 800 cm² by passing current of 0.2 ampere for 3 hours. Calculate the thickness of silver deposited.

(Density of silver = 10.47 g cm⁻³, Molar atomic mass of silver = 107.924 g mol⁻¹) **[Ans. : 2.9 × 10⁻⁴ cm]**

5. (a) Draw the diagram of standard hydrogen electrode. Write the electrode reaction.
 (b) Calculate the equilibrium constant for the reaction :

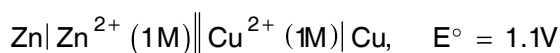
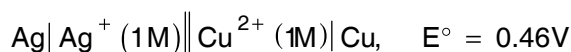


Given $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} = 1.44\text{V}$; $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.68\text{V}$.

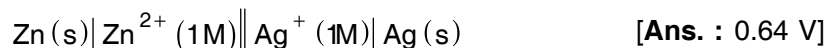
[Ans. : 7.6 × 10¹²]

NUMERICAL PROBLEMS

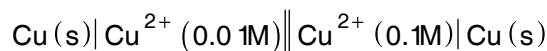
- *1. The emf of the following cells are:



Calculate emf of the cell



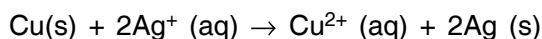
2. For concentration cell



- (a) Calculate the cell potential
(b) Will the cell generate emf when concentration becomes equal.

[Ans. : 0.295V, No.]

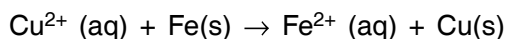
3. Calculate the equilibrium constant for the reaction at 25°C.



The standard cell potential for the reaction at 25°C is 0.46V.

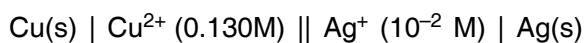
[Ans. : 4.0×10^{15}]

4. Calculate ΔG° for the reaction.



$$E_{\text{Cu}^{2+}/\text{Cu}}^\circ = +0.34\text{V}; E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44\text{V} \quad [\text{Ans. : } -150, 540 \text{ kJ}]$$

5. Conductivity of two electrolytic solutions of 0.1 M concentration of the substances A and B are 9.2×10^{-3} and $4.7 \times 10^{-4} \text{ S cm}^{-1}$, which one of these offer less resistance for the flow of current and which one is a stronger electrolyte?
6. Write the Nernst equation and calculate the emf of the following cell at 298K.



$$\text{Given } E_{\text{Cu}^{2+}/\text{Cu}}^\circ = +0.34\text{V}; E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80\text{V}. \quad [\text{Ans. : } 0.25\text{V}]$$

7. A zinc rod is dipped in 0.1M solution of ZnSO_4 . The salt is 95% dissociated at this dilution at 298K. Calculate the electrode potential

$$\left(E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76\text{V} \right). \quad [\text{Ans. : } -0.7902\text{V}]$$

8. For the electrode $\text{Pt}, \text{H}_2 (1 \text{ atm}) | \text{H}^+_{(\text{aq})} (XM)$, the reduction electrode potential at 25°C is -0.34V . Write the electrode reaction and calculate the value of X. How will you deduce the pH of solution from this result?

[Ans. : $X = 1.807 \times 10^{-6}$, $\text{pH} = 5.743$]

9. For what concentrations of $\text{Ag}^+ (\text{aq})$ will the emf of the given cell be zero at 25°C if concentration of $\text{Cu}^{2+} (\text{aq})$ is 0.1M ? Given

$$E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}. E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}.$$

Cell : $\text{Cu} (\text{s}) / \text{Cu}^{2+} (\text{aq}) // \text{Ag}^+ (\text{aq}) / \text{Ag} (\text{s})$ [Ans. 5.3×10^{-9}]

10. Zinc granules are added in excess to 500 mL of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potential of $\text{Zn}^{2+} | \text{Zn}$ and $\text{Ni}^{2+} | \text{Ni}$ are -0.75 V and -0.24 V respectively, find out the concentration of Ni^{2+} in solution at equilibrium.

[Ans. : $5.88 \times 10^{-18}\text{M}$]

11. The molar conductivity of 0.1M CH_3COOH solution is $4.6\text{S cm}^2 \text{ mol}^{-1}$. Calculate the conductivity and resistivity of the solution.

[Ans. : $0.00046 \text{ S cm}^{-1}$, $2174 \Omega \text{ cm}$]

12. The molar conductivities of NH_4^+ ion and Cl^- ion are $73.5 \text{ S cm}^2 \text{ mol}^{-1}$ and $76.255 \text{ cm}^2 \text{ mol}^{-1}$ respectively. The specific conductivity of 0.1 M NH_4Cl is $1.288 \times 10^{-2} \text{ Scm}^{-1}$. Calculate the dissociation constant of NH_4Cl .

[Ans. : 7.396×10^{-2}]

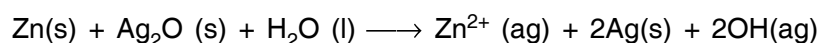
13. Molar conductivity at infinite dilution for NH_4Cl , NaOH and NaCl solution at 298K are respectively 129.8 , 218.4 and $108.9 \text{ Scm}^2 \text{ mol}^{-1}$ and Λ_m for 10^{-2} M solution of NH_4OH is $9.33 \text{ Scm}^2 \text{ mol}^{-1}$. Calculate the degree of dissociation of NH_4OH .

[Ans. : 0.039]

14. Write the Nernst equation and emf of the following cell at 298 K ; $\text{Pt}(\text{s}) / \text{Br}_2(\text{l}) | \text{Br}^-(0.010\text{M}) || \text{H}^+(0.030\text{M}) | \text{H}_2(\text{g}) (0.9 \text{ bar}) | \text{Pt}(\text{s})$. $E^\circ_{\text{Br}^-/\text{Pt}} = 1.0 \text{ 9V}$.

[Ans. : -0.88V]

15. In the button cells widely used in watches and other derices, the following reaction takes place :



Determine $\Delta_r G^\circ$ and E° for the reaction.

$$\text{Given : } \Delta_f G^\ominus (\text{Ag}_2\text{O}) = -11.20 \frac{\text{kJ}}{\text{mol}} / \Delta_f G^\ominus (\text{H}_2\text{O}) = -237.13 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G^\ominus (\text{Zn}^{2+}) = -147.06 \frac{\text{kJ}}{\text{mol}} / \Delta_f G^\ominus (\text{HO}^-) = -157.24 \frac{\text{kJ}}{\text{mol}}$$

$$[\text{Ans. : } \Delta_r G^\ominus = -213.21 \text{ KJ/mol}^{-1}, E^\ominus = 1.105 \text{ V}]$$

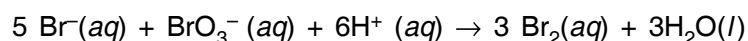
UNIT - 4

CHEMICAL KINETICS

QUESTIONS

VSA TYPE QUESTIONS (1 MARK)

1. Define the term 'rate of reaction'.
2. Mention the units of rate of reaction.
3. Express the rate of reaction in terms of $\text{Br}^- (aq)$ as reactant and $\text{Br}_2 (aq)$ as product for the reaction :

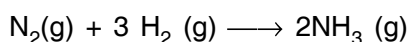


4. For a chemical reaction represented by $\text{R} \rightarrow \text{P}$ the rate of reaction is denoted by

$$\frac{-\Delta [\text{R}]}{\Delta t} \quad \text{or} \quad \frac{+\Delta [\text{P}]}{\Delta t}$$

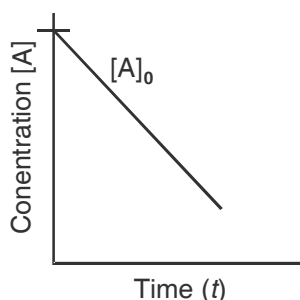
Why a positive sign (+) is placed before $\frac{\Delta [\text{P}]}{\Delta t}$ and not before $\frac{\Delta [\text{R}]}{\Delta t}$?

5. Express the rate of reaction in terms of disappearance of hydrogen and appearance of ammonia in the given reaction.

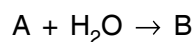


6. Why rate of reaction does not remain constant throughout?
7. Write the unit of first order rate constant of gaseous reaction if the partial pressure of gaseous reactant is given in bar.
8. For a zero order reaction :

$\text{R} \rightarrow \text{P}$, the change in concentration of reactant w.r.t. time is shown by following graph.



9. What will be the order of reaction, if the rate of reaction does not depend on the concentration of any of the reactant.
10. For the elementary step of a chemical reaction :



$$\text{rate} \propto [A]^1$$

What is the (i) Molecularity and (ii) Order of the reaction.

[Ans. : (i) 2 (ii) 1]

11. For a chemical reaction $A \rightarrow B$. The rate of the reaction is given as

Rate = $k [A]^n$, the rate of the above reaction quadruples when the concentration of A is doubled. What is the value of n? [Ans. : $n = 2$]

12. Mention one example of zero order reaction.

13. What is the value of the order of reaction of radioactive decay?

[Ans. : First order]

- *14. Express the relation between the half life period of a reactant and initial concentration for a reaction of n^{th} order.

$$\left[\text{Ans. : } t_{1/2} \propto \frac{1}{[A]_0^{n-1}} \right]$$

- *15. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction? [First order]

16. Suggest an appropriate reason for the observation : "On increasing temperature of the reacting system by 10 degrees, the rate of reaction almost doubles or even some times becomes five folds."

- *17. For a chemical reaction, activation energy is zero and at 300k rate constant is $5.9 \times 10^{-5} \text{ sec}^{-1}$, what will be the rate constant at 400k?

[Ans. : $5.9 \times 10^{-5} \text{ sec}^{-1}$]

- *18. Two reactions have identical values of E_a . Does this ensure that also they will have the same rate constant if run at the same temperature? Explain.

[Hint : Rate depends on the nature and concentrations of reactants and also pre-exponential factor.

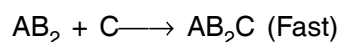
19. The rate constant of a reaction is given by the expression

$$k = Ae^{-E_a/RT}$$

Which factor in this expression should register a decrease so that the reaction proceeds rapidly?

20. For a chemical reaction rate constant $k = 5.3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ what will be the order of reaction? [Ans. : Zero order]

21. Write the rate law and order for the following reaction :



[Ans. : Rate = $k [AB_2] [C_2]$; Order = $1 + 1 = 2$]

SA (I) TYPE QUESTIONS (2 MARKS)

22. List four factors which affect the rate of a chemical reaction. State how each of these factors changes the reaction rate.

23. Differentiate between

- (a) Average rate and instantaneous rate of a chemical reaction.
(b) Rate of a reaction and specific rate of reaction.

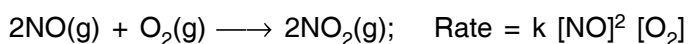
24. The rate law for the reaction $A + B \longrightarrow P$ is given by

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

On doubling the concentration of A and reducing the concentration of B to half of its original concentration, calculate the ratio of the new rate to the previous rate of reaction. [Ans. : 2^{n-m}]

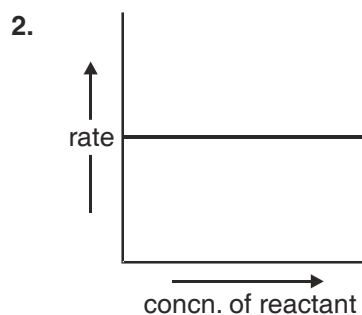
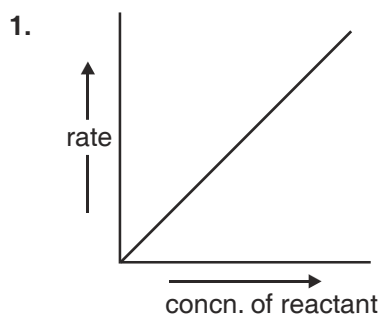
$$\left[\text{Hint : } \frac{\text{New rate}}{\text{Previous rate}} = \frac{k [2A]^n \left[\frac{B}{2}\right]^m}{k [A]^n [B]^m} \right]$$

25. For the reaction in a closed vessel :



If the volume of the reaction vessel is doubled, how would it affect the rate of the reaction? **[Ans. : Diminish to 1/8 volume of initial value]**

26. Explain with an example, what is a pseudo first order reaction?
27. Show that time required for 99.9% completion of the first order reaction is 10 times of $t_{1/2}$ for first order chemical reaction.
28. The graphs (1 and 2) given below are plots of rate of reaction verses concentration of the reaction. Predict the order from the graphs.

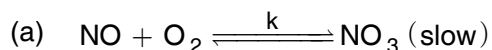
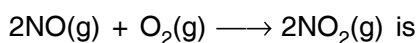


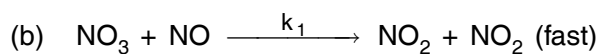
29. (a) For a reaction $\text{A} + \text{B} \rightarrow \text{Products}$, the rate law is given by

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

What is the order of reaction?

- (b) the conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y? **[Ans. : (a) 5/2; (b) 9 times]**
30. The possible mechanism for the reaction



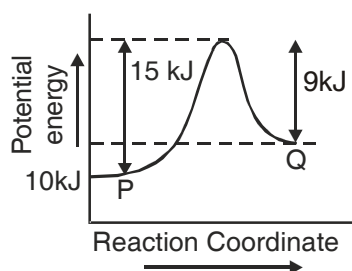


What is the predicted rate law and order of the reaction?

[Ans. : Rate = $k [\text{NO}]^2 [\text{O}_2]$; Order = 2 + 1 = 3]

SA (II) TYPE QUESTIONS (3 MARKS)

31. What is meant by zero order reaction? Derive an integrated rate equation for a zero order reaction.
32. (a) Write two points of difference between order and molecularity of a reaction.
(b) Write one point of difference between rate of reaction and rate constant.
33. Draw a graph between fraction of molecules and kinetic energy of the reacting species for two different temperatures :
(a) Room temperature
(b) Temperature 10°C higher than the room temperature
(c) Indicate the fraction of additional molecules which react at $(t + 10)^\circ\text{C}$.
34. The energy of activation for forward and backward reactions for a hypothetical reaction $\text{P} \rightarrow \text{Q}$ are 15 kJ/mol and 9 kJ/mol respectively. Potential energy of P is 10 kJ/mol as shown in the graph. Determine
(a) Threshold energy of the forward reaction.
(b) Potential energy of Q.
(c) Heat of reaction. [Ans. : (a) 25 kJ (b) 16 kJ (c) 6 kJ]



LONG ANSWER TYPE QUESTIONS (5 MARKS)

35. (a) A chemical reaction is of second order w.r.t. a reactant. How will the rate of reaction be affected if the concentration of this reactant is : (a) Doubled; (b) Reduced to 1/8th.

[Ans. : (a) Four times (b) 1/64]

- (b) From the following data for a chemical reaction between A and B at 300 K

[A] mol/L	[B] mol/L	Initial rate (mol L ⁻¹ sec ⁻¹)
2.5 × 10 ⁻⁴	3 × 10 ⁻⁵	5 × 10 ⁻⁴
2.5 × 10 ⁻⁴	6 × 10 ⁻⁵	4 × 10 ⁻³
1 × 10 ⁻³	6 × 10 ⁻⁵	1.6 × 10 ⁻²

Calculate (i) the order of reaction with respect to A and with respect to B. (ii) the rate constant at 300K.

36. (a) Draw a plot between log k and reciprocal of absolute temperature.
(b) The energy of activation for a chemical reaction is 100 kJ/mol. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on the rate of reaction at 20°C, if other things are equal.
37. (a) Derive the equation for rate constant of a first order reaction. What would be the units of the first order rate constant if the concentration is expressed in moles per litre and time in second?
(b) For first order chemical reaction half life period ($t_{1/2}$) is concentration independent. Justify the statement by using integrated rate equation.

NUMERICALS

38. The reaction $\text{SO}_2\text{Cl}_2(\text{g}) \xrightarrow{k} \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is a first order reaction with half life of 3.15×10^4 s at 575 K. What percentage of SO_2Cl_2 would be decomposed on heating at 575K for 90 min. [Ans. : 11.2%]

39. A certain reaction is 50% complete in 20 min at 300K and the same reaction is again 50% complete in 5 min at 350K. Calculate the activation energy if it is a first order reaction.

(R = 8.314J K⁻¹ mol⁻¹, log 4 = 0.602)

[Ans. : 24.206 kJ/mol]

40. For a chemical reaction $A \rightarrow B$, it was found that concentration of B increases by 0.2 mol L^{-1} in half an hour. What is the average rate of reaction. **[Ans. : $0.0066 \text{ mol L}^{-1} \text{ min}^{-1}$]**
41. In the reaction $R \rightarrow P$, the concentration of R decreases from 0.03M to 0.02 M in 25 minutes. Calculate the average rate of reaction using unit of time both in minutes and seconds. **[Ans. : $4 \times 10^{-4}\text{M min}^{-1}$, $6.66 \times 10^{-6} \text{ M s}^{-1}$]**
42. A first order reaction has a rate constant $1.15 \times 10^{-3} \text{ s}^{-1}$. How long will 5g of this reactant take to reduce to 3g? **[Ans. : $t = 444 \text{ s}$]**
43. The rate of reaction triples when the temperature changes from 20°C to 50°C . Calculate the energy of activation. [$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $\log 3 = 0.48$] **[Ans. : 12.59 kJ]**
- *44. A hydrogenation reaction is carried out at 550 K . If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K . Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1} .
[Hint : $k = Ae^{-E_a/RT}$. In the absence of catalyst, $E_a = x \text{ kJ mol}^{-1}$. In the presence of catalyst, $E_a = (x - 20) \text{ kJ mol}^{-1}$]
[Ans. : $E_a = 100 \text{ kJ mol}^{-1}$]
45. The rate constant for the first order decomposition of H_2O_2 is given by the following equation $\log k = 14.34 - 1.25 \times 10^4 \text{ K/T}$. Calculate E_a for this reaction and at what temperature will its half-life be 256 minutes. **[Ans. : $E_a = 239.34 \text{ kJ}$; $T = 670\text{k}$]**
46. Show that for a first order reaction, time required for 99% completion is twice for the time required for the completion of 90% of reaction.
47. The experimental data for the reaction $2A + B_2 \longrightarrow 2AB$, are as follows. Write probable rate expression.

$[A] \text{ mol/L}^{-1}$	$[B_2] \text{ mol/L}^{-1}$	Initial rate $\text{mol L}^{-1} \text{ sec}^{-1}$
0.5	0.5	1.6×10^{-4}
0.5	1.0	3.2×10^{-4}
1.0	1.0	3.2×10^{-4}

$$\left[\text{Ans. : } \frac{dx}{dt} = k[B_2] \right]$$

48. A reaction is 20% complete in 20 minutes. Calculate the time required for 80% completion of reaction, If reaction follows the first order kinetics.

[Ans. : 144 min]

49. The decomposition of phosphine $4\text{PH}_3(\text{g}) \longrightarrow \text{P}_4(\text{g}) + 6\text{H}_2(\text{g})$ has rate law;

Rate = $k [\text{PH}_3]$. The rate constant is $6.0 \times 10^{-4} \text{ s}^{-1}$ at 300K and activation energy is $3.05 \times 10^5 \text{ J mol}^{-1}$. Calculate the value of the rate constant at 310K. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

[Ans. : $30.97 \times 10^{-3} \text{ s}^{-1}$]

50. For the decomposition of azoisopropane to hexane and nitrogen at 543K, the following data is obtained.

t sec.	0	360	720
Pressure (atm.)	35.0	54.0	63.0

Calculate the rate constant.

[Ans. : $k_{360} = 2.17 \times 10^{-3} \text{ s}^{-1}$; $k_{720} = 2.24 \times 10^{-3} \text{ s}^{-1}$]

51. The decomposition of hydrocarbon follows the equation $k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K/T}}$ Calculate Ea.

[Ans. : $232.79 \text{ kJmol}^{-1}$]

UNIT 5

SURFACE CHEMISTRY

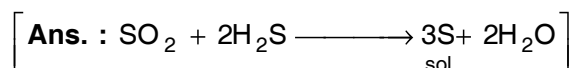
QUESTIONS

VSA TYPE QUESTIONS (1 MARK)

1. Why does a gas mixed with another gas not form a colloidal system?
2. Why adsorbate particles are attracted and retained on the surface of adsorbent?
3. Explain the terms sorption and desorption.
4. "Chemisorption is highly specific." Illustrate with an example.
5. "Adsorbents in finely divided form are more effective." Why?
6. Name two compounds used as adsorbent for controlling humidity.
[Ans. : Silica gel, Alumina gel]
7. Mention one shape-selective catalyst used to convert alcohol into gasoline.
8. 'Generally high temperature is favourable for chemisorption.' Why?
9. Name the catalyst used in the following process :
 - (a) Haber's process for the manufacture of NH_3 gas.
 - (b) Ostwald process for the manufacture of nitric acid.
10. Explain the relationship given by Freundlich in Freundlich adsorption isotherm.
11. Which group elements show maximum catalytic activity for hydrogenation reactions?

[Hint : 7–9 group elements]

12. Why gas masks are used by miners in coal mines while working?
13. Write the chemical reaction involved in the preparation of sulphur sol.



14. Name the enzyme which converts milk into curd. [Ans. : lactobacilli]
15. What are the optimum temperature and pH under which enzymes are highly active. [Ans. : Temperature 298–310K and pH – 5 to 7]
16. What are the physical states of dispersed phase and dispersion medium in foam rubber.
17. Identify the micelle in the following examples
- (a) Sulphur sol (b) Solution of KCl
- (c) Starch sol (d) $\text{C}_{17}\text{H}_{35}\text{COO}^-\text{Na}^+$

18. What is the composition of colloidal solution?
19. Why Tyndall effect is observed when colloidal solutions are viewed at right angles to the passage of light?
20. Why colloidal particles show Brownian movement?

[Hint : Due to unbalanced bombardment of the particles by the molecules of the dispersion medium]

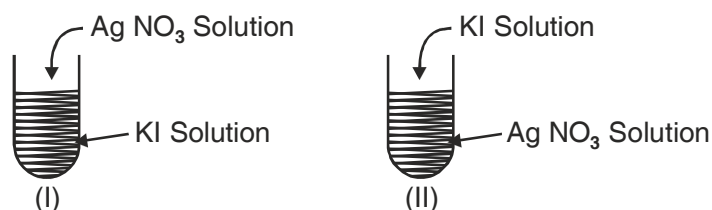
21. How can the ultrafiltration process of a colloidal solution be made faster?
22. State the sign of entropy change involved when the molecules of a substance get adsorbed on a solid surface. [Ans. : $\Delta S = -ve$]
23. Why is the ester hydrolysis slow in the beginning and becomes faster after some time.
24. Why does sky appear blue to us?
25. What happens when hydrated ferric oxide (+ve sol) and arsenious sulphide (–ve sol) are mixed in almost equal proportions?
- *26. Gelatin is generally added to ice-cream.

[Hint : Ice-cream is w/o emulsion and gelatin acts as emulsifier].

27. How lake test is based upon adsorption?
 [Hint : $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ has the capacity to adsorb the colour of blue litmus from the solution]
- *28. What is saturation pressure in Freundlich's isotherm?
29. Mention the two conditions for the formation of micelles.
 [Hint. : CMC and T_k]
- *30. 'Ultramicroscope does not provide any information about the size and shape of colloidal particles.' Why?
31. How Brownian movement is responsible for the stability of sols?
 [Hint : Stirring effect due to Brownian movement does not allow the particles to settle down.]
32. Which of the following is more effective in coagulating positively charged hydrated ferric oxide sol : (i) KCl (ii) CaSO_4 (iii) $\text{K}_3[\text{Fe}(\text{CN})_6]$.
33. State the purpose of impregnating the filter paper with colloidal solution.
34. Mention one use of ZSM-5 catalyst.

SA (I) TYPE QUESTIONS (2 MARKS)

35. Explain the effect of temperature on the extent of physical and chemical adsorption.
36. Define the term peptization and also mention its cause.
37. Arrange the gases CO , N_2 and CH_4 in increasing order of adsorption on the surface of charcoal in a closed vessel. Give reasons also.
 [Hint : $\text{N}_2 < \text{CO} < \text{CH}_4$ as critical temp. \propto extent of adsorption]
38. What will be the charge on colloidal solutions in the following cases.



Give reasons for the origin of charge.

39. What happens :
- When animal charcoal is added to a solution of methylene blue dye.
 - When aqueous solution of raw sugar is passed over beds of animal charcoal.
40. Write the factors upon which the catalytic reaction of shape-selective catalyst depends?
- [Hint : (a) Pore structure of the catalyst; (b) Size and shape of the reactant and product molecules.]
41. Mention two examples of emulsifying agents for o/w emulsions and w/o emulsions.
42. Suggest a mechanism of enzyme catalysed reaction along with the diagram.
43. What are the conditions for the occurrence of (a) Electrophoresis and (b) Electroosmosis?
44. A small amount of silica gel and a small amount of anhydrous calcium chloride are placed separately in two beakers containing water vapour. Name of phenomenon that takes place in both the beakers.
- [Hint : Silica gel – Adsorption, Anhydrous CaCl_2 – Absorption, as it forms $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)
45. Write the differences between adsorption and absorption?
46. How physisorption can be distinguished from chemisorption?
47. Classify the following reactions as homogeneous and heterogeneous catalysis :
- Vegetable oil (l) + H_2 (g) $\xrightarrow{\text{Ni(s)}}$ Vegetable ghee (s)
 - $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (aq) + H_2O (l) $\xrightarrow{\text{H}_2\text{SO}_4(\text{aq})}$
 $\text{C}_6\text{H}_{12}\text{O}_6$ (aq) + $\text{C}_6\text{H}_{12}\text{O}_6$ (aq)
48. In what way, these are different : (a) a sol and a gel (b) a gel and an emulsion.

49. State "Hardy Schulze Rule" with one example.
50. What is an emulsifying agent? What role does it play in forming an emulsion?
51. Define the terms :
- Helmholtz electrical double layer.
 - Zeta potential.
- *52. A graph between $\log\left(\frac{x}{m}\right)$ and $\log p$ is a straight line at an angle of 45° with intercept on the y-axis i.e. $(\log k)$ equal to 0.3010. Calculate the amount of the gas absorbed per gram of the adsorbent under a pressure of 0.5 atmosphere.
- Hint :** Refer to NCERT Text Book page 125, Fig. 5.2

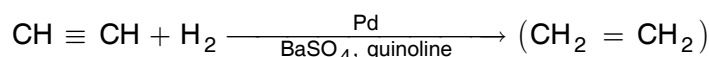
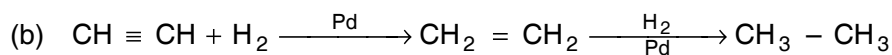
$$\frac{1}{n} = \tan 45^\circ = 1, \log k = 0.3010, k = 2, p = 0.5 \text{ atm.}$$

$$\frac{x}{m} = Kp^{\frac{1}{n}} = 2 \times (0.5)^1 = 1.0$$
- *53. Mention the two necessary conditions for the observation of Tyndall effect.
- *54. "The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles." Justify the statement by giving one example.
- *55. Account for the following :
- Artificial rain can be caused by spraying electrified sand on the clouds.
 - Electrical precipitation of smoke.
56. Write chemical equations for the preparation of sols :
- Gold sol by reduction.
 - hydrated ferric oxide sol by hydrolysis.
- *57. How can the two emulsions can be distinguished :
- oil in water type (O/W) and
 - water in oil type (W/O)

SA (II) TYPE QUESTIONS (3 MARKS)

58. What is meant by activation of the adsorbent? How is it achieved?
59. Write the difference between
- catalysts and enzymes
 - promoters and poisons (with the help of an example).
60. Write the steps of 'Modern Adsorption Theory of Heterogenous Catalysis.'
61. Mention the two important features of solid catalysts and explain with the help of suitable examples.
62. How are the following colloids different from each other in respect of dispersion medium and dispersed phase? Give one example of each type.
(a) An aerosol (b) A hydrosol (c) An emulsion.
63. What happens :
- by persistent dialysis of a sol.
 - when river water meets the sea water.
 - when alum is applied on cuts during bleeding.
64. Distinguish between multimolecular, macromolecular and associated colloids with the help of one example of each.
65. (a) How are emulsions useful in preparing photographic plates of films?
(b) Explain the process of electrical precipitation of smoke, with diagram.
66. (a) Which property of colloids is responsible for the sun to look red at the time of setting?
(b) C_2H_2 on addition with H_2 forms ethane in presence of palladium but if reaction is carried in the presence of barium sulphate and quinoline, the product is ethene and not ethane. Why?

[Ans. (a) Sun is at horizon and blue part of the light is scattered away by the dust particles as light has to travel a long distance through the atmosphere.



($BaSO_4$ -Quinoline act as poison. The catalyst in this case is not effective in further reaction].

UNIT 6

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

QUESTIONS

VSA TYPE QUESTIONS (1 MARK)

1. Name three metals which occur in native state in nature.
[Ans. : Au, Ag and Pt]
2. What are collectors in froth flotation process? Give one example.
[Ex. : Pine oil]
- *3. Give the names and formulae of three ores which are concentrated by froth floatation process.
[Ans. : Galena (PbS), Zinc blend (ZnS) cinnabar (HgS)]
4. Among Fe, Cu, Al and Pb, which metal (s) can not be obtained by smelting.
[Ans. : Al]
5. What is the thermodynamic criteria for the feasibility of a reaction?
[Ans. : ΔG should be $-ve$ or $\log k = +ve$]
- *6. Why CO is a better reducing agent than C at 673 K?
[Ans. : (CO, CO₂) line is lower than (C, CO) line and (C, CO₂) line in the Ellingham diagram. As a result free energy change during reduction using CO becomes more negative].
7. Indicate the temperature at which carbon can be used as a reducing agent for FeO.
[Ans. : $T > 1123\text{ K}$]
8. Why aluminium cannot be reduced by carbon?
[Hint : Al is stronger reducing agent than carbon]

9. Name the most important form of iron. Mention its one use.
[Ans. : Cast iron, for making gutter pipes, casting stoves, railway sleepers, toys etc.]
10. Name the impurities present in bauxite ore.
[Ans. : SiO_2 , Fe_2O_3 and TiO_2]
11. What is the composition of Copper matte?
[Hint : Cu_2S and FeS]
12. Which form of copper is called blister copper?
[Ans. : Solidified copper obtained from copper matte due to the evolution of SO_2 which has blister like appearance].
13. What are froth stabilizers? Give two examples.
[Ex. : Cresol and aniline].
14. A sample of galena is contaminated with zinc blend. Name one chemical which can be used to concentrate galena selectively by froth floatation method.
[Ans. : NaCN]
- *15. What does a steep increase in the slope of a line on Ellingham diagram indicates?
[Ans. : Phase transformation]
16. What are the constituents of German silver?
[Ans. : $\text{Cu} = 25\text{-}30\%$, $\text{Zn} = 25\text{-}30\%$, $\text{Ni} = 40\text{-}50\%$]
17. Why is froth floatation process selected for concentration of the sulphide ore?
[Ans. : Sulphide ore particles are wetted by oil (pine oil) and gangue particles by water]
18. Which form of iron is used in making anchors, chains and agricultural implements?
[Ans. : Wrought Iron]
19. Write the reaction involved in the extraction of copper from low grade ores.
[Ans. : First Step is leaching of ore with acid or bacteria then $\text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow \text{Cu}(\text{s}) + 2\text{H}^+(\text{g})$]
20. Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water. Why?

21. Zinc is used but not copper for the recovery of metallic silver from the complex $[\text{Ag}(\text{CN})_2]^-$, although electrode potentials of both zinc and copper are less than that of Ag. Explain why?

[Hint : Zinc reacts at faster rate as compared with copper, further zinc is cheaper than copper].

SA (I) QUESTIONS (2 MARKS)

- *22. What is hydrometallurgy? Give one example where it is used for metal extraction.

[Ans. : Leaching followed by reduction is called hydrometallurgy it is used in extraction of 'Ag'].

- *23. Name the process for the benefaction/concentration of (i) an ore having impurities lighter than it (ii) Sulphide ores.

24. What is cryolite? Mention its use in the extraction of aluminium.

[Ans. : Na_3AlF_6]

25. What is the role of following :

(a) SiO_2 in the metallurgy of Cu.

(b) CaCO_3 in the metallurgy of Fe.

26. Extraction of copper directly from sulphide ore is less favourable than from its oxide through reduction. Explain.

[Ans. : $2\text{Cu S(s)} + \text{C(s)} \rightarrow \text{CS}_2 \text{(l)} + 2\text{Cu(s)}$

$\text{CuO(s)} + \text{C(s)} \rightarrow \text{CO (g)} + \text{Cu(s)}$

ΔG value is more -ve in second case as compared with first case]

27. The graphite electrodes in the extraction of 'Al' by Hall-Heroult process need to be changed frequently. Why?

28. Write the chemical formulae of the following ores (a) Haematite (b) Magnetite (c) Limonite (d) Siderite.

[Ans. : (a) Fe_2O_3 (b) Fe_3O_4 (c) $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (d) FeCO_3]

29. Give equations for the industrial extraction of zinc from calamine.

[Ans. : $\text{ZnCO}_3 \rightarrow \text{ZnO} + \text{CO}_2$ (Calcination) $\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}$ (Reduction)]

30. Name the elements contained in anode mud during refining of copper. Why does it contain such elements?

[Ans. : Au and Ag. They are not oxidised at anode. Since they are less electropositive than copper.]

31. What kind of elements are suitable for purification by Chromotography?
32. Write the Chemical reactions taking place in different zones in the blast furnace for the extraction of iron from its ore.
33. How are impurities separated from bauxite ore to get pure alumina?
34. Why is the reduction of a metal oxide easier if metal formed is in liquid state at the temperature of radiation?

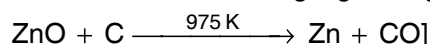
[Hint : ΔS is more positive when the metal is in liquid state as compared with solid state, so ΔG becomes more -ve]

35. Name the alloying element added to iron for making
(i) steel used in cutting tools and crushers.
(ii) steel used in making cables, measuring tapes and aeroplane parts.

[Ans. : (i) Chromium (ii) Nickel]

36. What is pyrometallurgy? Explain with one example.

[Ans. : A process of reducing a metal oxide by heating with either coke or some other reducing agent e.g., Al, Mg etc.



37. Write the method to produce Copper matte from copper pyrites.
*38. Copper can be extracted by hydrometallurgy but not zinc. Explain why?

[Hint : $E^\circ_{\text{Zn}^{2+}/\text{Zn}}$ is -ve, $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ is +ve]

- *39. Free energies of formation ΔG_f of MgO(s) and CO(g) at 1273K and 2273 K are given below:

$$\Delta G_f [\text{MgO(s)}] = -941 \text{ KJ mol}^{-1} \text{ at } 1273 \text{ K.}$$

$$\Delta G_f [\text{CO(g)}] = -439 \text{ KJ mol}^{-1} \text{ at } 1273 \text{ K.}$$

$$\Delta G_f [\text{MgO(s)}] = -314 \text{ KJ mol}^{-1} \text{ at } 2273 \text{ K.}$$

$$\Delta G_f [\text{CO(g)}] = -628 \text{ KJ mol}^{-1} \text{ at } 2273 \text{ K.}$$

On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for MgO(s).

[Ans. : For the reaction, $\text{MgO(s)} + \text{C(s)} \rightarrow \text{Mg(s)} + \text{CO(g)}$

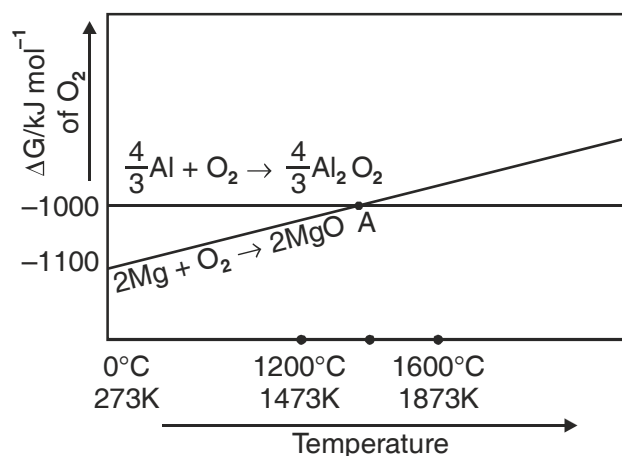
At 1273K, $\Delta G_r = \Delta G_f[\text{CO(g)}] - \Delta G_f[\text{MgO(s)}] = -439 - (-941) \text{ kJ mol}^{-1}$
 $= 502 \text{ kJ mol}^{-1}$

At 2273 K, $\Delta G_r = -628 - (-314) \text{ kJ mol}^{-1} = -314 \text{ kJ mol}^{-1}$

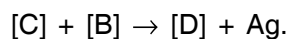
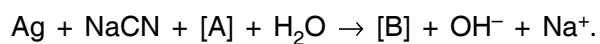
The temperature is 2273 K]

SA (II) TYPE QUESTIONS (3 MARKS)

- *40. State the principles of refining of metal by the following methods.
 (a) Zone refining (b) Electrolytic refining (c) Vapour phase refining.
41. How is pure copper obtained from its principle ore? Write the chemical reactions occurring during the extraction.
42. Name the method of refining of the following metals –
 (a) Hg (b) Sn (c) Cu (d) Ge (e) Ni (f) Zr
- [Ans. : (a) Distillation, (b) Liquation; (c) Electrolytic refining
 (d) Zone refining; (e) Mond Process (f) Van Arkel Process]
43. Suggest a condition under which :
 (i) Mg can reduce alumina (Al_2O_3)
 (ii) Al can reduce MgO.



- *44. The native silver forms a water soluble compound (B) with dilute aqueous solution of NaCN in the presence of a gas (A). The silver metal is obtained by the addition of a metal (C) to (B) and complex (D) is formed as a byproduct. Write the structures of (C) and (D) and identify (A) and (B) in the following sequence –



[Ans. : [A] = O₂

[B] = Na [Ag(CN)₂]

[C] = Zn

[D] = Na₂ [Zn (CN)₄]].

UNIT 7

The *p* – BLOCK ELEMENTS

POINTS TO REMEMBER

1. The electronic configuration of *p*-block elements is $ns^2 np^{1-6}$.
2. *p*-Block elements consist of all known nonmetals, metalloids and some metals.
3. First member of each group from 13-17 show a number of dissimilarities with other members of their group, the reason is small size, high electronegativity, non availability of d-orbitals for bonding and high ionisation enthalpy.
4. *p*-block elements exhibit highest group oxidation state equal to group number minus ten. The lower oxidation state shown by heavier members of the group is two units less than higher group oxidation state due to inert pair effect. The stability of higher oxidation state decreases while that of lower oxidation state increases down the group.
5. N_2 is a gas, diatomic due to ability to form multiple bonds, P, As., Sb exist as tetraatomic, P_4 , As_4 , Sb_4 having tetrahedral shape.
6. All the elements of group 15 form hydrides of type EH_3 in which element E is sp^3 hybridized.
7. P_4 forms a number of oxoacids. Then number of OH group attached to central P atom decides the basicity of acid.
8. Group 16 elements are called chalcogens (except Po).
9. Oxygen exhibits -2 oxidation state except in F_2O (+2), F_2O_2 (+1) and H_2O_2 (-1). As the electronegativity decreases down the group, the tendency to exhibit -2 oxidation state decreases.

10. Halogens have high values of electronegativities. They can combine with each other to form binary compounds called interhalogens compounds of the type XX' , XX'_3 , XX'_5 and XX'_7
11. All the noble gases have configuration $ns^2 np^6$ except He having $1s^2$ closed-shell configuration.

QUESTIONS

VSA TYPE QUESTIONS (1 MARK)

1. In group 15 elements, there is considerable increase in covalent radius from N to P but small increase from As to Bi. Why?
[Hint : Due to completely filled d- and f-orbitals.]
2. The tendency to exhibit - 3 oxidation state, decreases down the group in group 15 elements. Explain.
[Hint : Due to increase in size electronegativity decreases].
3. Maximum covalence of Nitrogen is '4' but the heavier elements of Group 15 show covalence greater than '4'. Why?
4. Nitrogen exists as a diatomic molecule with a triple bond between the two atoms, whereas the heavier elements of the group do not. Assign a reason.
[Hint : $p\pi-p\pi$ multiple bonds are formed by N due to its small size.]
5. The ionization enthalpies of group 15 elements are higher than those of group 14 and 16 elements in the corresponding period. Assign the reason.
6. The boiling point of PH_3 is lesser than NH_3 . Why?
7. NO_2 dimerises to form N_2O_4 . Why?
[Hint : Due to presence of odd electron on N]
8. Draw the structure of N_2O_5 molecule.
9. How does ammonia solution react with Ag^+ (aq)? Write the balanced chemical equation.

10. Why does NH_3 forms intermolecular hydrogen bonds but PH_3 does not?

[Hint : Due to strong electronegativity, small size of Nitrogen atom and presence of lone pair of electrons.]

11. Write disproportionation reaction of H_3PO_3 ?

12. How does NH_3 acts as a complexing agent?

[Hint : Metal hydroxides dissolved in excess of NH_4OH , Ammonia acts as Lewis base].

13. Why HF is the weakest acid and HI is the strongest.

[Hint : Values of dissociation constant.

$$K_a : (\text{HF}) = 7 \times 10^{-4} \quad (\text{HI}) = 7 \times 10^{11}$$

Intermolecular H-bonds in H-F and high bond dissociation enthalpy of H-F make it weakest and weak bond in H-I make it strongest.

14. Explain Halogens are strong oxidising agent.

[Hint : Ready acceptance of electron.]

15. Why is Bi(V) a stronger oxidant than Sb(V)?

[Hint : +3 oxidation state is more stable than +5 oxidation state in Bi].

16. Why SF_4 is easily hydrolysed, whereas SF_6 is resistant to hydrolysis?

[Hint : Water molecule can not attack 'S' atom due to steric hinderance and 'S' atom is also coordinately saturated of SF_6 molecule.]

17. Bond dissociation enthalpy of F_2 is less than that of Cl_2 . Why?

18. Write the reaction of PCl_5 with heavy water.

[Hint : $\text{PCl}_5 + \text{D}_2\text{O} \rightarrow \text{POCl}_3 + 2\text{DCl}$]

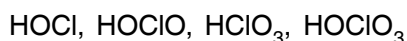
19. How many P – O – P bonds are there in cyclotrimetaphosphoric acid?

[Hint : 3 bonds]

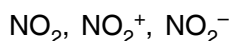
20. In group 16, the stability of +6 oxidations state decreases and that of +4 oxidation state increases down the group. Why?

[Hint : Inert pair effect]

21. Why we can not prepare HBr by heating KBr with sulphuric acid.
 [Hint : As HBr readily reduces H_2SO_4 forming Br_2]
22. Explain why sulphur disappears when boiled with aqueous solution of sodium sulphite.
 [Hint : Sulphur combines with Na_2SO_3 , forming soluble sodium thiosulphate.]
23. Write the equation for the decomposition of hydrogen peroxide in the presence of finely divided metal and MnO_2 as catalyst.
24. Fluorine exhibit only -1 oxidation state whereas other halogens exhibit +ve oxidation states also. Explain.
25. Arrange the following oxoacids of chlorine in increasing order of acidic strength.



- *26. The majority of known noble gas compounds are those of Xenon. Why?
- *27. "Hypophosphorus acid is a good reducing agent." Justify with an example.
 [Hint : $4\text{AgNO}_3 + \text{H}_3\text{PO}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Ag} + \text{HNO}_3 + \text{H}_3\text{PO}_4$.
- *28. Draw the structure of $\text{H}_4\text{P}_2\text{O}_7$ and find out its basicity?
 [Hint : Tetrabasic]
- *29. Arrange the following triatomic species in the order of increasing bond angle.



NO_2 has one non-bonding electron, NO_2^- has 2 non-bonding e^- , NO_2^+ has no non-bonding e^- on N atom. Bond angle of NO_2^+ is maximum but of NO_2^- minimum].

30. With what neutral molecule ClO^- is isoelectronic.
31. Draw the structure of $\text{H}_2\text{S}_2\text{O}_8$ and find the number of S-S bond if any.

32. What is cause of bleaching nature of Chlorine water? Explain it with chemical equation?

[Hint : Formation of nascent Oxygen]

- *33. The negative value of electron gain enthalpy of fluorine is less than that of chlorine.

[Hint. : Due to small size of F atom, there are strong inter electronic repulsions in the relatively smaller 2p orbitals of fluorine. So the incoming electron does experience less attraction than in Cl]

- *34. Which one of the following is not oxidised by O₃. State the reason.



[Hint. : KMnO₄ since Mn is showing maximum oxidation state of +7.]

SA (I) TYPE QUESTIONS (2 MARKS)

1. PCl₅ is known but PI₅ is not known Why?

[Hint : 5 Cl atom can be accommodated around P atom, I being larger in size cannot be accommodated.]

2. Why is red phosphorous denser and less chemically reactive than white phosphorous?
3. Give chemical reaction in support of the statement that all the bonds in PCl₅ molecule are not equivalent.

[Hint : PCl₅ + H₂O → POCl₃ + 2HCl]

4. Account for the following :

(a) XeF₂ has linear structure and not a bent structure.

(b) Phosphorous show marked tendency for Catenation.

5. Draw the structures of BrF₃, XeOF₄, XeO₃, N₂O₃ using VSEPR theory.
6. Write the conditions that favour the formation of ammonia gas along with the reactions involved in Haber's Process.

7. Write the chemical equations of the following reactions

(a) Glucose is heated with conc. H_2SO_4 .

(b) Sodium nitrate is heated with conc. H_2SO_4 .

Complete the following reactions :

8. (i) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{Heat}}$

(ii) $\text{NH}_4\text{Cl}(\text{aq}) + \text{NaNO}_2(\text{aq}) \longrightarrow$

9. (i) $\text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \longrightarrow$

(ii) $\text{FeCl}_3(\text{aq}) + \text{NH}_4\text{OH} \longrightarrow$

10. (i) $\text{Ca}_3\text{P}_2 + \text{H}_2\text{O}(\text{l}) \longrightarrow$

(ii) $\text{I}_2 + \text{HNO}_3(\text{conc.}) \longrightarrow$

11. (i) $\text{Ba}(\text{N}_3)_2 \xrightarrow{\text{Heat}}$

(ii) $4\text{H}_3\text{PO}_3 \xrightarrow{\text{Heat}}$

12. (i) $\text{PH}_4\text{I} + \text{KOH} \longrightarrow$

(ii) $\text{HgCl}_2 + \text{PH}_3 \longrightarrow$

13. (i) $\text{PCl}_3 + 3\text{H}_2\text{O} \longrightarrow$

(ii) $\text{S} + \text{H}_2\text{SO}_4(\text{conc.}) \longrightarrow$

14. (i) $\text{Al}_2\text{O}_3(\text{s}) + \text{NaOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow$

(ii) $\text{HCl} + \text{O}_2 \xrightarrow{\text{CuCl}_2}$

15. (i) $\text{Ca}(\text{OH})_2 + \text{Cl}_2 \longrightarrow$

(ii) $\text{XeF}_4 + \text{H}_2\text{O} \longrightarrow$

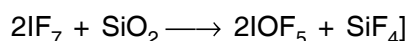
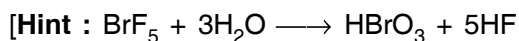
16. (i) $\text{Na}_2\text{SO}_3 + \text{Cl}_2 + \text{H}_2\text{O} \longrightarrow$
(ii) $\text{NaHCO}_3 + \text{HCl} \longrightarrow$
17. (i) $\text{XeF}_6 + \text{H}_2\text{O} \xrightarrow[\text{Hydrolysis}]{\text{Complete}}$
(ii) $\text{XeF}_6 + \text{H}_2\text{O} \xrightarrow[\text{Hydrolysis}]{\text{Partial}}$
18. (i) $\text{NO}_3^- + \text{Fe}^{2+} + \text{H}^+ \longrightarrow$
(ii) $\text{Zn} + \text{HNO}_3 \text{ (dil)} \longrightarrow$
19. (i) $\text{Zn} + \text{HNO}_3 \text{ (conc)} \longrightarrow$
(ii) $\text{P}_4 + \text{HNO}_3 \text{ (conc)} \longrightarrow$
20. (i) $\text{NH}_3 + \text{O}_2 \xrightarrow{\text{Pt/Rn}}$
(ii) $\text{P}_4 + \text{NaOH} + \text{H}_2\text{O} \longrightarrow$
21. (i) $\text{P}_4 + \text{SOCl}_2 \longrightarrow$
(ii) $\text{P}_4 + \text{SO}_2\text{Cl}_2 \longrightarrow$
22. (i) $\text{PbS} + \text{O}_3 \longrightarrow$
(ii) $\text{KI} + \text{H}_2\text{O} + \text{O}_3 \longrightarrow$
23. (i) $\text{MnO}_4^- + \text{SO}_2 + \text{H}_2\text{O} \longrightarrow$
(ii) $\text{S}_8 + \text{Cl}_2 \longrightarrow$
24. (i) $\text{NH}_3 \text{ (Excess)} + \text{Cl}_2 \longrightarrow$
(ii) $\text{NH}_3 + \text{Cl}_2 \text{ (Excess)} \longrightarrow$
25. (i) $\text{Cl}_2 + \text{NaOH} \text{ (Cold and dil)} \longrightarrow$
(ii) $\text{Cl}_2 + \text{NaOH} \text{ (Hot \& Conc)} \longrightarrow$

26. (i) $\text{Fe} + \text{HCl} \longrightarrow$
(ii) $\text{ClF} + \text{H}_2\text{O} \longrightarrow$
27. (i) $\text{U} + \text{ClF}_3 \longrightarrow$
(ii) $\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{Cl}_2 \longrightarrow$
28. (i) What is the covalency of N in N_2O_3 ?
(ii) Explain why phosphorus forms pentahalide whereas nitrogen and bismuth do not?
29. (i) The acidic character of hydrides of group 15 increases from H_2O to H_2Te . Why?
(ii) Dioxygen is a gas while sulphur (S_8) is a solid. Why?
30. (i) Interhalogen compounds are more reactive than halogens except F_2 . Why?
(ii) Give one important use of ClF_3 .
31. (i) Write the composition of bleaching powder.
(ii) What happens when NaCl is heated with conc. H_2SO_4 in the presence of MnO_2 . Write the chemical equation.
32. Arrange the following in the decreasing order of their basicity. Assign the reason :
- $\text{PH}_3, \text{NH}_3, \text{SbH}_3, \text{AsH}_3, \text{BiH}_3$.
- *33. A colourless and a pungent smelling gas which easily liquifies to a colourless liquid and freezes to a white crystalline solid, gives dense white fumes with ammonia. Identify the gas and write the chemical equation for its laboratory preparation. **[Hint : HCl]**
- *34. Complete following disproportionation reactions.
- (a) $\text{P}_4 + \text{NaOH} + \text{H}_2\text{O} \longrightarrow$
(b) $\text{HNO}_2 \xrightarrow{\text{H}^+}$

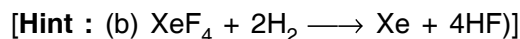
- *35. Suggest reason why only known binary compounds of noble gases are fluorides and oxides of Krypton, Xenon.

[Hint : F and O are most electronegative elements]

- *36. Which fluorinating agent are oftenly used instead of F_2 ? Write two chemical equations showing their use as fluorinating agents.



- *37. (a) Hydrolysis of XeF_6 is not regarded as a redox reaction. Why?
(b) Write a chemical equation to represent the oxidising nature of XeF_4 .



38. Write Chemical equation :

- (a) Cl_2 reacts with hot and conc. solution of NaOH.
(b) PtF_6 and Xenon are mixed together.

SA (II) TYPE QUESTIONS (3 MARKS)

1. (i) How is HNO_3 prepared commercially. Name the process.
(ii) Write chemical equations of the reactions involved.
(iii) What concentration by mass of HNO_3 is obtained.
2. (i) How does O_3 react with Lead sulphide, Write Chemical equation.
(ii) What happens when SO_2 is passed in acidified $KMnO_4$ solution.
(iii) SO_2 behaves with lime water similar to CO_2 .
3. Assign reason for the following :
- (i) Sulphur in vapour state exhibits paramagnetism.
(ii) F_2 is strongest oxidising agent among halogens.
(iii) In spite of same electronegativity oxygen forms hydrogen bond while chlorine does not.

4. Give appropriate reason for each of the following :
- Metal fluorides are more ionic than metal chlorides.
 - Perchloric acid is stronger than Sulphuric acid.
 - Addition of chlorine to KI solution gives it a brown colour but excess of Cl_2 makes it colourless.

[Hint :

- According to Fajan's Rule, bigger **ions** more polarised than the smaller ion by a particular cation.
- Oxidation state of Cl in HClO_4 is +7 while oxidation state of S in H_2SO_4 is +6, Hence OH bond easily breaks in the HClO_4 molecule.
- $$2\text{KI} + \text{Cl}_2 \longrightarrow 2\text{KCl} + \text{I}_2$$

Excess $5\text{Cl}_2 + \text{I}_2 + 6\text{H}_2\text{O} \longrightarrow 2\text{HIO}_3 + 10\text{HCl}$
Colourless.

5. Explain why :
- No chemical compound of Helium is known.
 - Bond dissociation energy of fluorine is less than that of chlorine.
 - Two S–O bonds in SO_2 are identical.
6. Out of the following hydrides of Group 16 elements, which will have :
- | | | |
|--------------------------|---------------------------|-----------------------------|
| (i) H_2S | (ii) H_2O | (iii) H_2Te |
|--------------------------|---------------------------|-----------------------------|
- lowest boiling point
 - highest bond angle
 - highest electropositive hydrogen.
7. (i) How is XeO_3 prepared from XeF_6 ? Write the chemical equation for the reaction.
- (ii) Draw the structure of XeF_4 .
8. (i) Thermal stability of hydrides of group 16 elements decreases down the group. Why?

- (ii) Compare the oxidising powers of F_2 and Cl_2 on the basis of bond dissociation enthalpy and hydration enthalpy of halide ions.
- (iii) Write the chemical equation for the reaction of copper metal with conc. HNO_3 .
- *9. An unknown salt X reacts with hot conc. H_2SO_4 to produce a brown coloured gas which intensifies on addition on copper turnings. On adding dilute ferrous sulphate solution to an aqueous solution of X and then carefully adding conc. H_2SO_4 along the sides of the test tube, a brown complex Y is formed at the interface between the solution and H_2SO_4 . Identify X and Y and write the chemical equation involved in the reaction.
- [Hint : X is NO_3^- salt].
10. Assign reason to the following :
- (i) Noble gases have large positive values of electron gain enthalpy.
- (ii) Helium has the lowest boiling point than any known substance.
11. Arrange the following in the order of the property indicated for each set –
- (a) F_2 , Cl_2 , Br_2 , I_2 – (Increasing bond dissociation energy).
- (b) HF, HCl, HBr, HI (Increasing acid strength).
- (c) NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3 (Increasing base strength).

[Hint :

- (a) F_2 has exceptionally low bond dissociation enthalpy. Lone pairs in F_2 molecule are much closer to each other than in Cl_2 molecule. Larger electron (–) electron-repulsion among the lone pairs in F_2 molecule make its bond dissociation enthalpy exceptionally low.
- (b) Depends upon H–X bond dissociation enthalpy as the size of atom increases, acid strength also increases from HF to HI.
- (c) Electron availability on the central atom 'E' in EH_3 decreases down the group.
- *12. A translucent white waxy solid (A) on heating in an inert atmosphere is converted to its allotropic form (B), Allotrope (A) on reaction with very dilute aqueous NaOH/KOH liberates a highly poisonous gas (C) having a rotten fish smell, with excess of chlorine forms D which hydrolyses to form compound (E) identify the compounds (A) to (E).

13. Write balanced equation for the following reactions :
- Zn is treated with dilute HNO_3 .
 - NaCl is heated with H_2SO_4 in the presence of MnO_2 .
 - Iodine is treated with conc. HNO_3 .
14. X_2 is a greenish yellow gas with pungent offensive smell used in purification of water. It partially dissolves in H_2O to give a solution which turns blue litmus red. When X_2 is passed through NaBr Solution, Br_2 is obtained.
- Identify X_2 , name the group to which it belongs.
 - What are the products obtained when X_2 reacts with H_2O ? Write chemical equation.
 - What happens when X_2 reacts with conc. NaOH . Give equation.
16. Assign the appropriate reason for the following:
- Nitrogen exist as diatomic molecule and phosphorous as P_4 , Why?
 - Why does $\text{R}_3\text{P} = \text{O}$ exist but $\text{R}_3\text{N} = \text{O}$ does not? (R = alkyl group).
 - Explain why fluorine forms only one oxoacid, HOF.

[Hint :

- Due to its small size and high electronegativity N forms $p\pi - p\pi$ multiple bond ($\text{N}\equiv\text{N}$). whereas P does not form $p\pi - p\pi$ bonds instead forms P - P single bond.
- Due to absence of d-orbitals, N cannot expand its covalence beyond four.
In $\text{R}_3\text{N} = \text{O}$, N should have a covalence 5 so the compound $\text{R}_3\text{N} = \text{O}$ does not exist.
- Due to high electronegativity and small size, F does not form oxoacids in which the oxidation state of F would be +3, +5, +7, it forms one oxoacid having +1 oxidation state of F.

LONG ANSWER TYPE QUESTIONS (5 MARKS)

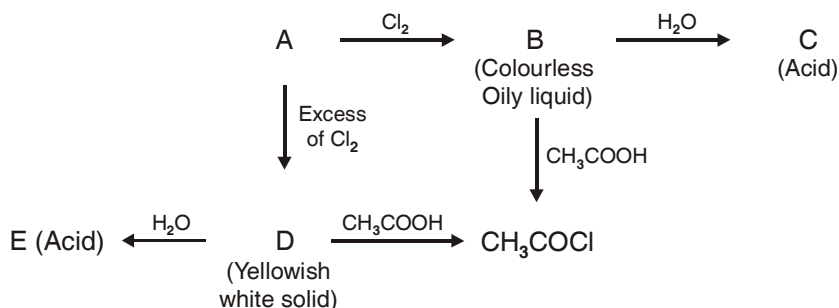
- How is PH_3 prepared in the laboratory? How is it purified? How does the

solution of PH_3 in water react on irradiation with light and on absorption in CuSO_4 ? How can you prove that PH_3 is basic in nature?

Write the chemical equations for all the reactions involved.

2. Assign a possible reason for the following :
 - (a) Stability of +5 oxidation state decreases and that of +3 oxidation state increases down the group 15 elements.
 - (b) H_2O is less acidic than H_2S .
 - (c) SF_6 is inert while SF_4 is highly reactive.
 - (d) H_3PO_2 and H_3PO_3 act as good reducing agents while H_3PO_4 does not.
 - (e) Noble gases have comparatively large size in their respective periods.
3.
 - (a) How is XeF_6 prepared from the XeF_4 ? Write the chemical equation for the reaction.
 - (b) Deduce the structure of XeF_6 from VSEPR theory.
 - (c) How does XeF_2 reacts with PF_5 ?
 - (d) Give one use each of helium and Neon.
 - (e) Write the chemical equation for the hydrolysis of XeF_4 .
4.
 - (a) Why does nitrogen show anomalous behaviour? Discuss the trend of chemical reactivity of group 15 elements with.
 - (a) Oxygen
 - (b) Halogens
 - (c) Metals
 - (b) H_3PO_2 is a dibasic acid. Why?
5.
 - (a) Arrange the following in the order of their increasing acid strength.
 - (a) Cl_2O_7 , SO_2 , P_4O_{10}
 - (b) How in N_2O gas prepared?
 - (c) Give one chemical reaction to show O_3 is an oxidising agent.

*6. Identify A, B, C, D and E in the following sequence of reactions



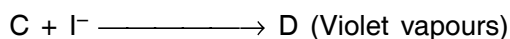
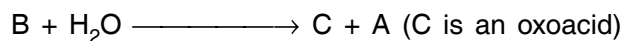
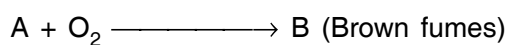
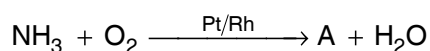
Complete the reactions of the above mentioned sequence.

[Hint : A is P₄].

*7. A white waxy, translucent solid, M, insoluble in water but soluble in CS₂, glows in dark. M dissolves in NaOH in an inert atmosphere giving a poisonous gas (N). Also M catches fire to give dense white fumes of O :

- Identify M, N and O and write the chemical equations of the reactions involved.
- M exist in the form of discrete tetrahedral molecule. Draw its structure.
- M on heating at 573 K is changed into other less reactive form, Q, which is non-poisonous, insoluble in water as well as in CS₂ and does not glow in dark, Identify Q and draw its structure.

8. Write the structure of A, B, C, D and E in the following sequence of reactions :



Complete reactions of the above mentioned sequence and name the process.

[Hint. : A is NO].

9. Give reason for each of the following :
- (a) Molten alumina is a poor conductor of electricity.
 - (b) Ammonia is a good complexing agent.
 - (c) Bleaching by SO_2 is temporary.
 - (d) PCl_5 is ionic in solid state.
 - (e) Sulphur in vapour form exhibits paramagnetism.
10. Knowing the electrons gain enthalpy value for $\text{O} \rightarrow \text{O}^-$ and $\text{O}^- \rightarrow \text{O}^{2-}$ as -141 and 720 kJ mol^{-1} respectively, how can you account for the formation of large number of oxides having O^{2-} species and not O^- ?
- [Hint :** Latice enthalpy of formation of oxides having O^{2-} more than compensates the $\Delta_{\text{eg}}H_2$ of oxygen.

UNIT 8

d – AND *f* – BLOCK ELEMENTS

POINTS TO REMEMBER

1. The elements belonging to group 3 to 12 are called *d*-block elements, the general electronic configuration is $(n - 1) d^{1-10} ns^{0-2}$. They are also called transition elements.
2. The elements of group 12 are not regarded as transition metals because they do not have partially filled $(n - 1)d$ subshell in the native state or in any combined state.
3. All the transition metals have **high density, hardness and other metallic characters due to unpaired electrons** and stronger metallic bonds and exhibit paramagnetism, those which contain no unpaired electron are diamagnetic.
4. Colour may be due to *d*–*d* transitions that occur in incomplete *d*–subshell in transition metal ions.
5. Transition elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands.
6. The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour.
7. The *f*-block elements or inner transition metals have electronic configuration $(n - 2) f^{1-14} (n - 1) d^{0-1} ns^2$, they are also called Lanthanoids and Actinoids.
8. Gradual decrease in atomic and ionic size in Lanthanoids or Actinoids is called Lanthanoid and actinoid contraction. Most of trivalent Lanthanoids are coloured. This is due to *f* – *f* transition.
9. All the Lanthanoids are rather soft and white; they react easily with H_2O .

QUESTIONS

VERY SHORT ANSWER TYPE QUESTIONS (1 MARK)

1. Write the electronic configuration of Cr^{3+} ion (atomic number of Cr = 24)?
2. State the cause of horizontal and vertical relationship in transition elements?
3. Explain $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue while ZnSO_4 is colourless?
4. Why is the third ionisation energy of Manganese ($Z = 25$) is unexpectedly high?

[Hint : The third electron is to be removed from stable configuration Mn^{2+} ($3d^5$). It requires higher energy.]

5. Which element among 3d- transition elements, exhibit the highest oxidation state?

[Hint : Mn (+7)]

6. Gold has completely filled d-orbitals ($5d^{10}$) in its ground state. How can you say that it is a transition element.
7. In 3d series ($\text{Sc} \rightarrow \text{Zn}$). Why the enthalpy of atomisation of Zn is low?

[Hint : Poor metallic bonding.]

8. Out of the following elements, identify the element which does not exhibit variable oxidation state?

Cr, Co, Zn.

9. The +3 oxidation state of Lanthanum ($Z = 57$), Gadolinium ($Z = 64$) and Lutetium ($Z = 71$) are especially stable. Why?
10. Mention one consequence of Lanthanoid Contraction?
11. The first ionization enthalpies of 5d- series elements is higher than those of 3d and 4d series elements why?

[Hint : Increasing value of effective nuclear charge due to lanthanoid contraction.]

12. Why Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state.

13. Nickel show an oxidation state zero in its complex $[\text{Ni}(\text{CO})_4]$, Assign a reason?
 [Hint : due to synergic bonding.]
14. Calculate the magnetic moment of Cu^{2+} ($Z = 29$) on the basis of “Spin-only” formula.
 [Hint : Spin formula $\mu = \sqrt{n(n + 2)}$ B.M.]
15. What is the shape of chromate ions?
 [Hint : Tetrahedral]
16. Why does vanadium pentoxide acts a catalyst?
 [Hint : In V_2O_5 , Vanadium shows variable oxidation sates.]
17. What are interstitial compounds?
18. The transition metals and their compounds are known for their catalytic activity. Give two specific reasons to justify the statement.
19. Write the chemical equation for the reaction of thiosulphate ions and alkaline potassium permanganate.
 [Hint : $8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow 8\text{MnO}_2 + 2\text{OH}^- + 6\text{SO}_4^{2-}$].
20. Mention the name and formula of the ore from which potassium dichromate is prepared.
 [Hint : FeCr_2O_4 (Chromite)].
21. Write the electronic configuration of Lu^{3+} (At. No. = 71).
22. What is the most common oxidation state of actinoids?
23. Write the names of the catalyst used in the :
 (a) Manufacture of sulphuric acid by contact process.
 (b) Manufacture of polythene.
24. Mention the name of the element among lanthanoids known to exhibit +4 oxidation state.
25. Name one ore of manganese and chromium.

26. Why is Cd^{2+} ion white?
- *27. How many bonds in the dichromate anion are equivalent?
- *28. Arrange the following monoxides of transition metals on the basis of decreasing basic character TiO , VO , CrO , FeO . [Hint : $\text{TiO} > \text{VO} > \text{CrO} > \text{FeO}$]

SHORT ANSWER TYPE QUESTIONS (2 MARKS)

1. Explain with chemical equation, when the yellow colour of aqueous solution of Na_2CrO_4 changes to orange on passing CO_2 gas?
2. The stability of Cu^{2+} (aq) rather than Cu^+ (aq) is much more. Why?
3. Indicate the steps in the preparation of
 - (a) $\text{K}_2\text{Cr}_2\text{O}_7$ from Chromite ore.
 - (b) KMnO_4 from Pyrolusite ore.
4. Give reason for : –
 - (a) In permanganate ions, all bonds formed between manganese and oxygen are covalent.
 - (b) Permanganate titrations in presence of hydrochloric acid are unsatisfactory.
5. Write complete chemical equations for
 - (a) oxidation of Fe^{2+} by $\text{Cr}_2\text{O}_7^{2-}$ in acidic medium
 - (b) oxidation of Mn^{2+} by MnO_4^- in neutral medium.
6.
 - (a) Why do transition metals show high melting points?
 - (b) Out of Fe and Cu, which one would exhibit higher melting point?

[Hint. (i) Strong interatomic bonding arising from the participation of ns and unpaired $(n - 1) d$ -electrons.

(ii) Fe has higher melting point due to presence of more unpaired electrons $3d$ -orbitals.

7. Describe giving reason which one of the following pairs has the property indicated :
- (a) Cr^{2+} or Fe^{2+} (stronger reducing agent).
- (b) Co^{2+} or Ni^{2+} (lower magnetic moments).
8. Of the ions Co^{2+} , Sc^{3+} , Cr^{3+} which one will give colourless aqueous solution and how will each of them respond to magnetic field and why?

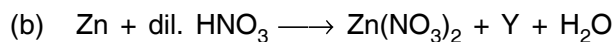
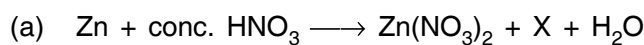
[Hint : Co^{2+} ($3d^7$); Cr^{3+} ($3d^3$); Sc^{3+} ($3d^0$)]

9. Complete the following equations :
- (a) $\text{MnO}_2 + \text{KOH} + \text{O}_2 \longrightarrow$
- (b) $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{KCl} \longrightarrow$
10. Mention two compounds that forms the basis of Ziegler-Natta catalyst. Give its one use.
11. Give two examples of oxoanions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.
12. For the first row transition metals the enthalpy of atomisation value are :

	<i>Sc</i>	<i>Ti</i>	<i>V</i>	<i>Cr</i>	<i>Mn</i>	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	<i>Cu</i>	<i>Zn</i>
$\Delta_a H^\ominus / \text{kJ mol}^{-1}$	326	473	515	397	281	416	425	430	339	26

Assign reason for the following :

- (a) Transition elements have higher values of enthalpies of atomisation.
- (b) The enthalpy of atomisation of zinc is the lowest.
13. Account for the following :
- (a) Copper shows its inability to liberate hydrogen gas from the acids.
- (b) Scandium ($Z = 21$) does not exhibit variable oxidation states.
14. Copper (I) compounds undergo disproportionation. Write the chemical equation for the reaction involved and give reason.
15. Iron (III) catalyses the reaction :



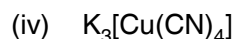
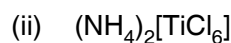
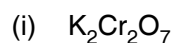
Identify X and Y and write balanced equations.

[Hint : X is NO_2 and Y is N_2O].

- *26. Titanium shows magnetic moment of 1.73 BM in its compound. What is the oxidation number of Ti in the compound?

[Hint : O.N. of Ti = +3].

27. From the following compounds (i) to (iv), find out the compound which is both paramagnetic and coloured.



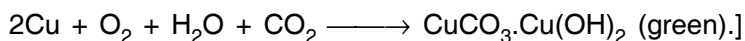
[Hint : (iii)]

- *28. Calculate the number of electrons transferred in each case when KMnO_4 acts as an oxidising agent to give (i) MnO_2 (ii) Mn^{2+} (iii) Mn(OH)_3 (iv) MnO_4^{2-} respectively.

[Hint : 3, 5, 4, 1].

- *29. Copper corrodes in moist air to produce a green layer on its surface, Explain the cause with suitable chemical reaction?

[Hint : Formation of basic copper carbonate)

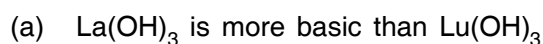


- *30. Calculate the number of moles of KMnO_4 that is needed to react completely with one mole of sulphite ion in acidic medium.

[Hint : 2/5 moles].

SHORT ANSWER TYPE QUESTIONS (3 MARKS)

1. Account for the following :



- (c) Most of transition metals do not displace hydrogen from dilute acids why?

[Hint : (a) Due to small size of Lu^{3+}].

2. Describe the oxidising action of Potassium Dichromate with following. Write ionic equations for its reaction with.

(a) Iodide ion (b) Iron (II) (c) H_2S .

3. (a) Deduce the number of 3d electrons in the following ions Fe^{3+} , Cu^{2+} .
(b) Why do transition metals forms alloys.
(c) Write any two characteristics of interstitial compounds.

- *4. In the following reaction, Mn(VI) changes to Mn(VII) and Mn(IV) in acidic solution.



- (a) Explain why Mn(VI) changes to Mn(VII) and Mn(IV).
(b) What special name is given to such type of reactions?
5. What happens when
(a) thiosulphate ions or KI react with alkaline KMnO_4 .
(b) oxalic acid (at 333 K) reacts with acidified KMnO_4
(c) sulphurous acid reacts with acidified potassium permanganate?

Write the chemical equations for the reactions involved.

6. (a) Write the general electronic configuration of inner transition elements.
(b) Which of the following atomic numbers are of inner transition series: 70, 80?
(c) Mention the common oxidation state of actinoids.
7. Name the catalysts used in the
(a) manufacture of ammonia by Haber's Process
(b) oxidation of ethyne to ethanol

(c) photographic industry.

- *8. Among TiCl_4 , VCl_3 and FeCl_2 - which one will be drawn more strongly into a magnetic field and why?

[Hint : Among these halides, the transition metal ion having maximum number of unpaired electrons will be drawn strongly into the magnetic field.

$\text{Ti}^{4+} = 3d^0$	no. of unpaired $e^- = 0$	$\mu = 0$
$\text{V}^{3+} = 3d^2$	no. of unpaired $e^- = 2$	$\mu = 2.76 \text{ BM}$
$\text{Fe}^{2+} = 3d^6$	no. of unpaired $e^- = 4$	$\mu = 4.9 \text{ BM}$

- *9. Account for the following :

- How are H_2O molecules bonded in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$?
- Silver chloride dissolves in excess of ammonia.
- Cuprous chloride is diamagnetic while cupric chloride is paramagnetic.

[Hint : (b) $\text{AgCl} + 2\text{NH}_3 \longrightarrow [\text{Ag}(\text{NH}_3)_2] \text{Cl}$ Complex –
[Diamminesilver (I) Chloride]

10. Draw the structures of chromate and dichromate ions. How many $-\text{Cr}-\text{O}$ bonds are identical in each ion.

LONG ANSWER TYPE QUESTIONS (5 MARKS)

1. A green compound 'A' on fusion with NaOH in presence of air forms yellow compound 'B' which on acidification with dilute acid, gives orange solution of compound 'C'. The orange solution when reacted with equimolar ammonium salt gives compound 'D' which when heated liberates nitrogen gas and compound 'A'. Identify compounds A to D and write the chemical equation of the reactions involved.

[Hint : 'A' = CrO_3 ; 'B' = Na_2CrO_4 ; 'C' = $\text{Na}_2\text{Cr}_2\text{O}_7$ 'D' = $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$]

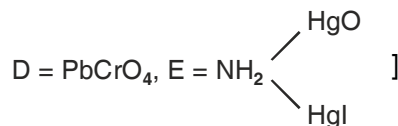
2. Assign reasons for the following :

- There is no regular trends in E° values of M^{2+}/M systems in 3d series.

- (b) There is gradual decrease in the ionic radii (M^{2+}) in 3d series.
 - (c) Majority of transition metals form complexes.
 - (d) Ce^{3+} can be easily oxidised to Ce^{4+}
 - (e) Tantalum and palladium metals are used to electroplate coinage metals.
3. Account for the following :
- (a) Actinoids displays variety of oxidation states.
 - (b) Yb^{2+} behaves as a good reductant.
 - (c) Cerium (iv) is a good analytical reagent.
 - (d) Transition metal fluorides are ionic in nature while as chlorides and bromides are covalent in nature.
 - (e) Hydrochloric acid attacks all the actinoids.
- *4. Explain by giving suitable reason :
- (a) $Co(II)$ is stable in aqueous solution but in the presence of complexing agent it is readily oxidised.
 - (b) Eu^{2+} , Yb^{2+} are good reductants whereas Tb^{4+} is an oxidant.
 - (c) Am and Cm have exceptional configuration in actinoids.
 - (d) Out of Cr^{2+} or Fe^{2+} , which one is the stronger reducing agent?
 - (e) The highest oxidation state is exhibited by oxoanions of a metal.
- [Hint : (d) Cr^{2+}]
5. When a white crystalline compound A is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 , a reddish brown gas B is evolved, which gives a yellow coloured solution C when passed through NaOH. On adding CH_3COOH and $(CH_3COO)_2Pb$ to solution C, a yellow coloured ppt. D is obtained. Also on heating A with NaOH and passing the evolved gas through K_2HgI_4 solution, a reddish brown precipitate E is formed.

Identify A, B, C, D and E and write the chemical equations for the reactions involved.

[Hint : A = NH_4Cl , B = CrO_2Cl_2 (g), C = Na_2CrO_4

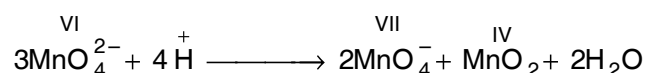


- *6. (a) Describe the preparation of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). Write the chemical equations of the reactions involved.
- (b) "The chromates and dichromates are interconvertible by the change in pH of medium." Why? Give chemical equations in favour of your answer.
7. Explain giving reasons :
- (a) Transition metals are less reactive than the alkali metals and alkaline earth metals.
- (b) Though transition metals have very high negative values of electrode potential still they are not good reducing agent.
- (c) Element in the middle of transition series have higher melting points.
- (d) The decrease in atomic size of transition elements in a series is very small.
- (e) What is effect of increasing of pH on $\text{K}_2\text{Cr}_2\text{O}_7$?
8. (a) Compare the chemistry of the actinoids with that of lanthanoids with reference to—
- (i) electronic configuration
- (ii) oxidation states
- (iii) chemical reactivity.
- (b) How would you account for the following—
- (i) of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.
- (ii) the lowest oxide of a transition metal is basic whereas highest is amphoteric or acidic.

9. (a) What is meant by disproportionation of oxidation state. Give one example.

(b) Explain why Europium (II) is more stable than Ce(II)?

[Hint : (a) When Particular state becomes less stable relative to other oxidation states, one lower and one higher it is said to undergo disproportionation e.g.



(b) Eu (II) = [Xe] 4f⁷ 5d⁰ – (4f subshell is half filled)

Ce (II) = [Xe] 4f¹ 5d⁰ – (5d Subshell is empty and 4f subshell has only one electron which can be easily lost.)]

10. (a) For M²⁺/M and M³⁺/M²⁺ systems the E^o values for some metals are as follows :

$$\text{Cr}^{2+}/\text{Cr} - 0.9\text{V}$$

$$\text{Cr}^{3+}/\text{Cr}^{2+} - 0.4\text{V}$$

$$\text{Mn}^{2+}/\text{Mn} - 1.2\text{V}$$

$$\text{Mn}^{3+}/\text{Mn}^{2+} + 1.5\text{V}$$

$$\text{Fe}^{2+}/\text{Fe} - 0.4\text{V}$$

$$\text{Fe}^{3+}/\text{Fe}^{2+} + 0.8\text{V}$$

Use this data to comment upon :

(i) The stability of Fe³⁺ in acid solution as compared to that of Cr³⁺ and Mn³⁺ and

(ii) the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese.

(b) How is the variability in oxidation states of transition metal different from that of the non transition metals? Illustrate with examples.

UNIT 9

CO-ORDINATION COMPOUNDS

QUESTIONS

VSA TYPE QUESTIONS (1 MARK)

1. Define coordination compounds?
2. Write the names of counter ions in
(i) Hg [Co (SCN)₄] and (ii) [Pt(NH₃)₄] Cl₂.
3. Calculate the oxidation state of nickel in [Ni(CO)₄] [Ans. : 0]
- *4. Calculate the coordination number of central atom in [Co(C₂O₄)₃]³⁻.
[Ans. : 6]
5. What is the coordination number of iron in [Fe(EDTA)]⁻? [Ans. : 6]
6. Write the name of a complex compound used in chemotherapy.
[Ans. : Cis-Platin. [Pt(NH₃)₂ Cl₂]
7. Name the compound used to estimate the hardness of water volumetrically.
[Ans. : Na₂ EDTA]
8. Give the IUPAC name of [Pt Cl₂ (NH₂CH₃) (NH₃)₂] Cl.
- *9. How many geometrical isomers are possible for the tetrahedral complex [Ni(CO)₄].
[Ans. : No isomer, as the relative positions of the unidentate ligands attached to the central metal atom are same with respect to each other].
10. Arrange the following in the increasing order of conductivity in solution.
[Ni(NH₃)₆]Cl₂; [Co(NH₃)₆]Cl₃ and [CoCl₂(en)₂] Cl

11. Arrange the following ligands in increasing order of Δ_0 (Crystal field splitting energy) for octahedral complexes :

Cl^- , NH_3 , I^- , CO , en.

12. Write I.U.P.A.C. name of Tollens' reagent.
13. Which is more stable? $\text{K}_3[\text{Fe}(\text{CN})_6]$ or $\text{K}_4[\text{Fe}(\text{CN})_6]$
14. Calculate the overall dissociation equilibrium constant for the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion. Given that overall stability constant (β_4) for this complex is 2.1×10^{13} .
[Ans. : 4.7×10^{-14}]

- *15. What is a Chelate ligand? Give one example.
16. Write the I.U.P.A.C. name of $\text{Li}[\text{AlH}_4]$.
17. Name one homogeneous catalyst used in hydrogenation of alkenes.
- *18. Name the types of isomerism show by coordination entity : $[\text{CrCl}_2(\text{Ox})_2]^{3-}$
- *19. $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ is coloured but on heating becomes colourless. Why?
- *20. Write the IUPAC name of ionization isomer of $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)] \text{Br}$
- *21. Write the formula and the name of the Coordinate isomer of $[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$.
[Ans. : $[\text{Cr}(\text{en})_3][\text{Co}(\text{CN})_6]$ Tris-[ethane -1, 2, diammine] chromium (III) hexacyanocobaltate (III)]

SA(I) TYPE QUESTIONS (2 MARK)

- *22. Write two differences between a double salt and a coordination complex with the help of an example.
23. Mention the main postulates of Werner's Theory.
24. Define (a) Homoleptic and (b) Heteroleptic complexes with the help of one example of each.
25. In the following coordination entity : $[\text{Cu}(\text{en})_2]^{2+}$
- (a) Identify the ligand involved and
- (b) Oxidation state of copper metal.
26. Are the bidentate ligands same as the ambidentate ligands? Justify with one example.

37. A complex is prepared by mixing CoCl_3 and NH_3 in the molar ratio of 1:4. 0.1 m solution of this complex was found to freeze at -0.372°C . What is the formula of the complex?

$$K_f \text{ of water} = 1.86^\circ\text{C/m}$$

[Hint : $\Delta T_f = K_f \times m = 1.86 \times 0.1 = 0.186^\circ\text{C}$.

$$\Delta T_f(\text{obs}) = 0.373^\circ\text{C}$$

ΔT_f (obs) is twice the theoretical value. This means each molecule of complex dissociates into two ions. $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2]\text{Cl}$.

- *38. Explain using Crystal Field Theory : The $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ion contains five unpaired electrons while $[\text{Mn}(\text{CN})_6]^{4-}$ ion contains only one unpaired electron.

SA (II) TYPE QUESTIONS (3 MARKS)

39. Account for the following —
- $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral.
 - $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is strongly paramagnetic whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ weakly paramagnetic.
 - $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is in outer orbital complex.
40. Compare the following complexes with respect to their shape, magnetic behaviour and the hybrid orbitals involved.
- $[\text{CoF}_6]^{3-}$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 - $[\text{Fe}(\text{CN})_6]^{4-}$
[Atomic Number : Co = 27, Cr = 24, Fe = 26]
41. Draw the structure of
- Cis-dichloridotetracyanochromate (II) ion
 - Mer-triamminetrichloridocobalt (III)
 - Fac-triaquatrininitrito-N-cobalt (III)

42. Name the central metal atom/ion present in (a) Chlorophyll (b) Haemoglobin (c) Vitamin B-12. [Ans. : (a) Mg (b) Fe; (c) Co.]

43. A metal complex having composition $\text{Cr}(\text{NH}_3)_4 \text{Cl}_2 \text{Br}$ has been isolated in two forms 'A' and 'B'. The form 'A' reacts with AgNO_3 solution to give white precipitate which is readily soluble in dilute aqueous ammonia, whereas 'B' gives a pale yellow precipitate which is soluble in concentrated ammonia solution. Write the formula of 'A' and 'B'. Also mention the isomerism which arises among 'A' and 'B'.

[Hint : A = $[\text{Cr}(\text{NH}_3)_4 \text{BrCl}] \text{Cl}$; B = $[\text{Cr}(\text{NH}_3)_4 \text{Cl}_2] \text{Br}$ ionisation isomerism].

44. Write the limitations of Valence Bond Theory.

45. Draw a sketch to show the splitting of *d*-orbitals in an octahedral crystal field state for a d^4 ion. How the actual electronic configuration of the split *d*-orbitals in an octahedral crystal field is decided by the relative values of Δ_0 and pairing energy (P)?

*46. For the complex $[\text{Fe}(\text{en})_2 \text{Cl}_2] \text{Cl}$ identify :

- (a) The oxidation number of iron.
- (b) The hybrid orbitals and the shape of the complex.
- (c) The magnetic behaviour of the complex.
- (d) The number of geometrical isomers.
- (e) Whether there is an optical isomer also?
- (f) Name of the complex. [At. no. of Fe = 26]

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

Identify the complex forming element and [A], [B], [C] and [D] complexes,

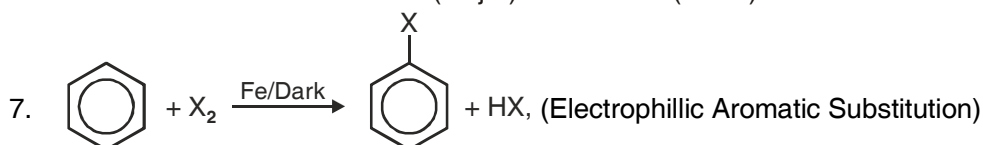
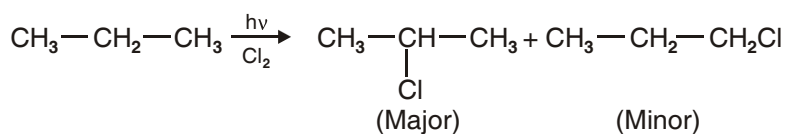
[Hint. : Nickel, [A] = $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$; [B] = $[\text{Ni}(\text{H}_2\text{O})_4 (\text{en})]^{2+}$;

[C] = $[\text{Ni}(\text{H}_2\text{O})_2 (\text{en})_2]^{2+}$; [D] = $[\text{Ni}(\text{en})_3]^{2+}$.

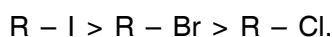
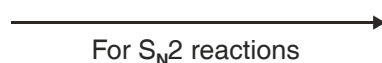
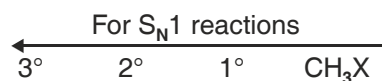
ORGANIC CHEMISTRY

SOME NOTEWORTHY POINTS

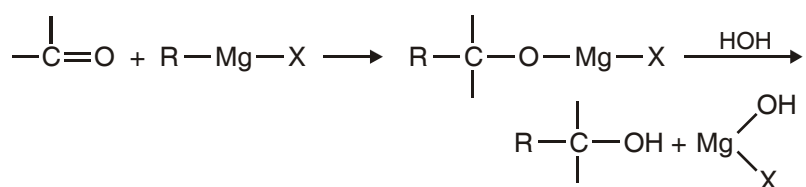
- In IUPAC naming, the sequence followed is
Prefixes in alphabetic order → Word Root → Pri Suffix → Sec. Suffix.
- If there are two or more functional groups, then priority will be given to one and second becomes prefix. $-\text{COOH} > -\text{SO}_3\text{H} > \text{anhydride} > \text{Ester} > \text{Acid halide} > \text{nitrile} > \text{aldehyde} > \text{ketone} > \text{alcohol} > \text{amine}$
- Anti Markownikov's addition takes place only with HBr.
- Order of reactivity w.r.t. acid : $\text{HI} > \text{HBr} > \text{HCl}$.
- Order of reactivity w.r.t. alcohols with Lucas reagent : $3^\circ > 2^\circ > 1^\circ$.
- $\text{R} - \text{H} + \text{X}_2 \xrightarrow{h\nu} \text{R} - \text{X} + \text{HX}$ The order of reactivities $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$.
Order of reactivity w.r.t. hydrogen atom abstracted is $3^\circ > 2^\circ > 1^\circ$.
Example :



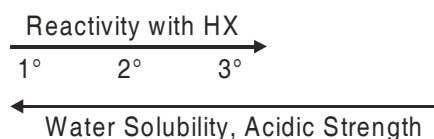
- Order of reactivity in S_N1 and S_N2 mechanism are as follows :



9. In case of optically active alkyl halide, S_N2 mechanism results in the inversion of configuration while S_N1 mechanism results in racemisation.
10. Aryl halides are much less reactive towards nucleophilic substitution reactions. Presence of electron withdrawing groups (like $-\text{NO}_2$) at *o*- and/or *p*-positions to halogen increases the rate of reaction.
11. Inductive Effect (+I and -I), Resonance Effect, Hyperconjugation, etc. play very important role in organic chemistry.
12. All the three type of monohydric alcohols (1° , 2° or 3°) except methanol can be prepared from Grignard Reagent



13. Alcohol



14. Presence of electron withdrawing group increases the acidic strength of alcohol, phenol and carboxylic acid while presence of electron donating group decreases the acidic strength.

E.W.G. : NO_2 , $-\text{X}$, $-\text{CN}$, COOH , etc., E.D.G. : $-\text{R}$, $-\text{OR}$, $-\text{OH}$, $-\text{NH}_2$

15. In electrophilic substitution in aromatic compound ring activating group like $-\text{OH}$, $-\text{NH}_2$, $-\text{OR}$, are *o*- and *p*- directing whereas ring deactivating groups

like $-\text{CHO}$, ---C=O , $-\text{COOH}$, $-\text{NO}_2$, $-\text{SO}_3\text{H}$ are *m*-directing. Halogens (X-) are electron withdrawing but are *o*- and *p*- directing.

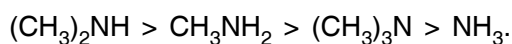
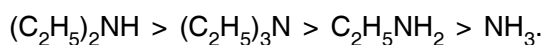
16. 3° alcohols are resistant to oxidation due to lack of α -hydrogen.
17. Acidic strength Alcohol < Phenol < Carboxylic acid, it is because of resonance stability of phenoxide and carboxylate ion. In carboxylate ion negative charge is delocalised over two oxygen atoms. while in phenoxide ion it is delocalised over one oxygen atoms and the benzene ring.

18. All organic compounds which form intermolecular H-bonds are water soluble.
19. Intermolecular H-bonds of *p*- and *m*- nitrophenol increases water solubility/ Acidic strength while intramolecular H-bonds in *o*-nitrophenol decreases these properties.
20. In the reaction of alkyl aryl ether (Anisole) with HI, the products are always alkyl halide and phenol, because O–R bond is weaker than O–Ar bond.
21. Ethers are stored in coloured bottles. In presence of sunlight they react with oxygen to form peroxide which may cause explosion on heating. Fe^{2+} can be used to detect and remove peroxide formed.
22. In reaction of toluene with CrO_3 , acetic anhydride is used to protect benzaldehyde as benzylidenediacetate to avoid further oxidation to benzoic acid.
23. Reactivity towards nucleophile of aldehyde and ketones.
 $\text{HCHO} > \text{CH}_3\text{CHO} > \text{CH}_3\text{CH}_2\text{CHO}$
 $\text{RCHO} > \text{R COR} ; \quad \text{ArCHO} > \text{Ar COR} > \text{Ar CO Ar}$
 because of (i) +I Inductive effect of –R group. (ii) Steric hindrance of –R and Ar. group.
24. Boiling points and melting points of various organic compounds depends on intermolecular forces of attraction which depend on following :
- Inter molecular/intramolecular H-bonding.
 - Dipole-Dipole interaction (Carboxyl and ether).
 - Molecular size
 - Surface area. (branching decreases surface area).
25. Benzaldehyde does not reduce Fehling's solution.
26. The more the K_a value, the lesser is the $\text{p}K_a$. A stronger acid has a higher K_a but a lower $\text{p}K_a$ value.
27. Acidic strength : $\text{HCOOH} > \text{C}_6\text{H}_5\text{COOH} > \text{CH}_3\text{COOH}$ because of +R and +I effect.
28. $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OH} \end{array}$ group in carboxylic acid is not a true carbonyl group because of resonance.

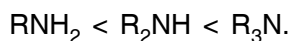


29. Basic character of aliphatic amines

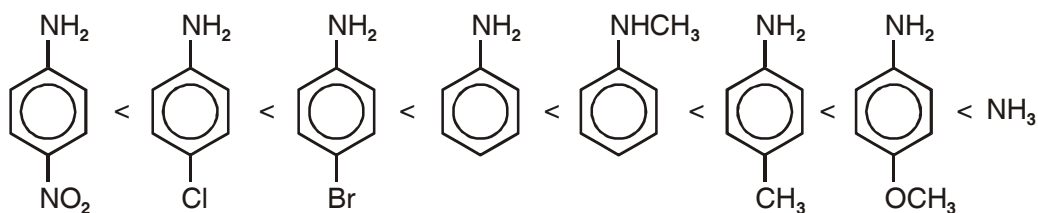
(a) In aqueous solution :



(b) In gaseous (vapour) state :



30. Basic character of aromatic amine



31. Hinsberg's reagent ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$) is used to separate the mixtures of 1°, 2° and 3° amines.

32. Sulphanilic acid exists as zwitter ion, therefore it is amphoteric in nature.

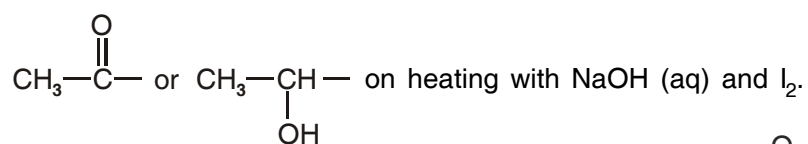
33. Aryl diazonium salts are more stable than alkyl diazonium salts.

34. Aniline and benzoic acid do not take part in Friedel-Craft Reaction.

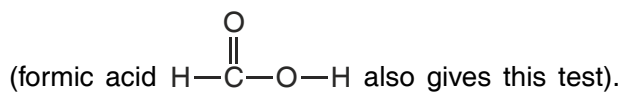
35. The more the basic character, the more is the K_b value and lesser is its $\text{p}K_b$ value.

USEFUL TIPS FOR IDENTIFICATION OF FUNCTIONAL GROUPS

- For identification of chloro, bromo or iodo alkanes, aq. KOH is added followed by AgNO_3 solution then precipitate of AgX is formed.
- Iodoform formation (CHI_3) test is given by all organic compounds having



- Tollens' reagent test is given by organic compound having $-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ group

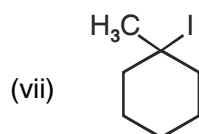
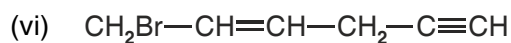
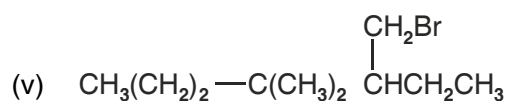
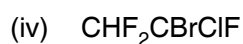
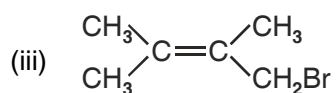
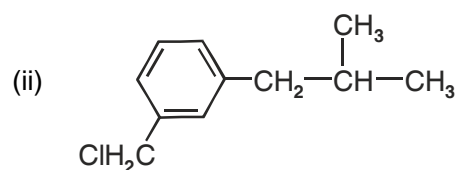
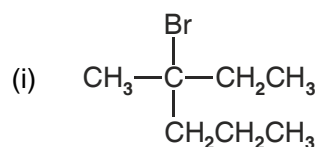


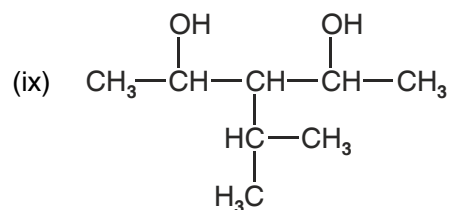
UNIT 10

HALO-ALKANES AND HALOARENES

QUESTIONS

1. Write the IUPAC names of the following compounds.





2. Write the structure of following halogen compounds

(i) D D T

(ii) Freon - 12

(iii) 1-Bromo 4-sec-butyl-2-methylbenzene.

(iv) p-Bromotoluene.

(v) Methylene chloride

(vi) Chloral

3. Arrange the following in the increasing order of property indicated :

(i) Bromomethane, bromoform, chloromethane, dichloromethane. (Increasing order of boiling points).

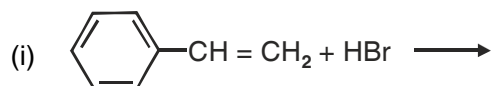
(ii) 1-Chloropropane, isopropyl chloride, 1-chlorobutane (Increasing order of b.pt.)

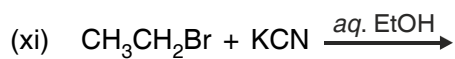
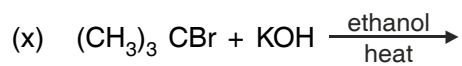
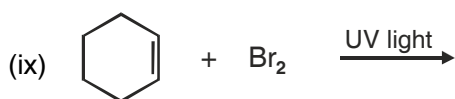
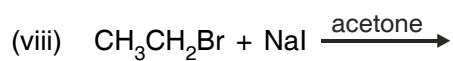
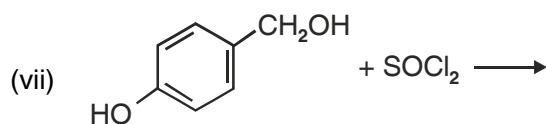
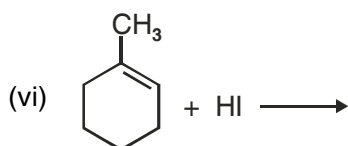
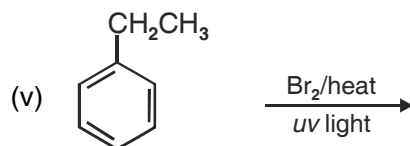
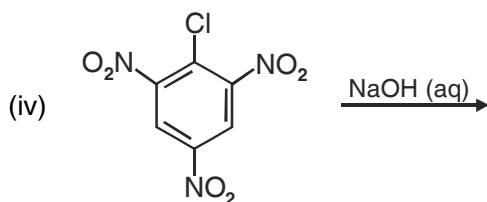
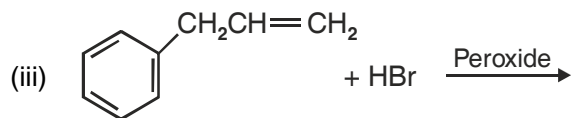
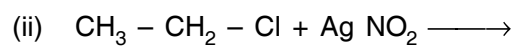
(iii) Dichloromethane, chloroform, carbon tetrachloride. (Increasing order of dipole moment).

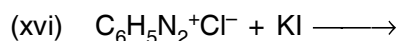
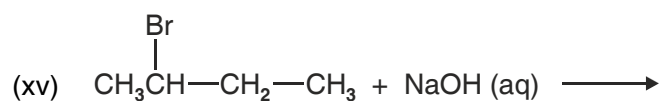
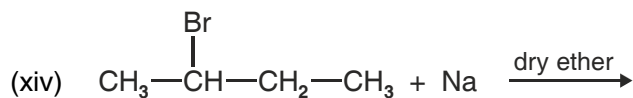
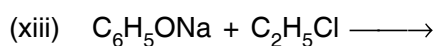
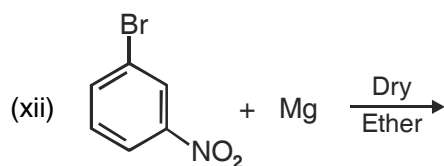
(iv) CH_3F , CH_3Cl , CH_3Br , CH_3I (Increasing reactivity towards nucleophilic substitution).

(v) o, m, p-dichlorobenzenes (Increasing order of melting points).

4. Complete the following reactions :



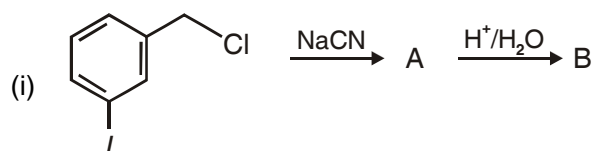


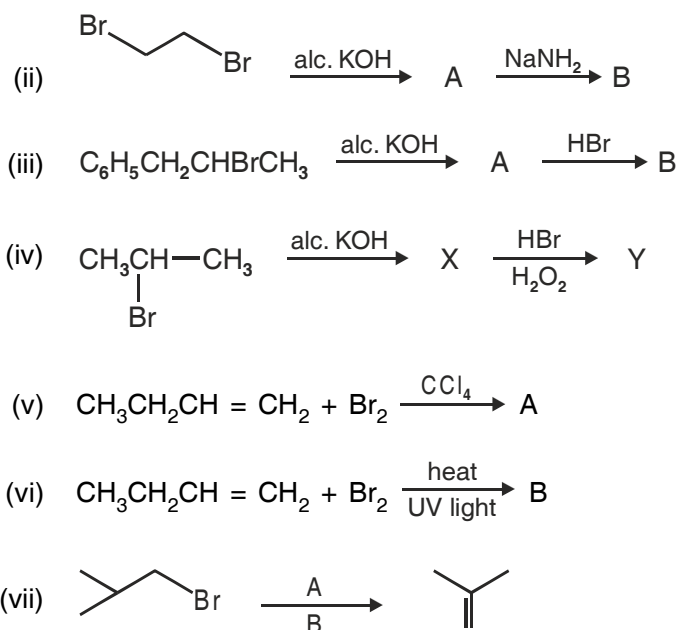


5. How will you bring about the following conversions?

- (i) Benzene to 3-bromonitrobenzene
- (ii) Ethanol to but-1-yne
- (iii) 1-Bromopropane to 2-bromopropane
- (iv) Benzene to 4-bromo-1-nitrobenzene
- (v) Aniline to chlorobenzene
- (vi) 2-Methyl-1-propene to 2-chloro-2-methylpropane
- (vii) Ethyl chloride to propanoic acid
- (viii) But-1-ene to n-butyl iodide
- (ix) Benzene to phenylchloromethane.
- (x) Tert-butyl bromide to isobutyl bromide.

6. Identify the products formed in the following sequence :

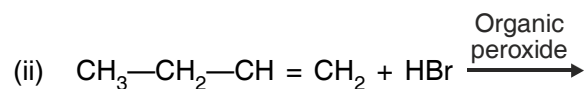
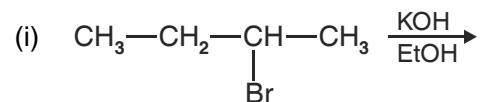


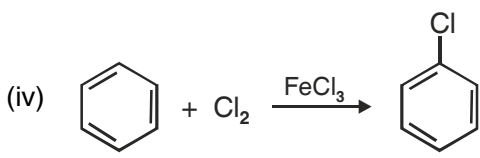


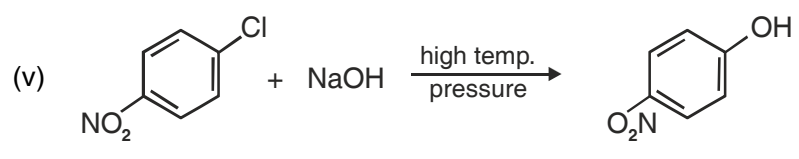
7. Explain the following reactions with suitable example :

- (i) Finkelstein reaction.
- (ii) Swarts reaction.
- (iii) Wurtz reaction.
- (iv) Wurtz-Fitting reaction
- (v) Friedel-Craft's alkylation reaction.
- (vi) Friedel-Craft's acylation reaction
- (vii) Sandmeyer reaction.

8. Write the major products and name the rule responsible for the formation of it.

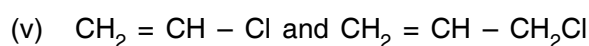
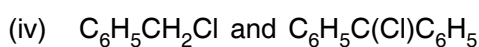
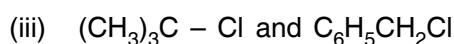
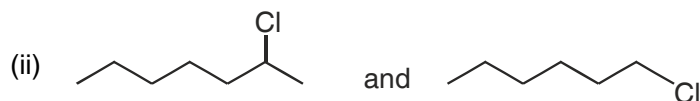
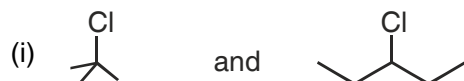


9. Write the difference between
- enantiomers and diastereomers
 - retention and inversion of configuration.
 - electrophilic and nucleophilic substitution reactions.
10. Give a chemical test to distinguish between the following pairs of compounds:
- Chlorobenzene and cyclohexylchloride.
 - Vinyl chloride and Ethyl chloride.
 - n*-Propyl bromide and Isopropyl bromide.
11. Give mechanism of the following reactions :
- $(\text{CH}_3)_3\text{C} - \text{Cl} + \text{OH}^- \longrightarrow (\text{CH}_3)_3\text{C} - \text{OH}$
 - $\text{CH}_3 - \text{Cl} + \text{OH}^- \longrightarrow \text{CH}_3 - \text{OH}$
 - $$\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{Cl} + \text{OH}^- \xrightarrow{\text{Ethanol}} \text{CH}_3 - \text{CH} = \text{CH}_2$$
 - 

(iv) c1ccccc1.ClCl>>Clc1ccccc1
 - 

(v) O=[N+]([O-])c1ccc(Cl)cc1.O[Na]>>O=[N+]([O-])c1ccc(O)cc1
12. Which compound in each of the following pairs will react faster in $\text{S}_{\text{N}}2$ reaction with OH^- and why?
- CH_3Br or CH_3I
 - $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl

13. In the following pairs which halogen compound undergoes faster S_N1 reaction?

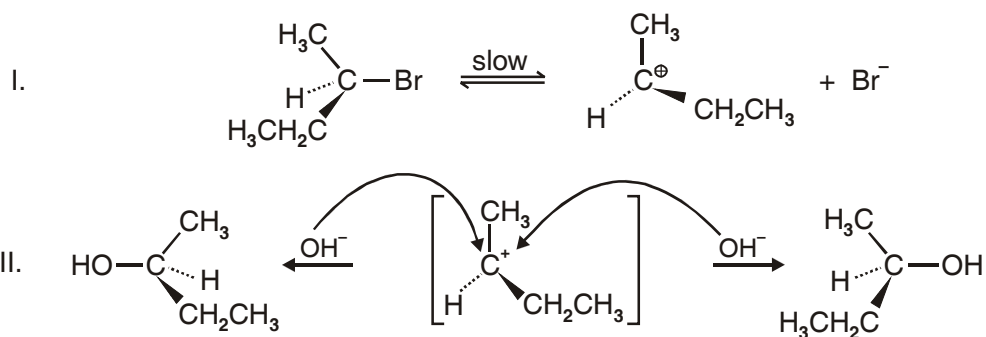


14. Give reasons for the following :

- (i) The bond length of C–Cl bond is larger in haloalkanes than that in haloarenes.
- (ii) Although alkyl halides are polar in nature but are not soluble in water.
- (iii) *t*-Butyl bromide has lower boiling point than *n*-butyl bromide.
- (iv) Haloalkanes react with KCN to form alkyl cyanide as main product while with AgCN alkylisocyanide is the main product.
- (v) Sulphuric acid is not used in the reaction of alcohol with KI.
- (vi) Thionyl chloride is the preferred reagent for converting ethanol to chloroethane.
- (vii) Haloalkanes undergo nucleophilic substitution reaction easily but haloarenes do not undergo nucleophilic substitution under ordinary conditions.
- (viii) Chlorobenzene on reaction with fuming sulphuric acid gives ortho and para chlorosulphonic acids.
- (ix) 2, 4-Dinitro chlorobenzene is much more reactive than chlorobenzene towards hydrolysis reaction with NaOH.
- (x) Grignard reagent should be prepared under anhydrous conditions.

- (xi) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
- (xii) Neopentyl bromide undergoes nucleophilic substitution reactions very slowly
- (xiii) Vinyl chloride is unreactive in nucleophilic substitution reaction.
- (xiv) An optically inactive product is obtained after the hydrolysis of optically active 2- bromobutane.

[Hint : The hydrolysis reaction occurs by S_N1 pathway. The carbocation is formed first which gives a mixture of (±) butan-2-ol in the second step].



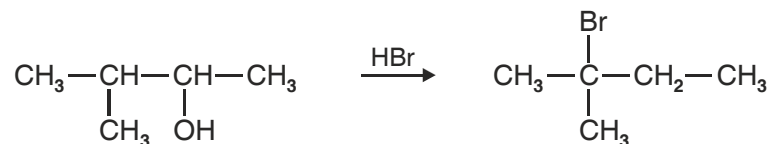
- (xv) Methyl iodide is hydrolysed at faster rate than methyl chloride.

15. Write the different products formed by the monochlorination of following compounds :

- (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- (ii) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$
- (iii) $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$

[Hint : (i) Two, (ii) four, (iii) three

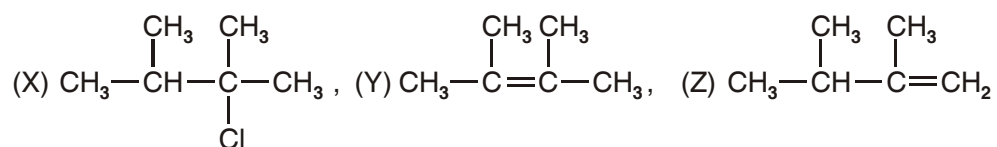
16. When 3-methylbutan-2-ol is treated with HBr, the following reaction takes places :



Give the mechanism for this reaction.

- *20. An alkyl halide X having molecular formula $C_6H_{13}Cl$ on treatment with potassium tert-butoxide gives two isomeric alkenes Y and Z. Both alkenes on hydrogenation give 2, 3-dimethylbutane. Identify X, Y and Z.

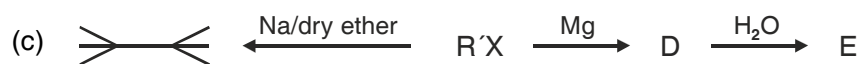
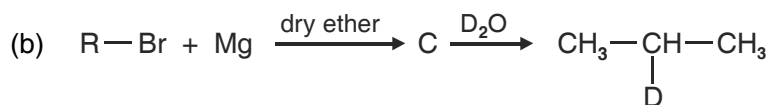
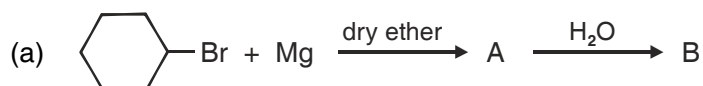
[Ans.



- *21. An organic compound (A) having molecular formula C_3H_7Cl on reaction with alcoholic solution of KCN gives compound B. The compound B on hydrolysis with dilute HCl gives compound C and C on reduction with H_2/Ni gives 1-aminobutane. Identify A, B and C.

[Ans. : A = $CH_3CH_2CH_2Cl$, B = $CH_3CH_2CH_2CN$, C = $CH_3CH_2CH_2CONH_2$

- *22. Identify A, B, C, D, E, R and R' in the following sequence of reactions :

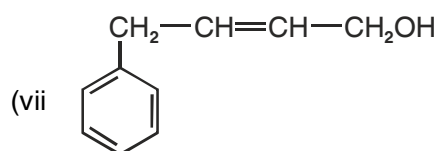
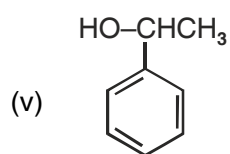
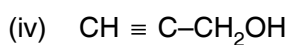
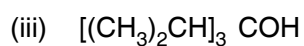
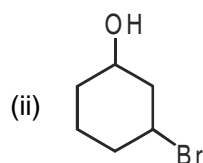
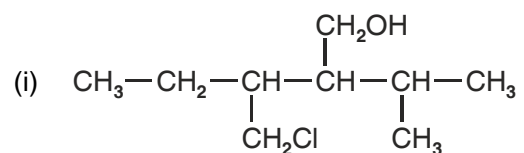


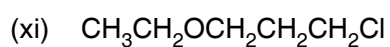
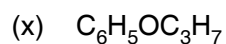
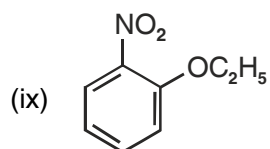
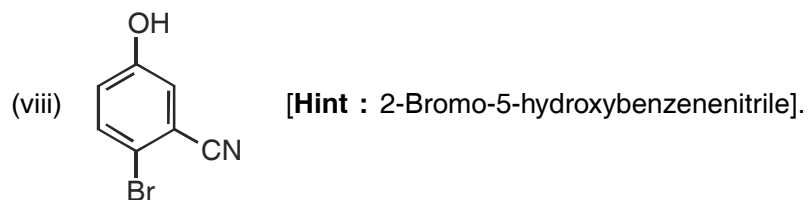
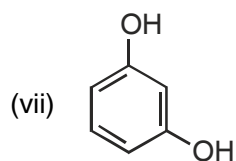
UNIT 11

ALCOHOLS, PHENOLS AND ETHERS

QUESTIONS

1. Write IUPAC names of the following compounds :





2. Write the structures of the compounds whose names are given below :

(i) 3, 5-Dimethoxyhexane-1, 3, 5-triol

(ii) Cyclohexylmethanol

(iii) 2-Ethoxy-3-methylpentane

(iv) 3-Chloromethylpentan-2-ol

(v) p-Nitroanisole

3. Describe the following reactions with example :

(i) Hydroboration oxidation of alkenes

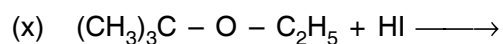
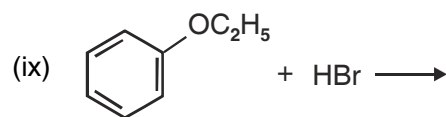
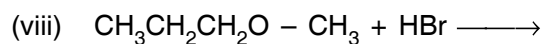
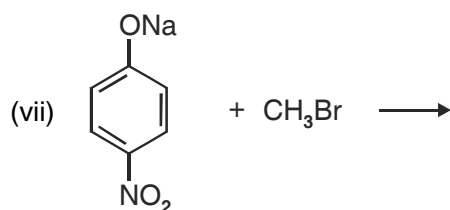
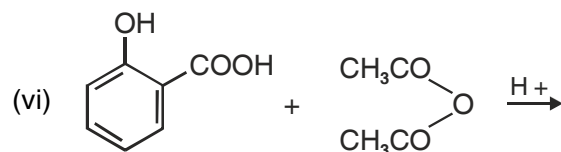
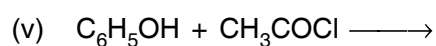
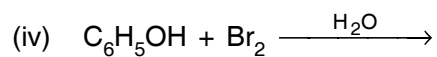
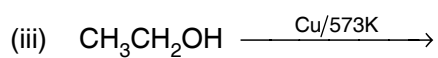
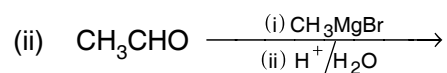
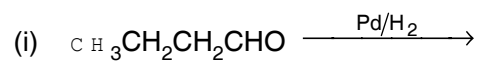
(ii) Acid catalysed dehydration of alcohols at 443K.

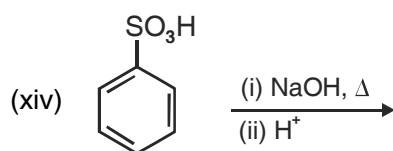
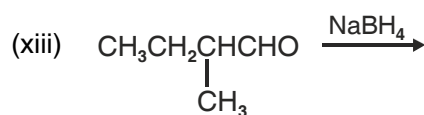
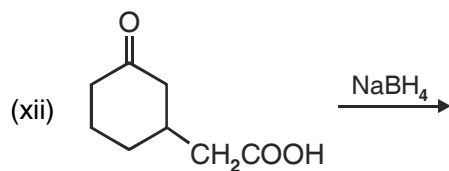
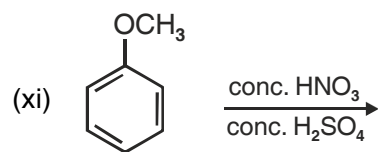
(iii) Williamson synthesis

(iv) Reimer-Tiemann reaction.

- (v) Kolbe's reaction
 (vi) Friedel-Crafts acylation of Anisole.

4. Complete the following reactions :





5. What happens when :

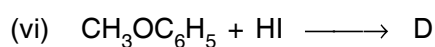
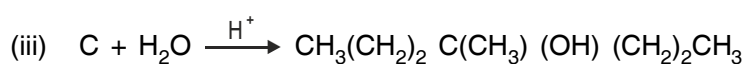
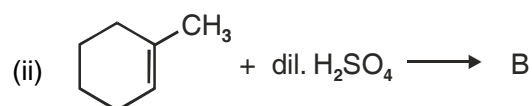
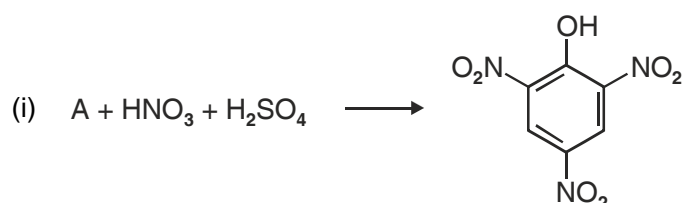
- (i) aluminium reacts with *t*-butylalcohol
- (ii) phenol is oxidised with chromic acid
- (iii) cumene is oxidised in the presence of air and the product formed is treated with dilute acid.
- (iv) phenol is treated with conc. HNO₃.
- (v) phenol is treated with chloroform in presence of dilute NaOH.

6. How will you convert

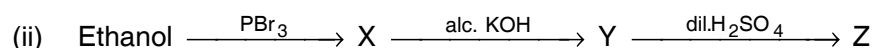
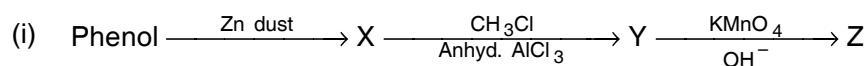
- (i) propene to propan-1-ol.
- (ii) anisole to phenol
- (iii) butan-2-one to butan-2-ol
- (iv) ethanal to ethanol

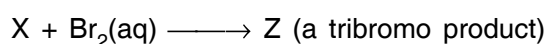
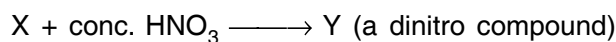
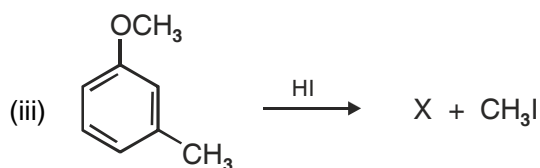
- (v) phenol to ethoxybenzene
- (vi) 1-Phenylethene to 1-Phenylethanol
- (vii) formaldehyde to cyclohexylmethanol
- (viii) butylbromide to pentan-1-ol.
- (ix) toluene to benzyl alcohol
- (x) 1-Propoxypropane to propyl iodide
- (xi) ethylbromide to 1-ethoxyethane
- (xii) methyl bromide to 2-methoxy-2-methylpropane
- (xiii) ethylbromide to ethoxybenzene
- (xiv) ethanol to benzylethyl ether.

7. Identify the missing reactant or product A to D in the following equations:



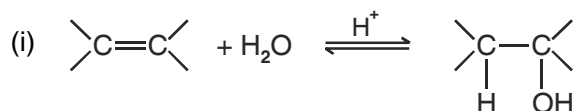
8. Identify X, Y and Z in the following sequence of reactions :



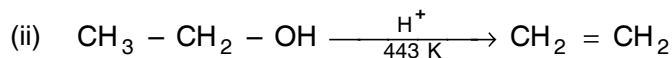


9. Describe the mechanism of Chemical reactions in which alcohol acts as a nucleophile or an electrophile.

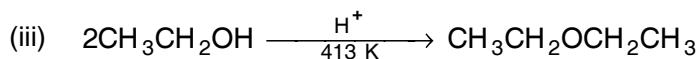
10. Write the mechanism for following reactions :



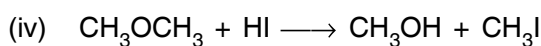
(acid catalysed hydration of alkenes)



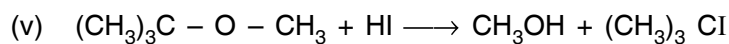
(acid catalysed dehydration of alcohols)



(acid catalysed nucleophilic substitution reaction)



(acid catalysed cleavage of ethers)



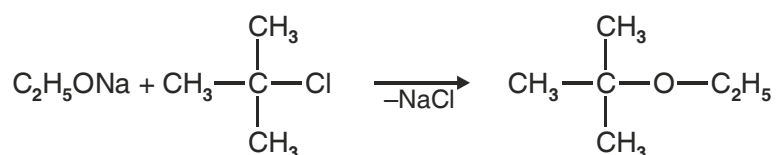
(acid catalysed cleavage of ethers)

11. Give reason for the following :

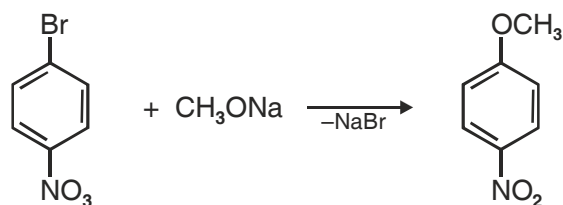
(i) The C–O–C bond angle in dimethylether is (111.7°)

(ii) Alcohols have higher boiling points than ethers of comparable molecular mass.

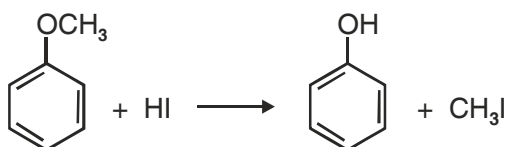
- (iii) Phenols are more acidic than alcohols.
- (iv) Nitrophenol is more acidic than o-methoxyphenol.
- (v) Phenol is more reactive towards electrophilic substitution reaction than benzene.
- (vi) Preparation of ether by treatment of alcohol with dilute H_2SO_4 is not a suitable method for the preparation of diisopropylether or tert butylether.
- (vii) The following is not an appropriate method for the preparation of t-butyl ethyl ether :



- (viii) The following is not an appropriate method for the preparation of 1-methoxy-4-nitrobenzene;



- (ix) o-Nitrophenol is steam volatile but p-nitrophenol is not.
- (x) Phenol is less polar than ethanol.
- (xi) The phenylmethylether reacts with HI to form phenol and iodomethane and not iodobenzene and methanol.



- (xii) Methanol is less acidic than water.
- (xiii) Alcohols can act as weak base as well as weak acids.
- (xiv) Phenols do not give protonation reaction readily.
- (xv) Alcohols undergo nucleophilic substitution reactions but phenols do not undergo nucleophilic substitution at C-1 carbon.
- (xvi) Absolute ethanol can not be obtained by fractional distillation of ethanol water mixture.

12. Arrange the following in the increasing order of property shown :

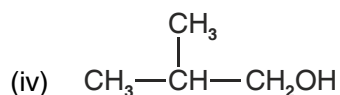
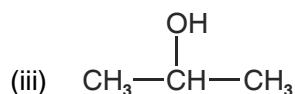
- (i) Methanol, Ethanol, Diethylether, Ethylene-glycol.
(Boiling points)
- (ii) Phenol, o-nitrophenol, m-nitrophenol, p-nitrophenol.
(Acidic strength)
- (iii) Dimethylether, ethanol, phenol.
(Solubility in water)
- (iv) n-butanol, 2-methylpropan-1-ol, 2-methylpropan-2-ol.
(Acidic strength)

13. Give a chemical test to distinguish between the following pair of compounds.

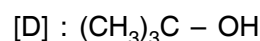
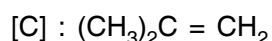
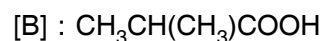
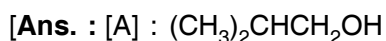
- (i) n-Propylalcohol and isopropylalcohol
- (ii) Methanol and ethanol
- (iii) Cyclohexanol and phenol.
- (iv) Propan-2-ol and 2-methylpropan-2-ol.
- (v) Phenol and anisole
- (vi) Ethanol and diethylether

*14. Which of the following compounds gives fastest, reaction with HBr and why?

- (i) $(\text{CH}_3)_3\text{C} - \text{OH}$
- (ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

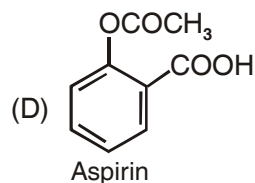
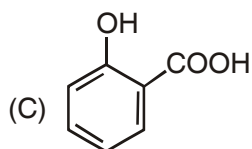
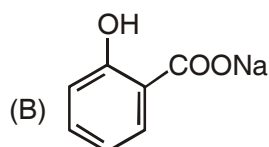
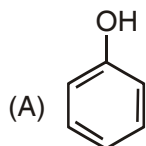


- *15. What is the function of ZnCl_2 (Anhyd) in Lucas test for distinction between 1° , 2° and 3° alcohols.
16. An alcohol A ($\text{C}_4\text{H}_{10}\text{O}$) on oxidation with acidified potassium dichromate gives carboxylic acid B ($\text{C}_4\text{H}_8\text{O}_2$). Compound A when dehydrated with conc. H_2SO_4 at 443 K gives compound C. Treatment of C with aqueous H_2SO_4 gives compound D. ($\text{C}_4\text{H}_{10}\text{O}$) which is an isomer of A. Compound D is resistant to oxidation but compound A can be easily oxidised. Identify A, B, C and D and write their structures.



- *17. An organic compound A having molecular formula $\text{C}_6\text{H}_6\text{O}$ gives a characteristic colour with aqueous FeCl_3 . When A is treated with NaOH and CO_2 at 400 K under pressure compound B is obtained. Compound B on acidification gives, compound C which reacts with acetyl chloride to form D, which is a popular pain killer. Deduce the structure of A, B, C and D. What is the common name of Drug D?

[Ans. :



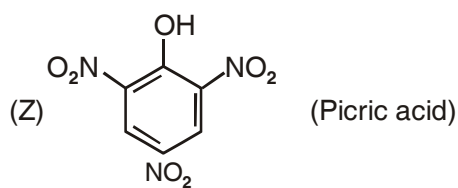
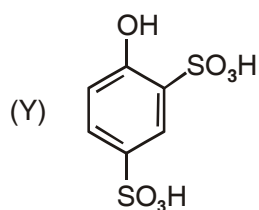
19. An ether A ($\text{C}_5\text{H}_{12}\text{O}$) when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis form compounds B and C.

Oxidation of B gives an acid D whereas oxidation of C gave a ketone E. Deduce the structures of A, B, C, D and E.

- [Ans. : (A) $\text{CH}_3\text{CH}_2\text{OCH} \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$
- (B) $\text{CH}_3\text{CH}_2\text{OH}$
- (C) $\text{CH}_3\text{CHOHCH}_3$
- (D) CH_3COOH
- (E) CH_3COCH_3

20. Phenol, when it first reacts with concentrated sulphuric acid forms Y. Y is reacted with concentrated nitric acid to form Z. Identify Y and Z and explain why phenol is not converted to Z by reacting it with conc. HNO_3 .

[Ans. :



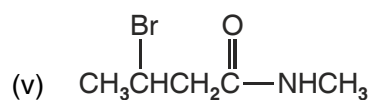
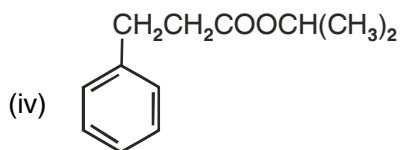
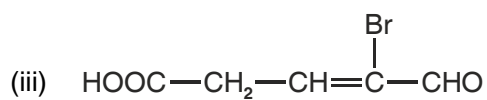
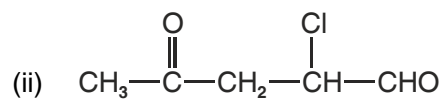
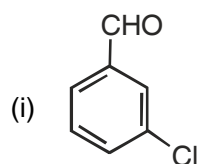
Phenol is not reacted directly with conc. HNO_3 because the yield of picric acid is very poor in this method.]

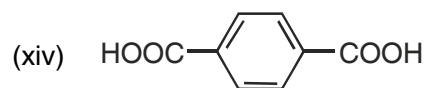
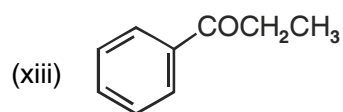
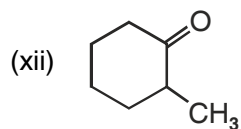
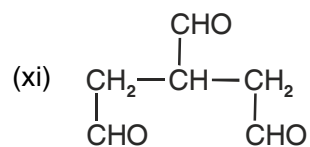
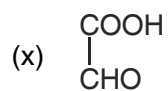
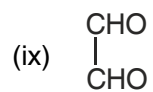
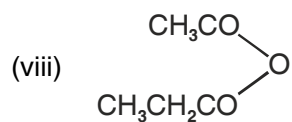
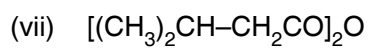
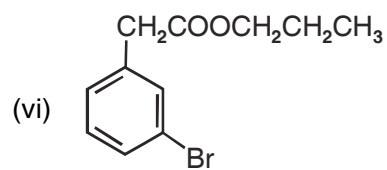
UNIT 12

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

QUESTIONS

1. Indicate the electrophilic and nucleophilic centres in acetaldehyde.
2. Write the IUPAC names of the following organic compounds :





3. Explain the following reactions giving one example in each :

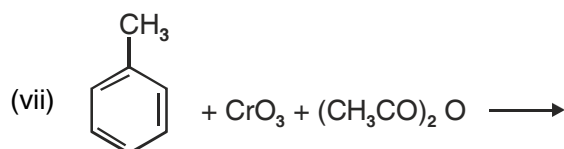
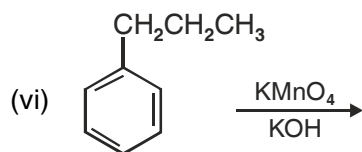
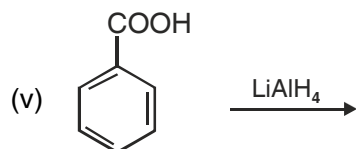
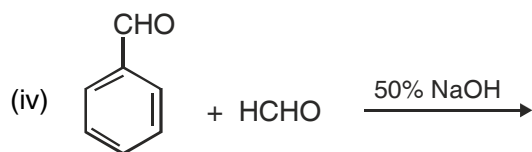
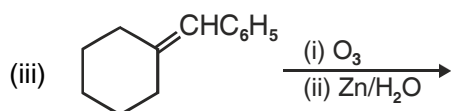
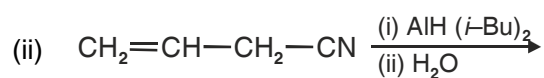
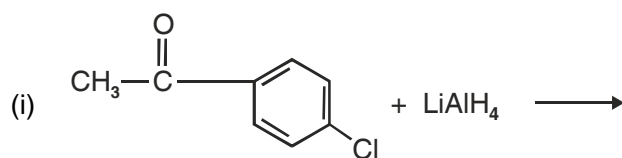
(i) Rosenmund reduction reaction

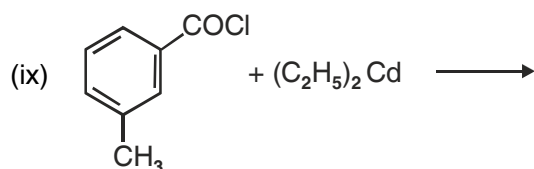
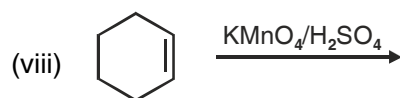
- (ii) Stephen reaction
 - (iii) Etard reaction
 - (iv) Gatterman-Koch reaction
 - (v) Aldol condensation
 - (vi) Cross Aldol condensation
 - (vii) Cannizzaro reaction
 - (viii) Decarboxylation reaction
 - (ix) Kolbe's reaction
 - (x) Hell-Volhard-Zelinsky reaction
 - (xi) Clemmensen reduction
 - (xii) Wolff-Kishner reduction
 - (xii) Haloform reaction.
4. How will you convert :
- (i) Isopropyl chloride to 2-methylpropionaldehyde.
 - (ii) benzene to benzaldehyde
 - (iii) benzoic acid to acetophenone
 - (iv) propene to propanal
 - (v) butanoic acid to 2-hydroxybutanoic acid
 - (vi) benzoic acid to m-nitrobenzyl alcohol
 - (vii) propanol to propene
 - (viii) propanol to butan-2-one.
 - (ix) methyl magnesium bromide to ethanoic acid
 - (x) benzoic acid to benzyl chloride
 - (xi) acetone to chloroform
 - (xii) acetylene to acetic acid

(xiii) formaldehyde to propanol

(xiv) acetophenone to 2-phenylbutan-2-ol

5. Complete the following reactions :





6. How will you prepare the following derivatives of acetone?

(i) 2, 4-DNP derivative

(ii) Schiff's base

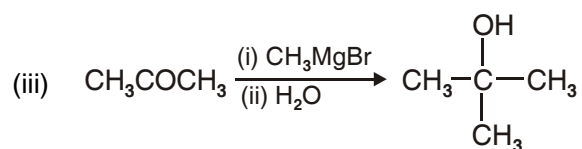
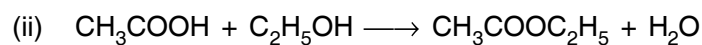
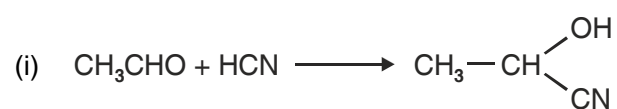
(iii) Oxime

7. Arrange the following in the increasing order of the property indicated

(i) CH_3CHO , HCHO , CH_3COCH_3 , $\text{C}_6\text{H}_5\text{CHO}$ (Reactivity towards HCN)

(ii) Propan-1-ol, propanone, propanal (boiling point)

8. Give the reaction mechanism for following reactions :



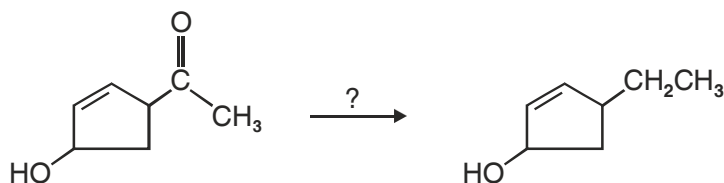
9. Give the chemical tests to distinguish between following pair of compounds:

- (i) Propanol and propanone
- (ii) Ethyl acetate and methyl acetate
- (iii) Benzaldehyde and benzoic acid
- (iv) Benzaldehyde and acetaldehyde
- (v) Formic acid and acetic acid
- (vi) Propanal and propanol
- (vii) Ethanoic acid and ethylethanoate

10. Give reason for the following :

- (i) The reactivity of aromatic aldehydes and ketones is less than that of aliphatic carbonyl compounds towards nucleophilic addition reactions.
- (ii) Benzaldehyde does not give Fehling's test.
- (iii) The α -H atoms in ethanal are acidic in nature.
- (iv) p-Nitrobenzaldehyde is more reactive than benzaldehyde towards nucleophilic addition reactions.
- (v) Acetic acid does not give sodium bisulphite addition product.
- (vi) For the formation of ethylacetate from acetic acid and ethanol in presence of sulphuric acid, the reaction mixture is heated to remove water.
- (vii) Chloroacetic acid has lower pka value than acetic acid.
- (viii) Monochloroethanoic acid is a weaker acid than dichloroethanoic acid.
- (ix) Benzoic acid is stronger acid than ethanoic acid.
- (x) Aldehyde are more reactive than ketones towards nucleophilic reagents.
- (xi) Benzaldehyde does not undergo aldol condensation.

- (xii) Formic acid reduces Tollens' reagent.
 - (xiii) Electrophilic substitution in benzoic acid takes place at m-position.
 - (xiv) Carboxylic acids do not give characteristic reactions of carbonyl group.
 - (xv) Formaldehyde gives Cannizzaro's reaction whereas acetaldehyde does not.
 - (xvi) Tert-butyl benzene cannot be oxidised with KMnO_4 .
 - (xvii) Bond length of $\text{C} = \text{O}$ in carboxylic acids is slightly larger than $\text{C} = \text{O}$ bond length in carbonyl compounds.
 - (xviii) There are two $-\text{NH}_2$ groups in semicarbazide. However, only one $-\text{NH}_2$ group is involved in the formation of semicarbazones.
 - (xix) Benzoic acid is less soluble in water than acetic acid.
 - (xx) Formic acid is a stronger acid than acetic acid.
- *11. You are given four different reagents Zn-Hg/HCl , $\text{NH}_2-\text{NH}_2/\text{OH}^-$ in Glycol, H_2/Ni and NaBH_4 . Select one reagent for the following transformation and give reasons to justify your answer.



[Hint : Zn-Hg/HCl and $\text{NH}_2-\text{NH}_2/\text{OH}^-$ are the appropriate reagents for converting $-\text{CO}$ group to $-\text{CH}_2$ group but HCl will also bring about dehydration of alcohol to form alkene. Therefore the most effective is $\text{NH}_2-\text{NH}_2/\text{OH}^-$ in glycol.

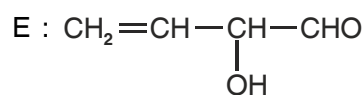
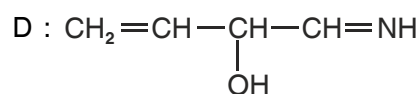
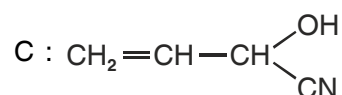
- *12. An organic compound (A) having molecular formula $\text{C}_5\text{H}_{10}\text{O}$ gives a positive 2, 4-DNP test. It does not reduce Tollens' reagent but forms an addition compound with Sodium hydrogen sulphite. On reaction with I_2 in alkaline medium, it forms a yellow precipitate of compound B and another compound C having molecular formula $\text{C}_4\text{H}_7\text{O}_2\text{Na}$. On oxidation with KMnO_4 , [A]

forms two acids D and E having molecular formula $C_3H_6O_2$ and $C_2H_4O_2$ respective. Identify A, B, C, D and E.

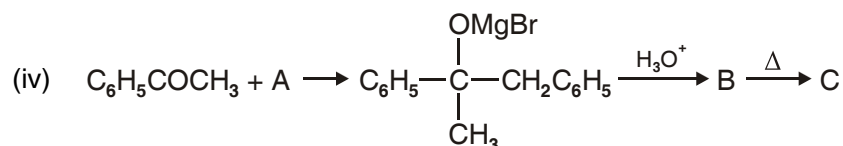
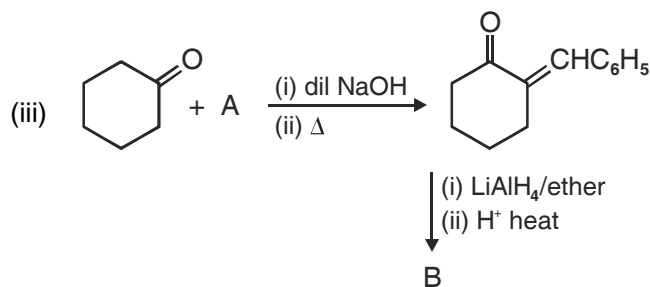
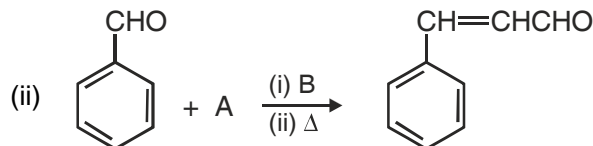
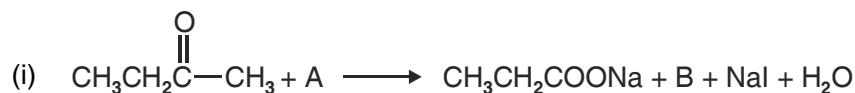
- *13. Formaldehyde and acetaldehyde on treatment with dil. NaOH form A which on heating changes to B. When B is treated with HCN, it forms C. Reduction of C with DIBAL- H yields D which on hydrolysis gives E.

[Ans. : A : $HOCH_2CH_2CHO$

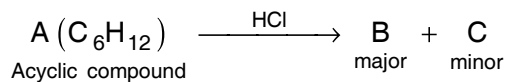
B : $CH_2 = CH - CHO$



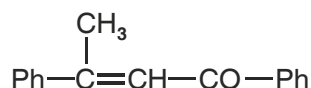
- *14. Identify the missing reagent/products in the following reactions :



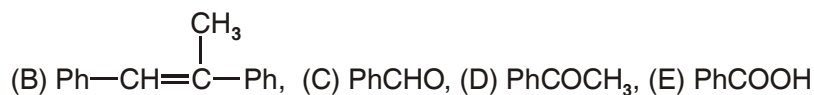
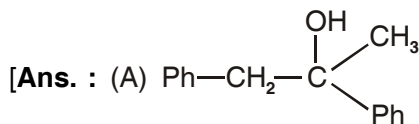
15. Identify A, B, C, D and E in the following sequences of reactions :



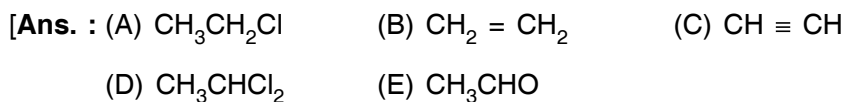
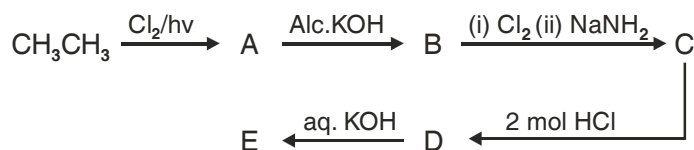
*16. A tertiary alcohol 'A' on acid catalyzed dehydration gave product 'B'. Ozonolysis of 'B' gives compounds 'C' and 'D'. Compound 'C' on reaction with KOH gives benzyl alcohol and compound 'E'. Compound 'D' on reaction with KOH gives α , β - unsaturated ketone having the following structure.



Identify A, B, C, D and E

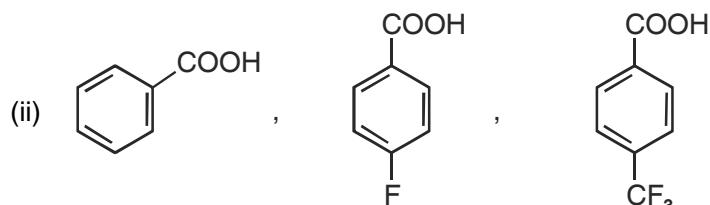


*17. Identify A, B, C, D and E in the following sequence of reactions :



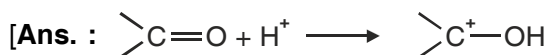
*18. Arrange the following acids in the order of increasing acidic strength

(i) Formic acid, benzoic acid, acetic acid



(iii) $\text{CH}_3\text{CH}_2\text{COOH}$, $\text{C}_6\text{H}_5\text{COOH}$, CH_3COOH , $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$

*19. During the reaction of a carbonyl compound with a weak nucleophile, H^+ ions are added as catalyst. Why?



H^+ ions get attached to oxygen atom and make carbonyl carbon more electropositive.]

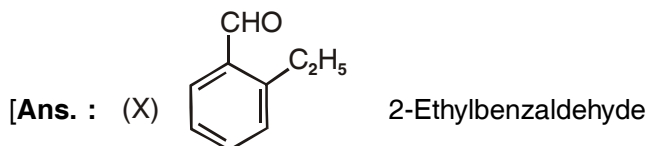
*20. During reaction of carbonyl compound with 2, 4-DNP reagent the pH of the reaction mixture has to be maintained between 3 and 4. Why?

[Ans. : H^+ ions increase the electrophilicity of carbonyl carbon. When H^+ ions are in excess, they protonate the NH_2 – group of 2, 4-DNP. After protonation $-\overset{+}{\text{N}}\text{H}_3$ group does not act as nucleophile.]

*21. An aromatic compound X with molecular formula C_9H_{10} gives the following chemical tests :

- (i) Forms 2, 4-DNP derivative
- (ii) Reduced Tollens' reagent
- (iii) Undergoes Cannizzaro reaction
- (iv) On vigorous oxidation gives 1, 2-benzenedicarboxylic acid.

Identify X and write its IUPAC name. Also write the reactions involved in the formation of above mentioned products.

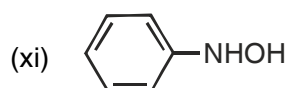
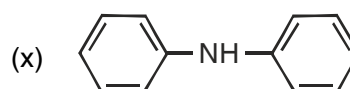
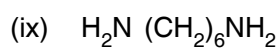
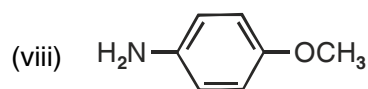
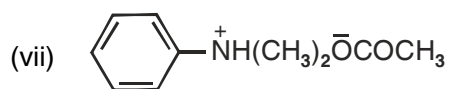
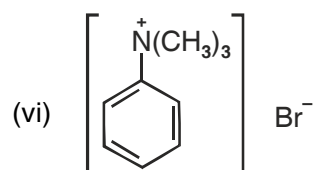
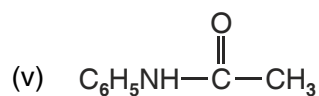
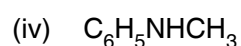
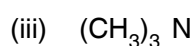
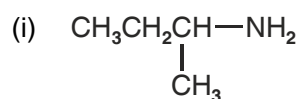


UNIT 13

AMINES

QUESTIONS

1. Write IUPAC names of the following amines :



2. Giving an example of each, describe the following reactions :

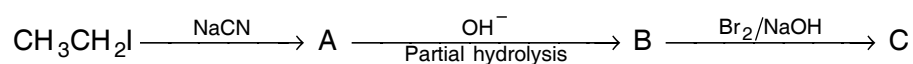
- Hoffman bromamide reaction
- Gabriel phthalimide synthesis

- (iii) Gatterman reaction
 - (iv) Coupling reaction
 - (v) Hoffman's ammonolysis
 - (vi) Carbylamine reaction
 - (vii) Acetylation of aniline.
3. Describe the test for identification of primary, secondary and tertiary amines. Also write the chemical equations of the reactions involved.
4. Arrange the following in the increasing order of given property :
- (i) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3 , (Basic strength in aqueous solution).
 - (ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and CH_3NH_2 . (Basic strength in gaseous phase).
 - (iii) Aniline, p-toluidine, p-nitroaniline. (Basic strength).
 - (iv) NH_4^+ , $C_6H_5NH_3^+$, p-F- $C_6H_5NH_3^+$. (Acid strength).
5. Identify A and B in the following reactions :
- (i) $CH_3CH_2Cl + NH_3$ (Excess) $\xrightarrow{373K}$ A
 - (ii) $CH_3CH_2Cl + NH_3$ $\xrightarrow{373K}$
(excess)
6. How will you bring about the following conversions?
- (i) Benzene to Aniline
 - (ii) Aniline to benzene
 - (iii) Ethanoic acid to ethanamine
 - (iv) p-Toluidine to 2-bromo-4-methylaniline.
 - (v) Methylbromide to ethanamine
 - (vi) Benzenediazonium chloride to nitrobenzene
 - (vii) Ethylamine to methylamine

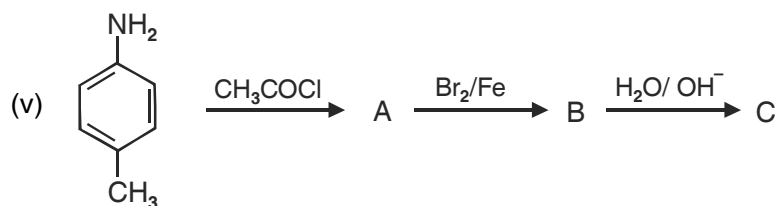
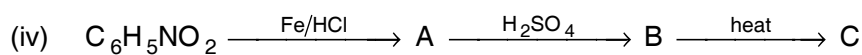
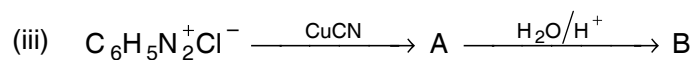
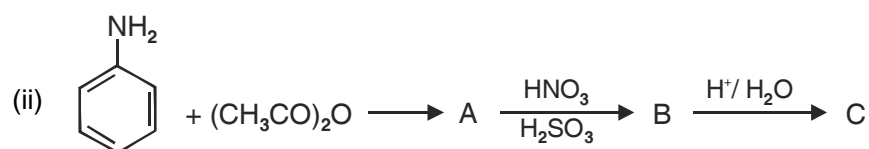
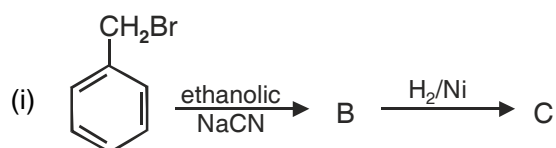
(ix) Benzene to sulphanic acid

(x) Hexanenitrile to 1-aminopentane.

7. Write the products formed in the following sequence of reactions :



8. Identify the missing reagent/product in the following reactions :



9. Give one chemical test to distinguish between the following pairs of compounds :

(i) Methylamine and dimethylamine

(ii) Secondary and tertiary amines

- (iii) Ethylamine and aniline
- (iv) Aniline and benzylamine
- (v) Methylamine and methanol
- (vi) Methylamine and N, N-dimethylamine
- (vii) Ethanol and ethanamine

10. Explain why :

- (i) The C–N–C bond angle in trimethyl amine is 108°
- (ii) The quaternary ammonium salts having four different alkyl groups are optically active
- (iii) Alkylamines are more basic than ammonia
- (iv) Aniline can not be prepared by Gabriel phthalimide synthesis
- (v) Gabriel phthalimide synthesis is preferably used for synthesising primary amines.
- (vi) Ethylamine is soluble in water but aniline is not
- (vii) Aniline is soluble in dilute HCl.
- (viii) Amines have lower boiling point than alcohols of comparable molecular masses.
- (ix) 1° Amines have higher boiling points than 2° amines which in turn, are higher boiling than 3° amines.
- (x) The pK_b value of benzeneamine is 9.33 while that of ammonia is 4.75.
- (xi) Aniline does not undergo Friedel-Crafts reaction.
- (xii) Aniline readily forms 2, 4, 6-tribromoaniline on reaction with bromine water.
- (xiii) Sulphanilic acid is soluble in water.
- (xiv) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

UNIT 14

BIOMOLECULES

POINTS TO REMEMBER

1. Carbohydrates are optically active polyhydroxy aldehydes or ketones or molecules which provide such units on hydrolysis.
2. They are broadly classified into three groups-monosaccharides, oligosaccharides and polysaccharides.
3. Glucose, the most important source of energy for mammals, is obtained by the digestion of starch.
4. Monosaccharides are held together by glycosidic linkages to form disaccharides or polysaccharides.
5. Proteins are the polymers of about twenty different α -amino acids which are linked by peptide bonds. Ten amino acids are called essential amino acids because they can not be synthesised in our body. Hence must be provided through diet.
6. Proteins perform various structural and dynamic functions in the organisms. Proteins, which contain only α -amino acids, are called simple proteins.
7. The secondary or tertiary structure of proteins get disturbed on change of pH or temperature and they are not able to perform their functions. This is called denaturation of proteins.
8. Enzymes are biocatalysts which speed up the reactions in biosystems. They are very specific and selective in their action and chemically all enzymes are proteins.
9. Vitamins are necessary food factors required in the diet. They are classified as fat soluble (A, D, E and K) and water soluble (B group and C).
10. Nucleic acid are responsible for the transfer of characters from parents to offsprings.

11. There are two types of nucleic acids DNA and RNA. DNA contains a five carbon sugar molecule called 2-deoxyribose and RNA contains ribose.
12. Both DNA and RNA contain adenine, guanine and cytosine. The fourth base is thymine in DNA and uracil in RNA. The structure of DNA is double stranded while that of RNA is a single stranded molecule.
13. DNA is the chemical basis of heredity and has the coded message for proteins to be synthesised.
14. There are three types of RNA *i.e.*, m-RNA, r-RNA and t-RNA which actually carry out the protein synthesis in the nucleus.
15. Human stomach does not have any enzyme capable of breaking cellulose molecules and thus we cannot digest cellulose.

QUESTIONS

VSA TYPE QUESTIONS (1 MARK)

1. Name polysaccharide which is stored in the liver of animals.
2. What structural feature is required for a carbohydrate to behave as reducing sugar?

[Hint : The carbonyl group of any one monosaccharide present in carbohydrate should be free]

3. How many asymmetric carbon atoms are present in D – (+) glucose?
4. Name the enantiomer of D-glucose.

[Hint : L-(–)-Glucose]

5. Give the significance of (+)-sign in the name D-(+)-glucose.

[Hint : (+) sign indicates dextrorotatory nature of glucose].

6. Give the significance of prefix 'D' in the name D-(+)-glucose.

[Hint : 'D' Signifies that –OH group on C-5 is on the right hand side]

7. Glucose is an aldose sugar but it does not react with sodium hydrogen sulphite. Give reason.

[**Hint** : The -CHO group reacts with -OH group at C-5 to form a cyclic hemiacetal].

8. Why is sucrose called invert sugar?

[**Hint** : When sucrose is hydrolysed by water the optical rotation of solution changes from positive to negative.]

9. Name the building blocks of proteins.

10. Give the structure of simplest optically active α -amino acid.

11. Name the α -amino acid which is not optically active.

12. Write the Zwitter ionic form of amino acetic acid.

13. Name the enzyme which catalyses the hydrolysis of maltose into glucose.

14. Give reason : Amylase present in the saliva becomes inactive in the stomach.

[**Hint** : In stomach the pH decreases.]

15. How would you explain the amphoteric behavior of amino acids.

[**Hint** : Amino acids are amphoteric due to the presence of both acidic and basic functional groups.]

16. Which forces are responsible for the stability of α -helix structure of proteins.

17. How are polypeptides different from proteins.

18. Which nucleic acid is responsible for carrying out protein synthesis in the cell.

19. The two strands in DNA are not identical but complementary. Explain.

[**Hint** : H-bonding is present between specific pairs of bases present in complementary stands.]

20. When RNA is hydrolysed, there is no relationship among the quantities of different bases obtained. What does this fact suggest about the structure of RNA.

[**Hint** : RNA is single stranded].

21. What type of linkage holds together the monomers of DNA and RNA.
[Hint :Phosphodiester linkage]
22. Mention the number of hydrogen bonds between adenine and thymine.
23. A child diagnosed with bone deformities, is likely to have with the deficiency of which vitamin?
24. Fat soluble vitamins A, D, E and K are stored in which part of body?
25. What is meant by the term DNA fingerprinting?
26. List two important functions of proteins in human body.
27. Name the vitamin responsible for coagulation of blood.
28. Except vitamin B₁₂, all other vitamins of group B, should be supplied regularly in diet. Why?
29. How is glucose prepared commercially?
30. What is the structural difference between glucose and fructose?
31. What is the difference between an oligosaccharide and a polysaccharide.
32. Give the Haworth projection of α -D-glucopyranose.

SA (I) TYPE QUESTIONS (2 MARKS)

1. What are anomers. Give the structure of two anomers of glucose.
2. What are the hydrolysis products of
 - (i) maltose
 - (ii) cellulose?
3. What are the two components of starch? Which one is water soluble?
4.
 - (i) Acetylation of glucose with acetic anhydride gives glucose pentaacetate. Write the structure of the pentaacetate.
 - (ii) Explain – Why glucose pentaacetate does not react with hydroxylamine?

[Hint : The molecule of glucose pentaacetate has a cyclic structure in which –CHO is involved in ring formation with OH group at C-5]

5. What are vitamins? How are they classified?
6.
 - (i) Why is sucrose called a reducing sugar?
 - (ii) Give the type of glycosidic linkage present in sucrose.
7. Classify the following as monosaccharides or oligosaccharides.
 - (i) Ribose
 - (ii) Maltose
 - (iii) Galactose
 - (iv) Lactose
8. Write the products of oxidation of glucose with
 - (a) Bromine water
 - (b) Nitric acid
9. State two main differences between globular and fibrous proteins.
10. Classify the following α -amino acids as neutral, acidic or basic.
 - (i) $\text{HOOC} - \text{CH}_2 - \text{CH}(\text{NH}_2) \text{COOH}$
 - (ii) $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH}(\text{NH}_2) \text{COOH}$
 - (iii) $\text{H}_2\text{N} - (\text{CH}_2)_4 - \text{CH}(\text{NH}_2) - \text{COOH}$
 - (iv) $\text{HN}=\underset{\text{NH}_2}{\text{C}} - (\text{CH}_2)_3 - \text{CH}(\text{NH}_2)\text{COOH}$
11. You have two amino acids glycine and alanine. What are the structures of two possible dipeptides that they can form?
12. What are essential and non essential amino acids? Give one example of each type.
13. Name four type of intermolecular forces which stabilize 2° and 3° structure of proteins.
 [Hint : Hydrogen bonds, disulphide linkages, vander Waals and electrostatic forces of attraction.]
14. Classify the following as globular or fibrous proteins.
 - (i) Keratin

- (ii) Myosin
 - (iii) Insulin
 - (iv) Haemoglobin.
15. What do you understand by
- (a) Denaturation of protein
 - (b) Specificity of an enzyme.
16. On electrolysis in acidic solution amino acids migrate towards cathode while in alkaline solution they migrate towards anode.
- [Hint : In acidic solution, COO^- group of amino acid zwitter ion is protonated and NH_3^+ groups is left unchanged while in basic solution deprotonation converts NH_3^+ to NH_2 and COO^- is left unchanged.]
17. (i) Name the disease caused by deficiency of vitamin D.
(ii) Why vitamin C cannot be stored in our body?
18. Define the terms hypervitaminosis and avitaminosis.
- [Hint : Excess intake of vitamin A and D causes hypervitaminosis while multiple deficiencies caused by lack of more than one vitamin are called avitaminosis]
19. Explain what is meant by :
- (i) a peptide linkage
 - (ii) a glycosidic linkage?
- [Hint : (i) Peptide linkage refers to the $-\text{CONH}-$ linkage formed by reaction between $-\text{COOH}$ group of one amino acid with $-\text{NH}_2$ group of the other amino acid.
(ii) Glycosidic linkage refers to $-\text{C}-\text{O}-\text{C}-$ linkage between two sugars formed by loss of H_2O .]
20. Give the sources of vitamin A and E and name the deficiency diseases resulting from lack of vitamin A and E in the diet.
21. What are the main functions of DNA and RNA in human body.

SA(II) TYPE QUESTIONS (3 MARKS)

1. How are carbohydrate classified?
2.
 - (i) Name four bases present in DNA.
 - (ii) Which of them is not present in RNA.
 - (iii) Give the structure of a nucleotide of DNA.
3. Differentiate between the following :
 - (i) Secondary and tertiary structure of protein.
 - (ii) α -Helix and β -pleated sheet structure of protein.
 - (iii) Fibrous and globular proteins.

UNIT 15

POLYMERS

POINTS TO REMEMBER

1. Polymers are defined as high molecular mass macromolecules, which consist of repeating structural units derived from the corresponding monomers.
2. In the presence of an organic peroxide initiator, the alkenes and their derivatives undergo addition polymerisation or chain growth polymerisation through a free radical mechanism. Polythene, teflon, orlon etc. are formed by addition polymerisation of an appropriate alkene or its derivative.
3. Condensation polymerisation reactions are shown by the addition of bi- or poly functional monomers containing -NH_2 , -OH and -COOH groups. This type of polymerisation proceeds through the elimination of certain simple molecules such as H_2O , NH_3 etc.
4. Formaldehyde reacts with phenol and melamine to form the corresponding condensation polymer products. The condensation polymerisation progresses through step by step and is called also step growth polymerisation.
5. Nylon, bakelite and dacron are some of the important examples of condensation polymers.
6. A condensation of two different unsaturated monomers exhibits copolymerisation. A copolymer like Buna-S contains multiple units of 1, 3-Butadiene and styrene.
7. Natural rubber is cis-1, 4-polyisoprene. It can be made more tough by the process of vulcanization with sulphur.
8. Synthetic rubbers like Buna-N are usually obtained by copolymerisation of alkene and 1, 3-Butadiene derivatives.

9. In view of potential environmental hazards of synthetic polymeric wastes certain biodegradable polymers such as PHBV and Nylon-2-Nylon-6 are developed as alternatives.

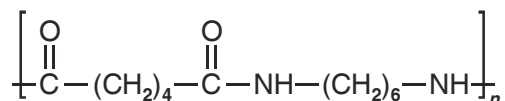
QUESTIONS

VSA TYPE QUESTIONS (1 MARK)

1. Define the term copolymer.
2. Identify homopolymer from the following examples Nylon-66, Nylon-6, Nylon-2-Nylon-6.
3. Give example of a natural polyamide, which is an important constituent of diet.

[Hint : Proteins]

4. Classify polythene and bakelite as thermosetting plastics or thermoplastics.
5. Among fibres, elastomers and thermosetting polymers which one has strongest intermolecular forces of attraction?
6. Why is bakelite called a thermosetting polymer.
7. Give the monomers of bakelite.
8. Identify the monomer in the following polymeric structure.



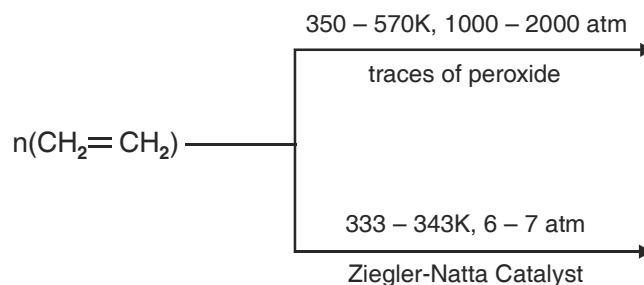
9. Nylon-2-Nylon-6 is a biodegradable polymer obtained from glycine, $\text{H}_2\text{N} - \text{CH}_2 - \text{COOH}$ and amino caproic acid, $\text{H}_2\text{N} - (\text{CH}_2)_5 - \text{COOH}$. Write the structure of this polymer.
10. Give two uses of teflon.
11. Name the polymer used for making insulation material for coating copper wire.

[Hint : PVC].

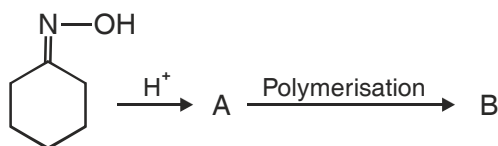
12. Write the name and structure of monomer of the polymer which is used as synthetic wool.
13. How is vulcanized rubber obtained?
14. Name the polymer used for making radio television cabinets and feeding bottles of children.
15. What do the digits 6 and 66 represent in the names nylon-6 and nylon-66?
16. Write the full form of PHBV.
17. Which of the following sets has all polymers capable of repeatedly softening on heating and hardening on cooling.
 - (i) Glyptal, Melamine, PAN.
 - (ii) PVC, Polystyrene, polythene.
 - (iii) Polypropylene, urea formaldehyde resin, teflon.
- *18. Why benzoyl peroxide is used as an initiator for chain growth polymerisation?
[Hint : It easily generates free radicals required for initiation of reaction.]

SA (I) TYPE QUESTIONS (2 MARKS)

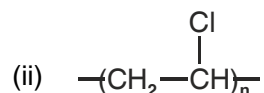
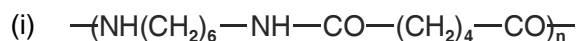
1. Give the structure of monomer of the polymer, neoprene. What is the advantage of neoprene over the natural rubber?
2. Classify the following as homopolymer or copolymer. Also classify them as addition or condensation polymers.
 - (i) $-(\text{NH}-\text{CH}(\text{R})-\text{CO})_n-$
 - (ii) $-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}}-\text{CH}_2)_n-$
3. Give the mechanism of polymerisation of ethene to polythene in presence of benzoyl peroxide.
4. Complete the following reactions :



5. (i) What is the difference between step growth polymer and chain growth polymer?
(ii) Give example of each type.
6. Identify the products A and B in the :



7. How can you differentiate between thermosetting and thermoplastic polymers.
8. Mention the type of intermolecular forces present in nylon-66. What properties do they impart to nylon?
[Hint : Strong intermolecular forces of attraction like Hydrogen bonding. This results in close packing of chains and thus impart crystalline nature to the fibres.]
9. What is the difference between linear chain and branched chain polymers. Explain giving examples.
10. Identify the polymer whose structure are given and mention one of their important use.



11. Arrange the following polymers in the order of increasing intermolecular forces :
- (i) Nylon-6,6, Buna-S, Polythene.
 - (ii) Nylon-6, Neoprene, Polyvinylchloride
12. Write the expanded form and give the structures of monomers for the following polymers:
- (i) PAN
 - (ii) PTFE
13. Novolac is the linear polymer which on heating with formaldehyde forms cross-linked bakelite. Write the structures of monomers and the polymer novolac.
14. Write the structure of following polymers and also give their main use :
- (a) Polystyrene
 - (ii) Melamine formaldehyde resin.
15. Identify the polymers used in the manufacture of paints and lacquers. Write the structure of the polymer and its monomers.
16. Can a copolymer be formed by both addition and condensation polymerisation? Explain with the help of examples.
17. What is the difference between an elastomer and a fibre? Give one example of each.
18. Write the structure of the monomer used in the synthesis of :
- (i) Nylon-6
 - (ii) Nylon-6, 6

SA (II) TYPE QUESTIONS (3 MARKS)

1. Differentiate between the following pairs :
- (i) Branched chain polymers and cross linked polymers.
 - (ii) Thermoplastic and thermosetting polymers.
 - (iii) Chain growth and step growth polymerisation.
2. List two uses each of the following polymers :
- (i) Nylon-2-Nylon-6.

- (ii) Urea-formaldehyde resin
 - (iii) Glyptal
3. (i) What is meant by biodegradable polymers?
- (ii) A biodegradable polymer is used in speciality packaging, orthopaedic devices and in controlled release of drugs. Identify the polymer and give its structure.
4. Polythene finds widespread use to make carry bags and also for manufacturing buckets and pipes.
- (i) Name the different types of polythene used for above mentioned applications.
 - (ii) What is the structural difference between these two types?
 - (iii) Write the method of preparation of high density polythene.

UNIT 16

CHEMISTRY IN EVERY DAY LIFE

POINTS TO REMEMBER

1. A drug is a chemical agent which affects human metabolism and provides cure from ailment. If taken in doses higher than recommended, these may have poisonous effect.
2. Use of chemicals for therapeutic effect is called chemotherapy.
3. Drugs usually interact with biological macromolecules such as carbohydrates, proteins, lipids and nucleic acids. These are called target molecules.
4. Drugs are designed to interact with specific targets so that these have the least chance of affecting other targets. This minimises the side effects and localises the action of the drug.
5. Drugs like analgesics, antibiotics, antiseptics, disinfectants, antacids and tranquilizers have specific pharmacological functions.
6. Antifertility drugs are used to control population. These contain a mixture of synthetic estrogen and progesterone derivatives.
7. Chemicals are added to food for preservation, enhancing their appeal and adding nutritive value in them.
8. Artificial sweetening agents like aspartame, saccharin etc. are of great value to diabetic persons and people who need to control their calories.
9. These days detergents are much in vogue and get preference over soaps because they work even in hard water.
10. Synthetic detergents are classified into three main categories namely anionic, cationic and non-ionic.

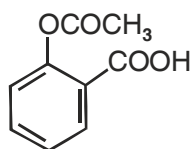
11. Detergents with straight chain of hydrocarbons are preferred over branched chain as the latter are non-biodegradable and consequently cause environmental pollution.
12. The unbranched hydrocarbon side chains of the detergent molecule are prone to attack by bacteria, so the detergents are bio-degradable and pollution is prevented.

QUESTIONS

VSA TYPE QUESTIONS (1 MARK)

1. Write the formula and IUPAC name of Aspirin.

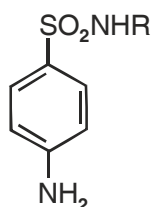
[Hint :



Common name-Aspirin

IUPAC name : 2-Acetoxybenzoic acid.]

2. Name two types of the drugs classified on the basis of pharmacological effect.
3. What is the role of Bithional in toilet soaps?
4. Why is sodium benzoate added to packed containers of jams and pickles?
5. Name the type of drugs having following structural formula :



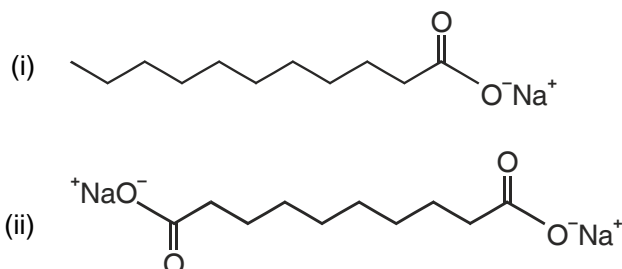
[Hint : Sulpha Drugs].

6. Why the receptors embedded in cell membranes show selectivity for one chemical messenger over the other?

[Hint : The active site of receptor has specific shape and specific functional groups which can bind only specific messenger which fits in.]

7. With reference to which classification has the statement 'ranitidine is an antacid' been given?
[Hint : Classification based on pharmacological effect.]
8. Give the name of medicine used for the treatment of syphilis.
[Hint : Salvarsan].
9. Give the composition of tincture of iodine.
10. How does aspirin act as analgesic?
[Hint : Aspirin inhibits the synthesis of prostaglandins which cause pain.]
11. Name the antiseptic agents present in dettol.
[Hint : Chloroxylenol and Terpineol].
12. What precaution should be taken before administering penicillin to a patient?
[Hint : To confirm, beforehand that the patient is not allergic to penicillin.]
13. Explain why aspirin finds use in prevention of heart attacks?
[Hint : Due to antibloodclotting activity.]
14. Mention one use of drug meprobamate.
[Hint : Antidepressant drug.]
15. Name the derivative of sucrose which tastes like sugar and can be safely used by weight conscious people.
16. Why synthetic detergents are preferred over soaps for use in washing machines?
[Hint : They work well even with hard water and not form any scum.]
- *17. How is acidity cured with cimetidine?
[Hint. : Cimetidine prevents the interaction of histamines with the receptors present in stomach wall.]
- *18. While antacids and antiallergic drugs interfere with the function of histamines, why do these not interfere with the function of each other?
[Hint. : Antacids and antiallergic drugs bind to the different receptor sites. Therefore they do not interfere with the function of each other].

19. Which of the following two compounds can be used as a surface agent and why?



[Hint : Compound (i) acts as a surface agent because its one end is hydrophobic while the other end is hydrophilic in nature.]

20. What type of drug is chloramphenicol?
21. Name a chemical used as an antiseptic as well as disinfectant.
22. Give two examples of antidepressants.

SA (I) TYPE QUESTIONS (2 MARKS)

1. What are antihistamines. Give two examples.
2. What are narcotic and nonnarcotic analgesics? Give one example of each.
3. Explain the following terms as used in medicinal chemistry :
 - (i) Target molecules
 - (ii) Enzyme inhibitors.
4. Give one important use of each of following :
 - (i) Equanil
 - (ii) Morphine
5. What are neurologically active drugs. Give two examples.
6.
 - (i) What are antibiotics?
 - (ii) What is meant by the term broad spectrum antibiotic?
7. From the given examples ciprofloxacin, phenelzine, morphine, ranitidine. Choose the drug used for
 - (i) treating allergic conditions
 - (ii) to get relief from pain

8. Why a drug should not be taken without consulting a doctor? Give two reasons.
9. State the main difference between bacteriostatic and bacteriocidal antibiotics. Give one example of each.
10. What are antifertility drugs? Name the constituents of an oral contraceptive.
11. What do you mean by nonbiodegradable detergents? How can we make biodegradable detergents?
- *12. If water contains dissolved calcium hydrogencarbonate, which out of soap and detergent will you prefer to use? Why?
 [Hint : We will use detergent because it will not form insoluble scum with Ca^{2+}]
- *13. What are sulpha drugs? What is their use? Give one example.
- *14. What are barbiturates? What is the action of barbiturates on human body?
 [Hint : Barbituric acid derivatives are called barbiturates. They are highly effective pain relieving agents.]
- *15. Write the structures of soaps obtained by the hydrolysis of following fats:
 - (i) $(\text{C}_{15}\text{H}_{31}\text{COO})_3\text{C}_3\text{H}_5$ – Glycerol palmitate
 - (ii) $(\text{C}_{17}\text{H}_{33}\text{COO})_3\text{C}_3\text{H}_5$ – Glycerol oleate.
 [Hint : (i) $\text{C}_{15}\text{H}_{31}\text{COO}^-\text{Na}^+$ (ii) $\text{C}_{17}\text{H}_{33}\text{COO}^-\text{Na}^+$]

SA (II) TYPE QUESTIONS (3 MARKS)

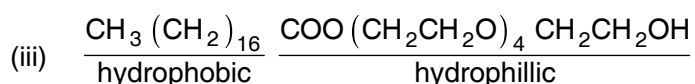
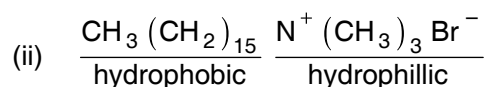
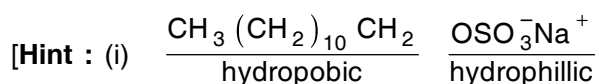
1.
 - (i) Why are artificial sweetening agents harmless when taken?
 - (ii) Name one such artificial sweetening agent.
 - (iii) Why is the use of aspartame as an artificial sweetener limited to cold foods?
2. Pick out the odd one amongst the following on the basis of their medicinal properties. Give suitable reason.
 - (i) Luminal, seconal, terfenadine, equanil.

- (ii) Chloroxylenol, phenol, chloramphenicol, bithional.
 - (iii) Sucralose, aspartame, alitame, sodium benzoate.
- [Hint : (i) Terfenadine is antihistamine other three are used as tranquilisers.
(ii) Chloramphenicol is a broad spectrum antibiotic. Other three have antiseptic properties.
(iii) Sodium benzoate is a preservative. Other three are artificial sweetners.]
3. Give the main function of following in the body of human beings.
 - (i) Enzymes
 - (ii) Receptor proteins
 - (iii) Neurotransmitter
 4. Identify the class of drug :
 - (i) Phenelzine (Nardin)
 - (ii) Aspirin
 - (iii) Cimetidine
 5. Give the pharmacological function of the following type of drugs:
 - (i) Analgesics
 - (ii) Tranquilizers
 - (iii) Antifertility drugs
 6. Give the name of medicine used in the treatments of following diseases:
 - (i) Typhoid
 - (ii) Joint pain (in Arthritis)
 - (iii) Hypertension
 7. Give the class of drugs to which these substances belong :
 - (i) Bithional
 - (ii) Amoxycillin
 - (iii) Salvarsan

8. How are antiseptics different from disinfectants? How does an antibiotic differ from these two? Give one example of each of them.
9. Explain the following terms with suitable examples :
- Cationic detergents
 - Anionic detergents
 - Nonionic detergents

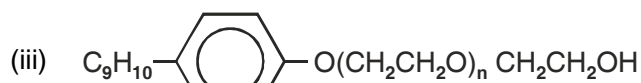
*10. Label hydrophilic and hydrophobic part in the following compounds :

- $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3^- \text{Na}^+$
- $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3 \text{Br}^-$
- $\text{CH}_3(\text{CH}_2)_{16}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n \text{CH}_2\text{CH}_2\text{OH}$



*11. Classify the following as cationic detergents, anionic detergents or nonionic detergents:

- $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3^- \text{Na}^+$
- $[\text{CH}_3 - (\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]^+ \text{Br}^-$



Where $(n = 5 - 10)$

- [Hint : (i) Anionic detergent. (ii) Cationic detergent.
(iii) Nonionic detergent.

12. Explain the term hyperacidity. Discuss two types of medicines used to check hyperacidity and their mode of action.
- *13. How do enzyme inhibitors work? Distinguish between competitive and non-competitive enzyme inhibitors.

[Hint : An enzyme inhibitor either blocks the active site of enzyme or changes the shape of the active site by binding at an allosteric site. They are of two types.

- (i) Competitive enzyme inhibitor – It competes with natural substance for their attachment on the active sites of enzymes.
- (ii) Noncompetitive enzyme inhibitor binds at allosteric site and changes the shape of the active site in such a way that the substrate can not recognise it.]

MODEL TEST PAPER – I (Solved)

(FOR SR. SCHOOL CERTIFICATE EXAMINATION - 2012)

CHEMISTRY (THEORY)

Time : 3 hours

Total Marks : 70

General Instruction

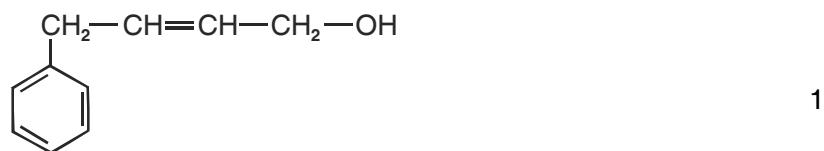
- (i) All questions are compulsory.
- (ii) Question number 1 to 8 are very short answer questions, carrying 1 mark each. Answer these in one word or about one sentence each.
- (iii) Question number 9 to 18 are short answer questions, carrying 2 marks each. Answer these in about 30 words each.
- (iv) Question number 19 to 27 are short answer questions, carrying 3 marks each. Answer these in about 40 words each.
- (v) Question number 28 to 30 are long answer questions, carrying 5 marks each. Answer these in about 70 words each.
- (vi) Use log table, if necessary.
- (vii) Use of calculator is not permitted.

1. Name the non-stoichiometric point defect responsible for colour in alkali metal halides. 1

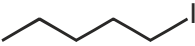
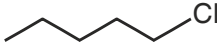
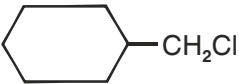
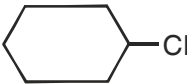
2. Write the IUPAC name of coordination isomer of the compound



3. Write IUPAC name of the following compound

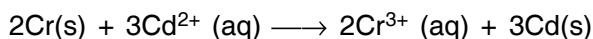


4. Chloroacetic acid has lower pKa value than acetic acid. 1

5. Write the structural formula of N, N-Dimethylethanamine. 1
6. What happens when D-glucose is treated with the following reagents? 1
- HI
 - Bromine water
7. How does vulcanisation change the character of natural rubber? 1
8. Differentiate between antagonists and agonists. 1
9. Explain the following terms with suitable examples :-
- Non-ionic detergents
 - Tranquilizers 2
10. Write the names and structures of the monomers used for getting the following polymers.
- PAN
 - Nylon-6 2
11. Which one in the following pairs undergoes S_N2 reaction faster and why?
-  or 
 -  or  2
12. Give suitable reasons for the following :
- Alkyl halides give cyanides with KCN but isocyanide with AgCN.
 - The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride. 2
13. Compare the following complexes with respect to shape and magnetic behaviour
- $[\text{Ni}(\text{CN})_4]^{2-}$
 - $[\text{NiCl}_4]^{2-}$ 2

14. Compare the chemistry of actinoids with that of lanthanoids with special reference to
- (a) Oxidation state
 - (b) chemical reactivity
- 2
15. Explain the following terms with a suitable example in each case
- (a) Shape selective catalysts
 - (b) electroosmosis
- Or**
15. Write the difference between
- (a) Physisorption and Chemisorption
 - (b) Catalyst and enzyme
- 2
16. What type of cell is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery while operating or in use.
- 2
17. Account for the following –
- (a) The vapour pressure of a solution of glucose in water is lower than that of pure water.
 - (b) Mixture of phenol and aniline shows (-)ve deviation from Raoult's law.
18. Write chemical equations for the preparation of sols :
- (a) Gold sol by reduction
 - (b) hydrated ferric oxide sol by hydrolysis
- 2
19. An element has a bcc structure with a cell edge of 288 pm. The density of the metal is 7.2 g cm^{-3} . How many atoms and unit cells are there in 208 g of the element.
- 3
20. At 300K, two solutions of glucose in water with concentration 0.01M and 0.001 M are separated by semipermeable membrane. On what solution pressure need to be applied to prevent osmosis? Also calculate magnitude of this applied pressure. [$R = 0.82 \text{ L atm mol}^{-1} \text{ K}^{-1}$]
- 3

21. Calculate the standard cell potential of the galvanic cell in which the following reaction take place :



Also calculate $\Delta_r G^\circ$ value for the reaction.

[Given $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74\text{V}$, $E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.4\text{V}$

$F = 96500\text{C mol}^{-1}$. 3

22. State briefly the principles which serve as basis for the following operations in metallurgy :

- (a) Zone refining
- (b) Vapour phase refining
- (c) Froth floatation process 3

Or

22. Describe the role of the following :

- (a) Depressant in froth floatation process
- (b) Cryolite in the metallurgy of aluminium
- (c) Silica in the extraction of copper from copper pyrites ore. 3

23. Arrange the following in the order of property indicated for each set :

- (a) NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3 (Decreasing basic strength)
- (b) F_2 , Cl_2 , Br_2 , I_2 (Increasing bond dissociation enthalpy)
- (c) H_2O , H_2S , H_2Se , H_2Te (Increasing bond angle) 3

24. Assign reason for the following :

- (i) The enthalpies of atomisation of transition elements are high.
- (ii) The metallic radii of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second series.

- (iii) With the same d-orbital configuration $[d^4]$ Cr^{2+} ion is a reducing agent but Mn^{3+} ion is an oxidising agent. 3

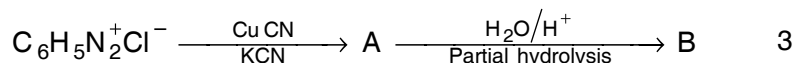
25. How will you convert :

- (i) Phenol to ethoxy benzene
(ii) butan-2-one to but-2-ene
(iii) 1-Propoxypropane to propyl alcohol 3

26. (a) Explain with suitable reasons :

- (i) Gabriel phthalimide synthesis is not used for the synthesis of aniline.
(ii) Although amino group is o, p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

(b) Identify the A and B in the following reactions :



27. (a) How are vitamins classified? Mention the deficiency diseases caused by lack of vitamin A and K.
(b) Write the Zwitter ionic form of amino acids. 3
28. (a) List two main differences between order and molecularity of a reaction.
(b) A certain reaction is 50% complete in 20 minutes at 300K and the same reaction is again 50% complete in 5 minutes at 350K. Calculate the activation energy if it is a first order reaction ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; $\log 4 = 0.6020$) 5

Or

28. (a) Justify the statement that for a first order reaction half-life period ($t_{1/2}$) is independent of the initial concentration of the reactant.
(b) For a chemical reaction at 800°C ,
 $2\text{NO} + 2\text{H}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$ the following data were obtained.

$[\text{NO}] \times 10^{-4} \text{ mol L}^{-1}$	$[\text{H}_2] \times 10^{-3} \text{ mol L}^{-1}$	Initial rate ($\text{mol L}^{-1} \text{ s}^{-1}$)
1.5	4.0	4.4×10^{-4}
1.5	2.0	2.2×10^{-4}
0.5	2.0	0.24×10^{-4}

What is the order of reaction w.r.t. NO and H₂? Also calculate the rate constant at 800°C. 5

29. (a) Assign reasons for the following :
- H₃PO₂ and H₃PO₃ act as good reducing agents while H₃PO₄ does not.
 - ICl is more reactive than I₂.
 - H₂S is less acidic than H₂Te.
- (b) Draw the structure of
- XeOF₄
 - H₂S₂O₇

5

Or

29. (a) Complete the following chemical equations
- $\text{P}_4(\text{s}) + \text{NaOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow$
 - $\text{I}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{O}_3(\text{g}) \longrightarrow$
- (b) Assign a reason for each of following :
- Bi(V) is a stronger oxidising agent than Sb(V).
 - Fluorine does not exhibit any positive oxidation state.
 - In solution of H₂SO₄ in water, the second dissociation constant K_{a2} is less than the first dissociation constant K_{a1}.

5

30. (a) Describe the following reactions
- Cannizzaro reaction
 - Cross Aldol condensation

(b) Give chemical tests to distinguish between :

(i) Phenol and benzoic acid

(ii) Acetophenone and benzophenone

(c) Arrange the following in increasing order of acid strengths :

$(\text{CH}_3)_2\text{CHCOOH}$, $\text{CH}_2\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$

5

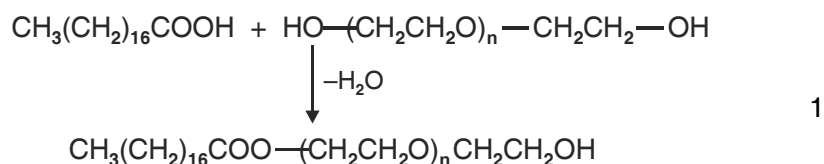
Or

30. An organic compound (A) $\text{C}_5\text{H}_{10}\text{O}$ gives positive 2, 4-DNP Test. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite. On reaction with iodine in presence of sodium hydroxide, yellow precipitate B and another compound C is formed. On oxidation with KMnO_4 it forms two acids D and E. Identify A, B, C, D and E.

MARKING SCHEME

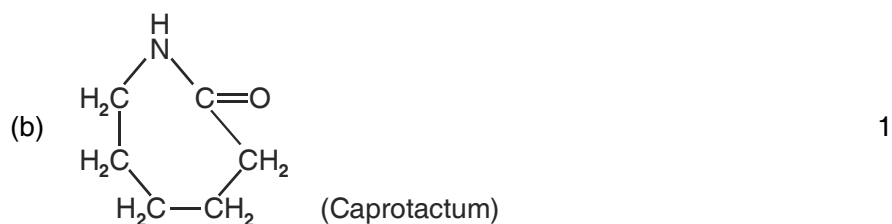
Q. No.	Value Points	Marks
1.	F-Center or Metal excess defect	1
2.	$[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$ Hexaamminechromium (III) –hexacyanocobaltate (III)	1
3.	$\begin{array}{c} \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{OH} \\ \\ \text{C}_6\text{H}_5 \end{array}$ 4-Phenylbut-2-en-ol	1
4.	Chloroacetic acid is stronger acid than acetic acid due to –I effect of chlorine atom. Therefore, it has lower $\text{p}K_a$ value.	1
5.	$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{N} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	1
6.	$\begin{array}{c} \text{CHO} \\ \\ (\text{CHOH})_4 \\ \\ \text{CH}_2\text{OH} \end{array} \xrightarrow{\text{HI}/\Delta} \text{C}_6\text{H}_{14} \text{ (hexane)}$	1/2
	$\begin{array}{c} \text{CHO} \\ \\ (\text{CHOH})_4 \\ \\ \text{CH}_2\text{OH} \end{array} \xrightarrow{\text{Br}_2 \text{ water}} \begin{array}{c} \text{COOH} \\ \\ (\text{CHOH})_4 \\ \\ \text{CH}_2\text{OH} \end{array}$ Gluconic acid	1/2
7.	In vulcanisation, sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened.	1
8.	Drugs that bind to the receptor site and inhibit its natural function are called antagonists. Drugs that mimic the natural messenger by switching on receptor, are called agonists.	1

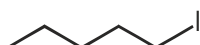
9. (a) Non-ionic detergents do not contain any ion in their constitution. One such detergent is formed when stearic acid reacts with polyethylene glycol. 1

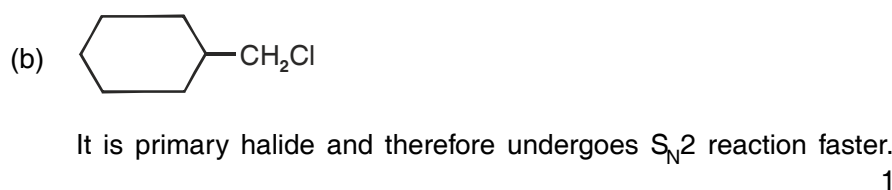


- (b) Tranquilizers are a class of chemical compounds used for the treatment of stress, and mild or even severe mental diseases e.g., chlordiazepoxide and meprobamate. 1

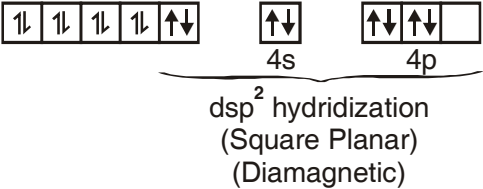
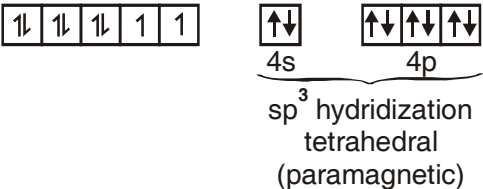
10. (a) $\text{CH}_2=\text{CH}-\text{CN}$ 1
(Acrylonitrile)



11. (a)  1
- As iodine is a better leaving group because of its large size, It will be released at a faster rate in the presence of incoming nucleophile. 1



12. (a) KCN is ionic compound and produces CN^- , so it combines with RX and gives cyanides as major product because of higher bond enthalpy of $\text{C}-\text{C}$ bond than that of $\text{C}-\text{N}$ bond, while with AgCN it gives isocyanide due to covalent nature of $\text{Ag}-\text{C}$ bond by attacking through N atom. 1

- (b) In chlorobenzene carbon is sp^2 hybridised while in cyclohexane it is sp^3 hybridised. Due to the more electronegativity difference in cyclohexyl chloride its dipole moment is higher than that of chlorobenzene. 1
13. (a) $[\text{Ni}(\text{CN})_4]^{2-}$
 $\text{Ni}_{28} [\text{Ar}]^{18} 4s^2 3d^8$
 $\text{Ni(II)} [\text{Ar}]^{18} 3d^8$
- 
- dsp² hybridization
(Square Planar)
(Diamagnetic) 1
- (b) $[\text{NiCl}_4]^{2-}$
 $\text{Ni}_{28} [\text{Ar}]^{18} 4s^2 3d^8$
 $\text{Ni (II)} [\text{Ar}]^{18} 3d^8$
- 
- sp³ hybridization
tetrahedral
(paramagnetic) 1
14. (a) All the lanthanoids exhibit a common stable oxidation state of +3. In addition some lanthanoids also show oxidation states of +2 and +4 where L_n^{2+} and L_n^{4+} have more stable $4f^0$, $4f^7$ or $4f^{14}$ configuration. Members of the actinoids family exhibit more variable oxidation states as compared to the elements belonging to lanthanoids. 1
- (b) Actinoids are more reactive than lanthanoids due to bigger size. 1
15. (a) Zeolites are known as shape selective catalysts, because their activity depends on pore size and shape of reactant molecules. 1

- (b) Electroosmosis : When the movement of colloidal particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is called electroosmosis. 1

Or

15. (a) Physisorption have weak Van der Waal attraction forces while in chemisorption there are stronger chemical bonds [40 kJ to 200 kJ/mol.] 1
- (b) Almost all the enzymes are globular proteins and used as biochemical catalyst while catalysts are chemical substance used for increasing the rate of chemical reactions. 1
16. (a) Lead storage battery is a secondary battery. ½
- Anode : $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \longrightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$ ½
- Cathode : $\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{PbSO}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l})$ ½
- Overall reaction :
- $\text{Pb(s)} + \text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq}) \longrightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$ ½
17. (a) Vapour pressure of pure water gets decreased by addition of non-volatile glucose, which covers some surface area and lesser surface area is available for vapourisation, of water molecules. 1
- (b) In this case the intermolecular hydrogen bonding between phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bonding between similar molecules. 1
18. (a) $2 \text{AuCl}_3 + 3\text{SnCl}_2 \longrightarrow 3\text{SnCl}_4 + 2\text{Au}$ (Gold sol). 1
- (b) $\text{FeCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O} + 3\text{HCl}$ 1
sol
19. Volume of the unit cell = $(288 \times 10^{-10} \text{ cm})^3$
= $2.39 \times 10^{-23} \text{ cm}^3$

$$\text{Volume of 208 g of the element} = \frac{\text{Mass}}{\text{Density}} = \frac{208\text{g}}{7.2\text{g cm}^{-3}} \quad 1$$

$$= 28.88 \text{ cm}^3$$

$$\text{No. of unit cells} = \frac{28.88 \text{ cm}^3}{2.39 \times 10^{-23} \text{ cm}^3 / \text{unit cell}} \quad 1$$

$$= 12.08 \times 10^{23} \text{ unit cells}$$

Since the unit cell is bcc therefore, number of atoms per unit cell is 2

$$\text{Total number of atoms in 208 of element} = 2 \times 12.08 \times 10^{23} \quad 1$$

$$= 24.16 \times 10^{23}$$

20. (a) For 0.01 M solution

$$\pi_1 = C_1 RT$$

$$\pi_1 = 0.01 \times 0.0821 \times 300 = 0.2463 \text{ atm.} \quad 1$$

For 0.001 M solution.

$$\pi_2 = 0.001 \times 0.0821 \times 300$$

$$= 0.02463 \text{ atm.} \quad \frac{1}{2}$$

(b) The solvent particles pass from dilute to concentrate solution, i.e., from 0.001M to 0.01 M solution. Therefore, pressure should be applied on 0.01m solution to prevent osmosis. $\frac{1}{2}$

(c) The magnitude of pressure applied = 0.2463 – 0.0246 = 0.2217 atm. 1

21. $\text{Cr} | \text{Cr}^{3+} || \text{Cd}^{2+} | \text{Cd}$

$$E^\circ_{\text{cell}} = E^\circ_{\text{R}} - E^\circ_{\text{L}}$$

$$= -0.4\text{V} - (-0.74\text{V}) = 0.34 \text{ V} \quad 1$$

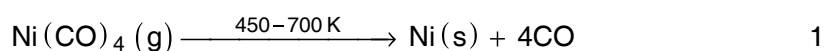
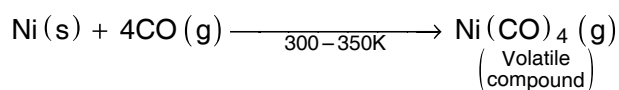
$$\therefore \Delta G^\circ = -nF E^\circ_{\text{cell}}$$

$$\Delta G^\circ = -6 \times 96500 \text{ C mol}^{-1} \times 0.34 \text{ V} = -6 \times 96500 \times 0.34 \text{ CV mol}^{-1} \quad 1$$

$$\Delta G^\circ = -196860 \text{ J mol}^{-1}$$

$$\Delta G^\circ = -196.86 \text{ kJ mol}^{-1} \quad 1$$

22. (a) **Zone Refining** : Impure metal rod is heated with circular heater from one end. The metal melts and on cooling the pure metal gets solidified while impurities go into the molten zone. 1
- (b) **Vapour Phase Refining** : The metal is converted to a volatile compound which on further heating breaks down to give pure metal.



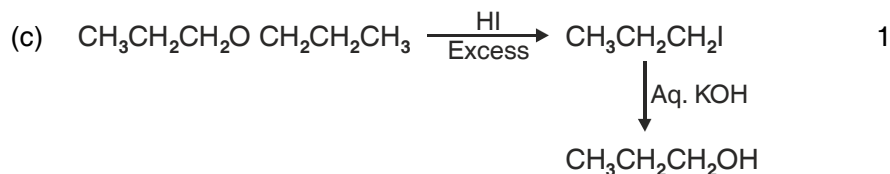
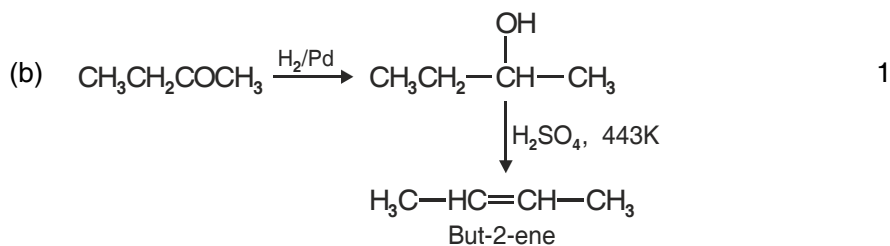
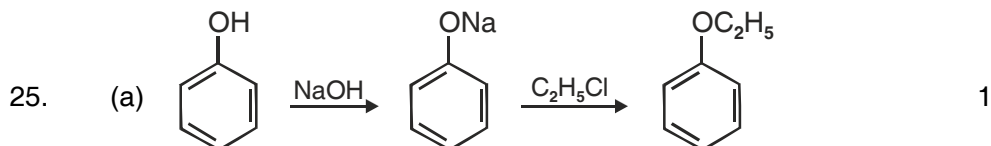
- (c) **Froth Floatation Process** : In this process sulphide ore particles are wetted with oil and rise to the surface along with the froth and are separated. The earthy matter wetted by water settles down at the bottom. 1

Or

22. (a) Depressant prevents the formation of froth of one ore in a mixture of two sulphide ores. 1
- (b) Cryolite is added to lower the melting point of the mix and brings conductivity. 1
- (c) Silica is used for removal of FeO as slag, FeSiO₃ in the metallurgy of copper. 1
23. Arrangement of the following compound in the order of property indicated for each set.
- (a) NH₃ > PH₃ > AsH₃ > SbH₃ > BiH₃ [Decreasing basic strength] 1
- (b) I₂ < F₂ < Br₂ < Cl₂ [Increasing bond dissociation enthalpy] 1
- (c) H₂Te < H₂Se < H₂S < H₂O [Increasing bond angle] 1
24. (a) Strong M–M interactions due to participation both ns and (n – 1) d electrons, the enthalpies of atomisation of transition elements are high. 1
- (b) Due to lanthanoid contraction the sizes of 5d series do not increase and remain almost the same as corresponding members of 4d series. 1

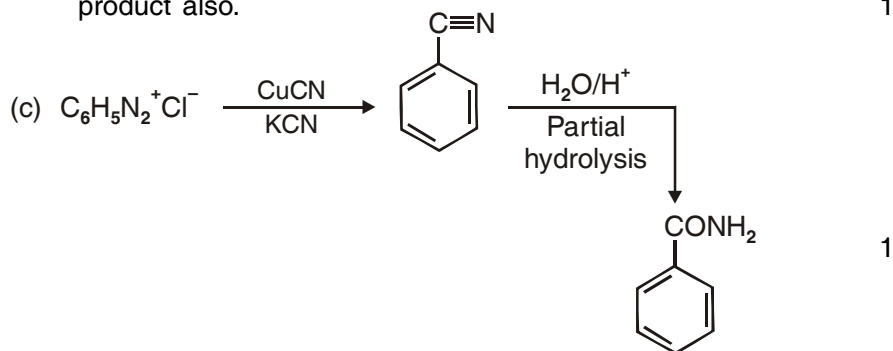
(c) Cr^{2+} is reducing agent because $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}}$ is negative. This is because of stable

t_{2g}^3 configuration of Cr^{3+} ion. On the other hand $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}}$ is positive due to extra stability of Mn^{2+} which has $[\text{Ar}] 3d^5$ configuration. 1

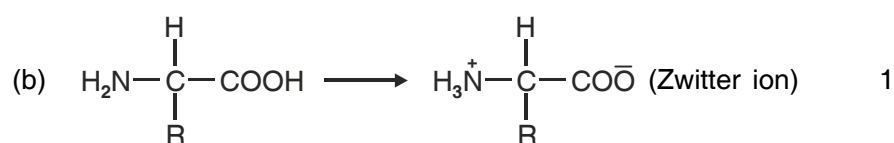


26. (a) $\text{Ar}-\text{X}$ does not exhibit nucleophilic substitution reaction readily due to partial double bond character of $\text{C}-\text{X}$ bond, therefore ArNH_2 cannot be prepared by Gabriel phthalimide process. 1

(b) Amino group is o, p-directing towards electrophilic substitution reaction but due to the formation of anilinium ion $-\text{NH}_3^+$ it gives m-product also. 1



27. (a) Vitamins are broadly classified as water soluble and fat soluble vitamins,
- Water soluble : B, C
- Fat soluble : A, D, E and K 1
- Deficiency disease of vitamin A is Night blindness
- Deficiency disease of Vitamin K is Increasing blood clotting time. $\frac{1}{2} \times 2$



28. (a)

<i>Order of Reaction</i>	<i>Molecularity of Reaction</i>
<ul style="list-style-type: none"> ● Order of reaction corresponds to sum of the exponents to which the concentration terms is raised in rate law expression. ● It may be zero. ● It may be fractional. ● It is experimentally determined. 	<ul style="list-style-type: none"> ● Molecularity corresponds to no. of reacting species in elementary reactions. ● It can never be zero. ● It can never be fractional ● It is a theoretical term. $\frac{1}{2} \times 4$

(b) $k = \frac{0.693}{t_{\frac{1}{2}}} \Rightarrow k_1 = \frac{0.693}{20 \text{ min}} = 0.03465 \text{ min}^{-1} \quad \frac{1}{2}$

$k_2 = \frac{0.693}{5 \text{ min}} = 0.1386 \text{ min}^{-1} \quad \frac{1}{2}$

$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \frac{1}{2}$

$\log \left[\frac{0.1386}{0.03465} \right] = \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{300\text{K}} - \frac{1}{350\text{K}} \right)$

1

$$E_a = 24205.8 \text{ J mol}^{-1} = 24.2 \text{ kJ mol}^{-1}$$

½

Or

28. (a) As per first order integrated rate law

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

Half-life period $t = t_{1/2}$

$$\text{when } [A] = \frac{[A]_0}{2}$$

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

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

It means half life period ($t_{1/2}$) is independent of the initial concentration. 2

(b) According to data using in a hypothetical equation : Rate = $k[\text{NO}]^x [\text{H}_2]^y$

$$\text{Rate}_1 = 4.4 \times 10^{-4} = k [1.5]^x [4.0]^y$$

$$\text{Rate}_2 = 2.2 \times 10^{-4} = k [1.5]^x [2.0]^y$$

$$\text{Rate}_3 = 0.24 \times 10^{-4} = k [0.5]^x [2.0]^y$$

Compare Rate_1 with Rate_2

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{4.4 \times 10^{-4}}{2.2 \times 10^{-4}} = \frac{k [1.5]^x [4.0]^y}{k [1.5]^x [2.0]^y}$$

$$2 = (2)^y$$

$$y = 1$$

Similarly by comparing Rate_2 and Rate_3

$$3^x = 3^2 \Rightarrow x = 2$$

$$\text{Rate} = k [\text{NO}]^2 [\text{H}_2]^1$$

$$0.24 \times 10^{-4} = k[0.5]^2 \times [2.0]^1$$

$$k = 4.88 \times 10^{-8} \text{ mol}^{-2} \text{ litre}^2 \text{ min}^{-1} \quad 1$$

29. (a) (i) H_3PO_4 exhibit +5 oxidation state which is highest oxidation state for phosphorus, so it does not act as a good reducing agent. 1
- (ii) I-Cl bond is weaker than I - I bond because the extent of overlapping is less. 1
- (iii) In H_2Te , H-Te bond is weaker than H-S bond in H_2S . So it is more acidic than H_2S . 1

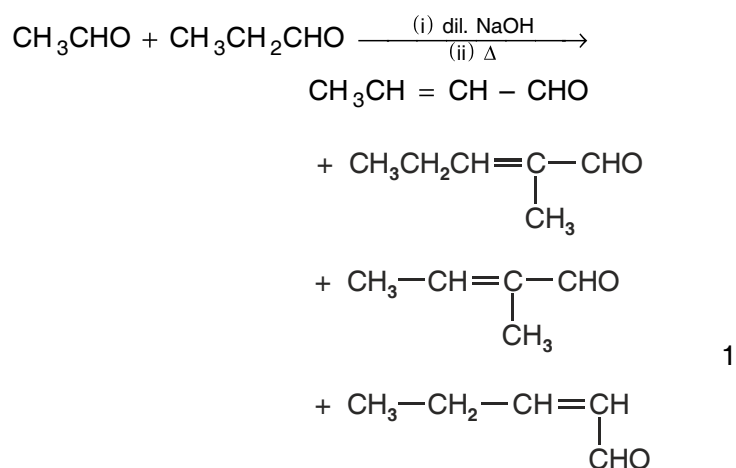


Or

29. (a) (i) $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$ 1
- (ii) $2\text{I}^- (\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{O}_3(\text{g}) \longrightarrow 2\text{OH}^- + \text{I}_2(\text{s}) + \text{O}_2(\text{g})$ 1
- (b) (i) Bi(V) is stronger oxidising agent due to greater magnitude of inert pair effect as compared to Sb(V) because of more diffused 4f orbitals present in bismuth. 1
- (ii) Fluorine always exhibits -1 oxidation state due to its highest electronegativity (4.0) in the periodic table. 1
- (iii) First ionisation of H_2SO_4 to H_3O^+ and HSO_4^- occurs almost completely. The ionisation of HSO_4^- to H_3O^+ and SO_4^{2-} is very difficult because HSO_4^- is an ionic species. That is why $K_{a_2} \ll K_{a_1}$. 1

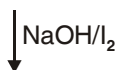
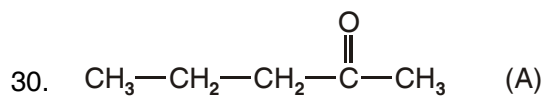
30. (a) (i) Cannizzaro reaction
 $\text{HCHO} + \text{HCHO} + \text{conc. KOH} \rightarrow \text{CH}_3\text{OH} + \text{HCOOK}$ 1

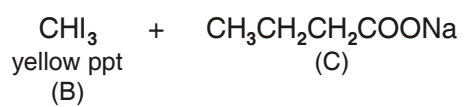
(ii) Cross Aldol Condensation



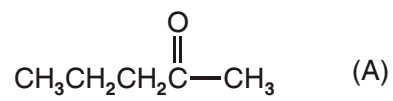
(b)	(i)	<i>Phenol</i>	<i>Benzoic acid</i>	
	(i)	It does not react with NaHCO_3 solution	It gives brisk effervescence of CO_2 gas.	1
	(ii)	<i>Acetophenone</i>	<i>Benzophenone</i>	
		Add NaOH and I_2 → yellow coloured ppt. of CHI_3 is formed.	Add NaOH and I_2 → No ppt. is formed	1
(c)		Increasing order of acid strengths. $(\text{CH}_3)_2\text{CHCOOH} < \text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH} < \text{CH}_3\text{CH}_2\underset{\text{Br}}{\text{CH}} - \text{COOH}$		1

Or

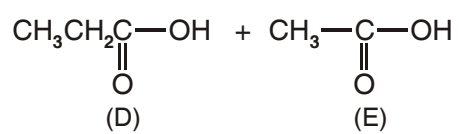




1



↓ oxidation



2

MODEL TEST PAPER – II

CHEMISTRY (THEORY)

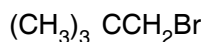
Time : 3 hours

Maximum Marks : 70

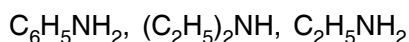
General Instructions :

- (i) All questions are compulsory.
- (ii) Marks for each question are indicated against it.
- (iii) Question number 1 to 8 are very short-answer questions and carry 1 mark each.
- (iv) Question number 9 to 18 are short-answer questions and carry 2 marks each.
- (v) Question number 19 to 27 are also short-answer questions and carry 3 marks each.
- (vi) Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
- (vii) Use Log Tables, if necessary. Use of calculators is not allowed.

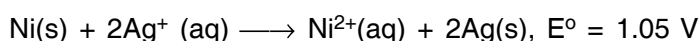
1. 'Crystalline solids are anisotropic in nature.' What does this statement mean?
2. Express the relation between conductivity and molar conductivity of a solution held in a cell.
3. Define 'electrophoresis.'
4. Draw the structure of XeF_2 molecule.
5. Write the IUPAC name of the following compound :



6. Draw the structure of 3-methylbutanal.
7. Arrange the following compounds in an increasing order of their solubility in water :



8. What are biodegradable polymers?
9. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere.
10. Determine the values of equilibrium constant (K_C) and ΔG° for the following reaction :



$$(1F = 96500 \text{ C mol}^{-1})$$

11. Distinguish between 'rate expression' and 'rate constant' of a reaction.
12. State reasons for each of the following :
- The N – O bond in NO_2^- is shorter than the N – O bond in NO_3^- .
 - SF_6 is kinetically an inert substance.

OR

State reasons for each of the following :

- All the P-Cl bonds in PCl_5 molecule are not equivalent.
 - Sulphur has greater tendency for catenation than oxygen.
13. Assign reasons for the following :
- Copper (I) ion is not known in aqueous solution.
 - Actinoids exhibit greater range of oxidation states than lanthanoids.
14. Explain the following giving one example for each :
- Reimer-Tiemann reaction
 - Friedel Craft's acetylation of anisole.
15. How would you obtain
- Picric acid (2, 4, 6-trinitrophenol) from phenol,
 - 2-Methylpropene from 2-methylpropanol?
16. What is essentially the difference between α -form of glucose and β -form of glucose? Explain.

17. Describe what you understand by primary structure and secondary structure of proteins.
18. Mention two important uses of each of the following :
- Bakelite
 - Nylon 6
19. Silver crystallizes in face-centered cubic unit cell. Each side of this unit cell has a length of 400 pm. Calculate the radius of the silver atom. (Assume the atoms just touch each other on the diagonal across the face of the unit cell. That is each face atom is touching the four corner atoms.)
20. Nitrogen pentoxide decomposes according to equation : $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$.

This first order reaction was allowed to proceed at 40 °C and the data below were collected :

$[\text{N}_2\text{O}_5]$ (M)	Time (min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

- Calculate the rate constant. Include units with your answer.
 - What will be the concentration of N_2O_5 after 100 minutes?
 - Calculate the initial rate of reaction.
21. Explain how the phenomenon of adsorption finds application in each of the following processes:
- Production of vaccum
 - Heterogeneous catalysis
 - Froth Floatation process

OR

Define each of the following terms :

- Micelles

- (ii) Peptization
- (iii) Desorption
22. Describe the principle behind each of the following processes :
- Vapour phase refining of a metal.
 - Electrolytic refining of a metal.
 - Recovery of silver ore was leached with NaCN.
23. Complete the following chemical equations :
- $\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \longrightarrow$
 - $\text{KMnO}_4 \xrightarrow{\text{heated}}$
 - $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{S} + \text{H}^+ \longrightarrow$
24. Write the name, stereochemistry and magnetic behaviour of the following:
(At.nos. Mn = 25, Co = 27, Ni = 28)
- $\text{K}_4 [\text{Mn}(\text{CN})_6]$
 - $[\text{Co}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_2$
 - $\text{K}_2 [\text{Ni}(\text{CN})_4]$
25. Answer the following :
- Haloalkanes easily dissolve in organic solvents, why?
 - What is known as a racemic mixture? Give an example.
 - Of the two bromoderivatives, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$ and $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$, which one is more reactive in $\text{S}_{\text{N}}1$ substitution reaction and why?
26. (a) Explain why an alkylamine is more basic than ammonia.
(b) How would you convert
- Aniline to nitrobenzene
 - Aniline to iodobenzene?
27. Describe the following giving one example for each :
- Detergents

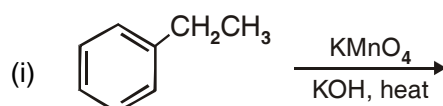
- (ii) Food preservatives
 - (iii) Antacids
28. (a) Differentiate between molarity and molality for a solution. How does a change in temperature influence their values?
- (b) Calculate the freezing point of an aqueous solution containing 10.50 g of MgBr_2 in 200 g of water. (Molar mass of $\text{MgBr}_2 = 184 \text{ g}$).
 K_f for water = $1.86 \text{ K kg mol}^{-1}$)

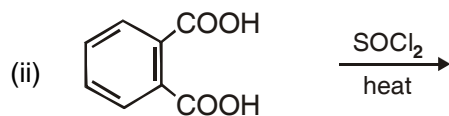
OR

- (a) Define the terms osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property? Explain.
- (b) Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250.0 g of water. (K_b for water = $0.512 \text{ K kg mol}^{-1}$,
 Molar mass of $\text{NaCl} = 58.44 \text{ g}$)
29. (a) Given chemical tests to distinguish between
- (i) Propanal and propanone,
 - (ii) Benzaldehyde and acetophenone.
- (b) How would you obtain
- (i) But-2-enal from ethanal,
 - (ii) Butanoic acid from butanol,
 - (iii) Benzoic acid from ethylbenzene?

OR

- (a) Describe the following giving linked chemical equations :
- (i) Cannizzaro reaction
 - (ii) Decarboxylation
- (b) Complete the following chemical equation :



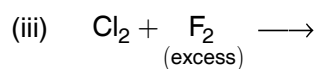
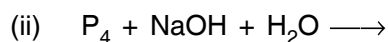


30. (a) Explain the following :

(i) NF_3 is an exothermic compound whereas NCl_3 is not.

(ii) F_2 is most reactive of all the four common halogens.

(b) Complete the following chemical equations :



OR

(a) Account for the following :

(i) The acidic strength decreases in the order $\text{HCl} > \text{H}_2\text{S} > \text{PH}_3$

(ii) Tendency to form pentahalides decreases down the group in group 15 of the periodic table.

(b) Complete the following chemical equations :

