

CHEMISTRY

PAPER – 1

(THEORY)

(Maximum Marks: 70)

(Time allowed: Three hours)

(Candidates are allowed additional 15 minutes for **only** reading the paper.
They must NOT start writing during this time.)

Answer all questions in Part I and six questions from Part II, choosing two questions from Section A, two from Section B and two from Section C.

All working, including rough work, should be done on the same sheet as, and adjacent to, the rest of the answer.

The intended marks for questions or parts of questions are given in brackets [].

Balanced equations must be given wherever possible and diagrams where they are helpful.

When solving numerical problems, all essential working must be shown.

In working out problems use the following data:

Gas constant $R = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1} = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$

$1 \text{ l atm} = 1 \text{ dm}^3 \text{ atm} = 101.3 \text{ J}$. $1 \text{ Faraday} = 96500 \text{ Coulombs}$.

Avogadro's number = 6.023×10^{23} .

PART I (20 Marks)

Answer all questions.

Question 1

(a) Fill in the blanks by choosing the appropriate word/words from those given in the brackets: [5]

(iodoform, acetaldehyde, positive, greater, acidic, acetone, disaccharide, negative, increases, glucose, decreases, chloroform, polysaccharide, lactose, lesser, basic, cationic hydrolysis, anionic hydrolysis)

- (i) Calcium acetate on heating gives _____ which gives _____ on heating with iodine and sodium hydroxide solution.
- (ii) On dilution of a solution, its specific conductance _____ while its equivalent conductance _____.
- (iii) Sucrose is a _____ and yields upon hydrolysis, a mixture of _____ and fructose.
- (iv) More _____ the standard reduction potential of a substance, the _____ is its ability to displace hydrogen from acids.
- (v) An aqueous solution of CH_3COONa is _____ due to _____.

This Paper consists of 7 printed pages and 1 blank page.

- (b) Complete the following statements by selecting the correct alternative from the choices given: [5]
- (i) In a face centered cubic lattice, atom (A) occupies the corner positions and atom (B) occupies the face centre positions. If one atom of (B) is missing from one of the face centered points, the formula of the compound is:
- (1) A_2B_5
 - (2) A_2B_3
 - (3) AB_2
 - (4) A_2B
- (ii) The half life period of a first order reaction is 20 minutes. The time required for the concentration of the reactant to change from 0.16 M to 0.02M is:
- (1) 80 minutes
 - (2) 60 minutes
 - (3) 40 minutes
 - (4) 20 minutes
- (iii) For a spontaneous reaction ΔG° and E° cell will be respectively:
- (1) -ve and +ve
 - (2) +ve and -ve
 - (3) +ve and +ve
 - (4) -ve and -ve
- (iv) The conjugate acid of HPO_4^{2-} is:
- (1) H_3PO_3
 - (2) H_3PO_4
 - (3) $H_2PO_4^-$
 - (4) PO_4^{3-}
- (v) The polymer formed by the condensation of hexamethylenediamine and adipic acid is:
- (1) Teflon
 - (2) Bakelite
 - (3) Dacron
 - (4) Nylon-66

(c) Answer the following questions:

[5]

- (i) Why the freezing point depression (ΔT_f) of 0.4M NaCl solution is nearly twice than that of 0.4M glucose solution?
- (ii) Identify the order of reaction from each of the following units of rate constant (k):
- (a) $\text{mol L}^{-1} \text{sec}^{-1}$
- (b) $\text{mol}^{-1} \text{L sec}^{-1}$
- (iii) Specific conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1} . Calculate its molar conductivity.
- (iv) Name the order of reaction which proceeds with a uniform rate throughout.
- (v) What are the products formed when phenol and nitrobenzene are treated separately with a mixture of concentrated sulphuric acid and concentrated nitric acid?

(d) Match the following:

[5]

- | | |
|------------------------------|------------------------------|
| (i) Diazotisation | (a) Bakelite |
| (ii) Argentite | (b) Nernst equation |
| (iii) Thermosetting plastics | (c) Aniline |
| (iv) Electrochemical cell | (d) Ethylenediamine |
| (v) Bidentate ligand | (e) Froth floatation process |

PART II (50 Marks)

SECTION A

Answer any two questions.

Question 2

- (a) (i) Determine the freezing point of a solution containing 0.625 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) dissolved in 102.8 g of water. [2]
(Freezing point of water = 273 K, K_f for water = $1.87 \text{ K kg mol}^{-1}$, at. wt. C = 12, H = 1, O = 16)
- (ii) A 0.15 M aqueous solution of KCl exerts an osmotic pressure of 6.8 atm at 310 K. Calculate the degree of dissociation of KCl. ($R = 0.0821 \text{ Lit. atm K}^{-1} \text{ mol}^{-1}$). [2]
- (iii) A solution containing 8.44 g of sucrose in 100 g of water has a vapour pressure 4.56 mm of Hg at 273K. If the vapour pressure of pure water is 4.58 mm of Hg at the same temperature, calculate the molecular weight of sucrose. [1]

- (b) (i) When ammonium chloride and ammonium hydroxide are added to a solution containing both Al^{3+} and Ca^{2+} ions, which ion is precipitated first and why? [2]
- (ii) A solution of potassium chloride has no effect on litmus whereas, a solution of zinc chloride turns the blue litmus red. Give a reason. [2]
- (c) How many sodium ions and chloride ions are present in a unit cell of sodium chloride crystal? [1]

Question 3

- (a) (i) Lead sulphide has face centered cubic crystal structure. If the edge length of the unit cell of lead sulphide is 495 pm, calculate the density of the crystal. (at. wt. Pb = 207, S = 32) [1]
- (ii) For the reaction: $2H_2 + 2NO \rightleftharpoons 2H_2O + N_2$, the following rate data was obtained: [3]

S.No.	[NO] mol L ⁻¹	[H ₂] mol L ⁻¹	Rate: mol L ⁻¹ sec ⁻¹
1	0.40	0.40	4.6×10^{-3}
2	0.80	0.40	18.4×10^{-3}
3	0.40	0.80	9.2×10^{-3}

Calculate the following:

- (1) The overall order of reaction.
- (2) The rate law.
- (3) The value of rate constant (k).

- (b) (i) The following electrochemical cell is set up at 298 K: [2]



Given $\rightarrow E^{\circ}Zn^{2+}/Zn = -0.761V$, $E^{\circ}Cu^{2+}/Cu = +0.339V$

- (1) Write the cell reaction.
- (2) Calculate the emf and free energy change at 298 K.

- (ii) Answer the following: [2]

- (1) What is the effect of temperature on ionic product of water (K_w)?
- (2) What happens to the ionic product of water (K_w) if some acid is added to it?

- (c) Frenkel defect does not change the density of the ionic crystal whereas, Schottky defect lowers the density of ionic crystal. Give a reason. [2]

Question 4

- (a) (i) Name the law or principle to which the following observations conform: [3]
- (1) When water is added to a 1.0 M aqueous solution of acetic acid, the number of hydrogen ion (H^+) increases.
 - (2) When 9650 coulombs of electricity is passed through a solution of copper sulphate, 3.175 g of copper is deposited on the cathode (at.wt. of Cu = 63.5).
 - (3) When ammonium chloride is added to a solution of ammonium hydroxide, the concentration of hydroxyl ions decreases.
- (ii) What is the difference between the order of a reaction and its molecularity? [2]
- (b) (i) Explain why high pressure is required in the manufacture of sulphur trioxide by contact process. State the law or principle used. [2]
- (ii) Calculate the equilibrium constant (K_c) for the formation of NH_3 in the following reaction: [1]
- $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
- At equilibrium, the concentration of NH_3 , H_2 and N_2 are 1.2×10^{-2} , 3.0×10^{-2} and 1.5×10^{-2} M respectively.
- (c) Explain the following: [2]
- (i) Hydrolysis of ester (ethyl acetate) begins slowly but becomes fast after sometime.
 - (ii) The pH value of acetic acid increases on addition of a few drops of sodium acetate.

SECTION B

Answer any two questions.

Question 5

- (a) Write the formula of the following compounds: [2]
- (i) Potassium trioxalatoaluminate(III)
 - (ii) Hexaaquairon(II) sulphate.
- (b) Name the types of isomerism shown by the following pairs of compounds: [1]
- (i) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
 - (ii) $[Co(en)_2Cl_2]^+$ and $[Co(tn)_2Cl_2]^+$
- (c) For the coordination complex ion $[Co(NH_3)_6]^{3+}$ [2]
- (i) Give the IUPAC name of the complex ion.
 - (ii) What is the oxidation number of cobalt in the complex ion?

- (iii) State the type of hybridisation of the complex ion.
- (iv) State the magnetic behaviour of the complex ion.

Question 6

- (a) Give balanced equations for the following reactions: [3]
- (i) Potassium permanganate is heated with concentrated hydrochloric acid.
 - (ii) Lead sulphide is heated with hydrogen peroxide.
 - (iii) Ozone is treated with potassium iodide solution.
- (b) Discuss the theory involved in the manufacture of sulphuric acid by contact process. [2]

Question 7

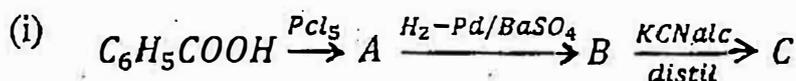
- (a) (i) What are the types of hybridisation of iodine in interhalogen compounds IF_3 , IF_5 and IF_7 , respectively? [3]
- (ii) Draw the structure of xenon hexafluoride (XeF_6) molecule and state the hybridisation of the central atom.
- (b) Give the balanced equations for the conversion of argentite (Ag_2S) to metallic silver. [2]

SECTION C

Answer any two questions.

Question 8

- (a) How can the following conversions be brought about:
- (i) Acetaldehyde to propan-2-ol. [1]
 - (ii) Nitrobenzene to p-aminoazobenzene. [1]
 - (iii) Acetic acid to methylamine. [2]
 - (iv) Aniline to benzene. [1]
- (b) (i) How will you distinguish between primary, secondary and tertiary amines by Hinsberg's test? [1]
- (ii) Why do alcohols possess higher boiling points as compared to those of corresponding alkanes? [1]
- (c) Identify the compounds A, B and C: [3]



Question 9

- (a) Give balanced equations for the following name reactions: [3]
- Friedel-Crafts reaction (alkylation)
 - Williamson's synthesis
 - Aldol condensation
- (b) Give chemical test to distinguish: [3]
- Ethyl alcohol and sec-propyl alcohol
 - Acetaldehyde and acetic acid
- (c) (i) Deficiency of which vitamin causes the following diseases: [4]
- Scurvy
 - Night blindness
- (ii) Write two differences between globular and fibrous proteins.

Question 10

- (a) An aliphatic unsaturated hydrocarbon (A) when treated with $\text{H}_2\text{SO}_4/\text{H}_2\text{SO}_4$ yields a compound (B) having molecular formula $\text{C}_3\text{H}_6\text{O}$. (B) on oxidation with concentrated HNO_3 gives two compounds (C) and (D). Compound (C) when treated with PCl_5 gives compound (E). (E) when reacts with ethanol gives a sweet smelling liquid (F). Compound (F) is also formed when (C) reacts with ethanol in the presence of concentrated H_2SO_4 . [4]
- Identify the compound A, B, C, D, E and F.
 - Give the chemical equation for the reaction of (C) with chlorine in the presence of red phosphorous and name the reaction.
- (b) Answer the following: [3]
- What is the common name of the polymer obtained by the polymerization of caprolactum? Is it addition polymer or condensation polymer?
 - Name the two organic compounds which have the same molecular formula $\text{C}_2\text{H}_6\text{O}$. Will they react with PCl_5 ? If they react, what are the products formed?
- (c) Give balanced equations for the following reactions: [3]
- Methyl magnesium bromide with ethyl alcohol.
 - Acetic anhydride with phosphorous pentachloride.
 - Acetaldehyde with hydroxylamine.