CHEMISTRY

PAPER – 1

(THEORY)

(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 cal deg^{-1} mol^{-1} = 8·314 JK^{-1} mol^{-1} = 0·0821 dm^3 atm K^{-1}mol^{-1}
1 l atm = 1 dm^3 atm = 101·3 J. 1 Faraday = 96500 Coulombs.
Avogadro's number = 6·023 $\times 10^{23}$.

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]**

(increases, decreases, positive, efficient, 68, non-efficient, no α-hydrogen, α-hydrogen, negative, Rosenmund's, greater, Cannizzaro, 74, common-ion effect, lesser, buffer action, diamagnetic, paramagnetic)

(i) The more _____ the standard reduction potential of a metal, the _____ is its ability to displace hydrogen from acids.

(ii) Both ccp and hcp are _____ packings and occupy about _____% of the available space.

(iii) Solubility of silver chloride _____ in the presence of sodium chloride because of _____.

(iv) Benzaldehyde undergoes _____ reaction on treatment with concentrated sodium hydroxide because it has _____ atom.

(v) The transition metals show _____ character because of the presence of unpaired electrons and Cu^+ is _____ because its electronic configuration is $[Ar]3d^{10}$.

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(b) Complete the following statements by selecting the **correct alternative from** the choices given: [5]

(i) The molal freezing point constant of water is 1·86 K kg mol^{-1} . Therefore, the freezing point of 0·1M NaCl solution in water is expected to be:

(1) -1·86°C
(2) -0·372°C
(3) -0·186°C
(4) +0·372°C

(ii) For a first order reaction the rate constant for decomposition of N_2O_5 is $6\times10^{-4}sec^{-1}$. The half-life period for the decomposition in seconds is:

(1) 11·55
(2) 115·5
(3) 1155
(4) 1·155

(iii) When acetaldehyde is treated with Grignard reagent, followed by hydrolysis the product formed is:

(1) Primary alcohol
(2) Secondary alcohol
(3) Carboxylic acid
(4) Tertiary alcohol

(iv) The geometry of XeF_6 molecule and the hybridization of Xe atom in the molecule is:

(1) Distorted octahedral and sp^3d^3
(2) Square planar and sp^3d^2
(3) Pyramidal and sp^3
(4) Octahedral and sp^3d^3

(v) In the complexes $[Fe(CN)_6]^{3-}$ and $[Pt(en)\ (H_2O)_2(NO_2)(Cl)]^{2+}$ the respective oxidation numbers of central metal atoms are :

(1) + 3 and +4
(2) +6 and +4
(3) +6 and +3
(4) +3 and +3

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(c) Answer the following questions: [5]

(i) What is the effect of temperature on the ionic product of water? How will it change the pH value of a neutral solution?

(ii) How many hours does it take to reduce 3 moles of Fe^{3+} to Fe^{2+} with 2·0 A current intensity?

(iii) How is urea prepared by Wohler synthesis?

(iv) Two liquids A and B form type II non ideal solution which shows a minimum in its temperature -mole fraction plot (T-χ diagram). Can the two liquids be completely separated by fractional distillation?

(v) The aqueous solution of sodium acetate is basic. Explain.

(d) Match the following: [5]

(i)	Disaccharide	(a)	Lucas reagent
(ii)	Carbylamine	(b)	Condensation polymer
(iii)	Dacron	(c)	Obnoxious smell
(iv)	Low spin complex, d^2sp^3	(d)	Sucrose
(v)	Anhydrous $ZnCl_2$ + conc.HCl	(e)	Hexaamminecobalt(III)ion

PART II (50 Marks)

Answer **six** *questions choosing* **two** *from* ***Section A,*** **two** *from* ***Section B*** *and* **two** *from* ***Section C.***

SECTION A

Answer any **two** *questions.*

Question 2

(a) (i) A solution containing 0·5 g of KCl dissolves in 100 g of water and freezes at – 0·24°C. Calculate the degree of dissociation of the salt. (K_f for water = 1.86°C) Atomic weights [K = 39, Cl = 35·5] [3]

(ii) If 1·71 g of sugar (molar mass = 342) are dissolved in 500 ml of an aqueous solution at 300 K, what will be its osmotic pressure? [1]

(iii) 0·70g of an organic compound when dissolved in 32g of acetone produces an elevation of 0·25°C in the boiling point. Calculate the molecular mass of organic compound (K_b for acetone = 1·72 K kg mol^{-1}). [1]

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(b) (i) What is the difference between order of a reaction and the molecularity of a reaction? [2]

(ii) A substance decomposes by following first order kinetics. If 50% of the compound is decomposed in 120 minutes, how long will it take for 90% of the compound to decompose? [2]

(c) Name the crystal structure of the copper metal. [1]

Question 3

(a) (i) Chromium metal crystallises with a body centered cubic lattice. The edge length of the unit cell is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g / cm^3? (atomic mass of Cr = 52·99) [2]

(ii) Why does sodium chloride on heating with sodium vapours acquire yellow colour? [1]

(iii) The equilibrium constant for the reaction: [1]

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \text{ at 715 K, is } 6{\cdot}0 \times 10^{-2}.$$

If, in a particular reaction, there are 0·25 mol L^{-1} of H_2 and 0·06 mol L^{-1} of NH_3 present, calculate the concentration of N_2 at equilibrium.

(iv) Calculate the concentration of OH^- ions in solution when $[H^+] = 6.2 \times 10^{-2} mol L^{-1}$. [1]

(v) State the Le Chatelier's principle. [1]

(b) For a crystal of sodium chloride, state: [2]

(i) The type of lattice in which it crystallises.

(ii) The coordination number of each sodium ion and chloride ion in the crystal lattice.

(iii) The number of sodium ions and chloride ions present in a unit cell of sodium chloride.

(iv) The structural arrangement of the sodium chloride crystal.

(c) Consider the following reaction: [2]

$N_2O_{4(g)} + \text{Heat} \rightleftharpoons 2NO_{2(g)}$

How is the composition of equilibrium mixture affected by:

(i) a change in temperature

(ii) a change in pressure

(iii) a change in concentration of N_2O_4

(iv) the removal of NO_2 from the reaction mixture

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Question 4

(a) The specific conductance of a 0.01 M solution of acetic acid at 298 K is 1.65×10^{-4} ohm^{-1} cm^{-1}. The molar conductance at infinite dilution for H^+ ion and CH_3COO^- ion are 349.1 ohm^{-1} cm^2mol^{-1} and 40.9 ohm^{-1} cm^2mol^{-1} respectively. Calculate: [3]

(i) Molar conductance of the solution.

(ii) Degree of dissociation of CH_3COOH.

(iii) Dissociation constant for acetic acid.

(b) (i) Calculate the e.m.f. of the following cell reaction at 298 K : [2]

$$Mg_{(s)} + Cu^{2+}(0.0001\ M) \rightarrow Mg^{2+}(0.001M) + Cu_{(s)}$$

The standard potential (E^0) of the cell is 2.71 V.

(ii) The solubility product (K_{sp}) of $BaSO_4$ is 1.5×10^{-9}. Calculate the solubility of barium sulphate in pure water and in 0.1 M $BaCl_2$. [2]

(c) Explain the following :

(i) When NH_4Cl and NH_4OH are added to a solution containing both, Fe^{3+} and Ca^{2+} ions, which ion is precipitated first and why? [2]

(ii) Dissociation of H_2S is suppressed in acidic medium. [1]

SECTION B

Answer any **two** *questions*

Question 5

(a) Write the IUPAC names of the following coordination compounds: [1]

(i) $[Cr(NH_3)_4(H_2O)_2]Cl_3$

(ii) $[PtCl_2(NH_3)_4][PtCl_4]$

(b) State the hybridization and magnetic property of $[Fe(CN)_6]^{3-}$ ion according to the valence bond theory. [1]

(c) (i) What type of isomers are $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$? Give a chemical test to distinguish between them. [2]

(ii) Write the structures of optical isomers of the complex ion $[Co(en)_2Cl_2]^+$ [1]

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Question 6

(a) Give balanced chemical equations for the following reactions: [3]

(i) Fluorine is passed through cold, dilute NaOH solution.

(ii) Hydrogen peroxide is treated with acidified $KMnO_4$ solution.

(iii) Sulphuric acid is treated with hydrogen sulphide.

(b) Draw the structure of xenon tetrafluoride molecule and state the hybridization of the central atom and the geometry of the molecule. [2]

Question 7

(a) Name the important ore of silver. Write all the steps and reactions involved in the Cyanide process for the extraction of silver from its ore. [3]

(b) Explain the following: [2]

(i) Why do transition metal ions possess a great tendency to form complexes?

(ii) The paramagnetic character in 3d-transition series elements increases upto Mn and then decreases.

SECTION C

Answer any **two** *questions.*

Question 8

(a) How can the following conversions be brought about:

(i) Glycerol to formic acid [1]

(ii) Chlorobenzene to phenol [1]

(iii) Diethyl ether to ethanol [1]

(iv) Phenol to aniline. [2]

(b) (i) How is iodoform prepared from ethanol? Give balanced equation. [1]

(ii) What will be the product formed when chlorobenzene is heated with sodium metal in the presence of dry ether? [1]

(c) Identify the compounds **A, B, C , D, E** and **F**: [3]

$$CH_3COCH_3 \xrightarrow[(O)]{Conc.HNO_3} A \xrightarrow{SOCl_2} B \xrightarrow{NH_3} C \xrightarrow{LiAlH_4} D$$

$$\xrightarrow{HNO_2} E \xrightarrow{CH_3COCl} F$$

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Question 9

(a) Give balanced equations for the following name reactions: [3]

(i) Reimer-Tiemann reaction.

(ii) Rosenmund reaction

(iii) Hoffmann's degradation reaction

(b) Give one chemical test to distinguish between the following pairs of compounds: [3]

(i) Ethylamine and diethylamine.

(ii) Acetaldehyde and benzaldehyde

(c) (i) Arrange the following compounds in the ascending order of their basic strength and give reasons for your answer: [2]

Methylamine, Aniline, Ethylamine, Diethyl ether

(ii) Name the monomers and the type of polymerization in each of the following polymers: [2]

(a) Polyester

(b) Bakelite

Question 10

(a) An organic compound A with molecular formula C_2H_7N on reaction with nitrous acid gives a compound B. B on controlled oxidation gives compound C. C reduces Tollen's reagent to give silver mirror and D. B reacts with D in the presence of concentrated sulphuric acid to give sweet smelling compound E. Identify A, B, C, D and E. Give the reaction of C with ammonia. [3]

(b) Give balanced equations for the following reactions: [4]

(i) How will you convert ethyl amine to methyl amine?

(ii) What is the effect of denaturation on the structure of proteins?

(iii) Name the nitrogen base residues present in DNA.

(c) Give balanced equations for the following reactions: [3]

(i) Aniline is treated with nitrous acid and HCl at low temperature.

(ii) Acetyl chloride is treated with ethyl alcohol.

(iii) Formaldehyde is treated with ammonia

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