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 $R = 1{\cdot}987$ *cal* $deg^{-1}\ mol^{-1} = 8{\cdot}314\ JK^{-1}\ mol^{-1} = 0{\cdot}0821\ dm^3\ atm\ K^{-1}mol^{-1}$

$1\ l\ atm = 1\ dm^3\ atm = 101{\cdot}3\ J.$ *1 Faraday = 96500 Coulombs.*

Avogadro's number $= 6{\cdot}023 \times 10^{23}$.

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]**

(Henry's, aldol condensation, absence, do not, ohm, Raoult's, increases, common ion effect, easily, three, solubility product, ohm^{-1}, two, four, $ohm^{-1}cm^2$, cannizzaro, $ohm^{-1}cm^{-1}$, zero, decreases, presence)

(i) Ideal solutions obey_____ law and they _____ form azeotropic mixtures.

(ii) Benzaldehyde undergoes _____ reaction due to _____ of α-hydrogen atom.

(iii) The solubility of silver chloride _____ in the presence of sodium chloride because of_____.

(iv) The unit of conductance is _____ and that of specific conductance is _____.

(v) When the concentration of a reactant of first order reaction is doubled, the rate becomes _____ times, but for _____ order reaction, the rate remains same.

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) Electrochemical equivalent is the amount of substance which gets deposited from its solution on passing electrical charge equal to:

(1) 96,500 Coulombs

(2) 1 Coulomb

(3) 60 Coulombs

(4) 965 Coulombs

(ii) The complex ion $[Ni(CN)_4]^{2-}$ is:

(1) Square planar and diamagnetic

(2) Tetrahedral and paramagnetic

(3) Square planar and paramagnetic

(4) Tetrahedral and diamagnetic

(iii) Wohler's synthesis is used for the preparation of:

(1) Glycine

(2) Amino acids

(3) Urea

(4) Proteins

(iv) When SO_2 gas is passed through acidified $K_2Cr_2O_7$ solution, the colour of the solution changes to:

(1) Red

(2) Black

(3) Orange

(4) Green

(v) In the equation $CH_3COOH + Cl_2 \xrightarrow[-HCl]{Red\ P} A$, the compound A is:

(1) CH_3CH_2Cl

(2) $ClCH_2COOH$

(3) CH_3Cl

(4) CH_3COCl

(c) Answer the following questions: [5]

(i) What is the order of reaction whose rate constant has the same unit as the rate of reaction?

(ii) What is the pH value of a solution whose hydroxyl ion concentration is 1×10^{-2} M?

(iii) Calculate the number of coulombs required to deposit 5·4g of Al when the electrode reaction is:

$$Al^{3+} + 3e^- \rightarrow Al$$ [Atomic Weight of Al = 27 g/mol].

(iv) Write the reaction to prepare acetaldehyde from hydrogen gas and an acid chloride.

(v) The edge length of unit cell of a body centered cubic (bcc) crystal is 352 pm. Calculate the radius of the atom.

(d) Match the following: [5]

(i)	Weak electrolyte	(a)	pH of a solution
(ii)	Colour in crystals	(b)	Iodoform
(iii)	Acetone	(c)	Tollen's reagent
(iv)	Sorensen	(d)	Ostwald dilution law
(v)	Ammonical silver nitrate	(e)	F - centre

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 10% aqueous solution of cane sugar (mol. wt. 342) is isotonic with 1·754% aqueous solution of urea. Find the molecular mass of urea. [2]

(ii) The molecular weight of an organic compound is 58 g mol^{-1}. What will be the boiling point of a solution containing 48 grams of the solute in 1200 grams of water? [2]

[K_b for water = 0·513°C kg $mole^{-1}$; Boiling point of water = 100°C.]

(iii) What will be the value of van't Hoff factor(i) of benzoic acid if it dimerises in aqueous solution? How will the experimental molecular weight vary as compared to the normal molecular weight? [1]

(b) (i) Determine the pH value of 0·001 M acetic acid solution if it is 2% ionised at this concentration. How can the degree of dissociation of this acetic acid solution be increased? [2]

(ii) The solubility product of $PbCl_2$ at 298K is $1{\cdot}7 \times 10^{-5}$. Calculate the solubility of $PbCl_2$ in g/lit. at 298K. [2]

Atomic Weights: [Pb = 207 and Cl = 35·5]

(c) Graphite is anisotropic with respect to conduction of electric current. Explain. [1]

Question 3

(a) (i) In a body centred and face centred arrangement of atoms of an element, what will be the number of atoms present in respective unit cells? Justify your answer with calculation. [2]

(ii) A compound AB has a simple cubic structure and has molecular mass 99. Its density is 3·4 g cm^{-3}. What will be the edge length of the unit cell? [2]

(b) (i) For the reaction: $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$; ΔH = −heat [2]

$K_e = 2{\cdot}5 \times 10^2$ at 298K

what will happen to the concentration of N_2 if:

(1) Temperature is decreased to 273K.

(2) Pressure is reduced.

(ii) In a first order reaction, 10% of the reactant is consumed in 25 minutes. Calculate: [2]

(1) The half-life period of the reaction.

(2) The time required for completing 87·5% of the reaction.

(c) Water acts as Bronsted acid as well as a Bronsted base. Give one example each to illustrate this statement. [2]

Question 4

(a) (i) Consider the following cell reaction at 298 K: [3]

$$2Ag^+ + Cd \rightarrow 2Ag + Cd^{2+}$$

The standard reduction potentials (E°) for Ag^+/Ag and Cd^{2+}/Cd are 0·80V and −0·40V respectively:

(1) Write the cell representation.

(2) What will be the emf of the cell if the concentration of Cd^{2+} is 0·1 M and that of Ag^+ is 0·2 M?

(3) Will the cell work spontaneously for the condition given in (2) above?

(ii) What is a buffer solution? How is it prepared? Explain the buffer action of a basic buffer with a suitable example. [2]

(b) Explain the following: [2]

(i) When NaCl is added to $AgNO_3$ solution, a white precipitate is formed.

(ii) An aqueous solution of ammonium chloride is acidic in nature.

(c) A 0·05 M NH_4OH solution offers the resistance of 50 ohms to a conductivity cell at 298K. If the cell constant is 0·50 cm^{-1} and molar conductance of NH_4OH at infinite dilution is 471·4 ohm^{-1} cm^2 mol^{-1}, calculate: [3]

(i) Specific conductance

(ii) Molar conductance

(iii) Degree of dissociation

SECTION B

Answer any **two** *questions*

Question 5

(a) Write the IUPAC names of the following: [2]

(i) $[CO(NH_3)_4SO_4]NO_3$

(ii) $K[Pt(NH_3)Cl_3]$

(b) What type of isomerism is exhibited by the following pairs of compounds: [1]

(i) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

(ii) $[Cr(SCN)(H_2O)_5]^{2+}$ and $[Cr(NCS)(H_2O)_5]^{2+}$

(c) How does $K_2[Pt\ Cl_4]$ get ionised when dissolved in water? Will it form precipitate when $AgNO_3$ solution is added to it? Give a reason for your answer. [2]

Question 6

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

(i) Silver nitrate is added to dilute solution of sodium thiosulphate.

(ii) Potassium dichromate is treated with acidified ferrous sulphate solution.

(iii) Phosphorous reacts with conc. sulphuric acid.

(b) How will you obtain pure potassium permanganate ($KMnO_4$) crystals from its ore, pyrolusite? Give the steps involved and the reactions. [2]

Question 7

(a) (i) Sulphur dioxide acts as an oxidizing agent as well as a reducing agent. Give one reaction each to show its oxidizing nature and its reducing nature. **[3]**

(ii) Explain why an aqueous solution of potassium hexacyanoferrate (II) does not give the test for ferrous ion.

(b) What is meant by Lanthanide contraction? Write the general electronic configuration of inner transition elements. **[2]**

SECTION C

Answer any **two** *questions.*

Question 8

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

(i) Acetaldehyde to acetaldehyde phenyl hydrazone. **[1]**

(ii) Benzoic acid to aniline. **[1]**

(iii) Methyl chloride to acetone. **[2]**

(iv) Benzene to benzene diazonium chloride. **[1]**

(b) (i) Glycerol (propane 1, 2, 3 triol) is more viscous than ethylene glycol (ethane 1, 2, diol). Explain. **[1]**

(ii) How can urea be detected by Biuret test? **[1]**

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

(i) $C_2H_5OH \xrightarrow{PCl_5} A \xrightarrow{KCN} B \xrightarrow{H_3O^+} C_2H_5COOH \xrightarrow[\Delta]{NH_3} C$

(ii) $C_6H_5COOH \xrightarrow{SOCl_2} A \xrightarrow{NH_3} B \xrightarrow{Br_2/KOH} C$

Question 9

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

(i) Benzoin condensation

(ii) Wurtz-Fittig reaction

(iii) Carbylamine reaction

(b) Give chemical test to distinguish: **[3]**

(i) Formaldehyde and acetaldehyde

(ii) Dimethyl ether and ethyl alcohol.

(c) (i) Write the structure of three ethers with molecular formula $C_4H_{10}O$. **[4]**

(ii) Starting with Grignard's reagent, how will you prepare propanoic acid?

Question 10

(a) An organic compound A has the molecular formula C_7H_6O. When A is treated with NaOH followed by acid hydrolysis, it gives two products B and C. When B is oxidized, it gives A, when A and C are each treated separately with PCl_5, they give two different products D and E. **[3]**

(i) Identify A, B, C, D and E.

(ii) Give the chemical reaction when A is treated with NaOH and name the reaction.

(b) Answer the following: **[4]**

(i) What do you observe when glucose solution is heated with Tollen's reagent?

(ii) Name the monomers and the type of polymerisation in each of the following polymers:

(1) Terylene

(2) Polyvinyl chloride

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

(i) Ethylamine with nitrous acid.

(ii) Diethyl ether with phosphorous pentachloride.

(iii) Aniline with acetyl chloride.