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.)*

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*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 1 atm = 1 dm^3 atm = 101.3 J.   1 Faraday = 96500 Coulombs.

PART I

*Answer **all** questions*

Question 1

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

(Raoult's, Arrhenius, lateral, sodium, magnesium, negative, positive, non-ideal, ideal, iron, copper, van't Hoff, s, p, ethanol, ethanoic acid, methanoic acid, methanol, propanoic acid.)

(i)   For a spontaneous change to take place, the ΔS of the system should be _____ and ΔG of the system should be _____.

(ii)   Hydrolysis of methyl propanoate gives _____ and _____.

(iii) Solutions which strictly obey _____ law are called _____ solutions.

(iv) π bonds are formed by the _____ overlap of _____ orbitals.

(v)   Zinc can displace _____ from $CuSO_4$ solution, but cannot displace _____ from $MgSO_4$ solution.

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

(i) The quantity of electricity required to deposit 1·15g of sodium from molten NaCl (Na=23, Cl = 35·5) is:

(1) 1 F

(2) 0·5 F

(3) 0·05 F

(4) 1·5 F

(ii) When acetic acid is reacted with calcium hydroxide and the product is distilled dry, the compound formed is:

(1) Calcium acetate

(2) Acetone

(3) Acetaldehyde

(4) Acetic anhydride

(iii) The [OH$^-$] concentration of a weak base is given by:

(1) ck_b

(2) $\sqrt{ck_b}$

(3) $\sqrt{k_b/c}$

(4) $\sqrt{k_b}$

(iv) In a plot of log k vs 1/T, the slope is:

(1) $- Ea/2·303$

(2) $Ea/2·303\ R$

(3) $Ea/2·303$

(4) $- Ea/2·303\ R$

(v) Among the following coordination compounds, the one giving a white precipitate with $BaCl_2$ solution is:

(1) $[Cr(H_2O)_5Br]SO_4$

(2) $[Cr(H_2O)_5SCN]$

(3) $[Co(NH_3)_5SO_4]Br$

(4) $[Pt(NH_3)_6]Cl_4$

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(c) Answer the following questions: [5]

(i) A solution X is prepared by dissolving three moles of glucose in one litre of water and a solution Y is prepared by dissolving 1.5 moles of sodium chloride in one litre of water. Will the osmotic pressure of X be higher, lower or equal to that of Y? Give a reason for your answer.

(ii) Give one example (equation) of a homogeneously catalysed reaction and name the catalyst.

(iii) Write the formula of the product formed when formaldehyde reacts with ammonia and name the product.

(iv) If the ionization (dissociation) constant of acetic acid is k_a, what will be the pH of a solution containing equal concentrations of acetic acid and sodium acetate?

(v) What is the electronic configuration of chromium atom ($Z = 24$)? Give a reason for your answer.

(d) Match the following: [5]

(i) Nernst equation   (a) Water

(ii) Lactic acid   (b) Constant volume

(iii) Amphiprotic solvent   (c) Ammonia

(iv) Lewis base   (d) Optical isomers

(v) Isochoric process   (e) Electrochemical cells

PART II

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 of urea in water has a boiling point of 100·18°C. Calculate the freezing point of the solution. (K_f for water is 1·86K kg mol^{-1} and K_b for water is 0·512 K kg mol^{-1}). [2]

(ii) A solution of lactose containing 8·45 g of lactose in 100g of water has a vapour pressure of 4·559 mm of Hg at 0°C. If the vapour pressure of pure water is 4·579 mm of Hg, calculate the molecular weight of lactose. [3]

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(b) (i) The molecular weight of H_2S is more than that of H_2O, but H_2S is a gas and H_2O is a liquid. Explain. [2]

(ii) When potassium cyanide reacts with water, will the resulting solution be acidic, alkaline or neutral? Justify your answer. [2]

(c) What is the hybridisation of the carbon atom in ethyne molecule? What is the H– C – H bond angle? [1]

Question 3

(a) (i) State the second law of thermodynamics in terms of the entropy of the universe. [1]

(ii) Calculate the maximum work that can be obtained from the given electrochemical cell constructed with two metals M and N. [3]

$$\left[E^{\circ}_{M^{+2}/M} = -0.76V, \ E^{\circ}_{N^{+2}/N} = +0.34V \right]$$

The cell reaction is $M + N^{+2} \rightarrow M^{+2} + N$

(b) (i) To precipitate group III cations NH_4Cl should be added to the solution before the addition of ammonium hydroxide. Explain why. [2]

(ii) A study of chemical kinetics of the reaction $A+B \rightarrow$ products, gave the following data at 25°C : [2]

Experiment	[A]	[B]	$\dfrac{d[Products]}{dt}$
1	1.0	0.15	4.20×10^{-6}
2	2.0	0.15	8.40×10^{-6}
3	1.0	0.20	5.60×10^{-6}

Find:

(1) The order of reaction with respect to A.

(2) The order of reaction with respect to B.

(3) The rate law.

(c) (i) What are F-centres in an ionic crystal? [1]

(ii) Why are crystals having F-centres paramagnetic? [1]

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Question 4

(a) (i) The central atom of methane and water is in the same state of hybridisation, but the shapes of the two molecules are different. Discuss. [2]

(ii) The conductivity of 0·2M KCl solution is 3×10^{-2} ohm^{-1} cm^{-1}. Calculate its molar conductance. [2]

(b) (i) Draw the valence shell molecular orbital diagram of oxygen molecule and predict its magnetic nature. [2]

(ii) Calculate the solubility of lead chloride in water, if its solubility product is $1·7 \times 10^{-5}$. [2]

    $(Pb = 206, Cl = 35·5)$

(c) For a crystal of diamond, state: [2]

(i) The hybridisation of the carbon atom.

(ii) The coordination number of each carbon atom.

(iii) The type of lattice in which it crystalises.

(iv) The number of carbon atoms present per unit cell.

SECTION B

Answer any two questions

Question 5

(a) Write the formulae of the following coordination compounds: [2]

(i) potassiumtetracyanonickel(0)

(ii) triamminetrinitrocobalt(III)

(b) $[CoF_6]^{3-}$ is a coordination complex ion. [2]

(i) What is the oxidation number of cobalt in the complex?

(ii) How many unpaired electrons are there in the complex?

(iii) State the magnetic behaviour of the complex.

(iv) Give the I.U.P.A.C. name of the complex.

(c) Draw the structural isomer of $[Co(NH_3)_5NO_2]Cl_2$ and name the type of isomerism. [1]

Question 6

(a) Give the equations for the conversion of argentite (Ag_2S) to metallic silver. [2]

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

    (i) Acidified potassium permanganate and oxalic acid.

    (ii) Ozone and mercury.

    (iii) Action of heat on a mixture of sodium chloride and concentrated sulphuric acid.

Question 7

(a) Explain why transition metals form complex compounds. [2]

(b) (i) What is the hybridisation of the chlorine atom in ClF_3 molecule? [2]

    (ii) Draw the structure of the molecule and state its geometry.

(c) Name the inert gases used for: [1]

    (i) Filling sodium vapour lamps.

   (ii) Obtaining light of different colours in neon signs.

SECTION C
Answer any two questions

Question 8

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

    (i) Ethanol to methylamine. [3]

    (ii) Benzene to phenol. [2]

(b) Complete the following reactions and name the reactions: [3]

    (i) $\underline{\hspace{2cm}} + 3I_2 + 4KOH \rightarrow CHI_3 + CH_3COOK + 3KI + 3H_2O$

    (ii) $C_3H_7NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} \underline{\hspace{2cm}} + 3KCl + 3H_2O$

(c) Name the type of polymerisation (addition or condensation) and name the monomers in each of the following polymers: [2]

    (i) Protein

    (ii) Polyethylene

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Question 9

(a) (i) What type of isomers are glucose and fructose? [1]

(ii) Name the functional group common to both glucose and fructose.

(b) (i) Identify the products A, B and C: [3]
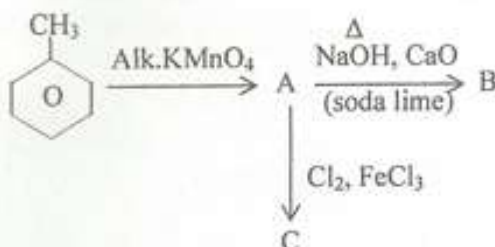
(ii) Identify the reagents X, Y and Z.

$$C_2H_5Cl \xrightarrow{X} C_2H_5CN \xrightarrow{Y} C_2H_5CH_2NH_2 \xrightarrow{Z} C_2H_5CH_2NHCOCH_3$$

[3]

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

(i) Benzaldehyde and hydroxylamine.

(ii) Benzoic acid and phosphorous pentachloride.

(iii) 1-butanol and hydrogen chloride.

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

(i) Methanal and ethanal.

(ii) Urea and benzoic acid.

Question 10

(a) An aliphatic hydrocarbon A on treatment with sulphuric acid in the presence of $HgSO_4$ yields a liquid B with molecular formula C_2H_4O. B on oxidation with acidified potassium dichromate yields C which gives effervescence with sodium bicarbonate. C when treated with $SOCl_2$ gives D. When D reacts with ethanol it gives a sweet smelling liquid E. E is also formed when C reacts with ethanol in the presence of conc. H_2SO_4. [4]

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

(ii) Draw the structure of the isomer of compound B.

(iii) Write the balanced equation for the conversion of A to B.

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(b) (i) The compound C_6H_{12} shows optical isomerism. Draw the structural formula of the [1] compound and name it.

(ii) Name *any three* types of isomerisms that the compound with molecular formula [3] C_4H_7Cl can give rise to. Also represent the structures of the compounds relevant to these isomers.

(c) Give equations to show what happens when a mixture of potassium cyanate and ammonium [2] sulphate is strongly heated. Name the reaction.

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