CHEMISTRY

PAPER 1

(THEORY)

Maximum Marks: 70
Time Allotted: Three Hours
Reading Time: Additional Fifteen minutes

Instructions to Candidates

1. You are allowed an **additional fifteen minutes** for **only** reading the question paper.
2. You must **NOT** start writing during the reading time.
3. This question paper has **11 printed pages and one blank page.**
4. It is divided into **four sections** and has **twenty one questions** in all.
5. Answer **all** questions.
6. **Section A** has **fourteen subparts**. Each question carries 1 mark.
7. While attempting **Multiple Choice Questions** in Section A, you are required to **write only ONE option as the answer.**
8. **Section B** has **ten questions.** Each question carries 2 marks.
9. **Section C** has **seven questions.** Each question carries 3 marks.
10. **Section D** has **three questions.** Each question carries 5 marks.
11. *Internal choices* have been provided in *one question each in Sections B, C and D.*
12. The intended marks for questions are given in brackets [ ].
13. All working, including rough work, should be done on the same sheet as, and adjacent to the rest of the answer.
14. Balanced equations must be given wherever possible and diagrams where they are helpful.
15. When solving numerical problems, all essential workings must be shown.
16. In working out problems, use the following data:

    Gas constant $R=1\cdot987 cal\ deg^{-1}mol^{-1}= 8\cdot314 JK^{-1}mol^{-1}= 0\cdot0821 dm^3 atmK^{-1}mol^{-1}$
    $1\ l\ atm =1 dm^3 atm=101\cdot3\ J,\ 1\ Faraday = 96500\ coulombs$
    Avogadro's number$= 6\cdot023\times10^{23}$

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1. Kindly read **aloud** the Instructions given on page 1 to all the candidates present in the examination hall.

SECTION A - 14 MARKS

Question 1

(A) Fill in the blanks by choosing the appropriate word(s) from those given in the [4×1] brackets:

[ethanol, $[Fe(H_2O)_6]^{2+}$, anode, d^2sp^3, Cannizzaro, reducing, cathode, sp^3d^2, iodine, $[Fe(CN)_6]^{4-}$, methanol, aldol, oxidising, manganese dichloride]

    (i) In electrochemical cells, the electrode having negative values of standard reduction potential acts as _____ while the electrode possessing positive values of standard reduction potential acts as _____ .

    (ii) The coordination compound _____ is an example of inner orbital complex and the hybridisation involved in the complex is _____ .

    (iii) Formaldehyde lacks α-hydrogen atom and thus forms sodium formate and _____ on reaction with conc. alkali. This reaction is known as _____ reaction.

    (iv) Since potassium permanganate is _____ in nature, it gives _____ on reaction with KI solution in acidic medium.

(B) Select and write the correct alternative from the choices given below. [7×1]

    (i) Ethylamine reacts with nitrous acid at low temperature to form:

        (a) $C_2H_5N_2^+Cl^-$, H_2O

        (b) C_2H_5OH, $C_2H_5NO_2$

        (c) C_2H_5OH, N_2, H_2O

        (d) C_2H_5OH, NH_3, H_2O

    (ii) Which one of the following statements are correct regarding the depression of freezing point?

        (P) The depression in freezing point is directly proportional to the amount of solute dissolved in solution.

        (Q) The depression in freezing point is inversely proportional to the amount of solute dissolved in solution.

        (R) Vapour pressure of the solution is more than that of pure solvent.

        (S) Vapour pressure of the solution is less than that of pure solvent.

        (a) Only (P) and (S) are correct.

        (b) Only (Q) and (R) are correct.

        (c) Only (Q) and (S) are correct.

        (d) Only (P) and (Q) are correct.

(iii) The amount of bromine required to completely convert 9·4 g of phenol into 2,4,6 tribromophenol is:
(Atomic weight of C = 12, H = 1, O = 16 and Br = 80)

 (a) 24 g

 (b) 48 g

 (c) 80 g

 (d) 96 g

(iv) Which one of the following statements is correct?

 (a) All amino acids are optically inactive.

 (b) All amino acids are optically active.

 (c) All amino acids are optically active except glutamic acid.

 (d) All amino acids are optically active except glycine.

(v) What type of structural isomerism exists between the following pair of coordination compounds?
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$ and $[Cr(H_2O)_5Cl]Cl_2.H_2O$

 (a) Ionisation isomerism

 (b) Hydrate isomerism

 (c) Coordination isomerism

 (d) Linkage isomerism

(vi) Given below are two statements marked Assertion and Reason. Read the two statements carefully and select the correct option.
Assertion: The use of phosphorus chlorides is preferred to thionyl chloride in the preparation of alkyl chlorides from alcohol.
Reason: Phosphorous chlorides give pure alkyl chlorides.

 (a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.

 (b) Both Assertion and Reason are true but Reason is not the correct explanation for Assertion.

 (c) Assertion is true and Reason is false.

 (d) Both Assertion and Reason are false.

(vii) Given below are two statements marked Assertion and Reason. Read the two statements carefully and select the correct option.
Assertion: The basic strength of hydroxides of lanthanoids decreases with an increase in their atomic number.
Reason: The size of trivalent cations of lanthanoids increases with an increase in their atomic number.

 (a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.

 (b) Both Assertion and Reason are true but Reason is not the correct explanation for Assertion.

 (c) Assertion is true and Reason is false.

 (d) Both Assertion and Reason are false.

(C) Read the passage carefully and answer the questions that follow. [3×1]

In the year 1889, Svante Arrhenius proposed that the dependence of the rate constant (k) of a reaction on temperature can be expressed by the following equation, known as the Arrhenius equation.

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

The calculation of E_a can be done by using the above equation in the following way:

$$log_{10}\, k = log_{10}\, A - \frac{E_a}{2 \cdot 303\, RT}$$

The above equation is similar to the equation for straight line i.e., $y = mx + c$. It can be used to calculate the value of E_a, by using either graphical method or rate constant method.

(i) The rate of a particular reaction triples when the temperature changes from 30° C to 60° C. Calculate the activation energy (E_a) of the reaction.

(ii) The slope of the line in the graph of $log_{10}\, k$ versus $\frac{1}{T}$ for a reaction is -4621. Calculate the energy of activation for the reaction. (Given: $R = 8 \cdot 314$ J K^{-1} mol^{-1})

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

SECTION B – 20 MARKS

Question 2 [2]

Sudeshna took her gold plated bangles to a goldsmith for cleaning and electroplating as they had become black due to constant exposure to dust and dirt. Calculate the amount of charge in coulombs needed for plating $1 \cdot 0$ g of gold on the bangles.

During electroplating, the following reaction takes place:

$$Au^{3+} + 3e^- \longrightarrow Au \quad \text{(Given: Atomic weight of Au} = 197 \text{ g mol}^{-1})$$

Question 3 [2]

An organic compound [A] having molecular formula C_3H_6O gives a positive iodoform test. On reduction by LiAlH$_4$, compound [A] forms compound [B]. Further, compound [B] reacts with SOCl$_2$ and forms compound [C]. On treatment with alcoholic KOH, compound [C] gives compound [D] which upon ozonolysis yields formaldehyde and acetaldehyde.

Identify the compounds [A], [B], [C] and [D].

Question 4 [2]

Write chemical equations to convert the following:

(i) Chlorobenzene to biphenyl

(ii) Chloroform to acetylene

Question 5 [2]

The half-life period for radioactive carbon, C^{14} is 5730 years. An ancient sample of wood has only 80% of C^{14} actively left in comparison to a living plant.
Estimate the age of the ancient wood sample.

Question 6 [2]

An aromatic compound [A] on heating with aqueous ammonia forms compound [B]. Upon heating with Br_2 and KOH, compound [B] forms compound [C] which has the molecular formula C_6H_7N.
Identify compounds [A], [B] and [C]. Name the reaction involved in conversion of compound [B] to compound [C].
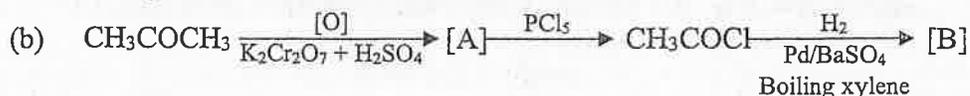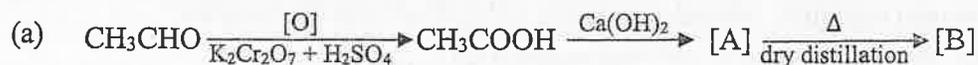
Question 7 [2]

Neha and Imran were given an assignment on the coordination complex $[Co(NH_3)_6]Cl_3$. They had to find the hybridisation involved and the magnetic behaviour of the complex compound. Neha found that the complex compound was of sp^3d^2 hybridisation and paramagnetic in behaviour whereas, Imran found that the complex compound was of d^2sp^3 hybridisation and diamagnetic in behaviour.

Evaluate the responses of Neha and Imran.

Question 8 [2]

(i) Identify the compounds [A] and [B] in the following reactions:

(a) $CH_3CHO \xrightarrow[K_2Cr_2O_7 + H_2SO_4]{[O]} CH_3COOH \xrightarrow{Ca(OH)_2} [A] \xrightarrow[\text{dry distillation}]{\Delta} [B]$

(b) $CH_3COCH_3 \xrightarrow[K_2Cr_2O_7 + H_2SO_4]{[O]} [A] \xrightarrow{PCl_5} CH_3COCl \xrightarrow[\substack{Pd/BaSO_4 \\ \text{Boiling xylene}}]{H_2} [B]$

OR

(ii) An aromatic organic compound [A] with the molecular formula C_7H_6O reduces Tollen's reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives compound [B] which has the molecular formula $C_7H_6O_2$. On reaction with sodium bi-carbonate, compound [B] forms brisk effervescence.
Identify the compounds [A] and [B]. Write the chemical reaction of compound [B] with sodium bi-carbonate.

Question 9 [2]

An organic compound [A] reacts with PBr_3 and forms compound [B] which reacts with magnesium in presence of ether and gives a Grignard's reagent. This Grignard's reagent reacts with CH_3CHO followed by hydrolysis to form secondary propyl alcohol.

Identify the compounds [A] and [B]. Write the chemical reaction to show how acetaldehyde is converted to secondary propyl alcohol.

Question 10   [2]

The specific conductivity of $0 \cdot 0025$ M acetic acid solution is $7 \cdot 95 \times 10^{-5}$ ohm^{-1} cm^{-1}.
Calculate the molar conductivity of this solution. If molar conductance for acetic acid is
$389 \cdot 5$ ohm^{-1} cm^2 mol^{-1} at infinite dilution (Λ_m^∞), what would be its degree of dissociation?

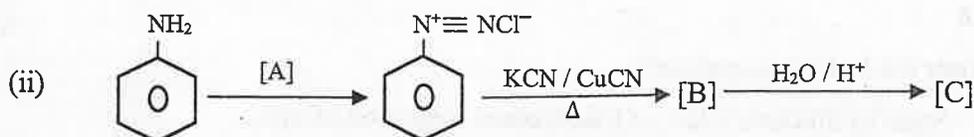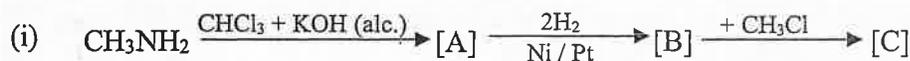**Question 11**   [2]

Write chemical tests to distinguish between the following pairs of compounds:

(i)   2-methylpropan-2-ol and propan-2-ol

(ii)   Ethanol and diethyl ether

SECTION C – 21 MARKS

Question 12   [3]

Identify [A], [B] and [C] in the following reactions:

(i) $CH_3NH_2 \xrightarrow{\text{CHCl}_3 + \text{KOH (alc.)}} [A] \xrightarrow[\text{Ni / Pt}]{2H_2} [B] \xrightarrow{+ \text{CH}_3\text{Cl}} [C]$

(ii)

Question 13   [3]

The colligative properties are properties of solutions which depend only upon the number
of solute particles irrespective of their nature. These properties help to calculate the
molecular weight of non-volatile, non-dissociating and non-associating solutes. If the
solute dissociates or associates, we get abnormal molecular weights. To account for
abnormal molecular weights of such solutes, van't Hoff factor (*i*) was introduced.

(i)   When $1 \cdot 90$ g of benzoic acid is dissolved in 26 g of benzene, it causes a
        depression in freezing point by $1 \cdot 60$ K. The molal depression constant for
        benzene is $4 \cdot 8$ K kg mol^{-1} and the molecular mass of benzoic acid is 122 g mol^{-1}.

        Calculate the degree of association of benzoic acid if it forms dimer in solution.

(ii)   Arrange the aqueous solution of the following compounds in the increasing order
        of value of van't Hoff factor:

                        Benzoic acid, Barium chloride, Urea

Question 14   [3]

Write chemical equations to illustrate the following name reactions:

(i)   Clemmensen's reduction

(ii)   Cross Aldol condensation

(iii) Kolbe's electrolytic reaction

Question 15   [3]

(i) $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[CoF_6]^{3-}$ is an outer orbital complex. Why? (Given: Atomic number of Co = 27).

(ii)   A coordination compound with molecular formula $CrCl_3.6H_2O$ precipitates two moles of AgCl with $AgNO_3$ solution. Write the structural formula of the compound.

(iii) Explain why an aqueous solution of $K_4[Fe(CN)_6]$ is not toxic whereas an aqueous solution of KCN is highly toxic.

Question 16   [3]

(i)   Answer the following questions:

   (a)   State Kohlrausch's law of independent migration of ions.

   (b)   Calculate the molar conductivity of an aqueous solution of $CaCl_2$ at infinite dilution. The ionic conductance of Ca^{2+} and Cl^- ions are $119 \cdot 0$ ohm^{-1} cm^2 mol^{-1} and $76 \cdot 3$ ohm^{-1} cm^2 mol^{-1} respectively.

   (c)   A galvanic cell has an electrode potential of $1 \cdot 10$ V. If an opposing potential of $1 \cdot 10$ V is applied to this cell, what will happen to the cell reaction and the current flowing through the cell?

                                                          OR

(ii)   Answer the following questions:

   (a)   What should be the sign (positive or negative) for E°_{cell} and ΔG° for a spontaneous redox reaction occurring under standard conditions?

   (b)   Why does molar conductance (Λ_m) of CH_3COOH increase drastically on dilution, while that of KCl increases gradually?

   (c)   How much charge is required in coulombs for the complete reduction of 1 mol of Cu^{2+} to Cu?

Question 17   [3]

(i)   What is observed when D-glucose is treated with bromine water? Write the chemical reaction.

(ii) Though vitamin C is found in fruits and vegetables, it cannot be stored in our body. Why?

(iii) What is a *peptide linkage*? Write an example to show peptide linkage.

Question 18   [3]

Following rate data was obtained at 298 K for the reaction A + B $\longrightarrow$ C + D

S.No.	Conc. of [A] mol L^{-1}	Conc. of [B] mol L^{-1}	Rate: mol L^{-1} sec^{-1}
1.	0·2	0·2	$6·0 \times 10^{-3}$
2.	0·6	0·4	$7·2 \times 10^{-2}$
3.	0·6	0·8	$2·88 \times 10^{-1}$
4.	0·8	0·2	$2·4 \times 10^{-2}$

Answer the following questions.

(i)   What is the order of reaction with respect to A and B?

(ii) Calculate the overall order of reaction.

(iii) Calculate the rate of reaction when [A] = 0·8 mol L^{-1} and [B] = 0·5 mol L^{-1}.

SECTION D – 15 MARKS

Question 19   [5]

Alcohols are the compounds that have one or more hydroxyl groups bonded to aliphatic carbon atoms while phenols are the compounds which have one or more -OH groups bonded to aromatic ring. Ethers are the compounds that have R-O-R as the functional group. They may be aliphatic as well as aromatic.

(i)   Write the chemical equation for the preparation of diethyl ether by Williamson's synthesis.

(ii) Explain why alcohols and ethers of comparable molecular mass have different boiling points.

(iii) Write the chemical reaction for the conversion of phenol to aniline.

(iv) Name the product obtained when ethyl alcohol is heated with conc. H_2SO_4 at 443 K.

(v)   Arrange water, ethanol and phenol in the increasing order of acidic nature. Give a reason for your answer.

Question 20 [5]

(i) Give a reason for each of the following:

    (a) Transition elements show high melting point.

    (b) Though Zr (z = 40) belongs to 4d transition series and Hf (z = 72) belongs to 5d transition series, yet the two cannot be separated easily.

    (c) Cu^{2+} and Fe^{3+} generally form coloured compounds.

(ii) Complete and balance the following reactions:

    (a) $K_2Cr_2O_7 + H_2SO_4 + Na_2SO_3 \longrightarrow$ _____ + _____ + _____ + _____

    (b) $KMnO_4 + H_2SO_4 + H_2S \longrightarrow$ _____ + _____ + _____ + _____

Question 21 [5]

(i) The pressure exerted by the vapour of a liquid at a particular temperature is known as the vapour pressure of the liquid at that temperature. When a non-volatile solute such as glucose is added to a volatile solvent like water, the vapour pressure of the solution decreases. F. Raoult (1887), a French chemist, studied the vapour pressure of several solutions. According to him, the vapour pressure of a solution depends on the temperature. A prior knowledge of the boiling points of different liquids helps in understanding their vapour pressure in solution.

Answer the following questions.

    (a) Write the Raoult's law for a solution containing a non-volatile solute.

    (b) What is an *ideal solution* and a *non-ideal solution*?

    (c) Calculate the vapour pressure of a solution containing 2 moles of glucose ($C_6H_{12}O_6$) in 900 g of water if the vapour pressure of pure water is 4·60 mm of Hg.

    (Given: Atomic weight of C = 12, H = 1 and O = 16)

    (d) Two liquids 'X' and 'Y' boil at 130° C and 180° C respectively. Which of the two liquids will have a higher vapour pressure at 90° C? Give a reason.

OR

(ii) (a) A solution of an organic compound is prepared by dissolving 34·2 g of solute in 500 g of water. Calculate the molecular mass of the solute and the freezing point of the aqueous solution.

       (Given: K_b for water = 0·52 K kg mol^{-1}, K_f for water = 1·86 K kg mol^{-1} and boiling point of aqueous solution = 100·104° C)

(b)   Calculate the osmotic pressure of 10% urea solution at 325 K.
(Given: Molecular mass of urea = 60 g mol^{-1}, R = 0·0821 L atm mol^{-1}K^{-1})

(c)   A person suffering from high blood pressure is advised to take minimum
quantity of common salt. Why?