Total number of printed pages-8

3 (Sem-4/CBCS) CHE HC 1

2024

CHEMISTRY

(Honours Core)

Paper: CHE-HC-4016

(Inorganic Chemistry-III)

Full Marks: 60

Time: Three hours

The figures in the margin indicate full marks for the questions.

1. Answer the following:

 $1 \times 7 = 7$

- (i) In transitional metal complexes the metal acts as
 - (a) Lewis acids
 - (b) Lewis bases
 - (c) Neutral compounds
 - (d) Amphoteric compounds (Choose the correct answer)

- (ii) Which oxidation state of Arsenic is most toxic?
- (iii) In which one of the following species does the transition metal ion have d^3 electronic configuration?
 - (a) $\left[Cr(NH_3)_6\right]^{3+}$
 - (b) $(Co(OH_2)_6)^{2+}$
 - (c) $[CoF_6]^{3-}$
 - (d) $[Fe(CN)_6]^{3+}$ (Choose the correct answer)
- (iv) What are macrocyclic ligands? Give one example.
- (v) Write the general valence shell electronic configuration of group 6 elements of the periodic table.
- (vi) In EDTA, total number of chelating rings are
 - (a) 5
 - (b) 3
 - (c) 4
 - (d) 6

(Choose the correct answer)

- (vii) Carbonic anhydrase is a zinc enzyme that catalyses the
 - (a) hydrolysis of the terminal peptide bond of a peptide chain
 - (b) hydration of CO_2 and dehydration of carbonic acid
 - (c) binding of dioxygen to haemoglobin
 - (d) None of the above processes (Choose the correct answer)
- 2. Answer the following:

2×4=8

- (i) " Cu^{2+} ions are coloured and paramagnetic, whereas Zn^{2+} ions are colourless and diamagnetic." Explain why.
- (ii) Draw the geometrical isomers of $\left[CrCl_2(en)_2 \right]^{2+}$ and state whether they are optically active or not.
- (iii) Write the full name and formula of the ligands whose abbreviations are given below:

dmg, acac, phen, edta

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 - (a) $\left[Cr(NH_3)_6 \right]^{3+}$ (b) $\left(Co(OH_2)_6 \right)^{2+}$

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- Write the full name and formula of the ligands whose abbreviations are given below:

dmg, acac, phen, edta

- (iv) How does Latimer diagram help to examine the thermodynamic feasibility of a species for disproportionation?
- 3. Answer **any three** questions from the following: 5×3=15
 - (i) "Transition metals act as good catalysts".

 Explain with proper reasons. Write the name of the transition metal which is used as catalyst in the Haber's process for synthesis of ammonia.

 4+1=5
 - (ii) Discuss the mechanism of dioxygen binding and release by haemoglobin.
 - (iii) "Octahedral complexes are more stable and more common than tetrahedral complexes." Explain.
 - (iv) What is lanthanide contraction? What causes lanthanide contraction? Why the lanthanides do not form oxocations?
 - (v) Discuss the magnetic character of square planer d^8 complexes with the help of crystal field theory.

- 4. Answer the following questions: $10\times3=30$
 - (i) Either
 - (a) The pairing energy for Mn^{3+} is $28,000 \ cm^{-1}$. The Δ_0 for the complexes $\left[Mn(H_2O)_6\right]^{3+}$ and $\left[Mn(CN)_6\right]^{3-}$ are 15,800 cm^{-1} and 38,500 cm^{-1} respectively. From these values identify the high-spin and low-spin complexes and write the electronic configuration.

3

- (b) Describe the preparation of KMnO₄ from pyrolusite ore. How does acidified permanganate solution react with the following species? Write the ionic equation for the reactions. 2+3=5
 - (i) Fe^{2+} ions
 - (ii) Oxalic acid
- (c) "The third ionization enthalpy of manganese is very high." Explain why.

- (d) Why is the separation of lanthanides difficult? Discuss the ion exchange method for the separation of lanthanides. 2+4=6
- (e) "Actinides have greater tendency to form complexes than lanthanides."Explain why.4

(ii) Either

(a) Explain the origin of Jahn-Teller distortion by crystal field theory. What are the conditions for Jahn-Teller distortion in the tetrahedral and octahedral complexes?

4+1+1=6

- (b) Compare the Jahn-Teller distortions in Ni(II) and Cu(II).
- (c) Explain why trans- $\left[Cu(en)_2 (H_2O)_2 \right]^{2+}$ is more stable than $cis-\left[Cu(en)_2 (H_2O)_2 \right]^{2+}$.

- (d) Write the general mechanisms by which a toxic metal can attack the human body. Give an account of the toxicity due to lead and mercury.

 3+2+2=7
- (e) "Excess as well deficiency of an essential metal is harmful to human body." Justify the statement with an example.

(iii) Either

- (a) Assign suitable reasons for the following:
 - I. The Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.
 - II. In the 3d series, the enthalpy of atomization of Zn^{2+} is the lowest.
 - III. Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured.

- IV. CrO is basic, Cr_2O_3 is amphoteric and CrO_3 is acidic in nature.
- V. $\left[Co(NH_3)_6 \right]^{3+}$ is more stable than $\left[Co(NH_3)_6 \right]^{2+}$.

Or

- (b) How are essential metals in biological system classified ? Mention each class with definition and write the name of each element present in it.
- (c) What is Na/K pump? Discuss the functioning of Na/K pump. 5

3 (Sem-4/CBCS) CHE HC 2

2024 CHEMISTRY

(Honours Core)

Paper: CHE-HC-4026

(Organic Chemistry-III)

Full Marks: 60

Time: Three hours

The figures in the margin indicate full marks for the questions.

- 1. Answer the following questions: $1 \times 7 =$
 - (a) Write aciform structure of nitromethan
 - (b) The aliphatic diazonium compounds at unstable, why?
 - (c) What is special isoprene rule?
 - (d) Mention one medicinal importance inicotine.

- (e) Arrange the following compounds in increasing order of aromatic character:Thiophene, pyrrole, benzene, furan
- (f) Mention two adverse effects of PAN on living organisms.
- (g) What class of alkaloid does nicotine belong to?
- 2. Answer **any four** of the following questions: $2 \times 4 = 8$
 - (a) Write the products formed in each of the following reactions:
 - (i) Cyanoethane is reduced with LiAlH₄
 - (ii) Nitrobenzene is heated with a mixture of conc. HNO_3 and conc. H_2SO_4
 - (b) Mention two synthetic applications of diazonium salts with their chemical reactions.
 - (c) Explain why Naphthalene gives
 1-Naphthalene sulphonic acid at low
 temperature and 2-Naphthalene
 sulphonic acid at high temperature.

- (d) Write down the different steps involved in Bischler-Napieralski reaction leading to synthesis of isoquinoline.
- (e) How can you show that
 - (i) α -terpineol is a 3° alcohol
 - (ii) geraniol has E-configuration
- (f) What product is formed in each case when citral is allowed to react with
 - (i) NaOH (aq)
 - (ii) KHSO₄
- 3. Answer **any three** questions from the following: 5×3=15
 - (a) Mention two nitrating agents employed in direct nitration of arenes? Explain the reaction mechanism of nitration of benzene. The 2,4,6-trinitrophenol is known as Picric acid although it does not contain a carboxyl group why?

2+2+1=5

- (b) Explain the role of resonance effect on basic properties of aliphatic amines with special reference to isomers of nitroanilines. Explain with appropriate structures, why N,N-dimethylpicramide is more basic than picramide. 3+2=5
- (c) Why does electrophilic substitution of Furan usually take place at C-2 position? Write Paal-Knorr synthesis of Furan. Write the product(s) of the following reaction. (structure and name).

 2+2+1=5

$$\begin{array}{c|c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \end{array}$$

- (d) Write the different products when anthracene is reacted with the following reactants: 1×5=5
 - (i) Sodium in THF
 - (ii) Sodium in amyl alcohol
 - (iii) Hydrogen gas over Ni
 - (iv) $Na_2Cr_2O_7/H_2SO_4$
 - (v) HNO3 in glacial acetic acid

(e) Write the product of the following reactions: 1×5=5

(a)
$$\Box$$
 CH₂NH₂ HNO₂ ?

(b)
$$\frac{H_2O_2}{\text{Acetic acid}}$$
?

(d) RX
$$\xrightarrow{\text{AgCN}}$$
 ?

(e)
$$\bigcap_{N}$$
 CrO_3 ?

- 4. Answer **any three** questions from the following: 10×3=30
 - (a) (i) Discuss the structural difference between nitroalkanes and alkyl nitriles. Discuss how one can be distinguished from the other.

 Mention two chemical tests.

2+3=5

- (ii) Elaborate the mechanism of diazotization of aniline. Mention one application of diazotization reaction. What happens when an aliphatic primary amine is diazotized?

 3+1+1=5
- (b) (i) Elaborate isocyanide test for amines with appropriate mechanism. How can reaction be stopped from further release of poisonous gas? Write the reaction.

 3+1+1=5
 - (ii) Why do aliphatic nitro compounds dissolve in aqueous alkali? Write the mechanism of Nef reaction.

2+3=5

- (c) (i) Explain why the electrophilic substitution in naphthalene takes place mainly at the 1-position? 2
 - (ii) How will you prepare
 2-nitronaphthalene starting from
 naphthalene?
 2
 - (iii) Write Haworth synthesis for phenanthrene.

- (iv) Explain the peri-hydrogen interaction in particularly in sulphonation of naphthalene. 3
- (d) (i) Give reasons for the following: 2+1+2=5
 - (a) Furan shows Diels-Alder cycloaddition
 - (b) Pyrrole readily polymerizes in presence of mineral acids
 - (c) Pyridine is less reactive in compare with benzene towards electrophiles.
 - (ii) Write the steps involved in the following conversion. Also mention the name of the synthesis. 4+1=5

$$\begin{array}{c|c} & CH_2R & ZnCl_2 \\ H & R & \end{array}$$

(e) (i) How many carbon atoms are present in sesqui and a diterpene?
Write a synthesis of geraniol. What products will be formed on ozonolysis of geraniol? 1+3+1=5

- (ii) Write four general properties of alkaloids. Mention a chemical test that is helpful in structue elucidation of an alkaloid. Draw the structure of nicotine and show how the nature of nitrogen atoms has been established. 2+1+1+1=5
- (f) (i) Name the type of hygrine alkaloid and its biological source. 2
 - (ii) Write two medicinal importances each of hygrine and reserpine.

2+2=4

- (iii) How is cocaine used as medicine?
- (iv) What is Emde's modification? 2

3 (Sem-4/CBCS) CHE HC 3

2024

CHEMISTRY

(Honours Core)

Paper: CHE-HC-4036

(Physical Chemistry-IV)

Full Marks: 60

Time: Three hours

The figures in the margin indicate full marks for the questions.

- 1. Answer the following questions: $1 \times 7 = 7$
 - (a) The molar conductance Λ_{NaOAC}° and Λ_{HCl}° at infinite dilution in water at 25°C are 91.0 and 426.2 Scm^2mol^{-1} respectively. To calculate Λ_{HOAC}° , the additional value required is
 - (i) Λ_{NaOH}°
 - (ii) Λ_{NaCl}°
 - (iii) Λ_{H_2O}
 - (iv) Λ_{KCl}

(Choose the correct answer)

- (b) Define specific conductance.
- (c) What is Ostwald's Dilution Law?
- (d) The pH of an aqueous solution is 4. Its OH^- is
 - (i) 10
 - (ii) 10^{-4}
 - (iii) 10⁻¹⁰
 - (iv) 10^{-14}

(Choose the correct answer)

- (e) Define Debye-Falkenhagen effect.
- (f) Which of the following molecule would have zero dipole moment?
 - (i) NH₃
 - (ii) m-dichlorobenzene
 - (iii) CH₃Cl
 - (iv) p-dichlorobenzene (Choose the correct answer)
- (g) The relative permeability $\mu_r > 1$ stands for
 - (i) Paramagnetic solids
 - (ii) Diamagnetic solids
 - (iii) Ferromagnetic solids
 - (iv) None of the above (Choose the correct answer)

- 2. Answer the following questions :
 - (a) Explain the variation of molar conductance with dilution for weak electrolyte.
 - (b) Name two types of concentration cells.
 - (c) How can dissociation constant of weak acid be determined from the measurement of conductance?
 - (d) Differentiate between paramagnetic and diamagnetic substances in terms of magnetic permeability and magnetic susceptibility.
- 3. Answer **any three** questions from the following: 5×3=15
 - (a) What is meant by transport number of an ion? How is it determined by moving boundary method? 1+4=5
 - (b) Explain saturated calomel electrode with the reactions when it is acting as anode and cathode as well.

 $2 \times 4 = 8$

- (c) At 25 °C, the specific conductance of carefully distilled water is 58.0×10^{-7} Sm^{-1} and λ_m° values for H^+ and OH^- ions are 349.8×10^{-4} and 198.5×10^{-4} $Sm^2 mol^{-1}$ respectively. Calculate the ionic product of water at 25°C. [Assume that λ_m differs very little from λ_m°]
- (d) Derive the relation between standard EMF and equilibrium constant of a cell reaction. The standard EMF of the cell $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ is 1·10 volts. Calculate the equilibrium constant of the cell reaction. Prove whether the reaction is feasible or not. 2+2+1=5
- (e) What is magnetic susceptibility? ExplainGouy's method for the measurement ofmagnetic susceptibility. 1+4=5

- 4. Answer **any three** questions from the following: 10×3=30
 - (a) Discuss Debye-Hückel theory of strong electrolytes. Explain relaxation effect and electrophoretic effect. How can Debye-Hückel-Onsager equation be utilized in the determination of equivalent conductance at infinite dilution for stong electrolytes.

3+4+3=10

- (b) Write the principle of conductometric titrations. Draw and explain the titration curves obtained in the conductometric titration of
 - (i) HCl with NaOH
 - (ii) CH3COOH with NaOH
 - (iii) CH3COOH with NH4OH and
 - (iv) AgNO3 with KCl

2+2+2+2=10

(c) Explain the construction and working of glass electrode for the determination of pH of a solution using this electrode.
 What are the limitations of a glass electrode?

(d) Derive Nernst equation for the measurement of EMF of an electrochemical cell. Consider an electrochemical cell

$$Fe(s) | Fe^{2+}(0.1M) | | Cd^{2+}(0.001M) | Cd(s)$$

- (i) Write the cell reaction
- (ii) Calculate the EMF of the cell
- (iii) Calculate ΔG° value of the cell reaction.

Given that $E_{Cd^{2+}|Cd}^{\circ} = -0.40 V$

$$E_{Fe^{2+}|Fe}^{\circ} = -0.44V$$

why does a cell stops working after some time? Explain with an example.

- (e) (i) What is molecular polarizability?
 - (ii) Derive the Clausius-Mossotti equation.
 - (iii) Define induced molar polarization.

(iv) Which of the following molecules obey Clausius-Mossotti equation? H_2O , NH_3 , CO_2 , CH_4

2+5+1+2=10

- (f) (i) How can you apply dipole moment of a molecule to calculate percentage ionic character of the molecule and to predict the shapes of molecules?
 - (ii) The dipole moment of $NH_3(g)$ is 1.46D and the bond angle HNH is 108°. Calculate the bond moment of the N-H bond.
 - (iii) How do you explain that the dipole moment of ethylchloride is considerably larger than that of chlorobenzene?

6+2+2=10