3 (Sem-4/CBCS) CHE HC1

2023

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) The compound which exhibits Jahn-Teller distortion is
 - (a) $[Mn(H_2O)_6]^{2+}$
 - (b) $[Mn(H_2O)_6]^{3+}$
 - (c) $[Cr(H_2O)_6]^{3+}$
 - (d) $[Fe(CN)_6]^{4-}$

(Choose the correct answer)

Contd.

- (ii) Which metal helps in blood clotting?
- (iii) For which of the following ions, colour is not due to a d-d transition?
 - (a) CrO_4^{2-}
 - (b) $Cu(NH_3)_4^{2+}$
 - (c) $Ti(H_2O)_6^{3+}$
 - (d) CoF_6^{3-} (Choose the correct answer)
- (iv) What is the main iron storage protein in biological system?
- (v) What type of isomerism is exhibited by the complex $[Co(NH_3)_5 NO_2]^{2+}$?
- (vi) Draw the structure of the following complex:Tri- μ -hydroxo bis [triammine chromium(III)]
- (vii) Which metal deficiency causes pernicious anemia?

- 2. Answer the following: 2×4=8
- (i) Explain why Ce^{+3} and Tb^{+3} are colourless but show strong absorption in UV region.
 - (ii) How does mercury cause toxicity in living system?
 - (iii) Why do transition metals show variable oxidation states?
- (iv) Determine the crystal field splitting energy Δ_0 of a d^6 complex having $10 \ Dq = 25{,}000 \ cm^{-1}$ and $P = 15{,}000 \ cm^{-1}$. Consider low spin complex.
- 3. Answer **any three** questions from the following: 5×3=15
 - (i) Using crystal field theory explain the difference in magnetic property of $[CoF_6]^{3-}$ and $[Co(CN)_6]^{3-}$.

3 0 (04 510 8080 4

- (ii) Comment on the spectral and magnetic properties of actinide elements compared to lanthanides.
- (iii) What is Na/K pump? Write the mechanism of action of Na/K pump.
- (iv) Given below is the Latimer diagram of manganese in acidic medium: 2+3=5

$$MnO_{4}^{-} \xrightarrow{+0.56} MnO_{4}^{2-} \xrightarrow{+2.26} MnO_{2} \xrightarrow{+0.95} Mn^{3+} \xrightarrow{+1.15} Mn^{2+} \xrightarrow{-1.19} Mn^{2+} Mn^{2+} \xrightarrow{-1.19} Mn^{2+} Mn^{2$$

- (a) Which species are likely to disproportionate and why?
- (b) Calculate standard reduction potential for the couple MnO_4^{2-}/Mn^{3+}
 - (v) Discuss the mechanism of binding of dioxygen with hemoglobin.
- 4. Answer **any three** questions from the following: 10×3=30
 - (i) Explain the bonding of $[Co(NH_3)_6]^{3+}$ with the help of molecular orbital theory. Draw the energy level diagram and also predict the magnetic property of the complex. 6+3+1=10

- (ii) (a) Explain the evidences in favour of the covalency of metal-ligand bonding in complexes.
- (b) What inferences can be drawn from the following reactions? 5

$$[Ni(CN)_4]^{2^-} + 4 * CN^- \longrightarrow [Ni(*CN)_4]^{2^-} + 4CN^- \text{ (very fast) } t_{1/2} = 30 \text{ sec}$$

$$[Mn(CN)_6]^{3^-} + 6 * CN^- \longrightarrow [Mn(*CN)_6]^{3^-} + 6CN^- \text{ (slow)} \qquad t_{1/2} = 1 \text{ hr}$$

$$[Cr(CN)_6]^{3^-} + 6 * CN^- \longrightarrow [Cr(*CN)_6]^{3^-} + 6CN^- \text{ (slowest) } t_{1/2} = 24 \text{ days}$$

- (iii) Write about the use of chelating compounds in medicinal chemistry.
- (iv) Answer the following questions regarding oxidation states exhibited by the first transition series elements:
- (a) List the oxidation states shown by each element indicating the unstable states within bracket.

5 0 10 4 0 10 120 120 1

- (b) All the elements except scandium exhibits a + 2 oxidation state whereas scandium exhibits a + 3 oxidation state only. Explain.
 - (c) Why do the elements at each end of the series exhibit minimum number of oxidation states and those in the middle show a maximum number of oxidation states?
- (d) Why are the higher oxidation states stabilised by oxide or fluoride? 3+2+3+2=10
- (v) What is lanthanide contraction and what is its cause? Discuss the separation of lanthanides using ion exchange method. Explain why La³⁺ is colourless but Lu⁴⁺ is orange red.

1+2+5+2=10

(vi) What special feature of Zn^{2+} makes it an excellent candidate for different enzymes? Write the structure and function of carbonic anhydrase enzyme with suitable diagram. 2+2+6=10

3 (Sem-4/CBCS) CHE HC2

2023

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: $1 \times 7 = 7$
 - (i) Draw and name the isomer of nitromethane.
 - (ii) Arrange the following in the decreasing order of basicity:

- (iii) Mention one medicinal importance of hygrine.
- (iv) Draw the Z-form of citral.
- (v) Write the product of the following:

RNC
$$\longrightarrow$$
 ?

- (vi) What happens when a mixture of acetylene and HCN is passed through red hot tube?
- (vii) What class of alkaloid does nicotine belong to?
- 2. Answer the following questions: 2×4=8
 - (a) Define terpenoids using special isoprene rule.
 - (b) Identify the products:

$$+ \underbrace{\begin{array}{c} \text{Diel-Alder reaction} \\ \text{O} \end{array}}_{\text{O}} [?] \xrightarrow{\text{CH}_{3}\text{Mgl}} [?]$$

(c) Write down the Paal-Knorr synthesis of the following:

- (d) Define and classify PAH.
- 3. Answer **any three** questions from the following: 5×3=15
 - (a) How will you prepare $CH_3CH_2NH_2$ by Gabriel synthesis? Elaborate Hinsberg test to distinguish $1^0,2^0$ and 3^0 amine. 2+3=5
 - (b) Alkylhalide reacts with KCN to give alkylcynide while it reacts with AgCN to give alkylisocynide. Explain with mechanism.
 - (c) Write Skraup synthesis of quinoline with mechanism.

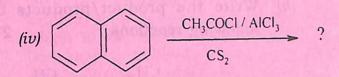
- (d) Give the structure and name of a 5-membered heterocyclic compound which shows Diel-Alder reaction. Write Diel-Alder reaction of your compound with maleic anhydride. 2+3=5
- (e) Write the structures of morphine and cocaine. Mention one medicinal use in each case. 2+2+1=5
- 4. Answer **any three** questions from the following: 10×3=30
 - (a) Mention a method of synthesis of naphthalene. Draw the resonating structures of naphthalene and apply Fries rule to identify the most stable structures. Explain why naphthalene undergoes electrophilic substitution reaction preferably at α-position. Write down the product of the following reaction:

$$\frac{\text{KMnO}_4/\text{H}^+}{2+2+2+3+1=10}$$

(b) Write the product/products of the following reactions: 2×5=10

(i)
$$CH_3$$
 CH_3 $CH_$

(iii)
$$CaO$$
 ?



$$(v) \qquad CH_2Cl_2/C_2H_5OC_2H_5$$

$$\Delta$$

- (c) (i) How will you confirm that citral contains an aldehydic group? 2
 - (ii) Propose a synthesis of citral from 6-methylhept-5-en-2-one.
 - (iii) Draw the structure of nicotine and identify the chiral carbon.
 - (iv) How will you establish the presence of pyridine nucleus in nicotine.
- (d) Write the mechanisms of the following: (any four) $2\frac{1}{2} \times 4 = 10$
 - (i) Hoffman degradation of amide
 - (ii) Reaction of diazotised aniline with alkaline β -naphthol
 - (iii) Chicibabin reaction

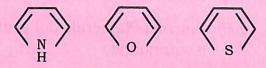
- (iv) Hydrolysis of alkyl cynide
- (v) Conversion of indole into quinoline
- (vi) Mannich reaction
- (vii) Bischler-Napieralskiol synthesis of isoquinoline
- (e) Starting from Ph-NO₂ (Nitrobenzene), how will you prepare the following? 2×5=10
 - (i) Ph-OH
 - (ii) Ph-COOH
 - (iii) Ph-H
 - (iv) Ph-Br
 - (v) Sym-tribromobenzene
- (f) (i) How can you detect the presence of amino group in anline using the diazotisation process? Write the reactions involved.

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(ii) What product is obtained when naphthalene is sulphonated at 80°C? What will happen if the temperature is raised to 165°C?

2

(iii) Arrange the following in order of decreasing reactivity towards electrophiles and explain: 2



(iv) How are terpenoids classified? Give one example each of the different class of terpenoids. 3

Total number of printed pages-8

3 (Sem-4/CBCS) CHE HC3

2023

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) What weight of AlF_3 salt be dissolved in 100 ml of solution so as to make the solution containing 1 eq/L?
 - (b) Define equivalent conductance.
 - (c) What is cell constant?
 - (d) What is transport number?

- (e) Ionic product of water at 25°C is approximately equal to
 - (i) $1 \times 10^{-7} (mol L^{-1})^2$
 - (ii) $2 \times 10^{-14} (mol/L)^2$
 - (iii) $1 \times 10^{-14} \text{ mol}^2 L^{-2}$
 - (iv) $1 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$ (Choose the correct answer)
- (f) Write two categories of electrochemical cell.
- (g) Which of the following hydrogen halides has most polar bond?
 - (i) HF
 - (ii) HBr
 - (iii) HCl
 - (iv) HI

(Choose the correct answer)

- 2. Answer following questions: $2\times4=8$
 - (a) Find the relationship between molar conductance and specific conductance in SI unit.

- (b) A perfectly cubical conductivity cell holds 0.94 cm³ of a solution between its electrodes. Determine its cell constants.
 - (c) What is relaxation effect?
 - (d) Write precisely on potentiometric titration.
- 3. Answer **any three** questions from the following: 5×3=15
 - (a) Discuss the Arhenius theory of electrolytic dissociation. Give evidence in support of the dissociation theory.

 3+2=5
 - (b) Write the principle of conductometric titrations. Discuss the characteristics of curves obtained in the titration of any two given below: 1+(2+2)=5
 - (i) HCl vs NaOH
 - (ii) CH₃COOH vs NaOH
 - (iii) HCl vs NH4OH
 - (iv) CH3COOH vs NH4OH

- (c) (i) What is ionic mobility? What is the effect of temperature on ionic mobility?
 - (ii) A potential of 12.0 volts was applied to two electrodes placed 20 cm apart. A dilute solution of NH₄Cl was placed between the electrodes when NH₄ is found to cover a distance of 1.6 cm in one hour. What is the mobility of NH₄ ion?
 - (d) (i) Derive a mathematical relation between the electrical energy of reversible galvanic cell and in free energy of the cell reaction. 3
 - (ii) What is half cell reaction ? Write the half cell reaction of the following cell: 2 $Zn |Zn^{2+}(aq)||Fe^{3+}(aq)|Fe^{2+}|Pl^{-}$
- (e) Briefly explain Gouy's method for the measurement of magnetic susceptibility.

- 4. Answer **any three** questions from the following: 10×3=30
 - (a) (i) How can you measure
 electrolytic conductance, specific
 conductance, equivalent
 conductance and molar
 conductance? Write the unit of
 cell constant (K) in SI unit.
 - (ii) The resistance of 0.01 M solution of an electrolyte was found to be 210 ohm at 25 °C. Calculate the molar conductance of the solution at 25 °C.

(Given : cell constant = $0.88 cm^{-1}$)

(iii) Specific conductance of an electrolyte solution decreases with dilution. Explain.

5+3+2=10

(b) (i) State and explain the Kohlrausch's law of independent migration of ions.

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- (ii) For the strong electrolytes NaOH, NaCl and $BaCl_2$ the molar ionic conductance at infinite dilution are 248.1×10^{-4} , 126.5×10^{-4} and 280.0×10^{-4} $S m^2 mol^{-1}$ respectively. Calculate \wedge_m^o for $Ba(OH)_2$.
- (iii) Illustrate the application of Kohlrausch's law. 5+2+3=10
- (c) (i) Illustrate how the solubility product of a sparingly soluble salt can be determined with the help of conductance measurement.
 - (ii) What is Ostwald dilution law?
 Write its verification, importance
 and limitations. 5+5=10
- (d) (i) Find the mean ionic activity of a uni-univalent electrolyte.
 - (ii) How can you calculate the equilibrium constant of a cell reaction of the type $aA + bB \Rightarrow cC + dD$?

(iii) Calculate the equilibrium constant of the cell reaction

$$2Ag^+ + Zn \implies 2Ag + Z_n^{2+}$$

occurring in the Zn - Ag cell at $25 \,^{\circ}C$ when $\left[Z_n^{2+}\right] = 0.10M$ and $\left[Ag^+\right] = 10M$. The EMF of the cell is found to be 1.62 volts.

- (e) (i) State and explain the Nernst equation.
 - (ii) Find out whether Zn and Ag would react with dilute H_2SO_4 acid or not.

Given:

$$E_{el}^{o} = 0 \text{ for } 2H^{+}, H_{2}(g); Pt$$
 $E_{el}^{o} = -0.76 \text{ V for } Zn^{2+}; Zn$
 $E_{el}^{o} = +0.80 \text{ V for } Ag^{+}; Ag$
 $4+(2\times3)=10$

(f) (i) How can you apply the dipole moment of a molecule to study its molecular structure?

(ii) Find the percentage of ionic character of HCl molecule using SI unit.

Given:

Internuclear distance $(r) = 127 \ pm$ Electronic charge = $1.6 \times .0^{-19} C$ Actual dipole moment = 3.44×10^{-30} coulomb metre.

- (iii) How can you distinguish diamagnetic substances and paramagnetic substances depending on the behaviour in a magnetic field?
- (iv) Explain polar and nonpolar convalent bonds.
- (v) Explain the variation of molar polarization with temperature.

2+2+2+2=10