[This question paper contains 4 printed pages.]

Sr. No. of Question Paper : 738 **G** **Your Roll No.....**

Unique Paper Code : 217501

Name of the Paper : CHHT-511 : Inorganic Chemistry – IV

Name of the Course : **B.Sc. (Hons.) Chemistry**

Semester : V

Duration : 3 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **five** questions in all.
3. **All** questions carry equal marks.

1. (a) Name the following complexes according to the IUPAC system of nomenclature.

   (i) $[ReH_3(P(C_6H_5)_3)_3]$

   (ii) $[Cr(OH)_2(H_2O)_4][AuCl_4]$

   (iii) $[Cl(NH_3)_3Co(NH_2)(OH)Co(NH_3)_3Cl]Cl_2$

   (iv) $[IrCl(NO_2)(en)(CH_3NH_2)_2]$

   (b) Write the formulae of the following complexes :

   (i) Tetraamminedichlororhodium(III)tetracyanozincate(II)

   (ii) Tetramethylammoniumheptaiodozirconate(IV)

   (c) Although gold and platinum have lower ionisation enthalpy than 3d transition elements yet they are noble metals. Explain.

   (d) Lanthanoids show sharp bands in the absorption spectra in contrast to transition elements, explain. (6,3,3,3)

P.T.O.

2. (a) Give all possible geometrical and optical isomers of the following :

(i) $[Co(NH_3)_3(H_2O)ClBr]^+$

(ii) Tris(glycinato)chromium(III)

(b) Draw the Molecular Orbital energy level diagram for a sigma bonded octahedral complex. Explain using MOT that 10 Dq value in $[Co(CN)_6]^{3-}$ ion is increased as a result of pi bonding.

(c) Actinides have a greater tendency to form complexes than lanthanides, explain. (6,6,3)

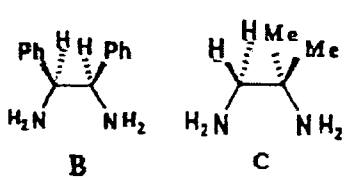
3. (a) Using the valence bond theory (i) assign the electronic configuration to the central metal atom, (ii) predict the type of hybridization involved, (iii) geometry, and (iv) the magnetic moment (in BM) for $[Cr(H_2O)_6]^{2+}$ and $[Cr(CN)_6]^{4-}$.

(b) In a square planar complex, the CFS of the d-orbital energies of a central metal ion decrease in the sequence:

$$d_{x2-y2} > d_{xy} > d_{z2} > d_{xz}, d_{yz}$$

Offer an explanation for the decreasing trend in energies.

(c) Platinum(II) forms a 4-coordinate complex (A) with one molecule of mesostilbenediamine (B) and one molecule of isobutylenediamine (C). It is possible to resolve the complex (A) into optically active isomers. Show that the result proves that the complex does not have tetrahedral geometry and that the result is consistent with square planar geometry.



B C

(d) Which complex ion is more stable $[M(en)_3]^{2+}$ or $[M(dien)_2]^{2+}$ and why ?

(en = ethylenediamine; dien = diethylenetriamine) (6,3,3,3)

4. (a) For the Fe^{2+}, the electron-pairing energy, P, is about 17,600 cm^{-1}. The values of Δ_0 for the complexes $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ are 10,500 cm^{-1} and 32,200 cm^{-1} respectively. Calculate the CFSE for these complexes corresponding to high-spin and low-spin states and predict the possible stable configurations. Give the electron compositions of the t_{2g} and e_g levels of each.

(b) What are 'allowed' and 'forbidden' transitions ? Solution of $[Fe(H_2O)_6]^{2+}$ ion is green but $Fe(CN)_6^{4-}$ is yellow in colour. Explain and characterize the origin of the transitions in these species.

(c) Arrange the following complex ions in the order of increasing Δ_0 giving reasons :

$[Ni(NH_3)_6]^{2+}$, $[Rh(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$.

(d) Lanthanide ions do not for complexes with amines in aqueous solutions. Give reason. (6,3,4,2)

5. (a) Ammonium metavanadate upon acidification with sulphuric acid forms an orange solid A which upon treatment with cone. Sodium hydroxide solution becomes a colourless solution B. When acid is added gradually to B at pH 9 an orange colour compound C is formed. Further addition of acid gives colour change to red and then brown precipitates of D. Identify A to D and write suitable reactions.

(b) Giving chemical equations, explain the following (Any **three**) :

(i) Ferrous sulphate reacts with potassium dichromate under acidic conditions and then potassium ferrocyanide is added.

(ii) V_2O_5 reacts with HCl and NaOH.

(iii) Titanium (II) alkoxides as useful reagents for fixation of nitrogen.

(iv) An aqueous solution of Co(II) chloride is treated with concentrated hydrochloric acid.

(c) Complex $[V(NO_2)_6]^{3-}$ is labile whereas complex $[Cr(NO_2)_6]^{3-}$ is inert in nature. Explain. (6,6,3)

P.T.O.

6. (a) Consider the Latimer diagram for Mn in acidic medium :

$$MnO_4^- \overset{+0.56V}{\text{---------}} MnO_4^{2-} \overset{+2.26V}{\text{--------}} MnO_2 \overset{+0.95V}{\text{--------}} Mn^{3+} \overset{+1.51V}{\text{--------}} Mn^{2+} \overset{-1.19V}{\text{----------}} Mn$$

Answer the following questions :

(i) Is there any tendency of Mn^{2+} to reduce to Mn ? Give reasons.

(ii) Calculate skip step EMF for MnO_2 to Mn^{2+}.

(iii) Which oxidation states of Mn are likely to disproportionate ?

(iv) Which is the most stable species ?

(b) Define Jahn Teller theorem. Which of the following high-spin complexes would you expect to exhibit a Jahn-Teller distortion ? Give reasons.

$[Cr(NH_3)_6]^{3+}$; $[MnCl_6]^{3-}$; $[Fe(H_2O)_6]^{3+}$

(c) Ce^{4+} is used as an oxidizing agent in volumetric analysis. Give reason.

(d) Which is stronger base $La(OH)_3$ or $Lu(OH)_3$? Why ? (6,4,3,2)

7. Attempt **any five** of the following :

(i) Why $[Mn(H_2O)_6]^{2+}$ is pale coloured ?

(ii) Though transition elements possess very high electrode potential yet they are not good reducing agents. Explain.

(iii) Explain the separation of lanthanides by cation exchange chromatography.

(iv) How is the magnetic behaviour of Gd^{3+} and Lu^{3+} different from the rest of the lanthanides ?

(v) Which one is more stable: AgI_2^- or AgF_2^-. Explain.

(vi) The magnetic moment of Cu(II) acetate in solid state is found to have magnetic moment 1.3 B.M. Explain.

(vii) What type of structure do you expect for Co_3O_4 and why ? Explain on the basis of CFT. (3×5)