

[This question paper contains 6 printed pages.]

915

Your Roll No.

B.Sc. (Hons.) / III

C

CHEMISTRY – Paper XIII

(Inorganic Chemistry – III)

Time : 3 Hours

Maximum Marks : 38

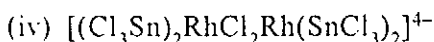
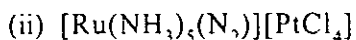
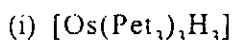
*(Write your Roll No. on the top immediately
on receipt of this question paper.)*

Attempt six questions in all.

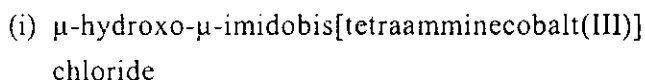
Q. No. 1 is compulsory and carries 8 marks.

All other carry 6 marks each.

1. (a) Give the IUPAC nomenclature for the following complexes :



(b) Write the formulae of the following complexes :



P.T.O.

(ii) Barium tetrafluorobromate(III)

(iii) Ammonium tetrachloroplatinate(II)

(c) The first purely inorganic chiral complex synthesized by Werner was $[\text{Co}\{(\text{OH})_2\text{Co}(\text{NH}_3)_4\}_3]\text{Br}_6$. Write the structure of this complex. (4,3,1)

2. (a) An octahedral complex *A* of the molecular formula $\text{CrCl}_3 \cdot 5\text{H}_2\text{O}$ has molar conductivity corresponding to 1:2 electrolyte. Dilute acidify solution of *A* on standing for many days changes to *B* having molar conductance corresponding to 1:3 electrolyte. Deduce structures of *A* and *B* on the basis of Werner's theory.

(b) Depict the structures of all possible isomers of $[\text{Rh}\{(\text{NH})_2\text{SO}_2\}_2(\text{H}_2\text{O})_2]$.

(c) Name the type of isomerism in the following pairs of isomers :

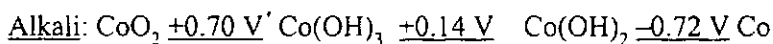
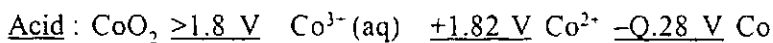
(i) $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ and $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NO}_2)_6]$

(ii) $[\text{Pt}(\text{dipy})(\text{SCN})_2]$ and $[\text{Pt}(\text{dipy})(\text{NCS})_2]$

(2,2,2)

3. (a) For a complex ion $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ the mean pairing energy P is found to be $28,000 \text{ cm}^{-1}$. If the magnitude of Δ_0 is $21,000 \text{ cm}^{-1}$, calculate the CFSE or the complex in configuration corresponding to high spin and low spin states. In which of the two states is the complex more stable.
- (b) The experimentally determined hydration energy for Mn^{2+} agrees with the calculated value. But for Fe^{2+} and Co^{2+} the experimentally determined hydration energy value is found to be higher than the calculated value.
- (c) The magnetic moment of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ was found to be 5.91 BM and of $[\text{Fe}(\text{CN})_6]^{3-}$ to be 1.91 BM. Account for, the above observation on the basis of valence bond theory. (2,2,2)
4. (a) With the help of molecular orbital theory explain the position of CO as a strong field ligand in spectrochemical series.
- (b) Which complex ion would show greater crystal field splitting and why ?
- (i) $[\text{PtCl}_4]^{2-}$ or $[\text{PdCl}_4]^{2-}$
- (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{Fe}(\text{CN})_6]^{3-}$

- (c) Transition metals and their compounds act as good catalysts. (2,2,2)
5. (a) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is violet in colour whereas TiO_2 is white.
- (b) Explain whether Mn_3O_4 and Fe_3O_4 will adopt a normal spinel structure or inverse spinel structure.
- (c) Why is the crystal field splitting in tetrahedral complexes (Δ_t) is only 4/9 of the corresponding splitting in octahedral field (Δ_0). (2,2,2)
6. (a) $\text{K}_2[\text{Ni F}_6]$ is diamagnetic while $\text{K}_3[\text{Co F}_6]$ is paramagnetic. Both have same d^6 configuration. Explain on the basis of CFT.
- (b) Given below are the Latimer diagrams for cobalt in acidic and alkaline media :



- (i) In which medium, acidic or alkaline is $\text{Co}(\text{IV})$ more stable ?

- (ii) In which medium, acidic or alkaline, can Co^{2-} be more easily oxidised to Co^{3+} ?
- (iii) Is there any species likely to undergo disproportionation. Explain.
- (c) An aq. solution of NiCl_2 is pale green, on adding ammonia colour changes to blue. When dimethyl glyoxime reagent is added to blue solution, red ppt is obtained. Explain these observations on the basis of crystal field theory. (1½,3,1½)
7. (a) A complex of a certain metal ion has a magnetic moment of 4.90 BM. Another complex of the same metal, in the same oxidation state, has a zero magnetic moment. The central metal ion could be : Cr (III), Mn (II), Fe (II), Fe (III), Co (II).
- (b) Predict the products A and B :
- (i) $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^{2-} + \text{NO}_2^- \longrightarrow \text{A}$
- (ii) A + $\text{NO}_2^- \longrightarrow \text{B}$
- (c) What is lanthanide contraction ? What is its effect on the chemistry of 5d series of transition elements ? (2,2,2)

8. (a) Both $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Cr}(\text{CN})_6]^{3-}$ are thermodynamically stable, yet the former is much more labile than the latter. Explain.
- (b) Explain the principle behind the separation of lanthanides by ion-exchange method.
- (c) Ce^{4+} acts as oxidising agent whereas Eu^{2+} as reducing agent. Explain.
- (d) Explain the amphoteric nature of V_2O_5 .

(2,2,1,1)