

2022

CHEMISTRY — HONOURS

Paper : CC-10

MURALIDHAR GIRLS' COLLEGE (Inorganic Chemistry)
LIBRARY

Full Marks : 50

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words
as far as practicable.*Answer **question no. 1** and **any eight** questions from the rest.1. Answer **any ten** questions :

1×10

- Find out the electronic state of an ion with 3F_4 ground term.
 - Cite an example of tetragonally compressed molecule.
 - What would be spin only magnetic moment of Mn^{3+} in $[Mn(H_2O)_6]Cl_3$?
 - Show the Scheme of preparation of *cis*- $PtCl_2(C_2H_4)(NH_3)$ from $[PtCl_4]^{2-}$.
 - Account for the dark red colour of $[Fe(bipy)_3]^{2+}$ (bipy = bipyridine).
 - Identify the metal ion(s) able to show Jahn-Teller effect in their high spin state :
Cr(II), Fe(II), Ni(II), Mn(IV), Mn(III)
 - Identify the transition(s) which are not allowed according to selection rule :
 $2s \rightarrow 2p$, $3p \rightarrow 3d$, $2s \rightarrow 3p$, $3s \rightarrow 3d$, $1s \rightarrow 2s$.
 - Find out the number of unpaired electron(s) in Gd ($z = 64$).
 - Arrange the following ligands in a spectrochemical series : H_2O , NH_3 , F^- , OH^- , CN^- , CO
 - State ground state term for Fe^{2+} .
 - Mention the M^{2+} ion in 3d-transition series, that possesses minimum ionic radius value in low spin state.
 - Give the structure of the complex 'A'. $[Pt(Cl)_3(NO_2)]^{2-} \xrightarrow{NO_2^-} A$.
- Using Orgel diagram, explain the possible transitions of $[Cr(H_2O)_6]^{3+}$ complex. Which transition corresponds to 10 Dq value?
 - Explain the order of LMCT transition energies : $MnO_4^- < TcO_4^- < ReO_4^-$.

3+2

Please Turn Over

3. (a) Pd(II) and Pt(II) form square planar complexes exclusively but Ni(II) forms square planar complexes under certain condition. Explain.
- (b) Δ_o for three hexaamines differs as follows :
- $[\text{Co}(\text{NH}_3)_6]^{3+} = 23000 \text{ cm}^{-1}$
- $[\text{Rh}(\text{NH}_3)_6]^{3+} = 34000 \text{ cm}^{-1}$
- $[\text{Ir}(\text{NH}_3)_6]^{3+} = 41000 \text{ cm}^{-1}$
- Identify the factor(s) involved for this difference. 3+2
4. (a) $10 Dq$ for $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ is known from electronic spectrum as 21000 cm^{-1} . The pairing energy of Mn(III) is 28800 cm^{-1} . Predict whether the complex is high spin or low spin and also calculate the CFSE value. 3+2
- (b) Cr(II) acetate monohydrate is diamagnetic. Explain. 3+2
5. (a) How will you separate lanthanides using ion-exchange methodology?
- (b) Estimation of activation energy for aquation reaction of octahedral Co(III) and Cr(III) complexes indicates that a pentagonal bipyramid intermediate path is followed by Cr(III), while for Co(III) the intermediate is a square pyramid. Comment on their mechanistic path. 3+2
6. (a) Addition of concentrated HCl to pale pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ changes its colour to blue but similar addition to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ has no effect. Justify this from the point of OSSE. 3+2
- (b) Explain the exceptional stability of +2 oxidation state of Eu ($z = 63$) and Yb ($z = 70$). 3+2
7. (a) Lanthanides show poor tendency to form complexes with π acid ligands while the same is greater for actinides. Explain.
- (b) In high spin octahedral and tetrahedral complexes of Co(II) three unpaired electrons are present; but magnetic moment for the octahedral complexes are 4.8-5.2 BM whereas for tetrahedral it is 4.2-4.8 BM.— Explain. 3+2
8. (a) Explain mechanistically the high substitution rate for square planar platinum (II) complexes in presence of a π -acid ligand.
- (b) Between two redox couples, $[\text{Co}(\text{NH}_3)_6]^{3+}/[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}/[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, which one is more oxidizing and why? Explain on the basis of CFT. 3+2
9. (a) Actinides show variety of oxidation states while lanthanides exhibit uniform (+3) oxidation state. Why is it so?
- (b) Fe^{3+} (aq) reacts rapidly with EDTA at room temperature, while Cr^{3+} (aq) reacts slowly. Comment. 3+2
10. (a) What is lanthanide contraction? Explain why Zr and Hf have similar properties although they belong to different periods.
- (b) Explain the variation of hydration energy of M^{2+} ion in 3d transition series. 3+2

11. (a) Both the metal ions in $K_3[CuF_6]$ and $K[AgF_4]$ possess d^8 electronic configuration but one is paramagnetic and the other is diamagnetic. Identify them with justification.
- (b) Predict the colour of the complex $[Ti(H_2O)_6]^{3+}$ [Given $\Delta_o = 20.000 \text{ cm}^{-1}$]. 3+2
12. (a) Explain the abrupt drop of $\log k_3$ value in the complexation of $[Cu(H_2O)_6]^{2+}$ with ethylenediamine at 30°C .
- $[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(H_2O)_4en]^{2+} + 2H_2O \quad \log k_1 = 10.72$
- $[Cu(H_2O)_4en]^{2+} + en \rightleftharpoons [Cu(H_2O)_2(en)_2]^{2+} + 2H_2O \quad \log k_2 = 9.31$
- $[Cu(H_2O)_2(en)_2]^{2+} + en \rightleftharpoons [Cu(en)_3]^{2+} + 2H_2O \quad \log k_3 = -0.90$
- (b) Establish the structure of $NiFe_2O_4$ and Mn_3O_4 as normal or inverse spinel. 3+2
13. (a) Justify the distorted octahedral structure of $[Cu(H_2O)_6](ClO_4)_2$
- (b) Explain antiferromagnetism through superexchange using a suitable example. 3+2

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