2022

CHEMISTRY — HONOURS

Paper : CC-10

(Inorganic Chemistry)

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.

1×10

1. Answer ***any ten*** questions :

   (a) Find out the electronic state of an ion with $^3F_4$ ground term.

   (b) Cite an example of tetragonally compressed molecule.

   (c) What would be spin only magnetic moment of Mn^{3+} in $[Mn(H_2O)_6]Cl_3$?

   (d) Show the Scheme of preparation of *cis*- $PtCl_2(C_2H_4)(NH_3)$ from $[PtCl_4]^{2-}$.

   (e) Account for the dark red colour of $[Fe(bipy)_3]^{2+}$ (bipy = bipyridine).

   (f) 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)

   (g) Identify the transition(s) which are not allowed according to selection rule :

   $2s \rightarrow 2p$, $3p \rightarrow 3d$, $2s \rightarrow 3p$, $3s \rightarrow 3d$, $1s \rightarrow 2s$.

   (h) Find out the number of unpaired electron(s) in Gd ($z = 64$).

   (i) Arrange the following ligands in a spectrochemical series : H_2O, NH_3, F^-, OH^-, CN^-, CO

   (j) State ground state term for Fe^{2-}.

   (k) Mention the M^{2+} ion in 3d-transition series, that possesses minimum ionic radius value in low spin state.

   (l) Give the structure of the complex 'A'. $[Pt(Cl)_3(NO_2)]^{2-} \xrightarrow{NO_2^-} A$.

2. (a) Using Orgel diagram, explain the possible transitions of $[Cr(H_2O)_6]^{3+}$ complex. Which transition corresponds to 10 Dq value?

   (b) Explain the order of LMCT transition energies : $MnO_4^- < TcO_4^- < ReO_4^-$. 3+2

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 :

   $[Co(NH_3)_6]^{3+} = 23000\ cm^{-1}$

   $[Rh(NH_3)_6]^{3+} = 34000\ cm^{-1}$

   $[Ir(NH_3)_6]^{3+} = 41000\ cm^{-1}$

   Identify the factor(s) involved for this difference. 3+2

4. (a) 10 Dq for $[Mn(H_2O)_6]^{3+}$ 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.

   (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 $[Co(H_2O)_6]^{2+}$ changes its colour to blue but similar addition to $[Ni(H_2O)_6]^{2+}$ has no effect. Justify this from the point of OSSE.

   (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, $[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}$ and $[Co(H_2O)_6]^{3+}/[Co(H_2O)_6]^{2+}$, 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^9 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 $\Delta_o = 20,000\ cm^{-1}$]. 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
