This question paper contains 4+2 printed pages]

Your	Roll	No.	
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1259

B.Sc. (Hons.)/III

A

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 carries 8 marks.

All other carry 6 marks each.

- 1. Explain with reasons any four of the following observations:
 - (a) Lanthanides show sharp line like bands in the absorption spectra while transition elements show broad bands.
 - (b) 4d and 5d elements usually form low spin complexes.
 - (c) The basic strength of lanthanide oxides, La₂O₃, decreases with increase in oxidation number.

P.T.O.

- (d) CrO₃ is strongly oxidizing but WO₃ is not.
- (e) Knowledge of magnetic moment is often necessary for a correct assignment of the electronic configuration according to valence bond theory.
- 2. (a) Name the following complexes according to IUPAC system of nomenclature:
 - (i) $[PtCl(NO_2)(en)(py)_2]SO_4$
 - (ii) [(CH₃)₄N]₃ [CrCl₆]
 - (iii) [Pt(py)₄] [PtCl₄]
 - (iv) $[CO_3Fe (CO)_3 Fe(CO)_3]$ 1×4
 - (b) Write the formulae of the following complexes:
 - (i) Aluminium dichloromethylplatinate (II)
 - (ii) μ-amido-μ-hydroxobis (tetraammine) dicobalt (III)

ion

- (a) The magnetic moments of [MnBr₄]²⁻ and [Mn(CN)₆]³⁻
 are 5.9 and 2.8 BM respectively. Using valence bond theory, assign geometries to these complexes.
 - (b) Which complex in each of the following pairs will have greater crystal field splitting and why?

$$[Fe(H_2O)_6]^{3+}$$
 Or $[Fe(CN)_6]^{3-}$ $[Co(CH_3)_6]^{3+}$ Or $[Rh(NH_3)_6]^{3+}$.

(c) From the following data, predict in which case it is easier to oxidize Fe(II) to Fe (III):

$$[Fe(H_2O)_6]^{3+} + e \longrightarrow [Fe(H_2O)_6]^{2+} \stackrel{E}{=}_0 = 0.70 \text{ V}$$

 $[Fe(CN)_6]^{3-} + e \longrightarrow [Fe(CN)_6]^{2-} \stackrel{E}{=}_0 = 0.36 \text{ V}$

- 4. (a) For $[Cr(H_2O)_6]^{2+}$, the mean pairing energy, P, is found to be 23500 cm⁻¹ and Δ_0 value is 13900 cm⁻¹.
 - (i) Calculate the CFSE for this complex corresponding to high-spin and low-spin states.
 - (ii) Which state is more stable?
 - (b) Is FeFe₃O₄ a normal or inverted spinel? Explain. 2
 P.T.O.

- 5. Giving reasons, account for the following:
 - (a) The magnitude of the crystal field splitting, Δ_p , in tetrahedral complexes is considerably less than that in octahedral fields.
 - (b) Ethylene diammine forms a more stable complex than its tetramethyl derivative.
 - (c) Actinides show a greater tendency to form complexes than lanthanides. 3×2
- 6. (a) Use the Latimer diagrams below to answer the following questions:

Acid:

$$MnO_4$$
 $\xrightarrow{0.56}$ MnO_4^{2-} $\xrightarrow{2.26}$ MnO_2 $\xrightarrow{0.95}$ Mn^{3+} $\xrightarrow{1.51}$ Mn^{2+} $\xrightarrow{-1.18}$ Mn

Alkali:

$$MnO_4$$
 $\xrightarrow{0.58}$ MnO_4^{2-} $\xrightarrow{0.60}$ MnO_2 $\xrightarrow{0.15}$ $Mn(OH)_3$ $\xrightarrow{-0.25}$ $Mn(OH)_2$ $\xrightarrow{-0.156}$ Mn

- (i) Find out the oxidation states in acidic medium which undergo disproportionation.
- (ii) In which medium, acidic or alkaline, is Mn (III) more stable?

- (b) In the crystal structure of CuF₂, Cu²⁺ ion is surrounded
 by six F⁻ with four F⁻ at a distance of 193 pm while
 two F⁻ at 227 pm. Explain giving reasons.
- 7. (a) Name the type of isomerism in each of the following pairs:
 - (i) $[Pd(py)_2(SCN)_2]$ and $[Pd(py)_2(NSC)_2]$
 - (ii) $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$
 - (b) Draw the structures of all possible isomers of [Co(en)₂Cl₂]⁺ ion.
 - (c) Giving chemical equations, state what happens when :
 - (i) Hydrogen peroxide is added to acidified potassium dichromate solution forming a blue colour.
 - (ii) Potassium permanganate is added to cold concentrated sulphuric acid. 3×2

8. (a) Which of the following complexes are expected to be labile according to valence bond theory:

 $[{\rm Cr}({\rm NH_3})_6]^{3+},\ [{\rm MnCl}_6]^{3-}\ \ {\rm and}\ \ [{\rm Co}({\rm CN})_6]^{3-}.$

- (b) Draw the MO energy diagram for the complex ion $[\text{Co(NH}_3)_6]^{3+}.$
- (c) $[FeF_6]^{3-}$ ion is colourless although iron (III) is a d^5 ion. Explain.

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