

[This question paper contains 6 printed pages.]

Sr. No. of Question Paper : 6015

D

Your Roll No.....

Unique Paper Code : 217501

Name of the Course : **B.Sc. (H) CHEMISTRY**
(ADMISSIONS OF 2010 AND ONWARDS)

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

Semester : V

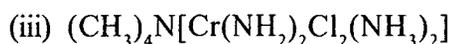
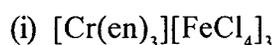
Duration : 3 Hours

Maximum Marks : 75

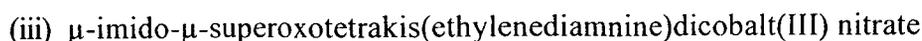
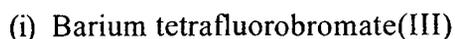
Instructions for Candidates

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

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



- (b) Write the formulae of the following complexes :



P.T.O.

- (c) Calculate the KJ mol^{-1} the crystal field theory stabilization energy (CFSE) attained by Fe^{2+} in an oxide environment. Given Δ_0 for Fe^{2+} in an oxide environment 124 KJ mol^{-1} . What will be CFSE in tetrahedral environment ?
- (d) A solution containing 0.319 g of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was passed through cation exchange resin in the acid form and the acid liberated was titrated with a standard solution of NaOH . This required 19.0 mL of 0.125 M NaOH . Find out the correct formula of the Cr(III) complex.

(Molecular weight of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is 266.5). (6,3,3,3)

2. (a) Explain the following :

- (i) FeI_3 does not exist in pure state.
- (ii) Insoluble CrCl_3 dissolve readily on addition of even trace of reducing agent.
- (iii) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue but $\text{Cu}(\text{CN})_4^{2-}$ is colorless.
- (iv) Among the lanthanide ions the magnetic moment of only Gd^{3+} is in agreement with the moment calculated from spin only formula. Why ?
- (v) $4d$ and $5d$ elements usually form low spin complexes. Why ?
- (vi) All the Cr-F bond lengths in $[\text{CrF}_6]^{3-}$ are equal but in $[\text{CrF}_6]^{4-}$ two Cr-F bond lengths are shorter than the remaining four.

(b) How will you distinguish between following isomers ?

- (i) cis-trans $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
- (ii) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ & $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ (12,3)

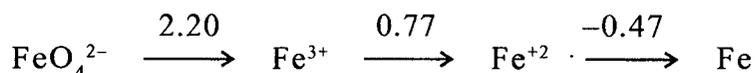
3. (a) An oxide (A) of an element when treated with Cl_2 in the presence of carbon gave compound (B) which fumes in moist air and hydrolyzed partially to give compound (C) when compound (B) is treated with alcohol in the presence of NH_3 compound (D) is formed. Identify compounds (A), (B), (C) and (D) and also write down the reaction involved it.
- (b) When Pentaamminecarbonatocobalt(III) complex is treated with NaNO_2 and dil. HCl unstable red color compound (A) is formed. If this compound is heated or conc. HCl is used a yellow colored stable compound (B) is formed. Both the compounds are isomers. Name the type of isomerism and also write down the structure of both the compounds.
- (c) On the basis of molecular orbital theory, explain the ability of cyanide and fluoride to produce large and small crystal field splitting energy respectively.
- (d) The absorption band of cerium(III) ion is broad, while that of other lanthanide ions is sharp. Explain. (6,3,3,3)
4. (a) An orange coloured compound (A) on heating gives green coloured compound (B) and oxygen. On acidification of compound (B) a compound (C) is formed. On treatment of compound (C) with zinc in the presence of dil. HCl a blue colored compound (D) is formed. Compound (D) on treatment with sodium acetate gives a red compound (E). Identify (A), (B), (C), (D) and (E). Discuss the structure and magnetic behavior of compound (E).
- (b) Using VBT predicts the molecular shape and magnetic moment of the following species :
- (i) $[\text{Ni}(\text{CN})_4]^{4-}$
- (ii) $[\text{Cr}(\text{NO}_2)_6]^{3-}$
- (iii) $[\text{CoCl}_4]^{2-}$

- (c) Work out the number of unpaired electrons in the ions : Nd^{3+} , Eu^{3+} and Dy^{3+} .
(Atomic number of Nd = 60; Eu = 63 and Dy = 66). (6,6,3)

5. (a) The crystal field splittings Δ are listed in the following three ammine complexes of cobalt. Explain the difference in Δ values.

Complex	$\Delta(\text{cm}^{-1})$
$[\text{Co}(\text{NH}_3)_6]^{3+}$	22 900
$[\text{Co}(\text{NH}_3)_6]^{2+}$	10 200
$[\text{Co}(\text{NH}_3)_4]^{2+}$	5 900

- (b) Would you predict that NiCr_2O_4 would adopt a normal spinel or an inverse spinel structure? Explain your reasoning.
- (c) Given below are the Latimer diagrams for Fe in acidic media :



Answers the following questions :

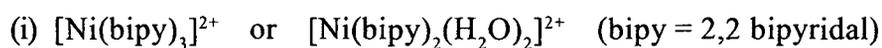
- (i) Why is FeO_4^{2-} a strong oxidizing agent?
 - (ii) Is there any state which undergoes disproportionation?
 - (iii) Is there any tendency of Fe^{2+} to reduce Fe?
- (d) Discuss each of the following observations :
- (i) High-spin Mn(II) complexes are only faintly colored, while low-spin complexes are quite strongly colored.
 - (ii) Explain ion exchange method for separation of lanthanides.

(3,3,3,6)

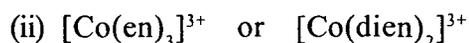
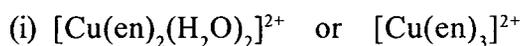
6. (a) The third ionization energy of chromium is 157 kJ mol^{-1} greater than that of vanadium, so it is harder to oxidise $\text{Cr}^{2+}(\text{g})$ than $\text{V}^{2+}(\text{g})$. But in aqueous solutions chromium(II) is more powerful reducing agent than vanadium(II). [Given the spectroscopic values of Δ_0 :

Vanadium ($\Delta_0(+2) = 12300 \text{ cm}^{-1}$, $\Delta_0(+3) = 18600 \text{ cm}^{-1}$) and chromium ($\Delta_0(+2) = 14100 \text{ cm}^{-1}$, $\Delta_0(+3) = 17000 \text{ cm}^{-1}$].

- (b) Explain Labile and inert complexes. Which one of the following is more labile? Justify your answer:



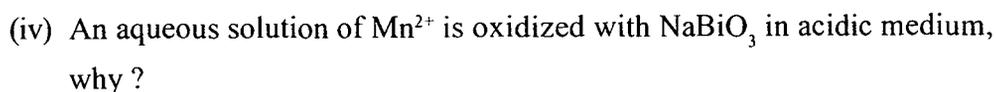
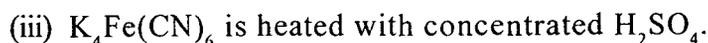
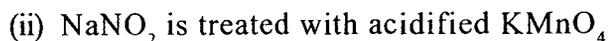
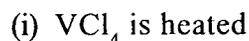
- (c) Explain why chelated complexes are more stable as compared to non-chelated complexes. Which one of the following is more stable? Justify your answer:



[en = ethylenediamine; dien = diethylenetriamine]

- (d) Actinides have a greater tendency to form complexes than lanthanides. Why?
- (e) Tetrahedral complexes are high spin, explain. (4,4,4,2,1)

7. (a) What happens when? Give balanced chemical equations:



- (b) Write down the formula, name and structure of a first pure inorganic optically active compound.
- (c) Write down all the possible isomers of $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{Cl}$ compound.
- (d) Although $\text{Co}^{2+}(\text{aq})$ forms a tetrachlorocomplex on treatment with conc. HCl , $\text{Ni}^{2+}(\text{aq})$ does not do so. Explain. (6,4,4,1)