# II Semester M.Sc. Examination, June 2015 (CBCS) CHEMISTRY <br> C-201: Inorganic Chemistry - II (Coordination Chemistry) 

Time: 3 Hours
Max. Marks : 70
Instruction : Answer question 1 and any five of the remaining.

1. Answerten questions of the following :
a) Which of the following metal complexes is expected to be subject to a John - Teller distortion ? Explain
i) $\left[\mathrm{CrF}_{6}\right]^{2-}$
ii) $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
b) Distinguish between kinetic and thermodynamic stability of metal complexes.
c) Account for the fact that CO stabilizes the low oxidation states of metal ions.
d) Calculate the CFSE of an octahedral Cr (III) complex for which

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\Delta_{0}=23,100 \mathrm{~cm}^{-1} \text { and } \mathrm{P}=17,200 \mathrm{~cm}^{-1} .
$$

e) Predict the geometries of complexes whose coordination numbers are 5 and 7 .
f) Mention the limitations of CFT.
g) Some value of Racah parameters are 920,760 and $1050 \mathrm{~cm}^{-1}$. Assign these values to the ions, $\mathrm{V}^{2+}, \mathrm{Cr}^{3+}$ and $\mathrm{Mn}^{4+}$. Explain your choice.
h) Arrange the given Russell - Saunders terms in increasing order of energy : ${ }^{3} \mathrm{P},{ }^{1} \mathrm{G},{ }^{1} \mathrm{P}$ and ${ }^{3} \mathrm{~F}$. Explain your answer.
i) Explain why lanthanides exhibit sharp absorption bands.
j) What is meant by spin cross over? Mention a system exhibiting it.
k) For $\mathrm{Hg}\left[\mathrm{Co}(\mathrm{SCN})_{4}\right]$, the value of corrected molar magnetic susceptibility was found to be $16.44 \times 10^{-6} \mathrm{cgs}$ at 300 K . Calculate its effective magnetic moment.
I) State and explain Kasha's rule.
2. a) What are metal chelates ? Explain with suitable examples.
b) Describe the formation constant of a metal complex by pH metric method.
c) The stepwise stability constant values for $\mathrm{Cu}^{2+} / \mathrm{NH}_{3}$ system are as follows : $\log k_{1}=4.25, \log k_{2}=3.56, \log k_{3}=2.96$ and $\log k_{4}=2.35$. Calculate the overall stability constant of $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$.
3. a) Explain any two experimental evidences for partial covalency in $M$-L bonding of complexes.
b) Sketch the MO energy level diagram for $\left[\mathrm{CoF}_{6}\right]^{3+}$ involving $\sigma$ bonding only.
c) Discuss how CFT explains color of a complex.
$(4+3+3)$
4. a) Show the spliting pattern of d-orbitals in octahedral and tetrahedral complexes. Explain why 10 Dq value of an octahedral complex is greater than that of a tetrahedral complex.
b) Discuss the bonding and structure of a metal nitrosyl.
c) Describe the stereochemical non-rigidity in $\mathrm{Fe}_{2} \mathrm{Cp}_{2}(\mathrm{CO})_{4}$.
5. a) Calculate the values of $B$ ' and $\beta$ for $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ which exhibits absorption bands at 10040, 16500 and $20920 \mathrm{~cm}^{-1}$. Assign these transitions (Given : B for free $\mathrm{Cr}^{3+}$ ion $=650 \mathrm{~cm}^{-1}$ )
b) Giving suitable examples, mention different types of charge transfer transitions. Explain why compounds exhibiting charge transfer transitions are intensely colored.
c) In what way Tanabe Sugano diagrams are different from Orgel diagrams?
6. a) Discuss the magnetic properties of actinide metal complexes.
b) Sketch the graph and explain the effect of temperature on magnetic susceptibility of ferromagnetic and antiferromagnetic compounds.
c) The complexes $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+},\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ and $\left[\mathrm{MnCl}_{4}\right]^{2-}$ have magnetic moments of nearly 5.9 BM. What does this tell you about electrons arrangement in these complexes? Why is the spin-only formula so precise in these complexes?
7. a) Discuss the preparation and bonding in phosphine complexes.
b) Give a brief account of self assembly in supramolecular chemistry.
c) Explain why an electronic transition for $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ is spin forbidden but for $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ is spin allowed?
8. a) With the help Jablonskii diagram, indicate the various photophysical processes.
b) With suitable examples, explain photo substitution and photo-redox reactions.
c) Draw the possible geometrical and optical isomers $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}\right]$.


