Reg. No. | | | | | | | | | |

CHH 501

Third Semester M.Sc. Degree Examination, December 2018
CHEMISTRY
(CBCS : 2016 – 17 Syllabus) (New Syllabus)
Coordination Chemistry

Time : 3 Hours Max. Marks : 70

Note : 1) *Answer **all** questions in Part – **A** and **any four full** questions from Part – **B**.*
2) *Figures to the **right** indicate marks.*

PART – A

1. Answer **all** questions. **(9×2=18)**

a) Find the ground term of the configurations $3d^5$ of Mn^{+2} and $3d^3$ of Cr^{3+}.

b) Account for the fact that the nature of the intensely coloured $KMnO_4$ and CrO_4^{2-}.

c) Distinguish between intramolecular and intermolecular photo oxidation-reduction reactions.

d) Calculate the magnetic moments of manganese (III) in both strong and weak octahedral fields.

e) Give the meaning of the terms magnetic susceptibility and molar susceptibility.

f) The free sulphate ion shows two IR active bands at 1104 and 613 cm^{-1}, but in complex $[Co(NH_3)_5SO_4]Br$, each band is split into two peaks. Why ?

g) Design two step synthesis of *cis*- and *trans*- $[Pt(NH_3)_2Cl_2]$ using *trans*-effect.

h) The ammonia molecule is replaced by ethylenediamine in $[Co(NH_3)_5Cl]^{2+}$ complex ion, the rate of equation of the complex is decreased. Why ?

i) What is the preferred mechanism of substitution reactions of octahedral coordination compounds ?

PART – B

Answer **any four full** questions: **(4×13 =52)**

2. a) State and explain Laporte orbital selection rule and spin selection rule.

   b) Explain, why an electronic transition for high spin $[Mn(H_2O)_6]^{2+}$ is spin forbidden, but for $[Co(H_2O)_6]^{2+}$ is spin allowed.

   c) Draw the Tanabe-Sugano diagram for $[Ni(OH_2)_6]^{2+}$ and calculate Δ_o and B for the same complex ion (Given absorption at 8500, 15400 and 26000 cm^{-1}). **(4+4+5=13)**

3. a) Explain the mechanism of photoredox reactions.

   b) What are charge transfer transitions ? How they are different from d-d transitions ?

   c) Explain solar energy conversion by taking $[Ru(bipy)_3]^{2+/3+}$ complex as an example. Discuss its applications. **(4+4+5=13)**

4. a) Calculate a value for μ_{eff} for $[Ni(H_2O)_6]^{2+}$ taking into account spin-orbit coupling (Given $\lambda = -315$ cm^{-1} and $\Delta_o = 8500$ cm^{-1}).

   b) Write briefly on magnetic properties of lanthanides and actinides.

   c) Indicate the changes that occur in the IR spectra of carbonate and perchlorate groups upon complexation. **(4+4+5=13)**

5. a) Discuss the Mossbauer spectra of $K_3[Fe(CN)_6]$, $Na_2[Fe(CN)_5NO]$, $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5NH_3]^{3-}$.

   b) Interpret the essential features of the EPR spectrum of bis-salicylaldimine copper (II) complex.

   c) The CO stretching frequencies for Ni $(CO)_4$, $Co(CO)_4^-$ and Fe $(CO)_4^{2-}$ are 2060, 1890 and 1790 cm^{-1}. Interpret these. **(5+4+4=13)**

6. a) Write briefly on the isomerization reaction involved in *cis*-and *trans*-$[Co(en)_2Cl_2]^+$.

   b) In the octahedral substitution reaction $[Co(NH_3)_5X]^{2+} + H_2O$, which ligand is expected to yield the larger rate constant for substitution X = F^- or I^- ? Explain.

   c) Explain the mechanism involved in those reactions where there is no M – L bond cleavage. **(5+4+4=13)**

7. a) Discuss the substitution in square planar complexes with respect to the influence of solvent, leaving group and entering group.

   b) Outline the mechanism of inner-sphere electron transfer reaction with suitable example.

   c) What are two electron transfer reactions ? How this reaction is useful in the preparation of coordination compounds ? **(5+4+4=13)**
