Q.P. Code : 60761

Second Semester M.Sc. Degree Examination, July 2019

(CBCS Scheme)

Chemistry

Paper C 201 – INORGANIC CHEMISTRY – II

Time : 3 Hours] *[Max. Marks : 70*

*Instructions to Candidates : Answer Question Number **1** and any **FIVE** of the remaining.*

1. Answer any **TEN** of the following : **(10 × 2 = 20)**

   (a) Enumerate the factors responsible for the steady decrease in stepwise stability constants of a reaction $M + n\,[L] \rightleftharpoons ML_n$.

   (b) Distinguish between kinetic and thermodynamic stability of metal complexes.

   (c) Among the following complexes $[Mn(CO_6)]^+$, $Cr(CO)_6$ and $[Fe(CO)_4]^{2-}$ indicate the complex with the shortest "CO" bond and the one with the shortest M-C bond distance.

   (d) Predict the geometries of metal complexes whose coordination number is 8. Give one example for each type.

   (e) How is ESR spectroscopy helpful in predicting the covalent character in metal complexes?

   (f) For $[CrL_6]^{2+}$ complex, Δ_0 and P are 13900 and 23500 cm^{-1}, respectively. Calculate CFSE for low and high-spin states.

   (g) What is meant by spin crossover?

   (h) Account for the room temperature lower magnetic moment of copper acetate.

   (i) Obtain the ground terms for d^2 and d^8 metal ions.

   (j) Calculate the total number of microstates for Ni^{2+} and Mn^{2+}.

   (k) What is the origin of the intense yellow collour of CrO_4^{2-} ?

   (l) Predict the products of the following reactions :

   (i) $MnC_p(CO)_3 + HSiCl_3 \xrightarrow{hr} ? + ?$

   (ii) $2[Mn(CO)_4Br]_2 \xrightarrow{hr} ? + ?$

2. (a) Explain the basis on which the spectrochemical series of ligands setup. Point out its limitations.

(b) What is Jahn-Teller distortion? Sketch and explain the splitting of metal d-orbitals in ML_6 complex, when M-2 bonds along the Z-axis are compressed and elongated.

(c) Illustrate the splitting of d-orbitals in square planar and octahedral crystal fields. **(3 + 4 + 3 = 10)**

3. (a) Construct the molecular orbital diagram of $[COF_6]^{3-}$ with only σ - bonding. Calculate the spin-only magnetic moment.

(b) Discuss stereochemical non rigidity in the complex $C_p(CO)Fe(\mu-CO)_2Fe(CO)C_p$.

(c) Describe the structure and bonding in metal dinitrogen complexes. **(4 + 3 + 3 = 10)**

4. (a) Discuss the factors that affect stability of metal complexes.

(b) Distinguish the bonding in

(i) linear M-NO group and angular M-NO group

(ii) metal hydride and metal dihydrogen complexes. **(5 + 5 = 10)**

5. (a) Explain briefly on the determination of stability constant of a metal complex by spectrophotometric method.

(b) $[Ni(H_2O)_6]^{2+}$ exhibits absorption bands at 8700, 14500 and 25000 cm^{-1}. Assign the transitions and calculate the values of 10 Dq, B and B' (given B for free Ni^{2+} ion = 1040 cm^{-1}).

(c) Explain the significance of Racah parameters. **(4 + 3 + 3 = 10)**

6. (a) Setup an Orgel diagram for a metal complex with d^7 electron configuration. What are the other electron configurations which this diagram can represent?

(b) State the selection rules in electronic spectroscopy. Discuss briefly on the mechanisms by which these rules are relaxed.

(c) Write briefly on the spectral properties of lanthanides. **(3 + 4 + 3 = 10)**

7. (a) Describe briefly on the determination of magnetic susceptibility by Gouy method.

(b) What is spin orbit coupling? Discuss its impact on magnetic properties of complexes.

(c) State and explain Kasha's rule. **(4 + 3 + 3 = 10)**

8. (a) With suitable examples, explain photosubstitution and photoredox reactions encountered in metal complexes.

(b) Sketch the graph and explain the effect of temperature on ferro and antiferromagnetic compounds.

(c) Explain the magnetic properties of $[Ni(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ using crystal field theory. **(4 + 3 + 3 = 10)**