M. Sc. Chemistry Examination, 2022

(4th Semester)

Inorganic Chemistry Special

Paper – XIV-I

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answer script for each Unit.

UNIT: I-4141

1. Justify the following statements: 5×3

   a) Diamagnetism originating from the spinning motion of the electron and nucleus is negligibly small compared to the orbital motions of the electrons.

   b) Temperature dependent molar magnetic susceptibility data for paramagnetic systems with weak antiferro- and ferromagnetic interactions help to determine Curie and Weiss Constants.

   c) The magnetic moment of $K_2[OsCl_6]$ increases from 1.44 B.M. to 1.94 B.M. when it is diluted with the isomorphous diamagnetic substances $K_2[PtCl_6]$.

   d) For the low spin octahedral complexes of Mn(III), Os(IV) and Ru(IV), μ_{obs} (at 300 K) follows the sequence: Mn(III) (3.5 B.M.) > Ru(IV) (2.65 B.M.) > Os(IV) (1.50 B.M.).

   e) $[Cr(CH_3COO)_2.H_2O]_2$ is diamagnetic.

2. Answer the following questions:

a) What do you mean by Lande Interval rule? Illustrate with Tb^{3+} ($\lambda = 202\ cm^{-1}$) system by considering only ground and first excited state. 1+2

b) Discuss briefly magnetic properties of NiO. 3

c) Calculate μ_{eff} for $[CoCl_4]^{2-}$ where 10 Dq = 3100 cm^{-1} and $\lambda = 172\ cm^{-1}$. 2

d) Calculate χ_{dia} for pyridine [Given atom contribution in 10^{-6} order in emu/mol, C(ring)= –6.24, H= –2.93, N (ring) = –4.61 and constitutive contribution in 10^{-6} order in emu/mol for pyridine = 0.5]. 2

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Answer all the questions

3. a) Explain the different radiative and non-radiative processes in the light of the Jablonski diagram when a molecule is excited by a photon. 2

b) What do you mean by Light Emission Sensitizer (LES)? Show schematically how LES functions. What are the essential criteria of an ideal LES? 3

c) What do you mean by zero-zero spectroscopic energy ($E_{0\text{-}0}$)? How can $E_{0\text{-}0}$ value of chemical species be estimated? $1\frac{1}{2}$

d) What happens if the photo-excited $*[Ru(bpy)_3]^{2+}$ complex is treated with $[Cr(CN)_6]^{3-}$ and $Cr(bpy)_3]^{3+}$? 2

e) What do you mean by chemiluminecence? How does it differ from photoluminescence? 2

f) $[Ru(bpy)_3](PF_6)_2$ is photochemically inert in water whereas $[Ru(bpy)_3](Cl)_2$ is photochemically labile in dichloromethane at room temperature. Suggest a probable reason of this experimental finding and predict the final product that can be obtained from $[Ru(bpy)_3](Cl)_2$ in dicholromethane. 2

4. a) What are the essential conditions for inner sphere electron transfer reactions? Reduction of $[Co^{III}(Cl)(NH_3)_5]^{2+}$ by Cr^{2+}_{aq} is much faster than reduction of $[Co^{III}(NH_3)_6]^{3+}$ although the thermodynamic driving forces appear to be similar for both reactions. Critically discuss. 2+4

b) For a common oxidant, if V^{2+}_{aq} reacts faster than Cr^{2+}_{aq} then we can conclude the occurrence of OSET process. Justify with at least one example. 4

c) For the self-exchange rate of the couple MnO_4^-/ MnO_4^{2-} it is observed that the following cations (M^+) increase the rate in the order: $Cs^+ \gg K^+ \approx Na^+ > Li^+$. Explain. $2\frac{1}{2}$