e) $[Ru(bpy)_3](PF_6)_2$ is photochemically inert in water but $[Ru(bpy)_3](Cl)_2$ is photochemically labile in dichloromethane at room temperature. Suggest a probable reason of the experimental finding and predict the final product that can be obtained from $[Ru(bpy)_3](Cl)_2$ in dicholromethane. $2\frac{1}{2}$

9. a) Consider the reduction of $[Co^{III}(NH_3)_5X]^{3+}$ by $[Cr(H_2O)_6]^{2+}$. Should we expect a difference in mechanism of electron transfer for X = NH_3 and H_2O ? Explain. 3

b) Give with proper explanation one example of an inner-sphere electron transfer reaction where bridging ligand is retained with the oxidizing centre. 3

c) Consider the reduction of $[Co^{III}(NH_3)_5X]^{3+}$ by $[Cr(H_2O)_6]^{2+}$. The rate of this reaction is much faster when X = SCN in comparison to when X = NCS. Explain. 3

d) Although Cr^{2+}_{aq} is a thermodynamically more powerful reducing agent than V^{2+}_{aq} but kinetically $V^{2+}{}_{aq}$ reduces faster, for example, Co(III) or Ru(III) complexes. What are the possible reasons for this observation ? $3\frac{1}{2}$

Ex/M.Sc./CH/4/I-4141/108/2017

M. Sc. Chemistry Examination, 2017

(4th Semester)

Inorganic Chemistry Special

Paper - XIV-I

Time : Two hours Full Marks : 50

25 marks for each Unit

Use a separate answerscript for each Unit.

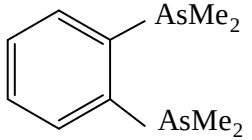
UNIT – I- 4141

Answer ***any five*** :

1. a) Given are the Pascal's constants and constitutive corrections for : 3+2

Atom	χ (dia) $\times 10^6$(cgs)
C	–6.0
H	–2.93
As(III)	–20.9
Constitutive corrections for atoms	λ X 10^6(cgs)
C (ring)	–0.24

Calculate the diamagnetic correction for



b) Describe the anomalous magnetic behavior in the light of solute-solute interaction.

2. Describe Gouy method for the determination of the molar ..... (χ_M) of a coordination compound. What is the standard used for such determination ? 5

3. Show that the perturbation theory is strong enough to predict the eigen values of the order of (2n+1) from the knowledge of eigen function of n^{th} order. 5

4. a) What do you understand by quenching of orbital angular momentum ? What are the conditions that should be satisfied to get orbital contribution from a d^n netal ion.

b) Magnetically Sm(III) and Eu(III) behave differently from Pm(III) and Tb(III). How can you justify this observation ? 3+2

5. a) Explain the terms ferromagnetism and antiferromagnetism. How would you rationalize the sign of J and nature of cooperative phenomena ?

b) How J is related to φ ($\angle$ Cu–Cl–Cu) and Cu–Cl bond distance (longer) for the chloro-bridged Cu(II) binuclear complexes. 3+2

6. Utilizing Van Vleck Equation derive the relation :

$$\mu_J = g\beta[J(J+1)]^{1/2}$$ 5

7. Derive the relationship :

$\chi_A = (Ng^2\beta^2/3kT)[1/(3+\exp(-2J/kT]$ for binuclear Cu(II) complexes and hence give the energies of different levels. 5

UNIT – I - 4142

Answer ***all*** the questions

8. a) What do you mean by Light Emission Sensitizers (LES) ? Show schematically how LES function ? What are the essential criteria of an ideal LES ? 3

b) Calculate the excited state redox potentials for the following couples :

i) $[Ru(bpy)_3]^{3+}/*[Ru(bpy)_3]^{2+}$ and

ii) $*[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{+}$

[Given : $E_{1/2}([Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+} = +1.26V$; $E_{1/2}([Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{+} = -1.28V$ and E_{0-0} = 2.12 eV) 2

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

d) What do you mean by chemiluminescence ? How does it differ from photoluminescence ? 2