M.Sc. Examination 2019
Semester - IV
Chemistry
Course: CH-807
(Inorganic Chemistry)

Time: Three Hours **Full Marks: 40**

Questions are of value as indicated in the margin.
Notations and symbols have their usual meanings.
Attempt ***any four*** questions.

1. a) Attempt ***any three*** 3×3

   (i) Outline the reaction mechanism of base hydrolysis of $\left[\mathrm{Co}\left(\mathrm{NH_3}\right)_5\right]^{2+}$.

   (ii) Draw the isomeric structures of $\left[\mathrm{CoCl}\left(\mathrm{NH_3}\right)\left(\mathrm{trien}\right)\right]^{2+}$ and compare their hydrolysis rates and predict the products.

   (iii) Explain and compare the reactivities of *cis*/*trans* isomers of $\left[\mathrm{Co^{III}}\left(\mathrm{en}\right)_2\,\mathrm{Cl}\left(\mathrm{X}\right)\right]^{n+}$ in aquation where the nonleaving group X is a strong π-acceptor ligand. Comment on the possibility of isomerization in their aquation process.

   (iv) How can you utilize the LEFR plot to support the mechanism of acid hydrolysis of $\mathrm{Co^{III}}$-ammine complexes?

   b) Give the Eyring equation to calculate $\Delta H^{\#}$ and $\Delta S^{\#}$. 1

2. a) Attempt ***any three*** 3×3

   (i) Give the spectral transitions in porphyrin system. Define Soret band.

   (ii) Comment on the role of proximal and distal histidine of haemoglobin.

   (iii) Explain and illustrate the effect of DPG (i.e. BPG) concentration in Hb (haemoglobin)-O_2 interaction.

   (iv) Draw the structure of oxy- and deoxy-forms of haemoglobin and comment on their magnetic properties.

   b) Draw the structure of oxidized and reduced forms of Fe_4S_4 ferredoxin. 1

3. a) Attempt ***any three*** 3×3

   (i) Explain and compare the water exchange rates of $\mathrm{V^{2+}}$ and $\mathrm{Ni^{2+}}$.

   (ii) For the $\mathrm{Co^{III}}$-complexes, the dissociative activation is preferred while for the $\mathrm{Cr^{III}}$-complexes, the associative activation is preferred. Explain.

   (iii) Draw the qualitative MO diagram for Fe-O_2 bent end-on mode of binding in the myoglobin-O_2 adduct and explain the chemical state of Fe- and coordinated O_2 in the said adduct.

   (iv) In absence of Mg(II)-incorporation, chlorophyll is fluorescent but Mg(II)-incorporation makes it phosphorescent. Explain.

   b) Name the important transition metals and their functions in photosynthesis. 1

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4. Attempt ***any four*** 2.5×4
   (i) What do you mean by normal and inverse spinel? Why K_2NiF_4 does not adopt the spinel structure?
   (ii) Compare the structure of $CuFe_2O_4$ and $CuCr_2O_4$ with proper reason.
   (iii) What are V- and H-centre defects in halide crystals?
   (iv) Why NaCl does not prefer interstitial defect?
   (v) Compare the defect clusters in fcc-Pt and bcc α-Fe.
   (vi) Comment on the position of Fermi level with the change in temperature and doping concentration for an n-type semiconductor.

5. Attempt ***any four*** 2.5×4
   (i) Briefly describe the temperature dependence of conductivity for an extrinsic semiconductor.
   (ii) $BaTiO_3$ is ferroelectric but not $CaTiO_3$: why?
   (iii) What are type-I and type-II superconductor? Demonstrate the perfect diamagnetic nature of a superconductor.
   (iv) Comment on the dielectric behaviour of KH_2PO_4 and $NH_4H_2PO_4$ with proper reason.
   (v) What is ferrielectricity? Cite an example.
   (vi) Comment on the field dependent electrical behaviour of $PbZrO_3$.

6. Attempt ***any four*** 2.5×4
   (i) Briefly explain ferromagnetism in Fe, Co and Ni using Bethe-Slate curve.
   (ii) How does a solid state reaction proceed? Explain with proper example.
   (iii) Describe epitactic and topotactic reaction with suitable example.
   (iv) Briefly describe the basic principles of thermal analysis techniques.
   (v) In thermogravimetric analysis ΔM is fundamental, not ΔT: why?
   (vi) Why do we need a reference in DTA?

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