Section A: This section contains ONE COMPULSORY question

Question 1 (30 marks)

(a). Valence Bond Theory (VBT) and Crystal Field Theory (CFT) are widely applied in understanding the chemistry of coordination compounds. Success of these theories is based on a number of assumptions. However, the same theories have limitations:

(i) State two assumptions for each of these theories. (4 mks)

(ii) Give two limitations that meet the applications of each of these theories. (4 mks)

(iii) Outline how each of these theories has failed or succeeded in explaining:

I. The origin of color in transition metal complexes (2.5 mks)

II. The temperature dependence of magnetic characteristics of transition metal complexes (3 mks)

(c). Give the meaning of the term reaction mechanism. (1 mk)

(d) The equation representing a substitution reaction between a coordinated compound and a ligand can be presented as shown below:

$EX_nY + Z \rightarrow EX_nZ + Y$

Where E is central species

X_n is n ligands of type X

Z is incoming ligand while Y is outgoing ligand

(i) The feasibility of such a reaction will be dependent on what factors? (2 mks)

(ii) Discuss briefly each of the following terms as applied in coordination chemistry:

I. Associative mechanism (A)

II. Dissociative mechanism (D)

III. Interchange mechanism (I)

IV. Spectator ligand (2.5 mks)

(iii). Give the reaction mechanisms A and D mentioned in (ii) above. (3 mks)

(iv). Briefly explain how the following factors influence the Associative (A) or Dissociative (D) processes.

I. Steric effects of attached ligands

II. Large central cation.

III. Strength of spectator ligands.

IV. Steric effect of incoming ligand (8 mks)

Section B: This section contains FOUR questions. Answer ONLY TWO questions.

Question 2 (20 marks)

(a). Explain each of the following concepts and give an example in each case:

(i) Complementary reaction

(ii) Non-complementary reaction

(4 mks)

(b) How is the actual electron transfer accomplished in an inner sphere redox mechanism? (2 mks)

(c) A metal species (d^7) in the 3rd row of the periodic table can form both tetrahedral and octahedral complexes. The metal species can form low spin or high spin complexes.

(i). Highlight the difference between a high spin complex and a low spin complex. (2 mks)

(ii). With the aid of boxes in representing orbitals, present the electronic configuration for the metal species if it forms:

I. Octahedral low spin complexes (1 mk)

II. Octahedral and tetrahedral high spin complexes (2 mks)

(iii). Write the hybridization of the complexes in (ii) II. above. (1 mks)

(iv). Compare and explain the stability between high spin and low spin complexes (2 mks)

(v). Explain why tetrahedral complexes only exist in outer sphere complex form. (2 mks)

(d) As ligands approach the central species in octahedral field, tetrahedral field, spherical field and square planar field, degeneracy of the 5 d orbitals is affected depending on the system. Sketch a diagram showing the energies of the d orbitals of the central species for the four systems. (4 mks)

Question 3 (20 marks)

(a) What is a coordination compound? How does this compare with a complex ion? (2 mks)

(b). Consider the following complexes:

I $K_4[Fe(CN)_6]$

II $[Cu(NH_3)_6](NO_3)_2$

III $[Co(NH_3)_5(SO_4)]^+$

IV $[Cd(H_2NCH_2CH_2NH_2)_2]Cl_2$

Give the meaning of each of the following terms as applied to coordination compounds:

(i) Central species (1 mk)

(ii) Donor atom (1 mk)

(iii) Monodentate ligand (1 mk)

(iv) Polydentate ligand (1 mk)

(c). In the complexes in (b) above, identify the

(i) Central species (2 mks)

(ii) Ligands (2 mks)

(iii) Group the ligands in the above complexes into monodentate and polydentate types (2 mks)

(iv) Explain any two characteristics that enable a ligand to be polydentate. (4 mks)

(v) Donor atoms in each of the ligands (2 mks)

(d). State the coordination number of the complexes in (b) above. (2 mks)

Question 4 (20 marks)

(a) Explain the type of reaction mechanism which square planar complexes predominantly follow during substitution reactions. (2 mks)

(b) What is meant by the term 'trans effect' as applied to square planar complexes? (2 mks)

(c) Starting with either square planar $[Pt(Cl)_4]^{2-}$ or $[Pt(NH_3)_4]^{2+}$, explain with the aid of appropriate equations how the Cis and Trans $Pt(NH_3)_2Cl_2$ can be prepared. (4 mks)

(d) Given the complex $[Co(NH_3)_5Cl]^{2+}$, give the general rate law which represent the hydrolysis of such a complex (describe the terms in the law). (2 mks)

(e) Outline a plausible mechanism when the complex in (d) above goes through hydrolysis under basic medium. (3 mks)

(f) In most cases of octahedral substitution reaction the dissociative (D or Id) mechanism is predominantly applicable. Explain why this is so. (3 mks)

(g) Give the reaction mechanism for the following reaction:

(i) Sn(II) + Hg(II) → Sn(IV) + Hg

(ii) 2Cr(II) + Tl(III) → 2Cr(III) + Tl(I)

(4 mks)

Question 5 (20 marks)

(a) In a free atom, the five d orbitals are degenerate. As ligands approach a central species in an octahedral field, tetrahedral field, spherical field and square planar field, the energy of the five d orbitals of the central species are raised in relation to the free central species:

(i) Diagrammatically present the five d orbitals clearly indicating the axes and symmetry of the orbitals. (5 mks)

(ii) Use the cube as the reference model to explain the d orbitals that are used in coordinate bonding in octahedral and square planar complexes. (6 mks)

(iii) Which orbitals are used in bonding when a tetrahedral complex is formed (3 mks)

(b) The complex ion $Ni(H_2O)_6^{2+}(aq)$ reacts with $NH_3(aq)$ and en(ethylene diamine; $NH_2CH_2CH_2NH_2$) to form the complexes $Ni(NH_3)_6^{2+}$ and $Ni(en)_3^{2+}(aq)$ respectively.

(i) What is the meant by the term chelate effect? (2 mks)

(ii) What can be said about the difference in stability of the two complexes formed? Explain your answer. (4 mks)