NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF APPLIED CHEMISTRY
END OF SEMESTER EXAMINATIONS - DECEMBER 2002
INORGANIC CHEMISTRY II - SCH1201
TIME: 3 HOURS

INSTRUCTIONS TO CANDIDATES

Answer **ALL** questions from Section A and **ANY THREE** from Section B.

Periodic Tables Required

SECTION A

1. What two properties would generally be important in a solvent for electrochemical reactions? (4 marks)

2. (a) State whether each of the following would act as an acid or a base in liquid HF:
(i) BF_3, (ii) SbF_5, (iii) CH_3COOH, (iv) H_2O.
In each case write an equation to show the basis for your answer. (8 marks)

(b) Explain, in terms of the hard and soft acid and base concept, which end of the SeCN- ion would be expected to co-ordinate to (i) Cr^{3+}, (ii) Pt^{2+}? (4 marks)

3. Would you expect Cd^{2+} to be coloured? Explain. (3 marks)

4. (a) Name the following co-ordination compounds according to the IUPAC rules:
(i) $[Co(NH_3)_6]Cl_2$ (ii) $K_2[PtCl_4]$ (iii) $K_4[PtCl_6]$ (6 marks)

(b) Draw structures for each of the following:

(i) *cis*- and *trans*-Dichlorobisethylenediaminecobalt(II).

(ii) *cis*-Tetramminechloronitrocobalt(II) ion.

(iii) *trans*-Tetramminechloronitritocobalt(II) ion. (8 marks)

5. Calculate, in terms of Δ_0, the ligand field stabilisation energies (LFSE's) of the following high-spin ions in their octahedral complexes: Fe^{2+}, Mn^{2+}, Mn^{3+}, Co^{2+}. (10 marks)

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6. Write expressions for the stepwise and overall formation constants for the complex ions $Ag(S_2O_3)^-$, and $Ag(S_2O_3)_2^{3-}$, and use them to explain the relationship between the two types of formation constant. (6 marks)

7. In ligand substitution reactions of the type

$$[ClPt(dien)]^+ + X^- \rightarrow [XPt(dien)]^+ + Cl^-$$

where dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$, no intermediate can be detected, and the rate of reaction is highly dependent on the nucleophilicity of X^-. Describe and classify the mechanism. (6 marks)

SECTION B

8. (a) For each of the following reactions, identify the product and balance the equation:

(i) $BF_3 + NH_3 \rightarrow$

(ii) $I^- + I_2 \rightarrow$

(iii) $OH^- + Zn(OH)_2 \rightarrow$ (6 marks)

(b) Name the class of reaction represented by all three of the above reactions in Lewis Acid/Base Theory, and classify each substance involved as acid, base or complex. (9 marks)

9. (a) With the aid of a sketch, show how the energies of the various metal d-orbitals are arranged in an octahedral ligand field, and how they change as two *trans*- ligands (lying along the +z and -z directions), are gradually remove to infinity. (7 marks)

(b) Use your diagram in (a) to describe the electronic structure of the following species:

(i) A six co-ordinate d^4 species which shows Jahn-Teller distortion from octahedral.

(ii) A four co-ordinate square-planar d^8 species. (8 marks)

10. (a) Explain with the aid of sketches the existence of *mer*- and *fac*- isomers of formula MA_3B_3. (6 marks)

(b) Draw all the distinct octahedral isomers of formula MA_3BCD, distinguishing between geometric and optical isomers. (9 marks)

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11. (a) The complex ion $NiCl_4^{2-}$ has two unpaired electrons, while $[Ni(CN)_4]^{2-}$ is diamagnetic. Propose structures (geometric and electronic) for these two complex ions that would account for this difference. (8 marks)

(b) The complex ion $[Fe(CN)_6]^{3-}$ is paramagnetic with one unpaired electron. The complex ion $[Fe(SCN)_6]^{3-}$ has five unpaired electrons. Explain this difference in terms of their *d*-electron configurations. Where do the ions CN^- and SCN^- lie in the spectrochemical series relative to each other? (7 marks)

12. (a) Why are the simplest carbonyls of Mn and Co binuclear? State their formulas and show that they satisfy the 18-electron rule.

(b) Write the formulas of the mononuclear metal carbonyls formed by V, Cr, Fe and Ni. Which one of these does not satisfy the 18-electron rule? Why does this element not form a binuclear carbonyl instead?

END OF QUESTION PAPER!!!!

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