



NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
END OF SECOND SEMESTER EXAMINATIONS – MAY 2004
INORGANIC CHEMISTRY II – SCH 1201
TIME: 3 HOURS

INSTRUCTIONS TO CANDIDATES

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

REQUIREMENTS: PERIODIC TABLES

SECTION A

1. (a) Explain what is meant by the terms weak acid and weak base when applied to a non-aqueous protic solvent HA. Include equations. (4 marks)
- (b) Sulphuric acid is a weak acid in acetic acid. Show this by means of an equation. (2 marks)
- (c) Sodium acetate is a strong base in acetic acid. Explain. (2 marks)

2. (a) Name the following compounds according to IUPAC rules
 - (i) $\text{Na}_2[\text{ZnCl}_4]$
 - (ii) $[\text{Cr}(\text{en})_3]\text{Cl}_3$ where $\text{en}=\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (4 marks)
- (b) Draw the structures of the following compounds
 - (i) cis-diamminetetrathiocyanatochromate(III)
 - (ii) Tris(oxalato)cobalt(III) nitrate (4 marks)

3. Name and sketch the two ideal co-ordination polyhedra for 5 co-ordination indicating which ligands are equivalent to one another in each structure. (5 marks)

4. Draw all the possible isomers of octahedral $[\text{CoCl}_2(\text{en})(\text{NH}_3)_2]^+$. What is the type of isomerism present in each case? (10 marks)

5. Predict the magnetic moment for octahedral complexes of Fe^{2+} with
 - (i) strong field ligands and
 - (ii) weak field ligands. (5 marks)

6. Plot the hydration enthalpy for the ions below against atomic number M , and relate the shape of the plot to the ligand field theory.

Ion M^{2+}	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$\Delta H_{\text{hydration}}$ (kJmol^{-1})	1598	1782	1895	1925	1862	1958	2079	2121	2121	2059

(8 marks)

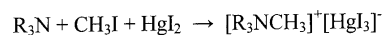
7. Explain why $[\text{Ni}(\text{en})_3]^{2+}$ is more stable than $[\text{Ni}(\text{NH}_3)_6]^{2+}$. (3 marks)

8. The reactions of $\text{Ni}(\text{CO})_4$ in which phosphanes replace CO to give complexes $[\text{Ni}(\text{CO})_3\text{PR}_3]$ occur at the same rate for different phosphanes PR_3 . Is the reaction associative or dissociative? Explain. (5 marks)

9. Outline a process, using chemical equations, by which either manganese or nickel is produced from its ore. (3 marks)

SECTION B

1. A certain organic compound, R_3N , was first treated with methyl iodide, and then the product was reacted with mercury(II) iodide, to give a crystalline co-ordination compound. The overall reaction was :



(a) Write equations for the two individual steps, identify the Lewis acids and Lewis bases involved, and classify each reaction step (as complex formation, displacement, etc) (8 marks)

(b) Which of the acids and bases in part (a) are "hard", and which are "soft". What is the general rule regarding binding preferences of hard and soft acids and bases? Explain whether the composition of the final product in (a) agrees with this rule. (7 marks)

2. Determine the electronic configuration and LFSE for each of the following complexes. Where relevant use the spectrochemical series to decide whether the complex is likely to be strong-field or weak-field.

(a) $[\text{Fe}(\text{CN})_6]^{3-}$ (5 marks)

(b) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (5 marks)

(c) $[\text{Ni}(\text{CO})_4]$ (tetrahedral). (5 marks)

3. For each of the following species: (i) $\text{Fe}(\text{CO})_5$, (ii) $\text{Mn}_2(\text{CO})_{10}$, (iii) $\text{V}(\text{CO})_6$, (iv) $[\text{Fe}(\text{CO})_4]^{2-}$
- (a) Name the species and draw its structure. (8 marks)
- (b) Assign an oxidation number to the central metal atom. (2 marks)
- (c) Count the number of valence electrons, and account for any deviation from the 18 electron rule. (5 marks)
4. Three co-ordination compounds were isolated, each with the empirical formula $\text{PtCl}_2 \cdot 2\text{NH}_3$. Compound A reacts slowly with solid Ag_2O to produce $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]^{2+}$, but does not react with ethylenediamine to give a chelate complex. Compound B does react with ethylenediamine to give $[\text{Pt}(\text{en})\text{Cl}_2]$. Compound C is an insoluble solid which, when ground with AgNO_3 , gives a solution containing $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$, and a new solid phase $\text{Ag}_2[\text{PtCl}_4]$. Draw the structures of compounds A, B and C, and name them. (15 marks)
5. The equilibrium constants for the successive reactions of ethylenediamine(en) with Co^{2+} , Ni^{2+} and Cu^{2+} are as follows:

Ion	$\log K_1$	$\log K_2$	$\log K_3$
Co^{2+}	5.89	4.83	3.1
Ni^{2+}	7.52	6.28	4.26
Cu^{2+}	10.55	9.05	-1

- a) i) Account for the general trend observed in the values of the successive formation constants.
- ii) How do you account for the very low K_3 value for Cu^{2+} ? (7 marks)
- b) i) Write an expression for the overall formation constant (β) for the formation of $[\text{Ni}(\text{en})_3]^{2+}$.
- ii) Calculate the overall formation constants (β) for $[\text{M}(\text{en})_3]^{2+}$ and arrange the complexes in order of decreasing stability. ($\text{M} = \text{Co}^{2+}$, Ni^{2+} and Cu^{2+}) (8 marks)

End of Question Paper!!!