

**DEPARTMENT OF APPLIED CHEMISTRY**

**END OF SEMESTER EXAMINATIONS - APRIL/MAY 1999**

**INORGANIC CHEMISTRY II - SCH 1201**

**TIME: 3 HOURS**

**INSTRUCTIONS TO CANDIDATES**

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

Atomic Mass Tables required.

**SECTION A**

- (a) Identify the conjugate bases corresponding to the following acids:  
(i)  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ , (ii)  $\text{HSO}_4^-$ , (iii)  $\text{CH}_3\text{OH}$ , (iv)  $\text{Si}(\text{OH})_4$ . (4 marks)

(b) Identify the conjugate acids corresponding to the following bases:  
(i) pyridine,  $\text{C}_5\text{H}_5\text{N}$ , (ii)  $\text{O}^{2-}$ , (iii)  $\text{CH}_3\text{COOH}$ , (iv)  $[\text{Co}(\text{CO})_4]^-$ . (4 marks)
- In order to show that HI is a stronger Bronsted acid than HBr, it is necessary to study equilibria in a non-aqueous solvent such as acetic acid,  $\text{CH}_3\text{COOH}$ . Using this example, explain:

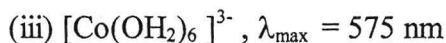
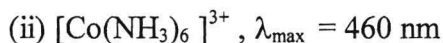
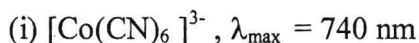
(a) The solvent-levelling effect that occurs in aqueous solution. (4 marks)

(b) The equilibria involved in comparing the acidity of HBr and HI in acetic acid. (4 marks)
- Explain why the density of mercury ( $13.6 \text{ g cm}^{-3}$ ) is significantly higher than that of cadmium ( $8.65 \text{ g cm}^{-3}$ ), whereas the density of cadmium is only slightly greater than that of zinc ( $7.14 \text{ g cm}^{-3}$ ). (4 marks)
- (a) Name the following complexes: (i)  $[\text{CoCl}(\text{NH}_3)_4(\text{OH}_2)]^{2+}$ , (ii)  $[\text{Fe}(\text{OH})(\text{OH}_2)_5]^{2+}$ . (2 marks)

(b) Determine the co-ordination numbers of the metal in the following ions:  
(i) dichlorobis(ethylenediamine)platinum(IV), (ii) tris(oxalato)ferrate(III) (2 marks)

(c) Write the formula for the following co-ordination compounds:  
(i) pentaamminesulphatocobalt(III) chloride, (ii) sodiumdiaquabis(oxalato)ferrate(III). (2 marks)
- The magnetic moment of an octahedral Co(II) complex is  $4.0 \mu_B$ . Determine the number of unpaired electrons, and hence deduce if this complex is high or low-spin, and give its corresponding electronic configuration. (5 marks)

6. (a) Estimate the ligand field splitting in the complexes:-

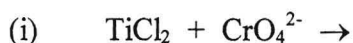


(Planck's constant,  $h = 6.626 \times 10^{-34} \text{ J s}$ ; Velocity of light,  $c = 2.998 \times 10^8 \text{ m s}^{-1}$ .)  
(12 marks)

(b) Use your results from part (a) to arrange the ligands in order of increasing ligand field strength.  
(2 marks)

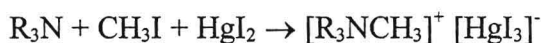
7. (a) Outline a process, using chemical equations, by which (i) nickel, (ii) manganese are prepared, from one of their ores.  
(6 marks)

(b) Predict the major products of the following reactions. (You need not balance the equations)



## SECTION B

8. A certain organic compound,  $\text{R}_3\text{N}$ , 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 "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)

9. (a) 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  $\text{PR}_3$ . Is the reaction associative or dissociative? Explain. (8 marks)
- (b) A Pt(II) complex of tetraethyldiethylenetriamine,  $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NEt}_2$ , is attacked by  $\text{Cl}^-$   $10^5$  times less rapidly than the diethylenetriamine,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ , analogue. Explain this observation in terms of associative activation. (7 marks)
10. 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  $\text{Ag}_2\text{O}$  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  $\text{AgNO}_3$ , 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)
11. Determine the electronic configuration and the ligand field stabilisation energy 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)
12. 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)

**END OF QUESTION PAPER!!!!**