0062

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

Semester 1 Examinations 2005 - 2006

Exam Code(s)	3BS9 and 3ER3
Exam(s)	Third Science Chemistry
Module Code(s)	CH307
Module(s)	Inorganic Chemistry
Paper No.	
Repeat Paper	
External Examiner(s)	Professor J.A.S. Howell
Internal Examiner(s)	Professor P. McArdle, Professor M. J. Hynes, Professor D. Cunningham and Dr. T. Higgins.

Instructions: **Answer 5 questions from section A and 2 questions from section B. Students are advised to spend 1 hour on section A and 1 hour on section B.**

Duration	**2 Hours**
No. of Pages	4 including this page
Department(s)	Chemistry
Course Director	Professor P. McArdle

Requirements:
MCQ
Handout
Statistical Tables
Graph Paper
Log Graph Paper
Other Material

Section A
(Answer 5 questions from section A)

1. Answer **each** of the following.

(a) What is the most stable oxidation state of chromium and what contributes largely to its stability in this state?

(b) What is the structure of the explosive blue product from the reaction of H_2O_2 with an acidified aqueous solution of Cr^{VI} followed by its extraction into ether and reaction with pyridine?

(c) Describe an industrial synthesis of TiO_2.

(d) Describe a major structural difference between $BaTiO_3$ and Na_2VO_3.

(e) Provide a solid state structural representation of **either** VF_5 or TiF_4.

[10 marks]

2. For **each** of the following give the metal valence electron count and identify which compounds are likely to be stable.

(a) $(\eta^5\text{-}C_5H_5)Co(CO)_2$

(b) $(\eta^6\text{-}C_6H_6)W(CO)(PPh_3)_2$

(c) $Mn(CO)_3(PPh_3)_2I$

(d) $(\eta^4\text{-buta-1,3-diene})Mn(CO)_2Br$

(e) $(\eta^3\text{-allyl})Ni(CO)_2PPh_3I$. **[10 marks]**

3. Define and give examples of **each** of the following.

(a) a transition metal organometallic compound

(b) an η^2-ligand

(c) a π–acid ligand

(d) a bridging carbonyl ligand

(e) a metal carbene complex **[10 marks]**

4. Answer **each** of the following.

(a) Comment on the fact that that the half-lives of the following two reactions are very similar.

$[PtCl_4]^{2-} + H_2O = [PtCl_3(H_2O)]^{1-} + Cl^-$

$[Pt(NH_3)_2Cl_2] + H_2O \rightleftharpoons [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$

(b) In water, the rate law for ligand substitution reactions of square planar Pt^{II} complexes has the following form where X is the leaving group and Y is the entering group.

$Rate = -d[PtL_3X]/dt = k_1[PtL_3X] + k_2[PtL_3X][Y]$

Sketch a mechanism that is consistent with this. Indicate fast and slow steps.

(c) The rate law for base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ is:

$Rate = -d[Co(NH_3)_5Cl^{2+}]/dt\ [OH^-]$

Sketch a mechanism that is consistent with this rate law.

(d) Clearly distinguish between "inner-sphere" and "outer-sphere" electron transfer reactions. **[10 marks]**

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5. Write the molecular formula and predict the geometry for the product of **each** of the following reactions.

(a) Ni^{2+} reacting with cyanide

(b) Ni^{2+} reacting with halide

(c) Pd^{2+} reacting with halide

(d) Co^{2+} reacting with iodide

(e) Cu^{2+} reacting with water. **[10 marks]**

6. Answer **each** of the following.

(a) Describe the alpha-helix structure in proteins

(b) Show how four different amino acid side chains coordinate to metal ions.

(c) Sketch the active site of the enzyme carboxypeptidase A.

(d) Sketch the active centre of a ferrodoxin protein **[10 marks]**

7. Describe four factors that influence the choice between tetrahedral and octahedral geometry for a coordination compound. **[10 marks]**

8. Answer **each** of the following;

(a) Give the colours of Cr^{2+} and Cr^{3+} aquo ions in HCl solution and the colour of an aqueous solution of $[CrO_4]^{2-}$ after addition of HCl.

(b) Give the products of the following reactions;
(i) ferrocene + $(CH_3CO)_2O$ + H_3PO_4 →
(ii) VO_3^- + Zn(Hg) →

(c) Give two factors which influence the rate of elution of the hydrolysis products of $[Cr(en)_2ox]^+$ on a cation exchange column (en = ethylenediamine and OX = oxalate).

(d) Use the spin only formula to predict the magnetic moment of bis(pentan-2,4-dionato)oxovanadium(IV).n-propylamine.

(e) Give the formulae of the complexes formed by copper(II) in the presence of excess ammonia.

[10 marks]

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Section B

(Answer 2 questions from Section B)

9. Answer **(a)** and **(b)**

(a) Describe the mechanism by which metal complex formation takes place in aqueous solution. **[12 marks]**

(b) Outline the important features of vanadium chemistry in the +4 and +5 oxidation states. **[13 marks]**

10. Answer **each** of the following;

(a) Describe the cone-angle construction suggested by Tolman and explain its uses. **[4 marks]**

(b) Briefly outline the difference between Schrock and Fischer type carbene complexes. **[5 marks]**

(c) Explain the terms oxidative addition and reductive elimination. Use the addition of MeI to Vaska's complex to illustrate oxidative addition. **[8 marks]**

(d) Explain why there are no stable neutral binary metal carbonyls for titanium or vanadium. **[8 marks]**

11. Answer **each** of the following.

(a) Explain the terms, σ-donor ligand, π-acceptor ligand , π-donor ligand. Give one example in each case. **[9 marks]**

(b) For the coordination cation, $[Cr(NH_3)_6]^{3+}$

(i) Draw a molecular orbital bonding scheme.

(ii) Label energy levels with appropriate symmetry symbols and as bonding, antibonding or non bonding.

(iii) Show the 10Dq energy transition

(iv) Show all valence electrons **[8 marks]**

(c) For the coordination anion, $[Cr(CN)_6]^{3-}$

(i) Draw a molecular orbital bonding scheme.

(ii) Label energy levels with appropriate symmetry symbols and as bonding, antibonding or non bonding.

(iv) Show the 10Dq energy transition

(v) Show all valence electrons

(vi) Highlight how this molecular orbital diagram differs from that in part **(b)**.

[8 marks]