GX302

Ollscoil na hÉireann, Gaillimh

National University of Ireland, Galway

SUMMER EXAMINATIONS, 2000

FINAL EXAMINATION FOR THE DEGREE OF B.Sc.(Honours)

(INCLUDING DENOMINATED DEGREES)

CHEMISTRY CH-401

Second Paper

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Professor. M. J. Hynes
Dr. T. Higgins

Time allowed: *Three* hours

(Answer *five* questions)

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

(a) Describe the principal differences that are found in the chemistry of metal carbene complexes of the Fischer and Schrock types. **[60 marks]**

(b) What are the steric interactions which can be used to explain the production of stereoregular polypropylene using metallocene catalysts. **[40 marks]**

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

(a) Give valence electron counts for the metal atom in each of the following and suggest whether the molecule might be stable. $(\eta^5\text{-}C_5H_5)_2WH_2$, $(\eta^5\text{-}C_5H_5)Cr(CO)_3$, $Fe(CO)_4Br_2$, $W(CO)_3(PPr^i_3)_2H_2$. **[40 marks]**

(b) Explain the following. The ^{1}H NMR spectrum of $(\eta^4$-cycloocta-1,3,5,7-tetraene$)Fe(CO)_3$ is simpler than might be expected at room temperature but becomes more complicated at low temperature. In contrast the ^{1}H NMR spectrum of $(\eta^4$-cyclohepta-1,3,5-triene$)Fe(CO)_3$ is more or less as expected over a wide temperature range. **[60 marks]**

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

(a) Show how Orgel diagrams may be used to interpret the uv-visible spectra of octahedral and tetrahedral complexes of $3d^2$ transition metal ions. Sketch and annotate typical spectra for both geometries. **[60 marks]**

(b) Describe the types of spectra exhibited by complexes of 3d transition metal ions. **[40 marks].**

4. "Eighteen electron systems rule supreme in determining the composition of stable carbonyl complexes of transition metal ions and atoms. However, this rule must be broken in the act of substitution".
Discuss the kinetics and mechanisms of the substitution reactions of metal carbonyl complexes in the light of the above statement. Use appropriate examples to illustrate your answer. **[100 marks]**

5. Discuss the following aspects of the chemistry of dioxygen.

(i) Metal dioxygen chemistry. **[20 marks]**

(ii) Metal dioxygen biochemistry. **[40 marks]**

(iii) Dioxygen activation in biological systems. **[40 marks]**

6. Discuss iron-sulphur and other non-haem iron proteins under the following headings.

(i) Structure. **[40 marks]**

(ii) Redox chemistry. **[40 marks]**

(iii) Catalytic chemistry. **[20 marks]**

7. Answer **(a)** and ***either*** **(b)** or **(c)**

(a) Outline in detail how x-ray diffraction intensity data are used in structure determination. **[70 marks]**

(b) The first four lines in the diffraction pattern of CsI are indexed as (1,1,0), (2,0,0), (2,1,1) and (2,2,0). Derive a scattering factor expression that accounts for the indexing. **[30 marks]**

(c) Provide an equivalent position diagram for the space group $P2_1/c$; the space group diagram is shown below. In the case of a complex crystallising in the space group $P2_1/c$, outline circumstances that would result in eight molecules existing in the unit cell. If a metal complex ML_2R_2 (M = metal; L and R are monodentate ligand) crystallises in this space group with two molecules per unit cell, suggest one set of possible positions for the metal atoms and indicate the consequences for the structure of the molecule.

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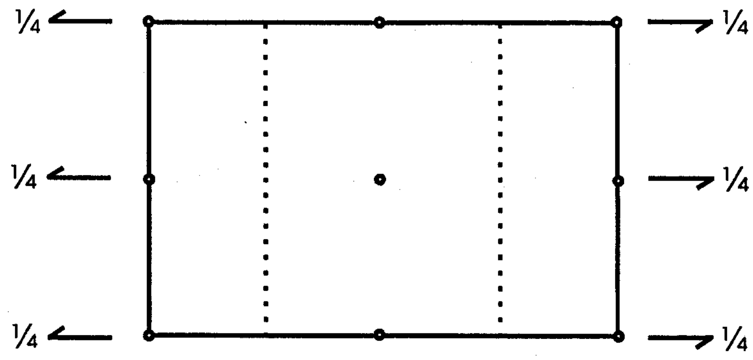

[30 marks]

8. Answer **(a)**, **(b)** and **(c)**.

(a) Outline briefly (do not supply mathematical details) how an expression for the magnetic moment of a molecule can be derived on the assumption that only the spin of the electron is contributing to the magnetism. **[40 marks]**

(b) Explain what is meant by ferromagnetic, antiferromagnetic and ferimagnetic behaviour and explain in qualitative fashion how ferromagnetic and antiferromagnetic alignment can occur through σ-bonding orbitals. Also explain how ferromagnetism and antiferromagnetism can be detected from detailed magnetic studies. Further show the extent to which structural information can be obtained from such detailed magnetic studies. **[50 marks]**

(c) An x-ray powder diffraction study of cubic MnO at 80°K revealed a unit cell parameter of 4.43 Å whereas a neutron diffraction pattern at the same temperature revealed a magnetic unit cell parameter of 8.86 Å. With the aid of an appropriate diagram indicate the significance of these combined observations. **[10 marks]**