IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2014, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

INORGANIC CHEMISTRY I

Thursday 19th June 2014, 09:30-11:45

PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR CORE COURSE.

USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

1.I1 – Molecular Structure

Answer parts a) **AND** b) and **EITHER** part c) **OR** d) of this question.

a) Answer **ALL** parts of this question.

i) Draw the structures of the octahedral isomers *cis*- and *trans*-$[FeCl_2(CO)_4]$ and show their rotational axes of symmetry.

(4 marks)

ii) Determine the point group of each isomer.

(2 marks)

iii) Which of the two isomers has an S_4 improper rotation? Show it on a sketch of the molecule.

(2 marks)

b) Answer **ALL** parts of this question.

i) Sketch and label the molecular orbital energy level diagram for the hypofluorite anion OF^-. On your diagram, include drawings of the atomic and molecular orbitals, and the electron occupancies.

(9 marks)

ii) What is the bond order of hypofluorite?

(1 mark)

iii) Is this ion diamagnetic or paramagnetic? Explain your answer.

(1 mark)

c) Using VSEPR theory, sketch and name the pseudostructures and structures of the following molecules and ions:

CCl_2 ClO_3^- ClF_5

(6 marks)

QUESTION CONTINUED OVERLEAF

d) Answer **ALL** parts of this question.

i) Write the Lewis structure, including resonance structures, for the carbonate ion, CO_3^{2-}.

(2 marks)

ii) Use VSEPR theory to predict its pseudostructure and structure.

(2 marks)

iii) Describe the hybridisation of the carbon atom in this ion and the nature of the bonding between the carbon and the oxygen atoms.

(2 marks)

1.I2 – Periodicity and Inorganic Reactivity

Answer **ALL** parts of this question.

a) Answer **ALL** parts of this question.

Suggest products for the reactions of the following elements with an excess of O_2, giving balanced equations in each case:

i) Na
ii) P_4
iii) Sb (at 100 ºC)

(5 marks)

b) Answer **ALL** parts of this question.

Sulfur trioxide is an extremely electrophilic reagent that rapidly reacts with any organic compound containing an electron donor group.

i) Suggest a synthesis of sulfur trioxide starting from elemental sulfur.

(2 marks)

ii) With reference to the structure of sulfur trioxide, give reasons for its high reactivity with organic compounds containing electron donor groups.

(2 marks)

iii) Sulfur trioxide forms a complex with pyridine (C_5H_5N) that can act as a milder source of sulfur trioxide for organic synthesis. Draw the structure of this complex and account for its reduced reactivity compared to sulfur trioxide.

(2 marks)

c) Answer **TWO** of the three parts i), ii) and iii) of this question.

i) The boron, nitrogen and carbon atoms in the molecule $B(NMe_2)_3$ are all coplanar. Draw the structure of this molecule identifying the hybridisation state of all non-hydrogen atoms, and discuss the nature of the bonding within the molecule. Also suggest reasons why $B(NMe_2)_3$ is less reactive than $Al(NMe_2)_3$.

(7 marks)

QUESTION CONTINUED OVERLEAF

ii) Discuss the reasons why Pb reacts with Cl_2 to give $PbCl_2$ rather than $PbCl_4$.

(7 marks)

iii) Account for the variation in bond strengths of the Group 17 diatomic molecules (shown below in kJ mol^{-1}), and provide a rough estimate for the bond strength in the interhalogen diatomic molecule BrF. Give your reasoning.

F_2	Cl_2	Br_2	I_2
158	242	192	151

(7 marks)

1.I3 – Coordination Chemistry

Answer **ALL** parts of this question.

a) Why are d-d electronic transitions in octahedral complexes generally weakly absorbing and give rise to broad UV-vis absorption bands?

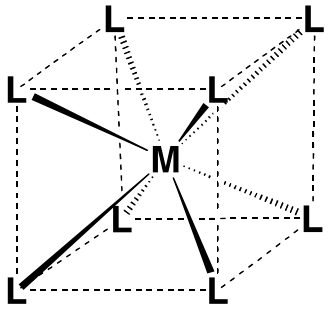
(10 marks)

b) Answer **ALL** parts of this question.

i) Using a simple crystal field approach, derive the d-orbital splitting diagram for a tetrahedral transition metal complex ML_4.

(3 marks)

ii) Discuss the similarities and the differences between the splitting diagrams for a tetrahedral ML_4 complex and a hypothetical ML_8 complex with a cubic coordination geometry (shown below). Comment on the magnitude of the splitting parameter Δ_c for cubic compared to Δ_t for tetrahedral geometry.



(4 marks)

iii) Determine the expected spin-only magnetic moment μ_{so} for the hypothetical cubic complex $[Os(CN)_8]^{3-}$.

(3 marks)

QUESTION CONTINUED OVERLEAF

c) Answer part i) **OR** ii) of this question.

i) Find the values for x and y in the following complexes by determining the oxidation state of the central metal from the experimental values of the effective magnetic moment μ_{eff}. Show your workings.

$[Cu(NH_3)_4]Cl_x$	μ_{eff} = 1.9 BM
$[Fe(NCMe)_6][PF_6]_y$	μ_{eff} = 4.9 BM

(5 marks)

ii) Describe the spectroscopic (UV-vis) and magnetic properties of $[ReO_4]^-$ and $[OsO_4]^-$.

(5 marks)