IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2013, 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

Tuesday 18th June 2013, 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 **BOTH** parts of this question.

i) Sketch and label the molecular orbital energy level diagram for the acetylide dianion $[C_2]^{2-}$. On your diagram, include drawings of the MOs and electron occupancies.

(9 marks)

ii) Using this MO diagram explain why the bond length in $[C_2]^{2-}$ (1.19 Å) is shorter than that in C_2 (1.24 Å).

(2 marks)

b) Using VSEPR theory, sketch the pseudostructures and structures of the following molecules:

BrF_3 SF_4 N_2H_4

(6 marks)

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

i) Draw the structure of *cis*-N_2H_2 and show its planes of symmetry. Determine the point group of this molecule.

(4 marks)

ii) Indicate the hybridisation of the N atoms in *cis*-N_2H_2.

(1 mark)

iii) Using Valence Bond theory, show a bonding scheme for *cis*-N_2H_2 (including sketches of the orbitals involved) based on the hybridisation you have suggested.

(3 marks)

QUESTION CONTINUED OVERLEAF

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

i) Draw the structure of $AlCl_3$ and show its rotational axes of symmetry. Determine the point group of this molecule.

(4 marks)

ii) Indicate the hybridisation of the Al atom in $AlCl_3$.

(1 mark)

iii) Using Valence Bond theory, show a bonding scheme for $AlCl_3$ (including sketches of the orbitals involved) based on the hybridisation you have suggested.

(3 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/compounds with an excess of H_2O, giving balanced equations in each case:

i) K
ii) BBr_3
iii) Borazine, $(HBNH)_3$

(3 x 2 marks)

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

The boiling points of the hydrogen halides are given below:

	HF	HCl	HBr	HI
b.p. (ºC)	20	-85	-66	-15

i) Briefly discuss and account for the variation in these boiling points.

(3 marks)

ii) Put these hydrogen halides in order of increasing acidity in water (*i.e.* decreasing pKa), giving your reasoning.

(2 marks)

c) Answer **TWO** of the following three parts of this question.

i) Compare and contrast the structures of and bonding in BF_3 and $[BF_4]^-$. Use your answer to explain why the B-F bond length is much shorter in BF_3 (1.30 Å) than in $[BF_4]^-$ (1.45 Å).

(7 marks)

ii) Reaction of SnF_4 with two mole equivalents of PMe_3 gives a new compound **A**. Draw the structure of **A,** indicating its geometry and stereochemistry. Would you expect CF_4 to react similarly with PMe_3 – give your reasoning.

(7 marks)

iii) Which of the following compounds are isoelectronic (with respect to valence electrons) and which are isostructural: SO_2, NO_2^+, SeO_2, TeO_2, ClO_2^+? Explain your answers.

(7 marks)

1.I3 – Coordination Chemistry

Answer **BOTH** parts of this question.

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

i) Discuss the factors affecting the crystal field splitting parameter (Δ) in transition metal complexes.

(5 marks)

ii) Discuss how the magnetic moment arises in transition metal complexes and how it can be determined.

(5 marks)

b) Answer **TWO** of the following three parts of this question.

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

$Na_x[Co(NO_2)_6]$	μ_{eff} = 1.8 BM (NO_2^- = nitro)
$K_2[Mn(IO_3)_y]$	μ_{eff} = 3.8 BM (IO_3^- = iodate)
$K_z[Mn(CN)_6]$	μ_{eff} = 2.2 BM (CN^- = cyanide)

(7.5 marks)

ii) The major band in the spectrum of the pink $[(Co(H_2O)_6]^{2+}$ has a maximum at 513 nm (ε = 5 L mol^{-1} cm^{-1}). On the addition of conc. HCl the solution turns blue due to the formation of $[CoCl_4]^{2-}$ and is more intensely coloured with an absorption maximum at 660 nm (ε = 550 L mol^{-1} cm^{-1}). Explain this observation.

(7.5 marks)

iii) Identify which has the larger CFSE (crystal field stabilisation energy) in each of the following pairs of transition metal complexes. Explain your reasoning.

$[Cr(H_2O)_6]^{2+}$ or $[Mn(H_2O)_6]^{2+}$
$[Ru(H_2O)_6]^{2+}$ or $[Fe(H_2O)_6]^{2+}$
$[Fe(H_2O)_6]^{3+}$ or $[Fe(CN)_6]^{3-}$

(7.5 marks)