

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 $[\text{C}_2]^{2-}$. On your diagram, include drawings of the MOs and electron occupancies.

(9 marks)

- ii) Using this MO diagram explain why the bond length in $[\text{C}_2]^{2-}$ (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:



(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, $(\text{HBNH})_3$

(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. ($^{\circ}\text{C}$)	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 pK_a), 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 $[\text{BF}_4]^-$. Use your answer to explain why the B-F bond length is much shorter in BF_3 (1.30 Å) than in $[\text{BF}_4]^-$ (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

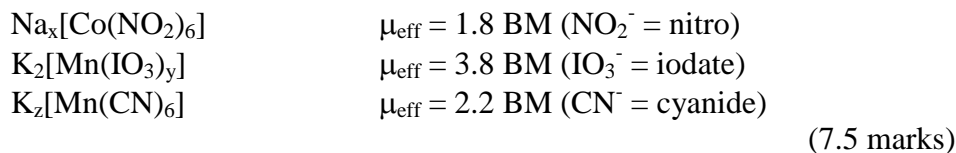
Answer **BOTH** parts of this question.

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.

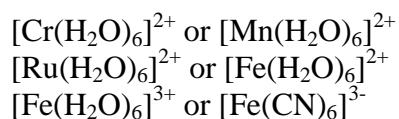
- i) Find the values x, y and z in the following complexes, by determining the oxidation state of the central metal from the experimental values of the effective magnetic moment μ_{eff} .



- ii) The major band in the spectrum of the pink $[(\text{Co}(\text{H}_2\text{O})_6)^{2+}]$ has a maximum at 513 nm ($\epsilon = 5 \text{ L mol}^{-1} \text{ cm}^{-1}$). On the addition of conc. HCl the solution turns blue due to the formation of $[\text{CoCl}_4]^{2-}$ and is more intensely coloured with an absorption maximum at 660 nm ($\epsilon = 550 \text{ L mol}^{-1} \text{ cm}^{-1}$). 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.



(7.5 marks)