

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JUNE 2015, for Internal Students of the
Imperial College of Science, Technology and Medicine**

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

ADVANCED CHEMISTRY THEORY IB

Inorganic Chemistry

Monday 15th June 2015, 09:30-11:45

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

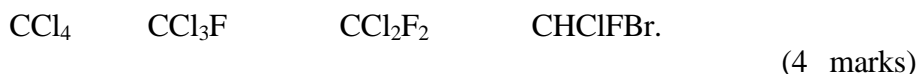
**USE A SEPARATE ANSWER BOOK FOR EACH
QUESTION. WRITE YOUR CANDIDATE NUMBER ON
EACH ANSWER BOOK.**

1.I1 – Molecular Structure

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

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

i) Assign the point groups to each of the following molecules:



ii) Using VSEPR draw the structure of B_2F_4 , show all its symmetry elements and assign its point group. (5 marks)

b) Sketch and label the molecular orbital energy level diagram for the linear anion $[\text{F}-\text{H}-\text{F}]^-$. On your diagram, include drawings of the atomic and molecular orbitals, label them and show the electron occupancies.

(NOTE: the energies for: F 2s is -43 eV, for F 2p is -20 eV and for H 1s is -14 eV) (9 marks)

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

i) Using VSEPR theory, sketch and name the pseudostructures and structures for KrF_2 and $[\text{XeF}_5]^-$. (4 marks)

ii) According to VSEPR theory, what are the two possible structures for SbF_5 ? Draw both structures. If the experimentally observed structure has a D_{3h} point group, what is its geometry? (3 marks)

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

i) Draw the structure of BH_3 and indicate the hybridisation of the B atom. (1.5 mark)

ii) BH_3 reacts with CO to yield BH_3CO . Draw the structure of BH_3CO and indicate the hybridisation of the B, C and O atoms. (2.5 marks)

iii) Using Valence Bond theory and the hybridisation you have suggested, show a bonding scheme for BH_3CO (including sketches of the orbitals involved). (3 marks)

1.I2 – Periodicity and Inorganic Reactivity

Answer **ALL** parts of this question.

a) Give one example for each of the following:

- i) A hypervalent molecule.
- ii) An electron deficient molecule.
- iii) A donor-acceptor complex.

(1 mark each)

b) For the following pairs of molecules state which one reacts rapidly with water. Give your reasoning and a fully balanced equation for the reaction.

- i) CCl_4 and SiCl_4 .

(6 marks)

- ii) SF_4 and SF_6 .

(6 marks)

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

- i) Explain from first principles why molten BeF_2 is not a conductor whilst MgF_2 , CaF_2 , SrF_2 and BaF_2 all conduct in the molten state.

(5 marks)

- ii) Using valence bond theory, compare and contrast the bonding in C_2H_6 and B_2H_6 .

(5 marks)

- iii) By considering their different structures, suggest why white phosphorus is soluble in the solvent CS_2 whereas red phosphorus is not.

(5 marks)

1.I3 – Coordination Chemistry

Answer **ALL** parts of this question.

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

- i) Briefly explain the origins of the Jahn-Teller distortion and how it affects the geometry in octahedral metal complexes.

(3 marks)

- ii) The complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ undergoes a Jahn-Teller distortion. Draw the two possible structures and the corresponding d-orbital splitting diagrams of the Jahn-Teller distortion for this complex. Explain, using Crystal Field Stabilisation Energy (CFSE) arguments, which distortion is most likely.

(8 marks)

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

- i) Depending on the ligand environment, octahedral iron(II) complexes can sometimes be in a spin crossover regime, which means that the high-spin and low-spin configurations of the complex are in an equilibrium. Determine the d-electron configuration and the magnetic moment spin-only value for both configurations.

(4 marks)

- ii) How will temperature affect the equilibrium?

(2 marks)

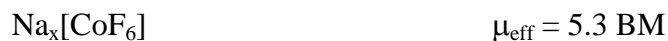
- iii) What will be the effect of raising the temperature on the UV-vis spectrum?

(2 marks)

QUESTION CONTINUED OVERLEAF

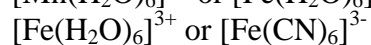
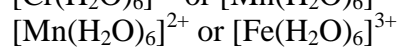
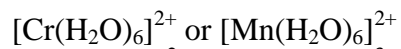
c) Answer **EITHER** part i) **OR** part ii) of this question.

- i) Find 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.



(6 marks)

- ii) Which of the following pairs of complexes has the largest CFSE (Crystal Field Stabilisation Energy)?



(6 marks)