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:

CCl_4 CCl_3F CCl_2F_2 CHClFBr.

(4 marks)

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 $[F\text{-}H\text{-}F]^-$. 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 $[XeF_5]^-$.

(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 valance 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 $[Ti(H_2O)_6]^{3+}$ 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.

$Na_x[CoF_6]$	μ_{eff} = 5.3 BM
$K_y[Fe(CN)_6]$	μ_{eff} = 2.3 BM
$K_z[Mn(CN)_5(OH)]$	μ_{eff} = 2.9 BM

(6 marks)

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

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

(6 marks)