IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2012, 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

Monday 18th June 2012, 09:30-11:30

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) Using VSEPR theory, sketch the predicted structures of XeF_4 and SeF_4.

(4 marks)

ii) Identify the rotational axes of symmetry and assign the point groups of these molecules.

(5 marks)

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

i) Sketch and label the molecular orbital energy level diagram for the linear cationic molecule $[BH_2]^+$. On your diagram, include drawings of the MOs and electron occupancies. (NOTE: the electronegativities of B and H are 2.01 and 2.20 respectively).

(8 marks)

ii) Comment on the bond order and the nature of the two B-H bonds.

(2 marks)

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

i) Indicate the hybridisation of each atom in CH_3CN.

(3 marks)

ii) Using Valence Bond theory, show a bonding scheme (including sketches of the orbitals involved) using the hybridization you have suggested.

(3 marks)

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

i) According to VSEPR theory, what are the two possible structures for AsH_5? Draw both structures.

(2 marks)

ii) The ^1H NMR spectrum of AsH_5 shows two different signals: a triplet (integrating to three protons) and a quartet (integrating to two protons). What is the point group of AsH_5? Explain your reasoning (NOTE: assume that only ^1H is NMR active).

(4 marks)

1.I2 – Periodicity and Inorganic Reactivity

Answer **BOTH** parts of this question.

a) BCl_3 is a monomer in the gas phase, whereas $AlCl_3$ dimerises to give Al_2Cl_6. Discuss the stereochemistry (*i.e.* shape), bonding and hybridisation of both BCl_3 and Al_2Cl_6. Suggest an explanation for their differing aggregation states.

(11 marks)

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

i) Discuss, using diagrams where appropriate, how phosphorous(III) compounds of general formula PR_3 can act as both Lewis Bases and Lewis Acids. For the pair of compounds PH_3 and PF_3 identify both the strongest Lewis Base and the strongest Lewis Acid. Give your reasoning.

(7 marks)

ii) Explain fully why the H-X-H bond angle is 104.5° in H_2O but only 92° in H_2S.

(7 marks)

iii) Discuss with reasoning why Tl reacts with excess to give TlCl rather than $TlCl_3$.

(7 marks)

1.I3 – Coordination Chemistry

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

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

i) Draw Lewis structures for the following ions: $[SCN]^-$ and $[PO_3]^{3-}$. Comment on the shapes of these molecules and include any resonance structures.

(5 marks)

ii) Use these Lewis structures to illustrate how these ions behave as ambidentate ligands.

(3 marks)

iii) Explain why d^8 transition metal ions often prefer square planar geometry.

(5 marks)

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

The standard enthalpies of formation and formation constants for $[Zn(NH_3)_2]^{2+}$ and $[Zn(en)]^{2+}$ are given below (en = ethylenediamine).

$$[Zn(OH_2)_2]^{2+} + 2\,NH_3 \rightleftharpoons [Zn(NH_3)_2]^{2+} + 2H_2O$$

$\Delta H = -28.03$ kJ mol^{-1}; $\log \beta_2 = 5.01$

$$[Zn(OH_2)_2]^{2+} + en \rightleftharpoons [Zn(en)]^{2+} + 2H_2O$$

$\Delta H = -27.6$ kJ mol^{-1}; $\log \beta_1 = 6.15$

i) Use the first of these equations to explain the difference between stepwise and overall formation constants.

(2 marks)

ii) Calculate the entropy change in each reaction.

(4 marks)

iii) Compare the thermodynamic parameters associated with these reactions, and explain any similarities and differences.

(6 marks)

QUESTION CONTINUED OVERLEAF

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

Cobalt(II) chloride undergoes a reversible reaction with water (indicated below):

$$[CoCl_2(OH_2)_2] + 4H_2O \rightleftharpoons [Co(OH_2)_6]Cl_2$$

intense blue ⇌ pink

i) Draw the crystal field splitting diagrams and calculate the magnetic moments (μ_{SO}) of both these compounds.

(6 marks)

ii) Explain the different factors that contribute to the observed colour change.

(6 marks)