IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2016, 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

Tuesday 14th June 2016, 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

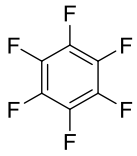
Answer **ALL** parts of this question.

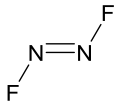
1) Using VSEPR theory, sketch and name the pseudostructures and structures for the following three molecules:

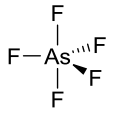
SCl_2 $[IF_4]^+$ $As(CH_3)_3$

(6 marks)

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







(3 marks)

Questions 3 to 6 are multiple choice – please use the multiple choice mark sheet provided for the following parts of this question. A correct answer will be given full marks. An incorrect answer will be given zero. Please only *mark* one answer per question.

3) Using the MO diagram of BN answer the following questions:

i) What is the correct electron configuration of BN?

A) $1\sigma^2\, 2\sigma^{*2}\, 3\sigma^2\, 4\sigma^{*2}\, 5\sigma^2 1\pi^2$

B) $1\sigma_g^2\, 1\sigma_u^{*2}\, 2\sigma_g^2\, 2\sigma_u^{*2}\, 3\sigma_g^2 1\pi_u^1$

C) $1\sigma_g^2\, 1\sigma_u^{*2}\, 2\sigma_g^2\, 2\sigma_u^{*2}\, 1\pi_u^4$

D) $1\sigma^2\, 2\sigma^{*2}\, 3\sigma^2\, 4\sigma^{*2}\, 1\pi^4$

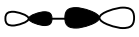
E) $1\sigma^2\, 2\sigma^{*2}\, 3\sigma^2\, 4\sigma^{*2}\, 1\pi^2\, 5\sigma^2$

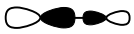
(2 marks)

QUESTION CONTINUED OVERLEAF

ii) Which of the following molecular orbitals is the HOMO in BN?

B—N

A) 

B) 

C) 

D) 

E) None of the above

(2 marks)

iii) Which one of the following statements is **true**:

A) The σ bonding molecular orbitals in BN are gerade (g)

B) In BN there is significant mixing between the different π orbitals

C) The 3σ molecular orbital in BN has a larger contribution from the N 2s orbital than from the B 2s orbital

D) The atomic orbitals of the B atom are lower in energy than those of the N atom

E) The 3σ molecular orbital in BN has a larger contribution from the B 2s orbital than from the N 2s orbital

(2 marks)

iv) What is the bond order of the anionic species $[BN]^-$?

A) 2.5

B) 2

C) 1.5

D) 1

E) None of the above

(2 marks)

QUESTION CONTINUED OVERLEAF

4) Which of the following molecules has an inversion centre (*i*) **AND** an S_4 axis?

A) SF_4

B) XeF_4

C) BF_3

D) NH_3

E) $SnCl_2$

(3 marks)

5) The hybridisation of nitrogen in $[NO_2]^+$, $[NO_2]^-$ and $[NF_4]^+$ respectively are:

A) sp, sp^3 and sp^2

B) sp, sp^2 and sp^3

C) sp^2, sp and sp^3

D) sp^2, sp^2 and sp^3

E) sp, sp and sp^3

(3 marks)

6) Which of the following statements is **false**:

A) When forming molecular orbitals from the overlap of two specific atomic orbitals, the bonding orbitals are always lower in energy than the antibonding orbitals.

B) The geometry of the water molecule can be rationalised correctly using valence bond theory.

C) One of the shortcomings of Molecular Orbital Theory is its inability to account for the paramagnetism of the oxygen molecule, O_2.

D) If a molecular orbital wavefunction changes sign on rotation by 180° about the internuclear axis, the orbtial is given the symmetry label π.

E) A σ-bond is symmetrical with respect to rotation about the bond axis.

(2 marks)

1I2 – Periodicity and Inorganic Reactivity

Answer **BOTH** parts of this question.

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

i) The energies (in kJ mol^{-1}) of single bonds for the Group 16 elements are:

O-O	S-S	Se-Se	Te-Te
142	264	172	126

Discuss and account for the variation in these bond energies.

(5 marks)

ii) Suggest a synthesis for sulphur dioxide giving a fully balanced equation. As part of your answer state the oxidation state of the sulphur atom in the reagents and products.

(2 marks)

iii) Sketch the structure and shape of sulphur dioxide and discuss (giving your reasoning) whether this molecule is capable of acting as a Lewis acid and / or a Lewis base.

(4 marks)

iv) Explain why at standard temperatures and pressures sulphur dioxide is a gas whereas selenium dioxide is a solid.

(4 marks)

b) Account for any **TWO** of the following **THREE** observations:

i) The infrared spectrum of diborane (B_2H_6) exhibits characteristic peaks at around ~2100 and 2500 cm^{-1}.

(5 marks)

ii) Graphite is a good electrical conductor whereas diamond is not.

(5 marks)

iii) NO_2 is a brown gas at room temperature that gradually turns colourless on cooling.

(5 marks)

1.I3 – Coordination Chemistry

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

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

i) Draw a labelled d-orbital splitting diagram for an octahedral complex (ML_6).

(2 marks)

ii) State which d-occupancies can show high and low spin states in octahedral complexes. Describe the factors that will favour a low spin configuration.

(5 marks)

iii) Starting from the ML_6 diagram drawn for part i), derive the d-orbital splitting diagram for a linear complex, ML_2.

(4 marks)

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

i) The nickel complexes shown below have different geometries. Suggest structures for these compounds and justify your reasoning.

$[NiCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$

(4 marks)

ii) Draw labelled d-orbital splitting diagrams for both of the complexes in part b) i). Calculate the effective magnetic moment (μ_{eff}) for each complex using the spin-only formula.

(4 marks)

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

i) Draw all potential isomers for the square planar, monometallic palladium complex $[PdX_2(PPh_3)_2]$, where X = $[SCN]^-$.

(3 marks)

ii) How might you differentiate and identify these isomers using the equipment available in an undergraduate teaching laboratory?

(3 marks)

d) Using arguments based on the spectroscopic selection rules, explain the observation that the intensity of the colour increases from left to right in the following series:

$$[Mn(OH_2)_6]^{2+} < [Mn(CN)_6]^{2-} < [MnO_4]^-$$

(6 marks)