

**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JUNE 2017, for Internal Students of the  
Imperial College of Science, Technology and Medicine**

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

**CHEM40001 INORGANIC CHEMISTRY 1**

**Thursday 29<sup>th</sup> June 2017, 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.**

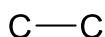
## Q1, Molecular Structure and Periodicity and Inorganic Reactivity

Answer **ALL** parts (I, II and III) of this question.

### PART I

Questions 1 to 10 are multiple choice. A correct answer will be given full marks. An incorrect answer will be given zero. Please only mark *one* answer per question.

1) Using the MO diagram of  $C_2$ , which of the following molecular orbitals is the LUMO:



E) None of the above

(2 marks)

2) For  $C_2$ , which of the following statements is **true**:

A) The  $\sigma$  bonding molecular orbitals in  $C_2$  are ungerade (u)

B) The bond order in  $C_2$  is 1.5

C) The following MO is unoccupied (i.e. does not have electrons):



D)  $[C_2]^{2-}$  is paramagnetic and has a bond order of 3

E) None of the above

(2 marks)

QUESTION CONTINUED OVERLEAF

3) Which of the following molecules has a horizontal mirror plane ( $\sigma_h$ ) **AND** a  $C_4$  axis?

- A) *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>ClBr]<sup>+</sup>
- B) B<sub>2</sub>H<sub>6</sub>
- C) SiCl<sub>4</sub>
- D) SF<sub>4</sub>
- E) None of the above

(2 marks)

4) In which one of the following compounds can the phosphorus centre neither act as a Lewis acid nor a Lewis base:

- A) PCl<sub>3</sub>
- B) PCl<sub>5</sub>
- C) PBr<sub>5</sub>
- D) PCl<sub>4</sub><sup>+</sup>
- E) PCl<sub>6</sub><sup>-</sup>

(2 marks)

5) Which of the following statements is **correct**:

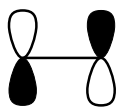
- A) The <sup>19</sup>F NMR spectrum (<sup>19</sup>F, I = ½ and 100% abundance) of XeOF<sub>2</sub> shows two sets of doublets
- B) In XeOF<sub>2</sub>, the Xe atom has a sp<sup>3</sup>d hybridisation
- C) The point group of XeOF<sub>2</sub> is D<sub>3h</sub>
- D) XeOF<sub>2</sub> has a trigonal planar structure
- E) None of the above

(2 marks)

QUESTION CONTINUED OVERLEAF

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

A) The following molecular orbital is *gerade* ( $\pi_g$ ):



B) Valence bond theory predicts that  $\text{CO}_2$  is linear and paramagnetic.

C) The relative order of some molecular orbitals in  $\text{N}_2$  changes as compared to  $\text{O}_2$  due to significant mixing.

D) If a molecular orbital wavefunction changes sign on rotation by  $90^\circ$  about the internuclear axis, the orbital is given the symmetry label  $\delta$ .

E) Valence bond theory can rationalise correctly the shape of  $\text{BF}_3$  by allowing the hybridisation of the 2s orbitals and two 2p orbitals.

(2 marks)

7) Which trend for increasing carbon-carbon bond distance in the allotropes of carbon is **correct**:

A) graphite <  $\text{C}_{60}$  (C=C) <  $\text{C}_{60}$ (C-C) < diamond

B) graphite <  $\text{C}_{60}$  (C=C) <  $\text{C}_{60}$ (C-C) < diamond

C)  $\text{C}_{60}$  (C=C) < graphite <  $\text{C}_{60}$ (C-C) < diamond

D)  $\text{C}_{60}$  (C=C) < graphite < diamond <  $\text{C}_{60}$ (C-C)

E)  $\text{C}_{60}$  (C=C) <  $\text{C}_{60}$ (C-C) < graphite < diamond

(2 marks)

8) In which compound is phosphorus in the **lowest** oxidation state:

A)  $\text{PCl}_4^+$

B)  $\text{P}_4\text{O}_6$

C)  $\text{POCl}_3$

D)  $\text{H}_3\text{PO}_4$

E)  $\text{PCl}_6^{--}$

(2 marks)

QUESTION CONTINUED OVERLEAF

9) Which of the following pair of compounds are **not** isostructural:

- A)  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$
- B)  $\text{CH}_4$  and  $\text{NH}_4^+$
- C)  $\text{BF}_3$  and  $\text{PCl}_3$
- D)  $\text{BF}_4^-$  and  $\text{PCl}_4^+$
- E) borazine and benzene

(2 marks)

10) Which trend in increasing reactivity for the given Group 16 halides is **correct**:

- A)  $\text{SF}_6 < \text{SeF}_6 < \text{TeF}_6 < \text{SF}_4$
- B)  $\text{SF}_4 < \text{TeF}_6 < \text{SeF}_6 < \text{SF}_6$
- C)  $\text{SF}_6 < \text{TeF}_6 < \text{SeF}_6 < \text{SF}_4$
- D)  $\text{TeF}_6 < \text{SeF}_6 < \text{SF}_6 < \text{SF}_4$
- E)  $\text{TeF}_6 < \text{SeF}_6 < \text{SF}_4 < \text{SF}_6$

(2 marks)

PART II – Answer **ALL** parts of this question

a) Sketch and label the molecular orbital energy level diagram for NO. Assume there is MO mixing in this molecule. On your diagram, include drawings of the atomic and molecular orbitals, and the electron occupancies.

(8 marks)

b) Discuss and account for the variation in these bond energies (in  $\text{kJ mol}^{-1}$ ):

N-O	N=O	P-O	P=O
142	607	355	544

(3 marks)

c) Suggest an approximate value for the bond strength in NO based on your answers to parts a) and b) above, giving your reasoning.

(2 marks)

d) Reaction of NO with  $\text{NO}_2$  at low temperature gives a blue liquid. Draw the structure of this new compound.

(2 marks)

QUESTION CONTINUED OVERLEAF

PART III – Answer **ALL** parts of this question

- a) Use VSEPR (showing your workings) to predict the structure of the chlorate anion ( $\text{ClO}_3^-$ ). In your answer include the oxidation state and the hybridisation state of the chlorine atom.  
(4 marks)
- b) On a diagram show all the symmetry operations for  $\text{ClO}_3^-$  and state its point group.  
(3 marks)
- c)  $\text{ClO}_3^-$  is very reactive and used commercially as a bleaching agent. However, perchlorate,  $\text{ClO}_4^-$ , is much less reactive. Account fully for this difference in reactivity.  
(5 marks)
- d) Explain, with reasoning, whether you would expect periodate,  $\text{IO}_4^-$ , to be more or less reactive than perchlorate.  
(3 marks)

## Q2, Coordination Chemistry

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

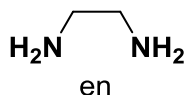
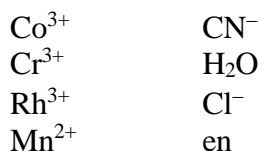
a) Answer **ALL** parts of this question.

The compound  $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$  adopts a trigonal bipyramidal structure.

- i) Draw the structures of all the isomers of this compound. (3 marks)
- ii) The isomer actually formed displays a single  $\nu(\text{CO})$  absorption in the infrared spectrum. State which structure is consistent with this observation and explain your reasoning. Why is this structure adopted in preference to the other possible isomers? (3 marks)
- iii) How could you differentiate between the isomers using proton-decoupled  $^{31}\text{P}$  NMR spectroscopy ( $^{31}\text{P}$ :I=  $\frac{1}{2}$ , 100% abundance)? Sketch the spectra, showing any coupling present (correct chemical shifts are not expected). (4 marks)

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

- i) From the options below, choose the combinations of metal ion and ligands that would give the octahedral complex with the largest crystal field splitting parameter ( $\Delta_{\text{oct}}$ ) value and the combination which would lead to the smallest  $\Delta_{\text{oct}}$  value. Explain your reasoning.



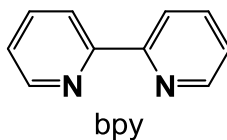
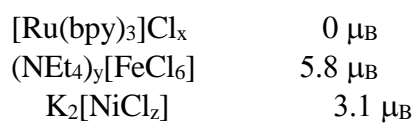
(5 marks)

- ii) For the two complexes chosen in part i), comment on the region of the UV-visible spectrum in which they would absorb as a result of d-d transitions. Predict the relative intensity of that absorption.

(4 marks)

QUESTION CONTINUED OVERLEAF

- c) Find the values of x, y and z in the following complexes by determining the oxidation state of the central metal from the experimental values of the magnetic moment,  $\mu_{\text{eff}}$  (in  $\mu_{\text{B}}$ )



(6 marks)

- d) In  $[\text{CuCl}_6]^{4-}$ , four Cu-Cl bond distances are 260 pm and two are 228 pm. Draw the structure of the complex and explain this observation using a fully-labelled crystal field splitting diagram for this complex.

(6 marks)