

# HONOUR SCHOOL OF NATURAL SCIENCE

## Part 1B Examination Sample Paper

### GENERAL INORGANIC CHEMISTRY

....., 9.30 *a.m.* to 12.30 *p.m.*

Candidates should answer **FIVE** questions of which **TWO** must be from Section A and **THREE** from Section B.

Please begin your answer to each question on a new page.

The numbers in square brackets indicate the marks the Examiners expect to assign to each part of the question. You may assume that, where there is a choice of parts, each part carries equal weight.

**Candidates should be aware of the availability of a table of physical constants and an alphabetic list of relative atomic masses**

The following abbreviations are used:  
Me = CH<sub>3</sub> –, Bu<sup>t</sup> = (CH<sub>3</sub>)<sub>3</sub>C –, Ph = C<sub>6</sub>H<sub>5</sub> –, Bu<sup>n</sup> = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> –,  
ethanoate = CH<sub>3</sub>CO<sub>2</sub><sup>–</sup>

DO NOT TURN OVER until told that you may do so.

# **Contents of paper**

## **Section A**

Questions 1-3 – Comparative chemistry of the elements and their compounds

## **Section B**

Question 4- Solid state chemistry

Question 5 – Reaction mechanisms

Question 6 – Spectroscopy and magnetism

Question 7 – Organometallic chemistry

Question 8 – Post transition metal chemistry, bioinorganic and inorganic NMR

## Section A

1. Compare and contrast the chemistry of the elements in *one* of the following pairs: [20]

K and Cu, B and Si, Be and Mg, Ni and Pd, O and S

2. Discuss points of interest in connection with *four* of the following compounds. [4 x 5]

$B_3N_3H_6$      $HArF$      $S_4N_4$      $K_2Pt(CN)_4Br_{0.33} \cdot 2H_2O$      $H_2O_2$   
 $BN$      $BaTiO_3$      $K_2ReH_9$      $Cu_2(\text{ethanoate})_4 \cdot 2H_2O$   
 $Ti(C_5H_5)_4$      $Cr(CO)_5(C(Bu^t)OMe)$      $U(C_8H_8)_2$

3. Answer *one* of the two parts (a) or (b)

(a) Discuss *three* of the following sets of observations. In each case provide further examples to indicate the extent to which they exemplify the chemistry of the *p*-block elements. [3 x 20/3]

(i) The N–N bond lengths (in pm) in the following nitrogen compounds:

$N_2$  110;     $N_2O$  113;     $H_2NNO_2$  143;  
 $N_2H_4$  145;     $N_2O_4$  175;     $N_2O_3$  186

(ii) The mean bond enthalpies (in  $\text{kJmol}^{-1}$ ) in some group 15 hydrides and chlorides:

	N	P	As	Sb
$EH_3$	391	321	297	254
$ECl_3$	193	322	309	314

(iii)  $\text{PCl}_5$  is thermally stable at  $200\text{ }^\circ\text{C}$ ,  $\text{AsCl}_5$  decomposes above  $-50\text{ }^\circ\text{C}$ ,  $\text{SbCl}_5$  is stable up to  $\sim 140\text{ }^\circ\text{C}$  while  $\text{BiCl}_5$  is unknown. The reduction potentials of some Group 15 elements at  $\text{pH} = 0$  are:

Couple	$E^\circ / \text{V}$
$\text{H}_3\text{PO}_4 / \text{H}_3\text{PO}_3$	$-0.28$
$\text{H}_3\text{AsO}_4 / \text{H}_3\text{AsO}_3$	$+0.56$
$\text{Bi}_2\text{O}_5 / \text{BiO}^+$	$+2.00$

(iv) The N(III), P(III) and As(III) oxides are acidic, Sb(III) oxide is amphoteric, while Bi(III) oxide is basic.

(b) Comment on the outcomes of *FOUR* of the following reactions [4 x 5]

(a) The reaction between an acidified aqueous solution of vanadium(V) and hydrogen peroxide produces an intensely-coloured red-brown species in solution.

(b) The reaction between titanium dioxide and *n*-butyl lithium in hexane produces a black solid. On exposure to moist air this product turns white.

(c) The reduction of  $\text{KReO}_4$  with potassium metal in ethanol produces a colourless oxygen-free and diamagnetic solid with a single resonance in the  $^1\text{H}$  NMR spectrum at  $-3.7\text{ ppm}$

(d) The reaction between sodium borohydride and iodine in a suitable solvent produces a second gaseous product in addition to  $\text{H}_2$ .

(e) Reduction of  $\text{Mo}_2\text{Cl}_{10}$  by sodium amalgam in the presence of  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  under nitrogen in THF produces, after removal of the solvent, an orange solid with an infrared band at  $1978\text{ cm}^{-1}$ .

(f) Chlorine gas reacts with a solution of tetrabutylammonium iodide in dichloromethane to produce yellow crystals. Overnight exposure of these to ultraviolet light results in the evolution of chlorine gas.

**End of Section A**  
**Section B**

4. Comment on *three* of the Parts (a) – (d). [3 × 20/3]

(a) MnO is an insulator whereas TiO is a metallic conductor.

(b) The electrical conductivity of NiO is a function of the partial pressure of O<sub>2</sub> in the atmosphere. For small values of  $x$ , Li <sub>$x$</sub> Ni<sub>1- $x$</sub> O has a higher conductivity than NiO.

(c) Y<sub>2</sub>O<sub>3</sub> is an electrical insulator. However, at 500 °C the electrical conductivity of the semiconductor Bi<sub>2</sub>O<sub>3</sub> is enhanced by the addition of Y<sub>2</sub>O<sub>3</sub> to form a solid solution. The conductivity of ZrO<sub>2</sub> is similarly enhanced when it is reacted with Y<sub>2</sub>O<sub>3</sub>.

(d) Ca should be an insulator because the atomic orbitals on a Ca atom are either empty or completely filled.

5. Answer *both* of the Parts (a) and (b).

(a) Interpret the data in *both* (i) and (ii).

(i) The rate constants determined for amine exchange in *trans*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)(NH<sub>2</sub>Et)] in methanol and hexane solutions. [5]

[Et <sub>2</sub> NH] (mol dm <sup>-3</sup> )	Rate constants / s <sup>-1</sup>	
	$k_{\text{obs}}$ (CH <sub>3</sub> OH)	$k_{\text{obs}}$ (hexane)
0.02	$0.9 \times 10^{-5}$	$0.3 \times 10^{-5}$
0.1	$0.9 \times 10^{-5}$	$1.4 \times 10^{-5}$
0.2	$0.9 \times 10^{-5}$	$2.8 \times 10^{-5}$

*Question continues*

(ii) The rate constants determined for the reduction of the Co(III) complexes by the Cr(II) complexes. [5]

Co(III) complex	Cr(II) complex	Rate constant / $\text{M}^{-1}\text{s}^{-1}$
$[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$	$[\text{Cr}(\text{bipy})_3]^{2+}$	$4.1 \times 10^4$
$[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$	$[\text{Cr}(\text{bipy})_3]^{2+}$	$1.1 \times 10^4$
$[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$	$[\text{Cr}(\text{OH}_2)_6]^{2+}$	$3.0 \times 10^5$
$[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$	$[\text{Cr}(\text{OH}_2)_6]^{2+}$	$1.9 \times 10^1$

(b) Comment on the rates and volumes of activation for water exchange of the following aquo ions. [10]

Complex	$k_{\text{exchange}} / \text{s}^{-1}$	$\Delta V^\ddagger / \text{cm}^{-3} \text{mol}^{-1}$
$[\text{Ca}(\text{OH}_2)_6]^{2+}$	$\approx 5 \times 10^9$	—
$[\text{Mn}(\text{OH}_2)_6]^{2+}$	$2.1 \times 10^7$	-5.4
$[\text{Fe}(\text{OH}_2)_6]^{2+}$	$4.4 \times 10^6$	+3.8
$[\text{Ni}(\text{OH}_2)_6]^{2+}$	$3.2 \times 10^4$	+6.1
$[\text{Al}(\text{OH}_2)_6]^{3+}$	$\approx 1$	—
$[\text{Ti}(\text{OH}_2)_6]^{3+}$	$1.8 \times 10^5$	-5.4
$[\text{Cr}(\text{OH}_2)_6]^{3+}$	$2.4 \times 10^{-6}$	—

*turn over*

6. Answer *two* of the Parts (i) – (iv).

[2 x 10]

(i) The following magnetic susceptibilities are measured at 298 K:

$$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \quad 4.2 \times 10^{-7} \text{ m}^3 \text{ kg}^{-1}$$

$$\text{K}_3[\text{Fe}(\text{CN})_6] \quad 7.7 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$$

Given the value  $NA\mu^0 \mu_B^2/3k = 1.57 \times 10^{-6} \text{ m}^3 \text{ K mol}^{-1}$ , calculate the effective magnetic moments  $\mu_{\text{eff}}/\mu_B$  for the two compounds (where  $\mu_B$  is the Bohr magneton), and account for the values you obtain.

$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$  is found to obey the Curie law well over a wide range of temperature, but not  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . Comment on this difference.

(ii) The table below gives the wavenumber ( $\nu$ ) and the order-of-magnitude extinction coefficient ( $\epsilon_{\text{max}}$ ) of the lowest-energy electronic absorption shown by the following five species, but not in the same order.

$\text{KFe}_2(\text{CN})_6$	$[\text{FeF}_6]^{3-}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
$[\text{FeCl}_4]^{2-}$	$[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$	

Identify the species A–E giving reasons for your choice.

Species	$\nu/\text{cm}^{-1}$	$\epsilon_{\text{max}} / \text{cm}^2 \text{ mol}^{-1}$
<b>A</b>	14200	<0.1
<b>B</b>	4050	100
<b>C</b>	8300	1
<b>D</b>	18 900	10
<b>E</b>	15 000	> $10^4$

*Question continues*

(iii) The lowest-energy intense ( $\epsilon > 10^4$ ) electronic absorption bands of some halide complexes are found at the following wavenumbers,  $\nu/10^3 \text{ cm}^{-1}$ :

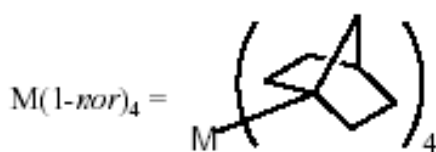
$[\text{CoCl}_4]^{2-}$	42.7	$[\text{CoBr}_4]^{2-}$	34.0	$[\text{ZnBr}_4]^{2-}$	48.6
$[\text{CoBr}_4]^{2-}$	34.0	$[\text{NiBr}_4]^{2-}$	28.4	$[\text{CdBr}_4]^{2-}$	48.6
$[\text{CoI}_4]^{2-}$	25.8	$[\text{CuBr}_4]^{2-}$	16.5	$[\text{HgBr}_4]^{2-}$	35.5

Identify the type of transition involved and comment on the trends observed.

Comment on the observation that  $[\text{CuI}_4]^{2-}$  has not been prepared.

(iv) Comment on the following data, showing the effective magnetic moments ( $\mu_{\text{eff}}/\mu_{\text{B}}$  per metal ion) found at room temperature for some tetrahedral complexes:

		$[\text{Mn}(1\text{-nor})_4]$	3.78		
	$[\text{FeO}_4]^{2-}$	3.71		$[\text{Fe}(1\text{-nor})_4]$	0
$[\text{CoCl}_4]^{2-}$	4.72	$[\text{Co}(1\text{-nor})_4]$	1.89	$[\text{Co}(1\text{-nor})_4]^-$	3.18



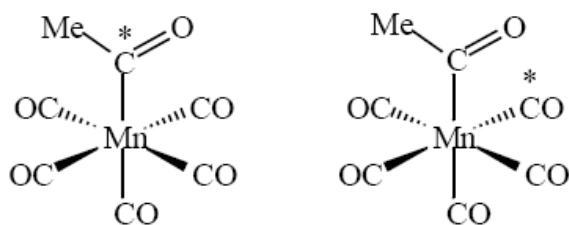
*turn over*

7. Answer *all* parts:

[3 x 20/3]

(a) Comment on the observations that  $\text{TiEt}_4$  decomposes at temperatures above  $-80^\circ\text{C}$  but  $\text{Ti}(\text{CH}_2\text{Ph})_4$  is stable at  $25^\circ\text{C}$ ; and that  $\text{FeMe}_2$  is not known while ferrocene is stable at  $300^\circ\text{C}$ .

(b) Predict the products from the decarbonylation of the two manganese compounds shown below.



(c) Draw a catalytic cycle for the hydrogenation of an olefin using the complex  $[\text{RhCl}(\text{PPh}_3)_3]$ , drawing the structures of the key intermediates involved and commenting on the reaction mechanisms for each stage of the cycle.

8. Answer TWO parts of the following:

a) Comment on TWO of the following observations, indicating to what extent they are typical for post transition metals in groups 12-14 and giving further examples of the behaviour illustrated. [2 x 5]

(i) Tin forms an extensive range of compounds in both the Sn(II) and Sn(IV) oxidation states, but the chemistry of Pb(IV) is much more limited than that of Pb(II).

*Question continues*

- (ii) Mercury forms solid chlorides with empirical formulae  $\text{HgCl}$  and  $\text{HgCl}_2$ .
- (iii) The structures of  $\text{SnO}$  and  $\text{SnS}$  show tin with tetragonal pyramidal and trigonal pyramidal coordination respectively

(b) Write short accounts of two of the following: [2 x 5]

- (i) The role of iron porphyrins in electron transfer and reversible oxygen binding.
- (ii) Co-enzyme  $\text{B}_{12}$
- (iii) The structures, spectroscopic and magnetic properties of biological iron sulphide clusters

c) Predict the specified NMR spectrum, taken in solution of TWO of the following:

[2 x 5]

- (i)  $^{19}\text{F}$  of  $[\text{SF}_5]^-$
- (ii)  $^1\text{H}$  of  $\text{P}(\text{SiH}_3)_2\text{H}$  (ignore coupling between  $^1\text{H}$  and the Si nucleus)
- (iii)  $^{31}\text{P}$  of *mer*- $[\text{RhCl}_3(\text{PPh}_3)_3]$  (with proton decoupling)

Nuclear spins and abundances:  $^{19}\text{F}$ :  $I = \frac{1}{2}$  (100%);  $^1\text{H}$ :  $I = \frac{1}{2}$  (100%);  $^{31}\text{P}$ :  $I = \frac{1}{2}$  (100%);  $^{103}\text{Rh}$ :  $I = \frac{1}{2}$  (100%). Assume that all other naturally occurring isotopes have  $I = 0$

*End of paper*