UNIVERSITY OF SWAZILAND SUPPLIMENTARY EXAMINATION ACADEMIC YEAR 2011/2012

# TITLE OF PAPER:

INTRODUCTORY INORGANIC CHEMISTRY

# **COURSE NUMBER:**

**C201** 

TIME ALLOWED: INSTRUCTIONS: THREE (3) HOURS THERE ARE SIX (6) QUESTIONS. ANSWER ANY FOUR (4) QUESTIONS. EACH QUESTION IS WORTH 25 MARKS.

A PERIODIC TABLE AND A TABLE OF CONSTANTS HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

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### **Question One**

a) What is the total number of orbitals that are present in a shell of principal quantum number n? (Hint: Begin with n = 1, 2 and 3 to recognize the pattern).

[4]

[16]

[4]

[3]

[5]

b) For each of the species given below, draw the Lewis structure. Use the Lewis structure to determine the overall geometry and the molecular shape of the species. Then determine the hybridization scheme for the central atom in the molecule.

i) NO<sub>3</sub><sup>-</sup> ii) SCl<sub>4</sub> iii) XeOF<sub>4</sub>

c) Describe the nature of  $\pi$  bonding and structure of P(SiH<sub>3</sub>)<sub>3</sub> molecule. Compare with the nature of bonding in P(CH<sub>3</sub>)<sub>3</sub>. [5]

#### **Question Two**

a) The Schrodinger equation may be written (in compact form) as

 $(KE + V)\psi = E\psi$ 

What do the terms KE, V,  $\psi$  and E stand for?

- b) Give the quantum numbers that are obtained from solving the Schrodinger equation.
- c) In the hydrogen atom the 3s and 3p orbitals have identical energies, but in the chlorine atom the 3s orbital lies at a considerably lower energy. Explain.
- d) The wave function of a certain orbital is roughly given by

$$\psi = (6-b)be^{-b/3}\cos\theta$$

where  $b = zr/a_0$  and  $a_0$  is the Bohr radius.

Using the above function answer the following questions.

- i) Pick out the radial part and the angular part of the function.
- ii) Draw a rough sketch of the plot of the angular part of the function. Show how you figure out the shape of your plots. [Hint: Evaluate the angular function along the +x, -x, +y, -y, +z and -z directions].

[13]

## **Question Three**

a) For each of the orbitals 1s, $2p_v$ and $3dz^2$ sketc	ch
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- i) the radial function R(r) [6]
- ii) The angular function [7]
- b) Using Slater's rules, calculate  $Z_{eff}$  for the valence electron in i)Ca and ii) Sr. Electron configurations of Ca and Sr are [Ar]4s<sup>2</sup> and [Kr]5s<sup>2</sup> respectively. The first ionization potentials of Ca and Sr are 6.113 and 5.695 eV (1 eV = 1.602 x 10<sup>-19</sup> J) respectively. Do their ionization energies seem to match the calculated effective nuclear charge values? Explain.

## **Question Four.**

- a) Illustrate, with the help of suitable orbital diagrams, how the LCAO approximation gives rise to **bonding** and **anti-bonding** orbitals for the following interactions:
  - i) an s orbital with an s orbital
  - ii) a **p** orbital with a **p** orbital to give  $\pi$  mo's

[Note that energy level diagrams are not required]

- b) Using valence orbitals only, draw the molecular orbital energy-level diagram for the diatomic molecule  $B_2$ . The electron configuration of B is [He]2s<sup>2</sup>2p<sup>1</sup>. Calculate the bond order of the molecule.
- c) Use the energy-level diagram you have drawn in b) above to write an electron configuration for each of the species: i)  $C_2$  ii)  $C_2^{2^-}$  iii)  $C_2^{8^-}$ . Which of these species do you expect to have any chance of existence? Give an explanation for your answer.

[10]

[7]

[8]

[12]

#### **Question Five**

(a) Sketch the Born-Haber cycle for the formation of a salt, MX<sub>2</sub>(s), from a metal, M(s), and a non-metal, X<sub>2</sub>(g)

[10]

b) Calculate the lattice energy of calcium chloride, CaCl<sub>2</sub>(s), that is obtained by reacting Ca(s) with Cl<sub>2</sub>(g), using the following data:

Standard enthalpy of formation of CaCl <sub>2</sub> (s)	-794 kJmol <sup>-1</sup>
Heat of sublimation of Ca(s)	+193 kJmol <sup>-1</sup>
Dissociation energy of Cl <sub>2</sub> (g)	+242 kJmol <sup>-1</sup>
Ionization energy $(I_1+I_2)$ of Ca(g) to Ca <sup>2+</sup> (g)	+1725 kJmol <sup>-1</sup>
Electron affinity of Cl(g)	-347 kJmol <sup>-1</sup>
	[4]

- c) Rationalise the following:
  - i) Ionic radii of the group II elements are smaller than their corresponding atomic radii. [2]
  - ii) Compounds of Be are much more covalent than those of the other group II counterparts. [5]

iii)  $PCl_5$  gas is known whereas  $NCl_5$  is not. [4]

#### **Question Six**

a) A group 2 metal X occurs naturally in great abundance as the carbonate. Metal X reacts with cold water forming compound D, which is a strong base. Aqueous solutions of D are used in qualitative tests for CO<sub>2</sub>. X combines with hydrogen gas, H<sub>2</sub>(g), to give a saline hydride, XH<sub>2</sub>, that is used as a drying agent. Identify X and D. Write the equations for the reaction of X with H<sub>2</sub>O and for the reaction of the hydride, XH<sub>2</sub>, with H<sub>2</sub>O. Write the equation of the reaction that takes place when an aqueous solution of D is used to test for CO<sub>2</sub>.

[10]

- b) Consider the compounds BaSO<sub>4</sub>, BCl<sub>3</sub>, PCl<sub>3</sub>, Mg(OH)<sub>2</sub>, SrH<sub>2</sub>, SiCl<sub>4</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> and KCl. Indicate which ones of the above compounds (when mixed with water)
  - i) are sparingly soluble
  - ii) are soluble without reaction
  - iii) react with water

For each of the species which react with water, write the balanced reaction equation involved.

## [9]

c) For each of the compounds given below, indicate whether the compound will produce an acidic, neutral or a basic solution when it is dissolved in water. Give the formulas of the major species that are formed upon dissolution of the compound.

i) Na<sub>2</sub>O ii) NaCl iii) SO<sub>3</sub>

[6]

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# **Useful relations**

At 298.15 K, RT = 2.4790 kJ mol<sup>-1</sup> and RT/F = 25.693 mV 1 atm = 101.325 kPa = 760 Torr (exactly) 1 bar = 10<sup>5</sup> Pa 1 eV = 1.602 18 × 10<sup>-19</sup> J = 96.485 kJ mol<sup>-1</sup> = 8065.5 cm<sup>-1</sup> 1 cm<sup>-1</sup> = 1.986 × 10<sup>-23</sup> J = 11.96 J mol<sup>-1</sup> = 0.1240 meV 1 cal = 4.184 J (exactly) 1 D (debye) = 3.335 64 × 10<sup>-30</sup> C m 1 T = 10<sup>4</sup> G 1 Å (angström) = 100 pm

# $1 \text{ M} = 1 \text{ mol dm}^{-3}$

# General data and fundamental constants

	Quantity	Symbol	Value
*	Speed of light	С	$2.997 925 \times 10^8 \text{ m s}^{-1}$
*	Elementary charge	е	$1.602\ 177 \times 10^{-19}\ C$
	Faraday constant	$F = eN_{\mathbf{A}}$	$9.6485 \times 10^4 \text{ C mol}^{-1}$
	Boltzmann constant	k	1.380 66 × $10^{-23}$ J K <sup>-1</sup> 8.6174 × $10^{-5}$ eV K <sup>-1</sup>
*	Gas constant	$R = kN_{\rm A}$	8.314 51 J K <sup>-1</sup> mol <sup>-1</sup> 8.205 78 × $10^{-2}$ dm <sup>3</sup> atm K <sup>-1</sup> mol <sup>-1</sup>
*	Planck constant	h $\hbar = h/2\pi$	6.626 08 × 10 <sup>-34</sup> J s 1.054 57 × 10 <sup>-34</sup> J s
*	Avogadro constant	NA	$6.022 \ 14 \times 10^{23} \ \text{mol}^{-1}$
	Atomic mass unit	u	$1.660\ 54 \times 10^{-27}\ \text{kg}$
*	Mass of electron	me	$9.109 \ 39 \times 10^{-31} \ \text{kg}$
*	Vacuum permittivity	ε <sub>0</sub> 4πε <sub>0</sub>	8.854 19 × 10 <sup>-12</sup> J <sup>-1</sup> C <sup>2</sup> m <sup>-1</sup> 1.112 65 × 10 <sup>-10</sup> J <sup>-1</sup> C <sup>2</sup> m <sup>-1</sup>
	Bohr magneton	$\mu_{\rm B} = e\hbar/2m_{\rm e}$	$9.274~02 \times 10^{-24} \text{ J T}^{-1}$
4	Bohr radius	$a_0 = 4\pi\varepsilon_0 \hbar^2/m_e e^2$	5.291 77 $\times$ 10 <sup>-11</sup> m
-	Rydberg constant	$R_{\infty} = m_e e^4 / 8h^3 c \varepsilon_0^2$	$1.097 \ 37 \times 10^5 \ \mathrm{cm}^{-1} = 1.097 \ 37 \times 10^5 \ \mathrm{cm}^{-1}$

## Prefixes

f	p n µ		μ	m	c	d	k	M	G
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The Periodic Table

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