UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2012/2013

TITLE OF PAPER: INTRODUCTORY INORGANIC CHEMISTRY

COURSE NUMBER: C201

TIME ALLOWED: THREE (3) HOURS

INSTRUCTIONS:

1. **There are six (6) questions. Answer any four (4) questions. Each question is worth 25 marks.**
2. **Begin the solution to each question on a new page**

A periodic table, a table of constants and a copy of Slater's Rules have been provided with this examination paper.

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Question One

a) Consider two **hydrogen-like** species, Li^{2+} and B^{4+}.

- i) Write the ground state electronic configuration for the two ions
- ii) In which one of the two species is the electron closer to the nucleus? Explain your answer.
- iii) Which atomic species has lower potential energy? Explain your answer.
- iv) Which atomic species has higher ionization energy?

[8]

b) If the minimum value of m_ℓ for an electron in an atom is –4, what is the smallest value of ℓ that the electron could have? What is the smallest value of n that an electron could have? **[2.5]**

c) Sketch pictures of two d orbitals in the xy-plane which coincides with the plane of the paper.

[5]

d) Consider the orbital function

$$\psi(r,\theta,\phi) = (4-\rho)\rho(e^{-\rho})\sin\theta\cos\phi$$

where $\rho=2zr/na_o$. Use this information to answer the following questions:

- i) Write down the angular, radial and the radial distribution functions. **[2.5]**
- ii) Evaluate the angular function in the directions, +x, -x, +y and –y and deduce the orientation of the orbital. [Help: In the directions +x, -x, +y and –y, the values of ϕ are 0°, 180°, 90° and 270° respectively].

[7]

Question Two

a) Given that the energy of an electron in an orbital corresponding to quantum number n is given by

$$E_n = - (Z^*)^2R_H/n^2,$$

derive the expression for the energy required to ionize an electron from any orbital with quantum number n.

[6]

b) For each of the 3s and $5d_{xz}$ atomic orbitals, sketch:

- a) The radial function R(r)
- b) The radial probability function P_r
- c) The angular function, $Y(\theta,\phi)$ in a suitable plane

In each case indicate the presence of the nodes, if any.

[13]

c). Give the electron configuration for the following:

i) Ru ii) Sm iii) As^{3-}

[6]

Question Three

a) For each of the following species, write the electronic configuration and determine the number of unpaired electrons:

i) Cu^{2+} ii) Mn^{2+} iii) Eu^{2+}

[9]

b) Calculate the effective nuclear charge for a valence electron in each of the atoms N, O and F. Explain your results in terms of any trends.

[7]

c) Outline the Born-Haber cycle and calculate the enthalpy of formation for CsI(s) given the following data:

Sublimation of Cs(s) .... +76.7 $kJmol^{-1}$
Sublimation of iodine...................................... +62.34 $kJmole^{-1}$
Ionization of Cs(g) .... +375.7 $kJmol^{-1}$
Dissociation of $I_2(g)$ .... +78.99 $kJmol^{-1}$
Electron affinity of I(g) .... –328 $kJmol^{-1}$
Lattice energy of CsI(s) .... – 758.1 $kJmol^{-1}$

[9]

Question Four

a) State the defining characteristics of each of the following:

i) A bonding sigma (σ) molecular orbital

ii) An anti-bonding sigma (σ*) molecular orbital

iii) A bonding pi (π) molecular orbital

[6]

b) State the orientation of the following orbitals for optimum overlap:

i) A sigma-type orbital ii) A pi-type orbital **[2]**

c) Suggest two ways by which atoms may be stabilized in compounds or molecules. Give one example of each case.

[3]

d) Sketch a molecular orbital energy level diagram for a cyanide ion, CN^-, and use the diagram to answer questions that follow below.

i) Write electronic configurations for the species CN, CN^-, NO and NO^+.

ii) Calculate bond orders for the species in i) above

iii) List the species in order of increasing bond length, starting with the one with the shortest bond length

[14]

Question Five

a) For each of the following species, determine overall geometry, molecular geometry and hybridization of atomic orbitals around the central atom.

i) SOF_4 ii) XeF_4

[8]

b) Consider the molecule XeO_3F_2, where Xe is the central atom.

i) Write at least four non-equivalent Lewis (i.e. resonance) structures.

ii) Use formal charges to determine which one of the structures from i) above is expected to be the most stable.

[10]

c) Sketch orbital diagrams illustrating the formation of pi bonds involving the following interactions:

i) p_π-p_π interactionii) p_π-d_π interaction

[7]

Question Six

a) Consider the elements Li, Be, B, N, F, Ne.

i) Which ones exist as diatomic molecules in the gaseous state at room temperature?
ii) Which one has the highest boiling point?
iii) Which ones form a chloride of formula $\mathbf{XCl_3}$?
iv) Which one has largest first ionisation energy?
v) Which has the smallest second ionisation energy?
vi) Which ones form hydrides that dissolve in water to give an alkaline solution?
vii) Which one forms an amphoteric hydroxide?
viii) Which one forms an amphoteric hydroxide?

[8]

b) Element Y has an atomic number of 31. Use your knowledge of chemical periodicity to answer the following questions about Y.

i) Write the electronic (s, p, d, f) configuration for Y.
ii) Is element Y in the's-block', 'p-block' or'd-block'?
iii) What is the principal oxidation number of Y?
iv) What is the probable formula of the oxide of Y?
v) Is the oxide of Y likely to be acidic, amphoteric or basic?
vi) Write the equation for a reaction which the oxide of Y would undergo with an aqueous solution of sodium hydroxide.

[8]

c) Each compound in **list 1** has a matching description in **list2**. Correctly match the partners. There is only one correct statement for each compound.

<u>**List 1**</u>	<u>**List 2**</u>
$CaCl_2$	Polymeric in the solid state
$Ca(OCl)_2$	Soda lime
$Be(OH)_2$	An oxidizing agent
CaO	Used in qualitative analysis for sulfates
$BaCl_2$	Hygroscopic solid, used for de-icing
$BeCl_2$	Amphoteric
MgO_2	Quicklime
$Ca(OH)_2/NaOH$	Bleaching powder

[4]

Slater's Rules:

1) Write the electron configuration for the atom using the following design;

(1*s*)(2*s*,2*p*)(3*s*,3*p*) (3*d*) (4*s*,4*p*) (4*d*) (4*f*) (5*s*,5*p*) etc

2) Any electrons to the right of the electron of interest contributes no shielding. (Approximately correct statement.)

3) All other electrons in the same group as the electron of interest shield to an extent of 0.35 nuclear charge units

4) If the electron of interest is an *s* or *p* electron: All electrons with one less value of the principal quantum number shield to an extent of 0.85 units of nuclear charge. All electrons with two less values of the principal quantum number shield to an extent of 1.00 units.

5) If the electron of interest is an *d* or *f* electron: All electrons to the left shield to an extent of 1.00 units of nuclear charge.

6) Sum the shielding amounts from steps 2 through 5 and subtract from the nuclear charge value to obtain the effective nuclear charge.

PHYSICAL CONSTANTS

Speed of light in a vacuum	c_0	2.99792458×10^{8} m s^{-1}
Permittivity of a vacuum	ϵ_0	$8.854187816 \times 10^{-12}$ F m^{-1}
	$4\pi\epsilon_0$	1.11264×10^{-10} c^2 N^{-1} m^{-2}
Planck constant	h	$6.6260755(40) \times 10^{-34}$ J s
Elementary charge	e	$1.60217733(49) \times 10^{-19}$ C
Avogadro constant	N_A	$6.0221367(36) \times 10^{23}$ mol^{-1}
Boltzmann constant	k	$1.380658(12) \times 10^{-23}$ J K^{-1}
Gas constant	R	8.314510(70) J K^{-1} mol^{-1}
Bohr radius	a_0	$5.29177249(24) \times 10^{-11}$ m
Rydberg constant	R_∞	$1.0973731534(13) \times 10^{7}$ m^{-1} (infinite nuclear mass)
	R_H	$1.09677759(50) \times 10^{7}$ m^{-1} (proton nuclear mass)
Bohr magneton	μ_B	$9.2740154(31) \times 10^{-24}$ J T^{-1}
	π	3.14159265359
Faraday constant	F	$9.6485309(29) \times 10^{4}$ Cmol^{-1}
Atomic mass unit	m_u	$1.6605402(10) \times 10^{-27}$ kg
Mass of the electron	m_e	$9.1093897(54) \times 10^{-31}$ kg or $5.48579903(13) \times 10^{-4}$ m_u
Mass of the proton	m_p	1.007276470(12) m_u
Mass of the neutron	m_n	1.008664904(14) m_u
Mass of the deuteron	m_d	2.013553214(24) m_u
Mass of the triton	m_t	3.01550071(4) m_u
Mass of the α-particle	m_α	4.001506170(50) m_u

CONVERSION FACTORS

To convert from units in the first column to units in columns 2 through 4, multiply by the factor given. For example, 1 eV = 96.4853 kJ/mol.

	cm^{-1}	**eV**	**kJ/mol**	**kcal/mol**
cm^{-1}	1	1.239842×10^{-4}	11.96266×10^{-3}	2.85914×10^{-3}
eV	8065.54	1	96.4853	23.0605
kJ/mol	83.5935	1.036427×10^{-2}	1	0.239006
kcal/mol	349.755	4.336411×10^{-2}	4.184	1

SOURCE: International Union of Pure and Applied Chemistry, I. Mills, ed., *Quantities, Units, and Symbols in Physical Chemistry,* Blackwell Scientific Publications, Boston, 1988, pp. 81-2, 85, inside back cover.

The Periodic Table

Period	1	2	3	4	5	6	7	8	9	10	11	12	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	La-Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	Ac-Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	......								
	s block		d block										p block					

Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 146.2	61 Pm 144.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
Actinides	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 241.1	96 Cm 244.1	97 Bk 249.1	98 Cf 252.1	99 Es 252.1	100 Fm 257.1	101 Md 258.1	102 No 259.1	103 Lr 262.1
	f block														