UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2015/2016

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.

PLEASE DO NOT OPEN THIS PAPER UNTIL AUTHORISED TO DO SO BY THE CHIEF INVIGILATOR.

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^o, 180^o, 90^o and 270^o 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_1.

[6]

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

a) The radial function R(r)
b) The radial distribution 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^- and CN^{3-}.

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

iv) State whether each of the species is paramagnetic or diamagnetic. Explain your answer.

[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) Draw a Lewis structure for each of the following, after determining the value of x:

(i) The cyclic silicate ion, $Si_xO_{12}^{8-}$

(ii) The cyclic silicate ion, $Si_xO_{18}^{12-}$

[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 ones form a chloride of formula $\mathbf{XCl_3}$?
iii) Which one has largest first ionisation energy?
iv) Which has the smallest second ionisation energy?
v) Which ones form hydrides that dissolve in water to give an alkaline solution?
vi) 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>
K	Polymeric in the solid state
F_2	Soda lime
$Be(OH)_2$	A superoxide
CaO	A covalent hydride
AsH_3	Reacts with water violently
$BeCl_2$	Amphoteric
CsO_2	Quicklime
$Ca(OH)_2/NaOH$	A strong oxidizing agent

[4]

d) Briefly discuss the diagonal relationship between Be and Al. Give two examples of chemical properties that illustrate their similarities.

[5]

C201 Data

Slater's Rules:

1) Write the correct electron configuration for the atom and organize the orbitals into groupings as follows:

(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 zero to shielding.

3) All other electrons in the same grouping (or same principal quantum number, **n**) 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:

> *Each of the electrons with one less value* (**n-1**)*of the principal quantum number shield to an extent of 0.85 units of nuclear charge. Each of thê electrons with two less values* (**n-2**) *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:

> *Each of the electrons to the left shield to an extent of 1.00 units of nuclear charge.*

6) Sum the shielding amounts from steps 2 through 4 or 5 and subtract from the nuclear charge value to obtain the effective nuclear charge:

$Z_{eff} = Z - S$

where

Z_{eff} = effective nuclear charge

Z = atomic number

S = shilelding constant

PERIODIC TABLE OF THE ELEMENTS

GROUPS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PERIODS	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12	TRANSITION ELEMENTS										26.982 Al 13	28.0855 Si 14	30.9738 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.0983 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.9415 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.9064 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.906 Rh 45	106.42 Pd 46	107.868 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.904 I 53	131.29 Xe 54
6	132.905 Cs 55	137.33 Ba 56	138.906 *La 57	178.49 Hf 72	180.948 Ta 73	183.85 W 74	186.207 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.967 Au 79	200.59 Hg 80	204.383 Tl 81	207.2 Pb 82	208.980 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	(223) Fr 87	226.025 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109									

* Lanthanide series	140.115 Ce 58	140.908 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.925 Tb 65	162.50 Dy 66	164.930 Ho 67	167.26 Er 68	168.934 Tm 69	173.04 Yb 70	174.967 Lu 71
** Actinide series	232.038 Th 90	231.036 Pa 91	238.029 U 92	237.048 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

Numbers below the symbol of the element indicates the atomic numbers. Atomic masses, above the symbol of the element, are based on the assigned relative atomic mass of ^{12}C = exactly 12; ( ) indicates the mass number of the isotope with the longest half-life.

SOURCE: International Union of Pure and Applied Chemistry, I. Mills, ed., *Quantities, Units, and Symbols in Physical Chemistry*, Blackwell Scientific Publications, Boston, 1988, pp 86-98.

Fundamental Physical Constants (six significant figures)

Avogadro's number	N_A	$= 6.02214\times10^{23}$/mol
atomic mass unit	amu	$= 1.66054\times10^{-27}$ kg
charge of the electron (or proton)	e	$= 1.60218\times10^{-19}$ C
Faraday constant	F	$= 9.64853\times10^{4}$ C/mol
mass of the electron	m_e	$= 9.10939\times10^{-31}$ kg
mass of the neutron	m_n	$= 1.67493\times10^{-27}$ kg
mass of the proton	m_p	$= 1.67262\times10^{-27}$ kg
Planck's constant	h	$= 6.62607\times10^{-34}$ J·s
speed of light in a vacuum	c	$= 2.99792\times10^{8}$ m/s
standard acceleration of gravity	g	$= 9.80665$ m/s^2
universal gas constant	R	$= 8.31447$ J/(mol·K)
		$= 8.20578\times10^{-2}$ (atm·L)/(mol·K)

Rydberg constant = 1.097×10^7 m^{-1}

SI Unit Prefixes

p	n	μ	m	c	d	k	M	G
pico-	nano-	micro-	milli-	centi-	deci-	kilo-	mega-	giga-
10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

Conversions and Relationships

Length
SI unit: meter, m

1 km = 1000 m
= 0.62 mile (mi)
1 inch (in) = 2.54 cm
1 m = 1.094 yards (yd)
1 pm = 10^{-12} m = 0.01 Å

Volume
SI unit: cubic meter, m^3

1 dm^3 = 10^{-3} m^3
= 1 liter (L)
= 1.057 quarts (qt)
1 cm^3 = 1 mL
1 m^3 = 35.3 ft^3

Pressure
SI unit: pascal, Pa

1 Pa = 1 N/m^2
= 1 kg/m·s^2
1 atm = 1.01325×10^5 Pa
= 760 torr
1 bar = 1×10^5 Pa

Mass
SI unit: kilogram, kg

1 kg = 10^3 g
= 2.205 lb
1 metric ton (t) = 10^3 kg

Energy
SI unit: joule, J

1 J = 1 kg·m^2/s^2
= 1 coulomb·volt (1 C·V)
1 cal = 4.184 J
1 eV = 1.602×10^{-19} J

Math relationships

$\pi = 3.1416$
volume of sphere = $\frac{4}{3}\pi r^3$
volume of cylinder = $\pi r^2 h$

Temperature
SI unit: kelvin, K

0 K = −273.15°C
mp of H_2O = 0°C (273.15 K)
bp of H_2O = 100°C (373.15 K)
T (K) = T (°C) + 273.15
T (°C) = [T (°F) − 32]$\frac{5}{9}$
T (°F) = $\frac{9}{5}T$ (°C) + 32