UNIVERSITY OF SWAZILAND

FINAL EXAMINATIONS 2014/2015

TITLE OF PAPER: INTRODUCTORY INORGANIC CHEMISTRY

COURSE NUMBER: C201

TIME ALLOWED: THREE (3) HOURS

INSTRUCTIONS: 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.

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

Question One

a) State the relationship between the Bohr orbit with n=1 and the wave mechanical orbital with n=1 for the hydrogen atom. Illustrate your answer with suitable diagrams. [4]

b) For the orbitals $4p_z$ and $5d_x$, sketch the diagrams, in two dimensions, corresponding to the following:

i) The radial probability function P(r)
ii) The angular function A(θ, φ)

[6]

c) What does the term penetration mean, and why is it important in understanding the energies of the s, p, d, and f orbitals (or electrons) with the same principal quantum number? [4]

d) Give the valence shell electron configuration, e.g. $[]ns^x np^y$, etc, of

i) Alkaline earth metals
ii) Halogens
iii) p-Block elements
iv) d-Block elements
v) Lanthanides

[11]

Question Two

a) What are the two main contributions to the cohesive energy of an ionic compound?

[3]

b) What is a Madelung constant? [2]

c) Prepare simple drawings of the following structures:

i) Two tetrahedra sharing an edge
ii) Two octahedra sharing a an edge
iii) Two octahedra sharing a vertex

[6]

d) Give an outline the Born-Haber cycle for the formation of $Mg_3N_2(s)$ starting with constituent elements in their standard states. Then calculate the electron affinity of the nitrogen atom in gaining three electrons to give the oxide N^{3-}, from the following data:

Standard enthalpy of formation of $Mg_3N_2(s)$ .... -461 $kJmol^{-1}$
Heat of sublimation of Mg(s) ....+150 $kJmol^{-1}$
Ionization of Mg(g) to $Mg^{2+}(g)$ ....+2170 $kJmol^{-1}$
Dissociation energy of $N_2(g)$ .... +473 $kJmol^{-1}$
Lattice energy of $Mg_3N_2(s)$ ....-12600 $kJmol^{-1}$

[14]

Question Three

a) Consider the series of diatomics O_2, O_2^+, O_2^-, and O_2^{2-}. Sketch a suitable molecular orbital energy-level diagram and use it to determine

i) Electronic configuration for each of the species
ii) How bond lengths and bond strength will vary among the species
iii) Magnetic properties of each of the species

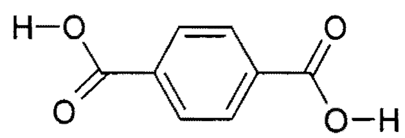
[20]

b) Although the molecule $OPCl_3$ is electronically saturated, the P-O bond length found in the compound is shorter than would be expected for a purely single bond. Draw Lewis structure of the molecule and explain how the P-O double bond character can arise (in the molecule). [5]

Question Four

a) With the help of appropriate structures, suggest the nature of hydrogen bonding present in the following species:

i) Hydrogen fluoride, HF
ii) 1,4-benzene dicarboxylic acid:



1,4-benzene dicarboxylic acid

[6]

b) Use balanced equations to illustrate what happens when the following species are dissolved in water:

i) KO_2

ii) Na_2O_2

iii) CaC_2

[7]

c) For each of the following, draw the Lewis structure and determine the hybridization for the central atom:

i) $[PO_4]^{3-}$ ii) OSF_4, where S is central atom iii) $A\ell_2Cl_6$ in solid state

[12]

Question Five

a) For each of the groups (of the periodic table) given below, state the common oxidation state(s) which occur in oxides, and give the formula, M_xO_y, of each of such oxides:

i) group 1 ii) group 2 iii) group 13 iv) group 14 v) group 15 [6]

b) Give a balanced equation for a reaction that is expected to take place when each of the following chlorides is added to water:

i) $SiCl_4$ ii) PCl_5 iii) $HCl(g)$ [6]

c) Give one example of an oxide and write a balanced reaction equation to illustrate its property as indicated below.

i) An acidic oxide that is soluble in water and show how it reacts with water
ii) A basic oxide that is soluble in water and show how it reacts with water
iii) An amphoteric oxide and show how it reacts with an acid and a base

[9]

Question Six

a) Identfy the species **A, B, C, D, E, F, G, H**, **I, J** and **K**:

i) Al_4C_3 + **A** ⟶ $Al(OH)_3$ + **B**

ii) **C** + Cl_2O_7 ⟶ $HClO_4$

iii) **D** + heat ⟶ BaO + **E**

iv) $Cl_2(aq)$ + **F** ⟶ **G** + $Br_2(aq)$

v) $SiCl_4$ + H_2O ⟶ **H + I**

vi) N_2O_5 + **J** ⟶ $2H^+$ + **K**

[11]

b) Draw Lewis structures for the following:

i) $[Si_2O_7^{6-}$, ii) $[SiO_3^{2-}]_n$

[4]

c) Use Slater's rules to estimate values of Z_{eff} for a valence electron in a) N atom and b) F atom. If the two values are different, explain why.

[10

Useful relations

At 298.15 K, $RT = 2.4790$ kJ mol^{-1} and $RT/F = 25.693$ mV

1 atm = 101.325 kPa = 760 Torr (exactly)

1 bar = 10^5 Pa

1 eV = $1.602\ 18 \times 10^{-19}$ J = 96.485 kJ mol^{-1} = 8065.5 cm^{-1}

1 cm^{-1} = 1.986×10^{-23} J = 11.96 J mol^{-1} = 0.1240 meV

1 cal = 4.184 J (exactly)

1 D (debye) = $3.335\ 64 \times 10^{-30}$ C m

1 T = 10^4 G

1 Å (ångström) = 100 pm

1 M = 1 mol dm^{-3}

General data and fundamental constants

Quantity	Symbol	Value
* Speed of light	c	$2.997\ 925 \times 10^8$ m s^{-1}
* Elementary charge	e	$1.602\ 177 \times 10^{-19}$ C
Faraday constant	$F = eN_A$	9.6485×10^4 C mol^{-1}
Boltzmann constant	k	$1.380\ 66 \times 10^{-23}$ J K^{-1} 8.6174×10^{-5} eV K^{-1}
* Gas constant	$R = kN_A$	$8.314\ 51$ J K^{-1} mol^{-1} $8.205\ 78 \times 10^{-2}$ dm^3 atm K^{-1} mol^{-1}
* Planck constant	h $\hbar = h/2\pi$	$6.626\ 08 \times 10^{-34}$ J s $1.054\ 57 \times 10^{-34}$ J s
* Avogadro constant	N_A	$6.022\ 14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\ 54 \times 10^{-27}$ kg
* Mass of electron	m_e	$9.109\ 39 \times 10^{-31}$ kg
* Vacuum permittivity	ε_0 $4\pi\varepsilon_0$	$8.854\ 19 \times 10^{-12}$ J^{-1} C^2 m^{-1} $1.112\ 65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\ 02 \times 10^{-24}$ J T^{-1}
* Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\ 77 \times 10^{-11}$ m
* Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	~~$1.097\ 37 \times 10^5$ cm^{-1}~~ = 1.09737×10^7 m^{-1}

Prefixes

f	p	n	µ	m	c	d	k	M	G
femto 10^{-15}	pico 10^{-12}	nano 10^{-9}	micro 10^{-6}	milli 10^{-3}	centi 10^{-2}	deci 10^{-1}	kilo 10^3	mega 10^6	giga 10^9

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.07	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	31 Ga Gallium 69.72	32 Ge Germanium 72.59	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.1	45 Rh Rhodium 102.9	46 Pd Palladium 106.4	47 Ag Silver 107.9	48 Cd Cadmium 112.4	49 In Indium 114.8	50 Sn Tin 118.7	51 Sb Antimony 121.8	52 Te Tellurium 127.6	53 I Iodine 126.9	54 Xe Xenon 131.3
55 Cs Cesium 132.9	56 Ba Barium 137.3	57 La Lanthanum 138.9	72 Hf Hafnium 178.5	73 Ta Tantalum 180.9	74 W Tungsten 183.9	75 Re Rhenium 186.2	76 Os Osmium 190.2	77 Ir Iridium 192.2	78 Pt Platinum 195.1	79 Au Gold 197.0	80 Hg Mercury 200.6	81 Tl Thallium 204.4	82 Pb Lead 207.2	83 Bi Bismuth 209.0	84 Po Polonium (210)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (257)	105 Db Dubnium (260)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 Ds Darmstadtium (269)	111 Rg Roentgenium (272)	112	(113)	114	(115)	116	(117)	(118)

58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium (147)	62 Sm Samarium 150.4	63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0
90 Th Thorium 232.0	91 Pa Protactinium (231)	92 U Uranium 238.0	93 Np Neptunium (237)	94 Pu Plutonium (242)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (249)	99 Es Einsteinium (254)	100 Fm Fermium (253)	101 Md Mendelevium (256)	102 No Nobelium (254)	103 Lr Lawrencium (257)

Key: 9 — Atomic number; F; Fluorine; 19.00 — Atomic mass

Metals

Metalloids

Nonmetals

The 1–18 group designation has been recommended by the International Union of Pure and Applied Chemistry (IUPAC) but is not yet in wide use. In this text we use the standard U.S. notation for group numbers (1A–8A and 1B–8B). No names have been assigned for elements 112, 114, and 116. Elements 113, 115, 117, and 118 have not yet been synthesized.

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:

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

> *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:

$Z_{eff} = Z - S$

where

Z_{eff} = effective nuclear charge

Z = atomic number

S = shilelding constant