UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATIONS

ACADEMIC YEAR 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.

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Question One

a) Give an explanation for each of the following:

i) The Bohr theory applies to Be^{3+} but not to Be^{2+}. **(1)**

ii) A wave function $f_1 = \psi$ has the same physical significance as its negative $f_2 = -\psi$. **(2)**

iii) The ionization energy of a Cu atom is smaller than that of a Cu^{2+} ion. **(2)**

b) Consider a diatomic molecule, PN, of phosphorus nitride. Taking the z axis as the internuclear axis, **sketch molecular orbitals described below**, arising from overlap of atomic orbitals on phosphorus with those on nitrogen. [The electronic configuration of a phosphorus atom is $[Ne]3s^2 3p^3$, while that of nitrogen is $[He]2s^2 2p^3$].

i) A bonding sigma (σ) molecular orbital (mo) from the overlap of an **s** orbital on phosphorus with an **s** orbital on nitrogen. **(2)**

ii) A bonding sigma mo arising from overlapping of a **p** orbital on phosphorus with a suitable **p** atomic orbital on nitrogen. **(2)**

iii) Two pi (or π) mo's, one bonding and another anti-bonding, both arising from overlap of a **d** orbital on phosphorus with a suitable **p** atomic orbital on nitrogen. **(4)**

c) Describe how $BeCl_2$ remedies its electron deficiency through polymerization **(7)**

d) Give reasons why compounds of Li are more covalent than those of the rest of group 1 elements. **(5)**

Question Two

a) Consider the 4f series of elements (in the periodic table) whose lightest member has Z=58 and contains one electron in the 4f sub-shell; the heaviest member of the series has a full 4f subshell. Use the above information to answer the questions that follow.

i) Give the electron configuration of the lightest member of the series. [Use the rare gas notation for the inner electrons].

ii) How many elements will be there in the series? Explain briefly.

iii) Give the electronic configuration(s) of the atom(s) with maximum number of unpaired electrons.

(9)

b) A selenium atom has the electronic configuration $[Ar]3d^{10}4s^{2}4p^{4}$. Calculate the effective nuclear charge for an electron

i) in a 4p orbital of Se

ii) in a 3d orbital of Se

(10)

c) Sketch the angular functions corresponding to the following orbitals:

i) $3dz^2$ ii) 3dxz

(6)

Question Three.

a) Using valence orbitals only (and neglecting 3d orbitals), draw a molecular orbital energy level diagram of the molecule, A_2, where each atom, A, has 3s and 3p orbitals as its valence orbitals. Use the diagram to answer the associated questions that follow below. **(6)**

i) Give the ground-state electron configurations and calculate the bond orders of S_2, P_2, and Cl_2. **(9)**

ii) Predict the order of increasing bond strength for the species in (i) above. **(2)**

iii) Figure out whether any of the species in (i) above are expected to be paramagnetic. **(3)**

b) Consider a molecule $H_2C{=}CH_2$. Use a suitable orbital diagram to illustrate how suitable atomic orbitals overlap to form a π (pi) bond. Draw two orbital diagrams, one corresponding to a **<u>bonding interaction</u>** and another corresponding to an **<u>anti-bonding interaction</u>**. **(5)**

Question Four

a) Suggest explanations for the following:

i) The group 2 elements are smaller than the corresponding group 1 elements. **(3)**

ii) M^{4+} ions are difficult to form for group 13 elements. **(3)**

iii) Li^{+} (0.76Å) and Mg^{2+} (0.72Å) have similar ionic radii and react with dinitrogen, N_2, in a similar manner. **(4)**

iv) $Be(OH)_2$ is amphoteric whereas $Ba(OH)_2$ is basic. **(5)**

v) When an aqueous solution of NaOH is added to a solution of $AlCl_3$, a precipitate appears which dissolves in excess base. **(4)**

vi) The molecule PCl_5 is known and is stable whereas the molecule NCl_5 is not known. **(6)**

Question Five

a) Draw the Lewis structure of each of the molecules given below. In each case, give the hybridization of the central atom. **(12)**

i) $[IF_6]^+$
ii) BrF_5

b) The p_π–p_π bond between C and O is stronger than Si and O. Why? **(3)**

c) Describe the bonding in B_2H_6 and Al_2Cl_6 both of which have structures that contain two bridging atoms **(10)**

Question Six

a) Write the Born-Haber cycle for the formation of $CaF_2(s)$ from the elements in their standard states. Given the following information, calculate the lattice energy.

Enthalpy of sublimation.................................... +172 $kJmol^{-1}$

Ionization energy of Ca(g) to $Ca^{2+}(g)$.................... +1640 "

Enthalpy of dissociation of $F_2(g)$ to 2F(g)............ +165 "

Electron affinity of F(g) to $F^-(g)$......................... –328 "

Enthalpy of formation (ΔH_f^o) of $CaF_2(s)$............... +1200 "

(11)

b) Complete and balance the equation for each of the following:

i) $CsF + IF_7 \rightarrow$

ii) Reaction involved in extraction of Br_2 from brine solution

iii) The reaction of P_4O_{10} with water

iv) $SiCl_4 + H_2O \rightarrow$

v) $CaF_2 + H_2SO_4 \rightarrow$

vi) $SO_3 + H_2O \rightarrow$

vii) $CaH_2 + H_2O \rightarrow$

(14)

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	1.096777×10^{7} m^{-1}
Bohr magneton	μ_B	$9.2740154(31) \times 10^{-24}$ J T^{-1}
	π	3.14159265359
Faraday constant	F	$9.6485309(29) \times 10^{4}$ C mol^{-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

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

PERIODIC TABLE OF THE ELEMENTS

GROUPS

TRANSITION ELEMENTS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9	10
1	1.008 H 1									
2	6.941 Li 3	9.012 Be 4								
3	22.990 Na 11	24.305 Mg 12								
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
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
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
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	

PERIODS	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1								4.003 He 2
2			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			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	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	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	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								

* 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.