# UNIVERSITY OF SWAZILAND

# FINAL EXAMINATION

# ACADEMIC YEAR 2011/2012

---

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)  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 $f_2 = -\psi$.  **(1)**

   iii) The 4s orbital in a Cu atom is larger (i.e. occupies more space) and lies at higher energy than the 4s orbital in a $Cu^{2+}$ ion.  **(3)**

b)  Consider a diatomic molecule, VN, of vanadium nitride. Taking the z axis as the internuclear axis, **sketch molecular orbitals described below**, arising from overlap of atomic orbitals on vanadium with those on nitrogen. [The electronic configuration of a vanadium atom is $[Ar]3d^3 4s^2$, while that of nitrogen is $[He]2s^2 2p^3$].

   i)   A bonding sigma ($\sigma$) molecular orbital (mo) from the overlap of a p orbital on vanadium with a suitable atomic orbital on nitrogen.  **(2)**

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

   iii) Two pi (or $\pi$) mo's, <u>one bonding and another anti-bonding</u>, both arising from overlap of a d orbital on vanadium with a suitable atomic orbital on nitrogen.  **(4)**

c)  Describe how $BF_3$ remedies its electron deficiency through delocalized $\pi$ bonding  **(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 $[Ar]3d^{10}4s^24p^4$. Calculate the effective nuclear charge for an electron

    **i)**    in a 4p orbital of Se

    **ii)**    in a 3d orbital of Se

**(10)**

**c)**     The angular function of a certain orbital is approximately given by $A(\theta,\phi)=\sin\phi\sin\theta$. In the xy plane $\theta = 90^\circ$, so that the function is reduced to a simpler orbital function

    $A(\theta, \phi) = \sin\phi$

Deduce the orientation of the orbital in the xy plane and sketch the corresponding orbital diagram. Indicate the presence of angular nodes, if any.

**(6)**

## Question Three.

**a)**     Using valence orbitals only (and neglecting 3d orbitals), draw a molecular orbital energy level diagram of the molecule, $AB$, where B is more electronegative than A, and each atom has 3s and 3p orbitals as its valence orbitals. Use the diagram to answer the associated questions that follow below. **Note:** Si, P, S and Cl have 3s and 3p as their valence subshells.     **(6)**

    **i)**    Give the ground-state electron configurations and calculate the bond orders of SiS, PS, and SCl.     **(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 $O=C=C=O$. Use suitable orbital diagrams to illustrate how suitable atomic orbitals overlap to form $\pi$ molecular orbitals. Draw two diagrams, one corresponding to **bonding interactions** and another corresponding to **anti-bonding interactions**.     **(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 KCN is added to a solution of Al$_2$(SO$_4$)$_3$, a precipitate of Al(OH)$_3$ forms.

**(4)**

**vi)** (SiH$_3$)$_3$N exhibits $\pi$ bonding whereas (CH$_3$)$_3$N does not. Use appropriate resonance structures to illustrate your answer.

**(6)**


## Question Five


**a)** Predict the structure of each of the molecules given below. In each case, give the hybridization of the central atom.

     i)  [IF$_6$]$^+$
     ii)  BrF$_5$

**(6)**


**b)** The p$_\pi$ – d$_\pi$ bond between S and O is stronger than Si and O. Why?     **(4)**


**c)** Describe the bonding in Ga$_2$H$_6$ and Ga$_2$Cl$_6$ both of which have structures that contain two bridging atoms     **(8)**


**d)** Write equations for the following processes involved in the extraction of the elements from their ores (or minerals):

     i)  Reduction of boron oxide by Mg

     ii)  The result of adding hot aqueous NaOH to a mixture of solid Al$_2$O$_3$ and Fe$_2$O$_3$

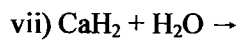     iii)  The reaction of CO$_2$ with Na[Al(OH)$_4$].

**(7)**

## 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.................................... $+172 \text{ kJmol}^{-1}$

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 $(\Delta H_f^o)$ 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) $CaC_2 + H_2O \rightarrow$

    vii) $CaH_2 + H_2O \rightarrow$

**(14)**

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

| s block | d block | | | | | | | | | | p block | | | | | |

**Lanthanides**

| 57<br>La<br>138.9 | 58<br>Ce<br>140.1 | 59<br>Pr<br>140.9 | 60<br>Nd<br>146.2 | 61<br>Pm<br>144.9 | 62<br>Sm<br>150.4 | 63<br>Eu<br>152.0 | 64<br>Gd<br>157.2 | 65<br>Tb<br>158.9 | 66<br>Dy<br>162.5 | 67<br>Ho<br>164.9 | 68<br>Er<br>167.3 | 69<br>Tm<br>168.9 | 70<br>Yb<br>173.0 | 71<br>Lu<br>175.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

**Actinides**

| 89<br>Ac<br>227.0 | 90<br>Th<br>232.0 | 91<br>Pa<br>231.0 | 92<br>U<br>238.0 | 93<br>Np<br>237.0 | 94<br>Pu<br>239.1 | 95<br>Am<br>241.1 | 96<br>Cm<br>244.1 | 97<br>Bk<br>249.1 | 98<br>Cf<br>252.1 | 99<br>Es<br>252.1 | 100<br>Fm<br>257.1 | 101<br>Md<br>258.1 | 102<br>No<br>259.1 | 103<br>Lr<br>262.1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

| f block |

## 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$^{-1}$ $= 1.986 \times 10^{-23}$ 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 | $F = eN_A$ | $9.6485 \times 10^4$ C mol$^{-1}$ |
| Boltzmann constant | $k$ | $1.380\ 66 \times 10^{-23}$ J K$^{-1}$ |
| | | $8.6174 \times 10^{-5}$ 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 | $h$ | $6.626\ 08 \times 10^{-34}$ J s |
| | $\hbar = h/2\pi$ | $1.054\ 57 \times 10^{-34}$ 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 | $\varepsilon_0$ | $8.854\ 19 \times 10^{-12}$ J$^{-1}$ C$^2$ m$^{-1}$ |
| | $4\pi\varepsilon_0$ | $1.112\ 65 \times 10^{-10}$ 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$^{-1}$ $= 1.09737 \times 10^7$ m$^{-1}$ |

## Prefixes

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

UNIVERSITY OF SWAZILAND
CHEMISTRY DEPARTMENT

*Compiled by Dr. N D Silavwe*

## 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.