University of Windsor
Chemistry and Biochemistry
Chemistry 59-250, Fall Term 2005

Assignment 1

Answer Key

Question #1
Oxidation States and RedOx Chemistry

Use the attached oxidation state (Frost) diagram to determine whether the following redox reactions will proceed and, if so, the oxidation states of the products. All reactions are in acidic conditions ($[H^+] = 1$) and there is no need to balance the equations.

(i) $Cl_2 + H_2O \rightarrow H^+ + Cl^- + O_2$

(ii) MnO_2 + oxalic acid $\rightarrow$ Mn(+2) + CO_2

(iii) Cu(+1) + acid $\rightarrow$ Cu(metal) + Cu(+2)

(iv) Fe(+3) + Cr(+2) $\rightarrow$ Fe(+2) + Cr(+3)

(v) calcium metal + oxalic acid $\rightarrow$ No Reaction

Identify the oxidation state of each atom in the following equations and balance the equations:

$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$
Cu(0) N(+5) Cu(+2), N(+5) N(+2)
3 Cu + 8 HNO_3 → 3 $Cu(NO_3)_2$ + 2 NO + 4 H_2O

$PO_3^{-3} + MnO_4^- + H^+ \rightarrow Mn(+2) + PO_4^{-3} + H_2O$
P(+3) Mn(+7) Mn(+2) P(+5)
5 PO_3^{-3} + 2 MnO_4^- + 6 H^+ → 2 Mn(+2) + 5 PO_4^{-3} + 3 H_2O

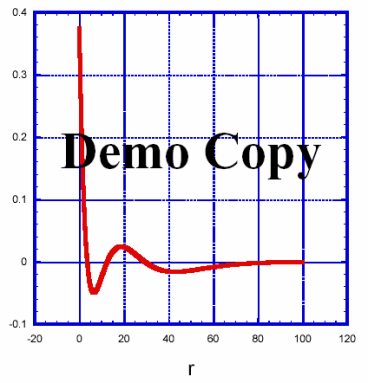
$Fe(+2) + MnO_4^- + H^+ \rightarrow Mn(+2) + Fe(+3) + H_2O$
Fe(+2) Mn(+7) Mn(+2) Fe(+3)
5 Fe(+2) + 1 MnO_4^- + 8 H^+ → 1 Mn(+2) + 5 Fe(+3) + 4 H_2O

Question #2
Quantum Numbers and Drawing Orbitals

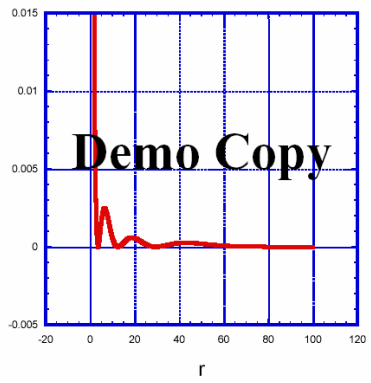
Provide appropriate quantum numbers for an electron in the following orbitals:

	n	ℓ	m_ℓ	m_s
(i) 4s	4	0	0	±1/2
(ii) $5p_x$	5	1	±1	±1/2
(iii) $4d_{z^2}$	4	2	0	±1/2
(iv) $3d_{x^2-y^2}$	3	2	±2	±1/2

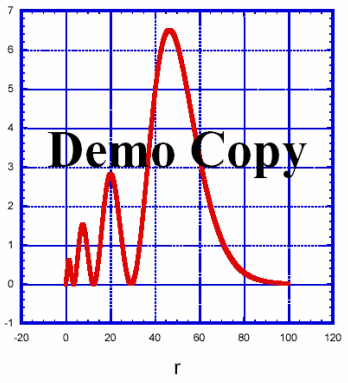
Draw reasonable plots (function vs. r) of the radial functions Ψ, Ψ^2 and $4\pi r^2\Psi^2$ for a 4s orbital.



Ψ



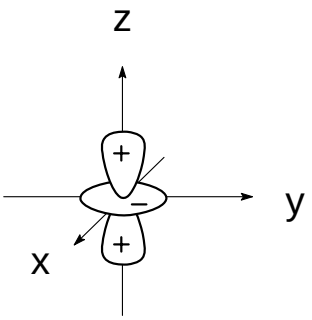
Ψ^2



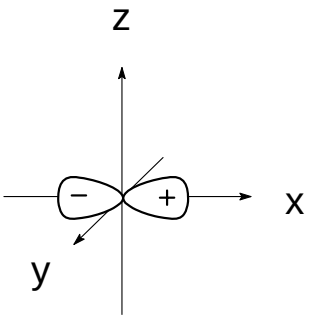
$4\pi r^2\Psi^2$

Draw reasonable representations, indicating their three-dimensional nature as best you can, of the following orbitals [specify the direction of the axes used and include sign of the phase (+ or -) of each lobe]:

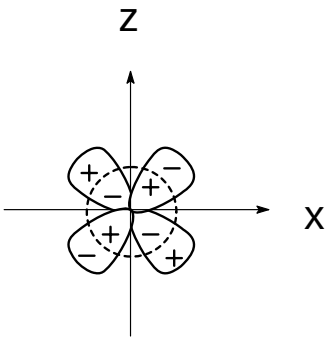
(i) $3d_{z^2}$



(ii) $2p_x$



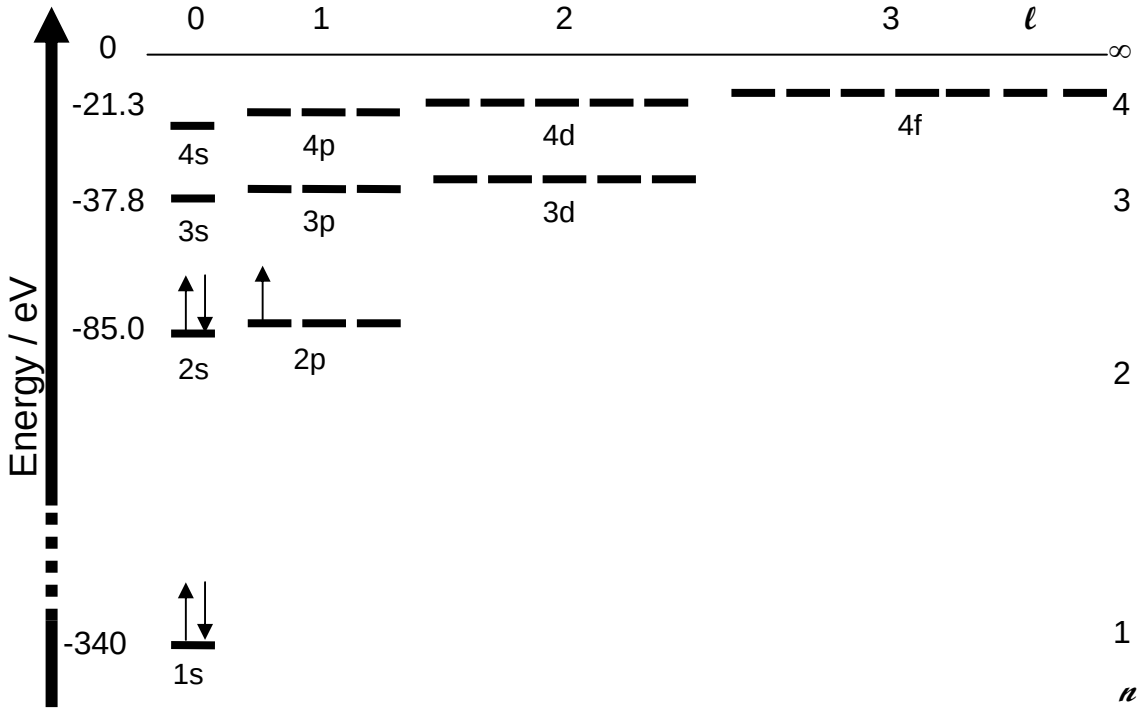
(iii) $4d_{xz}$



Question #3

Energy Level Diagrams and the Bohr Equation

Use the Bohr equation (ignore the correction for effective nuclear charge) to construct an energy level diagram for **boron**. Determine the energies for the first 4 shells and for n = ∞, label all subshells and don't forget to include the electrons.



Question #4

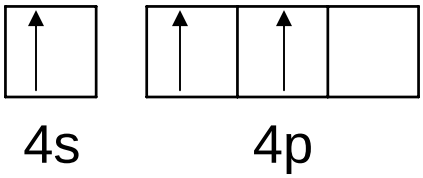
Electron Configurations, Ground States, Excited States and Forbidden States

(i) Write the complete electron configuration for the ground state of gallium.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^1$

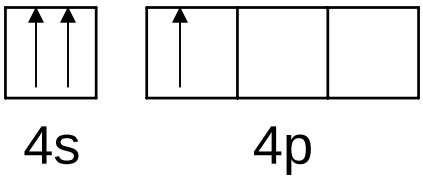
(ii) An "excited state" of an atom has a higher energy configuration than the ground state configuration. Put electrons in the valence orbitals (i.e. boxes) below to give an excited state electron configuration for gallium.

This is one example, any example that is "allowed", is not the ground state, and has 3 electrons should be OK.



(iii) A "forbidden state" of an atom has a hypothetical electron configuration that defies at least one of the rules we have discussed regarding allowed quantum numbers. Put electrons in the valence orbitals (i.e. boxes) below to give a forbidden electron configuration for gallium.

This is one example, any example that has 3 electrons and breaks the Pauli exclusion principle should be OK.



Question #5
Slater's Rules and Ionization Energies

Use Slater's rules to calculate σ, *Z** and the first ionization energy for **three** of the elements in group 14. Please show your calculations (that's the important part) and remember that the first ionization energy is found by the equation IP = 13.6 ($Z^{*2}/\mathbf{n}^2$). Compare your calculated ionization energies to the experimental values that I provided in class - is this method accurate for such predictions? Use the back of this page if extra space is required.

C:$(1s^2)(2s^2\ 2p^2)$
σ = (2 * 0.85) + (3 * 0.35) = 2.75
Z* = 6 – 2.75 = 3.25
IP = 35.9 eV (1 significant figure after decimal because of the Rydberg constant)

Si: $(1s^2)(2s^2\ 2p^6)(3s^2\ 3p^2)$
σ = (2 * 1.0) + (8 * 0.85) + (3 * 0.35) = 9.85
Z* = 14 – 9.85 = 4.15
IP = 26.0 eV

Ge: $(1s^2)(2s^2\ 2p^6)(3s^2\ 3p^6)(3d^{10})(4s^2\ 4p^2)$
σ = (10 * 1.0) + (18 * 0.85) + (3 * 0.35) = 26.35
Z* = 32 – 26.35 = 5.65
IP = 27.1 eV

Sn: $(1s^2)(2s^2\ 2p^6)(3s^2\ 3p^6)(3d^{10})(4s^2\ 4p^6)(4d^{10})(5s^2\ 5p^2)$
σ = (28 * 1.0) + (18 * 0.85) + (3 * 0.35) = 44.35
Z* = 50 – 44.35 = 5.65
IP = 17.4 eV

Pb: $(1s^2)(2s^2\ 2p^6)(3s^2\ 3p^6)(3d^{10})(4s^2\ 4p^6)(4d^{10})(4f^{14})(5s^2\ 5p^6)(5d^{10})(6s^2\ 6p^2)$
σ = (60 * 1.0) + (18 * 0.85) + (3 * 0.35) = 76.35
Z* = 82 – 76.35 = 5.65
IP = 12.1 eV

The predicted first ionization enthalpies (denoted IP above) are not very accurate (the experimental values are: C 11.3 eV ; Si 8.2 eV; Ge 7.9 eV; Sn 7.3 eV; Pb 7.4 eV). There are several reasons for this difference but the main one is that the model we are using to calculate Z* is too simple. Another major reason for the discrepancy is that we are using the Rydberg constant calculated for H (another simplification) instead of using the appropriate constant for each of the nuclei. I just wanted you to notice that the predictions are not accurate but the overall trend down the group is predicted qualitatively.