Practice Problems CH 07 7.1 to 7.5 AK

1. (6 points) Answer the following questions about ionization energies:
   (a) Why are ionization energies always positive quantities?
   (b) Why does the fluorine atom have a larger first ionization energy than the oxygen atom?
   (c) Why is the second ionization energy of an atom always greater than its first ionization energy?

a) ionization energy is the energy needed to remove an electron from an outermost shell. Since we are moving particles apart that are attracted to each other, it takes energy, an endo thermic process

b) nuclear charge (Z) increases across a row. Subshell shielding is not as effective as n (quantum shell) shielding. Therefore, the Z_{eff} is increasing across the row. Increasing Z_{eff} , increases the attractive forces between the electron and the nucleus. Since the Z of fluorine is greater than the Z of oxygen, the fluorine should have a larger $Z_{eff,}$ and therefore, a larger ionization energy.

c) Removing an electron reduces the shielding of the outer most electrons. As shielding decreases, Z_{eff} increases. When Z_{eff} increases, attraction increases for the outermost electron and more energy is needed to remove an electron. When a cation is created from an atom, the Z_{eff} increases as compared to the parent atom. Z_{eff} increases with increasing removal of outer electrons, increasing the ionization energy.

NOTE: although it might seem like b and c have the same answer, the processes occurring are different.

2. (6 points) The titanium (II) ion is iso-electronic with the calcium atom.
   (a) Are there any differences in the electron configurations of titanium (II) and calcium?

YES! This is the electron configuration of the atom Ti [Ar] $3d^2 4s^2$, when Ti loses and electron the new electron configuration looks like this. Ti^{2+} [Ar] $3d^2$. The calcium atom has the electron configuration of [Ar] $4s^2$. Electrons are lost from the highest n, l of the orbitals.

   (b) Will the 2s orbital in calcium be more stable than the 2s orbital in titanium?

The 2s orbital for Ca is less stable than the 2s orbital for Ti (and for that matter, the Ti^{2+} ion). The $2s_{Ca}$ has a lower Z for the same shielding as the Ti atom. This means that the Z_{eff} for the Ca is lower than Ti. Higher Zeff equal more stable subshells.

   (c) Will calcium and titanium (II) have the same number of unpaired electrons?

NO: Calcium has no unpaired electrons (box diagram!!), while Titanium has two unpaired electrons in the 3d subshell.

3. (**8 points**) Determine which of the following statements are true and explain why or why not based on shielding effects, quantum shielding, and/or Z_{eff}.

   a. Electron affinity of the Cesium atom is greater and more exothermic than the fluorine atom.

FALSE: EA is the energy released when an eltron is added to an outermost shell. The HIGHER the n value, for the same l the more likely the EA will be LESS exothermic. This means that atoms lower and to the left of the periodic table have less exothermic EA than atoms higher and to the right of the periodic table.
Cs has half-filled 6s subshell while F atom has an almost filled 2p subshell. The attractive force for the addition of an electron to complete the octet to form F^- is more exotermic then to form Cs^-. Cs has more n shielding even though the $Z_{Cs}>Z_F$.

   b. The ionization energy of an anion is larger than that of the parent atom.

FALSE: ionization energy is the energy needed to remove an electron from an outermost shell. The anion has a lower Z_{eff} then the parent atom because it has more shielding. Shielding reduces the attractive forces between the outermost electron anthe nucleus making the electron easier to remove.

   c. The lithium ion is larger than the rubidium ion

FALSE: Li and Li^+ are in a lower n value than Rb and Rb^+ [N=2 vs. n = 5]. The outermost electron is further away from the nucleus. Since the attractive force between the nucleus is inversely proportional to the radius, as the force decreases, the radius increases. Atoms and ions with larger n values have larger radii.

   d. The nitride anion is smaller than the fluorine atom

FALSE: since the N atom is larger than the F atom due to Z_{eff}, the addtion of electrons to the outer most shell to complete the octet in the formation of the nitride ion increases the shielding. This decreases the Z_{eff} of N and makes it even larger than the fluorine atom.

4. (5 points) Circle the best choice in the list:

Smallest radius: Ca^{2+}, Sr^{2+}, Ra^{2+}

	Ca^{2+}	Sr^{2}	Ra^{2+}
N	4	5	7

As n increases, the radius decreases because the outer most electron is further from the nucleus.

Lowest **second** ionization energy: Mg, Ne, Na

	Ne	Na	Mg
N	2	3	3

Z	10	11	12
e-configuration	[Ne}	[Ne]$3s^1$	[Ne]$3s^2$
1^{st} IE	[He]$2s^2 2p^5$	[Ne]	[Ne]$3s^1$
2^{nd} IE	[He]$2s^2 2p^4$	[He]$2s^2 2p^5$	[Ne]

The lowest IE would be Mg. Removing 2electrons from the outermost shells creates a noble gas shell for Neon. The highest would be Neon.

a. Smallest atom: Sn, I, At

	Sn	I	At
N	5	5	6

Radii decrease across a period and increase down a family, as a general trend. Since Sn and I are in the same row and Sn is in group 4A while I is in group 7A, I should be smaller than Sn. At is below I, so it should have a larger radius. The smallest atom would be iodine.

b. Impossible shell designation: 4g, 5d, 4p

4g, not because of the 'g' designation but because n=4 has only four allowed subshells, s, p, d, and f. A 'g' orbital first appears in the n=5 principal quantum shell.

c. Largest negative electron affinity: O, B, Na

Na would have the lowest EA while O would be largest: larges Z_{eff}, (O vs B), smallest n, larger l (Na vs O)

5. (8 points) Arrange the species in each group in order of **increasing** ionization potential, and explain in each case the reason for the sequence:

a. Fe, Fe^{2+}, Fe^{3+}

$IE_{Fe}<IE_{Fe(2+)}<IE_{Fe(3+)}$ As electrons are removed the Z_{eff} increases because shielding decreases. The attractive force for the electron to the nucleus increases; this is directly proportional to the IE. It is harder to remove an electron with an increasing Z_{eff}.

a. (2 points) .N, O, F

$IE_o<IE_N<IE_F$ Based on the periodic trend, one would expect that the ionization energy increases across the periodic table; but experimental values belie that notion. When we examine the box diagrams for nitrogen vs oxygen, we see that removing an electron from N to make N^+ destroys a half-filled shell. Half-filled shells are stable because the electron electron repulsions are minimized. Removing an electron from O to make O^+ creates a half-filled shell. This is more stable, and the electron is removed easier. Fluorine has the highest Z_{eff} in the period. As Z_{eff} increases, the attraction between the nucleus and the outermost electron increases; it takes more energy to remove the electron.

b. (2 points) K^+. Ar, Cl^-

$IE_{ACL(-)}<IE_{Ar}<IE_{K(+)}$ anions have the lowest ionization energy because they have the lowest Z_{eff}. It would be relatively easy to remove the electron compare to the other atoms and ions listed. Next would be Ar. Argon represents a completed noble gas shell. The electrons are attracted to the nucleus, so more energy has to be inputted in order to remove the outermost electron of argon to make the Ar^+ ion. The potassium ion would have the highest ionization energy. It is iso-electronic to argon, but has a larger Z (nuclear charge). Both have the same shielding, but the potassium ion has a larger Z_{eff}, making harder to remove the outer electron.

1) Supposed to be #4
   (5 points) Circle the best choice in the list:
   d. Smallest radius: Ni^{2+}, Pd^{2+}, Pt^{2+}

   e. Lowest second ionization energy: Ar, K□ Ca

   f. Smallest atom: Sn, I, Bi

   g. Impossible shell designation: 4g, 5d, 4p

   h. Most positive electron affinity: Ba, Sr, Cs

Atoms and ions in the same family have an increasing radius as the value of 'n' increases.

(see b for in the problem above), as electrons are removed and the noble gas core is 'mined' for electrons, the Z_{eff} increases making it more difficult to remove electrons. Calcium would have the lowest $\underline{2^{nd}}$ ionization energy because removing 2 electrons takes it to the noble gas core, but not beyond.

Radii decrease (general trend) across the periodic table, and increase down. Tin and iodine are in the same period. Tin is in group 4A while iodine is in group 7A. The Z_{eff} of tin is smaller than iodine, the attractive force is lower, because Z is lower (shielding not changing that much). Bismuth is in a larger n value. The radius of bismuth is larger than the other two atoms.

4g is an impossible shell, not because of the g designation (yes! This does exist-we did not cover it in class), but because the n=4 shell has only 4 subshells, 4s, 4p, 4d, 4f. the 'g' subshell starts with n=5.

Electron affinity increases with decreasing radii and n, and the emptier subshells. Ba and Sr have the same fill ns^2 while Cs is ns^1 . Cs has a place to add an electron while Ba and Sr do not. These atoms should have positive electron affinities. So the next question is, 'Which atom of the two, is even less likely to add an electron?" Barium is larger, it will not want an electron. It has the most positive electron affinity

6. (8 points) The first ionization energies for the period 2 elements are given below.   the values of the ionization energies for groups 3A and 6A drop slightly below the generally increasing trend.

Element	Li	Be	B	C	N	O	F	Ne
IE	520	899	800	1086	1402	1314	1681	2081

b. (4 points) Draw the box diagrams for the atoms Li, Be, O, and N.

	1s	2s	2p		
Li	↑↓	↑			
Be	↑↓	↑↓			
O	↑↓a	↑↓	↑↓	↑	↑
N	↑↓	↑↓	↑	↑	↑

c. (2 points) Draw the box diagrams for the ions that arise from the first ionization of nitrogen and oxygen.

	1s	2s	2p		
O	↑↓a	↑↓	↑	↑	↑
N	↑↓	↑↓	↑	↑	

(2 points) Based on electron configurations, Zeff, and any other trends, explain why the first ionization

The electron configuration of O^+ is iso-electronic to N. Removing an electron from the oxygen requires less energy because the electron configuration produced is more stable, electron-electron repulsions have been reduced. So even though the O atom has a higher Z_{eff} (and a smaller atom) than the N atom, the stabilizing factor of lowering electron-electron repulsions allows for a lower ionization energy. The nitrogen atom is destabilized when an electron is removed to create the N^+ ion. The half-filled shell is very stable, and this takes more energy to remove an electron.