Inorganic Chemistry with Doc M.

Day 2. Slater Shielding and Effective Nuclear Charge.

Topics:

1. Shielding, Slater's Rules, and effective nuclear charge, Z_{eff}
2. Pertaining to cations and anions
3. Pertaining to main group elements
4. Pertaining to transition metal elements
5. Periodic trends revisited
6. Ionic size (radius)

1a. Shielding values for the first 20 elements (H through Ca). We can estimate these quite simply. Here's how. Write the electron configuration by grouping the s and p electrons together: $(1s)^a\ (2s2p)^b\ (3s3p)^c$.

Problem:	**My work:**
a. P	$(1s)^2\ (2s2p)^8\ (3s3p)^5$
b. F	
c. Cl	
d. Mg	
e. C	

1b. Shielding is used to estimate how much the *other* electrons in an atom filter out the charge of the protons. For that reason, shielding always refers to one specific electron, typically a valence electron. Therefore, when we calculate shielding, we must not consider the electron in question. Rewrite the above electron configurations for the purpose of calculating the shielding value.

Problem:	**My work:**
a. P	$(1s)^2\ (2s2p)^8\ (3s3p)^4$
b. F	
c. Cl	
d. Mg	
e. C	

1c. Slater's Shielding Rules for valence electrons are:

- electrons in the same (nsnp) group contribute 0.35 towards the overall shielding
- electrons in the n-1 group contribute 0.85 towards shielding; n is the principle quantum number.
- electrons in the n-2 (and lower) group(s) contribute 1.00 towards the overall shielding

Slater's Shielding values are referred to by "S". Determine S for each of the following.

Problem:	**My work:**
a. P	$S = 2 \times 1 + 8 \times 0.85 + 4 \times 0.35 = 10.2$
b. F	
c. Cl	
d. Mg	
e. C	

1d. The effective nuclear charge, Z_{eff}, (also called Z*) is simply the atomic number, Z (the number of protons), - S. Determine Z_{eff} for each of the following. Remind yourself of the significance of the resulting value: for example, a valence electron on phosphorus sees/feels the attraction of 4.8 protons.

Problem:	**My work:**
a. P	$Z_{eff} = N - S = 15 - 10.2 = 4.8$
b. F	
c. Cl	
d. Mg	
e. C	

1e. Chemists are usually interested in valence electrons. However, Slater's Shielding Rules work for any core electrons as well as valence electrons. We add one more rule:

- electrons in higher groups to the electron in question, contribute nothing. That is to say, when the configuration is written in the format $(1s)^a\ (2s2p)^b\ (3s3p)^c$, and the electron in question was in the 2s2p group, electrons in the 3s3p group would not count.

Determine S and Z_{eff} for each of the following. Note in worked example (a) that the electron in question, a (2s2p) electron is not including in the shielding calculation. Also note that considering an s- or p-electron gives the same results.

Problem:	**My work:**
a. a 2s electron on P	*$S = 2 \times .85 + 7 \times 0.35 = 4.15$* *$Z_{eff} = N - S = 15 – 4.15 = 10.85$*
b. a 2p electron on Mg	
c. a 2s electron on Cl	

1f. One minor exception occurs when considering the shielding experienced by an electron in the 1s orbital. The main example of this is helium, but whenever considering a 1s electron as a core electron, a shielding of 0.30 works better than 0.35. So the first rule stated in 1c becomes edited slightly:

- electrons in the same (nsnp) group contribute 0.35 towards the overall shielding, except for electrons in the 1s orbital, for which 0.30 gives better results.

Determine S and Z_{eff} for each of the following.

Problem:	**My work:**
a. a 1s electron on He	
b. a 1s electron on Mg	

2. Cations and anions. Everything works according to the rules! Just keep track of the number of electrons doing the shielding — and continue to not count the electron in question. Write the electron configuration in Slater format and determine S and Z_{eff} for each of the following.

Problem:	**My work:**
a. a 2s electron on Na^+	$(1s)^2 (2s2p)^7$ $S = 2 \times .85 + 7 \times 0.35 = 4.15$ Z_{eff}, $= N - S = 11 – 4.15 = 6.85$
b. a 3p electron on Cl^-	

c. a 2p electron on Mg^{+2}	
d. a 1s electron on Li^+ (See 1f above!)	

3. Slater's Shielding Rules for Main Group elements. The rules we have learned for the first 20 elements apply to any *main group* element. The Slater electron configuration continues from $(1s)^a$ $(2s2p)^b$ $(3s3p)^c$:

$(1s)^a$ $(2s2p)^b$ $(3s3p)^c$ $(3d)^d$ $(4s4p)^e$ $(4d)^f$ $(4f)^g$ $(5s5p)^h$ $(5d)^i$ $(5f)^j$ $(6s6p)^k$ and so on

Write the electron configuration in Slater format and determine S and Z_{eff} for each of the following.

Problem:	**My work:**
a. a 4p electron on As	$(1s)^2$ $(2s2p)^8$ $(3s3p)^8$ $(3d)^{10}$ $(4s4p)^4$ S = 10 x 1.00 + 18 x 0.85 + 4 x 0.35 = 26.7 Z_{eff} = N - S = 33 – 26.7 = 6.3
b. a 5s electron on Sr	
c. a 5p electron on Cs^+	

4. Slater's Shielding Rules for Transition metals. We use the same general format for the Slater electron configuration as we did in 3, above. Note that the s-orbitals that are filled before each d group (4s before 3d, for example) are written to the right of d group (and will not contribute to the shielding). As before, do not include the electron in question in the Slater electron configuration.

$(1s)^a$ $(2s2p)^b$ $(3s3p)^c$ $(3d)^d$ $(4s4p)^e$ $(4d)^f$ $(4f)^g$ $(5s5p)^h$ $(5d)^i$ $(5f)^j$ $(6s6p)^k$ and so on

The rules are simpler for nd (and nf) electrons:

- electrons in the same (nd) group contribute 0.35 towards the overall shielding
- electrons in all groups to the left in the Slater configuration format contribute 1.00 towards the overall shielding

- electrons in all groups to the right in the Slater configuration format contribute nothing towards the overall shielding

Problem:	**My work:**
a. a 3d electron on Ni	$(1s)^2$ $(2s2p)^8$ $(3s3p)^8$ $\underline{(3d)}^7$ $(4s4p)^2$ S = 18 x 1.00 + 7 x 0.35 = 20.45 Z_{eff} = N - S = 28 – 20.45 = 7.55
b. a 3d electron on Mn	
c. a 4d electron on Ru	

5. Using the rules to predict periodic trends.

5a. Determine Z_{eff} for valence electrons in the series: Li, Be, B, C, N, O, F, and Ne. Plot Z_{eff} (y-axis) vs atomic number (x-axis).

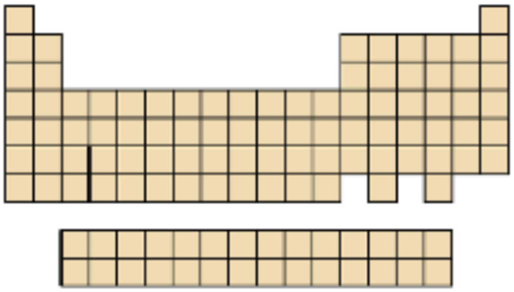
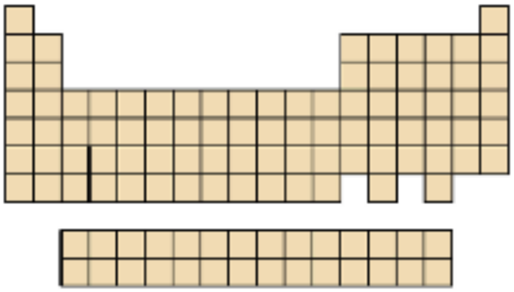
Z_{eff}	**Plot:**
Li	
Be	
B	
C	
N	
O	
F	
Ne	

5b. How does this plot compare in appearance to a plot of atomic radius vs. atomic number?

5c. Determine Z_{eff} for valence electrons in the series: Li, Na, K, and Rb.

Z_{eff}
Li
Na
K
Rb

Effective nuclear charge often "explains the big picture" when moving across the periodic table from left to right. Use arrows to show how Z* increases across the periodic table on both of these periodic tables. Next, use arrows to show how (1) atomic radius increases and (2) first ionization increases across the periodic table.

1. Atomic radius (size):	2. First ionization energy ($E \rightarrow E^+$)
	

5d. Add the vertical trend arrow for atomic radius and for first ionization energy to the periodic tables above. Z* does not explain this trend. What explains these two vertical trends?

1. Atomic radius (size): (Li → Cs)	2. First ionization energy ($E \rightarrow E^+$) (Li → Cs)

5e. Electron affinity is a measure of the energy released when an element adds an electron: $E + e^- \rightarrow E^-$ and is measured in kJ/mol. Unfortunately, due to historical reasons, electron affinity is often expressed in terms of how much energy is released when an electron is added. Thus, the electron affinity has positive values for exothermic processes. Aaaarg! One solution is to give the reaction and its associated ΔH value. Electron affinities are listed in order of atomic number in Appendix B-3 in our book (The 5th Edition of our book has placed all of Appendix B on line – I will distribute a copy of the B-3 in class). The values for Na and F are +52.9 kJ/mol and +328.0 kJ/mol, respectively. That means that the following are true:

$$Na + e^- \rightarrow Na^- \quad \Delta H = -52.9 \text{ kJ/mol}$$

$$F + e^- \rightarrow F^- \quad \Delta H = -328.0 \text{ kJ/mol}$$

The value for fluorine makes sense, however the value for Na is, perhaps, a surprise: Sodium atoms release energy when they add an electron to make the sodium anion! Write the electron configuration for Na and Na^- and also write the Z* for Na. Do these facts explain why adding an electron to sodium is exothermic? Explain.

5f. Peruse the table in Appendix B-3 (electron affinity). What elements do not want to add an electron? Identify two general "rules" for which adding an electron to an element is endothermic.

5g. OK, now lets return to ionization energies, $E \rightarrow E^+ + e^-$. Lets look closely at the second period Li through Ne and the first ionization energies as plotted in Figure 2-13. First note that the general trend follows what we've already noted: the first ionization energy increases as we move across the periodic table from left to right. Two elements, however, have lower first ionization energies than their previous elements, respectively. The first one is boron, B. Write the electron configuration for boron and propose an explanation for why its first ionization energy may be lower than that of beryllium.

The next troublemaker is oxygen. What is happening with oxygen?

6. Ionic size. The last topic in this chapter is the radius of ions, both cations and anions. In very general terms, "*Cations are small!*" and "*Anions are large!*" Ionic radii data are given in the book (Tables 2-9 – 2-12) and also Appendix B-1. Compare the atomic radius (Table 2-8) of a neutral element (pick one) with that of its cation.

6a. Circle the species with the largest radius and draw a box around the smallest radius in each series.

(i) Se^{-2} Br^{-} Rb^{+} Sr^{+2}
(ii) Y^{+3} Zr^{+4} Nb^{+5}
(iii) Co^{+4} Co^{+3} Co^{+2} Co
(iv) Na^{+} Ne F^{-}

Review for ACS Final Exam in Inorganic Chemistry: Periodic Trends

1. Which are listed in order of increasing electronegativity?
   - (a) F < Cl < Br < I
   - (b) O < S < Se < Te
   - (c) Al < Si < P < S
   - (d) I < Te < Sb < Sn
   - (e) Sn < As < S < F < He

2. Which correctly lists the elements in order of increasing ***third*** ionization energies?
   - (a) Al < Si < P < Mg
   - (b) Mg < Al < Si < P
   - (c) Al < P < Si < Mg
   - (d) P < Si < Al < Mg
   - (e) Si < P < Al < Mg

3. Which correctly lists the elements in order of increasing ionic radii?
   - (a) $I^{-} < Br^{-} < Cl^{-}$
   - (b) $F^{-} < O^{-2} < N^{-3}$
   - (c) $Na^{+} < Mg^{+2} < Al^{+3}$
   - (d) $O^{-2} < F^{-} < Na^{+}$
   - (e) $O^{-2} < F^{-} < Na^{+} < Ca^{+2}$

4. Which list contains only covalent oxides?
   - (a) CaO, CO_2, SO_3
   - (b) Al_2O_3, N_2O_4, P_2O_5
   - (c) K_2O, NO_2, SO_3
   - (d) MgO, Fe_2O_3, SiO_2
   - (e) CO_2, SO_3, ClO_2

5. First ionization energies can be described by a periodic trend. Which electron configuration is most likely to violate the predicted trend?
   - (a) $ns^2\ np^2$
   - (b) $ns^2\ (n-1)d^{10}\ np^3$
   - (c) $ns^2\ np^4$
   - (d) $ns^2\ np^5$
   - (e) $ns^2\ (n-1)d^{10}\ np^6$

Answers: C, C, B, E, C

Answers from Day 1.

1. Atomic radius/size decreases from left to right and increases from top to bottom.

2. For an initial approximation, the first ionization energy increases from left to right due to Z_{eff}, however it is easier to lose solitary electrons (np^1, nd^1, etc.) and the electron that makes the configuration one over half-filled (np^4, nd^6, etc.) for free atoms. Similarly, filled, empty and half-filled electrons are harder than expected to undergo a first ionization. For example, N (np^3) is harder than expected to ionize, while O (np^4) is easier. The trend from top to bottom within a family is for the first ionization energy to decrease, due to the fact that the orbital occupied by the valence electrons has a higher energy (higher n value).

3. Increases smoothly from L → R. Going downward, Z_{eff} increases from n = 1 → n = 3, then stalls out. Z_{eff} values going downward are not used to explain other periodic trends.

4. electronegativity increases from Fr to F (increases up and to the right). Group 8A (noble gases have zero electronegativity)

5. The general trend is for electron affinity to increase L → R. Electron affinity is tricky because some elements do not want another electron as much as you'd think. Filled sub-shell elements have zero electron affinity (ns^2, nd^{10}, np^6). Half-filled shells have slightly lower-than-expected electron affinities (nd^5, np^3). Electron affinity is largest for n = 3 elements, a balance between the more electronegative elements and atomic size.

6. Elements in Groups 1A → 10B (the first 12 columns of elements) are all equally metallic for all practical purposes. Among the main group elements in Groups 3A → 8A, metallic character increases as one descends a group or as one moves from right → left.

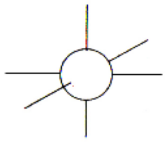
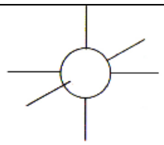
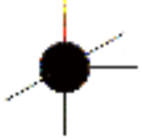
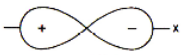
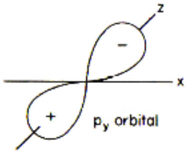
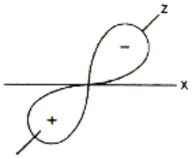
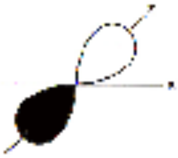
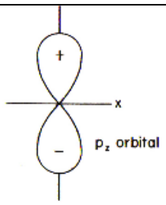
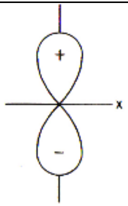
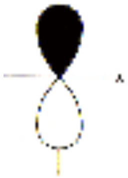
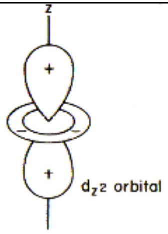
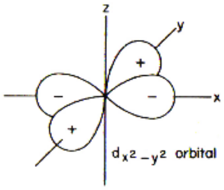
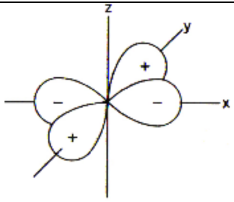
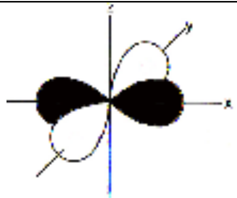
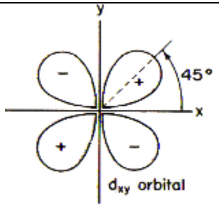
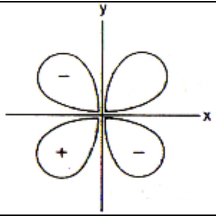
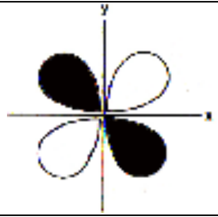
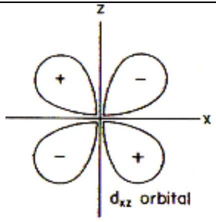
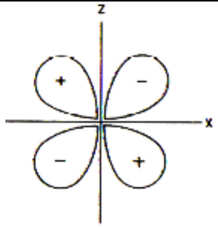
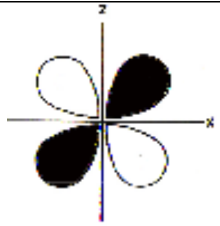
7. 1. alkali metals; 2. alkaline earth metals; 3. transition metals; 4. noble gases; 5. halogens; 6. chalcogens ; 7. pnicogens ; 8. lanthanides; 9. Actinides

8. 1. main group; 2. transition metals; 3. f-block elements (Note: the rare earths are the 15 lanthanides plus Sc and Y)

9.

		New
1A	I-A	1
2A	II-A	2
3B	III-A	3
4B	IV-B	4
5B	V-B	5
6B	VI-B	6
7B	VII-B	7
8B	VIII-B	8
9B	IX-B	9
10B	X-B	10
11B	XI-B	11
12B	XII-B	12
3A	III-A	13
4A	IV-A	14
5A	V-A	15
6A	VI-A	16
7A	VII-A	17
8A	VIII-A	18

10. gray color are the non-metals; white are the metalloids or semi-metals; and orange are the metals.

The d-orbitals	With label	Without label	Shaded
s-orbital	 s orbital		
p_x orbital	 p_x orbital		
p_y orbital			
p_z orbital			
d_{z^2} orbital			
$d_{x^2-y^2}$ orbital			
d_{xy} orbital			
d_{xz} orbital			
d_{yz} orbital