

**Inorganic Chemistry with Doc M. Group:** \_\_\_\_\_

**Names:** \_\_\_\_\_

## Day 2. Slater Shielding and Effective Nuclear Charge.

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:  $(1s)^a (2s2p)^b (3s3p)^c$ .

<b>Problem:</b>	<b>My work:</b>
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.

<b>Problem:</b>	<b>My work:</b>
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 the overall 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.

<b>Problem:</b>	<b>My work:</b>
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,  $Z_{\text{eff}}$ , (also called  $Z^*$ ) is simply the atomic number,  $Z$  (the number of protons), -  $S$ . Determine  $Z_{\text{eff}}$  for each of the following. Remind yourself of the significance of the resulting value: for example, a valence electron on phosphorus “sees” or “feels” the attraction of 4.8 protons.

<b>Problem:</b>	<b>My work:</b>
a. P	$Z_{\text{eff}} = N - S = 15 - 10.2 = 4.8$
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  $Z_{\text{eff}}$  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.

<b>Problem:</b>	<b>My work:</b>
a. a 2s electron on P	$S = 2 \times .85 + 7 \times 0.35 = 4.15$ $Z_{\text{eff}} = N - S = 15 - 4.15 = 10.85$
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  $Z_{\text{eff}}$  for each of the following.

<b>Problem:</b>	<b>My work:</b>
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  $Z_{\text{eff}}$  for each of the following.

<b>Problem:</b>	<b>My work:</b>
a. a 2s electron on $\text{Na}^+$	$(1s)^2 (2s2p)^7$  $S = 2 \times .85 + 7 \times 0.35 = 4.15$  $Z_{\text{eff}} = N - S = 11 - 4.15 = 6.85$
b. a 3p electron on $\text{Cl}^-$	
c. a 2p electron on $\text{Mg}^{+2}$	
d. a 1s electron on $\text{Li}^+$ (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  $(1s)^a (2s2p)^b (3s3p)^c$ :

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

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

<b>Problem:</b>	<b>My work:</b>
a. a 4p electron on As	$(1s)^2 (2s2p)^8 (3s3p)^8 (3d)^{10} (4s4p)^4$  $S = 10 \times 1.00 + 18 \times 0.85 + 4 \times 0.35 = 26.7$  $Z_{\text{eff}} = N - S = 33 - 26.7 = 6.3$
b. a 5s electron on Sr	
c. a 5p electron on Cs <sup>+</sup>	
d. the element two rows down from your group's element name (For example, Team Ne would do Kr.)	

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.

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

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

<b>Problem:</b>	<b>My work:</b>
a. a 3d electron on Ni	$(1s)^2 (2s2p)^8 (3s3p)^8 (3d)^7 (4s4p)^2$  $S = 18 \times 1.00 + 7 \times 0.35 = 20.45$  $Z_{\text{eff}} = N - S = 28 - 20.45 = 7.55$

b. a 3d electron on Mn	
c. a 4d electron on Ru	
d. Team Boron through Fluorine: Add 21 to your atomic number and do that element (Boron would do Mn); Teams from Periods 3 and 4, add 8 to your atomic number and do that element.	

5. Using the rules to predict periodic trends.

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

$Z_{\text{eff}}$	Plot:
Li	
Be	
B	
C	
N	
O	
F	
Ne	

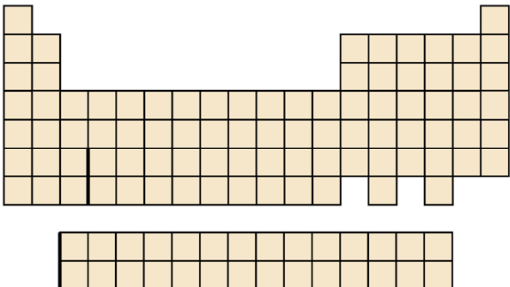
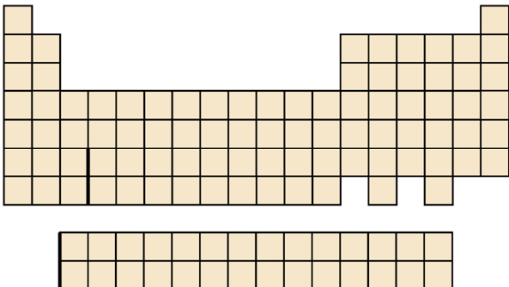
Q. How does this plot compare in appearance to a plot of atomic radius vs. atomic number? First ionization energy vs. atomic number?

5b. Determine  $Z_{\text{eff}}$  for valence electrons in the series: Li, Na, K, and Rb. Plot  $Z_{\text{eff}}$  (y-axis) vs atomic number (x-axis).

$Z_{\text{eff}}$	Plot:
Li	
Na	
K	
Rb	

Q. How does this plot compare in appearance to a plot of atomic radius vs. atomic number? First ionization energy vs. atomic number?

6. Periodic trends revisited. 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.

<p>1. Atomic radius (size):</p> 	<p>2. First ionization energy (<math>E \rightarrow E^+</math>):</p> 
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6b. 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?

<p>1. Atomic radius (size): (Li <math>\rightarrow</math> Cs)</p>	<p>2. First ionization energy (<math>E \rightarrow E^+</math>) (Li <math>\rightarrow</math> Cs)</p>
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6c. 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  $\Delta H$  value. Electron affinities are listed in order of atomic number in Appendix B-3 in our book. The values for Na and F are +52.9 kJ/mol and +328.0 kJ/mol, respectively. That means that the following are true:



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<sup>-</sup> and also write the Z\* for Na. Do these facts explain why adding an electron to sodium is exothermic? Explain.

6d. 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.

6e. 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?

Is this indicative of other members of boron’s and oxygen’s families? Discuss.

7. 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.

Repeat for any element and its anion:

## Review for ACS Final Exam in Inorganic Chemistry

### Periodic trends

- Which are listed in order of increasing electronegativity?
  - F < Cl < Br < I
  - O < S < Se < Te
  - Al < Si < P < S
  - I < Te < Sb < Sn
  - Sn < As < S < F < He
- Which correctly lists the elements in order of increasing *third* ionization energies?
  - Al < Si < P < Mg
  - Mg < Al < Si < P
  - Al < P < Si < Mg
  - P < Si < Al < Mg
  - Si < P < Al < Mg
- Which correctly lists the elements in order of increasing ionic radii?
  - I<sup>-</sup> < Br<sup>-</sup> < Cl<sup>-</sup>
  - F<sup>-</sup> < O<sup>-2</sup> < N<sup>-3</sup>
  - Na<sup>+</sup> < Mg<sup>+2</sup> < Al<sup>+3</sup>
  - O<sup>-2</sup> < F<sup>-</sup> < Na<sup>+</sup>
  - O<sup>-2</sup> < F<sup>-</sup> < Na<sup>+</sup> < Ca<sup>+2</sup>
- Which list contains only covalent oxides?
  - CaO, CO<sub>2</sub>, SO<sub>3</sub>
  - Al<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, P<sub>2</sub>O<sub>5</sub>
  - K<sub>2</sub>O, NO<sub>2</sub>, SO<sub>3</sub>
  - MgO, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>
  - CO<sub>2</sub>, SO<sub>3</sub>, ClO<sub>2</sub>
- First ionization energies can be described by a periodic trend. Which electron configuration is most likely to violate the predicted trend?
  - ns<sup>2</sup> np<sup>2</sup>
  - ns<sup>2</sup> (n-1)d<sup>10</sup> np<sup>3</sup>
  - ns<sup>2</sup> np<sup>4</sup>
  - ns<sup>2</sup> np<sup>5</sup>
  - ns<sup>2</sup> (n-1)d<sup>10</sup> np<sup>6</sup>

Answers: C, C, B, E, C