Chemistry 6011 Advanced Inorganic Chemistry I: From Atoms to Coordination Compounds Problem Set #2

## Chapter 5-

1. Write the MO electron configuration for the NO<sup>-</sup> ion.

a. What is the bond order?

b. Will the bond length be shorter or longer than in NO?

c. How many unpaired electrons will be present?

d. Will the unpaired electrons be concentrated more on the N or the O? Explain.

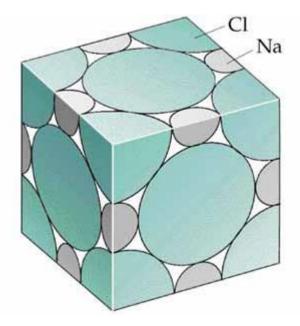
2. Predict the geometries of  $(CH_3)_2P(CF_3)_3$  and  $(CH_3)_3P(CF_3)_2$ . Do you expect these molecules to undergo Berry pseudorotation? Explain.

3. Miessler problems 5.1, 5.2, 5.8, 5.14

## Chapter 7-

1. Both CsCl and CaF<sub>2</sub> exhibit a coordination number of 8 for the cations. What is the structural relationship between the two lattices?

2. Identify the number of  $Na^+$  and  $Cl^-$  ions in the unit cell of sodium chloride illustrated below or in Figure 7.7a of your textbook. State how many formula units of NaCl the unit cell contains.



3. The measured density of NaCl is 2.167 g cm<sup>-3</sup>. From your answer to Problem 2 and your knowledge of the relationships among density, volume, Avogadro's number, and formula weight, calculate the volume of the unit cell and the length of the edge of the cell. Calculate the length  $r_+$  +  $r_-$  Check your answer,  $r_+$  +  $r_-$  against values in appendix B.

4. Using the Born-Haber cycle, calculate the heat of formation of potassium fluoride. You may have to look up some of the values that you need to perform this calculation. Please reference your source(s).

5. To ionize Mg to  $Mg^{2+}$  costs two times as much energy as to form  $Mg^+$ . The formation of  $O^{2-}$  is endothermic rather than exothermic as for  $O^-$ . Nevertheless, magnesium oxide is always formulated as  $Mg^{2+}O^{2-}$  rather than as  $Mg^+O^-$ .

a. What theoretical reason can be given for the  $Mg^{2+}O^{2-}$  formulation?

b. What simple experiment could be performed to prove that magnesium oxide was not Mg<sup>+</sup>O<sup>-</sup>?

6. The crystal structure of  $LaF_3$  is different from those discussed. Assume it is unknown. Using the equation of Kapustinskii, estimate the lattice energy.

7. Predict the structures of the following (i.e., to what mineral classes do they belong?):

a. MgCr<sub>2</sub>O<sub>4</sub>

b. K<sub>2</sub>MgO<sub>4</sub>

8. Why is graphite a good conductor whereas diamond is not? Both contain infinite lattices of covalently bound carbon atoms. To help answer this question please read pg. 272-274 entitled Diamond and Graphite in your textbook.

9. The energy levels of gallium are above those of germanium, which are above those of arsenic. Can you provide any arguments, data, etc., to substantiate this?

10. Using table 7.3, calculate the wavelength of light at which photoconduction will begin for a CdS light meter.

11. Cadmium sulfide is often used in the photometers of cameras to measure the available visible light. Suppose you were interested in infrared photography, use table 7.3 to suggest some compounds that might be suitable for an infrared photocell.

12. List the following in order of increasing boiling point:

H<sub>2</sub>O, Xe, LiF, LiI, H<sub>2</sub>, BaO, SiCl<sub>4</sub>, SiO<sub>2</sub>

13. Predict which of the following bonding interactions will be the stronger:

a. O=O or O-O

b. C-C or Si-Si

- c. Ne-Ne or Xe-Xe
- d.  $Li^+F^-$  or  $Mg^{2+}O^{2-}$  (ion pair)
- e. Li<sup>+</sup>F<sup>-</sup> or Ba<sup>2+</sup>Te<sup>2-</sup> (ion pair)

f. Li<sup>+</sup>F<sup>-</sup> or C-C (in diamond)

## Chapter 6-

Miessler problems 6.1, 6.6, 6.8, 6.9, 6.11, 6.15 (Skip part a &b), 6.21, 6.22, 6.26, 6.27, 6.31

A. Predict which way the following reactions will go in the gas phase:

 $\begin{array}{rcl} \mathrm{HI} &+& \mathrm{NaF} \iff \mathrm{HF} &+& \mathrm{NaI} \\ \mathrm{AlI}_3 &+& 3\mathrm{NaF} \iff \mathrm{AlF}_3 &+& 3\mathrm{NaI} \\ \mathrm{CuI}_2 &+& 2\mathrm{CuF} \iff \mathrm{CuF}_2 &+& 2\mathrm{CuI} \\ \mathrm{TiF}_4 &+& 2\mathrm{TiI}_2 \iff \mathrm{TiI}_4 &+& 2\mathrm{TiF}_2 \\ \mathrm{CoF}_2 &+& \mathrm{HgBr}_2 \iff \mathrm{CoBr}_2 &+& \mathrm{HgF}_2 \end{array}$ 

B. From Figure 10.1 determine how the following solutes will react with the solvents, and how the equilibria will lie, that is, will the solute be completely leveled or in equilibrium? State whether the solution formed in each case will be more acidic or more basic than the pure solvent.

| Solute            | Solvent       |
|-------------------|---------------|
| $H_2SO_4$         | Acetic Acid   |
| $H_2SO_4$         | Water         |
| $H_2SO_4$         | Ammonia       |
| Acetone           | Ammonia       |
| Acetone           | Water         |
| PhNH <sup>-</sup> | Ammonia       |
| PhNH <sup>-</sup> | Water         |
| PhNH <sup>-</sup> | Acetic Acid   |
| PhNH <sup>-</sup> | Sulfuric Acid |

C. Define the equations for the Latimer diagram of iron (Appendix B). Assume the conditions are acidic. Which steps are spontaneous?

Extra Credit:

- a. Write a one page analysis of the work performed to develop and characterize the purely inorganic, semiconducting double-helix structure.
- b. What would be the Born Haber cycle for a covalent molecule?