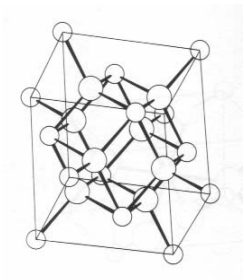


Very Short Answer Questions: (3 points each)

1. Ions generally increase in size with increases coordination number.
2. The picture to the right displays the fluorite lattice.
3. For a salt, increased polarization results in decreased water solubility.
4. The overlap integral, *S*, is given by the equation: $\int \psi_A \psi_B d\tau$.
5. The formula that gives the Mulliken-Jaffe electronegativity is ½(IE + EA).
6. Resonance occurs when more than one energetically reasonable structure can be drawn for a molecule.
7. Needing a nuclear reactor and large crystal size are the two major disadvantages of neutron diffraction.
8. The hybridization of a central atom in a molecule of trigonal bipyrimidal geometry is dsp^3.
9. IF_5 is a square pyramidal shaped molecule.
10. Water burns in the presence of molecular fluorine!

Discussion Questions: (You must show work to receive credit!)

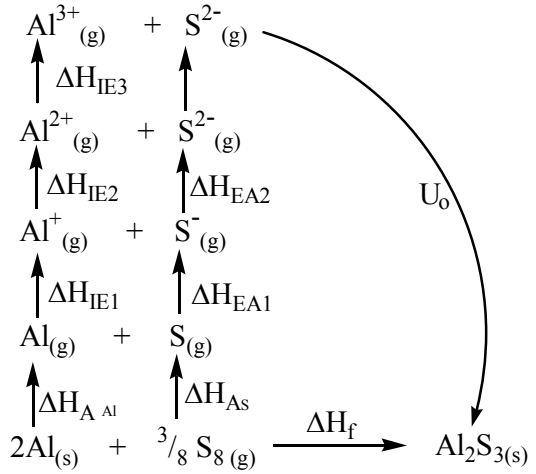
1. What are the three types of phosphorus? Describe their physical properties. (10 points)

   See handouts.

2. Which would be easier to thermally decompose $MgCO_3$ or $MgSO_4$? Propose a physical justification for your answer. (5 points)

   $MgCO_3$. Each oxygen on the CO_3^{2-} ion carries an average -2/3 charge while those on SO_4^{2-} carry a -½ charge. The oxidation state of C is +4 while for S it is +6. Thus the electron density on the carbonate oxygens is more polarizable (by an external cation) than is that on the sulfate oxygens. The result is that it is easier to remove an O and thermally decompose $MgCO_3$ than $MgSO_4$.

3. Write out the Born-Haber cycle for aluminum sulfide, write out the heat of formation equation, and define each term in it. (10 points)



ΔH_{IE} = ionization energy
ΔH_{EA} = electron affinity
U_o = lattice energy
ΔH_f = heat of formation
ΔH_{AAl} = heat of atomization, includes sublimation energy, gaseous bond energies
ΔH_{AS} = heat of atomization, includes appropriate terms for the anion

$$\Delta H_f = \Delta H_{A_S} + \Delta H_{IE1} + \Delta H_{IE2} + \Delta H_{IE3} + \Delta H_{A_S} + \Delta H_{EA1} + \Delta H_{EA2} + U_o$$

4. Consider the oxidation of fluorine gas: $F_2 \longrightarrow F_2^+ + e^-$. What is the major factor favoring this reaction and why? What is the major factor opposing this reaction and why? (10 points)

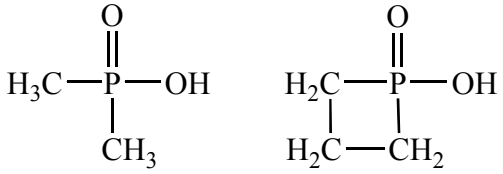
   Favoring - The fluorine molecule has 4 electrons in anti-bonding orbitals; removing one would strengthen the F-F bond.

   Opposing - The high electronegativity of fluorine is the dominating opposing force in this reaction.

5. Draw the most likely Lewis structures of $Me_2P(CF_3)_3$ and $Me_3P(CF_3)_2$. Which, if any, will undergo Berry pseudorotation? Provide the physical justification for your answer. (10 points)

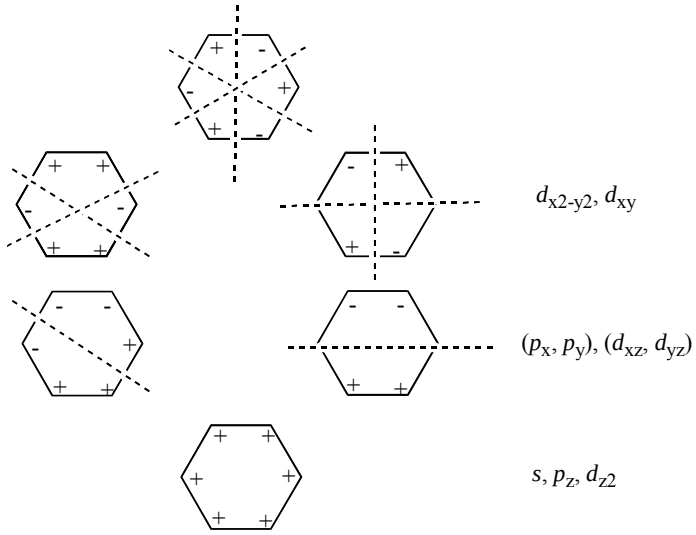
   Both should be trigonal bipyramids with CF_3 groups axial. Neither should undergo pseudorotation because each must place a CH_3 group in an axial position. This is not favored because the CF_3 is electron withdrawing. The hybrid orbitals that make up the axial positions are *pd* hybrids, while those in the equatorial positions are sp^2 hybrids. Thus, the latter draw considerably more electron density towards the nucleus and more electron rich groups will be more stable. For pseudorotation to occur, electron withdrawing CF_3 groups would have to bond to the more highly electronegative equatorial hybrids.

6. Which of the following should be more acidic? Provide the physical justification for your answer. (10 points)



   The cyclic acid is stronger. The bond angles in the cyclic structure are closer to 90º than tetrahedral. This means the presumed sp^3 hybridization of phosphorus can't result in identical orbitals bound to the attached groups. The smaller angle in the cyclic system requires that the hybrid bound to the carbon atoms contain more *p* character. Thus, the P-O bond will contain more *s*-character (recall *s* orbitals are more electronegative than *p* orbitals) which means electron density will be shifted away from the oxygen (and therefore hydrogen) making ionization easier.

7. Would you expect the distortions from idealized geometries to be larger for TeF_5^- or $TeCl_5^-$? What is the physical justification for your answer? (5 points)

   Fluorine is more electronegative than chlorine so it draws more electron density towards itself. This decreases the electron density near the Te center and the lone pair can expand to fill the gap. The result of which is to push the 4 planar F substituents away from the lone pair further than the chlorine substituents move in $TeCl_5^-$. Thus, the distortions in TeF_5^- are larger.

8. In a manner similar to that for $C_5H_5^-$, draw out the ligand group orbitals for benzene. Indicate the degeneracy for each energy level and provide which *d*-orbitals on a first row transition metal would interact constructively with each energy level. (10 points)