Inorganic Exam 2 **Name:**
Chm 451
29 October 2009

Instructions. Always show your work for full credit.

Molecular Orbitals

1. (4 pts) An unusual structure, and one for which there are probably no real examples is the hexagonal bipyramid – it features a plane of six B groups in the xy-plane in the shape of a regular hexagon. Another two B groups exist along the z-axis. (It is like a trigonal bipyramid only with six equatorial B groups.) Given that the symmetry operations for the D_{6h} character table listed below (the S operations are not included), determine the reducible representation for hexagonal bipyramidal AB_8.

D_{6h}	E	2 C_6(z)	2 C_3(z)	C_2(z)	3 C_2'	3 C_2''	i	σ_h(xy)	3 σ_d	3 σ_v
Γ	8									

2. During lecture, we worked out the molecular orbital diagram (σ-bonding only) for he molecule NO_2 in class. Let's start by redoing it here. The molecule has C_{2v} symmetry (AB_2E — bent). We can assume that oxygen's 2s orbitals are low enough in energy so we can ignore them and only concern ourselves with nitrogen's 2s and 2p orbitals and the three 2p orbitals from each oxygen. Oxygen's 2p orbitals have energies somewhat in between the energies of nitrogen's 2s and 2p orbitals. The C_{2v} character table is given here:

C_{2v}	E	C_2(z)	σ_v(xz)	σ_v(yz)	
A_1	1	1		1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

2a. (3 pts) Considering only σ-bonding interactions, start by sketching the two atomic orbitals of the oxygens that you plan to use to create the SALC set for the oxygen atoms.

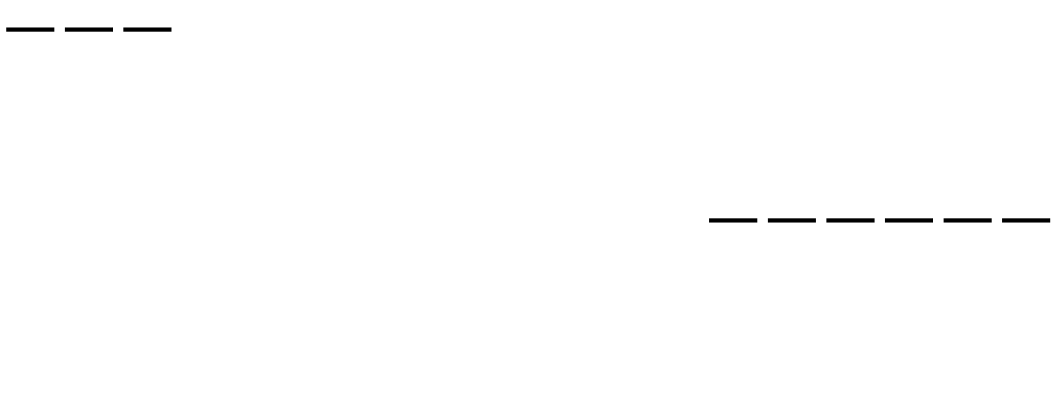
2b. (3 pts) Determine the reducible representation for the SALC set.

2c. (3 pts) Determine the irreducible representations from Γ.

2d. (3 pts) Determine what atomic orbitals on nitrogen also have the same symmetries as the irreducible representations determined above.

2e. (3 pts) Use what you know about the symmetry of nitrogen's 2s and 2p orbitals to match with the SALCs in order to create molecular orbitals. Sketch orbital drawings (balls and sticks) for the bonding and anti-bonding σ-manifold molecular orbitals.

2f. (4 pts) Create a MO energy diagram for σ-bonding — include the non-bonding orbitals.



2g. (6 pts) Now repeat the entire process for the π-manifold. Start with the 2p-orbitals on oxygen that can form π-bonds with nitrogen and use them to create a new SALC set for π-bonding. Determine the reducible representation and the irreducible representations.

2h. (3 pts) Sketch the new molecular orbitals that result from π-bonding. Make a new MO energy diagram showing only the π-MOs — leave off the σ-MOs sketched above. (In an actual workup, you would include both together, but this makes for messy pictures to grade.)

2i. (2 pts) Now compare your σ-manifold energy diagram with your π-orbital energy diagram. You will notice that some of the non-bonding orbitals from the σ-manifold energy diagram have become π-bonding in the π-manifold energy diagram. Identify the orbitals that are still non-bonding after σ and π have been considered.

Acids and bases.

3a. (2 pts) Sketch the Lewis dot structure for sulfur dioxide. You should get an AB_2E structure. As always, avoid expanding the octet.

3b. (3 pts) Sulfur dioxide is a gas that has a boiling point of -10 ^oC. Since this temperature is easily achieved with dry ice, some researchers have used SO_2 as an aprotic (without protons) solvent. Sulfur dioxide has the unique ability to act as a Lewis base or Lewis acid. Sketch SO_2 acting as a Lewis base with a Lewis acid of your own choosing.

3c. (3 pts) Sketch SO_2 acting as a Lewis acid with a Lewis base of your own choosing.

3d. (3 pts) Sulfur dioxide undergoes autodissociation. Write this equilibrium.

3e. (3 pts) If a Lewis acid is dissolved in SO_2, which species identified above will increase in concentration?

4. (3 pts) HSO_3F and HSO_3CF_3 are both strong acids that dissociate 100% in water. How might one establish which of these two acids is the strongest?

5. (3 pts) In class we saw the reaction between NH_3 and BF_3 in a clear gallon plastic bag. A while solid powder was formed. What was the solid and what sort of reaction took place?

Ionic Solids

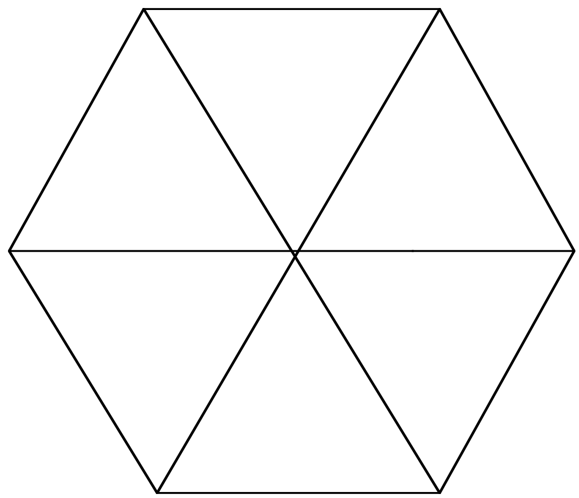
6. (6 pts) Nickel has a fcc unit cell and a density of 6.84 g/cm^3. What is the atomic radius of nickel?

7. (6 pts) What percentage of a simple cubic unit cell is occupied with atoms?

8. (6 pts) What is the radius of a tetrahedral hole in a fcc lattice in which the fcc spheres have a radius of r?

9. (3 pts) Nickel arsenide consists of arsenic anions in a hcp array and the nickel ions in the octahedral holes. What is the formula of nickel arsenide?

10. Continuing on with the hcp close-packed lattices, consider the figure below that represent the top view of one or more hcp unit cells.



10a. (2 pts) How many hcp unit cells are represented here?

10b. (2 pts) With "B" marks, indicate the centers of all of the B layer atoms in the diagram. Position matters!

10c. (2 pts) With "O" marks, indicate the centers of the octahedral holes as viewed from the top. Position matters!

10d. (2 pts) With "T" marks, indicate the centers of the tetrahedral holes as viewed from the top. Position matters!

11. (3 pts) Cobalt fluoride crystallizes in a close-packed array of fluoride ions with the cobalt ions filling one half of the octahedral holes. What is the empirical formula of this compound?

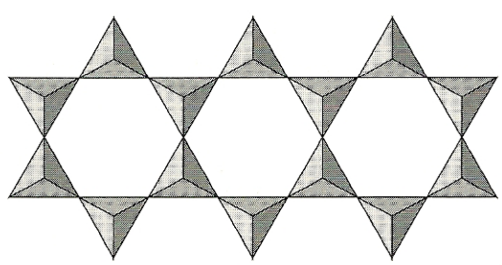
12. (3 pts) What is the formula for the compound that crystallizes with a cubic closest packed array of sulfur atoms, and that contains zinc ions in 1/8 of the tetrahedral holes and aluminum ions in 1/2 of the octahedral holes?

13. (3 pts) The rubidium cation has a radius of 148 pm and chloride has a radius of 181 pm. Predict which ionic lattice type, NaCl or CsCl is used by RbCl, with explanation. [Given: the radius ratio cutoffs are 0.225, 0.414, 0.732 and 1.00.]

14. (5 pts) What is the lattice energy for $MgCl_2(s)$? Use the following information, but note, in one instance you will need to switch the sign before you can use it!

First ionization energy of Mg: 738 kJ/mol Mg;
second ionization energy of magnesium 1451 kJ/mol Mg;
sublimation of magnesium (s → g): 148 kJ/mol Mg;
Cl-Cl bond energy: 243 kJ/mol Cl_2;
electron affinity for Cl: 349 kJ/mol Cl; and
$\Delta H_f(MgCl_2) = -642$ kJ/mol

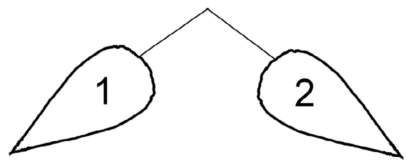
15. (3 pts) What is the empirical formula for this silicate anion?



Answers

D_{6h}	E	2 C_6(z)	2 C_3(z)	C_2(z)	3 C_2'	3 C_2''	i	σ_h(xy)	3 σ_d	3 σ_v
Γ	8	8	8	8	8	8	8	8	8	8

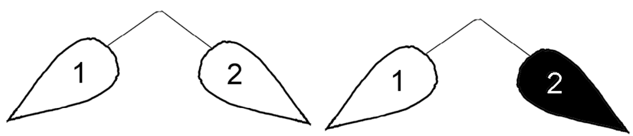
2a.



2b.

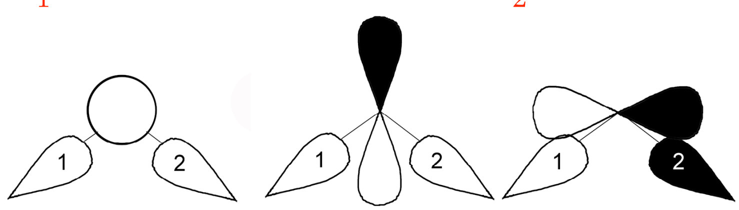
C_{2v}	E	C_2(z)	σ_v(xz)	σ_v(yz)	
Γ	2	0	0	2	z

2c. $A_1 + B_2$. The SALCs are shown below with $a_1$on the left and b_2 on the right:

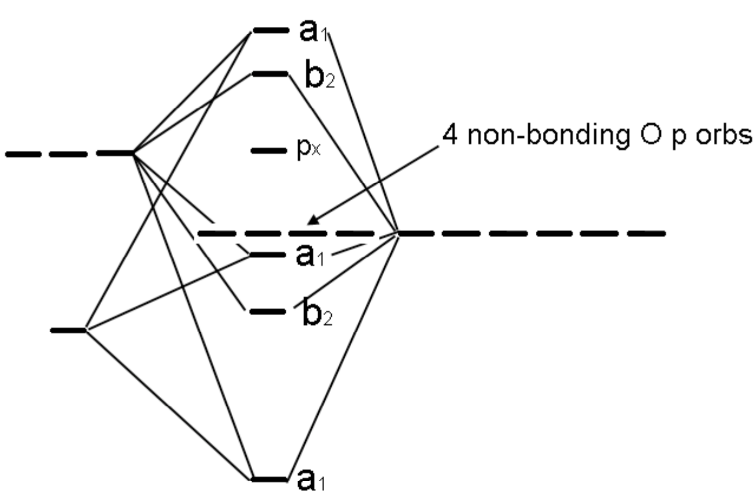


2d. a_1: 2s and $2p_z$; b_2: $2p_y$

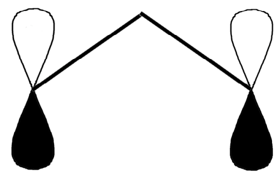
2e. The first two are a_1 MOs and the third one is the b_2. Note that there is only one



2f.



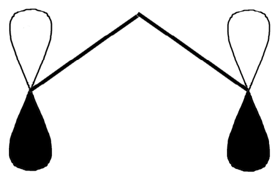
2g. Here are the two p-orbitals needed to make the two SALC sets

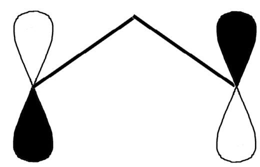


The above orbitals transform as A_2 and B_1

C_{2v}	E	C_2(z)	σ_v(xz)	σ_v(yz)	
Γ	2	0	0	-2	

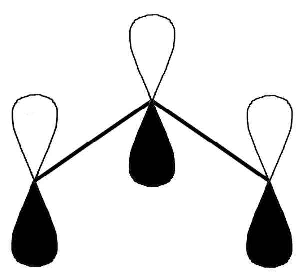
and give these SALCs:



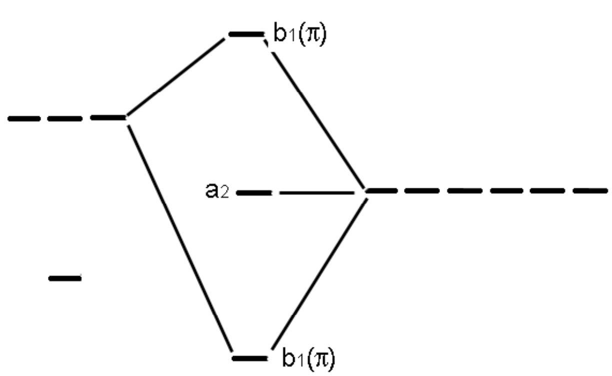


b_1 and a_2

There are no orbitals on the nitrogen that have a_2 symmetry, but there is the p_x on nitrogen with b_1 symmetry and that forms this MO: (also anti-bonding orbital – not shown)



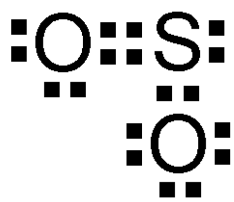
2h.



2i. There are two p-orbitals on oxygen that we have not used and they are non-bonding. Also, there is the a_2 SALC that is non-bonding.

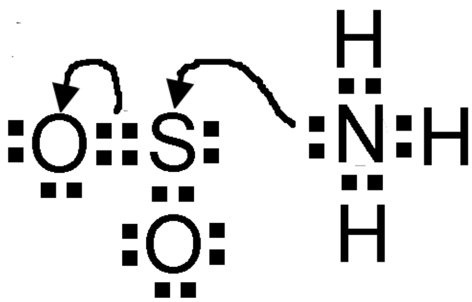
Acids and bases.

3a.



3b. $O_2S{:}BF_3$ or $O_2S{:}Al^{+3}$, for example.

3c.



3d. $2\ SO_2 \rightleftarrows SO^{+2} + SO_3^{-2}$

3e. SO^{+2}

4. determine their Ka values in a solvent that is harder to protonate such as glacial acetic acid

5. $H_3N{:}BF_3$, a Lewis acid-base reaction

Ionic Solids

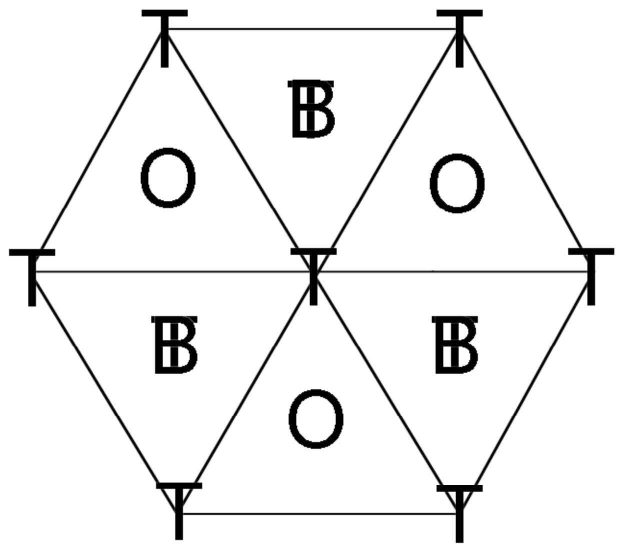
6. 136 pm

7. 52.4%

8. 0.225r

9. NiAs

10.



10a. three

11. CoF_2

12. $ZnAl_2S_4$

13. CsCl

14. -2524 kJ/mol $MgCl_2$

15. $Si_7O_{20}^{-12}$