Inorganic Exam 1   **Name:**
Chm 451
21 September 2010

Instructions. Always show your work where required for full credit.

1. (5 pts) The first ionization energies for the 2nd row elements generally increase from Li to Ne, however, there are two exceptions to the trend. List the two exceptions to the general trend and explain the reason for <u>one</u> of the exceptions.

2. (5 pts) Plot the relative electron affinities for the 2nd row elements Li, Be, B, C, N, O, F, and Ne. Label each dot in your plot.

3. (10 pts) Calculate the Slater shielding that occurs for these elements and ions. Simply set up the calculation, but do not perform the calculation.

Sulfur, S
Arsenic, As
A 3d electron on vanadium, V
Fluoride, F$^-$
A 3d electron on iron(II), Fe^{+2}

4. (4 pts) Circle the member of each series that is expected to have the largest effective nuclear charge.

A. Ge   As   Se   Br   Kr

B. B   C   N   Al   Si   P

C. Fe Fe^{+2} Fe^{+3}

D. O^{2-} F^- Ne S^{2-} Cl^- Ar

5. (18 pts) Sketch Lewis dot structures for each of these species and assign ABE formulas to each. Indicate if it is polar or not. Only expand the octet of the central atom when absolutely necessary.

A. SO_3^{2-}	B. NO_2	C. SO_2
	ABE formula: Polar? Yes No Resonance? Yes No	ABE formula: Polar? Yes No Resonance? Yes No
ABE formula:		
D. SeF_5^-	E. CO_3^{2-}	F. XeF_3^+
ABE formula: Resonance? Yes No	ABE formula: Resonance? Yes No	ABE formula: Resonance? Yes No

6. (6 pts) The fulminate ion, CNO^-, has nitrogen as a central atom. It is remarkably unstable — a dropping feather is enough to detonate silver fulminate. Sketch the three possible Lewis dot structures for CNO^-: one will have two double bonds and the other two will have one triple bond and one single bond. (In other words, the following partial structures: (1) C::N::O, (2) C:::N:O, and C:N:::O). Use formal charges to ascertain which structure is/are better. Indicate your choice.

7. (10 pts) Perform the following symmetry operations on the square pyramid shown below. Each time, start with the original structure and numbering system.

Original:

the E:	either C_4 rotation:	the C_2 rotation:	Either of the σ_v:	Either of the σ_d:

8. (15 pts) Indicate the principal rotation axis or the number of each of the following symmetry operations that exist for each of the following molecules and indicate the point group. The first one is done for you as an example. Hint: Sketch Lewis dot structure if you are uncertain of the structure!

	E	C_2	C_3	C_4	Other C_n	Principle rotation axis	i	σ_v	σ_h	Point group
H_2O	1	1	0	0	No	C_2	No	2	0	C_{2v}
NH_3										
BF_3										
XeF_4										
Br_2										
CO										

9. We discussed the MO diagram for O_2 in class. In the homework you answered questions about superoxide, O_2^- and peroxide, O_2^{-2}. Oxidation of O_2 has been done, although with great difficulty, resulting in the formation of O_2^+.
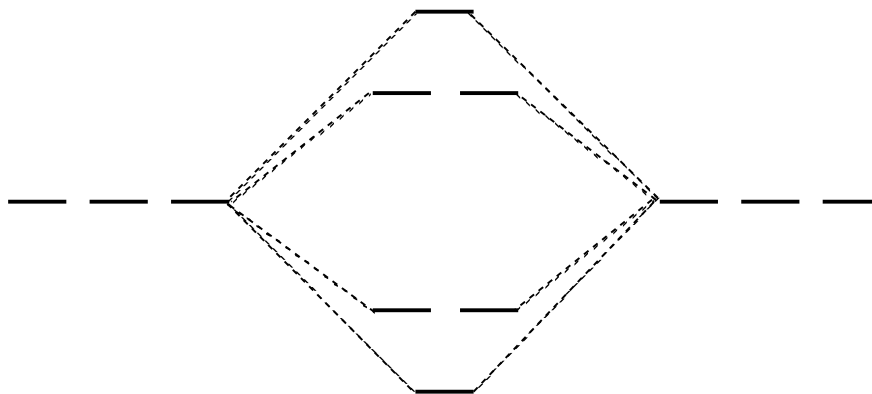
(a, 4 pts) Complete the MO diagram for O_2^+ by adding the appropriate number of electrons to the MO portion, labeling the atomic orbitals (2s or 2p) and every MO with either σ, σ^*, π or π^*.
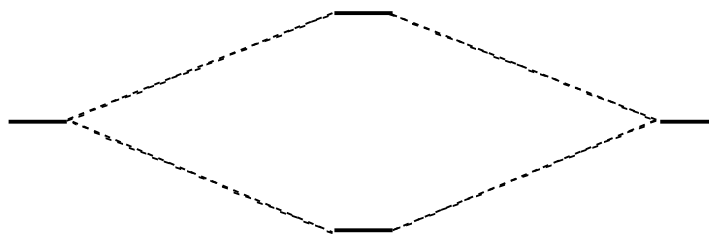

(b, 2 pts) Is O_2^+ paramagnetic or diamagnetic? Circle your answer.

(c, 2 pts) What is the bond order? Show calculation.

(d, 5 pts) Sketch a drawing of each MO next to the MO energy line. Use the appropriate atomic orbital shapes as components (circles for s-orbitals, bowtie shapes for p-orbitals)

10. (4 pts) In class we saw the production of singlet O_2 and its conversion to lower energy triplet O_2. The red light emitted had λ = 630 nm. Populate the MO diagram on the left for singlet O_2 and on the right for triplet O_2. Further labeling is not necessary.
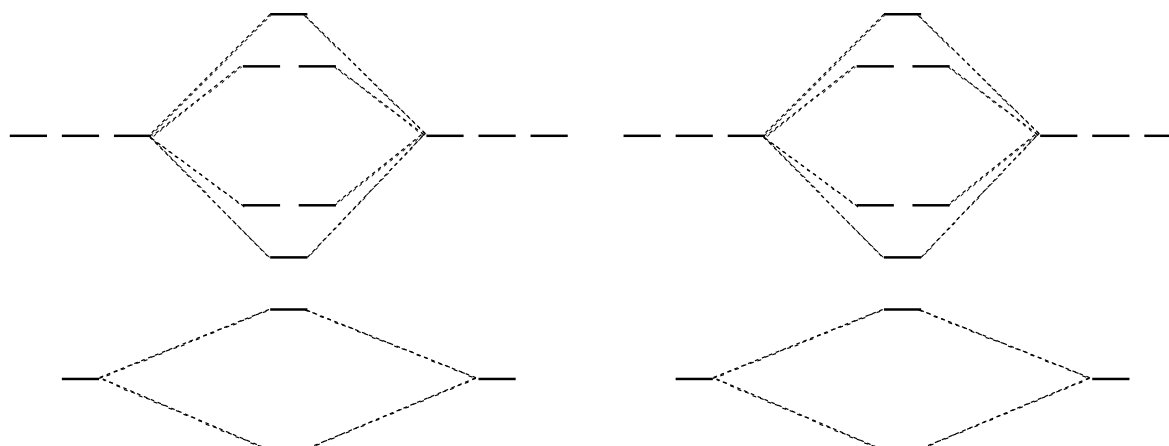
Answers

1. (a) boron and oxygen; (b) Boron has only one electron in the 2p orbitals and that is relatively easy to remove. The result is that boron's first ionization energy is lower than expected. Oxygen is similar, however this time, oxygen's 8th electron is one over a half-filled suborbital $2p^4$, and that 4th 2p electron is easier to remove than expected from the increasing effective nuclear charge alone.
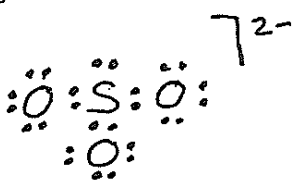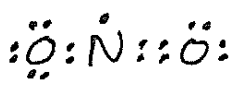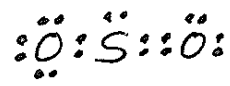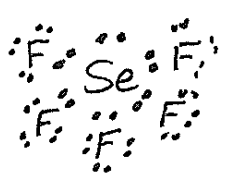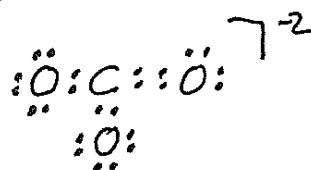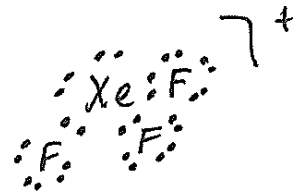
2. The trend for relative electron affinities ($E + e^- \rightarrow E^-$) is expected to increase when going from boron to carbon or oxygen to fluorine, for example, due to effective nuclear charge. What is surprising is that filled shells (Ne, $2p^6$) and subshells (Be, $2s^2$) have zero electron affinity. Nitrogen's ($2p^3$) is also small.
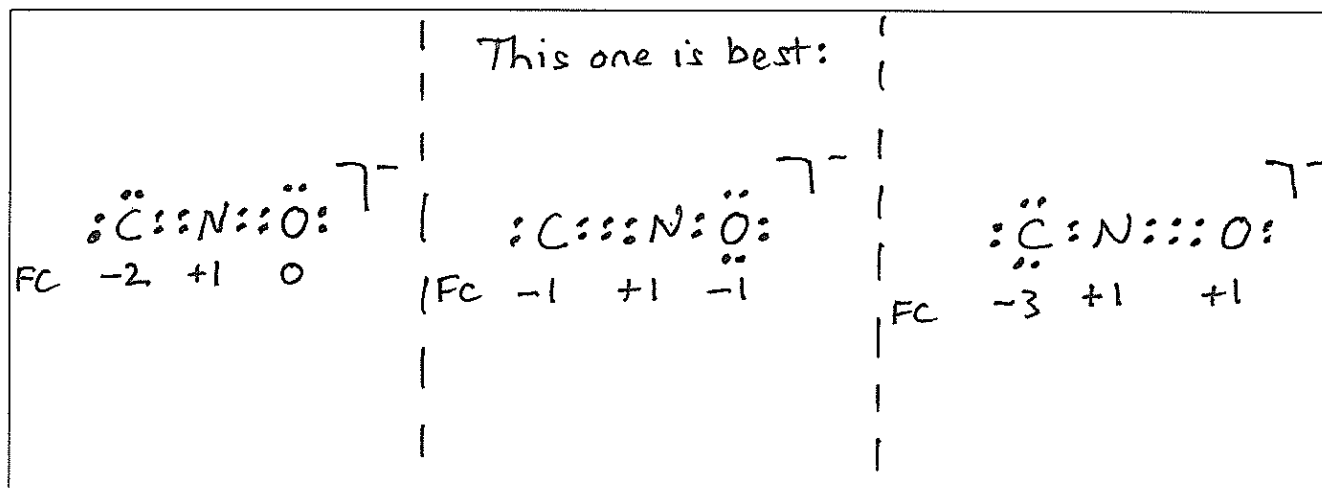
3.

S $(1s)^2$ $(2s2p)^8$ $(3s3p)^6$; Shielding = 2 x 1 + 8 x 0.85 + 5 x 0.35
As $(1s)^2$ $(2s2p)^8$ $(3s3p)^8$ $(3d)^{10}$ $(4s4p)^5$; Shielding = 10 x 1 + 18 x 0.85 + 4 x 0.35
3d electron on V $(1s)^2$ $(2s2p)^8$ $(3s3p)^8$ $(3d)^{10}$ $(4s4p)^5$; Shielding = 18 x 1 + 2 x 0.35
F^- $(1s)^2$ $(2s2p)^8$; Shielding = 2 x 0.85 + 7 x 0.35
3d electron on Fe^{+2} $(1s)^2$ $(2s2p)^8$ $(3s3p)^8$ $(3d)^5$ $(4s4p)^0$; Shielding = 18 x 1 + 5 x 0.35

4. A. Kr; B. P; C. Fe^{+3} D. Ar

5.

A. $SO_3{}^{2-}$	B. NO_2	C. SO_2
ABE formula: AB_3E	ABE formula: AB_2E Polar? (Yes) No Resonance? (Yes) No	ABE formula: AB_2E Polar? (Yes) No Resonance? (Yes) No
D. $SeF_5{}^-$	E. $CO_3{}^{2-}$	F. $XeF_3{}^+$
ABE formula: AB_5E Resonance? Yes (No)	ABE formula: AB_3 Resonance? (Yes) No	ABE formula: AB_3E_2 Resonance? Yes (No)

6.

This one is best:

$:\ddot{C}::N::\ddot{O}:$ ⌐⁻ $:C:::N:\ddot{O}:$ ⌐⁻ $:\ddot{C}:N:::O:$ ⌐⁻

FC −2 +1   0   FC −1 +1 −1   FC −3 +1 +1

7.

the E:	either C_4 rotation:	the C_2 rotation:	Either of the σ_v:	Either of the σ_d:
① ③ ② ④ ⑤	① ② ⑤ ③ ④	① ⑤ ④ ② ③	① ③ ④ ② ⑤	① ④ ⑤ ③ ②
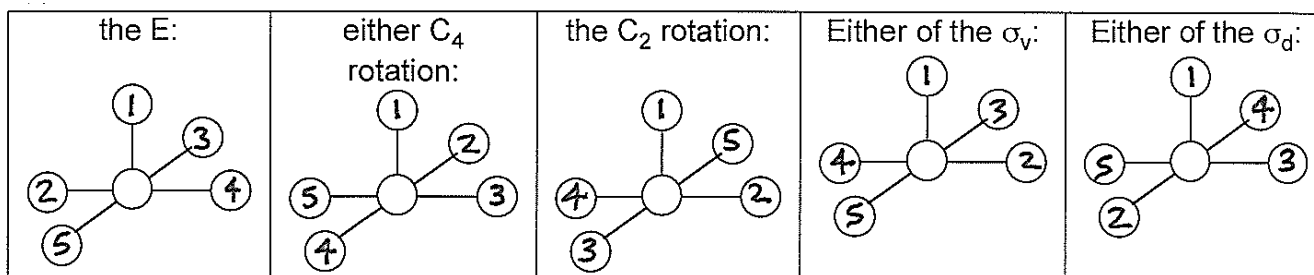
8.

	E	C_2	C_3	C_4	Other C_n	Principle rotation axis	i	σ_v	σ_h	Point group
H_2O	1	1	0	0	0	C_2	No	2	0	C_{2v}
NH_3	1	0	2	0	No	C_3	No	3	0	C_{3v}
BF_3	1	3	2	0	No	C_3	No	3	1	D_{3h}
XeF_4	1	5	0	2	No	C_4	Yes	2	1	D_{4h}
Br_2	1	∞	0	0	$C\infty$	$C\infty$	Yes	∞	1	$D\infty_h$
CO	1	0	0	0	$C\infty$	$C\infty$	No	∞	0	$C\infty_v$

9a.
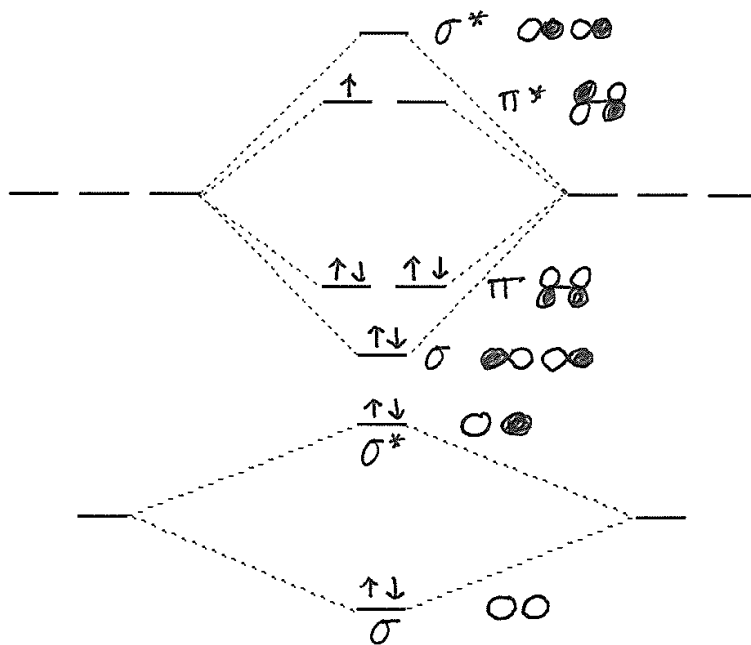
(b) paramagnetic

(c) bond order = (8 - 3)/2 = 2.5

(d) see drawing

10.