# Chm 451 Fall 2007
Exam 1   **Name:**

First ionization energy.

1a. (2 pts) Sketch the general trends (one big arrow across top and one down the side) for the first ionization energies on the periodic table
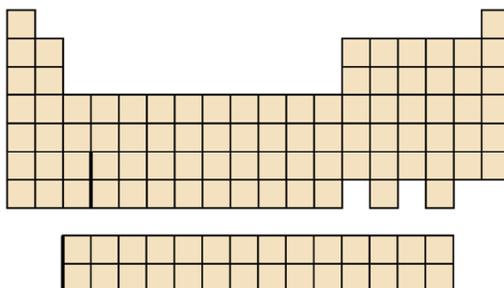
1b. (2 pts) What explains the general trend in first ionization energies as one moves across the periodic table? (in ten words or fewer)

1c. (2 pts) What explains the general trend in first ionization energies as one moves down the periodic table? (in ten words or fewer)

1d. (3 pts) First ionization energy does not change smoothly across any period. There are funny jogs here and there. Sketch the relative first ionization energies for the n = 3 period (sodium through argon)

Energy

Na   Mg   Al   Si   P   S   Cl   Ar
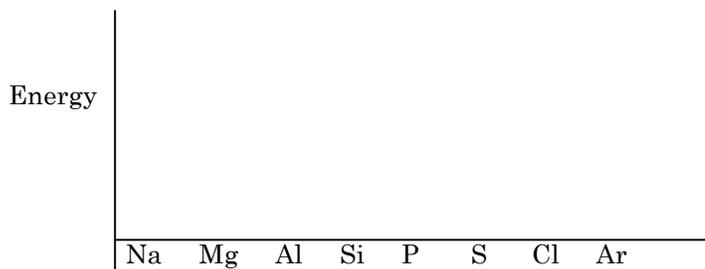
Electron affinity.

2a. (2 pts) What are the units on electron affinity?

2b. (2 pts) Is the generic reaction for electron affinity given by E $\rightarrow$ E$^+$ + e$^-$?   If not, fix it.

2c. (2 pts) Give an example of an element other than a noble gas that is expected to have an endothermic electron affinity.

The d-orbitals

3. (5 pts) Match these 3d-orbitals with their nodal planes. Each 3d orbital has two nodal planes.

| _____ | d_{xy} | A. Two nodal planes, one in the xy-plane and one in the yz-plane. |
_____	d_{xz}	B. Two nodal planes, one in the xz-plane and one in the yz-plane.
_____	d_{yz}	C. Two nodal planes, one in the xz-plane and one in the xy-plane.
_____	$d_{x^2-y^2}$	D. Two conical nodal planes, both having the z-axis at the centers of the cones.
_____	d_{z^2}	E. Two planes, both containing the z-axis and both midway between the x and y axes.

Slater shielding and estimating the effective nuclear charge

4. (6 pts) Estimate by calculation the shielding and the effective nuclear charge for a valence electron on

Element	Shielding	Effective nuclear charge
germanium		
cobalt		

Symmetry.

5. The most common geometric shape for AB_6 is the octahedron. For some rare cases, another geometry occurs: the trigonal prism. A top view of a trigonal prism is a triangle (left figure). The trigonal prism consists of two such triangles separated by a distance (right figure.)
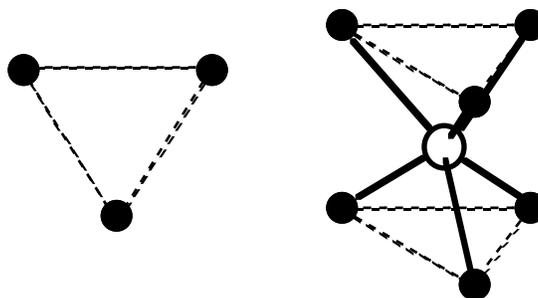
5a (2 pts) What is the primary rotation axis for the trigonal prism?

5b (2 pts) Are there other rotation axes? If so, how many and what kind?

5c (2 pts) Are there σ_v mirror planes? If so, how many?

5d (2 pts) Are there σ_h mirror planes? If so, how many?

5e (2 pts) Are there σ_d mirror planes? If so, how many?

5f (2 pts) Is there an inversion center?

5g (2 pts) Does the trigonal prism possess the identity symmetry element, E?

5h (4 pts) What is the point group for AB_6 as a trigonal prism?

Molecular orbital theory.

Cyanogen is a neutral radical with the formula CN. It is chemically similar to a halogen atom. For example, both Br and CN form anions Br^- and CN^- respectively, and both form dimers, Br_2 and $(CN)_2$, respectively.

6a. (5 pts) Sketch the molecular orbital energy diagram for CN. You may ignore sp-mixing. Start with atomic orbitals that are "about right" in terms of relative energies to each other (if you are not using your notes, just recall how the orbital energies changed in going across the periodic table, say from C to N.

Include all of the following:
  Label the atomic orbitals.
  Label the molecular orbitals.
  Populate the MO diagram with electrons

6b (5 pts) Sketch each MO using orbital sketches (s-orbitals as spheres and p-orbitals as dumbbells) with "+" and "– " labels.

6c (2 pts) Is cyanogen diamagnetic or paramagnetic?

6d (2 pts) Calculate the CN bond order for cyanogens.

Lewis dot structures.

7. (3 pts each) Sketch Lewis dot structures for each of the following. Write the ABE formula for each.

1. ClO_2^-	2. SF_4	3. $Sb(CH_3)_4^+$
4. PN_2^-	5. SeF_3^+	6. SF_6

8a. (2 pts) Sketch the Lewis dot structure of the bromate ion, BrO_3^- in such a way that no atom disobeys the octet rule.

8b (2 pts) Assign formal charges. What is the formal charge on bromine in your drawing?

8c (2 pts) Rearrange bonds in order to eliminate the separation of formal charge within the ion.

8d (2 pts) What is/are the argument(s) in favor of expanding the octet to reduce formal charge? What is/are the argument(s) against expanding the octet to reduce formal charge?

Forces.

9 (2 pts each) Predict the physical state (s, l or g) of each of these at room temperature. You must explain your rationale and/or show your work for credit — guesses count zero.

$KClO_2$	Zr
SF_4	black phosphorus (consists of sheets of phosphorus atoms)
XeO_2	HCl
BF_3	ICl_5

Answers.

1a. Increases L to R and bottom to top;   1b. increase in effective nuclear charge

1c. valence orbitals have larger n value and hence, higher energies making their removal to n = infinity less energy-demanding.

1d. The general trend is to increase, however $3p^1$ and $3p^4$ have lower than expected ionization energies because without them, the shells would be filled, empty or half-filled.

2a. kJ/mol;   2b. No, it is $E + e^- \rightarrow E^-$;   2c. Any Group II element or any member of the zinc triad.

3. B, A, C, E, D

4. Germanium: S = 26.35 protons and Z* = 5.65 protons; cobalt: S = 20.10 protons and Z* = 6.90 protons

5a C_3; 5b two C_3s and 3 C_2s; 5c three σ_v mirror planes; 5d one σ_h mirror plane; 5e zero σ_d mirror planes; 5f no inversion center; 5g yes; 5h D_{3h}

6a. Carbon on the left
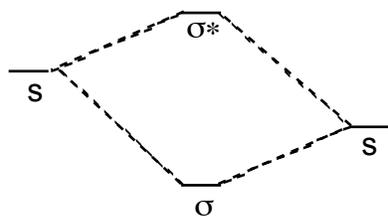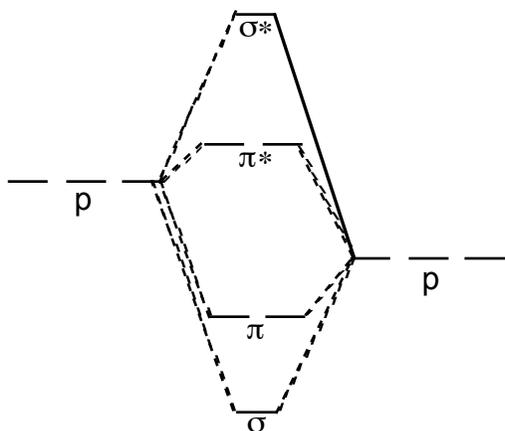
Populate the MO diagram with electrons: a total of 9 electrons filled up as: CN: $(\sigma_s)^2 (\sigma_s*)^2 (\sigma_p)^2 (\pi)^3 (\pi*)^0$ $(\sigma_p*)^0$

6b (5 pts) Sketch each MO using orbital sketches (s-orbitals as spheres and p-orbitals as dumbbells) with "+" and "−" labels.

σ_S   σ_S*

σp   σp*

π   π*
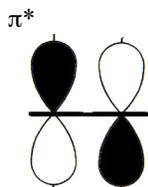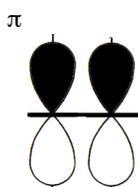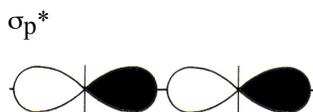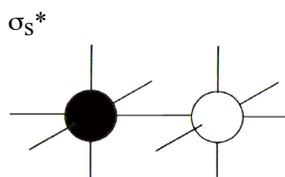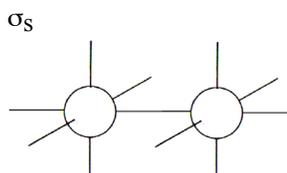
6c paramagnetic

6d 2.5

Lewis dot structures.
7. (3 pts each) Sketch Lewis dot structures for each of the following. Write the ABE formula for each.

1. AB_2E_2 2. AB_4E 3. AB_4 4. AB_2 5. AB_3E 6. AB_6

8a. AB_3E with no double bonds

8b Each oxygen is −1 and Br is +2.

8c Make two Br=O double bonds

8d In favor of expanding the octet: reduced formal charge, some evidence of shorter, stronger bonds
Against expanding the octet: beyond the n = 2 row, multiple bonds are not as common because the atoms
    are too far apart for the p-orbitals to overlap as efficiently. Also, the evidence on bond length and
    strength suggests that multiple bonding is not occurring to a great extent. The reality is likely
    somewhere in between.

9 (2 pts each) Predict the physical state (s, l or g) of each of these at room temperature. You must explain
your rationale and/or show your work for credit — guesses count zero.

$KClO_2$ is a solid: ionic

Zr is a metal and therefore a solid
SF_4 is polar with MM = 108: likely a gas

black phosphorus is network covalent and is a solid
XeO_2 is polar with MM = 163, it is likely a gas or possibly a liquid

HCl polar with MM = 36.5 therefore a gas
BF_3 is non-polar with MM = 64 therefore a gas

ICl_5 is polar (AB_5E) with MM = 304 therefore a solid or liquid.