CHEM 120
Spring 2006
Exam 1

Name: ____

Instructions
Write your answers in blue or black ink. Work done in pencil will be accepted, but you will not be able to appeal any apparent grading mistakes (except simple addition errors). Write neatly. If I can't read it, I can't grade it.

Show all work for full credit! For the word problems write your final answer in a complete sentence. Indicate what you are doing at important steps (you do <u>not</u> need to tell me about every mathematical manipulation you do). If you change your mind on a question, cross out the incorrect answer and clearly indicate your final answer.

There are **9** pages, none blank, and a periodic table. Possibly useful information may be found on page 9.

You may use the back of any page as additional workspace. Please indicate that you have done so.

Problem	Possible Points	Points Received	Estimated Time
1	17		10
2	10		6
3	12		5
4	23		7
5	20		7
6	10		5
7	4		5
8	4		5
Total	100		50
	Bonus		
	Grand Total		

1a. (6 Points) Cesium was discovered in mineral water in 1860 by Bunsen and Kirchoff. The name comes from the Latin *caesius*, which means "sky blue," describing the blue line they observed for this element at 455.5 nm. Calculate the frequency of this line.

Start with $\lambda \cdot \nu = c$ *and solve for* ν.

$$\nu = \frac{c}{\lambda} = \frac{2.9979245x10^{8}\ \text{m}\cdot\text{s}^{-1}}{455.5x10^{-9}\ \text{m}} = 6.581_{6}x10^{14}\ \text{s}^{-1}$$

The frequency of the line is 6.582x10^{14} s^{-1}.

b. (7 Points) Calculate the energy of a single photon of this light in eV.

Substitute the answer from part a into the equation $E = h \cdot \nu$.

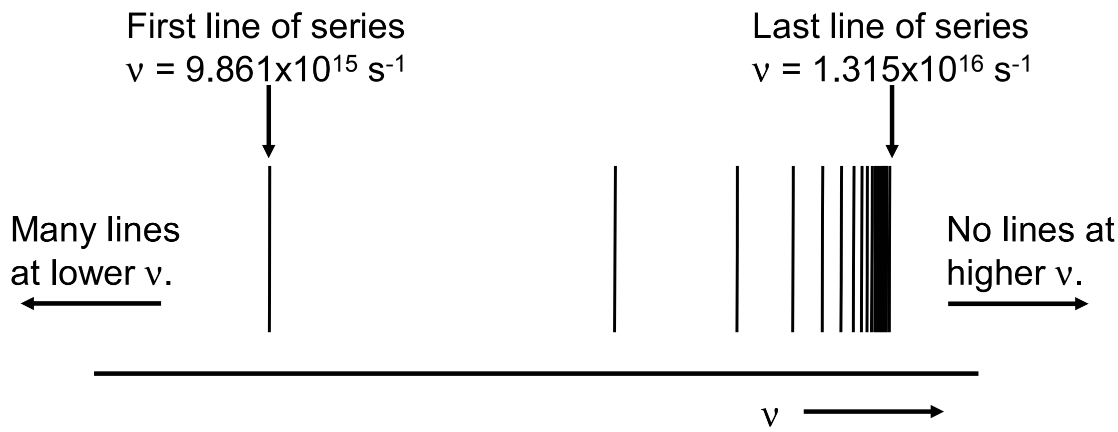
$$E = h\cdot\nu = \left(6.62608x10^{-34}\ \text{J}\cdot\text{s}\right)\left(\frac{1\,\text{eV}}{1.6022x10^{-19}\ \text{J}}\right)\left(6.518_{6}x10^{14}\ \text{s}^{-1}\right) = 2.722\ \text{eV}$$

A photon of this light has an energy of 2.722 eV.

c. (4 Points) Assume that this cesium line is caused by a transition of its single valence electron between states with different *n* and that the single electron in H can undergo the same transition. Explain why we would not expect these transitions to occur at the same energy.

For a one-electron atom, or ion, the energy of an electronic transition is given by the equation $\Delta E = -RZ^{2}\left(\frac{1}{n_{final}^{2}} - \frac{1}{n_{initial}^{2}}\right)$**. Since the n values are the same for both the hydrogen transition and the cesium transition, any energy difference must result from a difference in Z. Although only the valence electron is changing its energy in both atoms, in Cs there are 54 other electrons that shield the valence electron from the nucleus. Therefore, this electron does not feel the full +55 charge of the nucleus, but rather an effective nuclear charge that is somewhere between +55 and 0. H, on the other hand, feels the full +1 charge of the nucleus (Z* = Z). This difference in Z* will affect the energy at which a specific transition occurs. Orbitals with the same *n*, but different ℓ, will have different energies, depending on how well they can penetrate the shielding core electrons. This will affect the Cs transitions, but will not affect the H transitions (H has no core electrons).**

2. (10 Points) A portion of a one-electron ion's emission spectrum is shown below. Identify the ion.



The last line of any emission series for a one-electron system corresponds to a transition from the lowest unbound state (*n* = ∞) to some bound state (with a smaller *n*). Since there are no other lines at higher ν (higher E), the last line of this series must correspond to the largest energy jump that an electron can make in this system, namely the *n* = ∞ to *n* = 1 jump.

Start with the following equation (note the negative sign on hν, because this is an emission spectrum).

$$\Delta E = -h \cdot \nu = -RZ^2\left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right)$$

Substitute $n_{final} = 1$ and $n_{initial} = \infty$.

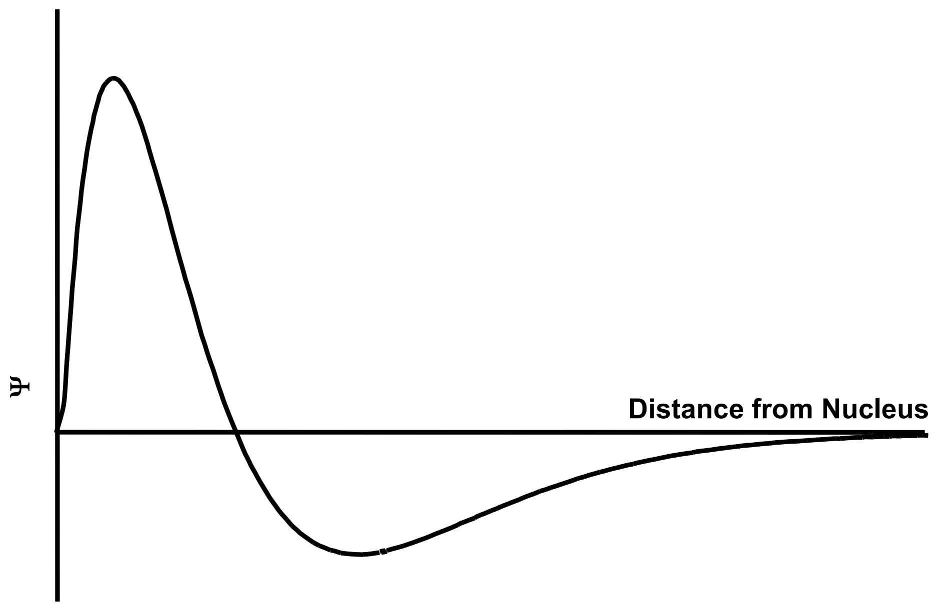
$$h \cdot \nu = RZ^2\left(\frac{1}{1_{final}^2} - \frac{1}{\infty_{initial}^2}\right) = RZ^2$$

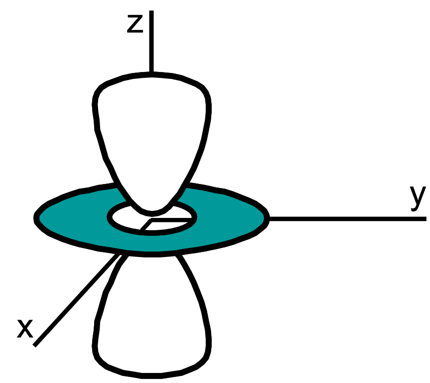
Solve for Z, substitute in the constants and evaluate.

$$Z = \sqrt{\frac{h \cdot \nu}{R}} = \sqrt{\frac{(6.62608x10^{-34}\ \mathrm{J \cdot s})(1.315x1016\ \mathrm{s}^{-1})}{2.178x10^{-18}\ \mathrm{J}}} = 2.000$$

With Z = 2, this spectrum must arise from the He^{+} ion.

3. (12 Points) The radial and angular portions of a certain H wavefunction are show below.





a. The number of radial nodes is/are **1**.

b. The number of angular nodes is/are **2**.

c. For this orbital ℓ equals **2**.

d. The possible m_ℓ values for this ℓ are **±2, ±1, 0**.

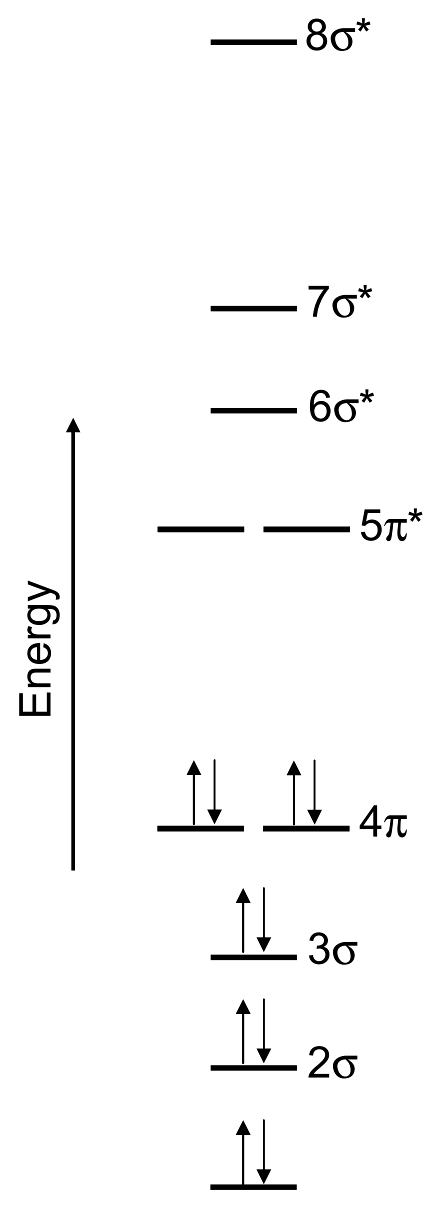
e. For this orbital *n* equals **4**. (There are n – ℓ – 1 radial nodes.)

f. The name of this orbital is $4d_{z^2}$.

g. When compared to an s orbital of the same *n* in the hydrogen atom, this orbital's energy is
greater than   less than   **the same as**   the s orbital's energy. (circle one)

h. When compared to an s orbital of the same *n* in the iron atom, this orbital's energy is
greater than   less than   the same as   the s orbital's energy. (circle one)

4. A partial MO diagram for acetylene, C_2H_2, is shown to the right. Note that only the molecular orbitals arising from the valence electrons are shown and that no atomic orbitals are shown. The numbers in the labels on each MO are just there to distinguish one from another.



a. (5 Points) Place the electrons in the diagram.

There are 10 valence electrons to place (2 C with 4 each and 2 H with 1 each).

b. (1 Point) Which orbital is the HOMO?

The 4π orbital is the HOMO.

c. (1 Point) Which orbital is the LUMO?

The 5π* is the LUMO.

d. (3 Points) What is the bond order in acetylene?

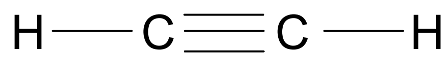
The bond order is one half the number of electrons in bonding MOs minus the number in antibonding MOs. In this case, this is (10-0)/2 = 5.

e. (3 Points) What kinds of bonds, and what number of each kind, are present in acetylene?

There are 3 σ bonds and 2 π bonds in acetylene.

f. (3 Points) Draw the Lewis dot structure of acetylene.

There are 10 valence electrons to place (see part a). Doing this and abiding by the Lewis dot structure rules gives the following.



g. (3 Points) Does your Lewis dot structure predict the same number of bonds as MO theory does? Explain any apparent discrepancies.

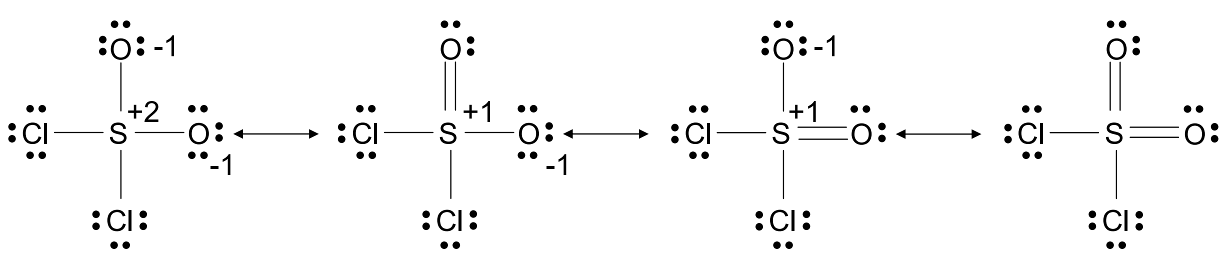
The Lewis dot structure predicts that there are five bonds in acetylene, the same as MO theory does.

h. (4 Points) Si and C are in the same group, however compounds of the type -Si≡Si- are very unstable and only recently have compounds of this type been successfully prepared. Explain why compounds of this type are common for C but rare for Si.

Orbital size increases down a group. So, Si orbitals are larger than C orbitals, which means that there will be poorer overlap between the Si orbitals and a weaker bond. If a bond is weaker it means that it is more reactive and the compound is less stable.

5a. (8 Points) Draw all four resonance structures for the compound SO_2Cl_2.

S	6
2 O	2 x 6 = 12
2 Cl	2 x 7 = 14
	32



Note that structures with a double bond to a Cl would place a positive charge on the Cl, and lead to structures which are not plausible according to the Electroneutrality Principle.

b. (5 Points) Calculate the formal charges for each different kind of atom in the resonance structures that you drew in part a. Write any non-zero formal charge next to the atom that bears that charge in that particular resonance structure.

All chlorines: formal charge = 7 – 6 – ½(2) = 0

Single bonded oxygens: formal charge = 6 – 6 – ½(2) = -1

Double bonded oxygens: formal charge = 6 – 4 – ½(4) = 0

S with four single bonds: formal charge = 6 – 0 – ½(8) = +2

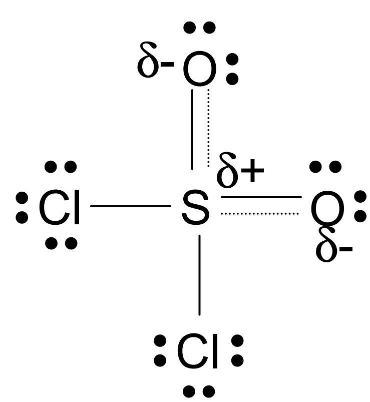
S with three single bonds and one double bond: formal charge = 6 – 0 – ½(10) = +1

S with two single bonds and two double bonds: formal charge = 6 – 0 – ½(12) = 0

c. (4 Points) Which structure do you expect to make the largest contribution to the resonance hybrid? Why?

The structure with the two double bonds is expected to make the largest contribution. This is because it minimizes formal charge, doesn't separate charge (because there isn't any), and has the maximum number of covalent bonds, all of which the Electroneutrality Principle states will lead to a favorable resonance structure.

d. (3 Points) Draw the resonance hybrid for this molecule and indicate which atoms have formal charge.



6. (10 Points) Give the electronic configuration of the following in spectroscopic notation. Indicate whether they are paramagnetic or diamagnetic.

Cu	**[Ar] $4s^1$ $3d^{10}$**	**paramagnetic**
Mg^+	**[Ne] $3s^1$**	**paramagnetic**
P^{3-}	**[Ne] $3s^2$ $3p^6$**	**diamagnetic**
Mn^{3+}	**[Ar] $3d^4$**	**paramagnetic**
C	**[He] $2s^2$ $2p^2$**	**paramagnetic**

7. (4 Points) Using what you know of the trends in ionization energy and electron affinity, explain why the metalloids do not lie in one group of the periodic table (like the halogens which are all in group 17) but run diagonally down the periodic table.

The metalloids behave both as metals and as nonmetals in their chemistry. Metals tend to lose electrons because they have low ionization energies, while nonmetals tend to gain electrons because of their high electron affinities. The observed behavior of the metalloids implies that their ionization energies must be very similar to that of a metal, while their electron affinities are similar to that of the nonmetals. Both the electron affinity and ionization energy decrease down a group and increase across a period. To keep the balance between ionization energy and electron affinity characteristic of a metalloid, they must run diagonally across the periodic table.

8. (4 Points) Which has the larger second ionization energy, lithium or beryllium? Why?

The second ionization energy of Li removes an electron from the filled core orbital (1s), while the second ionization energy of Be removes the last valence electron before the core. Because Z* is much higher for core electrons than valence electrons (shielding is less), it is more difficult to remove the negatively charged electron from the core.