

**CHEM 120**  
**Spring 2006**  
**Pre-Exam Assignment 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 not 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 **8** pages, none blank.

You may use your book to look up any needed physical constants, equations, etc. However, you may not work with anyone else, and you may not ask any other faculty members to help you with the specific questions given here. You may ask any chemistry faculty member for help on the concepts involved, and you may ask me anything you want.

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

Problem	Possible Points	Points Received
1	10	
2	5	
3	5	
4	10	
5	32	
6	16	
Free	22	22
Total	100	
	Bonus	
	Grand Total	

1. (10 Points) One line in the emission spectrum of  $\text{Be}^{3+}$  has a wavelength of 253.4 nm. If the transition that gives rise to this line starts from a state with  $n = 5$ , what is the principal quantum number of the lower-energy state involved in this transition? See the text, or the lecture notes, for the required equations and fundamental constants.

$\text{Be}^{3+}$  is a one-electron ion and behaves like H. The allowed energies of the electron in  $\text{Be}^{3+}$  are described by the following equation.

$$E_n = \left(-2.178 \times 10^{-18} \text{ J}\right) \left(\frac{Z^2}{n^2}\right)$$

The change in energy for an electron falling from a state with  $n = 5$  to another with a principal quantum number  $n$  will be given by the equation

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = \left(-2.178 \times 10^{-18} \text{ J}\right) \left(Z^2\right) \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2}\right).$$

The relationship between a photon's energy and its wavelength is  $E = \frac{hc}{\lambda}$  (derived from  $E = h\nu$  and  $\lambda\nu = c$ ).

Since the energy of the light emitted must equal the energy change for the electron, we can write the following.

$$-\frac{hc}{\lambda} = \left(-2.178 \times 10^{-18} \text{ J}\right) \left(Z^2\right) \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2}\right)$$

Solve this equation for  $\frac{1}{n_{\text{initial}}^2}$

$$\frac{1}{n_{\text{final}}^2} = \frac{hc}{\left(2.178 \times 10^{-18} \text{ J}\right) \left(Z^2\right) \lambda} + \frac{1}{n_{\text{initial}}^2}$$

Substituting in  $n_{\text{final}} = 5$  and  $Z = 4$  gives

$$\frac{1}{n_{\text{final}}^2} = \frac{\left(6.62608 \times 10^{-34} \text{ J}\cdot\text{s}\right) \left(2.99792458 \times 10^8 \text{ m}\cdot\text{s}^{-1}\right)}{\left(2.178 \times 10^{-18} \text{ J}\right) \left(4\right)^2 \left(253.4 \times 10^{-9} \text{ m}\right)} + \frac{1}{25}$$

$$\frac{1}{n_{\text{final}}^2} = 2.249_5 \times 10^{-2} + 4.000 \times 10^{-2} = 6.249_5 \times 10^{-2}$$

Solving for  $n_{\text{final}}$  gives

$$n_{\text{final}} = 4.000$$

**The final state has  $n = 4$ .**

2. (5 Points) Which is higher in energy: the 2s or the 2p orbital in hydrogen? Is this also true for helium? Explain.

**In the hydrogen atom the orbital energy depends only on  $n$  because there is only the interaction between the single electron and the nucleus. Since the 2s and 2p orbitals have the same  $n$ , they are degenerate.**

**This is not true for helium, or any other atom with more than one electron, because the electron-electron interactions (electron-electron repulsion, shielding and exchange) cause this degeneracy to be lifted such that the orbital energy depends on both  $n$  and  $\ell$ . If one of the two electrons were placed in either the 2s or the 2p orbital, it would be shielded by the electron in the 1s orbital. However, the electron in the 2s orbital would have a higher effective nuclear charge,  $Z^*$ , because it can penetrate the shielding 1s electron to a greater extent than the 2p ( $\psi_{2s}$  is not zero at the nucleus, while  $\psi_{2p}$  is zero at the nucleus). Because a 2s electron has a higher  $Z^*$  it will have a lower energy than the electron in the 2p orbital.**

3. (5 Points) Use the equation for the  $2p_z$  wavefunction given in Table 12.1 of your text to demonstrate that the maximum probability of finding the electron lies along the z axis and that it is zero in the xy-plane. See Figure 12.15 and Table 12.1 in the text for the definition of the coordinate system and parameters used in the equation, respectively.

The wavefunction for a  $2p_z$  orbital is  $\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{5/2} r e^{-Zr/2a_0} \cos\theta$ .

**When  $\theta = 90^\circ$ ,  $\cos\theta = 0$  and the entire wavefunction is 0 no matter what values  $\phi$  or  $r$  take. Since, the wavefunction will be 0 wherever  $\cos\theta$  is 0 (i. e., the xy plane) the probability of finding an electron ( $\psi^2$ ) in the xy plane is zero. As  $\theta$  gets closer to 0 (the z axis)  $\cos\theta$  approaches its maximum value of 1 and the entire wavefunction approaches its maximum value for any given  $r$ .**

*The wavefunction will be at a maximum when its first derivative with respect to  $\theta$  is 0. So, differentiating the wavefunction with respect to  $\theta$  and setting this equal to zero gives*

$$\frac{d\psi_{2p_z}}{d\theta} = -\left(\frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{5/2} r e^{-Zr/2a_0}\right) \sin\theta = 0$$

$$\sin\theta = 0$$

*This relationship is satisfied when  $\theta = 0^\circ$  and  $\theta = 180^\circ$ , which corresponds to the z axis.*

4. (10 Points) The photoelectric effect for Mg metal has a threshold frequency of  $8.95 \times 10^{14} \text{ s}^{-1}$  (i. e.,  $\nu_0$ ). Can Mg be used in photoelectric devices that sense visible light? Perform a calculation and explain.

**The threshold frequency corresponds to light with just enough energy to promote an electron from a bound state to an unbound state (in other words, just move it far enough away that it essentially doesn't interact with the nucleus anymore).**

*Start with Einstein's equation for the photoelectric effect and solve it for  $E_{\text{kinetic}} = 0$ , which will give the minimum frequency of incident light that will dislodge an electron.*

$$E_{\text{kinetic}} = h\nu - h\nu_0$$

$$0 = h\nu - h\nu_0$$

$$\nu = \nu_0$$

*So, we get that the minimum frequency to dislodge the electron is  $\nu_0$ . Light with a frequency greater than, or equal to, this frequency will cause an electron to be promoted to an unbound state and move away with some kinetic energy. But does this correspond to visible light?*

**Figure 12.3 in the book gives the range of visible light as being  $4 \times 10^{-7} \text{ m}$  to  $7 \times 10^{-7} \text{ m}$ . Because energy is inversely related to wavelength, the highest energy visible light has a wavelength of  $4 \times 10^{-7} \text{ m}$ . Convert this wavelength to frequency using the relationship  $\lambda\nu = c$ .**

$$\nu = \frac{c}{\lambda} = \frac{2.99792458 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{4 \times 10^{-7} \text{ m}} = 7.5 \times 10^{14} \text{ s}^{-1}$$

**This frequency is less than the minimum required to promote an electron to an unbound state. We, therefore, conclude that Mg could not be used in photoelectric devices that sense visible light because visible light does not have enough energy to free an electron.**

5. The  $\text{CN}^-$  ion binds strongly to many metals and it is the strong bond formed between  $\text{CN}^-$  and the iron in hemoglobin which is responsible for the ion's extreme toxicity.

a. (8 Points) Draw the Lewis dot structure for  $\text{CN}^-$  and determine the formal charge on each atom. Based on the formal charge, which end of the  $\text{CN}^-$  ion would you expect to interact more strongly with a positively charged metal ion?

1 C	4
1 N	5
-1 charge	1
<hr/>	
Total	10



$$\text{formal charge on C} = 4 - 2 - \frac{1}{2}(6) = -1$$

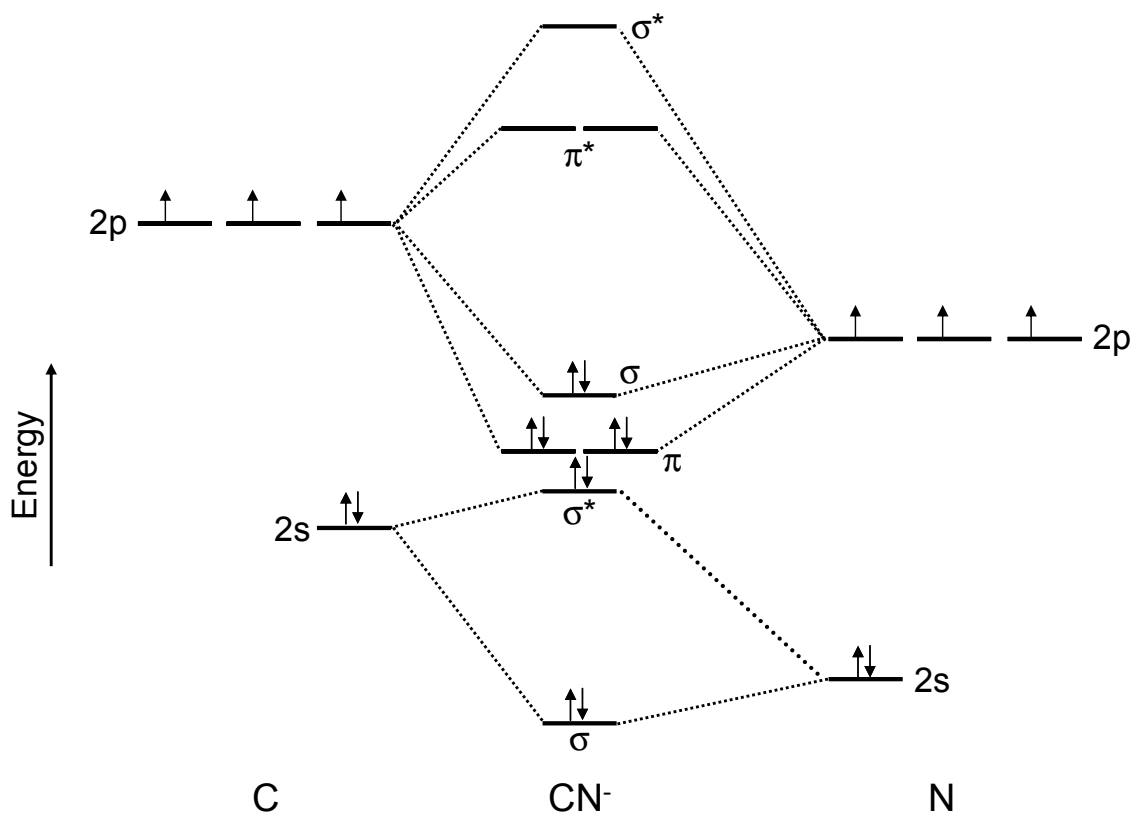
$$\text{formal charge on N} = 5 - 2 - \frac{1}{2}(6) = 0$$

**Since the negative charge on  $\text{CN}^-$  is formally on the C atom, it is expected that the C end of the ion would interact strongly with a positively charged metal ion.**

b. (4 Points) Based solely on electronegativity, which end of the  $\text{CN}^-$  would you expect to interact more strongly with a positively charged metal ion?

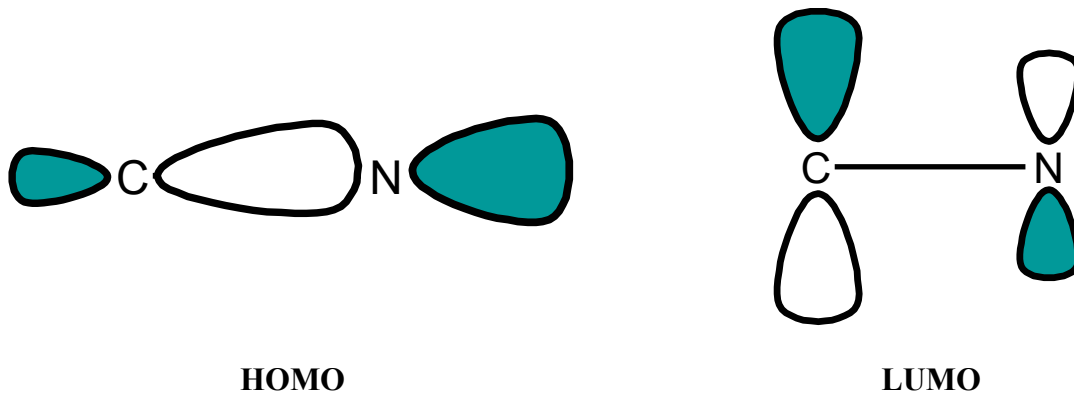
**Nitrogen is more electronegative than C and we would expect that the electrons in the bond will be pulled more toward it. This would make the nitrogen end of the ion carry most of the negative charge and interact most strongly with a positive charge.**

c. (5 Points) The partial MO energy level diagram for  $\text{CN}^-$  is shown below. Complete the diagram (you can place the extra electron either on C or on N initially).



*The electronic configuration of C is  $[\text{He}] 2s^2 2p^2$  and for N it is  $[\text{He}] 2s^2 2p^3$ . For simplicity, the extra electron has been placed on C.*

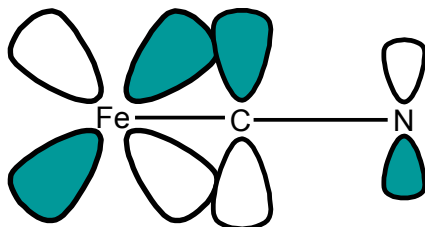
d. (5 Points) Draw qualitative pictures of the HOMO and of the LUMO for  $\text{CN}^-$ . For  $\pi$ , or  $\pi^*$ , orbitals, draw only one of the pair. Don't forget the effect that the energy difference between the atomic orbitals on C and the atomic orbitals on N has on the wavefunctions.



e. (4 Points) Based only on the MO diagram, predict which end of  $\text{CN}^-$  will bind to a positive metal ion. Explain your reasoning. Hint: use your answer to parts c and d.

**The HOMO contains the electrons with the highest energy, and are thus the most likely to be donated. The HOMO in  $\text{CN}^-$  is predominantly made up of a N 2p atomic orbital, which means most of the electron density in this MO is around the N atom. Because the electrons are around the N, we expect the N end of the ion to be negative and it would be more favorable for this end to interact with a positively charged metal ion.**

f. (3 Points) In reality  $\text{CN}^-$  binds to transition metal cations through the carbon, which is not what you would have predicted from MO theory. The problem is that we forgot something in our MO treatment, and that was the metal ion. Assume that we are looking at the interaction between  $\text{CN}^-$  and  $\text{Fe}^{3+}$  and that  $\text{CN}^-$  will donate the two electrons in its HOMO to the  $\text{Fe}^{3+}$ . When this happens there will be two additional interactions between the  $\text{Fe}^{3+}$  and the  $\text{CN}^-$  LUMO. Draw one of them. Hint: think about what the valence orbitals for  $\text{Fe}^{3+}$  are.



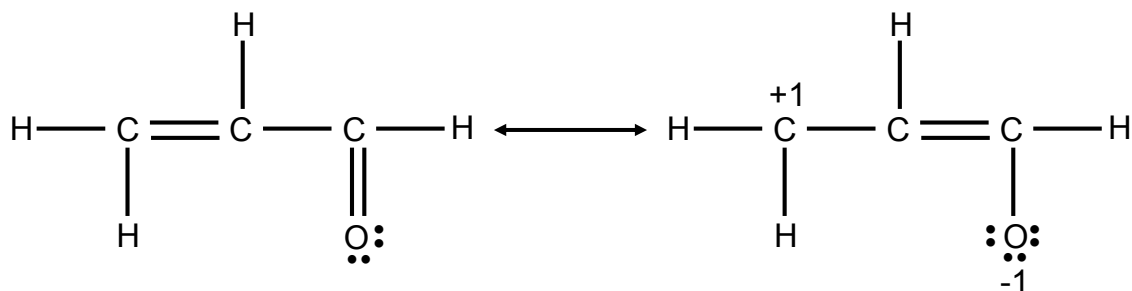
*There will be overlap between one of the  $\text{Fe}^{3+}$ 's valence d orbitals and the  $\pi^*$  LUMO of the  $\text{CN}^-$  which results in two new MOs the bonding one shown and an antibonding one (not shown).*

g. (3 Points) How would the interaction between  $\text{Fe}^{3+}$  and  $\text{CN}^-$ , described in part f, affect the bond order of the  $\text{CN}^-$ ? Why?

**The electronic configuration of  $\text{Fe}^{3+}$  is  $3d^5$ . This means that each d orbital is occupied by one electron. When the interaction in part f happens the electron on the  $\text{Fe}^{3+}$  now finds itself in an orbital that is very much an antibonding molecular orbital with respect to  $\text{CN}^-$  (we can think of this interaction between the  $\text{Fe}^{3+}$  3d orbital and the  $\text{CN}^- \pi^*$  MO as formally placing an electron in the  $\text{CN}^- \pi^*$ ). This decreases the bond order in  $\text{CN}^-$  because there is now some electron density in the  $\pi^*$  orbital. Remember that in MO Theory bond order is half the number of electrons in bonding orbitals minus the number in antibonding orbitals. In this case we are essentially placing some fraction of an electron into the  $\text{CN}^- \pi^*$  orbital and thereby lowering its bond order.**

*Note that when the  $\text{CN}^-$  HOMO interacts with an  $\text{Fe}^{3+}$  d orbital to form the C–Fe bond, two new MOs are formed; one bonding and one antibonding. The net effect is that the two electrons in the bonding  $\text{CN}^-$  HOMO are still in a bonding MO, and thus do not change the bond order in  $\text{CN}^-$ . You should also note that this was not the interaction that was asked about in this question!*

6. Acrolein,  $C_3H_4O$ , is used in the manufacture of plastics. It has the arrangement of atoms shown below and two possible resonance structures.



a. (4 Points) Fill in the missing electrons to complete the Lewis dot structures.

3 C	3 x 4 = 12
4 H	4 x 1 = 4
1 O	1 x 6 = 6
Total	22

b. (4 Points) Calculate the formal charge on each atom (show your work below). If a formal charge is not zero, write it next the atom in the appropriate resonance structure above.

**All H are the same:  $FC = 1 - 0 - 1/2(2) = 0$**

**Double bonded O:  $FC = 6 - 4 - 1/2(4) = 0$**

**Single bonded O:  $FC = 6 - 6 - 1/2(2) = -1$**

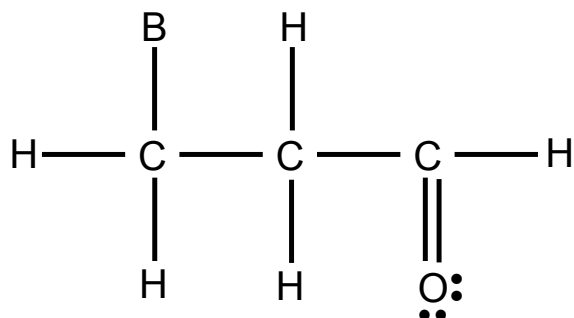
**C with two single bonds and one double bond:  $FC = 4 - 0 - 1/2(8) = 0$**

**C with three single bonds:  $FC = 4 - 0 - 1/2(6) = +1$**

c. (4 Points) Which resonance structure contributes the most to the resonance hybrid structure of acrolein? Explain.

**The one on the left contributes the most because it minimizes formal charge, does not separate formal charge and has the maximum number of covalent bonds. The one on the right does none of these things.**

d. (4 Points) Acrolein reacts with Lewis bases to give compound like that shown below where B stands for the Lewis base. How might this fact force you to modify your answer to part c?



**A Lewis base donates a pair of electrons, and because electrons are negatively charged, this donation will preferentially occur where there is a positive charge. Since the Lewis base ends up on the C which is predicted to have a formal +1 charge in the less-favorable resonance structure in part a, we must conclude that that C has some amount of positive charge and that that resonance structure is contributing to the resonance hybrid of acrolein.**