Chem 131 **Name**_____
Exam 2, Ch 11, 12, 26 **February 29, 2012**
100 Points

Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions.

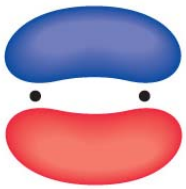
Part 0: Warmup. 4 points each

1. The compound SF_4 has a see-saw molecular geometry. How would valence bond theory describe the hybridization of the sulfur atom?

   a. sp^2
   b. sp^3
   c. sp^3d
   d. sp^3d^2
   e. sp^2d^2

   Answer ____C_____

2. The figure below is a representation of what type of orbital?



   a. σ bonding molecular orbital
   b. σ antibonding molecular orbital
   c. π bonding molecular orbital
   d. π antibonding molecular orbital
   e. sp^3 hybrid orbital

   Answer ____C_____

Part I: Complete all of problems 3-6

3. Define **<u>three</u>** of the following in a maximum of three sentences per item: (12 points)

   a. functional group: A small group of atoms in an organic molecule that have a characteristic structure and <u>reactivity</u>.

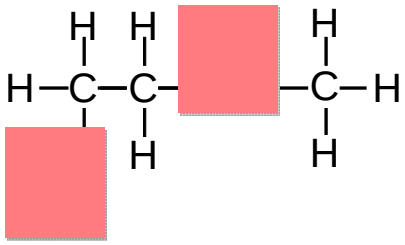
   b. hybrid orbital: An orbital, formed by a melding of atomic orbitals, adopted by an atom in a molecule to lead to the experimentally observed molecular shape.

   c. triple point: Temperature and pressure where the solid, liquid, and gas phases of a substance are in equilibrium.

   d. unit cell: Smallest repeating unit of a crystalline lattice.

4. Draw the structure of any compound that contains an *amine* and an *ester* and has the molecular formula $C_4H_9NO_2$. (6 points)

There are several possible answers, here is one. The ester and amine functional groups are shaded in pink:



5. Match each compound below to its boiling point. Clearly justify your decision; no credit will be given without a clear justification of your reasoning. (14 points)

a. methyl ethyl ether ($CH_3CH_2OCH_3$), mm = 60.1 g/mol
b. n-propanol ($CH_3CH_2CH_2OH$), mm= 60.1 g/mol
c. n-butane ($CH_3CH_2CH_2CH_3$) , mm = 58.1 g/mol
d. propylamine ($CH_3CH_2CH_2NH_2$) , mm = 59.1 g/mol

i. 97.2° C
ii. 10.8° C
iii. -0.5° C
iv. 48.5° C

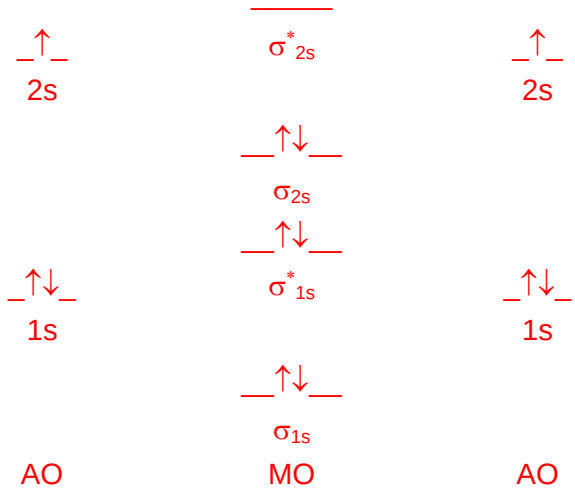
Compound	methyl ethyl ether ($CH_3CH_2OCH_3$),	n-propanol ($CH_3CH_2CH_2OH$)	n-butane ($CH_3CH_2CH_2CH_3$)	propylamine ($CH_3CH_2CH_2NH_2$)
Inter-molecular forces present	dispersion dipole-dipole (C-O)	dispersion dipole-dipole (C-O, O-H) hydrogen bonding	dispersion	dispersion dipole-dipole (C-N, N-H) hydrogen bonding
Boiling Point	10.8° C	97.2° C	-0.5° C	48.5° C

For molecules of comparable mass, boiling point typically increases as the strength of the intermolecular forces for the compound increases. Of the four compounds, n-butane can only participate in dispersion forces, which are the weakest of the IM forces. Therefore, we would expect it to have the lowest boiling points. The remaining molecules all have polar functional groups, and can participate in dipole-dipole interactions. Since methyl ethyl ether cannot participate in hydrogen bonding while propanol and propylamine can, we would expect the ether to have the next highest boiling point. Now we need to discriminate between the two compounds that can participate in hydrogen bonding (propanol and propylamine). Since oxygen is more electronegative than nitrogen, we would expect the resulting bond and molecular dipole to be greater in the propanol than in the propylamine. This should lead to stronger intermolecular interactions with the alcohol than the amine-containing compound. As a result, we would expect propanol to have the highest boiling point, with propylamine having the second highest:

Compound	Boiling Point
methyl ethyl ether	10.8° C
n-propanol	97.2° C
n-butane	-0.5° C
propylamine	48.5° C

6. The starship *Enterprise* is powered by dilithium (Li_2). Based on *molecular orbital theory*, should Li_2 be a stable molecule? Justify your answer with a MO diagram. (10 points)

Consider the MO diagram shown at right. Each Li atom has electron configuration $1s^2 2s^1$. So, there are a total of six electrons to consider. After building the MO diagram, we see that Li_2 should have a bond order of 1 [(4-2)/2]. This leads us to believe that Li_2 should be a somewhat stable molecule.

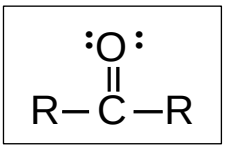


7. When drawing Lewis structures, we run into problems with compounds like ozone and benzene. With compounds like these, we have to invoke the concept of resonance and realize that the Lewis approach does provide a realistic picture of the electron distribution in these compounds. Molecular orbital theory does not have this same shortcoming. What fundamental assumption limits Lewis (and valence bond) theory and how does MO theory avoid this problem? (10 points)

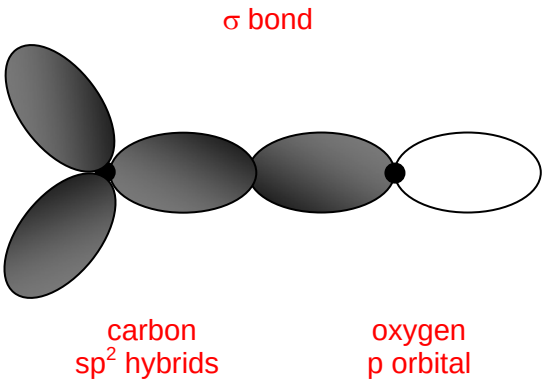
The Lewis and valence bond models are built around the notion that a bond consists of a pair (or pairs) of electrons shared between two atoms. Since MO theory addresses the entire molecule at once with a molecular orbital, it is possible for electrons to be delocalized throughout the molecules, as opposed to being pinned down between pairs of atoms.

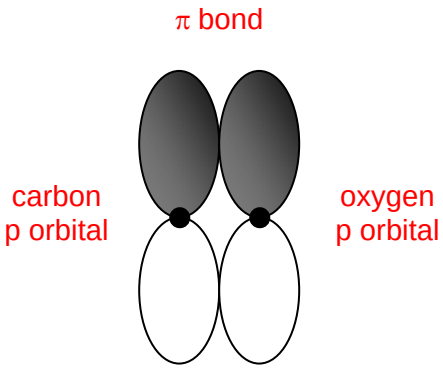
Part II. Answer three (3) of problems 8-11. Clearly mark the problem you do not want graded. 14 points each.

8. Many organic functional groups contain an oxygen atom double-bonded to a carbon, as shown at the right. Using *valence bond theory*, describe how the double bond is formed between the carbon and the oxygen. Indicate which orbitals on each atom participate and account for all electrons shared between the C and O atoms. Drawings may be useful in your description.



The key consideration here is the hybridization around the carbon atom. In this structure, the carbon takes on a trigonal planar geometry, which, in valence bond theory would imply sp^2 hybridization. As a result of this hybridization, there are three equivalent sp^2 hybrid orbitals oriented in a trigonal planar arrangement around the carbon, with one unhybridized p orbital oriented perpendicular to the sp^2 hybrids. Because of this geometry, it is possible for the carbon to share two pairs of electrons with the oxygen atom. One pair is shared in a sigma bond as shown in the figure on the left below. The sigma bond involves one of the sp^2 hybrid orbitals on carbon and a p orbital on oxygen (it must be a p orbital because the oxygen 2s orbital is filled!). The second pair of electrons is shared in a pi bond that results from side-to-side overlap of the unhybridized p orbital on carbon and the corresponding p orbital on oxygen (figure on the right below).





9. Silver forms a face-centered cubic structure as a solid. If the density of silver is 10.6 g/cm^3, what is the atomic radius of solid silver, in picometers (1 pm = 10^{-12} m)?

NOTE: There are multiple ways to approach this problem. Here is one.

We need to determine the number of atoms housed in the unit cell, as well as the volume of the unit cell, then translate that information to a radius of a silver atom.

In a fcc lattice, the unit cell holds (8 corner atoms)(1/8) + (6 face atoms)(1/2) = 4 atoms

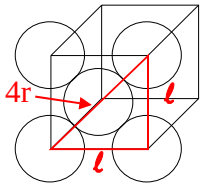
We can get the volume of the unit cell from the density:

$$\frac{1\ cm^3}{10.6\ \cancel{g\ Ag}} \times \frac{107.870\ \cancel{g\ Ag}}{1\ \cancel{mol\ Ag}} \times \frac{1\ \cancel{mol\ Ag}}{6.02 \times 10^{23}\ \cancel{atoms}} \times \frac{4\ \cancel{atoms}}{1\ unit\ cell} = \frac{6.762 \times 10^{-23}\ cm^3}{unit\ cell}$$

Since the unit cell is a cube, the length of one side is the cube root of this volume:

$$\ell = (6.762 \times 10^{-23}\ cm^3) = 4.074 \times 10^{-8}\ cm \text{ or:}$$

$$4.074 \times 10^{-8}\ cm \times \frac{10^{10}\ pm}{1\ cm} = 407.4\ pm$$



With the length of a side, we can use the structure of the fcc lattice and some right-triangle math to find the length of the diagonal and the radius of a gold atom:

$$\ell^2 + \ell^2 = (4r)^2$$

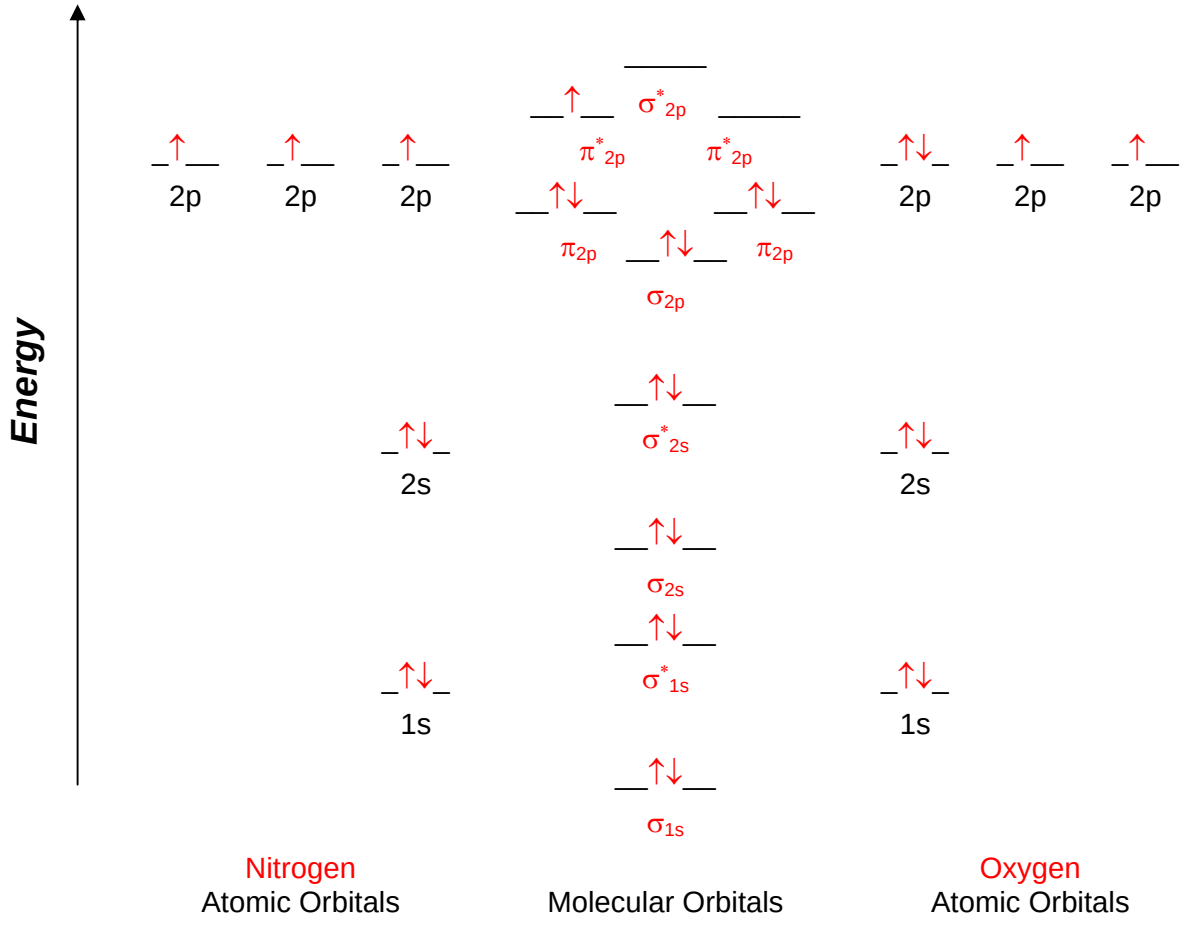
$$2\ell^2 = 16r^2$$

$$r = (2\ell^2/16)^{1/2}$$

r = 144.0 pm

10. Answer the following questions regarding the nitric oxide, NO:

a. Complete the MO diagram below for NO. You may assume that the distribution of molecular orbitals is similar to that in O_2. (6 points)



b. What is the bond order for NO? (2 points)

½(10-5) = 2.5

c. Is NO paramagnetic? Why or why not? (3 points)

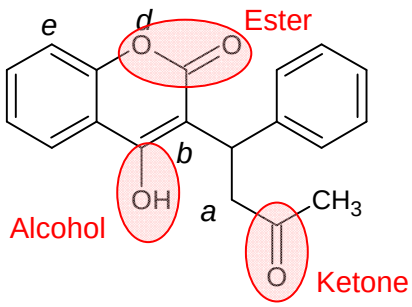
Because NO has an unpaired electron it is paramagnetic.

d. Would you expect the NO^+ ion to be more or less stable than NO? Why? (3 points)

NO (15 e^-): $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^1$
NO^+ (14 e^-): $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4$

The removal of the antibonding electron from the π^*_{2p} orbital would cause the bond order for NO^+ to increase (it would be 3), resulting in a *more stable* species.

11. Answer the following regarding warfarin, an anticoagulant also known as coumadin. Note: the two unshared electron pairs on each oxygen have been omitted for clarity.



a. Circle and name three functional groups in the compound. (4 points)

b. What is the molecular formula for warfarin? (2 points)

$C_{19}H_{16}O_4$

c. How many sigma bonds are there in warfarin? (2 points)

There are 41 sigma bonds.

d. How many pi bonds? (2 points)

There are 9 pi bonds.

e. Identify the hybridization of each of the atoms noted below: (4 points)

Carbon *a*: ____sp^3_____

Carbon *b*: ____sp^2_____

Oxyden *d*: ____sp^3_____

Carbon *e*: ____ sp^2_____

Possibly Useful Information

$a^2 + b^2 = c^2$	$N_A = 6.02 \times 10^{23}\ mol^{-1}$	henway = 2 to 3 pounds

1 1A													13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.00794	2 2A																	2 He 4.00260
3 Li 6.941	4 Be 9.01218												5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B		13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9381	26 Fe 55.847	27 Co 58.9332	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80	
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 131.29	
55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)	
87 Fr (223)	88 Ra 226.025	89 †Ac 227.028	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Rg (272)								

*Lanthanide series	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)