Chem 4A, Fall 2010
Midterm Exam 2, October 18, 2010.
Prof. Head-Gordon, Prof. Saykally

Name: KEY GSI: ____________

Grade:
1. (4 points) ______
2. (9 points) ______
3. (6 points) ______
4. (6 points) ______

Total: ______

Closed book exam. There are 6 pages. Calculators are OK. Show all working.
Use back side of pages for scribble paper. Don't spend too much time on any one problem.
Adjust brain-waves for constructive interference of your Chem 4A knowledge and go!

Some possibly useful facts and figures:

$R = 8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}$	$R = 0.082057\ \text{L atm mol}^{-1}\ \text{K}^{-1}$
$h = 6.6261\times 10^{-34}$ J s	M(H) = 1.0079 amu
$c = 2.9979 \times 10^{8}\ \text{m s}^{-1}$	M(O) = 15.994 amu
$m_e = 9.1094 \times 10^{-31}$ kg	M(Ca) = 40.078 amu
$N_0 = 6.0221 \times 10^{23}\ \text{mol}^{-1}$	molar volume at STP = 22.4 L

Some possibly relevant equations:

Planck relation:	$E = h\nu$	
de Broglie relation:	$p = h/\lambda$	
wave equation:	$c = \nu\lambda$	
uncertainty principle	$\Delta p \Delta x \geq h/4\pi$	
hydrogen atom	$E_n = -\frac{Z^2}{n^2} R_\infty$	$R_\infty = 2.18 \times 10^{-18} J$
linear momentum	$p = mv$	
kinetic energy	$T = \frac{1}{2}mv^2 = p^2/2m$	
perfect gas law	$PV = nRT$	
Boltzmann and gas constants	$k_B = R/N_0$	

1. (4 points) Atomic electronic structure and periodic properties.

(a) (1 point) Write the electron configuration of the C atom. Do you expect it to be diamagnetic or paramagnetic?

$1s^2 2s^2 2p^2$ or $[He]2s^2 2p^2$

This will be paramagnetic because of Hund's rule which states that there should be unpaired electrons in the 2p orbital:

(b) (1.5 points) The electron affinity is the negative of the stabilization energy when an atom or molecule gains an extra electron. Give a reason for whether you expect the electron affinity of N to be larger or smaller than that of C.

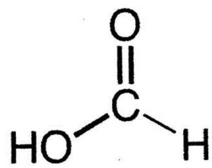
(c) (1.5 points) The ionization energy is the energy cost to remove an electron from an atom or molecule. Give a reason for whether you expect the ionization energy of N to be greater than or smaller than that of C.

The ionization energy for N will be greater than that of C.

Again, N has a stronger Z_{eff} because of incomplete shielding by the 2p-electrons.

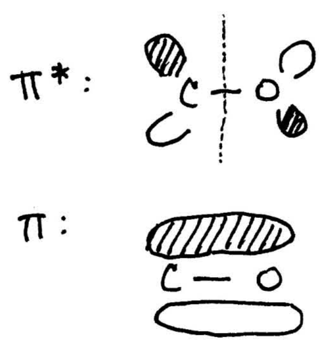
2. (9 points) Molecular orbitals in methanoic acid (HCOOH) and methanoate anion ($HCOO^-$) (the trivial names are formic acid and formate anion respectively).

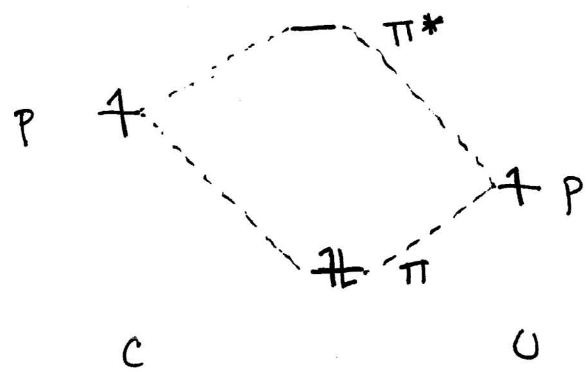
(a) (1 point) Write Lewis structure(s) for HCOOH, and determine the steric number of the central C atom, and the appropriate hybrids for use on C and the 2 O atoms.



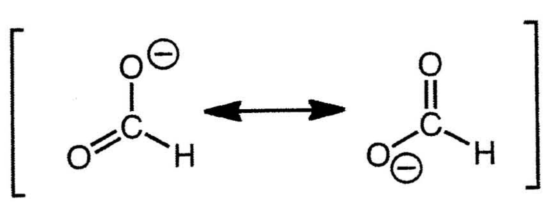
Steric number on carbon = 3
Use sp^2 hybrids on C and the O with a double bond.
Use sp^3 hybrids on the oxygen singly bonded to carbon.

(b) (2 points) Sketch the shape (boundary surface) of the π and π* molecular orbitals that describe π interactions in HCOOH. Also draw an energy level diagram showing the AO and MO energies, and which MO's are occupied.



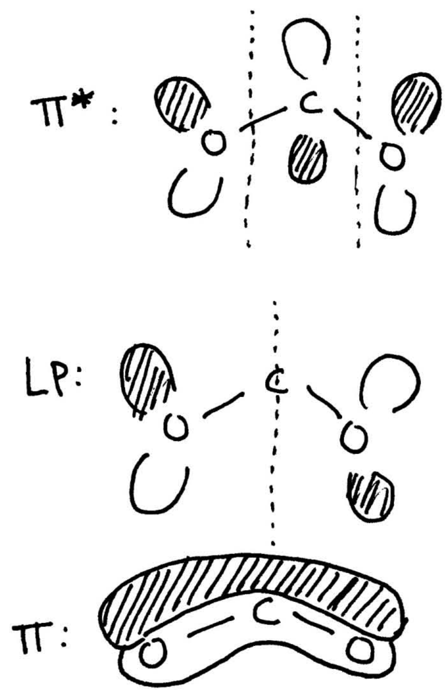


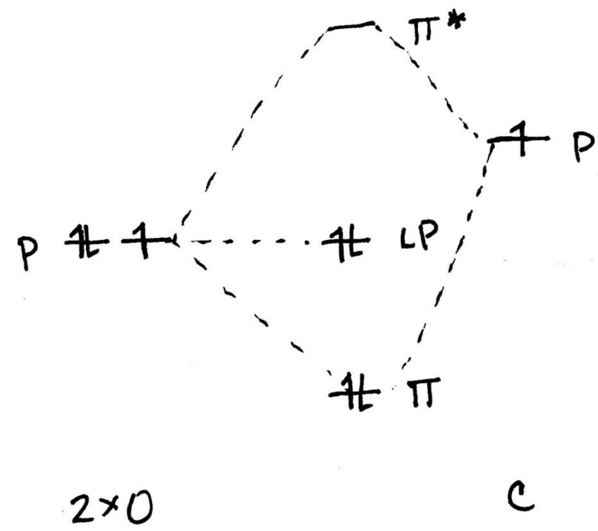
(c) (1.5 points) Write Lewis structure(s) for the $HCOO^-$ anion, determine the steric number of the central C, and discuss the hybrid orbitals that should be used on the central C atom and the 2 O atoms.



Steric number on C = 3
Use sp^2 hybrid orbitals on the C and both O's.

(d) (3 points) Sketch the shape (boundary surface) of the π and π^* molecular orbitals that describe π interactions in $HCOO^-$. Also draw an energy level diagram showing the AO and MO energies, and which MO's are occupied.



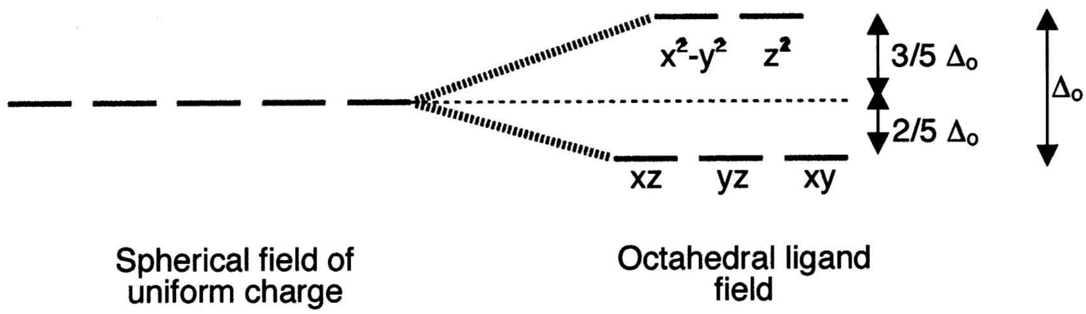


(e) (1.5 points) If the C=O bond is 1.23 Å and the C-O bond is 1.36 Å in HCOOH, use your MO diagrams from parts (b) and (d) above to explain what you think the bond-length in $HCOO^-$ should be.

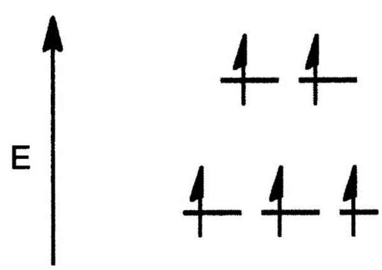
The bond length in $HCOO^-$ should be 1.295 Å, the average of the two bond lengths. This is because the π MO in $HCOO^-$ spans both C-O bonds, effectively leading to a bond order of 1.5.

3. Chemical bonding in transition metal complexes

(a) (2 points) Draw how the energies of the 5 d orbitals (xy, xz, yz, z^2, x^2-y^2) are altered due to an octahedral ligand field. Show how the energy levels are raised or lowered vs the field of a uniform shell of charge, in terms of the energy level splitting, Δ_0.

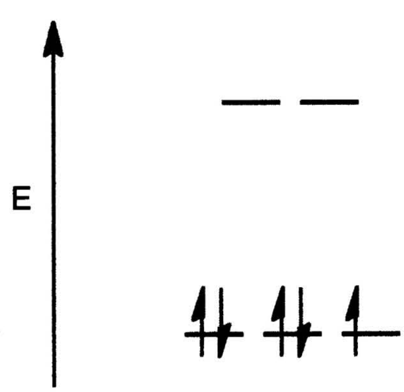


(b) (2 points) The Fe^{3+} ion has 5 d electrons. Predict how many electrons are unpaired when the ion is surrounded by an octahedral set of weak field ligands, such as water. Include an energy level diagram.



There will be 5 unpaired electrons.

(c) (2 points) Predict the number of unpaired electrons in $Fe(CN)_6^{3-}$, with a diagram, and explain the reason for any differences with the results you have predicted in part (b) above.



There will be 1 unpaired electron.

CN^- is a strong field ligand. This leads to a bigger split in Δ_o, which makes a low-spin configuration more favorable.

4. (6 points) Calcium (Z=20; *m*=40.078 amu), is an alkaline earth metal that reacts with water, in a milder version of the reactions we demonstrated with the alkali metals like sodium and potassium.

(a) (1 point) Write a balanced chemical equation, showing all products (one is a gas)

$$Ca_{(s)} + 2\,H_2O_{(l)} \rightarrow Ca(OH)_{2\,(aq.)} + H_{2\,(g)}$$

(b) (2 points) What mass of calcium is necessary to produce 3 L of gas at a pressure of 1 atm and a temperature of 30.0°C?

$$PV = nRT$$

$$\frac{PV}{RT} = n = \frac{(1\,atm)(3\,L)}{(0.082057\,\frac{L\,atm}{mol\,K})(303\,K)} = 0.1207\,mol\ H_2$$

$$0.1207\,mol\ H_2\left(\frac{1\,mol\ Ca}{1\,mol\ H_2}\right)\left(\frac{40.078\,g\ Ca}{mol\ Ca}\right) = \boxed{4.8\,g}$$

(c) (1 point) Suppose the 3L of gas was forced into a 1L container, which was cooled to 0°C. What would be the pressure inside the container be (in atm)?

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$= \frac{(0.1207\,mol)(0.082057\,\frac{L\,atm}{mol\,K})(273\,K)}{1\,L}$$

$$= \boxed{2.7\,atm}$$

(d) (2 points) Given that the average energy per molecule in the kinetic theory is $3k_BT/2$, obtain an expression for the root mean square speed, and use this to find the root mean square speed of the molecules inside the 0°C container.

$$\frac{3k_BT}{2} = \frac{1}{2}m\bar{v}^2$$

$$\sqrt{\frac{3k_BT}{m}} = \bar{v}$$

$$\sqrt{\frac{3RT}{m\cdot N_0}} = \bar{v}$$

*This expression is per molecule, so $m\cdot N_0$ = molar mass.

$$\sqrt{\frac{3RT}{MM}} = \bar{v}$$

$$\sqrt{\frac{3(8.3145\,J\,mol^{-1}K^{-1})(273\,K)}{2.02\,g\,mol^{-1}}} = \bar{v}$$

$$\sqrt{\frac{3(8.3145\,J)(273)}{2.02\,g}} = \bar{v}$$

$$\sqrt{\frac{3\times 8.3145\,kg\,m^2s^{-2}\times 273}{2.02\,g}} = \bar{v}$$

$$\sqrt{\frac{3\times 8.3145\,kg\,m^2s^{-2}\times 273}{2.02\,g\left(\frac{1\,kg}{1000\,g}\right)}} = \bar{v}$$

$$\boxed{1838\,m\,s^{-1} = \bar{v}}$$