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5.111 Principles of Chemical Science  
Fall 2008

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**Second Hour Exam****5.111**

Write your name below. **Do not open the exam until the start of the exam is announced.** The exam is closed notes and closed book.

1. Read each part of each problem carefully and thoroughly.
  2. Read all parts of each problem. **MANY OF THE LATTER PARTS OF A PROBLEM CAN BE SOLVED WITHOUT HAVING SOLVED EARLIER PARTS.** However, if you need a numerical result that you were not successful in obtaining for the computation of a latter part, make a physically reasonable approximation for that quantity (and indicate it as such) and use it to solve the latter parts.
  3. A problem that requests you to “calculate” implies that several calculational steps may be necessary for the problem’s solution. You must show these steps clearly and indicate all values, including physical constants used to obtain your quantitative result. Significant figure usage must be correct.
  4. If you don’t understand what the problem is requesting, raise your hand and a proctor will come to your desk.
  5. Physical constants, formulas and a periodic table are given on the last page. You may detach this page **once the exam has started.**
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Suggested time

1. 14 minutes (30 points) \_\_\_\_\_
2. 8 minutes (12 points) \_\_\_\_\_
3. 8 minutes (20 points) \_\_\_\_\_
4. 12 minutes (27 points) \_\_\_\_\_
5. 8 minutes (11 points) \_\_\_\_\_

**Total (100 points)** \_\_\_\_\_

Name \_\_\_\_\_

**1. (30 points) Lewis structures and VSEPR theory**

Draw the **most stable** Lewis structure for each of the following molecules, subject to the information given for each. Be sure to **include the lone pairs** and, if applicable, draw any **resonance forms** that are equal in energy. **Indicate any nonzero formal charges.**

(a) (i) (6 points) Draw the Lewis structure of  $\text{POCl}_3$ . Include any relevant resonance forms, and indicate any nonzero formal charges.

(ii) (2 points) Name the geometry around the phosphorus atom.

(b) (8 points) Draw the Lewis structure of  $(\text{NCNH})^{-1}$  (atom order as indicated). Include any relevant resonance forms, and indicate any nonzero formal charges.

(c) (i) (6 points) Draw the Lewis structure of  $(\text{SO}_3)^{2-}$ . Include any relevant resonance forms, and indicate any nonzero formal charges.

(ii) (2 points) Name the geometry around the sulfur atom.

(iii) (3 points) Circle the one value that best describes the O-S-O bond angle in  $(\text{SO}_3)^{2-}$ .

< 90°; 90°; > 90°; < 109.5°; 109.5°; > 109.5°; < 120°; 120°; > 120°; < 180°; 180°; > 180°

(iv) (3 points) Is  $(\text{SO}_3)^{2-}$  a **polar** or a **non-polar** molecule?

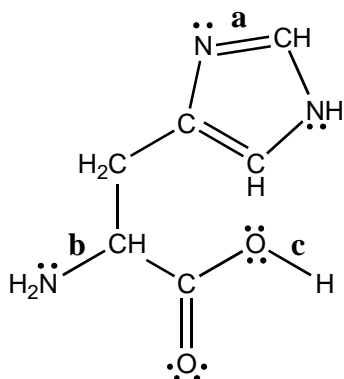
2. (12 points) **Ionic bonds**

KF has an ionic bond with a bond length of 0.217 nm. Calculate the  $\Delta E$ , in kJ/mol, for the **formation** of a KF bond from the neutral atoms K and F. For this calculation, assume that the potassium and fluorine ions are point charges. IE and EA information for K and F is provided in the table below.

	Ionization energy (kJ/mol)	Electron affinity (kJ/mol)
potassium (K)	418	48
fluorine (F)	1680	328

3. (20 points) **Hybridization**

(a) (12 points) The structure of the amino acid histidine is provided below. For the indicated bonds, a-c, write the symmetry of each bond, and give the hybrid or atomic orbitals (with their principal quantum numbers) that overlap to form each of the bonds. Where appropriate, include the x, y, or z designations with the orbitals.



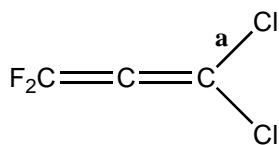
N-C bond a:

N-C bond b:

O-H bond c:

(b) (8 points)

(i) For the molecule below, indicate the symmetry in the C-Cl bond (labeled **a**), and give the hybrid or atomic orbitals (with their principal quantum numbers) that overlap to form the bond. If appropriate, include the x, y, or z designations with the orbitals.



C-Cl bond a:

(ii) Do the chlorine atoms in the  $F_2C=C=CCl_2$  molecule above lie in the **same plane** as the fluorine atoms or in a **perpendicular plane** to the fluorine atoms? Briefly explain your answer (with words or a picture).

**4. (27 points) Molecular orbital theory**

**(a) (21 points)**

(i) (9 points) Draw an energy correlation diagram for the molecular orbitals of the **valence electrons** in CN. Label the atomic and molecular orbitals, including the x, y and z designations where appropriate. The relative ordering of the energies of the states must be correct. **Use the full space available** to spread out your energy levels so that the labels for the orbitals fit easily.

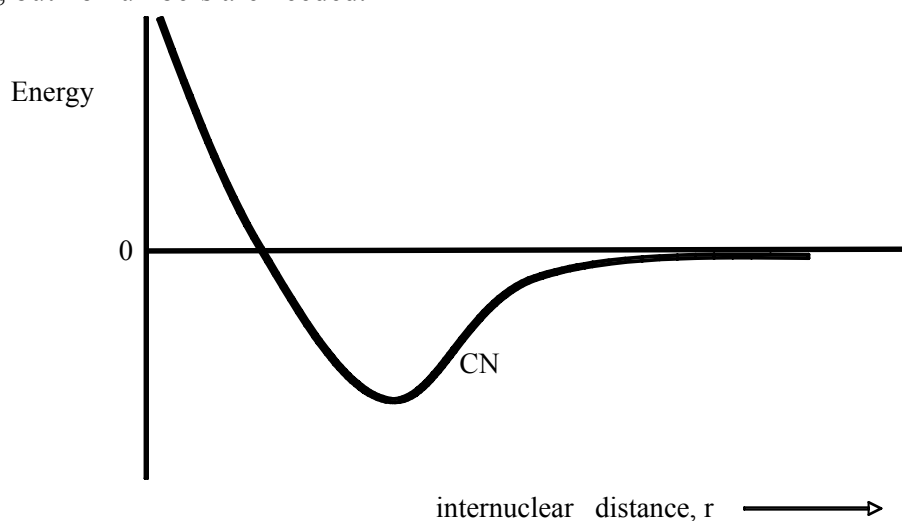
(ii) (2 points) Of the CN molecular orbitals **occupied by valence electrons**, name the orbitals that have a nodal plane along the internuclear (bond) axis.

(ii) (4 points) Determine the bond order of the cyanide molecule, CN, *and* the cyanide **ion**,  $\text{CN}^{-1}$ .

BO of CN:

BO of  $\text{CN}^{-1}$ :

(iii) (4 points) Below is an energy diagram of the CN covalent bond in a neutral CN molecule. On the same graph, plot the energy vs. internuclear distance,  $r$ , of the CN covalent bond in a  $\text{CN}^{-1}$  **ion**. Indicate the equilibrium bond distances with arrows. The **relative** values of the bond distances and energies must be correct, but no numbers are needed.



(iv) (2 points) Which of the following are radical species: CN,  $\text{CN}^{-1}$ , both, or neither?

(b) (6 points)

Write the **valence** electron configuration for  $\text{O}_2$ .



5. (11 points) **Thermochemistry**

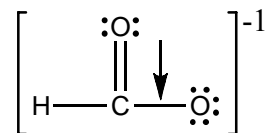
(a) (7 points) Consider the reaction below for the conversion nitrogen dioxide to nitric oxide and O<sub>2</sub>.



	$\Delta H_f^\circ$ (kJ/mol)
NO <sub>2</sub> (g)	+33.18
NO(g)	+90.25

Calculate  $\Delta H^\circ$  (per mol of O<sub>2</sub> formed) for the reaction at 298 K.

(b) (4 points) Using the table of mean bond enthalpies provided, predict the bond enthalpy (in kJ/mol) for the CO bond marked with an arrow in the molecule below.



Bond	Mean Bond Enthalpy (in kJ/mol)
C-H	412
C-C	348
C=C	612
C-O	360
C=O	743

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- $c = 2.99792 \times 10^8 \text{ m/s}$
- $h = 6.62608 \times 10^{-34} \text{ J s}$
- $N_a = 6.02214 \times 10^{23} \text{ mol}^{-1}$
- $1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}$
- $m_e = 9.10939 \times 10^{-31} \text{ kg}$
- $e = 1.60218 \times 10^{-19} \text{ C}$
- $U(r) = (z_1 z_2 e^2) / (4\pi\epsilon_0 r)$
- $\epsilon_0 = 8.8542 \times 10^{-12} \text{ C}^2 / (\text{Jm})$
- Electronegativity =  $(IE + EA) / 2$
- $\Delta G = \Delta H - T\Delta S$

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