5.111 Principles of Chemical Science

Fall 2008

Second Hour Exam- Answer Key **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**.

	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)	_____

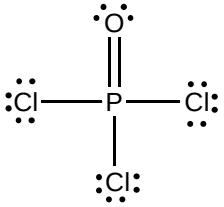
Total (100 points) _____

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 $POCl_3$. Include any relevant resonance forms, and indicate any nonzero formal charges.

32 valence electrons
40 electrons needed to fill valence shells
8 bonding electrons } after valence shell expansion, 10 bonding electrons and 22 lone pair electrons
24 lone-pair electrons } (eliminating all formal charges)

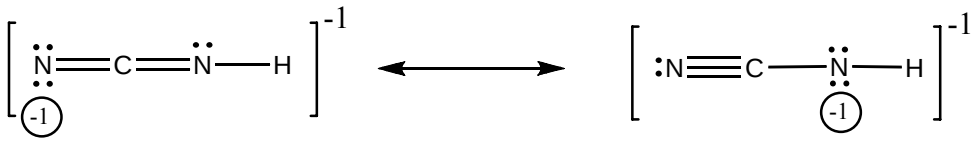


(ii) (2 points) Name the geometry around the phosphorus atom.

tetrahedral

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

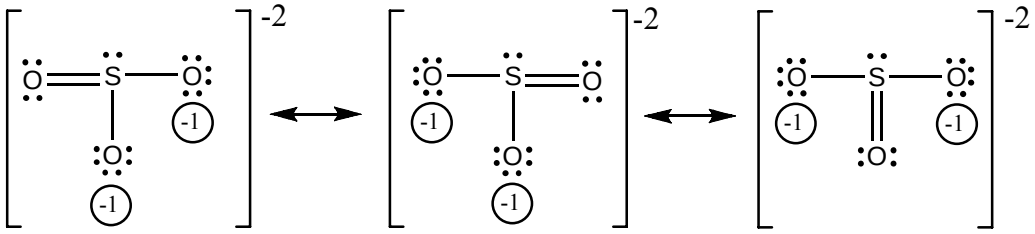
16 valence electrons
26 electrons needed to fill valence shells
10 bonding electrons
6 lone-pair electrons



Formal charges are circled on atoms where the FC is not zero.

(**c**) (i) (6 points) Draw the Lewis structure of $(SO_3)^{-2}$. Include any relevant resonance forms, and indicate any nonzero formal charges.

26 valence electrons
32 electrons needed to fill valence shells
6 bonding electrons } after valence shell expansion, 8 bonding electrons and 18 lone pair electrons
20 lone-pair electrons } (eliminating all formal charges)



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

trigonal pyramidal

(iii) (2 points) Circle the one value that best describes the O-S-O bond angle in $(SO_3)^{-2}$.

$< 90°$; $90°$; $> 90°$; (circled) $< 109.5°$; $109.5°$; $> 109.5°$; $< 120°$; $120°$; $> 120°$; $< 180°$; $180°$; $> 180°$

(iv) (2 points) Is $(SO_3)^{-2}$ a **polar** or a **non-polar** molecule?

polar

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

KF has an ionic bond with a bond length of 0.217 nm. Calculate the ΔE, 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

Overall: $K + F \rightarrow KF$

First calculate the ΔE for the formation of an ionic bond from the two ions:

$K^+ + F^- \rightarrow KF$

$$U(r) = \frac{z_1 z_2 e^2}{4\pi\varepsilon_o r} = \frac{(-1)\,(1)\,(1.602 \times 10^{-19}\ C)^2}{4\pi\,(8.854 \times 10^{-12}\ C^2 J^{-1} m^{-1})(0.217 \times 10^{-9}\ m)}$$

$U(r) = -1.063 \times 10^{-18}$ J

$$U(r) = -1.063 \times 10^{-18}\ J \times \frac{kJ}{1000\ J} \times \frac{6.022 \times 10^{23}}{mol} = -640.1\ kJ/mol$$

$U(r) = -640.1$ kJ/mol

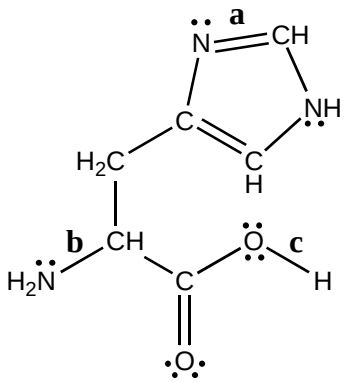
$\Delta E_{total} = IE_K - EA_F + U(r)$

$K \rightarrow K^+ + e^- \equiv IE_K$	418 kJ/mol
$F + e^- \rightarrow F^- \equiv -EA_F$	-328 kJ/mol
$K^+ + F^- \rightarrow KF \equiv U(r)$	-640.1 kJ/mol
$K + F \rightarrow KF$	-550.1 kJ/mol

-550. kJ/mol or -5.50×10^{-2} kJ/mol

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: **σ(N2sp^2, C2sp^2)**

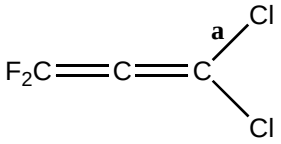
π(N2p$_y$, C2p$_y$) or π(N2p$_x$, C2p$_x$)

N-C bond b: **σ(N2sp^3, C2sp^3)**

O-H bond c: **σ(O2sp^3, H1s)**

(**b**) (8 points)

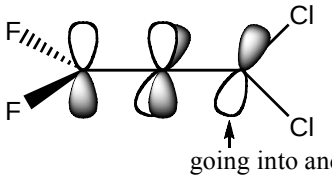
(i) For the molecule below, indicate the symmetry in the C-Cl bond (labeled **a**), and give the hybrid or atomic orbitals (with their principal quantum numbers) that overlap to form the bond. If appropriate, include the x, y, or z designations with the orbitals.



C-Cl bond a: **σ(C2sp^2, Cl3p$_z$)**

(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).

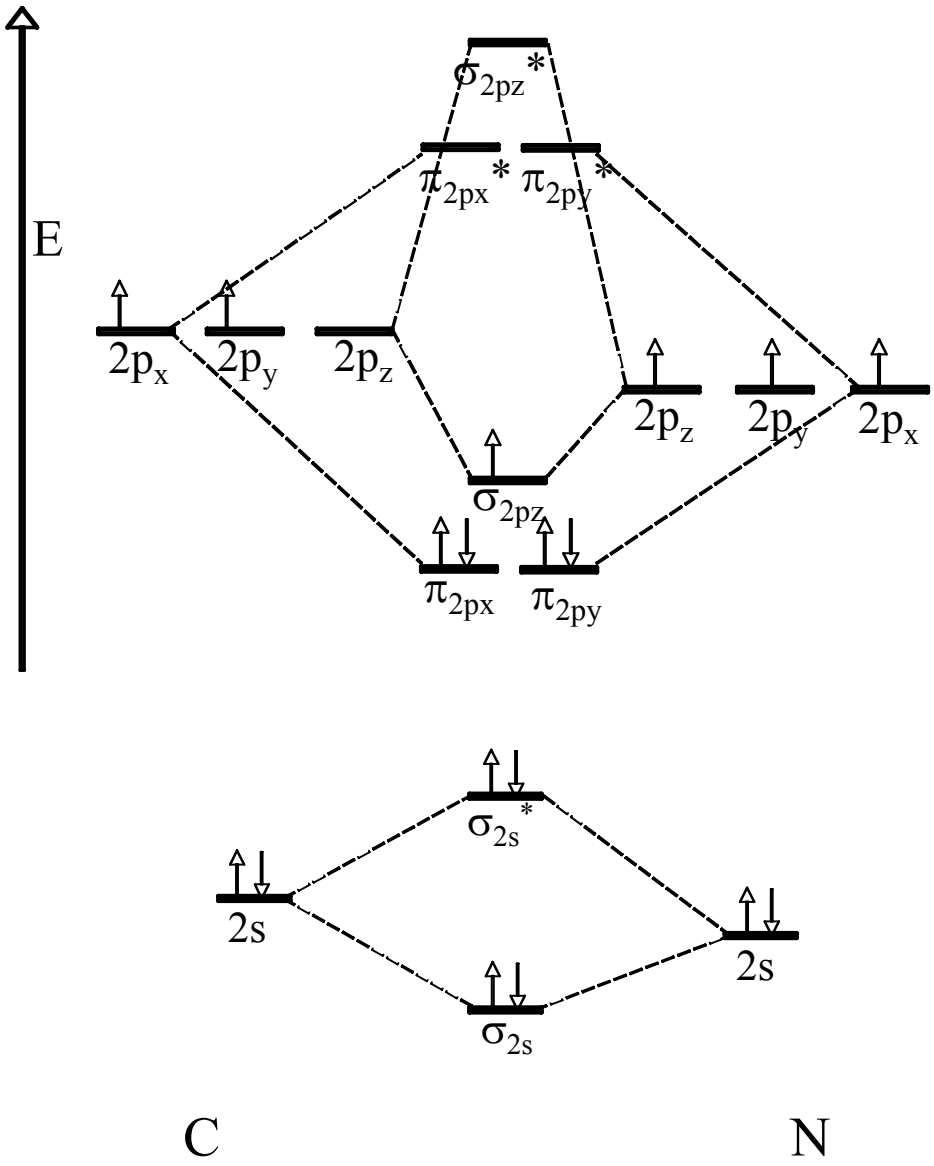
perpendicular plane. The p-orbitals in the two sp^2-hybridized carbon atoms are perpendicular to each other (p$_y$ and p$_x$), meaning the F-C-F bonds and the Cl-C-Cl bonds also lie in perpendicular planes.



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.

$\pi 2p_x$ and **$\pi 2p_y$**

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

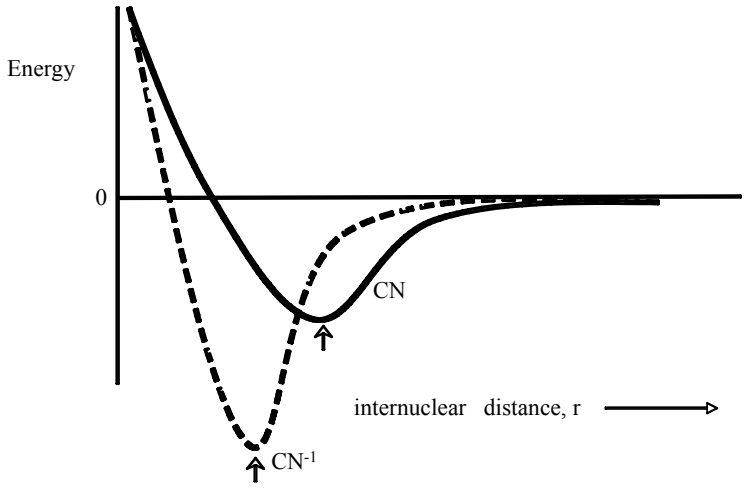
½(# of bonding electrons-# of anti-bonding electrons)

BO of CN: ½(7-2) = **2.5**

BO of CN^{-1}: ½(8-2) = **3**

(iv) (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 **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.

Note: this question is graded based on your answer to part (iii), since it depends on bond order.



(v) (2 points**)** Which of the following are radical species: CN, CN^{-1}, both, or neither?

CN is the only radical species.

(b) (6 points)

Write the **valence** electron configuration for O_2.

(12 valence electrons)

$(\sigma 2s)^2(\sigma 2s^*)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi 2p_x^*)^1(\pi 2p_y^*)^1$

5. (11 points) **Thermochemistry**

(**a**) (7 points) Consider the reaction below for the conversion nitrogen dioxide to nitric oxide and O_2.

$$\mathbf{2NO_2(g) \rightarrow 2NO(g) + O_2(g)}$$

	$\Delta H_f°$ (kJ/mol)
$NO_2(g)$	+33.18
NO(g)	+90.25

Calculate ΔH^o (per mol of O_2 formed) for the reaction at 298 K.

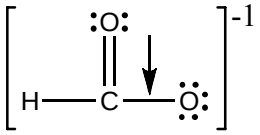
$\Delta H_r° = \Sigma \Delta H_f°(\text{products}) - \Sigma \Delta H_f°(\text{reactants})$

$\Delta H_r° = [2\Delta H_f°(NO) + \Delta H_f°(O_2)] - [2\Delta H_f°(NO_2)]$

$\Delta H_r° = [2(90.25 \text{ kJ/mol}) + (0)] – [2(33.18 \text{ kJ/mol})]$

$\Delta H_r°$ = 114.1 kJ or 114.14 kJ (also ok to have kJ/mol, since the questions says per mol of O_2)

(**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.



Note: the C-O bond is a 1½ bond (not a single bond) due to resonance.

360 kJ/mol < bond enthalpy < 743 kJ/mol

It is also fine if a student calculated a number, as long as it is above 400 and less than 700 kJ/mol (ie. 552 kJ/mol).

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

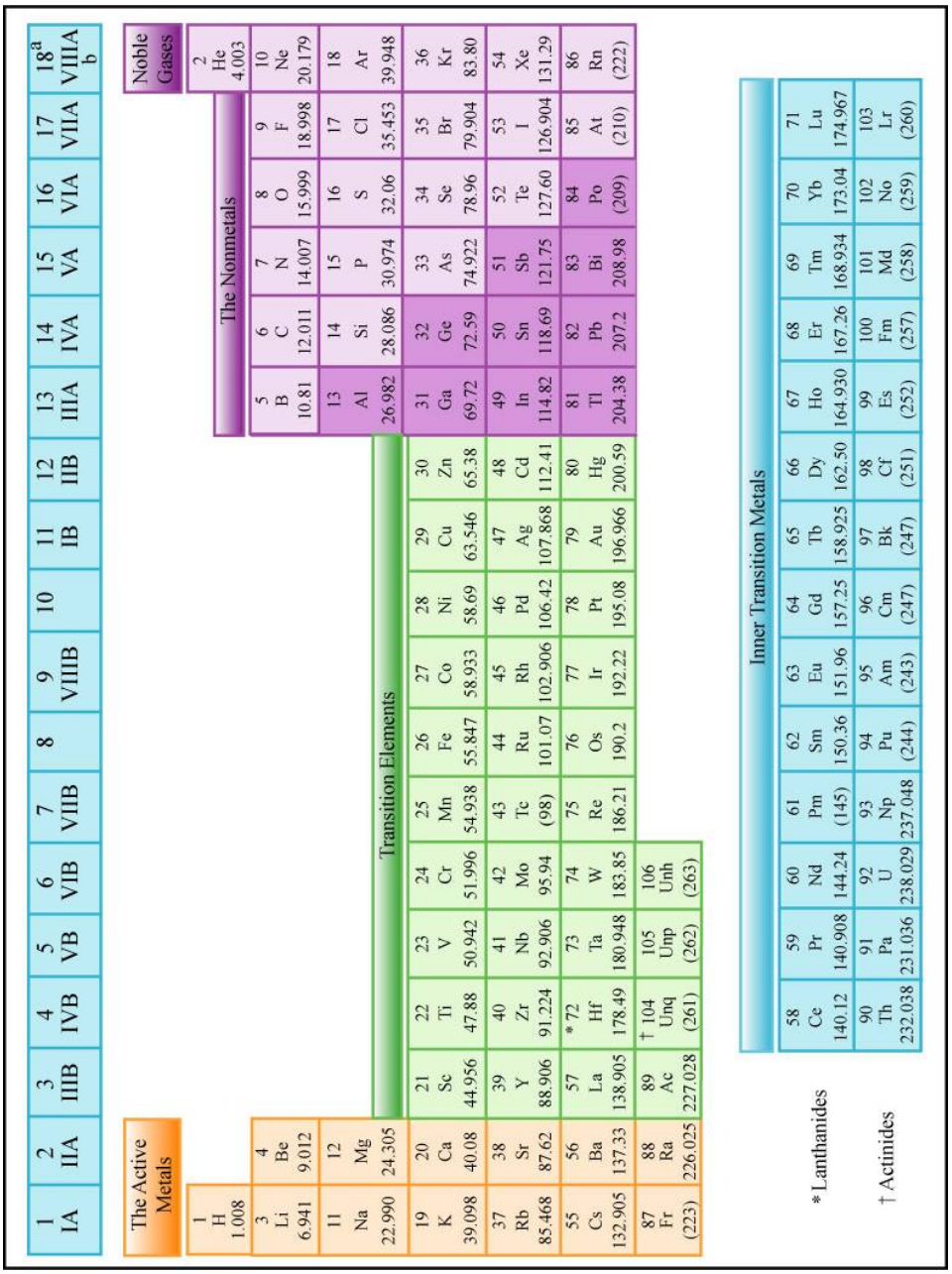


Image by MIT OpenCourseWare

$c = 2.99792 \times 10^{8}$ m/s

$h = 6.62608 \times 10^{-34}$ J s

$N_a = 6.02214 \times 10^{23}$ mol^{-1}

1 eV = 1.60218×10^{-19} J

$m_e = 9.10939 \times 10^{-31}$ kg

$e = 1.60218 \times 10^{-19}$ C

$U(r) = (z_1 z_2 e^2)/(4\pi\varepsilon_0 r)$

$\varepsilon_0 = 8.8542 \times 10^{-12}$ C^2/(Jm)

Electronegativity = (IE + EA)/2

$\Delta G = \Delta H - T\Delta S$