Practice Exam 2 Key – Fall 2014

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Write your name and your TA's 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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1.   Lewis structures / VSEPR   1a, 1b   (12 points) page 2 _____

                                                1c, 1d   (18 points) page 3 _____

2.   Ionic bonds   2a, 2b   (15 points) page 4 _____

3.   Hybridization   3a, 3b, 4a (26 points) page 5 _____

4.   Molecular orbitals   4b   (15 points) page 6 _____

5.   Periodic Trends   5a, 5b   (12 points) page 7 _____


                                Total (100 points)   _____

Name   ANSWER KEY

TA   _____

1. (30 points) **Lewis structures and VSEPR theory**
 (a) For the molecule N_2O, consider four possible structures below:

-1   +1
$\ddot{N}=N=\ddot{O}$
:$\ddot{N}$:

+1   -1
:$N\equiv N-\ddot{O}$:

-1   +2 -1
$\ddot{N}=O=\ddot{N}$

+2 -2
:$N\equiv O-\ddot{N}$:
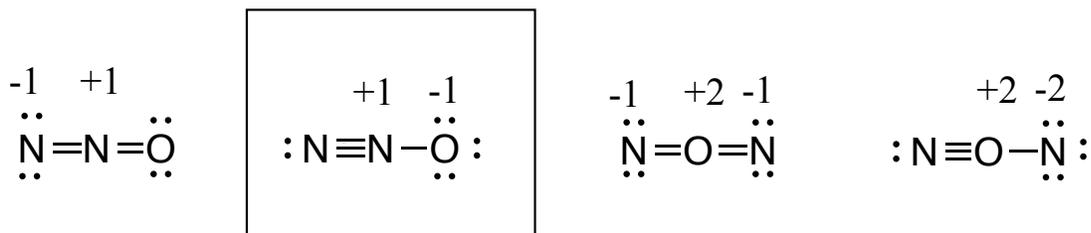
(Note: negative charge on the more electronegataive atom)

   (i) (3 points) Given the information from experiment that N_2O is a **polar molecule**, circle the most accurate statement below. <u>Briefly explain your reasoning</u>.

The atom arrangement is NNO.

The atom arrangement is NON.

More information is needed to determine the atom arrangement.

Explain: NON is symmetric and therefore not a polar molecule.

   (ii) (5 points) On all of the four structures above, indicate any nonzero **formal charges**. Based on formal charge alone, **box** the structure that you predict to be most stable.

(b) (i) (4 points) Complete the **most stable** Lewis structure for $[PO_4H]^{2-}$ (atom connectivity indicated below) by filling in **lone pairs and/or multiple bonds** on the structure drawn. Indicate any nonzero **formal changes**. You do NOT need to draw resonance forms, if any.

2-
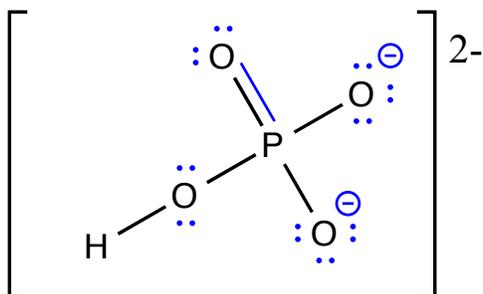
32 valence electrons (including the 2- charge)
42 – 32 = 10 bonding electrons (5 bonds)
32 – 10 = 22 lone pair electrons (11 lone pairs)

Note that to minimize FC, you must expand the P octet, which results in 6 bonds and 10 lone pairs.

(Note: double bond could be to any of the terminal oxygens)

(ii) (2 points) What is the steric number of phosphorus (P) in this molecule? SN = 4 (4 oxygens bonded to P and no lone pairs)

2

(c) (i) (6 points) Draw the **most stable** Lewis structure of $(C_2H_3O_2)^{1-}$ and indicate any **non-zero formal charges**. There are <u>no oxygen-oxygen bonds</u> in this structure, and there is a <u>single methyl (CH_3) group</u>. Include **lone pairs**, and if applicable, draw any **resonance forms** that are equal in energy.

24 valence electrons (including the 1- charge)
38 – 24 = 14 bonding electrons (7 bonds)
24 – 14 = 10 lone pair electrons (5 lone pairs)
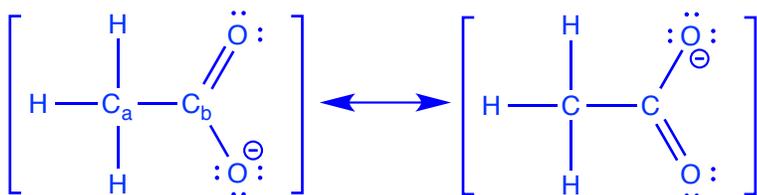
(ii) (4 points) Describe the <u>geometry</u> around each of the two carbon atoms in your structure above. For clarity, label your carbons "C_a" and "C_b" in your structure.

C_a is tetrahedral
C_b is trigonal planar

(d) Consider the Lewis structure below in which unspecified element A is bound to three Cl atoms.
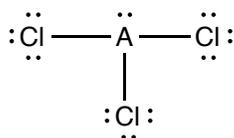
(i)   (2 points) Write the SN number
4

(ii)   (2 points) Give the geometry of the molecule
trigonal pyramidal (not trig. pyr.)

(iii)   (2 points) Circle the one value that best describes the Cl-A-Cl bond angle.

< 90°;   90°;   > 90°;   **< 109.5°;**   109.5°;   > 109.5°;   < 120°;   120°;   > 120°

(iv)   (2 points) Circle any element(s) that could be "A" in the structure above.

boron (B);   carbon (C);   **nitrogen (N);**   sulfur (S); iodine (I);   **arsenic (As)**

3

2. (15 points) **Ionic bonds**

element	ionization energy	electron affinity
Potassium (K)	418 kJ/mol	48 kJ/mol
Fluorine (F)	1680 kJ/mol	328 kJ/mol
Chlorine(Cl)	1255 kJ/mol	349 kJ/mol

(a) (12 points) The ionic bond length for KF is 0.217 nm. Calculate the energy (in units of kJ/mol) required to dissociate a single molecule of KF into the neutral atoms K and F, using information provided above. For this calculation, assume that the potassium and fluorine ions are point charges.

First calculate the ΔE for dissociation into ions: (-U(r))

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

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

$U(r) = -1.0\underline{6}3 \times 10^{-18}$ J
$-U(r) = 1.0\underline{6}3 \times 10^{-18}$ J

Next, convert -U(r) to kJ/mol.
$(1.0\underline{6}3 \times 10^{-18}$ J$) \times ($kJ$/1000$ J$) \times (6.022 \times 10^{23}/mol) = 64\underline{0}.2$ kJ/mol

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

$K^+ + e^- \rightarrow K \equiv -IE_K$ — $- 418$ kJ/mol

$F^- \rightarrow e^- + F \equiv EA_F$ — $+ 328$ kJ/mol

$KF \rightarrow K^+ + F^- \equiv -U(r)$ — $+ 64\underline{0}.2$ kJ/mol
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$+550.2$ kJ/mol

550. kJ/mol

(b) (3 points) The ionic bond length for KCl is 0.267 nm. Without doing any calculations, predict whether the energy required to dissociate a single molecule of KCl into **charged atoms K^+ and Cl^-** is more or less than the energy required to dissociate a single molecule of KF into **charged atoms K^+ and F^-**. Briefly explain your answer.

Energy to dissociate KCl into ions is less. There is an inverse relationship between U(r) and r. With a longer bond, U(r) is smaller.

3. (16 points) **Hybridization and Hydrogen Bonding**
(a) (10 points) The structure of the neurotransmitter dopamine is shown. 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.

O-H bond A: σ **(O2sp^3, H1s)**

C-C bond B: σ **(C2sp^2, C2sp^3)**

C-N bond C: σ **(C2sp^3, N2sp^3)**

C=C bond D: σ **(C2sp^2, C2sp^2)**
π **(C2py, C2py) or π (C2px, C2px)**
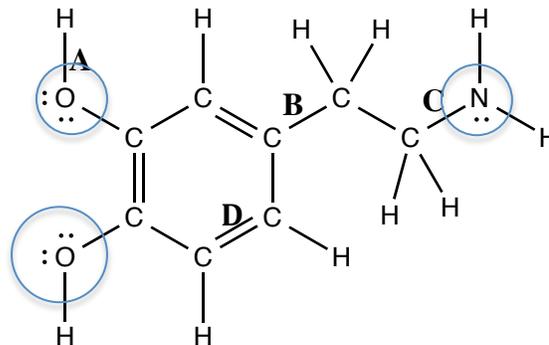
(b) (6 points) Circle all of the central atoms with bond angles <109.5°

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4. (23 points) **Molecular orbital theory**
(a) (i) (4 points) Write the **valence electron configuration** for the molecule N$_2$.

$(\sigma 2s)^2(\sigma 2s^*)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$
or $(\sigma 2s)^2(\sigma 2s^*)^2(\pi 2p_y)^2(\pi 2p_x)^2(\sigma 2p_z)^2$
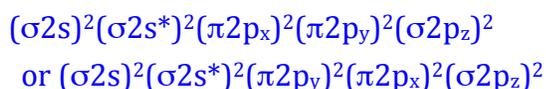
(ii) (3 points) Calculate the bond order for N$_2$.

BO = ½(# of bonding electrons - # of anti-bonding electrons)
BO = ½(8 − 2) = **3**

(iii) (3 points) Which molecule would you expect to have a **shorter** NN bond, N$_2$ or H-N=N-H? Briefly justify your answer.

N$_2$ should have the shorter NN bond, since triple bonds are stronger than double bonds.

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(b) (i) (7 points) Draw an energy correlation diagram for the molecular orbitals of the **valence electrons in F_2**. Label the atomic and molecular orbitals, including the x, y and z designations where appropriate. Use the full space available to spread out your energy levels so that the labels for the orbitals fit easily.
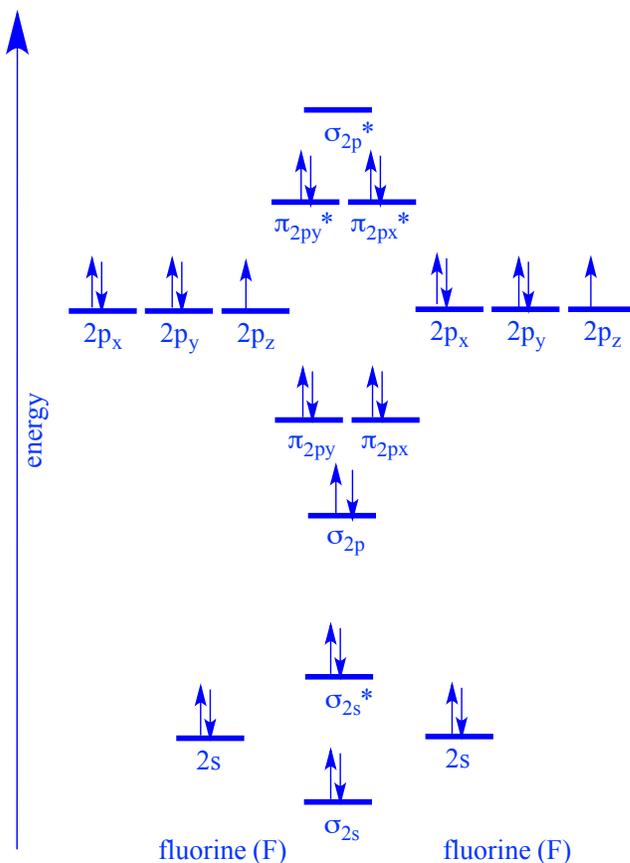
(ii) (2 points) What is the bond order for F_2?

B.O. = ½ (8-6) **= 1**

(ii) (6 points) Arrange the following from lowest to highest ionization energy: F, F_2 and F_2^{1-}. Briefly justify your answer.

lowest IE _____ F_2^{1-}, F_2, F_____ *highest IE*

Based on the MO diagram above, F_2^{-1} has its highest energy electron in the highest energy orbital, so it will require the least ionization energy to remove an electron. In contrast, F has its highest energy electrons in the lowest energy orbital of the choices listed.

5. (12 points) **Periodic trends**

(**a**) (6 points) Consider the **second** ionization energies (IE_2) for the following 3rd row elements: Si, S, Mg, Al.

   (**i**) Which has the highest IE_2?   S

   (**ii**) Which has the third highest IE_2?   Si

(**b**) (3 points) Rank the following from **smallest to largest** radius: **Mg^{2+}, Ca, Ca^{2+}**

   smallest... Mg^{2+}, Ca^{2+}, Ca....largest

(**c**) (3 points) Very briefly explain WHY atomic radius decreases as you go across a row in the periodic table.

Z_{eff} increases as Z increases within the same shell. As Z effective increases, the electrons are held closer to the nucleus and the atomic radius decreases.

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

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

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

1 eV $= 1.60218 \times 10^{-19}$ J

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

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

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

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

Electronegativity = $(IE + EA)/2$

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

Periodic Table of the Elements

Legend: Metals, Semimetals, Nonmetals

Group I:
- 1, 1.0079, H, Hydrogen
- 3, 6.941, Li, Lithium
- 11, 22.990, Na, Sodium
- 19, 39.098, K, Potassium
- 37, 85.468, Rb, Rubidium
- 55, 132.91, Cs, Cesium
- 87, (223), Fr, Francium

Group II:
- 4, 9.0122, Be, Beryllium
- 12, 24.305, Mg, Magnesium
- 20, 40.078, Ca, Calcium
- 38, 87.62, Sr, Strontium
- 56, 137.33, Ba, Barium
- 88, (226), Ra, Radium

Transition elements:
- 21, 44.956, Sc, Scandium
- 22, 47.867, Ti, Titanium
- 23, 50.942, V, Vanadium
- 24, 51.996, Cr, Chromium
- 25, 54.938, Mn, Manganese
- 26, 55.845, Fe, Iron
- 27, 58.933, Co, Cobalt
- 28, 58.693, Ni, Nickel
- 29, 63.546, Cu, Copper
- 30, 65.409, Zn, Zinc
- 39, 88.906, Y, Yttrium
- 40, 91.224, Zr, Zirconium
- 41, 92.906, Nb, Niobium
- 42, 95.94, Mo, Molybdenum
- 43, (98), Tc, Technetium
- 44, 101.07, Ru, Ruthenium
- 45, 102.91, Rh, Rhodium
- 46, 106.42, Pd, Palladium
- 47, 107.87, Ag, Silver
- 48, 112.41, Cd, Cadmium
- 71, 174.97, Lu, Lutetium
- 72, 178.49, Hf, Hafnium
- 73, 180.95, Ta, Tantalum
- 74, 183.84, W, Tungsten
- 75, 186.21, Re, Rhenium
- 76, 190.23, Os, Osmium
- 77, 192.22, Ir, Iridium
- 78, 195.08, Pt, Platinum
- 79, 196.97, Au, Gold
- 80, 200.59, Hg, Mercury
- 103, (262), Lr, Lawrencium
- 104, (261), Rf, Rutherfordium
- 105, (262), Db, Dubnium
- 106, (266), Sg, Seaborgium
- 107, (264), Bh, Bohrium
- 108, (277), Hs, Hassium
- 109, (268), Mt, Meitnerium
- 110, (281), Uun, Ununnilium
- 111, (272), Uuu, Unununium
- 112, (285), Uub, Ununbium

Group III:
- 5, 10.811, B, Boron
- 13, 26.982, Al, Aluminum
- 31, 69.723, Ga, Gallium
- 49, 114.82, In, Indium
- 81, 204.38, Tl, Thallium

Group IV:
- 6, 12.011, C, Carbon
- 14, 28.086, Si, Silicon
- 32, 72.64, Ge, Germanium
- 50, 118.71, Sn, Tin
- 82, 207.2, Pb, Lead
- 114, (289), Uuq, Ununquadium

Group V:
- 7, 14.007, N, Nitrogen
- 15, 30.974, P, Phosphorus
- 33, 74.922, As, Arsenic
- 51, 121.76, Sb, Antimony
- 83, 208.98, Bi, Bismuth

Group VI:
- 8, 15.999, O, Oxygen
- 16, 32.065, S, Sulfur
- 34, 78.96, Se, Selenium
- 52, 127.60, Te, Tellurium
- 84, (209), Po, Polonium

Group VII:
- 9, 18.998, F, Fluorine
- 17, 35.453, Cl, Chlorine
- 35, 79.904, Br, Bromine
- 53, 126.90, I, Iodine
- 85, (210), At, Astatine

Group VIII:
- 2, 4.0026, He, Helium
- 10, 20.180, Ne, Neon
- 18, 39.948, Ar, Argon
- 36, 83.798, Kr, Krypton
- 54, 131.29, Xe, Xenon
- 86, (222), Rn, Radon

Lanthanide series:
- 57, 138.91, La, Lanthanum
- 58, 140.12, Ce, Cerium
- 59, 140.91, Pr, Praseodymium
- 60, 144.24, Nd, Neodymium
- 61, (145), Pm, Promethium
- 62, 150.36, Sm, Samarium
- 63, 151.96, Eu, Europium
- 64, 157.25, Gd, Gadolinium
- 65, 158.93, Tb, Terbium
- 66, 162.50, Dy, Dysprosium
- 67, 164.93, Ho, Holmium
- 68, 167.26, Er, Erbium
- 69, 168.93, Tm, Thulium
- 70, 173.04, Yb, Ytterbium

Actinide series:
- 89, (227), Ac, Actinium
- 90, 232.04, Th, Thorium
- 91, 231.04, Pa, Protactinium
- 92, 238.03, U, Uranium
- 93, (237), Np, Neptunium
- 94, (244), Pu, Plutonium
- 95, (243), Am, Americium
- 96, (247), Cm, Curium
- 97, (247), Bk, Berkelium
- 98, (251), Cf, Californium
- 99, (252), Es, Einsteinium
- 100, (257), Fm, Fermium
- 101, (258), Md, Mendelevium
- 102, (259), No, Nobelium

5.111 Principles of Chemical Science

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