# CHEM-651: Advanced Inorganic Chemistry I

*Midterm I – October 4th, 2012*

NAME Solution Set

Answer each question to the best of your ability. Partial credit will be awarded where appropriate. You are not permitted to use any supplemental materials other than what is included in this test booklet. Calculators are not needed and are not permitted to be used. **PLEASE DO NOT REMOVE ANY PAGES FROM THIS EXAM.**

Write all your answers directly in this test booklet and show all work where necessary.

Good Luck!

1. _____ (10 pts)
2. _____ (10 pts)
3. _____ (24 pts)
4. _____ (10 pts)
5. _____ (22 pts)
6. _____ (16 pts)
7. _____ (8 pts)
8. _____ (5 pts)

Total _____

1. Please answer each of the following questions dealing with solutions to the Schrödinger equation, $\Psi(n, l, m_l)$. Please keep your answers succinct – two sentences or less (10 pts)

   (a) What information about an orbital is conveyed by each of the quantum numbers for the three-number solution to the Schrödinger equation? Be sure to make clear which property correlates with each quantum number (3 pts)

   n - size + energy of orbital
   l - orbital shape
   $m_l$ - orbital spatial orientation

   (b) How does the energy of the $3d_{xy}$ orbital in the hydrogen atom compare to the energy of the $3p_x$ orbital of hydrogen? Please explain your answer. (3 pts)

   For a $1e^-$ system the energy of 3p + 3d is the same. Orbitals of the same principle QN are of the same energy unless there are shielding effects

   (c) How does the energy of the 1*s* orbital of hydrogen compare to the energy of the 1*s* orbital of carbon? Please explain your answer. (2 pts)

   The effective nuclear charge experience by $e^-$ in carbon 1s is larger than for hydrogen. ∴ the carbon 1s orbital is lower in energy

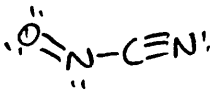
   (d) What is the ground-state electron configuration of a gas-phase $Cr^{2+}$ ion? What is the multiplicity of this species? (2 pts)

   $[Ar]4d^4$ → Quintet

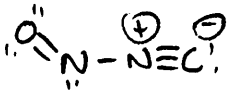
2. Three isomers having the empirical formula $N_2CO$ are known: ONCN (Nitrosyl Cyanide), ONNC (nitrosyl isocyanide) and NOCN (isonitrosyl cyanide). See *Angew. Chem. Int. Ed.* **1997**, *36*, 1707. (10 pts)

   (a) Draw the most important resonance structure for each of these isomers (3 pts).
   (b) Determine the formal charges on each atom (3 pts).

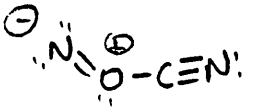
a) Nitrosyl Cyanide



Nitrosyl isocyanide



Isonitrosyl Cyanide



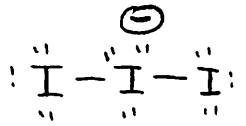
b) Formal Charges shown above

   (c) Which of the three isomers do you predict to be most stable? Please provide a brief explanation for your reasoning. (4 pts)

Nitrosyl Cyanide is most stable because all formal charges are zero.

3. Provide the lowest energy VSEPR structure for each of the following. Indicate whether the species is polar or non-polar and if polar, denote the direction of the dipole moment. Lastly, please indicate the point group to which the molecule belongs. (24 pts)

(a) $I_3^-$

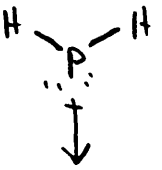


Nonpolar

$D_{\infty h}$

linear

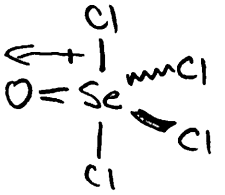
(b) $PH_2^-$



$C_{2v}$

Polar

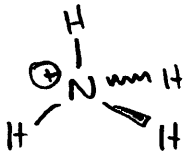
(c) $SeOCl_4$ (Se is central atom)



$C_{2v}$

Polar

(d) $NH_4^+$

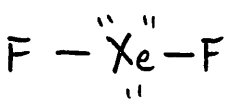


$T_d$

Nonpolar

(e) $XeF_2$

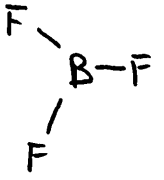
$D_{\infty h}$



Nonpolar

(f) $BF_3$

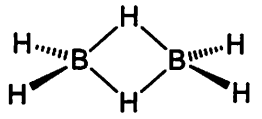
$D_{3h}$



Nonpolar

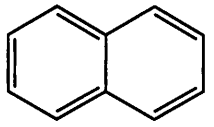
4. Determine the point groups of the following. For cases in which the structure is not provided, determine the ideal structure based on VSEPR analysis. (10 pts)

(a) Diborane



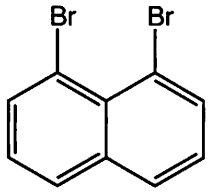

$D_{2h}$

(b) Naphthalene



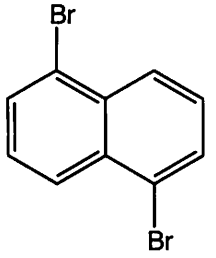
$D_{2h}$

(c) 1,8-dibromonaphthalene



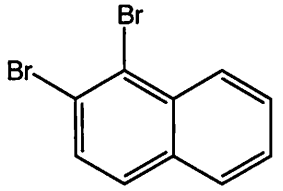

$C_{2v}$

(d) 1,5-dibromonaphthalene

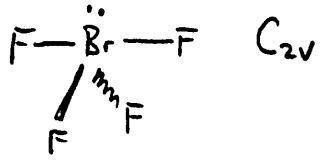



$C_{2h}$

(e) 1,2-dibromonaphthalene




$C_s$

(f) $[BrF_4]^+$ ⟹  $C_{2v}$

(g) *mer*-$Mo(CO)_3Cl_3$ $C_{2v}$

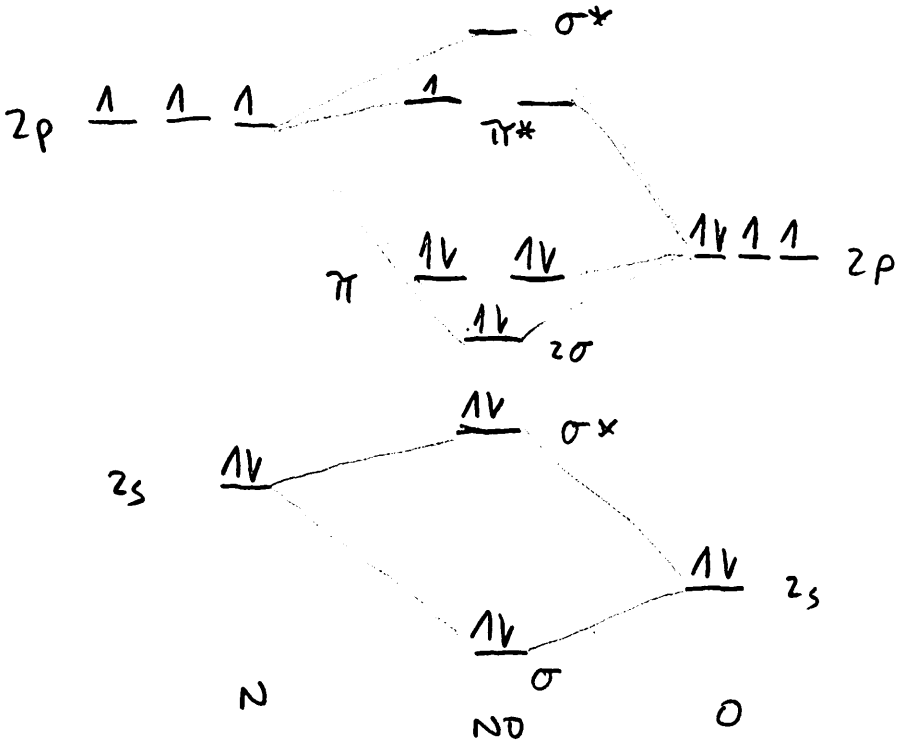
(h) *fac*-$Mo(CO)_3Cl_3$ $C_{3v}$

(i) $p_x$ $C_{\infty v}$

(j) $d_{xy}$ $D_{2h}$

5. Nitric Oxide (NO) is a biologically relevant species that has been shown to serve as a neurotransmitter and vasodilator. (22 pts)

(a) Prepare a molecular orbital energy level diagram for NO. Be sure to show how atomic orbitals combine to form the MOs. (10 pts)




(b) Based on you MO diagram, predict the bond order and multiplicity of NO. (2 pts)

BO = 2.5, Multiplicity = 2 (doublet)

(c) $NO^+$ and $NO^-$ are also known to exist. Based on the MO diagram you constructed in part (a) predict the trend in nitrogen-oxygen bond length (from smallest to longest) for these three species. (3 pts)

$NO < NO^+ < NO^-$

Short ⟶ long

(d) What are the predicted multiplicities of $NO^+$ and $NO^-$? How would you expect each of these species to behave in a magnetic field? (4 pts)

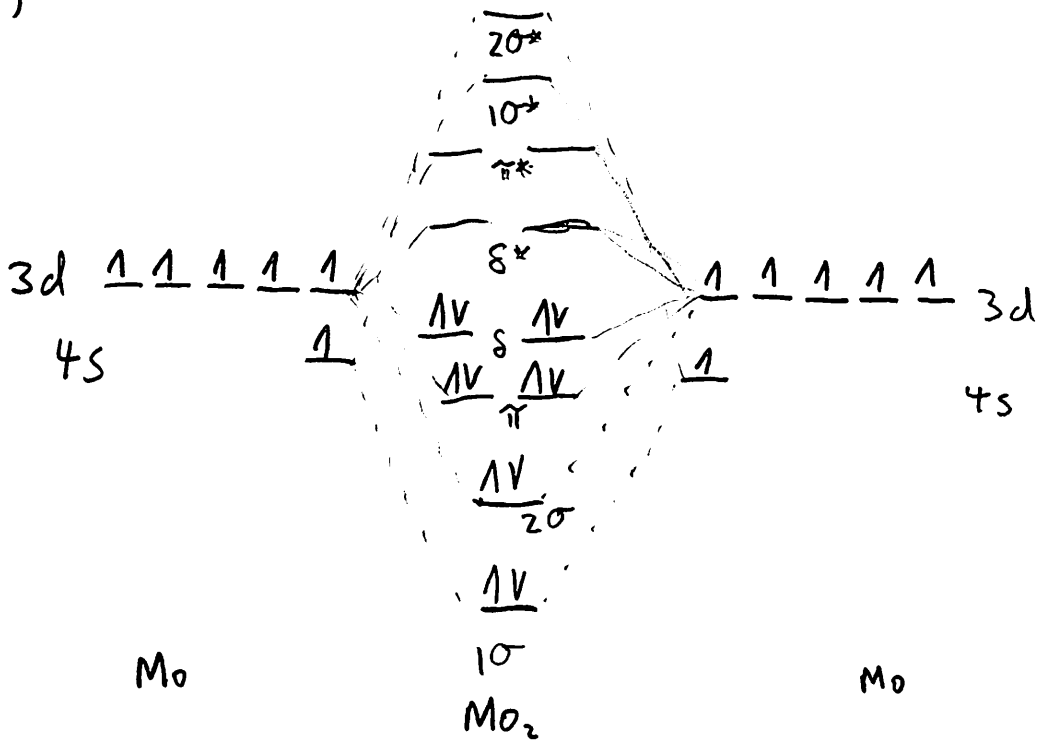
$NO^+$ → Singlet Repelled from magnetic field

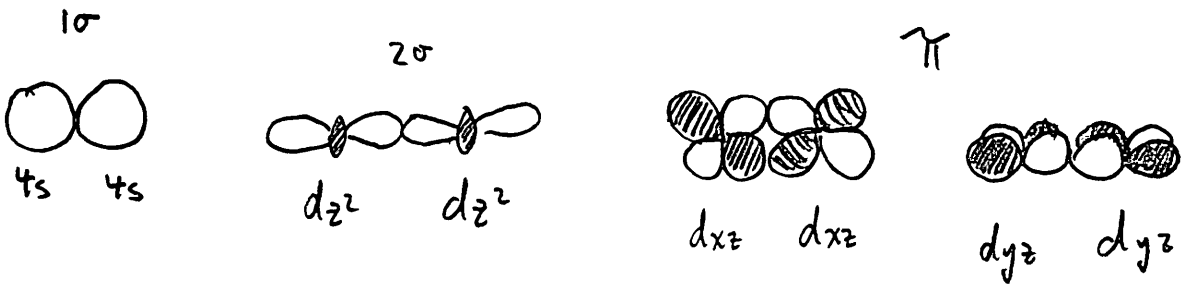
$NO^-$ → Triplet Attracted to magnetic field

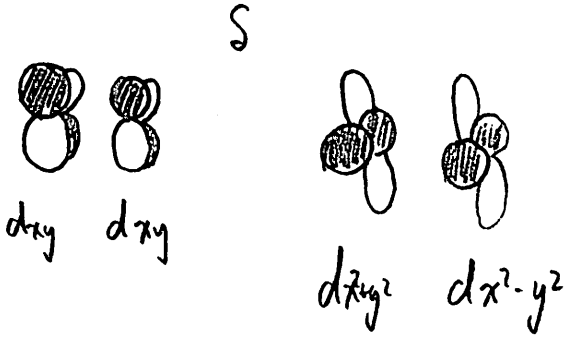
6. We saw in class that metals can be involved in multiple bonding with other metals. This was first demonstrated by F. A. Cotton and coworkers for $[Re_2Cl_8]^{2-}$ in which a metal-metal quadruple bond was observed. It has been shown that photolysis of $Mo(CO)_6$ in the gas phase produces the dimer $Mo_2(g)$ (*J. Mol. Spec.* **1978**, *73*, 430-440). The results of this experiment indicate that this Group 6 transition metal dimer has a bond order of six! (16 pts)

   (a) Prepare a MO diagram that details the valence bonding of this molecule. Please be sure to label all atomic and molecular orbitals. (10 pts)
   (b) Sketch the six individual metal-metal bonding interactions that exist for $Mo_2$. Please label the atomic orbitals that you use in each case. (3 pts)
   (c) Label each interaction as being either a σ, π or δ bond. (3 pts)

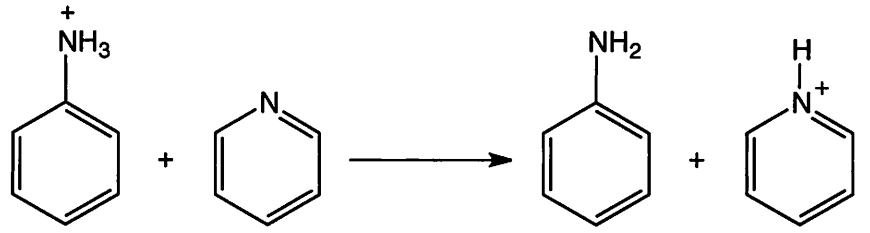
a)



7. Consider the following proton transfer reaction and corresponding proton affinities. For this problem, you may assume that entropic factors are negligible such that $\Delta G^\circ = 2.303\ RT\ pK \approx \Delta H^\circ$, where R is the universal gas constant (8.31 J $K^{-1}$ $mol^{-1}$).



| $pK_a = 4.6$ aqueous | PA = 953 kJ/mol gas phase | PA = 899 kJ/mol gas phase | $pK_a = 5.2$ aqueous |
|---|---|---|---|

(a) Is the above reaction spontaneous in aqueous solution? Please explain your answer. (3 pts)

Yes pKa of anilinium < pKa pyridinium ∴
Proton transfer is thermodynamically downhill

(b) Determine the free energy change for the proton transfer in the gas phase. Is the proton transfer spontaneous as written? (5 pts)

$Ph\text{-}\overset{+}{N}H_3 \longrightarrow Ph\text{-}NH_2 + H^+$ PA = 899 KJ/mol

$Py + H^+ \longrightarrow Py\text{-}\overset{+}{H}$ PA = -953 KJ/mol

$Ph\text{-}NH_3^+ + Py \longrightarrow Py\text{-}\overset{+}{H} + Ph\text{-}NH_2$ $\Delta H^\circ = -54$ KJ/mol

$\Delta G^\circ \sim \Delta H^\circ = -54$ KJ/mol

Reaction is downhill + spontaneous.

8. Extra Credit: Provide the correct symbol for each of the missing elements below (note: there are ten missing elements in total). (5 pts)

# PERIODIC TABLE OF THE ELEMENTS

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H 1.0079 | | | | | | | | | | | | | | | | | 2 He 4.00260 |
| 3 Li 6.941 | 4 Be 9.01218 | | | | | | | | | | | 5 B 10.81 | 6 C 12.011 | 7 N 14.0067 | 8 O 15.9994 | 9 F 18.9984 | 10 Ne 20.179 |
| 11 Na 22.9898 | 12 Mg 24.305 | | | | | | | | | | | 13 Al 26.9815 | 14 Si 28.0855 | 15 P 30.9738 | 16 S 32.06 | 17 Cl 35.453 | 18 Ar 39.948 |
| 19 K 39.0983 | 20 Ca 40.08 | 21 Sc 44.9559 | 22 Ti 47.88 | 23 V 50.9415 | 24 Cr 51.996 | 25 Mn 54.9380 | 26 Fe 55.847 | 27 Co 58.9332 | Ni | 29 Cu 63.546 | 30 Zn 65.39 | Ga | 32 Ge 72.59 | 33 As 74.9216 | 34 Se 78.96 | 35 Br 79.904 | 36 Kr 83.80 |
| Rb | Sr | 39 Y 88.9059 | 40 Zr 91.224 | Nb | 42 Mo 95.94 | 43 Tc (98) | 44 Ru 101.07 | Rh | 46 Pd 106.42 | 47 Ag 107.868 | 48 Cd 112.41 | 49 In 114.82 | 50 Sn 118.71 | 51 Sb 121.75 | 52 Te 127.60 | 53 I 126.905 | 54 Xe 131.29 |
| 55 Cs 132.905 | 56 Ba 137.33 | 57 La 138.906 | Hf | 73 Ta 180.948 | 74 W 183.85 | Re | 76 Os 190.2 | 77 Ir 192.22 | 78 Pt 195.08 | Au | 80 Hg 200.59 | 81 Tl 204.383 | 82 Pb 207.2 | Bi | 84 Po (209) | 85 At (210) | 86 Rn (222) |
| 87 Fr (223) | 88 Ra 226.025 | 89 Ac 227.028 | 104 Unq (261) | 105 Unp (262) | 106 Unh (263) | 107 Uns (262) | 108 Uno (265) | 109 Une (266) | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 58 Ce 140.12 | 59 Pr 140.908 | 60 Nd 144.24 | 61 Pm (145) | 62 Sm 150.36 | 63 Eu 151.96 | 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 |
| 90 Th 232.038 | 91 Pa 231.036 | 92 U 238.029 | 93 Np (237) | 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 (260) |