

NAME: _____ Section: _____ Student Number: _____

Spring 2014

Chemistry 2000 Midterm #1A - ANSWERS

_____/50 marks

- INSTRUCTIONS:
- 1) Please read over the test carefully before beginning. You should have 7 pages of questions, a blank “overflow” page and a periodic table page.
 - 2) If your work is not legible, it will be given a mark of zero.
 - 3) Marks will be deducted for incorrect information added to an otherwise correct answer.
 - 4) Calculators are not permitted.
 - 5) You have 90 minutes to complete this test.
-

Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until after 8:00pm Mountain Time on Tuesday, February 11th, 2014. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/50 on this exam and removal of the “overwrite midterm mark with final exam mark” option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____

Date: _____

Course: CHEM 2000 (General Chemistry II)

Semester: Spring 2014

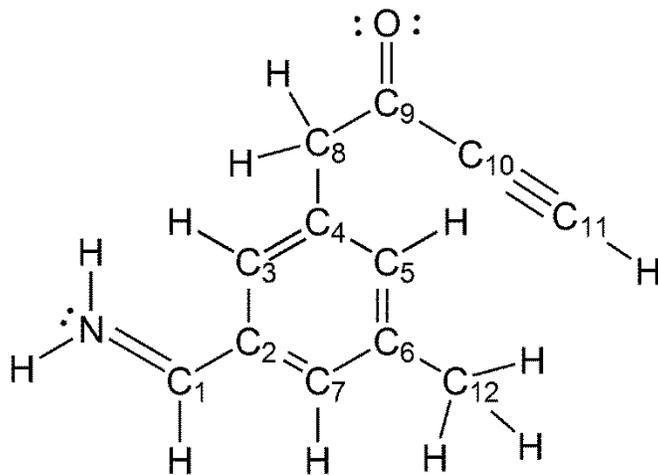
The University of Lethbridge

Question Breakdown

Q1	/ 5
Q2	/ 24
Q3	/ 15
Q4	/ 6

Total	/ 50
--------------	------

1. Consider the following molecule in accordance with valence bond theory: [5 marks]



(a) What is the hybridization for each of the carbon atoms in this molecule? [3 marks]

Carbon #	Hybrid orbital	Carbon #	Hybrid orbital
C ₁	sp^2	C ₇	sp^2
C ₂	sp^2	C ₈	sp^3
C ₃	sp^2	C ₉	sp^2
C ₄	sp^2	C ₁₀	sp
C ₅	sp^2	C ₁₁	sp
C ₆	sp^2	C ₁₂	sp^3

(b) How many σ bonds are there in this molecule? [1 mark]

26

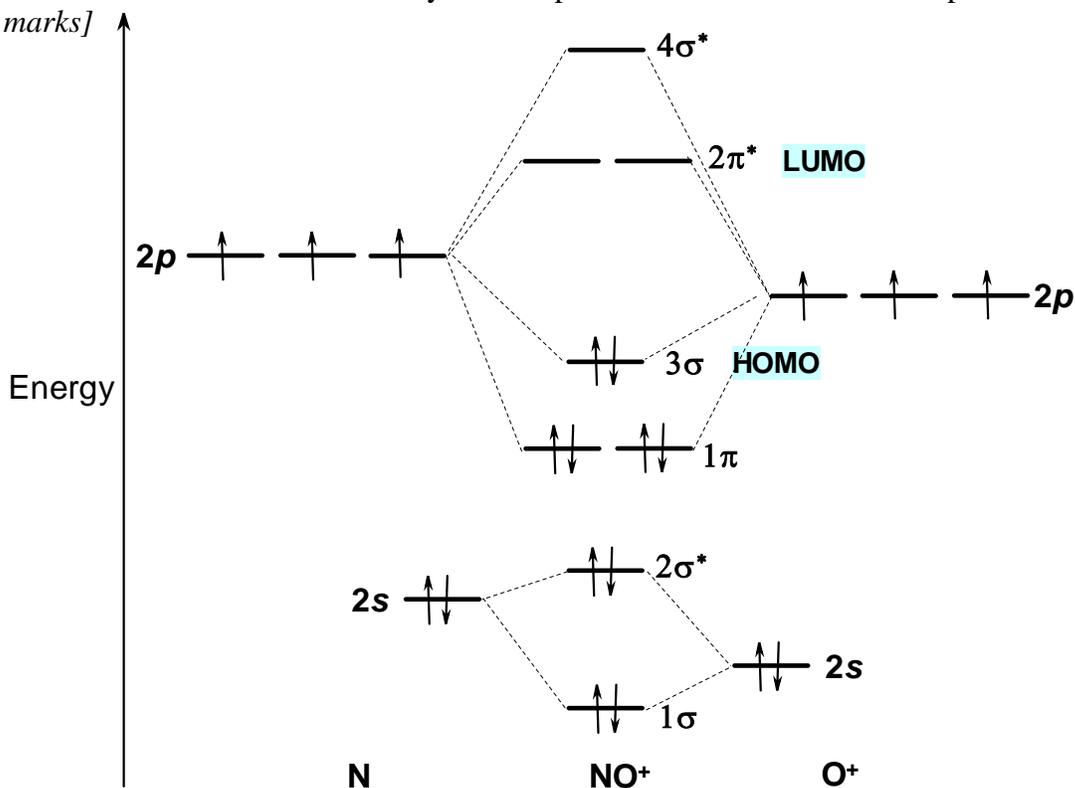
(c) How many π bonds are there in this molecule? [1 mark]

7

2. [24 marks]

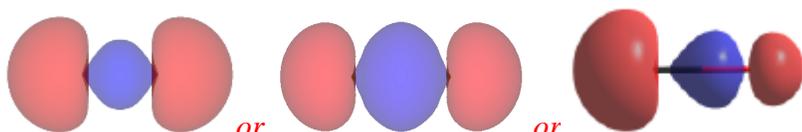
- (a) Construct a valence molecular orbital diagram for NO^+ . Label all atomic and molecular orbitals on your diagram and include tie lines to show the linear combinations that form each molecular orbital. Place the correct number of valence electrons into the atomic orbitals as well as the molecular orbitals. It is not necessary to draw pictures of the orbitals for this part of the question.

[9 marks]



- (b) On the diagram above, clearly label the highest occupied molecular orbital(s) of NO^+ as the “HOMO”(s). In the space below, draw a picture of this/these molecular orbital(s). Clearly indicate the phase, location of the nuclei, and relative amounts of electron density on each atom.

[3 marks]



are acceptable. If the student put the 1π orbital higher in energy than the 3σ then I needed to see pictures of the π bonding orbitals

- (c) On the diagram above, clearly label the lowest unoccupied molecular orbital(s) of NO^+ as the “LUMO”(s). In the space below, draw a picture of this/these molecular orbital(s). Clearly indicate the phase, location of the nuclei, and relative amounts of electron density on each atom.

[3 marks]



Needed to show both x-axis

and y-axis

NAME: _____ Section: _____ Student Number: _____

2. continued

(d) Write the valence orbital occupancy (i.e. electron configuration) in line notation for NO^+ .

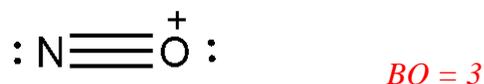
[1 mark]



(e) Provide a molecular formula for one neutral diatomic molecule that is isoelectronic with NO^+ . [1 mark]



(f) Draw the Lewis structure for NO^+ . What N–O bond order does your Lewis diagram predict? [2 marks]



$BO = 3$

(g) What bond order does your MO treatment predict for NO^+ ? Does it agree with the bond order from the Lewis diagram? [2 marks]

$$B.O. = \frac{1}{2}(8 - 2) = 3 \text{ Yes it agrees with the Lewis diagram}$$

(h) What is the bond order if we add an electron to NO^+ (i.e. what is the bond order in NO)? [1 mark]

It will go into an antibonding orbital, so the bond order will do down $(1/2)(8-3) = 2.5$

(i) Is the N–O bond strengthened or weakened in NO versus NO^+ ? Briefly explain why or why not. [1 mark]

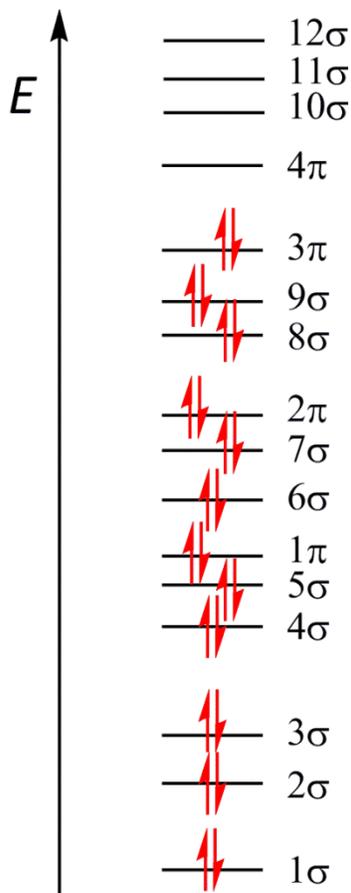
The N-O bond is weakened because the electron is going into an antibonding orbital.

(j) Which of the following molecules is paramagnetic: NO^+ , NO , NO^- . [1 mark]

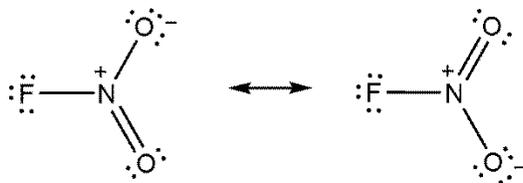
NO , NO^- are both paramagnetic.

3. [15 marks]

The valence molecular orbital diagram for planar nitryl fluoride, NO₂F (nitrogen is the central atom) is shown below. Note that the σ or π character of each MO is indicated, but NOT the nature of the overall interaction (i.e. whether it has bonding, antibonding, or non-bonding character).



(a) Draw the Lewis structure of NO₂F. Include any possible resonance structures for this molecule. [2 marks]

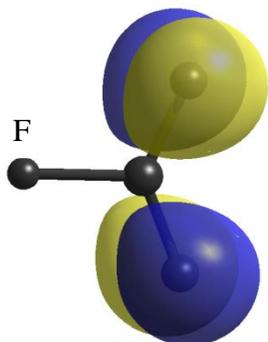


(b) What is the N–O bond order in NO₂F according to your Lewis structure(s)? [1 mark]

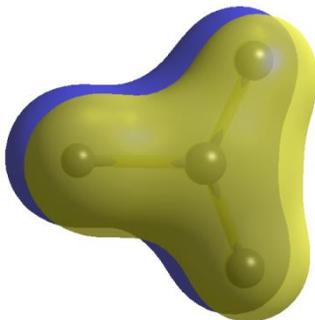
N–O bond order = 1.5 = (3 shared electron pairs/2 bonded atom pairs)

3. continued

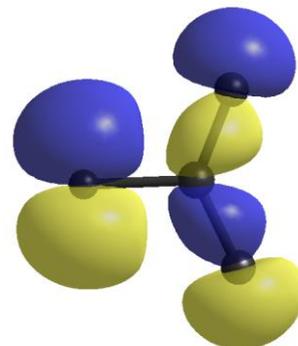
(c) Five orbital pictures for NO₂F are provided below (they are all in the same orientation). Four of them belong to π MOs, while one is a σ MO. In the space below each picture, identify the four π MOs and one σ MO, and assign the correct labels for the π MOs only (the sigma MO can just be labeled as σ to differentiate it from the π MOs). [5 marks]



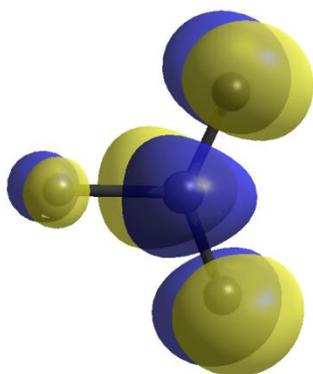
3π



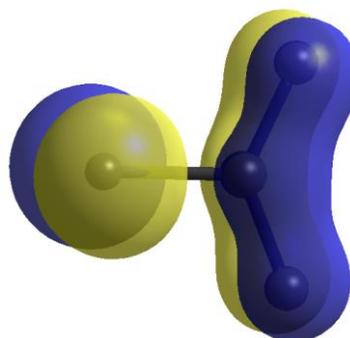
1π



sigma (σ) orbital



4π



2π

NAME: _____ Section: _____ Student Number: _____

3. continued.

(d) Of the four π MOs shown: [4 marks]

Which should be considered as bonding π MOs? Justify your answer.

1 π as it is the combination of an in-phase p atomic orbital on all four atoms.

2 π should be considered as more bonding than nonbonding or antibonding, as it has in-phase p atomic orbital contributions from both N-O groups which should lower the energy and off-set the weakly nonbonding or likely antibonding interaction between N-F.

Which should be considered as antibonding π MOs? Justify your answer.

4 π as it is the out-of-phase combination of p atomic orbitals on all four atoms

Which should be considered as non-bonding π MOs? Justify your answer.

3 π as there is no electron density on either N or F and the out-of-phase contributions from p orbitals on the two O atoms look more like their constituent AOs rather than an MO.

(e) Fill in the valence electrons for the MO diagram of nitryl fluoride. How many electrons are in σ MOs? How many are in π MOs? [2 marks]

18 electrons in σ MOs and 6 electrons in π MOs

(f) How many normal modes of vibration should NO_2F have? [1 mark]

3N - 6 (nonlinear) so 3(4) - 6 = 6 modes of vibration

NAME: _____ Section: _____ Student Number: _____

4. [6 marks]
Provide definitions for the following terms, and where appropriate give an example of each.

(a) intrinsic semiconductor

They are semiconductors without any dopant added to them. They have medium sized band gaps. A small fraction of the electrons in the valence band can be excited into the conduction band, meaning they are moderately good conductors of electricity. The holes left in the valence band can also carry current as other electrons in the valence band can be excited into them.

Examples: Silicon or germanium

(b) extrinsic semiconductor

A semiconductor that has had an impurity (or dopant) added in order to increase their conductivity. The dopants can either provide extra "holes" or extra electrons. N-type semiconductor have been doped to have extra electrons. P-type semiconductors have been doped to have extra holes.

Examples: Silicon doped with either boron or phosphorous or gallium, etc.

(c) ultraviolet photoelectron spectroscopy

When an atom or molecule is ionized using photons of energy = ultraviolet light.

Ionization using a PE spectrometer allows us to observe the vibrational levels of the atomic or molecular ion, according to Koopmans theorem where the ionization energy of an electron in a particular orbital is equal to the negative of its orbital energy ($-I_i = \epsilon_i$). We can measure E_K and calculate the orbital energy of occupied orbitals:

$$-I = \epsilon_i = E_K - h\nu$$

NAME: _____ Section: _____ Student Number: _____

Overflow Page

If you use this page for any answers, please clearly indicate which question is being answered and make sure you note on the page for the question itself that the answer continues here.

Chem 2000 Standard Periodic Table

1																	18																														
1.0079 H 1																		4.0026 He 2																													
6.941 Li 3	9.0122 Be 4											10.811 B 5	12.011 C 6	14.0067 N 7	15.9994 O 8	18.9984 F 9	20.1797 Ne 10																														
22.9898 Na 11	24.3050 Mg 12	3	4	5	6	7	8	9	10	11	12	26.9815 Al 13	28.0855 Si 14	30.9738 P 15	32.066 S 16	35.4527 Cl 17	39.948 Ar 18																														
39.0983 K 19	40.078 Ca 20	44.9559 Sc 21	47.88 Ti 22	50.9415 V 23	51.9961 Cr 24	54.9380 Mn 25	55.847 Fe 26	58.9332 Co 27	58.693 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.9216 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36																														
85.4678 Rb 37	87.62 Sr 38	88.9059 Y 39	91.224 Zr 40	92.9064 Nb 41	95.94 Mo 42	(98) Tc 43	101.07 Ru 44	102.906 Rh 45	106.42 Pd 46	107.868 Ag 47	112.411 Cd 48	114.82 In 49	118.710 Sn 50	121.757 Sb 51	127.60 Te 52	126.905 I 53	131.29 Xe 54																														
132.905 Cs 55	137.327 Ba 56	La-Lu	178.49 Hf 72	180.948 Ta 73	183.85 W 74	186.207 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.967 Au 79	200.59 Hg 80	204.383 Tl 81	207.19 Pb 82	208.980 Bi 83	(210) Po 84	(210) At 85	(222) Rn 86																														
(223) Fr 87	226.025 Ra 88	Ac-Lr	(261) Rf 104	(262) Db 105	(263) Sg 106	(262) Bh 107	(265) Hs 108	(266) Mt 109	(281) Dt 110	(283) Rg 111																																					
<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <tr> <td>138.906 La 57</td> <td>140.115 Ce 58</td> <td>140.908 Pr 59</td> <td>144.24 Nd 60</td> <td>(145) Pm 61</td> <td>150.36 Sm 62</td> <td>151.965 Eu 63</td> <td>157.25 Gd 64</td> <td>158.925 Tb 65</td> <td>162.50 Dy 66</td> <td>164.930 Ho 67</td> <td>167.26 Er 68</td> <td>168.934 Tm 69</td> <td>173.04 Yb 70</td> <td>174.967 Lu 71</td> </tr> <tr> <td>227.028 Ac 89</td> <td>232.038 Th 90</td> <td>231.036 Pa 91</td> <td>238.029 U 92</td> <td>237.048 Np 93</td> <td>(240) Pu 94</td> <td>(243) Am 95</td> <td>(247) Cm 96</td> <td>(247) Bk 97</td> <td>(251) Cf 98</td> <td>(252) Es 99</td> <td>(257) Fm 100</td> <td>(258) Md 101</td> <td>(259) No 102</td> <td>(260) Lr 103</td> </tr> </table>																		138.906 La 57	140.115 Ce 58	140.908 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.965 Eu 63	157.25 Gd 64	158.925 Tb 65	162.50 Dy 66	164.930 Ho 67	167.26 Er 68	168.934 Tm 69	173.04 Yb 70	174.967 Lu 71	227.028 Ac 89	232.038 Th 90	231.036 Pa 91	238.029 U 92	237.048 Np 93	(240) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103
138.906 La 57	140.115 Ce 58	140.908 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.965 Eu 63	157.25 Gd 64	158.925 Tb 65	162.50 Dy 66	164.930 Ho 67	167.26 Er 68	168.934 Tm 69	173.04 Yb 70	174.967 Lu 71																																	
227.028 Ac 89	232.038 Th 90	231.036 Pa 91	238.029 U 92	237.048 Np 93	(240) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103																																	

Developed by Prof. R. T. Boeré