

NAME: \_\_\_\_\_ Section: \_\_\_\_\_ Student Number: \_\_\_\_\_

Spring 2012

**Chemistry 2000 Practice Midterm #1A**

\_\_\_\_\_/ 50 marks

- INSTRUCTIONS:
- 1) Please read over the test carefully before beginning. You should have 4 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.
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**Confidentiality Agreement:**

I agree not to discuss (or in any other way divulge) the contents of this exam until after 8pm Mountain Time on Monday, February 13<sup>th</sup>, 2012. 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 2012

The University of Lethbridge

**Question Breakdown**

<b>Q1</b>	/ 12
<b>Q2</b>	/ 4
<b>Q3</b>	/ 6
<b>Q4</b>	/ 6
<b>Q5</b>	/ 22

<b>Total</b>	/ 50
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1. As you know, the noble gases are very unreactive. There are, in fact, two distinct reasons why a substance might be unreactive:

1. Molecules made from that substance might be unstable.  
e.g. In class, we saw the MO explanation for the nonexistence of Ne<sub>2</sub>.
2. Molecules made from the unreactive substance might be stable in complete isolation, but react with each other (or with other materials) in a thermodynamically favorable manner.

In other words, reactions like  $2 \text{NeX} \rightarrow 2 \text{Ne} + \text{X}_2$  might be favorable for any X.

These two cases can be distinguished experimentally, because in the first case we can't make the molecule at all, while in the second we can make it in specially designed experiments in the gas phase at ultralow pressures and detect it spectroscopically. **[12 marks]**

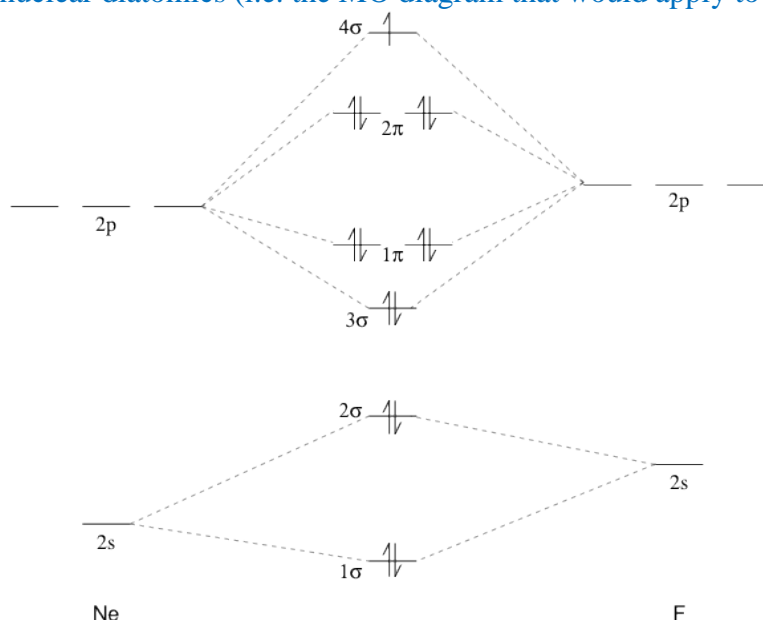
(a) Using the data in the table, construct a valence MO energy level diagram for NeF. *[10 marks]*

*Your diagram should include all valence electrons.*

*Label all orbitals, but you do not need to draw pictures of them.*

Orbital energies (Ry)		
	2s	2p
F	-2.95	-1.37
Ne	-3.56	-1.59

The 2s and 2p orbitals in the two atoms are well separated in energy, so the MO diagram is a bit like a distorted version of the "normal" MO diagram for homonuclear diatomics (i.e. the MO diagram that would apply to F<sub>2</sub>):



The 1σ, 3σ and 1π are bonding orbitals. The 2σ, 4σ and 2π are antibonding. The predicted bond order would therefore be

$$\text{Bond order} = \frac{1}{2}(8 - 7) = \frac{1}{2}.$$

(b) Based on your valence MO energy level diagram, state whether or not NeF is a stable molecule, and briefly justify your answer. Is Reason #1 or Reason #2 applicable to the lack of reactivity of Ne with F<sub>2</sub>? *[2 marks]*

While this is not a very strongly bonded molecule, it should be stable. We would therefore predict that Reason #2 would apply to NeF. In other words, reactions of this molecule with almost anything else should be spontaneous.

NAME: \_\_\_\_\_ Section: \_\_\_\_\_ Student Number: \_\_\_\_\_

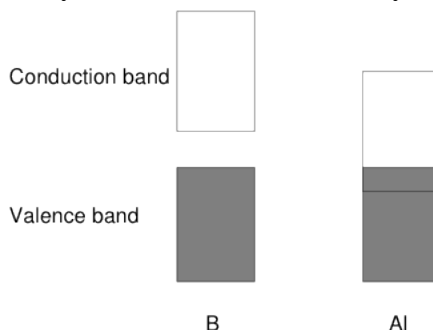
2. Briefly explain how photoelectron spectroscopy works. What information does photoelectron spectroscopy give us about a molecule's orbitals? **[4 marks]**

*Due to poor performance on this question (suggesting poor understanding of this topic), this sample answer has more detail than required for full marks (particularly in the last two points).*

- In photoelectron spectroscopy, a sample is irradiated with light of a single wavelength (short enough that a photon has enough energy to ionize a molecule).
- When a photon strikes a molecule, an electron is ejected (thereby ionizing the molecule). This uses some of the photon's energy; the remaining energy becomes electron kinetic energy, which is measured. This can be represented mathematically as  $E_{\text{photon}} = h\nu = I + K$  where  $I$  is the molecule's ionization energy and  $K$  is the ejected electron's kinetic energy. Since  $h\nu$  is known and  $K$  is measured,  $I$  can be readily calculated:  $I = h\nu - K$
- The energy of an orbital is the negative of the ionization energy (to remove an electron from that orbital), so photoelectron spectroscopy gives us the energy of the valence orbitals of an atom or molecule.
- Furthermore, photoelectron spectroscopy can be used to indicate whether an orbital is bonding, nonbonding or antibonding by comparing the vibrational spectrum of the neutral molecule to that of the ionized molecule (i.e. the cation):
  - If the electron ejected was in a bonding orbital, the bond order becomes smaller and the potential curve for the bond becomes shallower. Less energy will be required to excite the molecule into a higher vibrational mode (as indicated on the vibrational spectrum). Also, the lines on the photoelectron spectrum will appear closer together relative to a signal for an antibonding orbital.
  - If the electron ejected was in an antibonding orbital, the bond order becomes larger and the potential curve for the bond becomes steeper. More energy will be required to excite the molecule into a higher vibrational mode (as indicated on the vibrational spectrum). Also, the lines on the photoelectron spectrum will appear farther apart relative to a signal for a bonding orbital.
  - If the electron ejected was in a nonbonding orbital, there will be no change to the bond order and the potential curve for the bond will not change much. Therefore, the vibrational spectrum will not change much either. The signal on the photoelectron spectrum will often appear as a single line (or one tall line with a very few small peaks after it).
- Finally, the shape of each signal on the photoelectron spectrum indicates whether an orbital has sigma or pi symmetry. Sigma orbitals tend to give signals that are tall and have fewer lines. Pi orbitals tend to give signals that are shorter with more lines.

NAME: \_\_\_\_\_ Section: \_\_\_\_\_ Student Number: \_\_\_\_\_

3. Boron is an intrinsic semiconductor, while aluminium is a metal. **[6 marks]**  
(a) Sketch the band diagrams implied by this information. Clearly label each band. **[4 marks]**



- (b) Briefly discuss the feature(s) of these diagrams that cause the different electrical properties of boron and aluminium. **[2 marks]**

In boron, there is a filled valence band, and a small gap between this band and the conduction band. In aluminium, the two bands overlap.

4. **[6 marks]**

- (a) When valence bond theory is applied to  $\text{OF}_2$ , what is the hybridization of the central atom? **[3 marks]**  
*Show any work you do in arriving at your answer to this question.*

$\text{sp}^3$

*For full marks it was necessary to show the Lewis structure for  $\text{OF}_2$  and indicate that the tetrahedral electron group geometry (steric number = 4) requires that the O in  $\text{OF}_2$  be  $\text{sp}^3$  hybridized.*

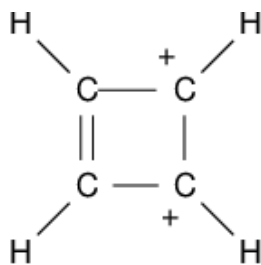
- (b) Briefly explain what hybridization is and why it is necessary in valence bond theory. **[3 marks]**

Hybridization involves the combination of valence atomic orbitals on a single atom to give the same number of hybridized atomic orbitals. These hybridized atomic orbitals can then be used to create directional bonds consistent with the electron group geometry predicted by VSEPR.

Hybridization is necessary because in VB theory each bond is considered separately and it is not possible to use different atomic orbitals (s and/or p orbitals) on a single atom to create bonds with the correct bond angles (e.g.  $109.5^\circ$  for tetrahedral) and equivalent energies.

NAME: \_\_\_\_\_ Section: \_\_\_\_\_ Student Number: \_\_\_\_\_

5. The following is a Lewis diagram for one resonance structure of the cyclobutenediylum dication ( $C_4H_4^{2+}$ ): [22 marks]



- (a) How many **valence**  $\sigma$  MOs and how many **valence**  $\pi$  MOs would this ion have? [2 marks]

\_\_\_16\_\_\_ valence  $\sigma$  MOs      \_\_\_4\_\_\_ valence  $\pi$  MOs

*Divide the valence atomic orbitals into sigma-symmetric and pi-symmetric categories.*

*There will be one valence sigma MO for every valence sigma-symmetric AO.*

*There will be one valence pi MO for every valence pi-symmetric AO.*

*All four carbon atoms are trigonal planar, so they each have a sigma-symmetric 2s orbital, two sigma-symmetric 2p orbitals and one pi-symmetric 2p orbital.*

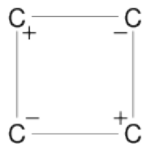
*Each hydrogen atom has one sigma-symmetric 1s orbital.*

*Sigma-symmetric AOs = (1s(H)  $\times$  4) + (2s(C)  $\times$  4) + (2p<sub>x</sub>(C)  $\times$  4) + (2p<sub>y</sub>(C)  $\times$  4) = 16*

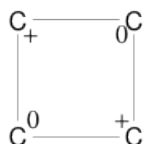
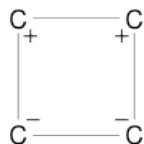
*Pi-symmetric AOs = (2p<sub>z</sub>(C)  $\times$  4) = 4*

- (b) Draw all the  $\pi$  MOs. You can either sketch each MO, or you can use the symbols +/-/0 to describe the contributions of the p orbitals on each atom. [4 marks]

Antibonding:

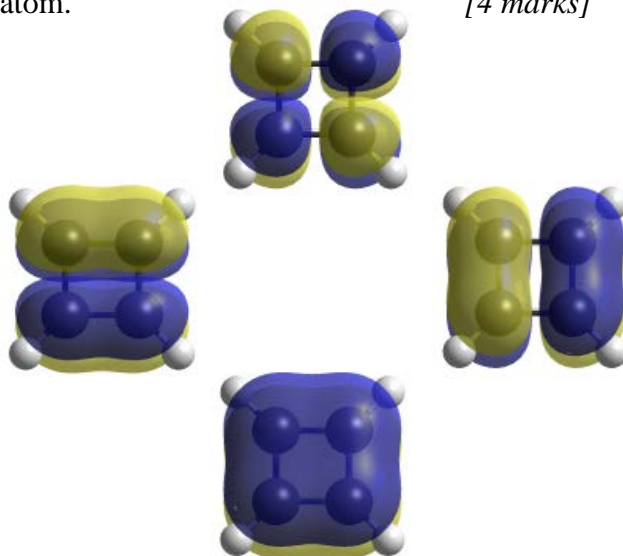
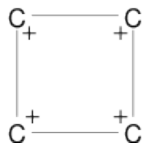


Nonbonding:



**or**

Bonding:



- (c) Next to each MO that you drew in part (b), classify it as bonding, antibonding, or nonbonding. [4 marks]  
*see part (b)*

- (d) How many valence  $\pi$  electrons are there in the cyclobutenediylum dication? [1 mark]

2

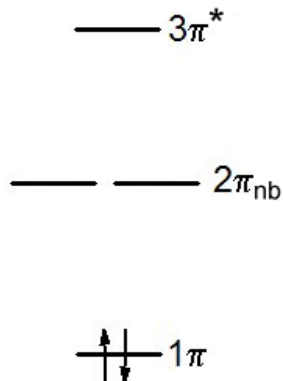
*$C_4H_4^{2+}$  has 18 valence  $e^-$ . (4 per C; 1 per H; subtract 2 for the +2 charge = 16 + 4 - 2 = 2)*

*16 of the valence  $e^-$  are used in sigma bonding (8 sigma bonds at two  $e^-$  each).*

*Therefore, 2 valence  $e^-$  remain to be used in the pi system.*

NAME: \_\_\_\_\_ Section: \_\_\_\_\_ Student Number: \_\_\_\_\_

- (e) Sketch a valence  $\pi$  MO energy level diagram based on your classification of the MOs in part (b) of this question. Label each MO and populate your diagram with electrons. [4 marks]



- (f) Calculate the carbon-carbon bond order in this ion ( $\sigma$  and  $\pi$  combined). [2 marks]

$\sigma$  bond order = 1

$$\pi \text{ bond order} = \frac{1}{2} (\pi \text{ bonding electrons} - \pi \text{ antibonding electrons}) = \frac{1}{2} (2 - 0) = 1$$

# C-C links 4

$$\text{total bond order} = \sigma \text{ bond order} + \pi \text{ bond order} = 1 + 1 = 2 \text{ or } 1.25$$

- (g) Is this ion paramagnetic or diamagnetic? [1 mark]

diamagnetic

*There are no unpaired electrons so the net electron spin is zero.*

- (h) Would bonding be stronger, weaker, or about the same if the ion gained two  $\pi$  electrons? Explain. Note that adding two electrons would give you a neutral molecule called cyclobutadiene. [3 marks]

Bonding should be about the same if the ion gains two  $\pi$  electrons.

Those electrons would go into the nonbonding  $2\pi$  orbitals. Nonbonding electrons do not affect bond order, so adding nonbonding electrons will not affect bond strength.

- (i) What molecular property could you measure and compare in the dication and in the neutral molecule to confirm your theoretical prediction in part (h)? [1 mark]

Bond length. If the bond order does not change, the bond length should not change.

*Properties like magnetism were not acceptable answers to this question as they did not relate to the change (or lack of change) in bond order.*

# Chem 2000 Standard Periodic Table

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