

University of Windsor  
 Chemistry and Biochemistry  
 Chemistry 59-450, Winter Term 2007

### Final Examination

Do all questions in the exam booklets that have been provided. The exam has a total of 200 points.

#### Question #1 [20 points]

(a) Use the following bond energies to estimate the stability of the salt  $[\text{N}_5]^+[\text{N}_3]^-$  with respect to molecular nitrogen. Be sure to use appropriate drawings and equations to justify your answer. [10]

N–N: 160 kJ mol<sup>-1</sup>

N=N: 419 kJ mol<sup>-1</sup>

N/N: 945 kJ mol<sup>-1</sup>

(b) Using the information from part (a) and the bond energies listed below, use isodesmic equations to justify the allotropes observed for **nitrogen and phosphorus** under standard conditions. [10]

P–P: 200 kJ mol<sup>-1</sup>

P=P: 310 kJ mol<sup>-1</sup>

P/P: 490 kJ mol<sup>-1</sup>

#### Question #2 [25 points]

(a) What is the “double bond rule”? Explain why was it proposed and explain how sterically-demanding substituents stabilize some types of “unfavourable” multiple-bonded compounds. [15]

(b) Explain why SF<sub>4</sub> is so reactive (for example in its hydrolysis or its reaction with carboxylic acids) whereas SF<sub>6</sub> is essentially inert. [10]

Potentially relevant bond energies are:

O–H: 460 kJ mol<sup>-1</sup>    S–F: 285 kJ mol<sup>-1</sup>    S=O: 500 kJ mol<sup>-1</sup>    H–F: 565 kJ mol<sup>-1</sup>

C–O: 360 kJ mol<sup>-1</sup>    C=O: 800 kJ mol<sup>-1</sup>    C–F: 485 kJ mol<sup>-1</sup>    C–C: 350 kJ mol<sup>-1</sup>

**Question #3 [20]**

Explain the following observations using all appropriate arguments:

- (a) Under standard inert-atmosphere conditions,  $\text{AsF}_5$  is a stable compound while  $\text{AsCl}_5$  is very unstable. [10]
- (b)  $\text{H}_2\text{O}_2$  has an O-O bond length of 1.48 Å while  $\text{F}_2\text{O}_2$  has an O-O bond length of 1.22 Å. [10]

**Question #4 [35]**

- (a) In the gas phase  $\text{PCl}_5$  has the structure that one would predict on the basis of VSEPR theory; describe and draw that structure. [3]
- (b) In the solid state  $\text{PCl}_5$  adopts an alternative structure that produces two different signals in the  $^{31}\text{P}$  NMR spectrum indicating two different phosphorus environments. Explain this observation and describe the solid-state structure. [10]
- (c) In the gas phase  $\text{BeH}_2$  has the structure that one would predict on the basis of VSEPR theory; describe and draw that structure. [2]
- (d) In the solid state  $\text{BeH}_2$  adopts a different structure; draw that structure and describe the bonding in that structure using an appropriate bonding model. [10]
- (e) Use Wade's rules to predict the structure of the anion  $[\text{Sn}_5]^{2-}$ . Please show your work. [10]

**Question #5 [30]**

- (a) Justify the statement: "The chemistry of the s-block elements is much less diverse than the chemistry of the p-block elements." Provide one example of a useful reaction based on the chemistry of an s-block element. [10]
- (b) Please explain why Fluorine is sometimes described as the most reactive element. Provide as many valid arguments as possible. [10]
- (c) Justify the statement: "Some of the 'Noble Gases' are not really 'Noble'." Provide an example of at least one type of compound that illustrates the statement and explain why there are more compounds containing Xe than any of the other group 18 elements. [10]

**Question #6 [30]**

(a) Describe the bonding in the molecule NO and the cation  $\text{NO}^+$  using Lewis structures and appropriate molecular orbital models. [10]

(b) Describe the bonding in the molecule  $\text{S}_2\text{N}_2$  using Lewis structures and appropriate molecular orbital arguments. [10]

(c) Describe the bonding in the molecule obtained when two NO molecules dimerize and explain the similarities and differences between this molecule and  $\text{S}_2\text{N}_2$ . [10]

**Question #7 [20]**

(a) Explain the following observation:  $\text{Cl}_3\text{BNMe}_3$  has a B-N distance of 1.575 D, while  $\text{B}(\text{NMe}_2)_3$  has a B-N distance of 1.439 D and  $\text{Me}_2\text{BNMe}_2$  has a B-N distance of 1.375 D. [10]

(b) Explain the following observations regarding lithium compounds we examined in class: LiCl has a typical salt-type structure,  $(\text{C}_5\text{H}_5)\text{Li}$  has a linear (column-like) structure and  $(\text{H}_3\text{C})\text{Li}$  has a cube-shaped cluster structure. [10]

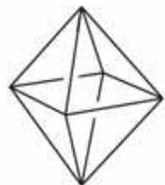
**Question #8 [20]**

(a) Where should the element Hydrogen be placed in the periodic table? Justify your answer(s). [10]

(b) What are the properties that make the element Carbon so uniquely important to chemistry. [10]



$n = 5$   
Trigonal  
bipyramid



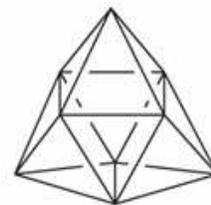
$n = 6$   
Octahedron



$n = 7$   
Pentagonal  
bipyramid



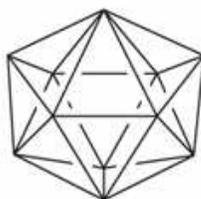
$n = 8$   
Dodecahedron



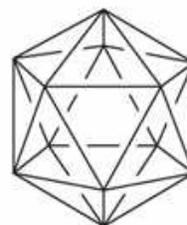
$n = 9$   
Tricapped  
trigonal prism



$n = 10$   
Bicapped  
square-antiprism



$n = 11$   
Octadecahedron



$n = 12$   
Icosahedron