Chemistry 322 **Name _____**
Dr. Clark
Spring 2006
Examination II

INSTRUCTIONS

1. This exam consists of 11 pages, one sheet of scratch paper, several pages of useful information, and a periodic table. If a page is missing, let me know immediately.

2. PRINT your name NOW at the top of ALL pages.

3. Part A is worth 32 points. Part B is worth 28 points. Part C is worth 15 points.

4. You will have up to 90 minutes to complete this exam. Check your work after completing the exam. **Please show all your work and be certain that all your explanations are given as complete sentences.**

5. **On the grading chart at the bottom of this page, CIRCLE the numbers of the questions that you would like to be graded for Parts A and B. BEFORE YOU HAND IN YOUR EXAM, CHECK THAT YOU HAVE CIRCLED THE CORRECT NUMBER OF QUESTIONS FOR PARTS A (4) and B (2).**

Part A 1 (ALL)		**/08 pts.**
2		**/08 pts.**
3		**/08 pts.**
4		**/08 pts.**
5		**/08 pts.**
Part B 6 (ALL)		**/15 pts.**
7		**/12 pts.**
8		**/12 pts.**
Part C 9 (ALL)		**/16 pts.**
TOTAL		**/75 pts.**

PART A. (32 points) **BASIC QUESTIONS**. Answer **QUESTION #1 and THREE of the next FOUR questions**, e.g. 1/2/3/4, 1/2/3/5, 1/3/4/5, etc. Write your answer in the space provided. SHOW YOUR WORK & WRITE EXPLANATIONS IN COMPLETE SENTENCES.

1. In addition to periodic trends such as ionization energy, electron affinity, and electronegativity that were discussed earlier in the course, several other examples of periodic trend-like behavior have been described more recently. These include (i) the Uniqueness Principle (a.k.a. the "first row anomaly"), (ii) the "inert-pair" effect, and (iii) the "diagonal effect."

For any 2 of these additional trends above, provide clear and concise descriptions of the meaning of these periodic characteristics. In recording your answer, be sure to provide the factors that are responsible for the physical basis/origin of these features.

2. Predict if the molecule P_2 can exist by constructing an appropriate molecular orbital diagram. If you determine that P_2 can exist, discuss whether this is a likely form of phosphorous at ambient conditions.

3. For each pair of compounds, circle the one that meets the description given.

a. The strongest Lewis base

NCl_3 $N(CH_2CH_3)_3$

b. The strongest Arrhenius acid

CF_3SO_3H $HClO_4$

c. The solvent in which HCl is most acidic

H_2O CH_3COOH

g. The hardest Lewis base

AsH_3 SbH_3

d. The weakest Arrhenius acid

H_2SeO_2 H_2SeO_3

e. The softest Lewis base

$As(C_6H_5)_3$ $P(C_6H_5)_3$

f. The strongest Arrhenius acid

$[Ru(H_2O)_6]^{2+}$ $[Ru(H_2O)_6]^{3+}$

g. The hardest Lewis acid

V^{2+} V^{3+}

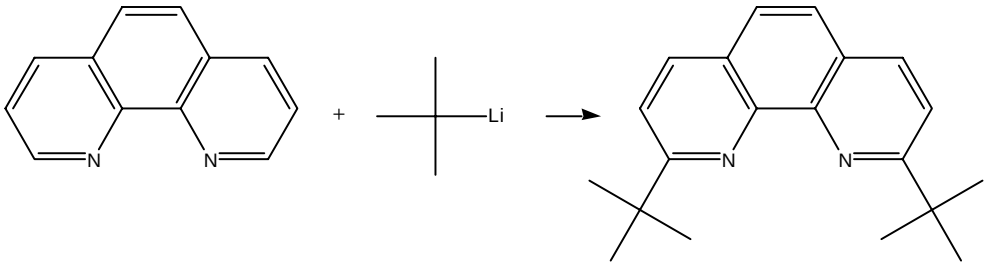
4. Liquid ammonia can be used as a solvent for reactions at low temperature.

a) What is the strongest acid possible in ammonia solvent?

b) What is the strongest base possible in ammonia solvent?

c) HF (pK_a~3) is a weak acid, but when dissolved in ammonia, HF behaves as a strong acid. Write an equation to represent the acid/base equilibrium that occurs and explain why HF appears to be a strong acid in ammonia solvent.

5. As shown in the scheme below, our good friend Bob plans to carry out the alkylation of phenanthroline using butyl lithium as the alkylating agent. Should he carry out this reaction in chloroform, toluene, or ethanol? Explain your choice.



Part B (27 points) **COMPETENCY QUESTIONS.** Answer **QUESTION 6 and EITHER QUESTION 7 or 8**. SHOW YOUR WORK AND WRITE EXPLANATIONS IN FULL SENTENCES.

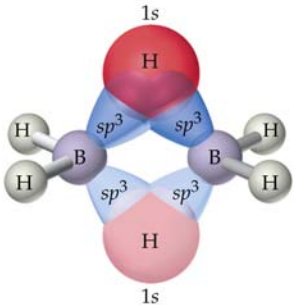
6. a) In question #1, you were asked to describe the meaning of the (i) Uniqueness Principle, (ii) the "inert-pair" effect, and/or (iii) the "diagonal effect." Based on the presentation/summary you prepared for this class, provide and discuss an example of a manifestation of one of these effects for the main group on which you presented.

b) Answer 2 of the next 8 parts regarding the chemistry of the main groups.

Group 1: Describe 3 reasons/properties of why Lithium is a good choice for use in batteries.

Group 2: Provide 2 specific examples of how and why biological molecules utilize Gp. 2 metals in many life processes.

Group 13: Many boranes use hydrogen as a bridging ligand. One example is diborane that is shown to the right. Why might the use of a bridging hydrogen ligand help stabilize boron-containing compounds in terms of their electron configurations?



Group 14: The physical properties of the Group 14 elements vary greatly, owing to their diverse array of applications. Classify each member of the group as a metal, metalloid, or non-metal, and name one important application of each element.

Group 15: The electron affinities of the group 15 elements are all fairly poor, particularly for nitrogen. Explain why this is generally the case for the family, as well as why nitrogen has a particularly poor affinity compared to other members of Gp. 15.

Group 16: One important allotrope of oxygen is ozone. What is the structure of ozone, and how are gases such as NO_2 likely responsible for depleting the ozone layer? A complete answer will involve the discussion of appropriate chemical reactions.

Group 17: Despite being diatomic molecules, the states of matter of F_2, Cl_2, Br_2, and I_2 vary substantially at ambient conditions. Explain why this is true on the basis of intermolecular forces and average kinetic energy.

Group 18: Some day our natural supply of He will run out. Briefly describe how (i) helium is produced by the sun and (ii) how we can generate supplies of this most wondrous element.

c) (2 pts. – Extra Credit) In class, we read an excerpt from a book chapter entitled "The Origin of the Elements." In this excerpt, the author describes a bit of nuclear chemistry and how the age of stars can be determined. At one point, he states the structure of a star is like an onion. What does he mean by this?

7. The superoxide anion, O_2^-, is one of several potentially toxic oxygen radicals that is formed as our bodies metabolize oxygen. Answer the questions below about the superoxide anion.

a) Construct a molecular orbital diagram of the superoxide anion, filling in the correct number of electrons into the molecular orbitals. Be sure to label each molecular orbital with its bond type, the atomic orbitals it was generated from, and whether it is bonding or antibonding (e.g. σ_{2s}, π_{2p}^*).

b) Making reference to your MO diagram from part a), compare and contrast the bond orders of dioxygen (O_2), the superoxide anion (O_2^-), and the peroxide anion (O_2^{2-}). Which of these three species has the strongest O-O bond? the longest O-O bond? Explain.

c) Sketch a diagram of the lowest unoccupied molecular orbital (LUMO) of O_2^-.

8. For the following solution equilibria, predict if the products or the reactants will be favored. Give your reasoning in each case, referring explicitly to acid/base concepts discussed in this course.

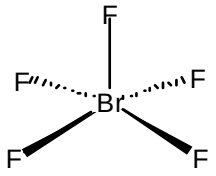
a) $AgF(aq) + LiI(aq) \rightleftarrows AgI(s) + LiF(aq)$

b) $2\ Fe(OCN)_3(aq) + 3\ Fe(SCN)_2(aq) \rightleftarrows 2\ Fe(SCN)_3(aq) + 3\ Fe(OCN)_2(aq)$

(NOTE: The OCN^{1-} and SCN^{1-} ligands are both -1 polyatomic anions and bond to iron through the oxygen and sulfur atoms, respectively.)

Part C (16 points) **MASTERY QUESTION.** Answer the following question in the space provided. SHOW ALL YOUR WORK AND WRITE EXPLANATIONS IN COMPLETE SENTENCES.

9. a) Using the group theoretical approach to bonding, find the irreducible representations of the symmetry adapted linear combinations (SALCs) of the F orbitals of appropriate energy that will form sigma bonds with the orbitals of Br. In recording your answer, clearly indicate how you determined which F orbitals were of the correct energy (and symmetry) to interact with Br.



(square pyramidal geometry)

b) Using the SALCs that you generated above, construct a molecular orbital diagram for sigma bonding in BrF_5. (NOTE: You may assume that the Br d orbitals are not involved in bonding. Also, since you are only considering those SALCs that form σ bonds on this MO diagram, SALCs that lead to the formation of π bonds will be depicted as non-bonding MOs. Be sure to show ALL non-bonding MOs on your diagram.)

c) For the four fluorine atoms that form the base of the square pyramid, determine the irreducible representations of the π SALCs AND state which orbitals on the central Br interact with the SALCs. Rationalize your choices by explicit reference to the appropriate character table.

Scratch Paper