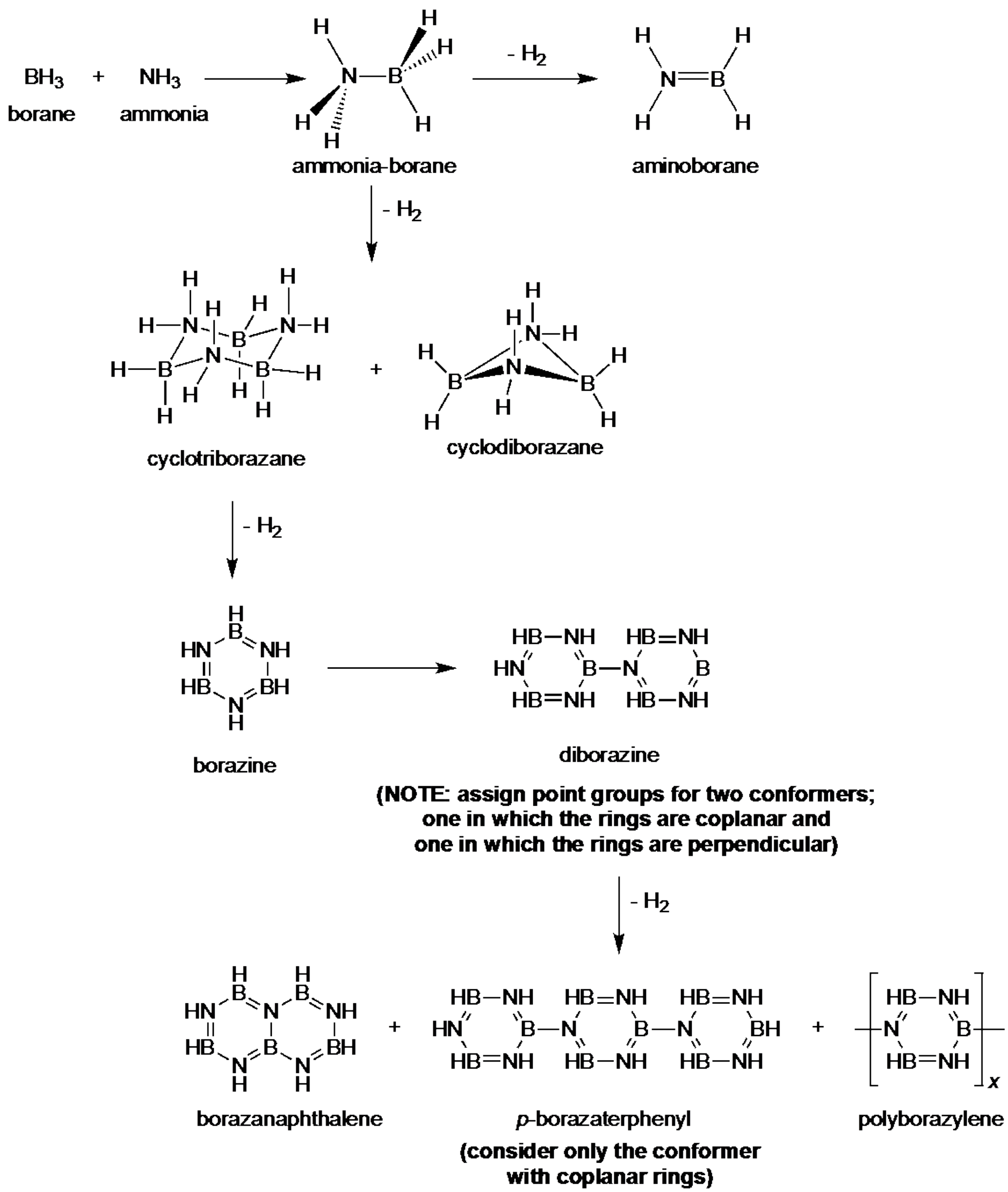
Recommended Reading: 5.1 – 5.7, **15.2-15.11** (3rd/4th edition)

Ch 102 – Problem Set 3
Due: Thursday, April 27 – *Before Class*

Problem 1 (2 points)

A) On-board storage of hydrogen is a major obstacle for the use of hydrogen as a clean-burning transportation fuel. Ammonia-borane is an appealing candidate for chemical hydrogen-storage applications. Amine-borane adducts can be readily synthesized from free amines and boranes. Thermal decomposition of ammonia-borane adducts yields hydrogen and a mixture of aminoborane and borazine products. Draw two resonance structures for aminoborane; given these structures, discuss the propensity to make oligomers.



B) Give the point group for cyclotriborazane, cyclodiborazane, diborazine, and *p*-borazaterphenyl (see notes under drawings). For polyborazylene, determine the 1-D space symmetry class (assume planar geometry); highlight unit cell and asymmetric unit. Also, determine the 2-D space group of the fully dehydrogenated $(BN)_x$ product (assume a graphene-like structure); highlight unit cell and asymmetric unit.

C) Using the equation below, calculate the hydrogen capacity (wt%) of ammonia-borane. Be sure to show how you arrived at your answer for full credit.

$$X\ H_3B{-}NH_3 \xrightarrow{[cat]} 3X\ H_2 + (BN)_X$$

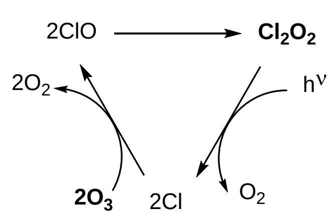
Bonus: D) For ammonia-borane to be a viable hydrogen storage material, recharging with H_2 of spent storage material must be practical (i.e. hydrogenation of the dehydrogenated products to yield ammonia-borane). While some of the dehydrogenated products can be easily hydrogenated, this reverse process becomes more challenging as the extent of dehydrogenation increases. In particular, polyborazylene is a challenging substrate to re-hydrogenate to afford ammonia-borane. Speculate on why this is the case.

Problem 2 (2 points)

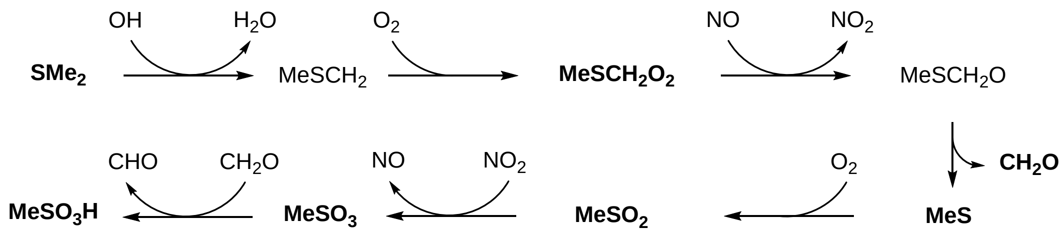
For all the bolded compounds below,

a) Draw the best Lewis dot structure(s). If applicable, draw at least one with hypervalency and one without, clearly labeling which is which. Label formal charges and oxidation states.
b) Identify the point group of the molecule. Is the molecule chiral?
c) Give the VSEPR structure of every atom in your structure bonded to multiple atoms, and indicate bond angles (e.g. 109.5º, <120º, >90º).
d) Indicate whether the molecule has closed shell or open shell electronic configuration.

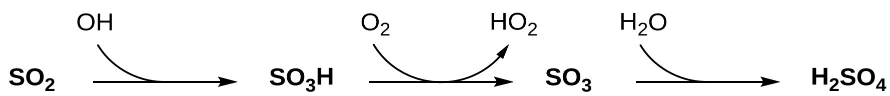
An important component of the upper atmosphere is ozone, which adsorbs UV light harmful to life on the surface. Human emissions, however, have depleted the ozone layer, forming a hole over Antarctica; when discovered, the hole was so large that satellite instruments were rejecting the measurements as being impossible. One mechanism for the breakdown of ozone involves atmospheric ClO (Seinfeld, J. H., Pandis, S.N., *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd ed.; Wiley: Hoboken, 2006.). Crutzen, Molina, and Rowland won the Nobel Prize in 1995 for their work on atmospheric ozone chemistry (Nobelprize.org. The Nobel Prize in Chemistry 1995. http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1995/ (accessed April 20, 2017).



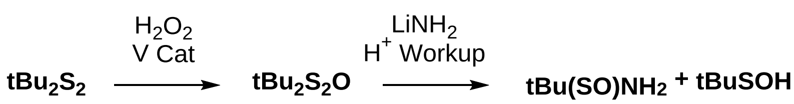
One minor component of our atmosphere is sulfur, which can exist in several oxidation states. The biggest natural component of sulfur is dimethyl sulfide, which is emitted by marine phytoplankton and must be oxidized before it is soluble enough in water to return to the surface. Below is one common mechanism of dimethyl sulfide oxidation, resulting in the formation of methanesulfonic acid (MSA).



A major component of human emissions is sulfur dioxide. This chemical is oxidized in the atmosphere and is a significant cause of acid rain (Seinfeld, J. H., Pandis, S.N., *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd ed.; Wiley: Hoboken, 2006.).



Interesting sulfur chemistry does not just occur in the atmosphere. The petroleum impurity di-*tert*-butyl disulfide can be converted to *tert*-butanesulfonamide, which can act as an ammonia surrogate in the synthesis of chiral amines (Weix, D. J.; Ellman, J.A. *Org. Lett.*, **2003**, *5* (8), pp 1317–1320), (Ellman, J. A.; Owens, T. D.; Tang, T. P. *Acc. Chem. Res.*, **2002**, *35* (11), pp 984–995).



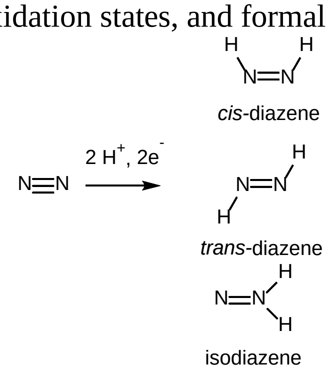
Problem 3 (2 points)

In class we discussed a series of biological reactions which convert nitrate (NO_3^-) into reduced nitrogen oxides (NO_2^-, NO, N_2O) and nitrogen. We further mentioned a class of enzymes known as nitrogenases which catalyze the reduction of N_2 by 6 e^- to form NH_3.

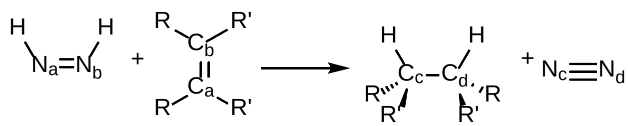
$$N_2 \xrightarrow[\text{nitrogenase}]{6H^+,\ 6e} NH_3$$

Similar to how there are various N_xO_y species which are intermediates in the reduction of NO_3^- to N_2, there can be different intermediate N_XH_y species in the reduction of dinitrogen to ammonia.

A) A putative early intermediate species in reduction of dinitrogen has the chemical formula N_2H_2 and is the product of formal delivery of 2 equivalents of H^+ and e^- to N_2. N_2H_2 can exist as three isomers shown below known as *cis*-diazene, *trans*-diazene and isodiazene. For each of the diazene isomers draw a Lewis structure and assign electron counts, oxidation states, and formal charges for all atoms.



B) *Cis*-diazene can be used in organic chemistry in the hydrogenation of olefins. For the reaction below assign electron counts and oxidation states for all the $N_{(a\text{-}d)}$ and $C_{(a\text{-}d)}$ atoms in the reactants and products. Which species acts as the oxidant and which acts as the reductant?



C) Diazene can react with other diazene molecules via a disproportionation reaction to a generate a further downstream potential intermediate hydrazine (N_2H_4) which is the product of formal delivery of 4 equivalents of H^+ and e^- to N_2. Write a balanced reaction for the reaction of N_2H_2 to generate N_2H_4. Assign oxidation states for all atoms in the products and reactants. Indicate which reagent acts as the oxidant and which acts as the reductant.

D) In low-power monopropellant rocket engines N_2H_4 is the only fuel source and energy is generated by passing N_2H_4 over a catalyst bed where the following reactions occur.

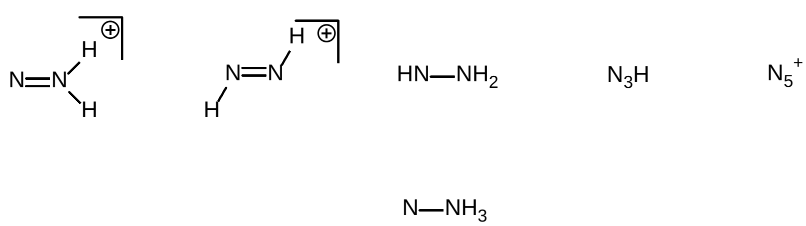
$$3\ N_2H_4 \longrightarrow 4\ NH_3 + N_2$$

$$N_2H_4 \longrightarrow H_2 + N_2$$

$$4\ NH_3 + N_2H_4 \longrightarrow 3\ N_2 + 8\ H_2$$

The first two reactions are highly exothermic producing large volumes of hot gases from small amounts of liquid N_2H_4 to generate thrust. The third reaction is endothermic and generates thrust through greatly increasing the number of gaseous molecules. For each of the three reactions assign electron counts and oxidation states for all N and H atoms in the reactants and products. Indicate which reagent(s) are the oxidant and reductant in each reaction.

E) For the following N_xH_y species draw a Lewis structure (with formal charges labelled) and any relevant resonance structures. Indicate which of your resonance structures is most reasonable and give the reason(s). Indicate whether the compound is expected to be diamagnetic or paramagnetic.



Problem 4 (2 points)

Part A

The bonding in LiF and HF was discussed in class. For this problem also consider HCl. Electronic structure calculations were performed with Gaussian, and the molecular orbitals of interest are depicted on page 5 vertically for the three species. Based on the atomic orbital contributions to the molecular orbitals, assign by visual inspection each MO diagram to LiF, HF, or HCl. (Hint: take into consideration the energies of the atomic orbitals involved) Clearly label which side corresponds to which atom (ie what are the identities of A and B for each case?). Briefly explain your assignments. For each horizontal set of three MOs also assign the axial symmetry using the A-B bond as the axis.

Part B

The first ionization energies of BF and N_2 are 11.06 eV and 15.57 eV respectively.

a) Draw a molecular orbital diagram for each molecule using the concept of axial symmetry (take into account the energy of the valence atomic orbitals). Fill in the appropriate number of electrons and identify the symmetry of each orbital (□ or □) and label it as bonding, nonbonding (nb) or antibonding (*).

b) Label the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

c) Explain the difference in ionization energy for these isoelectronic species based on the atomic orbital character of the highest occupied molecular orbital.

d) Images of several molecular orbitals of BF and N_2, calculated with Gaussian, are depicted on page 6. Based on the atomic orbital contributions to the molecular orbitals, assign by visual inspection each MO diagram to BF or N_2. What are the identities of A and B for each case? Explain.

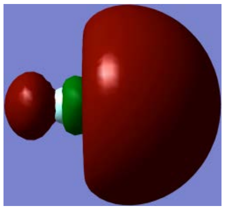
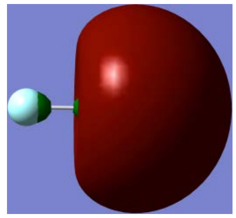
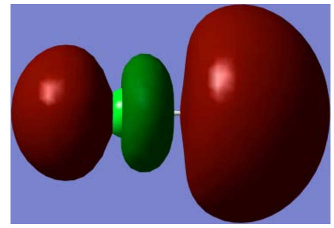
e) Based on the MO diagrams and atomic orbital contributions, which species do you expect to bind better to BH_3? Which one would you expect to have a stronger interaction with a molecule displaying a filled orbital of □ symmetry of appropriate energy.

Note: Gaussian output files for these calculations are available on the course website (Moodle). Visualization using the software is allowed for this problem.

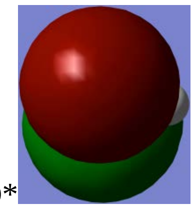
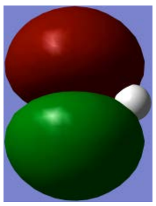
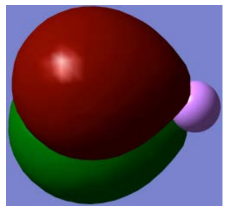
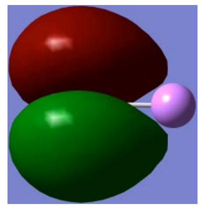
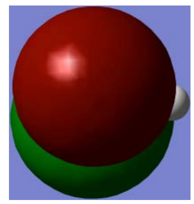
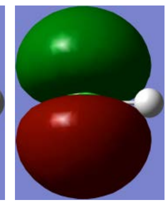
For Problem 4, Part A:

i) **A—B** ii) **A—B** iii) **A—B**

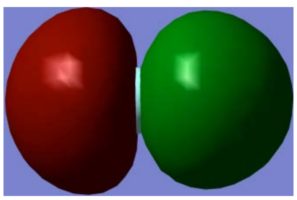
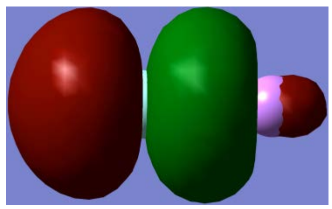
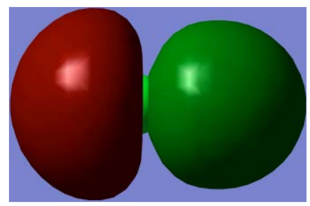
LUMO*

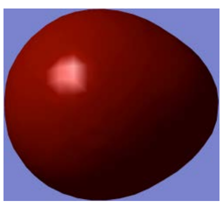
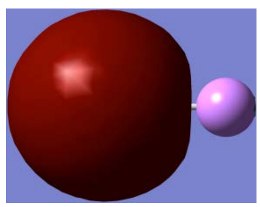
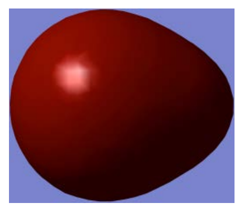
HOMO*
(degenerate set of two molecular orbitals)

HOMO-1

HOMO-2

*LOMO = lowest unoccupied molecular orbital

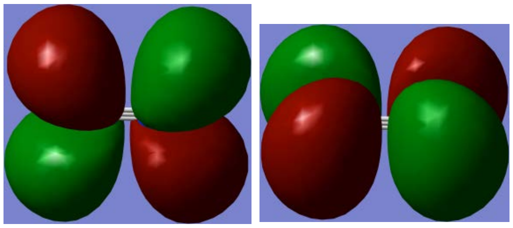
*HOMO = highest occupied molecular orbital

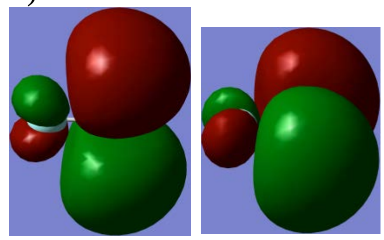
For Problem 4, Part B:

i) **A—B**

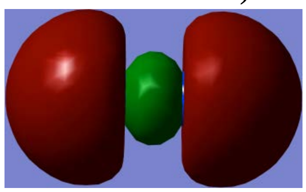
ii) **A—B**

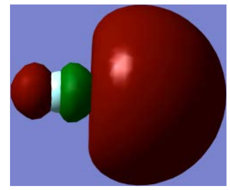
LUMO
(degenerate set of two molecular orbitals)



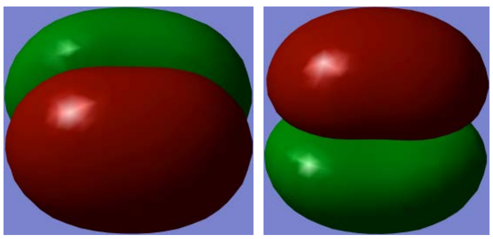


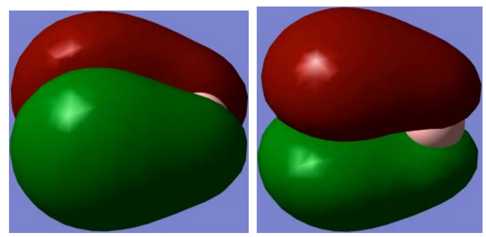
HOMO



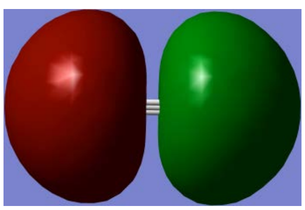


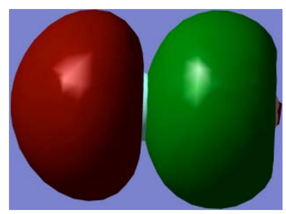
HOMO-1
(degenerate set of two molecular orbitals)



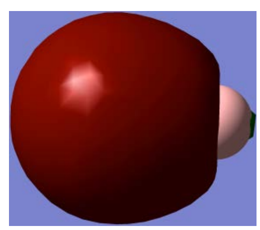


HOMO-2





HOMO-3



Problem 5. (2 points) ***Read the instruction below and format file names properly***

Pick a topic of interest from the recommended reading in bold. Prepare two power point slides including relevant descriptive chemistry (background on synthesis, applications, reactivity, properties, trend, etc, as applicable), some concepts presented in class (point group assignment, symmetry elements, etc) and some application of the provided software (for example, highlight symmetry elements / operations). Turn in a printout of the slides with your problem set, and email the TAs the slides in pdf format by 12:00 noon on the due date. Please format file names as "FirstName_LastName_PSET#" and include your name on the first slide.