Chem 233: Problem Set #1 (on Chapter 1)

1. What type of hybridization is used by each non-hydrogen atom in the substances shown below?

2. Draw Lewis (or Kekule) structures for all substances shown below. For those substances in E through H, draw all possible constitutional isomers.

   A. HNO₂      E. C₄H₁₀      I. NO₂⁺      M. CS₂
   B. H₂SO₃     F. C₄H₈      J. C₂H₅⁺     N. CO₃²⁻
   C. BF₃       G. C₄H₆      K. NH₂⁻
   D. PH₃       H. C₄H₈Cl₂   L. HSO₃⁺

3. Predict the molecular shape and bond angles for each substance given in question #2.

4. Draw a Lewis structure for CH₃CN and identify what type of hybridization each atom uses during bonding. Use valence bond theory and draw orbital pictures showing what orbitals are involved in the formation of the covalent bonds in CH₃CN.
σ-bond due to head-on overlap between valence atomic orbitals or hybrid orbitals. 
π-bond due to sideways overlap between hybrids or valence atomic orbitals.

5. Consider the singly occupied orbitals shown below. Decide whether each set of orbitals, when overlapped along the specified direction, will lead to formation of a σ-type bond, a π-type bond, or neither type bond.

σ-bond

π-bond

Neither

π-bond

σ-bond

Remember:

σ-bond has e-density along the bond connecting the 2 atoms.
π-bond has e-density above and below the bond connecting the 2 atoms.

Note: At an appropriate time, answer keys to each problem set will be posted on the Chem 233 website (www.chem.wvu.edu/chem15.Babb). The problem sets will give you an idea of how questions will be asked on the exams. Work through each problem set before looking at the posted answer key. Problem sets are not all inclusive. Material that can be easily learned will not be included on the problem set but may still appear on the exam.
KEY Questions #2 & #3 Problem Set #1 - Chem 333

2A. 

\[ \text{HNO}_3 \quad \text{valence} = 1+5+2(6) = 18 \]

[Structure of HNO₃]

\[ \text{MS} = \text{Bent} \quad \angle \leq 120^\circ \text{ (a little less due to lone pair e-)} \]

3B. 

\[ \text{H}_2\text{SO}_3 \quad \text{valence} = 2+6+3(6) = 26 \]

[Structure of HClO₄]

\[ \text{MS} = \text{Trigonal Planar} \quad \angle = 109.5^\circ \text{ (exactly)} \]

3C. 

\[ \text{BF}_3 \]

[Structure of BF₃]

\[ \text{MS} = \text{Tetrahedral} \quad \angle = 109.5^\circ \]

3D + 3D. 

\[ \text{PH}_3 \quad \text{valence} = 5+3(1)-8 \]

[Structure of PH₃]

\[ \text{MS} = \text{Pyramidal} \quad \angle \leq 109.5^\circ \]

3E + 3E. 

\[ \text{C}_4\text{H}_{10} \quad \text{C}_4\text{H}_{8} \]

[2 Constitutive Isomers]

\[ \text{MS} = \text{Tetrahedral (about each C)} \quad \angle = 109.5^\circ \]

2 Constitutive Isomers. 

[5 Constitutive Isomers]

\[ \text{MS} = \text{Tetrahedral about each sp}^3 \text{ hybridized C} + \text{Trigonal Planar about each sp}^2 \text{ hybridized C.} \]

\[ \angle = \text{Theoretical about all tetrahedal C} = 109.5^\circ \text{ about all trig planar C} = 120^\circ \]
8 different constit. isomers

\[ \text{MS} = \text{Tetrahedral about each } \text{sp}^3 \text{C} \]
\[ \text{Trigonal planar about each } \text{sp}^2 \text{C} \]
\[ \text{Linear about each } \text{sp} \text{C} \]
\[ \angle \delta = 109.5^\circ \text{ about each } \text{sp}^3 \text{C} \]
\[ 120^\circ \text{ about each } \text{sp}^2 \text{C} \]
\[ 180^\circ \text{ about each } \text{sp} \text{C} \]

Theoretical bond \( \mu \) isings may not have these bond \( \mu \)s (see Chapter 4)

9 different constit. isomers.

\[ \text{MS} = \text{Tetrahedral about each C} \]
\[ \angle \delta = 109.5^\circ \]
\[ \text{DI} + 3\text{I} \quad \text{NO}_2^- + \text{e}^- = 5 + 2(6) - 1 = 16\text{e}^- \quad \text{MS} = \text{Linear} \quad \theta = 180^\circ \]

\[ \text{DI} + 3\text{I} \quad \text{C}_2\text{H}_5^- + \text{e}^- = 2(4) + 5(1) - 1 = 12\text{e}^- \quad \text{MS} = \text{tetrahedral about } \text{sp}^3\text{C} + \text{trigonal planar about } \text{sp}^2\text{C} \quad \theta = 109.5^\circ \text{ about } \text{sp}^3\text{C} + 120^\circ \text{ about } \text{sp}^2\text{C} \]

\[ \text{DI} + 3\text{I} \quad \text{NH}_2^- + \text{e}^- = 5 + 2 + 1 = 8\text{e}^- \quad \text{MS} = \text{Bent} \quad \theta = 109.5^\circ \]

\[ \text{DI} + 3\text{I} \quad \text{HSO}_3^- + \text{e}^- = 1 + 6 + 3(6) - 1 = 24\text{e}^- \quad \text{MS} = \text{Trigonal Planar} \quad \theta = 120^\circ \]

\[ \text{DI} + 3\text{I} \quad \text{CS}_2 \quad \text{e}^- = 4 + 2(6) = 16\text{e}^- \quad \text{MS} = \text{Linear} \quad \theta = 180^\circ \]

\[ \text{DI} + 3\text{I} \quad \text{CO}_3^{2-} \quad \text{MS} = \text{Trigonal Planar} \quad \theta = 120^\circ \]
6. For each line (skeletal) structure shown below, write a structural formula that includes all hydrogen atoms.

7. Draw the following structural formulas as line (skeletal) structures.
8. Calculate formal charges for each atom indicated with an arrow.

\[ 4 - \frac{6}{2} - 2 = \boxed{2} \]

\[ H_3C-C≡C: \quad H_3C-C-H \quad CH_3 \quad H_3C-C-H \quad CH_3 \quad CH_3 \]

\[ 4 - \frac{6}{2} - \phi = \boxed{1} \]

\[ 4 - \frac{6}{2} - \phi = \boxed{1} \]

\[ 5 - \frac{8}{2} - \phi = \boxed{1} \]

\[ 6 - \frac{6}{2} - 2 = \boxed{1} \]

\[ 6 - \frac{6}{2} - 2 = \boxed{1} \]

\[ CH_3-C=CH \quad CH_3 \quad H_3C \]

\[ \boxed{1} \]

\[ H_3C-C=CH \quad CH_3 \quad H_3C \]

\[ CH_3-C=CH \quad CH_3 \quad H_3C \]

\[ 6 - \frac{6}{2} - 2 = \boxed{1} \]

\[ OH_2 \]

\[ 6 - \frac{6}{2} - 2 = \boxed{1} \]

\[ \boxed{1} \]

\[ 10 - N=O \quad \leftrightarrow \quad 10 - N=O \quad \boxed{1} \]

\[ \boxed{1} \quad \boxed{1} \quad \boxed{1} \quad \boxed{1} \quad \boxed{1} \]

\[ \boxed{1} \quad \boxed{1} \quad \boxed{1} \quad \boxed{1} \quad \boxed{1} \]

\[ \boxed{1} \quad \boxed{1} \quad \boxed{1} \quad \boxed{1} \quad \boxed{1} \]

9. Draw all possible resonance structures for nitrite, \( NO_2^- \). Calculate the formal charges on all atoms in each resonance structure. Show with curved arrows how one resonance structure is converted to the other by movement of electron pairs. Draw a picture of the resonance hybrid and indicate the N-O bond orders in this hybrid. \( \#e^- = 5 + 2(6) + 1 = 18e^- \quad 10 - N-O \quad \boxed{1} \)

10. Draw all possible resonance structures for each of the following. Indicate whether each resonance structure is of equivalent energy to the original.

A. \( \begin{array}{c} \text{N} \\ H_3C-C=H \end{array} \)

B. \( \includegraphics[width=1cm]{image} \)

C. \( \includegraphics[width=1cm]{image} \)

D. \( \includegraphics[width=1cm]{image} \)

E. \( \includegraphics[width=1cm]{image} \)

F. \( \includegraphics[width=1cm]{image} \)

An next page.
A. More $^-$ away from negative.
More only $^\pm$ and $^-$ pairs.
C, N, O often have more than $^-$.

B. More $^-$ toward positive.
Move only $^-$ and lone pairs.
Resonance structures II, III and IV are of different energy than original.

C. Resonance structures I and VII have some energy.
II and VI not but different than original.
III and V not.
Resonance structure IV has different energy than original.
D. Original resonance structure had one unpaired e⁻ and so all others must have one unpaired e⁻.

E. Structure III and IV are of equal energy, but all (II - IV) are of different energy than original.

Move e⁻ away from negative.

Can't draw because C would have more than 8 e⁻.

Structure II is a different energy than I. It is more stable than I.

Structure III is also of different energy than both II and IV.

F. Resonance structures II and III are of different energy than I. Structure II is more stable than I and III.