TOPIC F PROBLEMS

1) Draw a bond energy diagram (a graph of potential energy versus distance between the nuclei) for the bond in O_2, which has a bond energy of 495 kJ/mol and a bond distance of 121 pm.

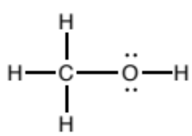
2) Draw Lewis structures for each of the following molecules. For each molecule, the first atom in the formula is the central atom and all other atoms are bonded to it.

a) CH_4 b) PCl_3 c) PBr_5 d) COF_2 e) SOF_2 f) SeF_4

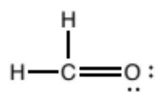
3) Draw Lewis structures for each of the following polyatomic ions. If there are multiple resonance structures for an ion, you only need to draw one of the resonance structures.

a) NO_2^- b) NH_4^+ c) BF_4^- d) CO_3^{2-} e) CN^- f) O_2^{2-}
g) ClO_4^- h) SeO_4^{2-} i) IF_4^-

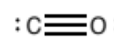
4) Consider each of the following molecules:



methanol



formaldehyde



carbon monoxide

a) What is the bond order of the carbon-oxygen bond in each molecule?
b) Which molecule has the largest carbon-oxygen bond energy?
c) Which molecule has the largest carbon-oxygen bond distance?
d) Would you expect the carbon-hydrogen bond distances in methanol and formaldehyde to be equal, or will they be significantly different? If they are different, which molecule should have the larger C-H bond distances?

5) For each of the bond types in parts a through d below, answer the following questions. You may refer to the table of electronegativity values in the textbook.

- Are these bonds polar?
- If they are polar, which atom is positively charged (if any)?

a) The C–Cl bonds in CCl_4 b) The O–Cl bonds in OCl_2
c) The C–H bonds in CH_4 d) The C–C bond in C_2H_6

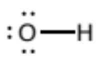
6) Using the bond dissociation energy values in the text, calculate an approximate value of ΔH for the reaction: $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$.

7) Xenon is one of the "inert gases", but it can form a number of compounds, including xenon trioxide (XeO_3). When heated, xenon trioxide breaks down explosively into the elements:

$$2\ XeO_3(g) \rightarrow 2\ Xe(g) + 3\ O_2(g) \qquad \Delta H = -804\ kJ$$

Use this value and the bond dissociation energy for the bond in O_2 to calculate a value for the xenon-oxygen bond energy. Give your answer in kJ/mol.

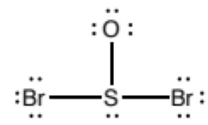
8) For each of the following molecules, determine the formal charge on each atom. (In your answer, draw the Lewis structure and write all non-zero formal charges next to the corresponding atoms.)



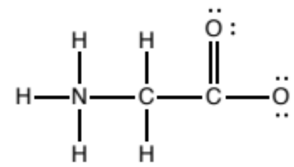
hydroxide ion

carbon monoxide

fulminic acid

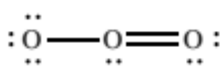


thionyl bromide

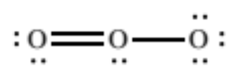


glycine

9) There are two resonance structure for the ozone molecule, O_3; these structures are shown below.



structure #1



structure #2

a) A student says "sometimes each bond in O_3 is the same strength as the bond in O=O, and sometimes it's the same strength as the central bond in H–O–O–H." Is this an accurate statement? Explain your answer.

b) Another student says "when O_3 looks like structure #1, the bond on the left is longer than the bond on the right." Is this an accurate statement? Explain your answer.

10) This problem asks you to compare two ions: NO_2^+ and NO_2^-. In both of these ions, the nitrogen is the central atom.

a) One of these ions requires two resonance structures to represent it accurately. Which one is it? Draw the two reasonable resonance structures for this ion.

b) For the other ion, there are three resonance structures that satisfy the octet rule. Draw these three resonance structures for this ion.

c) The ion in part b actually requires just one Lewis structure to depict it accurately. Which structure is this, and why is this the only structure you need?

d) Which are shorter: the nitrogen-oxygen bond distances in NO_2^+, or the nitrogen-oxygen bond distances in NO_2^-? Or do the two ions have equal N–O bond distances? Explain your answer.

11) There are two ions that have the empirical formula CNO^-. The <u>cyanate</u> ion has the three atoms in the order N–C–O, while the <u>fulminate</u> ion has the three atoms in the order C–N–O.

a) Draw all of the resonance structures that satisfy the octet rule for each ion. Include all non-zero formal charges in your structures.

b) Based on formal charges, which of these resonance structures would you expect to make a significant contribution to the actual structures of the cyanate and fulminate ions?

c) Based on your resonance structures for the cyanate ion, which atom (or atoms) carries the negative charge?

d) Repeat part c for the fulminate ion.

12) Draw all of the reasonable resonance structures that satisfy the octet rule for each of the following substances, and tell which structures will be major contributors to the actual structure of the molecule or ion.

a) CO_3^{2-}

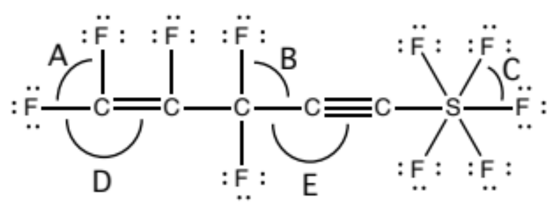
b) HCO_3^- (the H is attached to one of the O atoms in CO_3^{2-})

c) H_2CO_3 (each H is attached to one of the O atoms in CO_3^{2-})

13) Each of the three substances in the previous problem contains three carbon-oxygen bonds. For each substance, which carbon-oxygen bonds are the same length?

14) Rank the bonds labeled A through E in order of carbon-carbon bond distance, starting with the shortest bond distance. Be sure to consider resonance!

15) What are the approximate values (in degrees) for the bond angles labeled A through E in the molecule below?



16) For each of the following pairs of molecules, one molecule is polar while the other is not. Tell which molecule is polar, and justify your answer using Lewis structures and VSEPR.

a) CO_2 and SO_2 b) NCl_3 and BCl_3 c) SiF_4 and SeF_4 d) IF_5 and PF_5

17) What is the hybridization on each of the following atoms?

a) The nitrogen atom in NH_3

b) The phosphorus atom in PF_5

c) The carbon atom in CO_2

d) The carbon atom in CH_2O

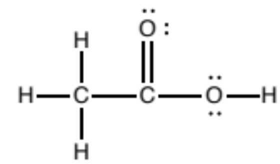
e) The iodine atom in IF_5

f) The nitrogen atom in NO_2^-

18) List all of the valence orbitals in each of the atoms listed in the previous problem, and tell how many of each there are. Do not list orbitals on the outer atoms.

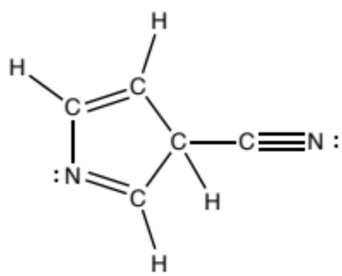
19) According to the valence-bond model, what atomic orbitals overlap to form each of the following chemical bonds?

a) The H–Br bond in HBr
b) The I–I bond in I_2
c) A C–F bond in CF_4
d) The C–H bond in HCN
e) A C–Cl bond in $COCl_2$
f) The C–C bond in acetic acid (the molecule on the right)
g) The C–O single bond in acetic acid



20) According to the valence-bond model, what atomic orbitals hold the nonbonding electrons in a molecule of water?

21) Questions a through d (on the next page) refer to the molecule below.



a) How many sigma bonds and how many pi bonds are there in this molecule?
b) What atomic orbitals form the carbon-nitrogen double bond? Tell whether each orbital is involved in a sigma bond or a pi bond.
c) What atomic orbitals form the carbon-nitrogen triple bond? Tell whether each orbital is involved in a sigma bond or a pi bond.
d) What atomic orbitals contain the nonbonding electrons?

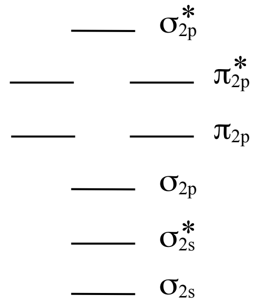
22) Draw pictures showing how each of the following MOs is formed by combining the specified atomic orbitals. Include the signs of the lobes for each atomic orbital.

a) a sigma bonding MO that is formed by two 2s orbitals
b) a sigma bonding MO that is formed by a 1s orbital and a 2p orbital
c) a sigma antibonding MO that is formed by two 2p orbitals
d) a pi antibonding MO that is formed by two 2p orbitals

23) A d orbital and a p orbital can combine to form molecular orbitals in several different ways. Draw a picture of the overlap between these two atomic orbitals that would produce each of the following molecular orbitals. Include the signs of the lobes for each atomic orbital.

a) a sigma bonding MO   b) a sigma antibonding MO
c) a pi bonding MO   d) a pi antibonding MO

24) The molecular orbital energy diagram for the valence orbitals of the NO^- ion is shown below. Use this diagram to answer the following questions.

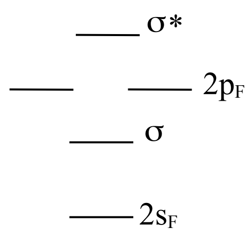


a) What is the bond order in NO^-?

b) Is NO^- diamagnetic, or is it paramagnetic? How can you tell?

c) Which has the larger bond distance, NO^- or NO? Assume that this energy diagram also applies to NO.

25) The molecular orbital energy diagram for the valence orbitals of HF is shown below. Use this diagram to answer the following questions. Note that the orbitals labeled $2s_F$ and $2p_F$ are nonbonding orbitals on the fluorine atom; electrons in these orbitals do not affect the bond order.



a) Based on this diagram, what is the bond order in HF?

b) Is HF diamagnetic, or is it paramagnetic? How can you tell?

c) How many nonbonding electrons are there in HF?

d) Draw a picture that shows how the σ orbital is formed from atomic orbitals on hydrogen and fluorine.

e) If an electron were removed from the HF molecule, how would the bond energy be affected?