CHEM 121
Supplemental Questions for Bonding

1. Iodine forms several different polyatomic ions with fluorine. Two of these ions are IF_2^+ and IF_2^-.

a. Draw Lewis dot structures for IF_2^+ and IF_2^-. If necessary, show all resonance structures.

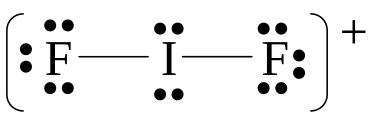
Determine number of valence electrons.

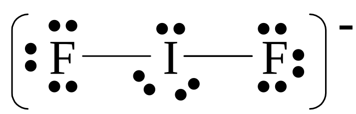
IF_2^+

I	**7**
2 F	**2 x 7**
+1 charge	**-1**
	20

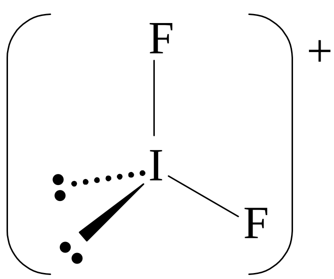
IF_2^-

I	**7**
2 F	**2 x 7**
-1 charge	**+1**
	22

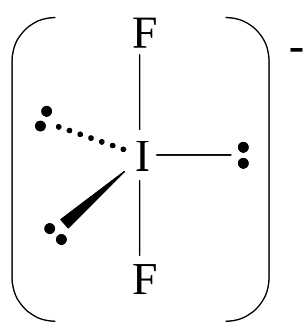




b. Draw the electron pair geometry for each ion. Write the name of the geometry below the structure.

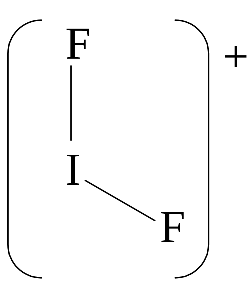


tetrahedral

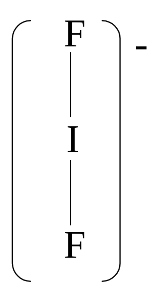


trigonal bipyramidal

c. Draw the molecular geometry of each ion. Write the name of the geometry below the structure.



bent

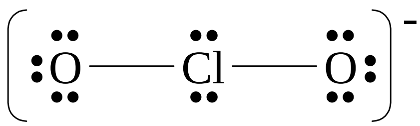


linear

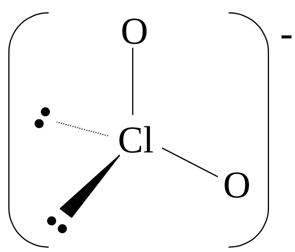
2a. Draw a Lewis dot structure for the chlorite ion, ClO_2^-, <u>assuming no resonance</u>.

Determine number of valence electrons.

Cl	**7**
2 O	**2 x 6**
-1 charge	**1**
	20

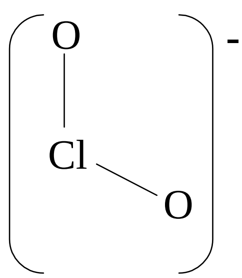


b. Draw the electron pair geometry of ClO_2^- and give the name of this geometry.



tetrahedral

c. Draw the structure of ClO_2^- and give the name of this geometry.



bent

d. What is the ideal O-Cl-O angle in ClO_2^-? Will the actual angle be smaller or larger than this? Why?

The ideal O-Cl-O bond angle is 109.5°, but the actual O-Cl-O bond angle will be smaller because the lone pairs repel the bonding pairs, forcing them together.

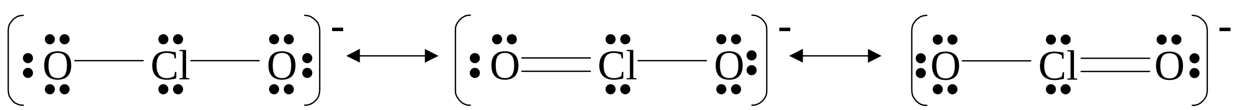
e. Calculate the formal charges in ClO_2^-. What are the oxidation numbers of each element in this ion? Why might the formal charges and the oxidation numbers be different?

$$FC_{Cl} = 7 - [4 + 1/2(4)] = +1 \qquad FC_O = 6 - [6 + 1/2(2)] = -1$$

The oxidation number of Cl is +3, and both oxygens are -2 *(by simply applying the rules from last semester)***.**

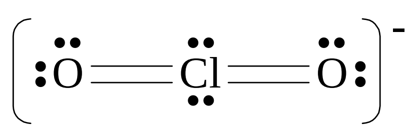
The formal charges and oxidation numbers may be different because of the way each method counts electrons. Formal charges assume all bonds are purely covalent (electrons are equally shared in a bond) and lone pairs belong to the atom on which they are placed in a Lewis dot structure. Oxidation numbers assume that the electrons in a bond belong solely to the more electronegative atom.

f. Draw the <u>three</u> most important resonance structures for ClO_2^-. Indicate which one or ones will contribute the most to the hybrid structure of ClO_2^- and briefly explain why.



The last two make the largest contribution to the resonance hybrid structure of ClO_2^- because they have the greatest number of bonds, place formal charges of zero on Cl and the O which is double bonded to the Cl, and places a -1 charge on the other O.

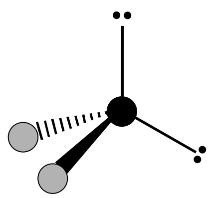
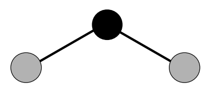
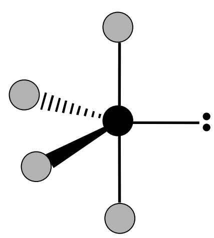
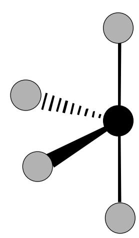
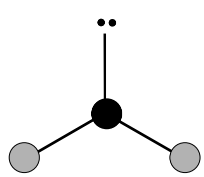
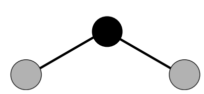
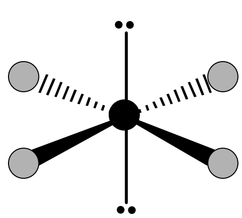
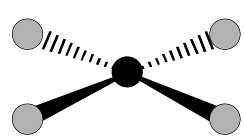
There is another resonance structure, and it makes a smaller contribution to the resonance hybrid, because it places a -1 formal charge on the least electronegative atom.



g. Why can you draw these additional resonance structures?

Cl can have an expanded octet.

3a. Name the given electron pair geometries. Draw and name the structure that derives from the electron pair geometry. Indicate the hybridization on the central atom. Atoms are shown as filled circles and lone pairs are shown as dots.

Electron Pair Geometry	Molecular Geometry	Hybridization
 **tetrahedral**	 **bent**	**sp^3**
 **trigonal bipyramidal**	 **see-saw**	**sp^3d**
 **trigonal planar**	 **bent**	**sp^2**
 **octahedral**	 **square planar**	**sp^3d^2**

b. Place the following bonds in order of increasing bond length.

F - H   C - H   B - H   O - H   N- H

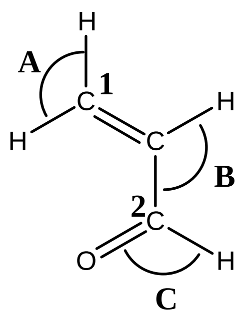
F - H   O - H   N- H   C - H   B - H

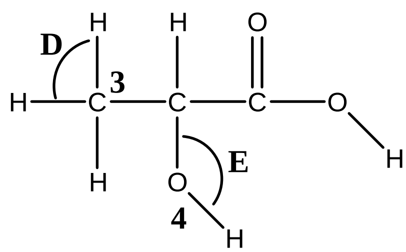
c. Place the following in order of decreasing bond length.

C ≡ N   C - N   C = N

C - N   C = N   C ≡ N

d. Indicate the hybridization of the indicated atoms (denoted by numbers) and give approximate values for the bond angles (denoted by letters) in the compounds shown below.





Bond Angles (°)		Hybridization	
A:	**120**	**1:**	**sp^2**
B:	**120**	**2:**	**sp^2**
C:	**120**	**3:**	**sp^3**
D:	**109.5**	**4:**	**sp^3**
E:	**<109.5**		

4. The fulminate anion has the structural formula CNO^-. It is an isomer of the cyanate anion, structural formula NCO^-.

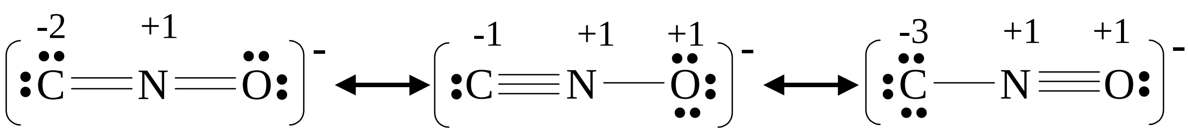
a. Fulminate and cyanate are **constitutional** isomers.

b. Draw all possible resonance structures for the fulminate anion.

Determine the total number of valence electrons.

CNO^-

C	**4**
N	**5**
O	**6**
-1 charge	**+1**
	16



(A) **(B)** **(C)**

c. Calculate the formal charges for the different atoms in each resonance structure. Indicate those charges on the appropriate resonance structure.

For resonance structure A

$FC_C = 4 - [4 + 1/2(4)] = -2$

$FC_N = 5 - [0 + 1/2(8)] = +1$

$FC_O = 6 - [4 + 1/2(4)] = 0$

For resonance structure B

$FC_C = 4 - [2 + 1/2(6)] = -1$

$FC_N = 5 - [0 + 1/2(8)] = +1$

$FC_O = 6 - [6 + 1/2(2)] = -1$

For resonance structure C

$FC_C = 4 - [6 + 1/2(2)] = -3$

$FC_N = 5 - [0 + 1/2(8)] = +1$

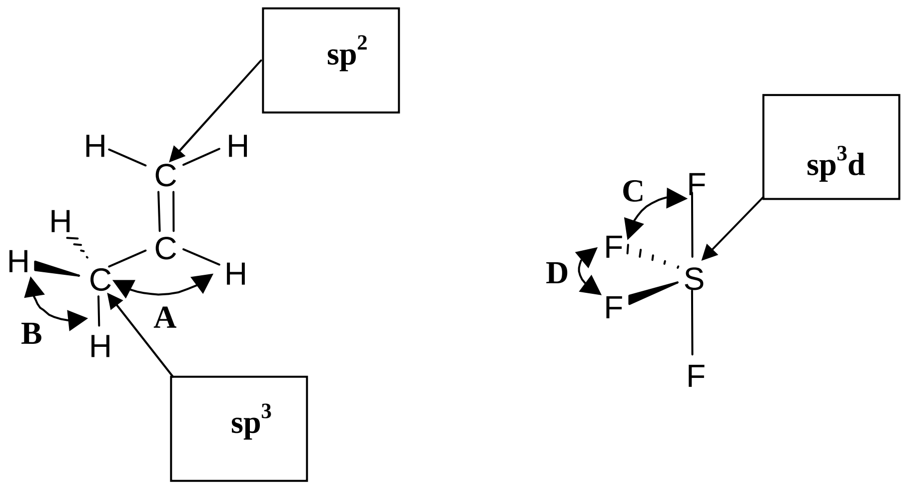
$FC_O = 6 - [2 + 1/2(6)] = +1$

Formal charges are shown on the resonance structures in part b.

d. The fulminate anion is very unstable. Given your answer in part c, suggest a reason for this.

The fulminate anion can't have any resonance structure that obeys the Electroneutrality Principle. All three structures separate charge, although structure B is the best at minimizing the formal charges. Structures A and C have large formal charges on the C. These structures also put these large negative formal charges on the least electronegative atom in the ion (C). Structure C also puts a formal positive charge on the most electronegative atom in the ion (O).

5. Give values for the indicated bond angles in this pair of molecules, be as specific as possible. In the boxes write the hybridization of the atom in question.



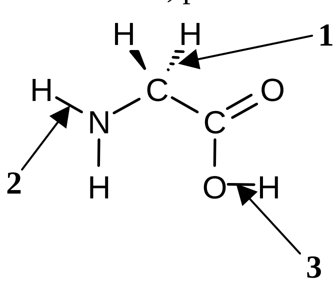
A: **120°**

B: **109.5°**

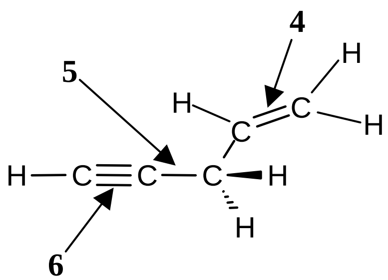
C: **< 90°**

D: **< 120°**

6. For each molecule, place the numbered bonds in order of increasing bond lengths.



3, 2, 1 (atomic radii increase in the order O, N, C)

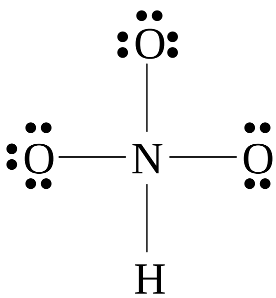


6, 4, 5 (triple bond is shortest, single bond longest)

7a. The chemical formula for nitric acid is written as HNO_3, but this doesn't tell us whether the H is attached to the nitrogen or to one of the oxygens. Draw a Lewis dot structure where the H is attached to the N (and the oxygens are all bound to the N). Include all appropriate resonance structures, if any. **Hint:** read the whole question before answering part a.

Number of electrons to place

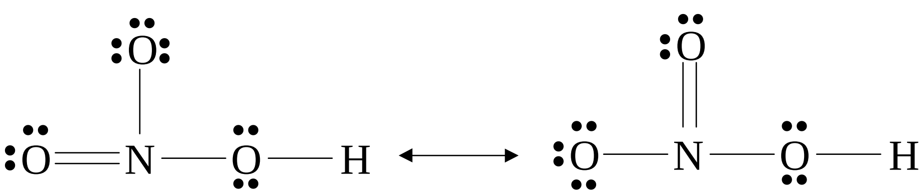
3 O	**3 x 6**
N	**5**
H	**1**
Total	**24**



The octet on one of the oxygens can not be completed. We could draw "resonance structures", making each of the oxygens in turn have an incomplete octet. This is not, however, really necessary.

b. Draw a Lewis dot structure where the H is attached to one of the O (and all the oxygens are bound to the N). Include all resonance structures, if any.

The electron count is the same as above.



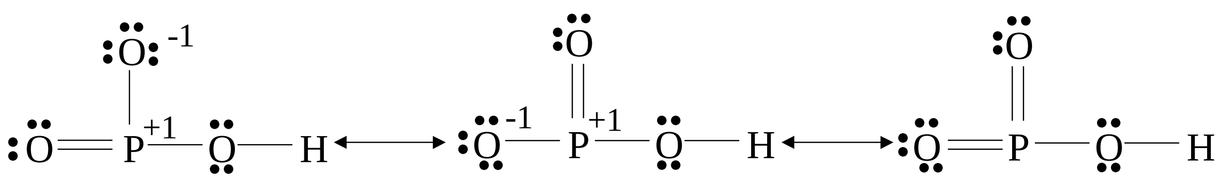
c. Which of the two structures (the one you drew in part a, or the one in part b) can not be the correct Lewis dot structure for HNO_3? Briefly explain why.

The first one (in part a) can not be correct since one of the oxygens has an incomplete octet.

d. The acid HPO_3 exists and it is isoelectronic with HNO_3. Draw the Lewis dot structure for this compound, again including all resonance structures. Calculate the formal charges in each resonance structure and use these to explain which one of the resonance structures contributes most to the resonance hybrid.

Isoelectronic means that two molecules have the same number of electrons (and usually the same shape).

We can then take the resonance structures in part b for HNO_3 and directly write two resonance structures for HPO_3. A third resonance structure can be written because P can have an expanded octet.

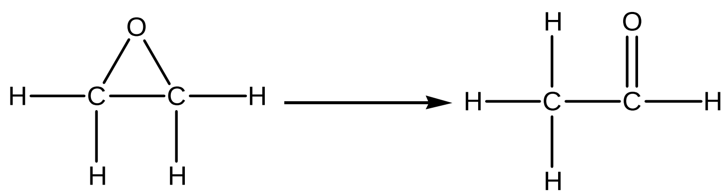


The formal charges are shown on each resonance structure.

The third resonance structure contributes the most, because it has minimized formal charge and has the maximum number of covalent bonds, as required by the Electroneutrality Principle.

No resonance structures may be drawn in which there is a double bond between the phosphorous and the oxygen that is attached to the H. This would place a formal positive charge on the oxygen, and violate the Electroneutrality Principle.

8a. An isomerization reaction converts one isomer to another. Using the bond dissociation energies found at the end of the test, estimate ΔH for the isomerization of ethylene oxide (a gas) to acetaldehyde (a liquid).



$\Delta H = \Sigma D$ (bond broken) - ΣD (bonds formed)

$\Delta H = 2\ D_{C\text{-}O} + D_{C\text{-}H} - D_{C\text{-}H} - D_{C=O}$

$\Delta H = 2\ (358) + 413 - 413 - 732$ kJ/mole

$\Delta H = -16$ kJ/mole

ΔH for this reaction is approximately -16 kJ/mole

b. Explain why the ΔH value that you calculated in part a is only an estimate.

The tabulated D values are averages of ΔH for breaking bonds in many compounds in the gaseous state. If one of the molecules involved in the reaction has bonds that are significantly different from the average, the predicted ΔH will be inaccurate (FYI this is the case with the reactant). There will also be inaccuracies introduced if one or more of the molecules is not a gas, as is in this example.

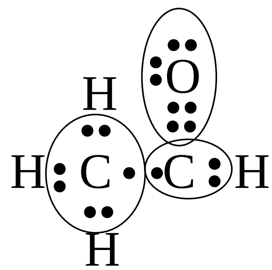
c. The compounds in part a are **constitutional (or structural)** isomers.

d. Calculate the formal charges and the oxidation numbers for each atom in acetaldehyde. Are they the same? Should they be? Note that all the bonds are shown, but no lone pairs are!

The formal charges in acetaldehyde are all zero.

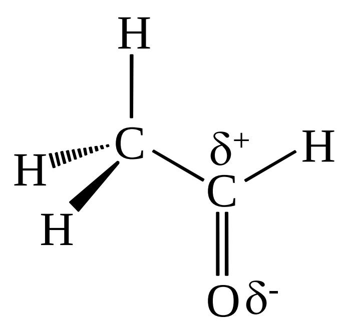
By the rules of oxidation numbers from CHEM 120, the oxidation number of H is +1 and the oxidation number of O is -2. Since the sum of the oxidation numbers for each element must be 0, the two oxidation numbers of the two carbons must sum to -2, but we don't know if they are both -1 or some other combination that sums to -2..

The oxidation numbers on the carbons can be calculated using the definition of oxidation number (electrons in bonds belong to more electronegative atom). This is shown schematically below. Note that the electrons in the C-C bond are split equally between the two carbons because these atoms have the same electronegativity.



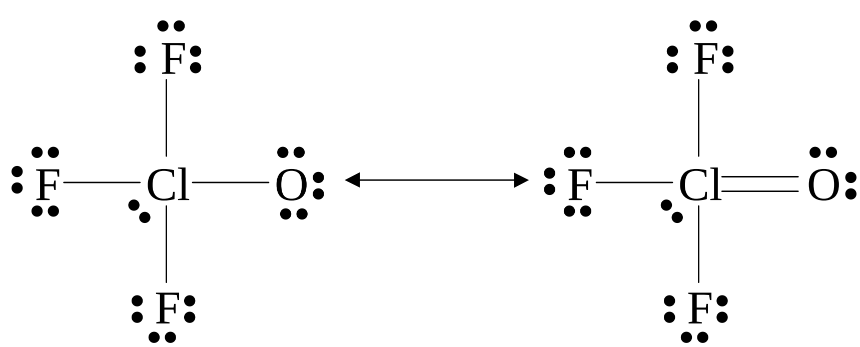
When drawn this way it is clear that the tetrahedral C has 7 electrons (3 more than it started with) and the trigonal planar C has 3 electrons (1 less than it started with). Therefore, the tetrahedral C has an oxidation number of -3 and the trigonal planar C has an oxidation number of +1.

e. Draw the structure for acetaldehyde that clearly shows the distribution of charge within the molecule (use either the crossed arrow or δ notation). Is this molecule polar?

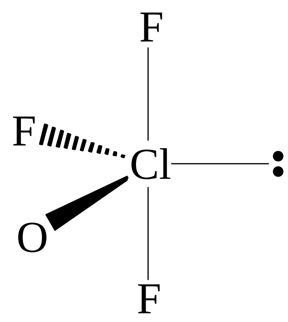


This is a polar molecule.

9a. Draw the Lewis dot structure of the compound ClF_3O. Show any contributing resonance structures.

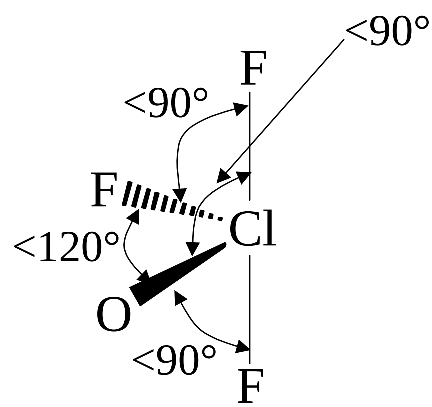


b. Draw the electron pair geometry of ClF_3O and give the name of this geometry.



trigonal bipyramidal

c. Draw the structure of ClF_3O. Indicate any bond angle that deviates from the ideal predicted by VSEPR. Give its approximate value and why it is not ideal.



All angles in this compound are expected to be distorted from the ideal values because the lone pairs repel the bonding pairs and thus force the atoms together; decreasing the bond angles.

d. What is the hybridization of the Cl in ClF_3O? What is the hybridization of O?

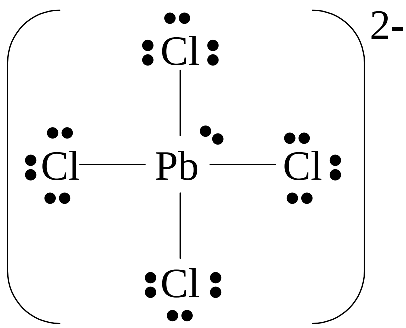
The hybridization of Cl is sp^3d, while the hybridization of O is not defined (it would be sp^2 in the resonance structure with the double bond, or sp^3 hybridized in the resonance structure with the single bond).

e. You could have drawn another structure of ClF_3O with the same number and types of bonds, but with a different arrangement of the atoms in space. These compounds are examples of isomers known as **diastereomers**.

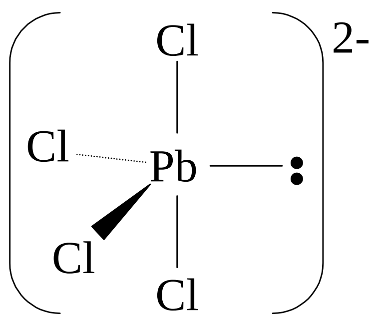
10a. Draw the Lewis dot structure of the $PbCl_4^{2-}$ ion.

$PbCl_4^{2-}$

Pb	**4**
4 Cl	**4 x 7**
-2 charge	**+2**
	34

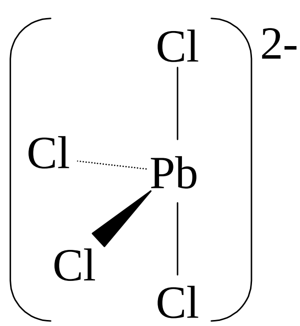


b. Draw the electron pair geometry of the $PbCl_4^{2-}$ ion. Write the name of this geometry below your picture.



trigonal bipyramidal

c. Draw the structure of this ion. Write the name of this geometry below your picture.



see-saw

d. Calculate the formal charges for the different atoms in this ion.

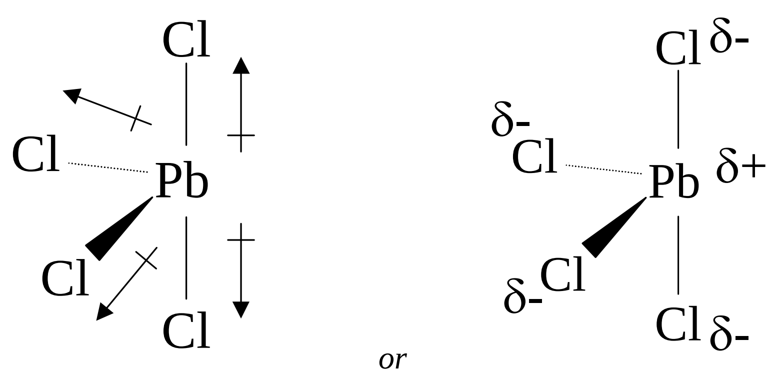
$FC_{Pb} = 4 - [\ 2 + 1/2(8)] = -2$

$FC_{Cl} = 7 - [6 + 1/2(2)] = 0$

e. Are the formal charges you calculated in part d a reasonable description of the charge distribution in $PbCl_4^{2-}$? Is there a better way to describe the electron distribution? In either case, explain your answer.

The formal charge calculation places the full -2 charge for the ion on the Pb. This is not reasonable because Pb is the least electronegative atom in the ion (because it is a metal).

A better way to describe the charge distribution is to consider electronegativity. Cl is more electronegative than Pb, so the electrons in a Cl - Pb bond are pulled toward the Cl. This creates a small positive charge on the Pb and a small negative charge on the Cl.



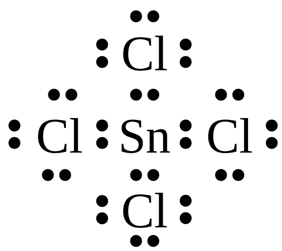
f. What are the oxidation numbers of the different atoms in $PbCl_4^{2-}$? Why are they not the same as the formal charges you calculated in part d?

The oxidation number of Pb is +2 and that of each Cl is -1 (calculated using CHEM 120 rules).

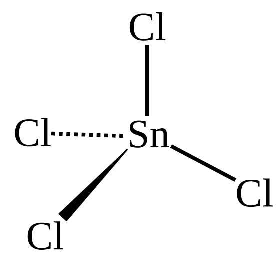
Formal charges consider the electrons in the bonds to be equally shared between the two atoms. Oxidation numbers consider the electrons in a bond to be on the more electronegative atom. The formal charge treats a bond as purely covalent, while the oxidation number treats it as purely ionic.

11a. What is the molecular structure of $SnCl_4$?

Sn	**4**
4 Cl	**4 x 7**
Total	**32**



electron pair geometry (tetrahedral)



molecular geometry (tetrahedral)

b. What are the formal charges in $SnCl_4$?

$FC_{Sn} = 4 - [0 + 1/2(8)] = 0$

$FC_{Cl} = 7 - [6 + 1/2(2)] = 0$

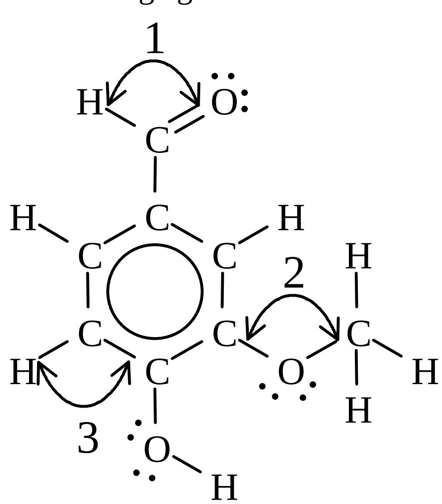
c. What are the oxidation numbers in $SnCl_4$?

Sn^{4+}, Cl^{-}

d. Is $SnCl_4$ polar? Why or why not?

$SnCl_4$ is non-polar. There is an electronegativity difference between the Sn and the Cl, and thus the Sn-Cl bond is polar. But the molecule is symmetric, so it can not be polar.

12. The structure of vanillin, the flavoring agent in vanilla extract, is shown below.



a. Give approximate values for the three bond angles indicated.

1: 120°

2: <109.5°

3: 120°

b. Indicate the shortest carbon-oxygen bond in the molecule.

The carbon-oxygen double bond is the shortest carbon-oxygen bond in the molecule.

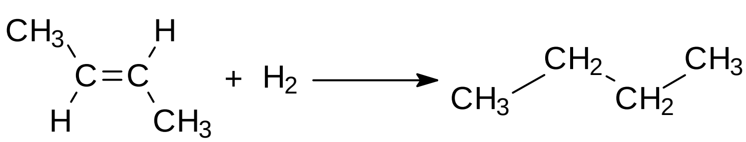
c. Indicate the most polar bond in the molecule.

The oxygen-hydrogen bond is the most polar (largest electronegativity difference).

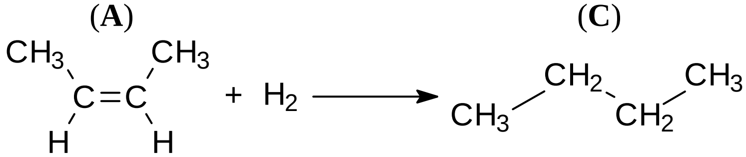
d. In general will a carbon-hydrogen single bond be longer or shorter than an oxygen-hydrogen single bond? Why?

The general trend for atomic size (covalent radius) is that it decreases across the periodic table. Since oxygen's covalent radius will be smaller than carbon's, the hydrogen will be closer to oxygen than carbon. This means that the carbon-hydrogen single bond will be longer than an oxygen-hydrogen single bond.

13. Compounds **A** and **B** react with H_2 to give compound **C**, as shown below.



(**A**) (**C**)



(**B**) (**C**)

a. **A** and **B** are examples of isomers known as **diastereomers**.

b. Using bond dissociation energies calculate ΔH for either the reaction of compound **A** with H_2, or the reaction of compound **B** with H_2. Be sure you specify which one you are doing.

Can do either one, they are the same.

Bonds broken: 1 C=C, 1 H-H

Bonds formed: 1 C-C, 2 C-H

$\Delta H = \Sigma(D_{bonds\ broken}) - \Sigma(D_{bonds\ formed}) = (602. + 436.) - (346. + 2(413.))\ kJ$

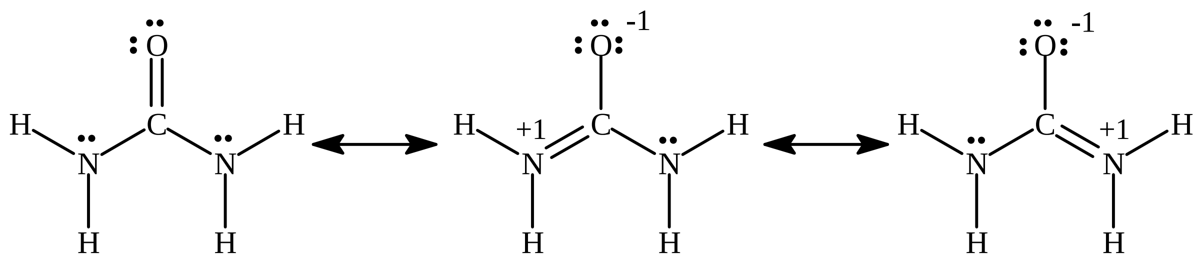
$\Delta H = -134.\ kJ$

ΔH for this reaction is estimated to be -134. kJ.

c. Explain why ΔH for these reactions are expected to be the same.

These compounds are diastereomers, which means they have the same number and types of bonds, but differ only in the arrangement of the atoms in space. Because the same bonds are being broken and formed in the reactions, we expect ΔH for these reactions to be the same.

14a. Urea is a byproduct of metabolism and is a major component of urine. The three resonance structures shown below may be drawn for urea.



Fill in the missing electrons in the above resonance structures. Indicate non-zero formal charges on each atom as appropriate.

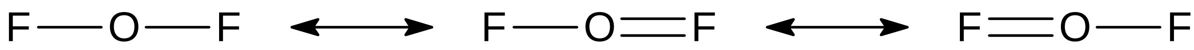
b. Which resonance structure(s) will make the largest contribution to the resonance hybrid structure of urea? Why?

The first resonance structure will make the largest contribution, because it minimizes formal charges according to the electroneutrality principle.

c. The carbon-nitrogen bonds in urea have been found experimentally to be slightly shorter than the average carbon-nitrogen single bond. What can you conclude from these data?

The other two resonance structures (with separated formal charges) do contribute to the resonance hybrid structure of urea, but not as much as the structure without the separation of formal charge.

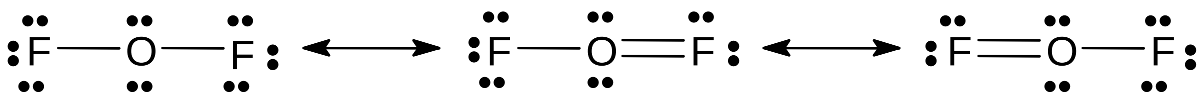
15. Fluorine alone can oxidize oxygen. The product of this reaction is OF_2. A fellow general chemistry student has written the three resonance structures for OF_2 shown below.



(A) (B) (C)

a. Place the missing electrons on the structures.

OF_2	
O	**6**
2 F	**2 x 7**
	20



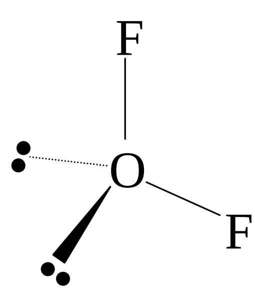
(A) (B) (C)

b. Explain why resonance structures **B** and **C** are not correct. (Hint: don't simply state that F only forms one bond, but explain more fully.)

In both structures B and C oxygen exceeds 8 valence electrons, but it is a second row element which can not have an expanded octet.

Both structures B and C place a formal positive charge on F, the most electronegative atom, in violation of the Electroneutrality Principle.

c. Using only resonance structure **A**, draw the electron pair geometry of OF_2. Write the name of the electron pair geometry under your drawing.

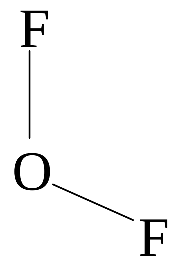


tetrahedral

d. What is the hybridization of the oxygen atom in OF_2?

The oxygen in sp^3 hybridized.

e. Draw the structure of OF_2. Write the name of this geometry below your picture.



bent

f. Estimate the F - O - F bond angle in OF_2.

It is less than 109.5° because of the effect of the lone pairs on the bonding pairs.

g. Is OF_2 a polar molecule? Explain.

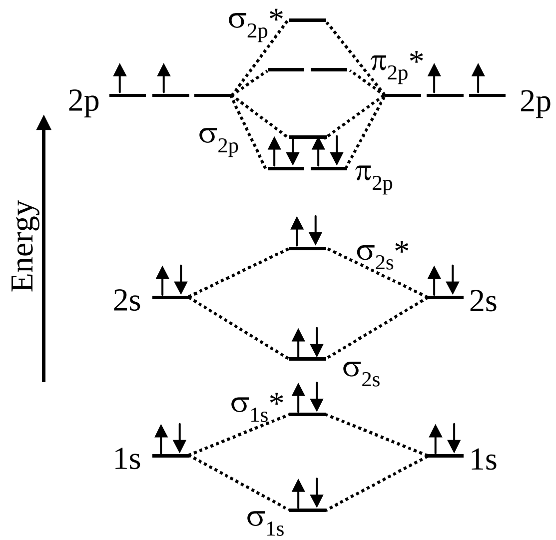
There are no formal charges in OF_2, but F is more electronegative than O, so the O-F bonds will be polar. The polarity of the O-F bonds places a small negative charge on the F and a small positive charge on the O. Since the molecular geometry of OF_2 is asymmetric (bent), this results in charges that are asymmetrically distributed, and so OF_2 is polar.

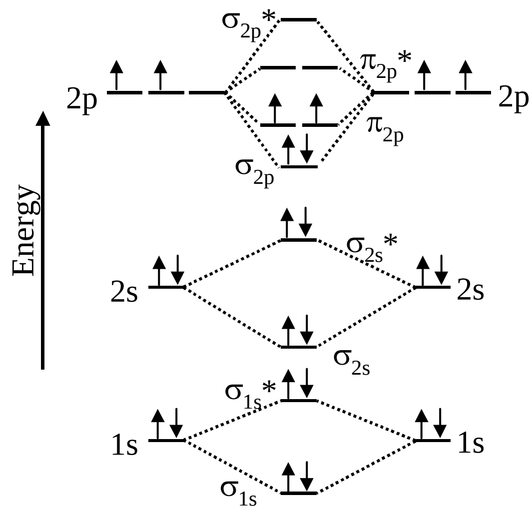
h. Why might OF_2^+ be formed, but not OF_2^-?

OF_2^+ will have a total of 19 valence electrons, which can be placed without exceeding an octet of electrons on any atom. This would give a free radical.

OF_2^- will have a total of 21 valence electrons, which can not be placed without exceeding an octet on any atom.

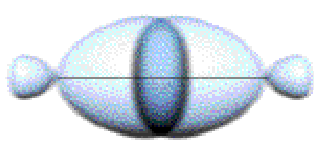
16a. The C_2 molecule is diamagnetic. Which of the following two possible MO energy level diagrams is correct for C_2?



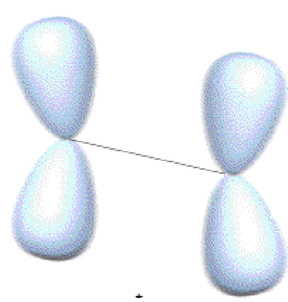


The diagram on the left is correct for C_2.

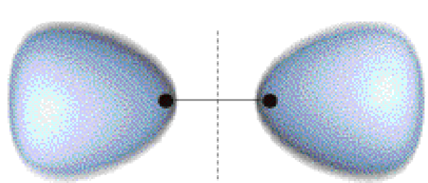
b. Identify the following molecular orbitals, be as specific as you can.



σ_p

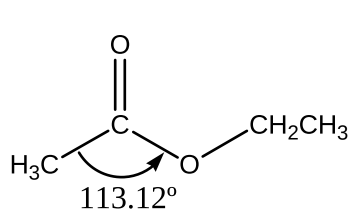


π_p*

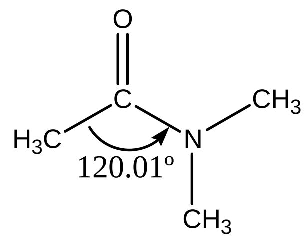


σ_s*

17. In ethyl acetate (compound **A**) the C-O bond length in the carbonyl group is 1.206 Å (1 Å = 1×10^{-10} m), and the C-C-O bond angle is 113.12º, while in N, N-dimethylacetamide (compound **B**) the C-O bond length is 1.239 Å and the C-C-N bond angle is 120.01º.

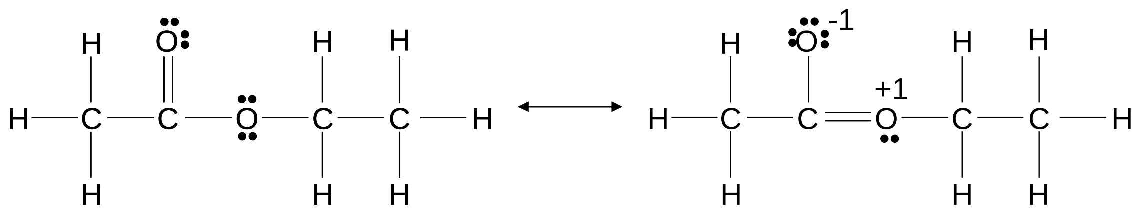


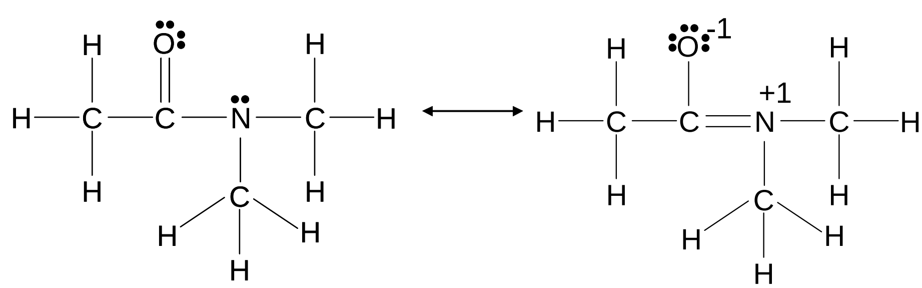
(A)



(B)

a. Draw Lewis dot structures for both compounds, showing the contributing resonance structures (each compound has two). Indicate formal charge when it is not zero (show relevant calculations).





$FC_O = 6 - [4 + \frac{1}{2}(4)] = 0$ *(C=O)*
$FC_O = 6 - [2 + \frac{1}{2}(6)] = +1$ *(C=O-C)*
$FC_O = 6 - [6 + \frac{1}{2}(2)] = -1$ *(C-O single bond)*

$FC_N = 5 - [4 + \frac{1}{2}(6)] = 0$ *(no double bond)*
$FC_N = 5 - [0 + \frac{1}{2}(8)] = +1$ *(double bond)*

The formal charge on all other atoms is zero.

b. Use VSEPR theory to explain the observed difference in the C-O bond lengths and in the given bond angles.

The shorter C-O bond length in the carbonyl portion of compound (A) indicates that the C-O bond has more double bond character, and thus the first resonance structure shown for it makes the largest contribution to the resonance hybrid of (A).

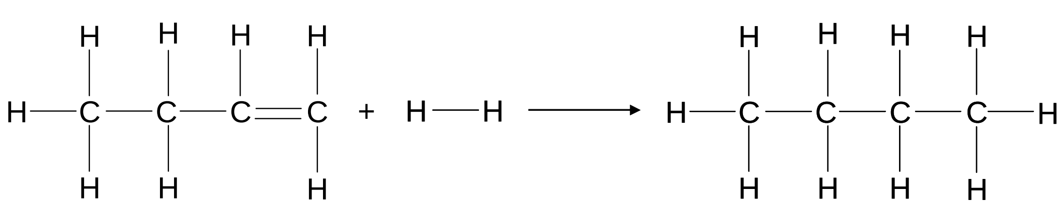
For compound (B), the longer C-O bond length indicates that the C-O bond has less double bond character and must result from the second resonance structure contributing more.

Since in compound (A) we know that the carbonyl C-O bond has more double bond character (from the bond length), there should be more repulsion between the bonding pairs in the C-O bond and the other bonding pairs (the C-C and the other C-O bonds). This should lead to the observed decreased C-C-O bond angle as the "fat" double bond tries to push the other bonds out of the way. The electronegativity difference between the C and the O will pull electron density away from the carbonyl C, and decrease the bonding pair-bonding pair repulsion. This would also lead to a decrease in the C-C-O bond angle.

For compound (B), the C-O bond has less double bond character, and so pushes on the other bonds less strongly. But, the C-N bond has more double bond character, and it must be repelling the electrons in the other bonds. Finally, there are the electronegativity differences to consider. The effect should be the same as that discussed above; a decrease in the C-C-N bond angle. Since the C-C-N bond angle is essentially 120^o, we must conclude that all of these different effects balance each other out and lead to no net distortion of the structure.

18a. There are four compounds with the chemical formula C_4H_8: 1-butene, 2-methylpropene, *cis*-2-butene and *trans*-2-butene. Based on gas-phase bond dissociation energies, we would expect all of these compounds to have the same ΔH_{rxn} for hydrogenation (which is the reaction with H_2 to give an alkane). Calculate ΔH for the hydrogenation of 1-butene and explain why it should the same as that for the other compounds.

The relevant reaction is



In this reaction one C=C, and one H-H bond are broken, while one C-C and two C-H bonds are formed.

$$\Delta H = D_{C=C} + D_{H\text{-}H} - 2\ D_{C\text{-}H} - D_{C\text{-}C} = 602 + 436 - 2(413) - 346\ kJ/mole$$

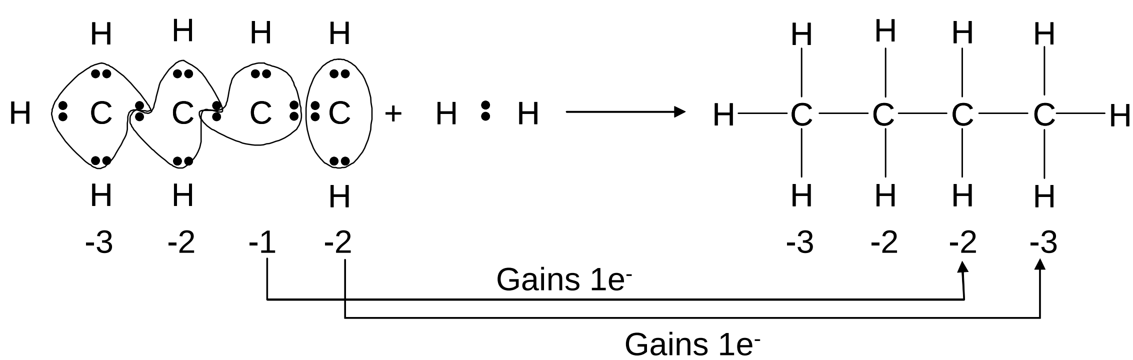
ΔH = -134 kJ/mole

ΔH for the hydrogenation reaction is estimated to be -134 kJ/mole.

In all of the compounds the same number and types of bonds are broken and formed. Because this method of estimating ΔH considers only the numbers and types of bonds broken and formed, ΔH will be the same for all of the compounds.

b. The hydrogenation of 1-butene may also be thought of as a redox reaction. From the Lewis dot structure of 1-butene and the product of the hydrogenation (butane), calculate the oxidation numbers of the carbons. Indicate which carbons change oxidation number, and identify the oxidant and the reductant.

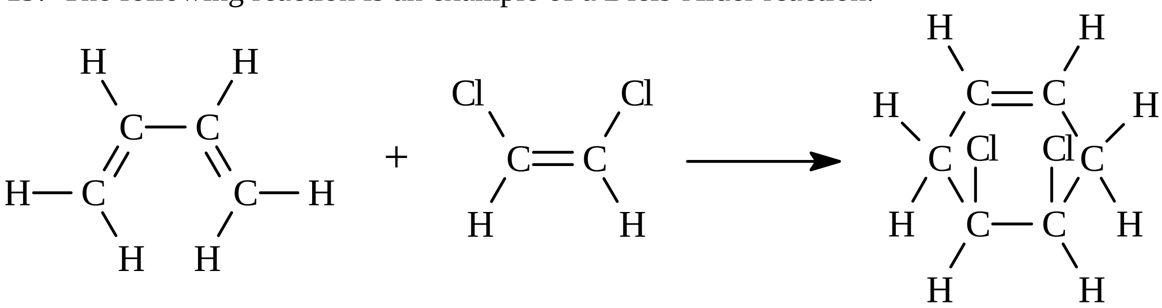
Oxidation numbers for each C atom are shown below. The oxidation number of all H atoms bonded to a C atom is +1, and the oxidation number of H in H_2 is zero (because it is the elemental form of hydrogen).



To calculate oxidation numbers from a Lewis dot structure first count the electron according to the following rules: count all electrons in lone pairs as belonging to the atom on which the lone pair resides, count all electrons in bonds as belonging to the more electronegative atom, and if the atoms are the same, split the electrons evenly. The oxidation number is then the number of valence electrons in the neutral atom minus the total number of electrons determined using the rules. The results of these calculations are shown above. *Note that you only had to do the calculation once, and then realize that there were similarities between the alkene and the alkane.*

1-Butene gains two e-, and is reduced, so it is the oxidant. H2 loses two e-, so it is oxidized, and is the reductant.

19. The following reaction is an example of a Diels-Alder reaction.



(**A**)

a. Estimate ΔH for this reaction from gas-phase bond dissociation energies.

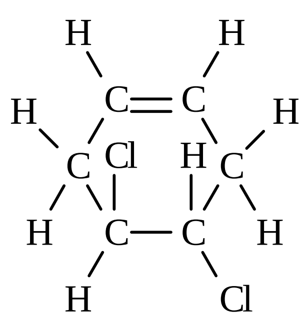
Bonds broken: 3 C=C, 1 C-C
Bonds formed: 1 C=C, 5 C-C

$\Delta H = \Sigma\ (D_{bonds\ broken}) - \Sigma\ (D_{bonds\ formed})$
$\Delta H = 3\ C{=}C + 1\ C{-}C - 1\ C{=}C - 5\ C{-}C$
$\Delta H = 3\ (602) + 1\ (346) - 5\ (346) - 1(602)\ kJ$
$\Delta H = -180\ kJ$

For this reaction ΔH is estimated to be -180 kJ.

You can also do this by breaking all the bonds in the reactants and then forming all the bonds in the product. A third alternative is to note that overall we break 2 C=C, net, and form 4 C-C, net.

b. Compound (**A**), above, and compound (**B**), below, are isomers. What kind of isomers are they?



(**B**)

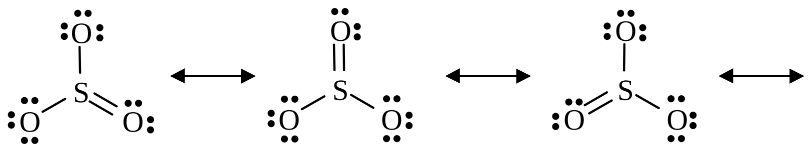
These compounds are diastereomers.

c. Estimate ΔH for the conversion of compound (**A**) to compound (**B**).

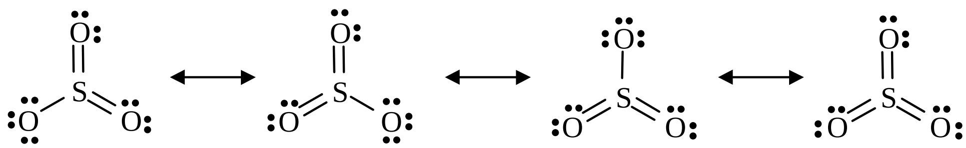
The bonds broken are the same as the bonds formed, so ΔH = 0 for the isomerization reaction.

20. SO_3 is an atmospheric pollutant that results from the oxidation of SO_2 by oxygen.

a. Draw the Lewis dot structure of SO_3. If resonance is possible, draw all contributing resonance structures.



(1) (2) (3)



(4) (5) (6) (7)

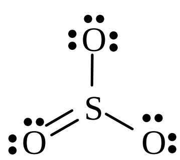
Resonance structures 4 - 7 can be written because S can have an expanded octet.

b. Calculate the formal charges for each atom in SO_3.

In structures 1 - 3, S has a formal charge of +2 = 6 - [0 + 1/2(8)]
In structures 4 - 6, S has a formal charge of +1 = 6 - [0 + 1/2(10)]
In structure 7, S has a formal charge of 0 = 6 - [0 + 1/2(12)]

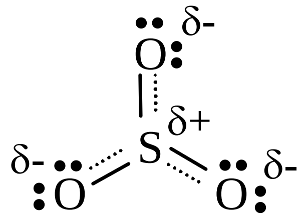
Doubly bonded O have a formal charge of 0 = 6 - [4 + 1/2(4)]
Singly bonded O have a formal charge of -1 = 6 - [8 + 1/2(2)]

c. Draw and name the electron pair geometry of SO_3.

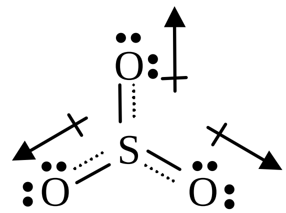


The electron pair geometry of SO_3 is trigonal planar (only one resonance structure shown).

d. Draw and name the structure of SO_3, including resonance and distribution of charge, if any.



or



The structure of SO_3 is trigonal planar.

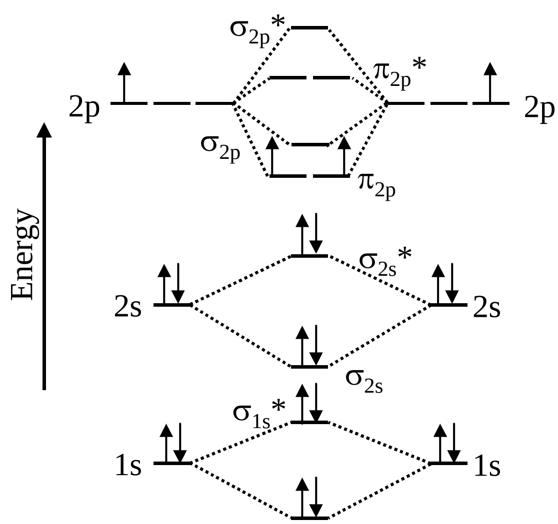
e. Is SO_3 a polar molecule? Explain.

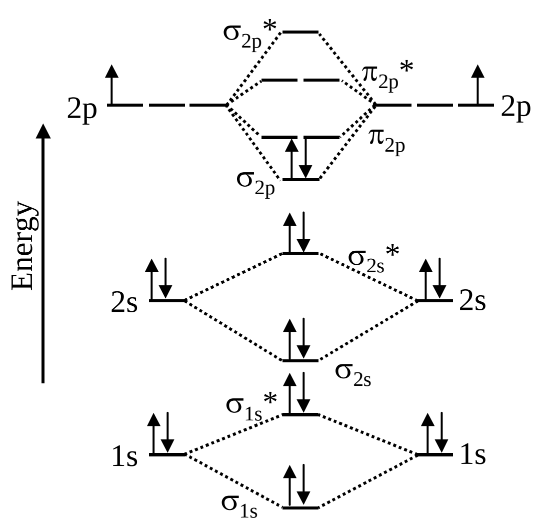
SO_3 has formal charges and polar bonds, but the charge is symmetrically distributed, so SO_3 is non-polar.

f. SO_3 is a greenhouse gas, what must be true?

SO_3 must absorb infrared light because it has an asymmetric vibration.

21. In class we discussed how the molecular orbital energy level diagram for O_2 and F_2 is what we expected, with σ_{2p} lower in energy than π_{2p}. For all other homonuclear diatomics of the second period the π_{2p} is lower in energy than σ_{2p}. Fill in both molecular orbital energy level diagrams shown below for B_2, and use the diagrams to explain what property (or properties) of B_2 prove(s) that π_{2p} is lower in energy than σ_{2p} for these elements.

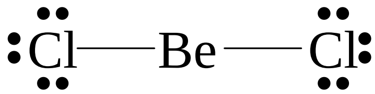




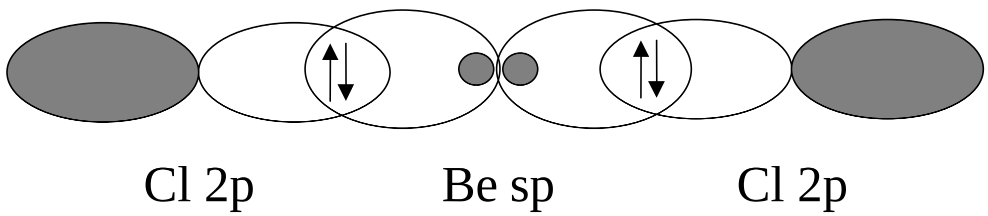
The magnetic properties of B_2 will provide direct evidence for the MO energy level diagram. If the diagram on the left is correct, then B_2 will be paramagnetic. If the diagram on the right is correct, then B_2 will be diamagnetic.

22a. Using valence bond theory, qualitatively sketch the orbitals involved in bonding in the molecule $BeCl_2$. Be sure to show all parts of all orbitals, and show the electrons involved as arrows on each orbital.

Start with the Lewis dot structure.



The electron pair geometry is linear, as is the molecular geometry. This means the Be is sp hybridized.



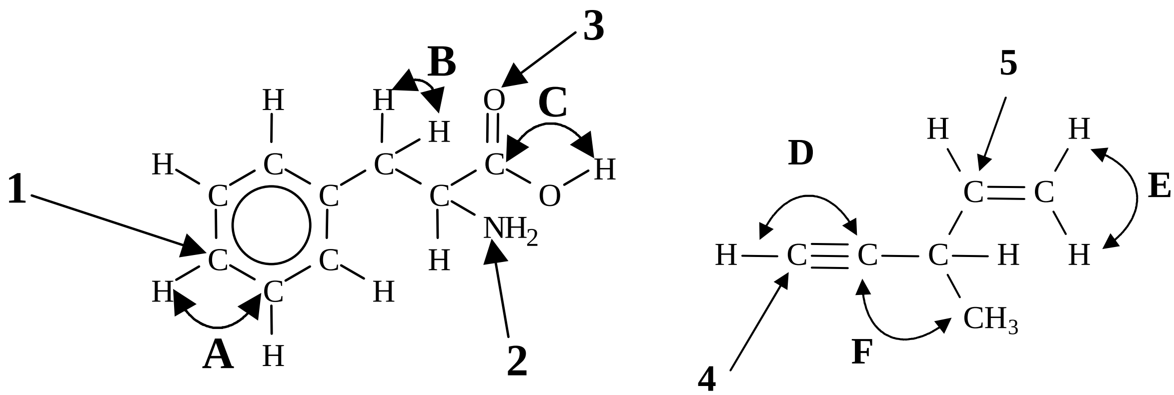
b. What hybrid orbitals are present on the Be atom? **sp hybrid orbitals**

c. Why must hybridization be invoked in valence bond theory to describe bonding in $BeCl_2$?

Hybridization is invoked so that the correct number of orbitals, with the proper orientation, required for overlap (i. e. form bonds) with the Cl 2p orbitals be present. Hybridization is also required so that the Pauli exclusion principle will be followed.

You might have been tempted to write double bonds between the Be and the Cl atoms, because Be does not have a complete octet. You can't do this because it would place formal +1 charges on the Cl atoms and a formal -2 charge on the Be, which would violate the electroneutrality principle. In MO theory you would need to consider the interaction between the empty Be p orbitals and the full Cl p orbitals. You can also consider this interaction in valence bond theory, but you still need to use ideas from MO theory.

23. Identify the bond angles (letters) and hybridization (numbers) in each of these molecules. How many π bonds are there in each molecule? How many σ?



1	**sp^2**
2	**sp^3**
3	**sp^2**
4	**sp**
5	**sp^2**

A	**120º**
B	**109.5º**
C	**<109.5º**
D	**180º**
E	**120º**
F	**109.5º**

There are 23 σ bonds in the compound on the left, and 13 σ bonds in the compound on the right.

The compound on the left has either 2 or 4 π bonds. If you consider the benzene ring to have three double bonds than it is 4 π bonds, but if you consider this as a single delocalized π bond, then there are only 2 π bonds. The compound on the right has 3 π bonds.