

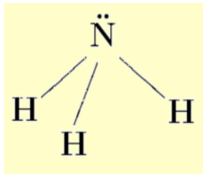
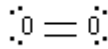
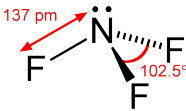
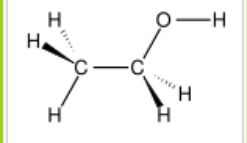
CH301 Fall 2009 Worksheet 7 Answer Key

1. How can you decide whether a bond is polar or not? If a molecule has polar bonds, does that make the molecule polar?

A polar bond is between two atoms with different electronegativities. One atom with hog the electrons, giving it a slightly negative charge, denoted δ^- . The other atom will have a slightly positive charge, δ^+ . A molecule with polar bonds may not be polar overall.

Symmetry of the molecule can cancel out the dipoles created by the polar bonds. For example, BF_3 has three polar bonds but all these polar bonds are in the same plane and cancel each other out. If you replace one of the F with another atom then there would be polarity in the molecule because the electronegativities would not cancel out.

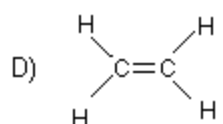
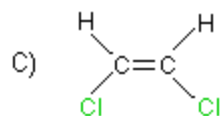
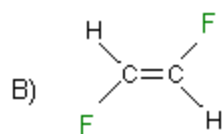
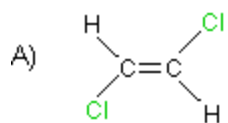
2. Fill in the chart and then rank the molecules in order of increasing polarity.

Draw structure	<p>NH_3</p> 	<p>O_2</p> 	<p>NF_3</p> 	 <p>Chemical structure of ethanol</p>
Calculate ΔEN of all bonds	$\Delta\text{EN} = 3 - 2.2 = .8$	$\Delta\text{EN} = 2.5 - 2.5 = 0$	$\Delta\text{EN} = 4 - 3 = 1$	$\Delta\text{EN C-H} = 2.5 - 2.2 = .3$ $\Delta\text{EN C-O} = 3.5 - 2.5 = 1$ $\Delta\text{EN O-H} = 3.5 - 2.2 = 1.3$
Polar or nonpolar molecule?	Polar	Nonpolar	Polar	Polar and nonpolar ends

$\text{O}_2 < \text{C}_2\text{H}_5\text{OH} < \text{NH}_3 < \text{NF}_3$

Homomuclear diatomic molecules are never polar.

3. Rank the following in order of increasing polarity:



$D = B = A < C$

Molecule C is the only one where the dipoles do not cancel out.

4. Explain how carbon, with only 2 unpaired electrons, can form 4 bonds to fulfill its octet. Account for any energy changes (if you're putting in energy, where is it then released). What kind of hybrid orbitals will carbon then form?

One of the electrons in the 2s orbital is promoted to the 2p orbital, giving carbon the electronic configuration of $[\text{He}]2s^1 2p^3$. Now there are 4 unpaired electrons that can bond. Promoting an electron takes energy, but the amount of energy released when bonds form compensates this. Also, only a small amount of energy is needed to initially promote the electron to the 2p orbital. If the electrons stay in the 2s and 2p orbitals then we would see 2 different types of bonds, but we know that we only see one type. In order to form 4 bonds these electrons will then hybridize their orbitals to form four sp^3 hybrid orbitals.

5. Group 14 elements can all form four bonds. However, as you go down the periodic table it gets harder for them to form multiple bonds with one another like carbon can. Explain why carbon is so special.

As you go down the periodic table the atom radii increases (see these trends are still important!), which means that they are too big to have significant pi overlap.

6. Explain how each of the hybrid orbitals are constructed. Account for the electron arrangement in the shape of molecules.

sp

sp^2

sp^3

sp^3d

sp³d²

First recognize which atomic orbitals are blending to form hybrid orbitals. Remember that electrons like to be as far away as possible from each other, so the hybrid orbitals are going to distribute with the maximum angle of separation as possible.

sp: a linear arrangement of electron pairs requires two hybrid orbitals, and so an s-orbital and a p-orbital are mixed to form two sp hybrid orbitals.

sp²: seen in trigonal planar molecules, one s-orbital and two p-orbitals mix to form three sp² hybrid orbitals. These hybrids all lie in the same plane and point toward the corners of an equilateral triangle.

sp³: tetrahedral, an s-orbital and three p-orbitals mix together to give four sp³ hybrid orbitals that point to a corner of a tetrahedron.

sp³d: trigonal bipyramidal, a d orbital is included in this hybrid orbital because the central atom has to accommodate for 5 electron pairs. There are only four sp³ hybrid orbitals, so we must include the d now. An s-orbital, three p-orbitals and a d-orbital blend together.

sp³d²: octahedral, central atoms that have 6 electron pairs to account for must use another d orbital. So, an s-orbital, three p-orbitals and two d-orbitals blend together to make six hybrid sp³d² hybrid orbitals.

7. Is it possible to have more hybrid orbitals than atomic orbitals of an atom?

No, orbitals are not added or reduced when hybridizing atomic orbitals.

8. For formic acid, HCOOH:

Draw the Lewis structure

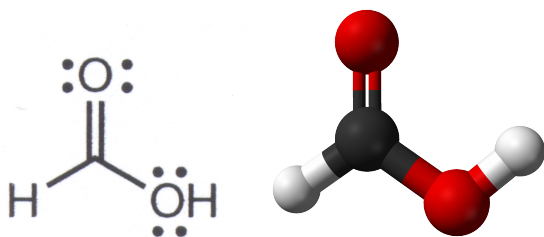
Use VSEPR to determine the geometry

Identify bond angles

Identify hybrid orbitals

How many sigma and pi bonds? (Hint: There is an -OH group.)

Answer:



The carbon atom has three sigma bonds and no lone pairs, the oxygen atoms and hydrogen surround it in a trigonal planar arrangement, with bond angles of 120°. The oxygen of the -OH group is in the plane with carbon, but the hydrogen of the -OH is not. Oxygen has two lone pairs and two sigma bonds, so it has four regions of electron density. Thus, the oxygen of the -OH group has a tetrahedral electron arrangement, with bond angles of 109.5°.

Since there is a double bond between carbon and one of the oxygens a p-orbital from the oxygen will form a pi bond with the non-hybridized p orbital of carbon. The three sigma bonds around carbon are sp² hybridized. The O of the -OH group has four regions of electron density, so it is sp³ hybridized.

9. The bond angle of an sp^3 hybridized atom is 109.5° and that of an sp^2 hybridized atom is 120° . Should the bond angle increase or decrease between two hybrid orbitals when the s-character of a hybrid orbital increases?

Increase. As more orbitals are hybridized the hybrid orbital looks less like an s orbital. So an sp hybrid orbital looks most like an s-orbital and an sp^3d^2 hybrid orbital looks least like an s orbital. Since sp looks the most like an s-orbital and there are only two sp hybrid orbitals they have the highest bond angle.

10. Why does valence bond theory not account for bonding in polyatomic molecules like CH_4 ?

VB theory says that bonds are formed when unpaired electrons in valence-shell atomic orbitals pair by atomic orbital overlap end-to-end to form sigma bonds or side-to-side to form pi bonds. However, carbon only has 2 unpaired valence electrons but as we see with methane, CH_4 , it forms four bonds. This is why we see hybridization of orbitals, so that we can have four unpaired electrons. In the case of methane these hybrid orbitals are sp^3 .

11. Explain the difference between sigma and pi bonds. What types of orbitals are involved in each?

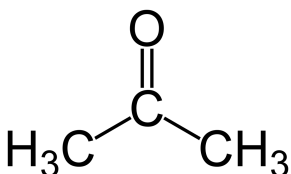
Sigma bonds are areas of electron density along the axis between the contributing atoms. Sigma bonds can form between s orbitals, p orbitals, and all hybrid orbitals. Pi bonds are areas of electron density off the axis between the contributing atoms. Pi bonds can be formed by p orbitals.

12. Explain why hybrid orbitals make sigma bonds.

S orbitals can only form sigma bonds because they form areas of electron density that surround the nucleus of the atoms, so the bonds formed by them can only be along the axis. All hybrid orbitals have some s character, so they form sigma bonds.

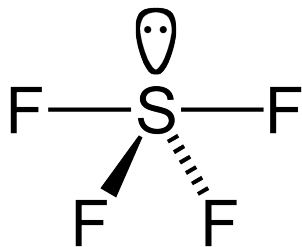
For questions 13 through 15: Draw the Lewis dot structure for the given compound. How many sigma bonds? How many pi bonds? Name the contributing orbitals.

13. CH_3COCH_3 (Acetone)



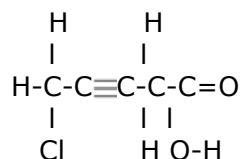
9 sigma bonds: 6 $1s-sp^3$ (between H-C), 3 sp^3-sp^2 (between C-C and C-O)
1 pi bond: $2p-2p$ (between C-O)

14. SF_4



4 sigma bonds formed by sp^3 from fluorine and dsp^3 from sulfur hybrid orbitals

15. $CH_2ClCCCH_2COOH$



12 sigma bonds: 5 $1s\text{-}sp^3$ (between H-C and H-O), 1 $sp^3\text{-}sp^3$ (between C-Cl), 2 $sp^3\text{-}sp$ (C-C), 1 $sp\text{-}sp$ (C-C), 2 $sp^3\text{-}sp^2$ (C-C and C-O), and 1 $sp^2\text{-}sp^2$ (C-O)
 3 pi bonds: $2p\text{-}2p$ (2 C-C and C-O)

16. How do we know that hybrid orbitals exist?

If hybrid orbitals did not form, spectroscopy would show two separate peaks for the bonds in methane - one for the sigma bond formed by the $1s\text{-}2s$ bond and one taller peak for the $1s\text{-}2p$ bond. However, spectroscopy shows one peak, so hybrid orbitals that all have the same energy must form.

17. Draw the molecular orbitals for Ne_2 . Calculate the bond order. Use MO theory to explain why this diatom does not exist.

See page 111 of the course notes for the Molecular Orbitals

$$\text{Bond Order} = (10 - 10) / 2 = 0$$

Because the bond order is equal to 0, no bond forms. This occurs because the number of bonds and antibonds formed cancel each other out.

18. Rank the following diatoms and diatomic ions in order of decreasing bond order.

a. B_2 , C_2 , N_2

$\text{N}_2 > \text{C}_2 > \text{B}_2$

b. Be_2 , F_2 , O_2

$\text{O}_2 > \text{F}_2 > \text{Be}_2$

c. O_2^+ , O_2 , O_2^-

$\text{O}_2^+ > \text{O}_2 > \text{O}_2^-$

d. N_2^+ , N_2 , H_2

$\text{N}_2 > \text{N}_2^+ > \text{H}_2$

19. Rank the following diatoms and diatomic ions in order of decreasing bond length.

a. B_2 , C_2 , N_2

$\text{B}_2 > \text{C}_2 > \text{N}_2$

b. Be_2 , F_2 , O_2

Be_2 (does not form a bond)

$\text{O}_2 > \text{F}_2$

c. O_2^+ , O_2 , O_2^-

$\text{O}_2^+ > \text{O}_2 > \text{O}_2^-$

d. N_2^+ , N_2 , H_2

$\text{H}_2 > \text{N}_2^+ > \text{N}_2$

Remember: Bond length decreases with increasing bond order

20. Draw the molecular orbitals for B_2 and F_2 . Which one is a magnet?

See page 111 of the course notes for the Molecular Orbitals.

B_2 is a magnet.