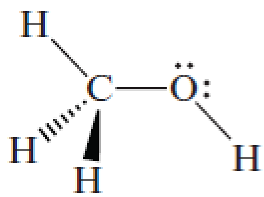
CHEMISTRY 111 – Section 1 NAME: ANSWER KEY
Exam #3 December 9, 2013

$$\ln\frac{P_2}{P_1} = \frac{\Delta H^\circ_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

R = 8.314 J/K·mol 760 mmHg = 1 atm

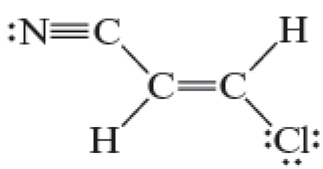
Q1. What type of hybrid orbitals are used for the carbon and oxygen atoms in methanol?



C: sp^3 (4 structural pairs) *O: sp^3 (4 structural pairs)*

Q2. How many sigma and pi bonds are in the following molecule and indicate hybrids:

Single bonds are sigma bonds

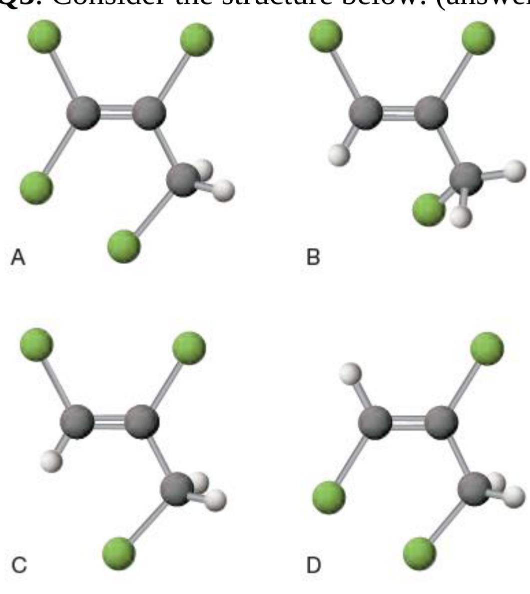


Hybrids on left C: *sp (2 structural pairs)*
hybrids on right C: *sp^2 (3 structural pairs)*

 # sigma bonds: 6

 # pi bonds: 3 (each multiple bond has 1 sigma bond and any additional bonds are pi bonds

Q3. Consider the structure below. (answers: isomers, conformers, no relation)



B and C represent: *conformers (rotate about a single bond)*

C and D represent*: isomers (rotate about a double bond)*

A and D represent: *no relation (different formulas)*

For the pair that are isomers, what stops one form from easily converting to the other form?

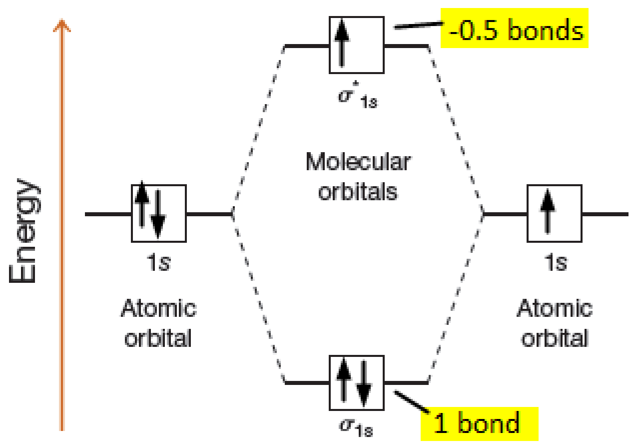
The C-C pi bond would need to be broken to rotate the left side by 90^o. This is because the two p_z orbitals need to be aligned for the pi interaction.

Q4. According to molecular orbital theory, what is an antibond?

A molecular orbital that is higher in energy than the atomic orbitals used to form it. When electrons occupy this type of orbital, the molecule is destabilized because the electrons would be at lower energy if the bonding atoms were farther apart.

Q5. Fill electrons into in the MO diagram below for He_2^+ ion.

What is the bond order for this ion? *0.5 (i.e. ½)   There are 3 valence electrons; 2 in a bonding orbital and 1 in an antibonding orbital..*



Q6. Which of the following forces are responsible for holding HBr in the liquid state? Circle all that apply.

~~Ion-ion~~	~~Ion-dipole~~	**Dipole-dipole**
~~H-bonding~~	**Induced dipole-Induced dipole**	~~H-Br Covalent Bonds~~

Explanation: HBr does not do hydrogen bonding and it is not ionic. It is polar so it exhibits induced dipole – induced dipole forces (as does everything) and dipole-dipole forces. It does have H-Br covalent bonds but those hold a single molecule together; they do not hold one molecule near another molecule.

Q7. If a compound has weak intermolecular forces, the…

a. vapor pressure will be *high*
b. enthalpy of vaporization will be *small*
c. boiling point will be *low*

Q8. Rank each of the following sets of compounds in terms of intermolecular force strength:

A: $CH_3CH_2NH_2$ **B:** CH_3CH_2F **C:** $CH_3CH_2CH_3$ **D:** CH_3CH_3

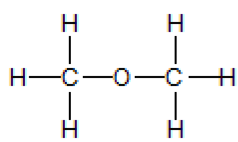
Weakest *D* < *C* < *B* < *A* < Stronger

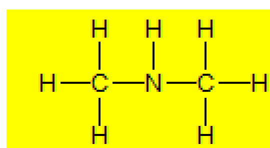
HF HCl, HBr, HI

Weakest *HCl* < *HBr* < *HI* < *H*F < Stronger

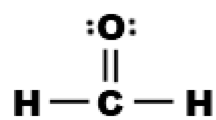
$CH_3CH_2NH_2$ and HF will form strong hydrogen bonds.

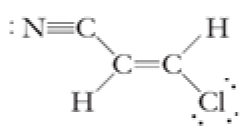
Q9. For which of the following compounds would hydrogen bonding be expected to play an important role in holding the molecules in the liquid state. Circle all that apply.





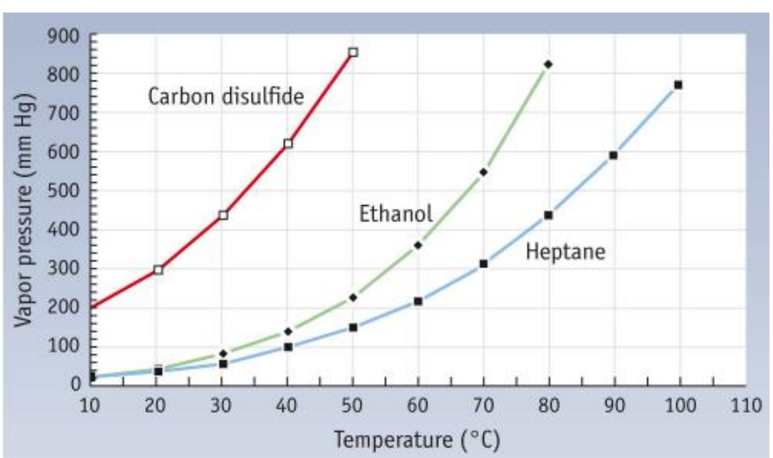
H—H





due to the N-H bond

Q10. Use the vapor pressure curves to answer the following questions.



a. What is the vapor pressure of ethanol when the temperature is 70 °C.

550 mm Hg

b. What is the normal boiling point of carbon disulfide?

about 46°

c. Which of the three has the weakest intermolecular forces?

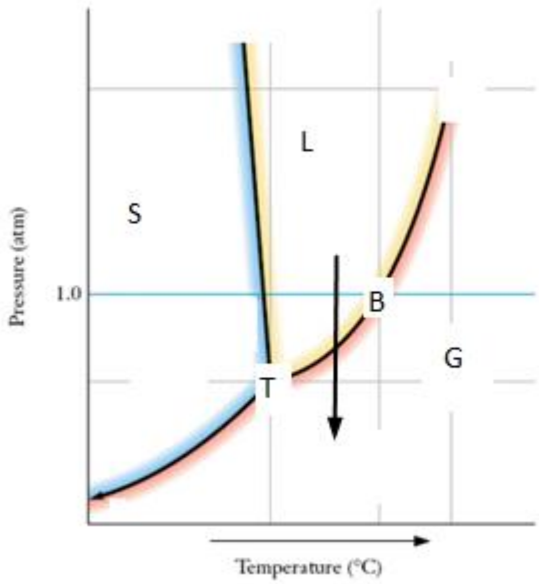
Carbon disulfide

d. Which compounds has the largest enthalpy of vaporization?

heptane

e. Draw a new curve on the graph for a compound with stronger intermolecular forces than the compounds depicted. *Draw to the right of heptane.*

Q11. Consider the phase diagram below.



a. Label the regions for gas, liquid and solid.

b. Draw an arrow for the transition that occurs when the liquid evaporates at constant temperature.

c. Write a "T" on top of the triple point.

d. Write a "B" showing the normal boiling point. *Spot where liquid/gas curve passes through 1.0 atm.*

e. Which is more dense:
the liquid (applying pressure to the solid moves it to the liquid phase)

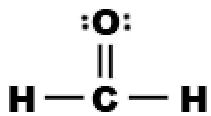
Q12. The vapor pressure of acetic acid at 10 ^oC is 43.5 mm Hg, and at 50 ^oC is 156.5 mm Hg. Use this to determine the enthalpy of vaporization of acetic acid.
You must show all your work.

$$\ln\frac{156.5\text{ mm Hg}}{43.5\text{ mm Hg}} = \frac{\Delta H_{vap}}{8.314\text{ J/K}\cdot\text{mol}}\left[\frac{1}{283.15\text{ K}} - \frac{1}{323.15\text{ K}}\right]$$

$$\ln 3.59 = 1.2803 = \frac{\Delta H_{vap}}{8.314\text{ J/K}\cdot\text{mol}}\left[4.372\times10^{-4}\right]$$

$$\Delta H_{vap} = 24{,}300\text{ J} = 24.3\text{ kJ}$$

Q13. The Lewis structure of formaldehyde is shown below. Give a full description of the bonding of ethene using Valence bond theory. In particular, note the types of bonds present and what orbitals overlap to create those bonds. Draw a diagram that shows what you mean and label it.



Q14. The solubility tables say nothing about the relative solubility of salts of rubidium or strontium. Predict which would be more soluble: RbCl or $SrCl_2$? Fully explain your answer in terms of enthalpy and entropy of dissolution.

$SrCl_2$ is expected to be less soluble. Here's why:

Dissolving involves separating the cation from the anion and hydrating each of those ions with water molecules.

The main difference in the compounds is that Sr^{2+} has a 2+ charge and Rb^{+} has a 1+ charge.

Enthalpy: It takes more energy to separate the ions in $SrCl_2$ than in RbCl. Countering that, Sr^{2+} forms stronger bonds to surrounding water molecules. So, the enthalpy differences between Rb^{+} and Sr^{2+} largely offset. The extra energy needed to separate Sr^{2+} from Cl^{-} is gained back by forming stronger bonds to H_2O molecules.

Entropy: Both salts have similar entropy changes with respect to the entropy of the ions themselves. Each ion starts out in a solid and ends up moving independently from the other ions. This favors dissolution equally for both salts.

Hydration of the ions differs. Sr^{2+} will hydrate many more water molecules than will Rb^{+}. Therefore, Sr^{2+} causes a larger entropy decrease in water molecules and this disfavors $SrCl_2$ from dissolving compared with RbCl.

Q15. If a compound has trigonal planar geometry, what type of hybrid orbitals does the central atom use?

Must be sp^2 hybrid orbitals.

Can a compound have trigonal planar electron pair geometry and have a lone pair on the central atom?

Yes. An example of this is ozone, O3. The central atom has 2 bonded atoms and 1 lone pair. It therefore has three structural pairs and a trigonal planar electron pair geometry.

Can a compound have trigonal planar molecular geometry and have a lone pair on the central atom?

No. The lone pair would force the three bonded atoms downward to form a trigonal pyramid.

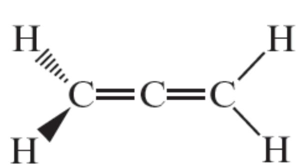
Q16. According to valence bond theory, electrons occupying a hybrid orbital can play two roles in the compound. What are they?

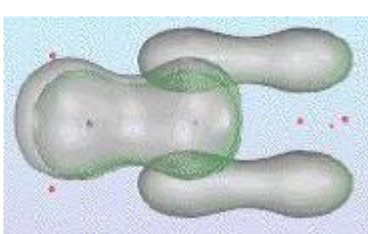
Hybrid orbitals are used to form sigma bonds and also to hold lone pairs of electrons.

What role do electrons in unhybridized p orbitals play?

Unhbridized p orbitals are used to formpi bonds, but are also sometimes empty of electrons.

Q17. Consider the Lewis structure of allene. Remember that Lewis structures do not imply shape- they just show the locations of the valence electrons. Each CH_2 end of the molecule forms a trigonal plane. Do you expect the two CH_2 groups to be in the same plane, or to be perpendicular? Give a one sentence explanation of why.





Each terminal CH_2 group has a C using sp2 hybrid orbitals. Each therefore has a single unhybridized p orbital that it uses to form a pi bond. The central C atom has sp hybrid orbitals and therefore has 2 unhybridized p orbitals it uses to form 2 pi bonds, one to the left carbon and the other to the right carbon.

If the central C uses its $2p_y$ orbital to form a pi bond to the left carbon, it must then use its $2p_z$ orbital to form a pi bond to the right carbon. Therefore the pi bonds going to either side are at right angles to each other and the two CH_2 fragments are perpendicular.

Q18.

Why don't water and oil mix?

What is responsible for proteins folding?

What is responsible for the formation of micelles, which form from surfactant molecules in water?

Q19. Are paper towels hydrophilic, hydrophobic, or both?

Give a molecular-scale explanation for why paper towels absorb water. What does the water absorption imply about the molecular structure of the paper towels?

Paper towels are hydrophilic. They therefore most likely contain many hydrogen bonding groups. On the molecular scale, the paper has (most likely) –O-H groups that can form hydrogen bonds to water. Those hydrogen bonds are most likely just as strong as those between water molecules.

Q20. Explain the shape of drops. Why are droplets not flatter? Why are droplets not completely spherical?

Droplet shape is a contest between surface tension and gravity. Surface tension tries to form a spherical shape. Gravity tries to push that shape as flat as possible. The stronger the IMFs (or the weaker the gravity), the more spherical the drop.

Surface tension comes about through intermolecular forces. Molecules on the surface have fewer interactions (simply because they are near fewer molecules) so they are less stable. Therefore, the liquid is most stable when it has the lowest surface area. A sphere has the smallest surface area for a given volume.

Bonus consideration: the stronger the IMFs between the liquid and the solid it is sitting on, the less spherical the droplet.