Name ______________________________ Team ID # ______________________

Team Name ______________________________________

2024 WUCT: Team Exam

April 6th, 2024
2:15 p.m. – 3:15 p.m.

1 HOUR will be allowed for the exam. The examination contains **7** questions on **25** numbered pages, including the last **SCRATCH PAGE**.

TURN IN THE ENTIRE EXAM (INCLUDING THE SCRATCH PAGE) WHEN YOU ARE FINISHED!

Please fill in the numbers of your 6-digit team ID:

Team ID

9	9	9	9	9	9
8	8	8	8	8	8
7	7	7	7	7	7
6	6	6	6	6	6
5	5	5	5	5	5
4	4	4	4	4	4
3	3	3	3	3	3
2	2	2	2	2	2
1	1	1	1	1	1
0	0	0	0	0	0

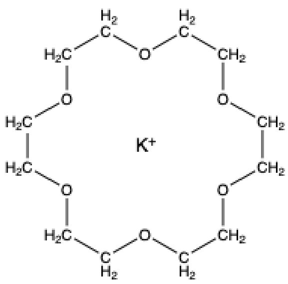
Exam Points Breakdown:

1. (15 pts)
2. (16 pts)
3. (14 pts)
4. (18 pts)
5. (12 pts)
6. (15 pts)
7. (10 pts)
Total Points: (100 pts)

2024 WUCT: Team Exam

This exam consists of 7 questions and is worth 100 points. You will complete this exam as a team. You will have 1 hour to take the exam. The only allowed resources for this exam are a calculator and the provided equation sheet. You may NOT use any other notes or books. You must show your work and box your final answer to receive credit for a problem. NOTE: If you get the answer to an early part of a question incorrect but later use that answer for a subsequent part of the question, you can still earn full credit for those subsequent parts. Please write your answer in the designated space on the answer sheet. If you need additional space for a problem, you may use the blank scratch page at the end of the exam. Make sure to clearly indicate in the problem's designated space where the rest of your work can be found. Any work anywhere other than the exam or the scratch page will not be graded. Dark pencil or pen is preferred.

<u>Problem #1</u>: ***(15 points)***
In 1987, Charles Pedersen won the Nobel Prize in Chemistry for his discovery of crown ethers. Crown ethers are a special type of molecule that can encapsulate metal cations of varying sizes. The structure of crown ether 18-crown-6 is shown below. The 18 represents the total number of oxygen and carbon atoms, and the 6 is the number of oxygen atoms.

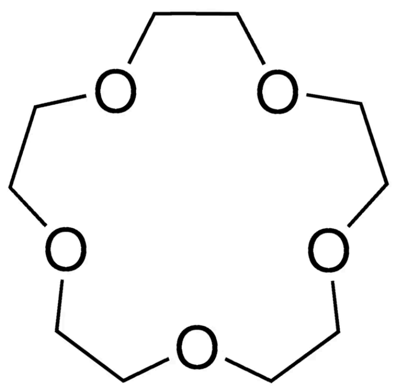


a. Given that cations can be found inside crown ether, why do you think that these large molecules bind the small ions so well? Explain your reasoning in 2-3 sentences. ***(2 points)***

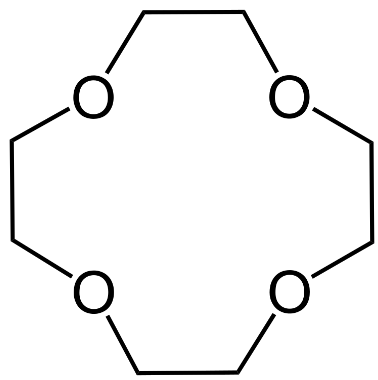
b. Which of the following would be able to bind to a crown ether? **Circle** all that apply. For this question, assume that all of the following compounds can fit inside a crown ether. ***(1 point)***

A. NH_4^+
B. Mg^{2+}
C. Cl^-
D. H_2O
E. CH_3OH
F. CCl_4

c. 18-crown-6 can solubilize $KMnO_4$ in organic solvents by helping to steal the K^+ ion away from its anion, such that the salt has to dissociate. However, 15-crown-5 is used to dissolve Na^+ ions, and 12-crown-4 is better for solvating salts containing Li^+ ions. Give one possible explanation for why this is so. ***(2 points)***



15-crown-5



12-crown-4

d. The binding of crown ethers to small compounds is an example of host-guest chemistry. This is a general term for the phenomenon of a larger "host" molecule binding to a smaller "guest" molecule. Host-guest binding can be described by an equilibrium reaction with the equilibrium constant of K_a, which is given the special name of the association constant.

$$\text{Host Molecule} + \text{Guest Molecule} \rightleftharpoons \text{Host-Guest Complex} \ (K = K_a)$$

In this scenario, the host molecule is 18-crown-6, and the guest molecule is the potassium cation. You start with 0.14 mol of K^+, 0.35 mol of the 18-crown-6 molecule, and 0.28 mol of the host-guest complex in 100 mL of solution. If the value of K_a is 1×10^6, what is the equilibrium concentration of the free potassium cation? Briefly explain if this value makes sense. ***(7 points)***

e. If the K_a of 18-crown-6 at 298 K is 1×10^6, what is the dissociation constant K_d at 48 ℃? (Hint: $K_d = \frac{1}{K_a}$). Assume the enthalpy change for the association reaction is -25.57 kJ/mol and remains constant across the temperature range of change. ***(3 points)***

Problem #2: ***(16 points)***

The *Bohr model* of the atom was the first model that incorporated quantum theory to describe a one-electron system. It shows the atom as a central nucleus containing protons and neutrons, with the electron in circular orbitals at specific distances from the nucleus. The allowed orbital radii can be described by the equation $r = \frac{n^2 a_0}{Z}$, where a_0 is the Bohr radius of 52.9 pm. The allowed orbital energies can be described by the equation $E = \frac{-Z^2 R_y}{n^2}$, where R_y is Rydberg's constant of 2.178×10^{-18} J.

a. Using the Bohr model:

   i. Compute the radius of electron orbit for the 1st excited state H-atom in nm. ***(2 points)***

   ii. Compute the ionization energy for Be^{3+} in J. ***(2 points)***

   iii. A laser is used to excite an Li^{2+} ion in its ground state to the fourth excited state. What is the wavelength of the incoming photon in nm? ***(2 points)***

Another quantum mechanical model, the *hydrogen atom model*, can be used to describe a one-electron system in which a single electron interacts with the nucleus, where the radius of orbit is probabilistic within an orbital. Different wavefunctions (ψ) can be used to describe the electron in this system when it is in different orbitals.

For this question, you will be working with an electron in the 1s orbital. The ψ for the 1s orbital is $\psi = \frac{1}{\sqrt{4\pi}} 2(\frac{1}{a_0})^{\frac{3}{2}} e^{-\frac{r}{a_0}}$. The expectation value of radius describes the average distance at which you will find the electron in this orbital. This value can be described by the equation below:

$$< r >= \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \psi^* r \, \psi \, r^2 sin\theta dr d\theta d\phi$$

In the equation, ψ represents the wavefunction that describes the hydrogen atom system. $\psi*$ is the complex conjugate of ψ. A complex conjugate simply inverses complex numbers. For instance, the complex conjugate of 2i is -2i. If an equation does not have any complex numbers, $\psi*$ will be equal to ψ.

b. Set up the equation for solving the expectation value of radius. ***(1 point)***

c. Given the following relationships:

i. $\int_0^{2\pi} \int_0^{\pi} \frac{1}{4\pi} sin\theta d\theta d\phi = 1$

ii. $\int_0^{\infty} e^{-\frac{2r}{a_0}} r^3 dr = \frac{3a_0^4}{8}$

Solve for the expectation value of radius. Leave your answer in terms of a_0. ***(2 points)***

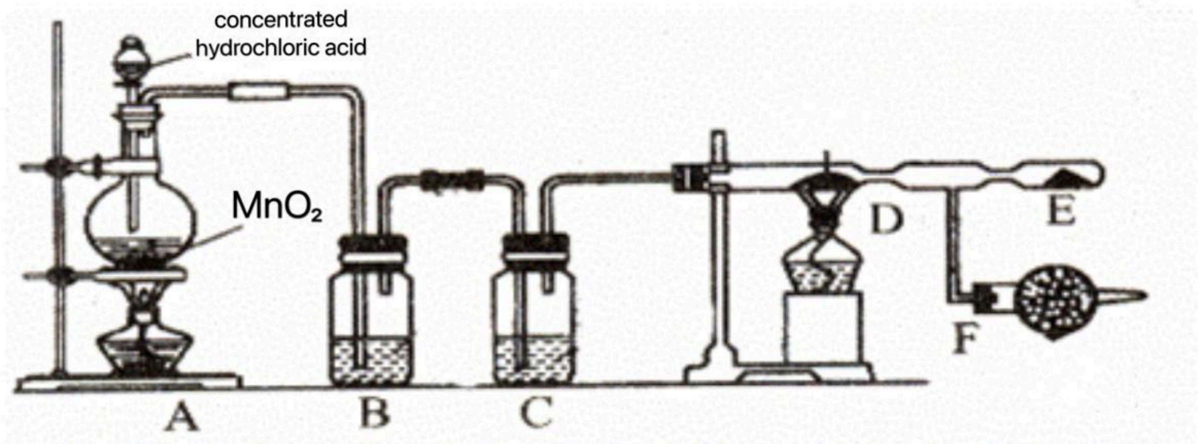
d. The most probable distance describes the distance at which you are most likely to find the electron in this orbital. It can be treated like a relative maximum in the probability distribution (P(r)) of the wavefunction (ψ). If P(r) = $\psi^* \psi r^2$, when is the probability distribution at a maximum? Leave your answer in terms of a_0. (Hint: what is the slope of P(r) at a relative maximum?) ***(3 points)***

e. What is the relationship between $< r >$ and the most probable distance? Draw a probability distribution graph that shows this relationship. ***(2 points)***

f. Can either of these two models, the Bohr model or the hydrogen atom model, be used for B^{3+}? Why or why not? ***(2 points)***

<u>Problem #3</u>: ***(14 points)***
Aluminum chloride ($AlCl_3$) is an important catalyst for organic reactions. It readily deliquesces, or absorbs moisture, when exposed to air. It sublimes at a temperature of 192.4℃.

In laboratories, the following apparatus can be used for $AlCl_3$ synthesis, where D has 0.80 g kitchen aluminum foil in it.



The reaction proceeds as follows: $2Al + 3Cl_2 \rightarrow 2AlCl_3$.

a. The skeleton equation of the reaction in flask A is shown below. Balance the equation and determine how many moles of electrons are transferred if 1.12 L Cl_2 is produced. Assume STP conditions. ***(3 points)***

$$\_HCl + \_MnO_2 \rightarrow \_H_2O + \_Cl_2 + \_MnCl_2$$

b. In reactor B, a saturated $NaCl$ solution is used to absorb any residual HCl gas in the Cl_2 product from flask A. Using knowledge of equilibrium, justify the use of saturated $NaCl$ solution and include necessary equations. Hint: chlorine reacts reversibly with water to form hydrochloric acid and hypochlorous acid. ***(2 points)***

c. The drying tube F contains soda lime, which is a granulated mixture of calcium oxide and sodium hydroxide. Briefly list two purposes of employing this apparatus. Be sure to include both what it does and what would happen if it was absent. (***2 points)***

d. Right on top of the letter "D", there is a narrowing in the tube. What simple measure could be taken if $AlCl_3$ solidifies and clogs up that tube? ***(1 point)***

e. After the reaction in D is completed, all solidified $AlCl_3$ is collected to calculate the purity of the kitchen aluminum foil. The $AlCl_3$ sample is dissolved in water to make a 50 mL solution. 1 mL of that solution is taken out and further diluted to 100 mL. 1 mL of 1 M K_2CrO_4 solution is then added to the diluted solution. After that, titration is performed using 0.1 M $AgNO_3$ solution.

	K_{sp}	Solubility	Appearance
$AgCl$	1.8×10^{-10}	1.7×10^{-5} mol/L	White solid
Ag_2CrO_4	2.0×10^{-12}	8×10^{-5} mol/L	Brown red solid

Given the information above, describe what you expect to observe at the endpoint of the titration. ***(2 points)***

f. Consider only the reaction between silver ions and chloride ions. If 11.30 mL $AgNO_3$ is used to reach the endpoint, determine the purity of the kitchen aluminum foil in % (no need to show your work). Assume impurities stay unreacted. ***(2 points)***

g. In acidic solutions, CrO_4^{2-} is converted into $Cr_2O_7^{2-}$ and can react with chloride: $Cr_2O_7^{2-} + 14H^+ + 6Cl^- \rightarrow 2Cr^{3+} + 7H_2O + 3Cl_2$. How would this affect the value of the calculated purity? **Circle** your answer. ***(2 points)***

i. Larger than the true purity value
ii. No effect
iii. Lower than the true purity value
iv. Cannot be determined

<u>Problem #4</u>: *(18 points)*
Lewis structure requires all atoms to follow the octet rule whenever possible, but a wide range of exceptions exist. For neutral molecules, the number of electrons that the center atom can have can be determined by the sum of its valence electrons and the absolute value of its oxidation number. For example, the S in SO_2 has $6 + |+4| = 10$ electrons around it.

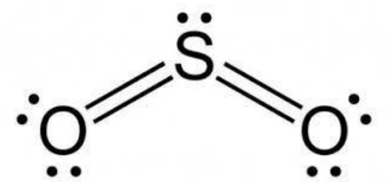
a. Use the formula given to calculate the number of electrons around the center atoms of the following molecules. ***(3 points)***

   $POCl_3$ NO_2 BH_3

b. For which molecule are the conclusions made about it in part (a) obviously wrong? Explain why and draw the correct Lewis structure for that molecule. Draw every equivalent resonance structure, and label all formal charges. ***(3 points)***

c. Explain with Lewis structure drawings why $AlCl_3$ tends to dimerize and $BeCl_2$ tends to polymerize. Use arrows to show coordinate bonds. ***(2 points)***

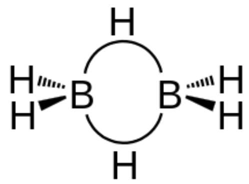
d. The violation of the octet rule could be explained by frontier molecular orbital theory. Take SO_2 as an example again.



Since every atom is sp^2 hybridized, the three unused p orbitals constitute a group of three delocalized pi bonds across the whole molecule, which contain the four excess electrons. This group of pi bonds is named Π_3^4, for there are 3 central atoms and 4 electrons participating in bonding. Name the groups of pi bonds for the following molecules. ***(2 points)***

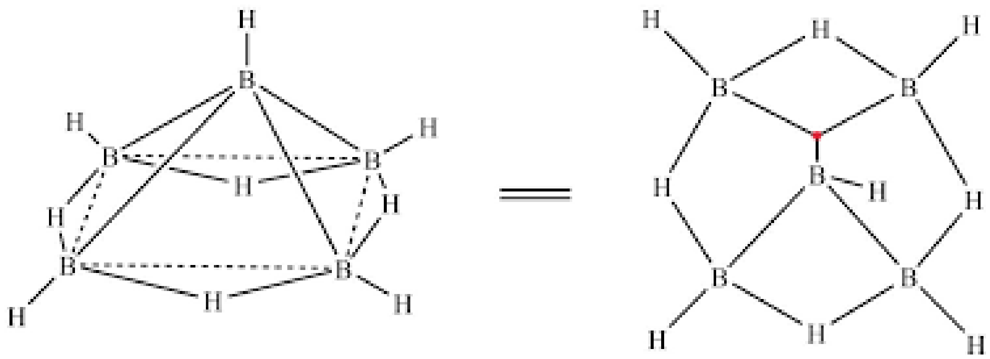
SO_3 ClO_2

What is the deal with electron-deficient species then? Take the borane series for example. The structure of diborane (B_2H_6) is shown below. The two boron atoms and the hydrogen between them each contribute one orbital to form a molecular bonding orbital, which contains two electrons. This MO is called a hydrogen bridge bond. Due to the bond arcs, it is also known as a bent bond, a banana bond, or a three-center bond.

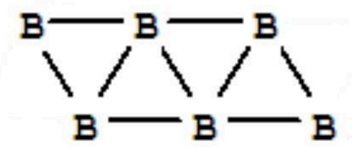


e. Do you expect the bond angle between the two banana bonds to be more or less than 109°? Why? ***(2 points)***

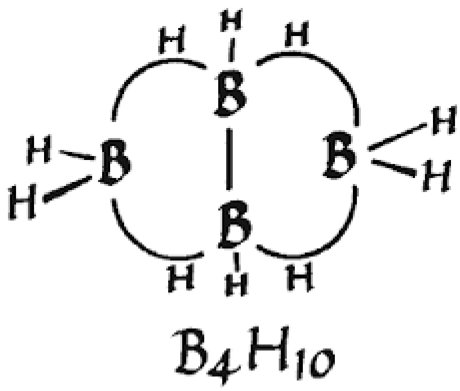
f. Comparing the formation of hydrogen bridge bonds, explain how the center boron atom in pentaborane (B_5H_9) achieves an octet. ***(2 points)***

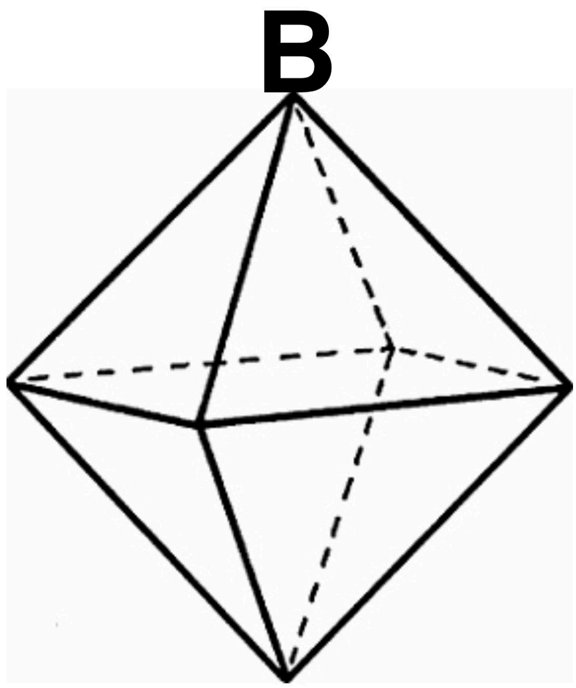


g. Given the boron framework of hexaborane (B_6H_{12}), work out its Lewis structure. Following the example of diborane, put the symbol of hydrogen (H) on a B-B bond to symbolize a bridge bond. You do not need to show other types of three-center bonds. (Hint: in hexaborane, there are 6 three-center bonds and 8 terminal B-H bonds.) ***(2 points)***



h. What do you expect is the geometry of tetraborane (B_4H_{10})? Put the symbol for boron (B) at appropriate vertices of the given octahedron to indicate the molecular geometry of tetraborane. One position is already given. ***(2 points)***





<u>Problem #5</u>: *(12 points)*

Hydrogen halides are inorganic compounds which are all gases at room temperature and Arrhenius acids with a general formula HX, where X can be fluorine, chlorine, bromine, iodine, astatine, or tennessine. For your chemistry class, you need to synthesize a hydrogen halide.

$$H_2(g) + X_2(g) \rightarrow 2\,HX(g)$$

a. For the above reaction, propose a mechanism. Note that the X-X bond is weak and can break apart into active radicals which react with H_2. Your mechanism will have three parts, with the first step being X_2 breaking into 2 X• ($k = k_1$), second step being a reversed reaction of the first step ($k = k_{-1}$), and the third step being a product formation step ($k = k_2$) ***(3 points)***

b. Assume the first step of the mechanism is the slow, rate determining step. Find the rate law equation based on this information. ***(1 point)***

c. Now assume the third step was the rate determining step, and the first two steps are in rapid equilibrium. Revise your rate law equation based on this information. ***(2 points)***

d. Find the expected rate law using steady state approximation. ***(3 points)***

e. Imagine there is a mixture of F_2, Cl_2, Br_2, and I_2, all in the gas phase at the same temperature. Of these, what gas has the greatest average velocity (moves the fastest)? ***(2 points)***

f. Find the root mean square velocity of X_2 that you identified from part e at 298 K in m/s. (Assume that F_2, Cl_2, Br_2, and I_2 are all gases at 298 K). If you did not answer the previous question, assume that X_2 is Br_2 gas. ***(1 point)***

Problem #6: ***(15 points)***
Polymers are large macromolecules that are composed of identical repeating units called monomers. There are many different natural polymers, including silk, proteins, and DNA. However, this question will focus on synthetic polymers, which are built by engineers and scientists through a wide variety of techniques. You use polymers all the time, whether it is the polyester in your favorite shirt, the non-stick Teflon pan you use to cook dinner, or the nylon in your dental floss. All the plastics you use in your everyday life are polymers: polyethylene in grocery store plastic bags, polystyrene in styrofoam to-go boxes, etc. This question will walk you through some of the fundamental concepts of polymer chemistry.

a. When a polymer is synthesized, chains of many different lengths are formed at the same time. To characterize the average molecular weight, chemists can find the mean molecular weight of all the different chains. Using the data given below, what is the average molecular weight of this sample of polymers? ***(2 points)***

Number of polymers of a given molecular weight (N_i)	Molecular weight (M_i) (g/mol)
1	250,000
4	375,000
6	415,000
9	575,000
12	650,000
14	725,000
13	800,000
7	850,000
5	925,000
2	975,000

b. Another measure of the molecular weight of a sample of polymers of different sizes is the weight average molecular weight. This value is based on the weight fraction of each chain size. The weight fraction of a certain length chain in a polymer sample is the proportion of the total mass that the specific chain length represents. In mathematical terms,

$$weight\ fraction = \frac{N_i M_i}{sum\ of\ all\ N_i M_i}$$

The weight average molecular weight is found by summing the products of the weight fraction of a particular length and the molecular weight of that particular length. Using the same data above, find the weight average molecular weight of the same polymer sample. ***(2 points)***

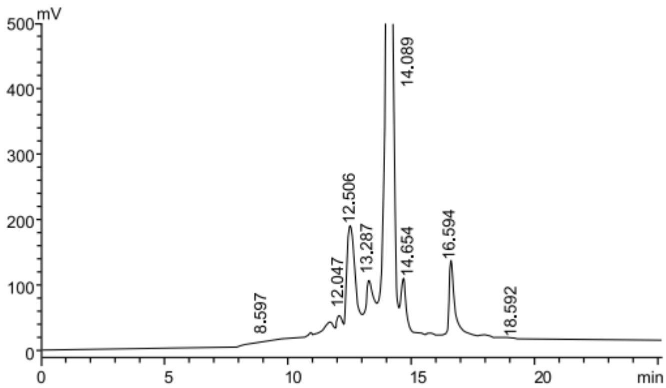
c. One method that polymer chemists use to separate and analyze polymers of different sizes is size exclusion chromatography. Size exclusion chromatography involves running a solution of the polymer sample through a porous solid material.

   i. Using what you know about chromatography in general and the set-up given here, what are the mobile and solid phases in this form of chromatography? ***(2 points)***

      Mobile phase:
      Solid phase:

   ii. Do larger or smaller polymers come through a column of this porous material first? Explain your answer in 2-3 sentences. (Hint: Consider which polymers can interact with the pores and which ones cannot, and how this impacts their elution order.) ***(2 points)***

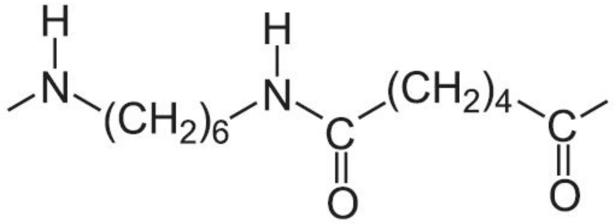
   iii. A plot known as a chromatogram is shown below. The x-axis is how long it takes for the polymer chain to elute. What do the peaks represent? ***(2 points)***



iv. How do you think the above chromatogram would change if the pores in the solid material were too small to let any polymers through? ***(1 point)***

d. Some polymer chains have both rigid crystalline regions and more flexible amorphous regions. Together, these different types of regions give polymers unique properties. Only polymer chains with at least one crystalline region can melt. However, all polymers have what is known as a glass transition temperature, when chains start to slide past each other.

i. Looking at the chemical structure of Nylon below, why do you think separate polymer chains tend to stack together? ***(1 point)***



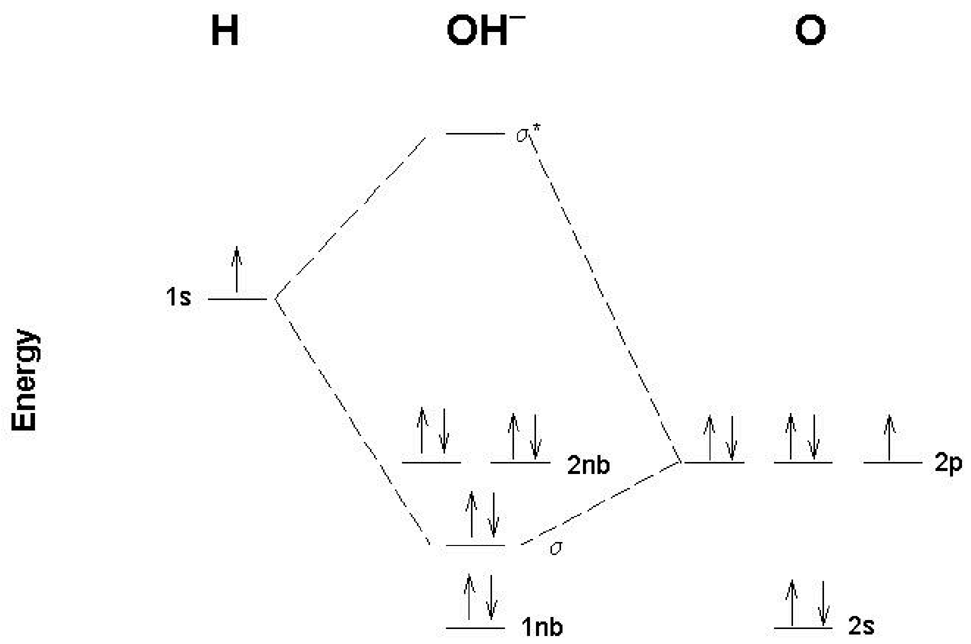
ii. The glass transition temperature is the temperature at which polymer chains just start to slide past each other. Why do you need to input energy to cause chains of Nylon to move past each other? Explain your answer in 1-2 sentences. ***(1 point)***

iii. For polystyrene, which value would you expect to be greater and why? ***(2 points)***

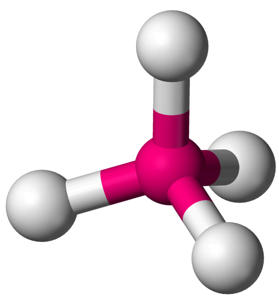
Melting temperature of a polymer	Glass transition temperature of a polymer

<u>Problem #7</u>: *(10 points)*
Molecular orbital theory is a theory used to describe the electronic structure and properties of molecules based on principles of quantum mechanics. A molecular orbital diagram illustrates the combination of atomic orbitals from individual atoms into molecular orbitals within a molecule.

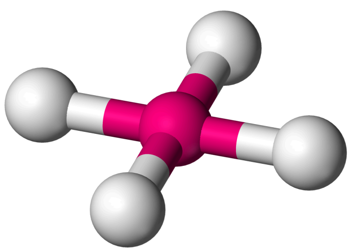
For example, the molecular orbital diagram for OH^- is shown.



You know that methane (CH_4) has tetrahedral geometry, but what if it actually had square-planar geometry instead?



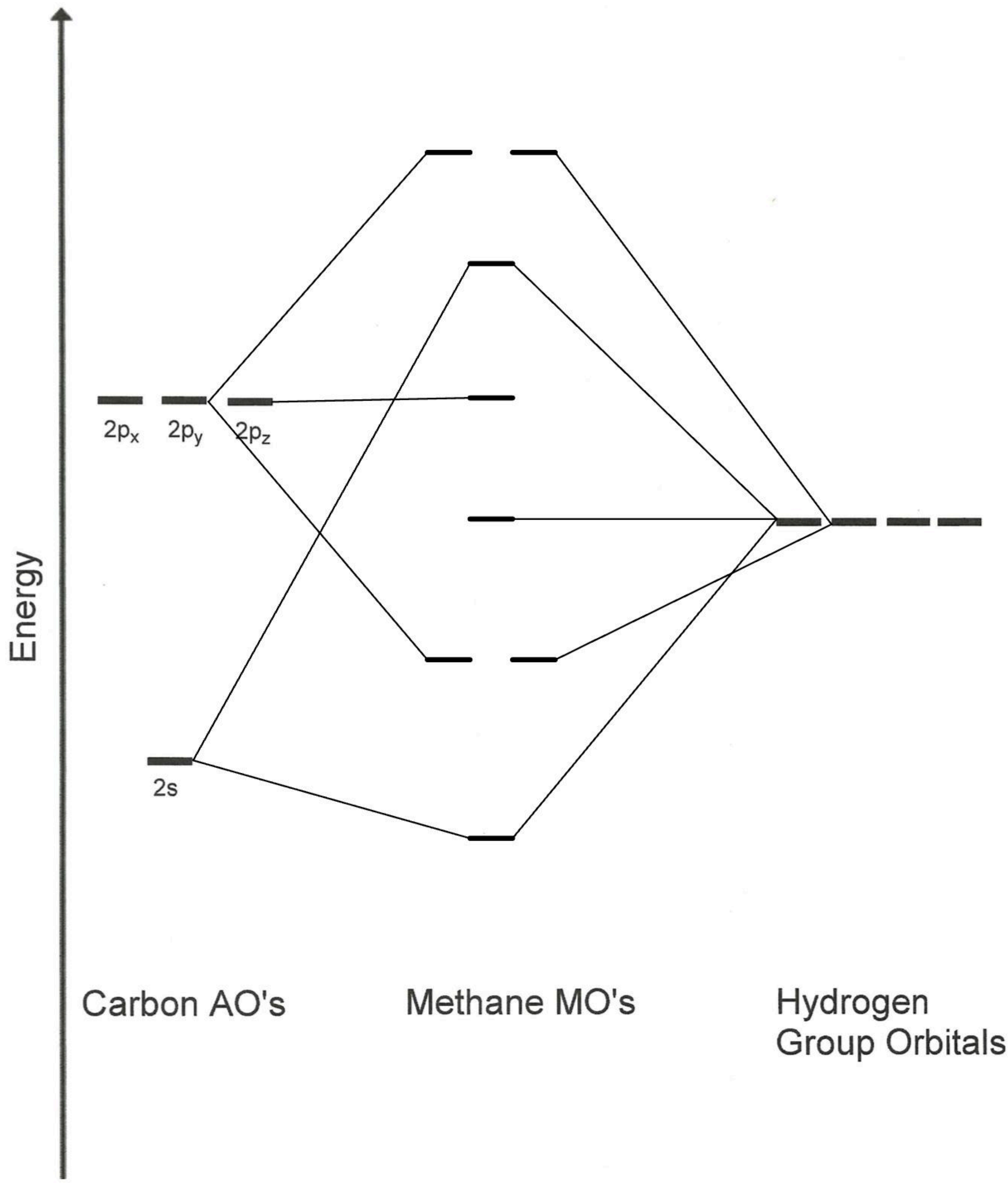
Tetrhedral



Square-planar

This would lead to methane having a MO diagram shown below.

a. Fill in the MO diagram of square-planar methane. ***(3 points)***



b. What is the bond order of each individual C-H bond in square-planar methane? ***(2 points)***

c. Given that the tetrahedral MO diagram of methane results in a bond order of 1 for each C-H bond, explain why the preferred structure of methane is tetrahedral. Use orbitals and bond energy arguments to support your explanation, and clarify why the bond order of tetrahedral methane is consistent with its spatial configuration. ***(5 points)***

Scratch Paper