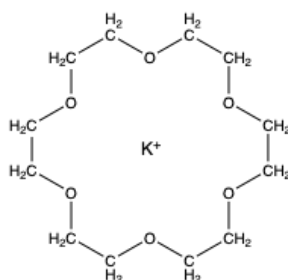


# 2024 WUCT: Team Exam

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.

## **Problem #1: (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.



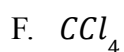
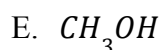
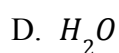
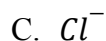
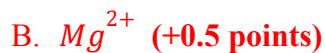
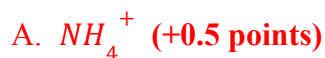
- a. Given that cations can be found inside crown ether, why do you think that these large molecules bind the small ions so well? Explain your reasoning in 2-3 sentences. (2 points)

Due to the significant electronegativity difference between oxygen and carbon, the C – O bonds in the ring are highly polarized, with the oxygen atoms carrying partial negative charges. These negatively charged oxygen atoms experience electrostatic attractions to the positively charged metal cations. As a result, the binding between the cation and the oxygen atom is strong.

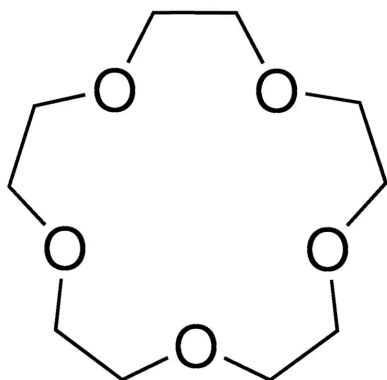
**+1 point for mentioning electronegativity difference or bond polarity (+0.5 points for only mentioning the lone pairs on oxygen)**

**+1 point for mentioning attraction between positive cations and partially negative-charged oxygens**

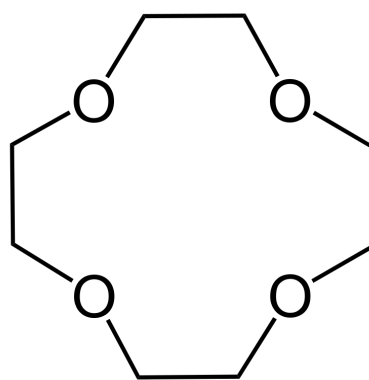
- b. Which of the following would be able to bind to a crown ether? **Circle** all that apply. For this question, assume that all of the following compounds can fit inside a crown ether. (1 point)



- 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



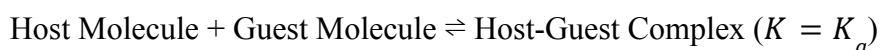
12-crown-4

According to periodic trends in atomic sizes,  $Li^+$  is smaller than  $Na^+$ , which is smaller than  $K^+$ . This trend is due to the increasing principal quantum number of the valence orbital such that as you go down a column of the periodic table, the valence orbital of the atom or ion is larger in size. Smaller ions will be better solvated by crown ethers with smaller cavities, while larger ions are better solvated by crown ethers with larger cavities.

+1 point for mentioning periodic trends in atomic sizes

+1 point for mentioning the size agreement between crown ether cavity size and ion size

- 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.



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  $1 \times 10^6$ , what is the equilibrium concentration of the free potassium cation? Briefly explain if this value makes sense. (7 points)

$$K_a = 1 \times 10^6$$

$$[K^+] = \frac{0.14 \text{ mol}}{0.100 \text{ L}} = 1.4 \text{ M}$$

$$[\text{crown}] = \frac{0.35 \text{ mol}}{0.100 \text{ L}} = 3.5 \text{ M}$$

$$[H - G] = \frac{0.28 \text{ mol}}{0.100 \text{ L}} = 2.8 \text{ M} \quad (H - G: \text{Host-Guest Complex})$$

$K_a$  is too large to do approximation method  $\rightarrow$  push over to the right +1 point



ICE Table +2 points

	18 - crown - 6	$K^+$	H - G
I	3.5 M	1.4 M	2.8 M
C	-1.4 M	-1.4 M	+1.4 M
I'	2.1 M	0 M	4.2 M
C'	+x	+x	-x
E	2.1 M + x	x	4.2 M - x

$$K'_a = \frac{[K^+][crown]}{[H-G]} \quad (K'_a \text{ is the equilibrium constant of the reverse reaction of}$$

Host-guest binding reaction)

$$K'_a = \frac{1}{K_a} = \frac{1}{1 \times 10^6} = 1 \times 10^{-6}$$

$$1 \times 10^{-6} = \frac{x \cdot (2.1+x)}{4.2-x} \quad \text{+1 point}$$

$$(1 \times 10^{-6})(4.2 - x) = x^2 + 2.1x$$

$$(4.2 \times 10^{-6}) - x(1 \times 10^{-6}) = x^2 + 2.1x$$

$$x^2 + 2.100001x - (4.2 \times 10^{-6}) = 0 \quad \text{+1 point}$$

$$x = \frac{-2.100001 \pm \sqrt{(2.100001)^2 - (4 \cdot 1 \cdot (-4.2 \times 10^{-6}))}}{2}$$

$$x = 1.99999714 \times 10^{-6}$$

$$[K^+] = x = 1.99999714 \times 10^{-6} \text{ M}$$

$$[K^+] = 1.99999714 \times 10^{-6} \text{ M} \quad \text{+1 point}$$

Explanation: This value makes sense because there should not be much free potassium with the high binding constant. +1 point

**+1 point for identifying the large equilibrium constant and using the pushing-over method**

**+2 points for ICE table (+1 for correctly showing the pushing over; +1 for obtaining the correct equilibrium concentrations of each species)**

**+1 point for setting up the correct equation (need to use the correct equilibrium constant; can use either front or reverse reaction) e.g.  $1 \times 10^{-6} = \frac{x \cdot (2.1+x)}{4.2-x}$**

**+1 point for showing the process of solving the x using the correct quadratic equation or the correct application of successive approximations.**

**+1 point for calculating the correct value for  $[K^+]$**

**+1 point for correct explanation**

- e. If the  $K_a$  of 18-crown-6 at 298 K is  $1 \times 10^6$ , what is the dissociation constant  $K_d$  at 48 °C? (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)**

$$K_d \text{ at } 298 \text{ K} = \frac{1}{1 \times 10^6} = 1 \times 10^{-6} \quad \text{+0.5 points}$$

$$\Delta H_d = +25.57 \text{ kJ/mol} \quad \text{+0.5 points}$$

Van't Hoff equation

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln(K_2) - \ln(K_1) = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln(K_2) = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \ln(K_1)$$

$$\ln(K_2) = \frac{-(25.57 \text{ kJ/mol})}{(0.00831451 \text{ kJ/mol K})} \left(\frac{1}{(48+273.15)\text{K}} - \frac{1}{(298 \text{ K})}\right) + \ln(1 \times 10^{-6}) \quad \text{+1 point}$$

$$\ln(K_2) = -13.07159974$$

$$K_d(48 \text{ }^\circ\text{C}) = K_2 = 2.104148381 \times 10^{-6} \approx 2.10 \times 10^{-6} \quad \text{+1 point}$$

**+0.5 points for calculating the correct  $K_d$  at 298 K**

**+0.5 points for calculating the correct  $\Delta H_d$**

**+1 point for setting up the correct Van't Hoff equation**

**+1 point for the correct  $K_d(48 \text{ }^\circ\text{C})$**

**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  $2.178 \times 10^{-18}$  J.

a. Using the Bohr model:

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

$$r = \frac{n^2 a_0}{Z} = \frac{2^2 (52.9 \text{ pm})}{1} = 211.6 \text{ pm} = 0.2116 \text{ nm}$$

**+1 point for correctly plugging into equation, +1 point for correct final answer (and units)**

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

$$\Delta E = -Z^2 R_y \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -4^2 (2.178 \times 10^{-18} \text{ J}) \left( 0 - \frac{1}{1} \right) = 3.49 \times 10^{-17} \text{ J}$$

**+1 point for correctly plugging into equation, +1 point for correct final answer**

- 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)

$$\Delta E = -Z^2 R_y \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -3^2 (2.178 \times 10^{-18} \text{ J}) \left( \frac{1}{5^2} - \frac{1}{1} \right) = 1.88 \times 10^{-17} \text{ J}$$

$$E = \frac{hc}{\lambda}$$

$$1.88 \times 10^{-17} \text{ J} = \frac{(6.626 \times 10^{-34} \text{ Js})(2.998 \times 10^8 \frac{\text{m}}{\text{s}})}{\lambda}$$

$$\lambda = 1.06 \times 10^{-8} \text{ m} = 10.6 \text{ nm}$$

**+1 point for finding energy difference**

**+1 point for finding the correct wavelength in nm**

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 ( $\psi$ ) 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  $\psi$  for the 1s orbital is  $\psi = \frac{1}{\sqrt{4\pi}} 2\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$ . 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:

$$\langle r \rangle = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \psi^* r \psi r^2 \sin\theta dr d\theta d\phi$$

In the equation,  $\psi$  represents the wavefunction that describes the hydrogen atom system.  $\psi^*$  is the complex conjugate of  $\psi$ . A complex conjugate simply inverts 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  $\psi$ .

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

$$\langle r \rangle = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \left( \frac{1}{\sqrt{4\pi}} 2\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} \right)^2 r^3 \sin\theta dr d\theta d\phi$$

**+1 point for setting up the equation**

- c. Given the following relationships:

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

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

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

$$\langle r \rangle = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \left( \frac{1}{\sqrt{4\pi}} 2\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} \right)^2 r^3 \sin\theta dr d\theta d\phi = \int_0^{2\pi} \int_0^{\pi} \frac{1}{4\pi} \sin\theta d\theta d\phi \int_0^{\infty} 4\left(\frac{1}{a_0}\right)^3 e^{-\frac{2r}{a_0}} r^3 dr = \frac{3a_0}{2}$$

**+2 points for correct answer**

- 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 ( $\psi$ ). 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)

$$P(r) = \frac{1}{4\pi} 4 \left(\frac{1}{a_0}\right)^3 e^{-\frac{2r}{a_0}} r^2$$

$$\frac{dP}{dr} = \frac{1}{4\pi} 4 \left(\frac{1}{a_0}\right)^3 \left[ \left(-\frac{2}{a_0}\right) e^{-\frac{2r}{a_0}} r^2 + e^{-\frac{2r}{a_0}} 2r \right]$$

$$0 = -\frac{1}{a_0} r^2 + r$$

$$r = a_0$$

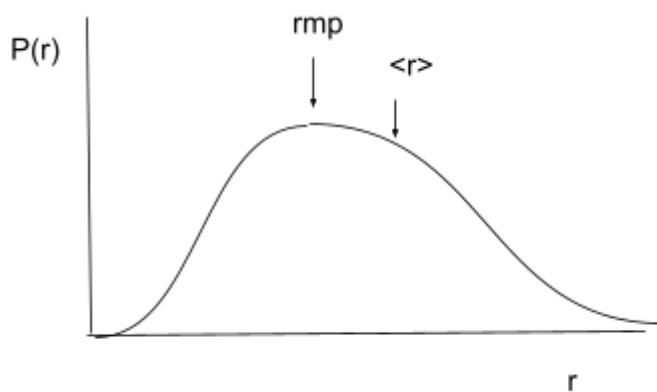
+1 point for setting up  $P(r)$

+1 point for setting derivative equal to 0

+1 point for correct final answer

- e. What is the relationship between  $\langle r \rangle$  and the most probable distance? Draw a probability distribution graph that shows this relationship. (2 points)

$\langle r \rangle$  is greater than the most probable distance



+1 point for saying  $\langle r \rangle$  is greater

+1 point for showing graph skewed to the right



- 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)

No, it cannot because  $B^{3+}$  has two electrons and the hydrogen atom model doesn't account for electron repulsions

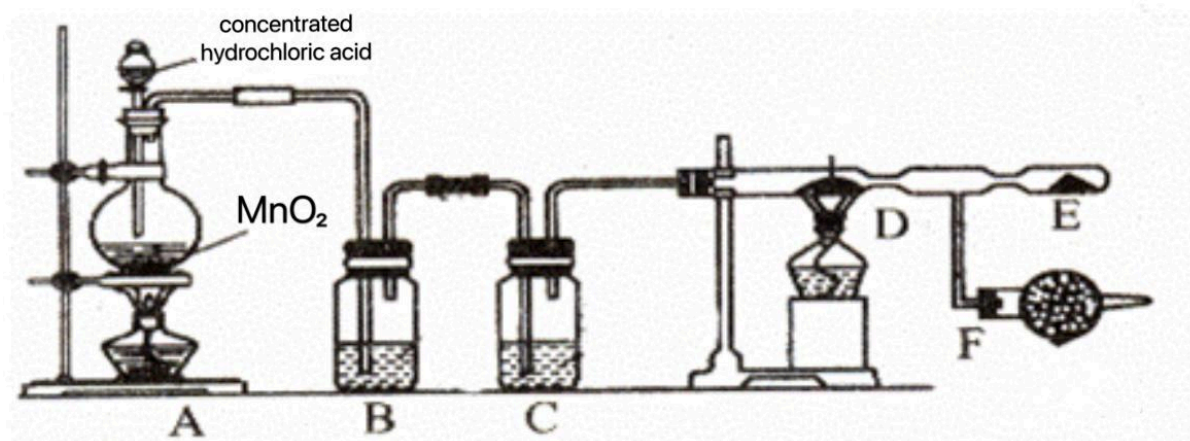
**+1 point for saying no**

**+1 point for explaining why**

**Problem #3: (14 points)**

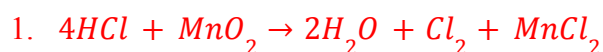
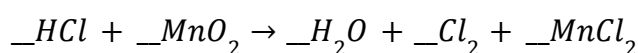
Aluminum chloride ( $AlCl_3$ ) is an important catalyst for organic reactions. It readily deliquesces, or absorbs moisture, when exposed to air. It sublimes at a temperature of  $192.4^\circ C$ .

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)



2.  $PV = nRT$

$$(1 \text{ atm})(1.12 \text{ L}) = n(0.08206 \frac{\text{atmL}}{\text{molK}})(273.15 \text{ K})$$

$$n = 0.05 \text{ mol } Cl_2 \text{ produced}$$

$$0.1 \text{ mol } Cl^- \text{ reacted}$$

$$0.1 \text{ mol electrons transferred}$$

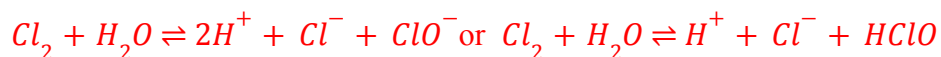
**+1 point for balancing equation**

**+1 point for using  $PV=nRT$  to get the moles of  $Cl_2$  (using  $V(1 \text{ mol gas})=22.4 \text{ L}$  at STP is acceptable)**

**+1 point for converting the moles of  $Cl_2$  to the moles of electrons and correct**

**final answer**

- b. In reactor B, a saturated  $\text{NaCl}$  solution is used to absorb any residual  $\text{HCl}$  gas in the  $\text{Cl}_2$  product from flask A. Using knowledge of equilibrium, justify the use of saturated  $\text{NaCl}$  solution and include necessary equations. Hint: chlorine reacts reversibly with water to form hydrochloric acid and hypochlorous acid. (2 points)



In a saturated  $\text{NaCl}$  solution,  $[\text{Cl}^-]$  is high, causing the equilibrium of the reaction above to shift to the left (towards  $\text{Cl}_2$ ) to relieve the stress caused by the excess  $\text{Cl}^-$  ions. This means more  $\text{Cl}_2$  will be formed from the equilibrium reaction, effectively preventing  $\text{Cl}_2$  from dissolving in water.

**+1 point for writing out the equation**

**+1 point for correct explanation**

- 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)

Absorb unreacted chlorine so that the toxic gas isn't released to the atmosphere.

Prevent moisture in the air from entering E and ruining the product.

Serve as an outlet for gas so that the apparatus doesn't explode.

**+1 point for every correct answer (max: +2 points)**

- d. Right on top of the letter "D", there is a narrowing in the tube. What simple measure could be taken if  $\text{AlCl}_3$  solidifies and clogs up that tube? (1 point)

Heat the clogging with flame. ( $\text{AlCl}_3$  readily sublimates at a temperature of  $192^\circ\text{C}$ )

**+1 point for correct answer**

- 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
$AgCl$	$1.8 \times 10^{-10}$	$1.7 \times 10^{-5}$ mol/L	White solid
$Ag_2CrO_4$	$2.0 \times 10^{-12}$	$8 \times 10^{-5}$ mol/L	Brown red solid

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

Brown red precipitates (+1 point) in white cloudy solution (+1 point) and doesn't dissolve back in 30 seconds (+1 point).

+1 point for every correct answer (max: +2 points)

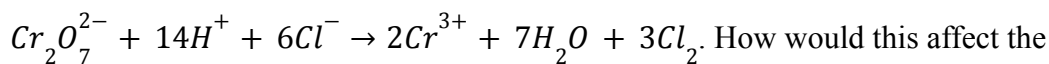
- f. Consider only the reaction between silver ions and chloride ions. If 11.30 mL  $AgNO_3$  is used to reach the endpoint, determine the purity of the kitchen aluminum foil in % (no need to show your work). Assume impurities stay unreacted. (2 points)

$$\frac{11.30 \times 10^{-3} \times 0.1 \times 50}{3} \times 26.982 = 0.508161 \text{ g Al}$$

$$\frac{0.508161}{0.80} \approx 63.5\% \text{ (answers within 63\%-64\% are all acceptable)}$$

+2 points for correct answer

- g. In acidic solutions,  $CrO_4^{2-}$  is converted into  $Cr_2O_7^{2-}$  and can react with chloride:



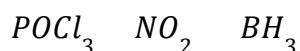
How would this affect the value of the calculated purity? Circle your answer. (2 points)

- Larger than the true purity value
- No effect
- Lower than the true purity value (+2 points)
- Cannot be determined

**Problem #4: (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  $\text{SO}_2$  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)

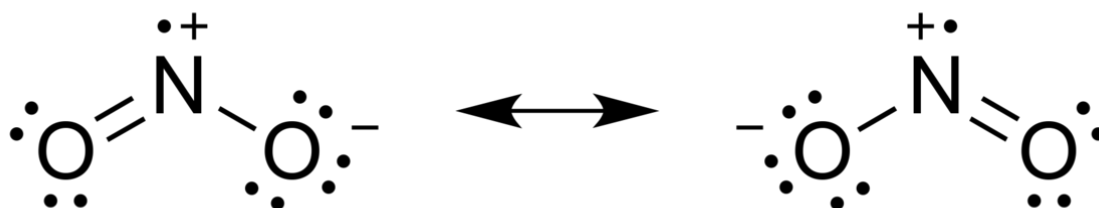


$\text{POCl}_3$ : 10;  $\text{NO}_2$ : 9;  $\text{BH}_3$ : 6

**+1 point for every right answer**

- 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)

$\text{NO}_2$ . Only elements from row 3 or beyond could have more than 8 electrons, because they have empty d orbitals that could contain the excess electrons.



**+1 point for correctly identify  $\text{NO}_2$**

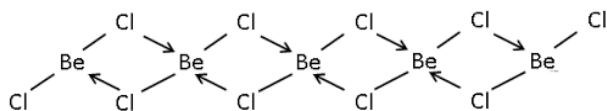
**+1 point for correct explanation**

**+1 point for drawing correct lewis structure and the corresponding resonance structure**

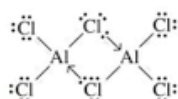
- c. Explain with Lewis structure drawings why  $AlCl_3$  tends to dimerize and  $BeCl_2$  tends to polymerize. Use arrows to show coordinate bonds. (2 points)

Answer:

$BeCl_2$ :



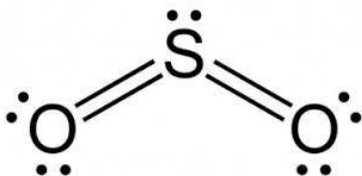
$AlCl_3$ :



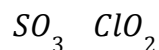
+1 point for the correct drawing of  $AlCl_3$

+1 point for the correct drawing of  $BeCl_2$

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



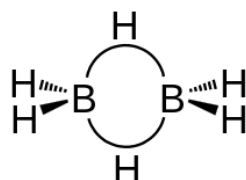
Since every atom is  $sp^2$  hybridized, the three unused p orbitals constitute a group of three delocalized pi bonds across the whole molecule, which contain the four excess electrons. This group of pi bonds is named  $\Pi_3^4$ , for there are 3 central atoms and 4 electrons participating in bonding. Name the groups of pi bonds for the following molecules. (2 points)



Answer:  $SO_3$ :  $\Pi_4^6$  ;  $ClO_2$ :  $\Pi_3^5$

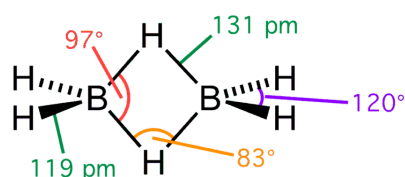
+1 point for each correct answer

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.



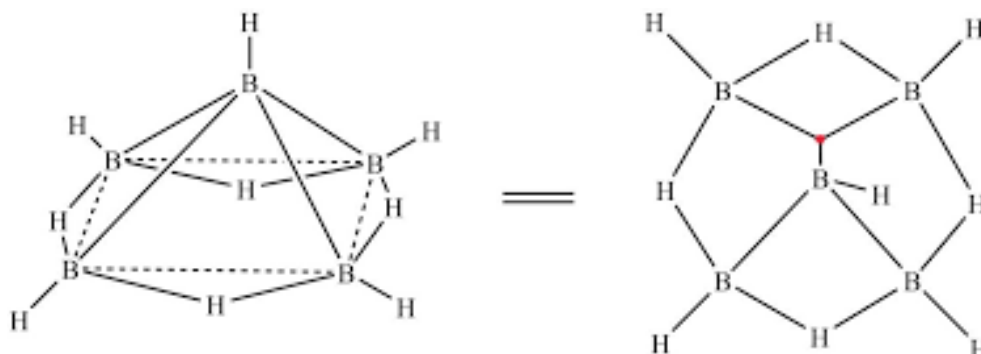
- e. Do you expect the bond angle between the two banana bonds to be more or less than  $109^\circ$ ? Why? (2 points)

Less. The banana bond is a 3 center 2 electron bond, so its electron density is smaller than the pure B-H bond, which is a 2 center 2 electron bond. The bonds with lower electron density repel each other less strongly. Therefore, the bond angle between the two banana bonds should be less than  $109^\circ$ .



**+1 point for correct answer**  
**+1 point for correct explanation**

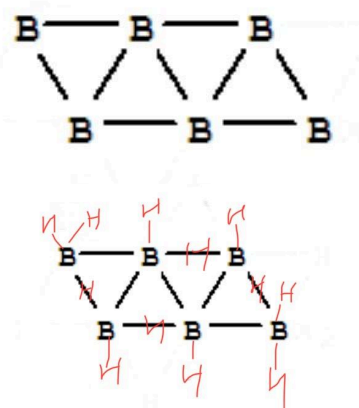
- f. Comparing the formation of hydrogen bridge bonds, explain how the center boron atom in pentaborane ( $B_5H_9$ ) achieves an octet. (2 points)



One B-H bond and two B-B bonds contain 6 electrons. (+1 point)

The three adjacent boron atoms each contribute a ( $sp^3$  hybrid) orbital to form a three-center bond, which contains 2 electrons. (+1 point)

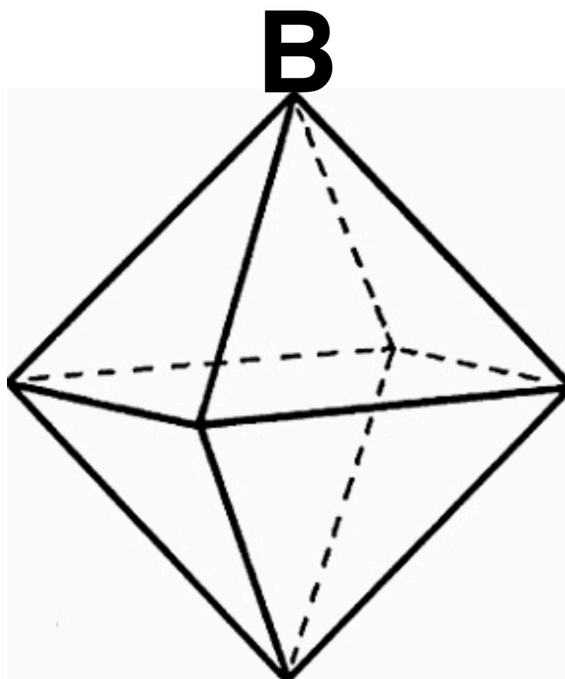
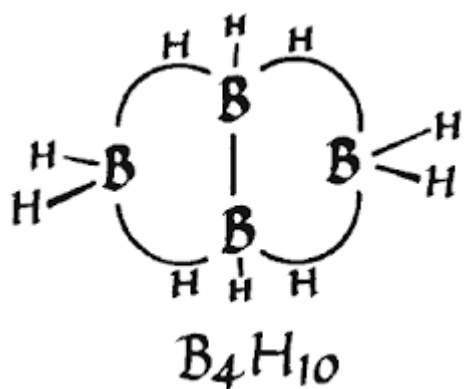
- g. Given the boron framework of hexaborane ( $B_6H_{12}$ ), work out its Lewis structure. Following the example of diborane, put the symbol of hydrogen (H) on a B-B bond to symbolize a bridge bond. You do not need to show other types of three-center bonds. (Hint: in hexaborane, there are 6 three-center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



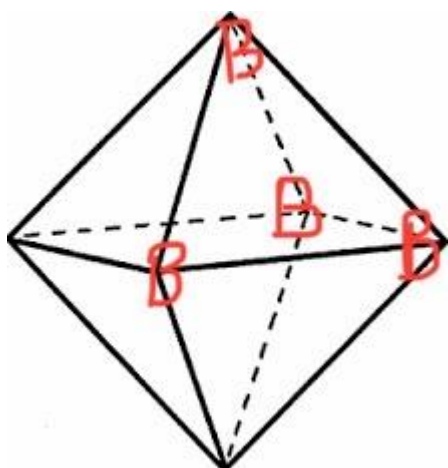
**+1 point for completely correct terminal bonds**  
**+1 point for completely correct bridge bonds**



- 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)



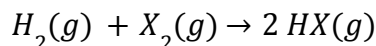
Answer:



+2 points for correct positioning of borons (other positions are possible as long as four borons form a tetrahedron)

**Problem #5: (12 points)**

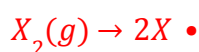
Hydrogen halides are inorganic compounds which are all gases at room temperature and Arrhenius acids with a general formula HX, where X can be fluorine, chlorine, bromine, iodine, astatine, or tennessine. For your chemistry class, you need to synthesize a hydrogen halide.



- 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<sub>2</sub>. Your mechanism will have three parts, with the first step being X<sub>2</sub> 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)**



$$\text{Rate} = k_1[X_2]$$

**+1 point for correct rate equation**

- 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)**

$k_1$  and  $k_{-1}$  are in equilibrium.

$$k_1[X_2] = k_{-1}[X \cdot]^2$$

$$[X \cdot] = \sqrt{\frac{k_1[X_2]}{k_{-1}}} \quad \text{+1 point}$$

For the third step:

$$\text{Rate} = k_2[H_2][X \cdot]^2$$

$$\text{Plugging in for } [X \cdot]: \text{Rate} = \frac{k_1 k_2}{k_{-1}} [X_2][H_2] \quad \text{+1 point}$$

**+1 point for correct expression of [X•]**

**+1 point for correct final rate equation**

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

a.  $\frac{d[X^*]}{dt} = k_1 \cdot [X_2]$  +0.5 points

b.  $-\frac{d[X^*]}{dt} = k_{-1}[X \cdot]^2 + k_2[H_2] \cdot [X \cdot]^2$  +0.5 points

c.  $k_1 \cdot [X_2] = k_{-1}[X \cdot]^2 + k_2[H_2] \cdot [X \cdot]^2$

d.  $[X \cdot]^2 = \frac{k_1[X_2]}{k_{-1}+k_2[H_2]}$  +1 point

e.  $\text{Rate} = k_2[H_2][X \cdot]^2 = \frac{k_2 k_1 [H_2][X_2]}{k_{-1} + k_2 [H_2]}$  +1 point

a. +0.5 points for correct  $\frac{d[X^*]}{dt}$

b. +0.5 points for correct  $-\frac{d[X^*]}{dt}$  (or +1 point if correct c equation is given, then no points for a and b)

d. +1 point for correct  $[X \cdot]^2$

e. +1 point for correct rate law expression

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)

$F_2$ , because it is the lightest

+1 point for identifying the correct halide

+1 point for correct justification

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)

$$F_2: V = \sqrt{3RT \frac{1}{0.038 \text{ kg/mol}}} = 442.3 \text{ m/s}$$

$$Cl_2: V = \sqrt{3RT \frac{1}{0.071 \text{ kg/mol}}} = 323.8 \text{ m/s}$$

$$Br_2: V = \sqrt{3RT \frac{1}{0.160 \text{ kg/mol}}} = 215.7 \text{ m/s}$$

$$I_2: V = \sqrt{3RT \frac{1}{0.254 \text{ kg/mol}}} = 171.1 \text{ m/s}$$

+1 point for correct value for the root mean square (based on the gas that they identified in part e or  $Br_2$  gas if they didn't answer part e)

**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

Total = 73 polymers

$$\text{Average molecular weight} = (1/73)(250,000) + (4/73)(375,000) + (6/73)(415,000) + (9/73)(575,000) + (12/73)(650,000) + (14/73)(725,000) + (13/73)(800,000) + (7/73)(850,000) + (5/73)(925,000) + (2/73)(975,000) = 688904.109589 \text{ g/mol}$$

**+1 point for finding mean**

**+1 point for correct value: 688,904 g/mol**

- 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,

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

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)

$$\text{Total of } N_i M_i = 50,290,000$$

$$\text{Weight Average Molecular Weight} = \left( \frac{1 \cdot 250000}{50290000} * 250000 \right) + \left( \frac{4 \cdot 375000}{50290000} * 375000 \right) + \left( \frac{6 \cdot 415000}{50290000} * 415000 \right) + \dots$$

$$\text{Weight Average Molecular Weight} = 728168.622 \text{ g/mol}$$

**+1 point for writing out the equation for weight average molecular weight**

**+1 point for the correct answer of 728,169 g/mol**

- 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:

Mobile phase: Solution of polymer sample

Solid phase: Porous solid material

**+1 point for correct mobile phase**

**+1 point for correct solid phase**

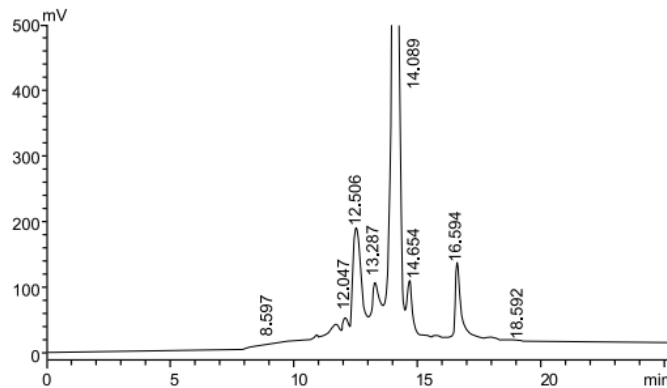
- ii. Do larger or smaller polymers come through a column of this porous material first? Explain your answer in 2-3 sentences. (Hint: Consider which polymers can interact with the pores and which ones cannot, and how this impacts their elution order.) (2 points)

This form of chromatography works on the principle that smaller polymers will get stuck in the pores and move through the porous material more slowly. Thus, **larger polymers will go straight through the column and come out first.**

**+1 point for (large polymers comes out first)**

**+1 point for (small polymers get stuck in pores)**

- 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)



The peaks represent the polymers of different chain lengths coming out of the column, with larger polymers come out first and the smaller polymers come out later. The heights of the peaks indicate the relative amounts of polymer of each length

**+1 point for correctly identifying that each peak corresponds to a polymer of a certain chain length**

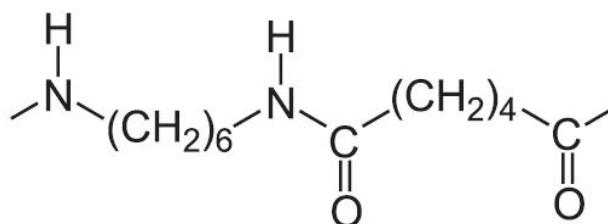
**+1 point for explaining that the peak heights represent the relative amounts of polymer of each chain length**

- 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)

If the pores were too small, all the polymers would run through at the same time, so there would be no separation between the peaks in the chromatogram. The chromatogram would be 1 large peak on the far left (low time).

**+1 point for stating that there will be 1 single peak**

- 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)**



**Hydrogen bonds** between the N-H and C=O keep the Nylon chains together. A series of intermolecular hydrogen bonds are strong enough to hold chains “in Parallel.”

**+1 point for stating Hydrogen bonds**

- 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)**

Energy needs to be added to break hydrogen bonds. Once hydrogen bonds are broken, the separate chains can move past each other.

**+0.5 points for stating that energy is needed to break hydrogen bonds**  
**+0.5 points for explanation that hydrogen bonds need to break to slide chains against each other**



- 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

I would expect the **melting temperature to be higher** because the melting temperature breaks up the rigid crystalline structure in polystyrene. The glass transition temperature represents the amount of energy required for chains to just begin to wiggle past each other.

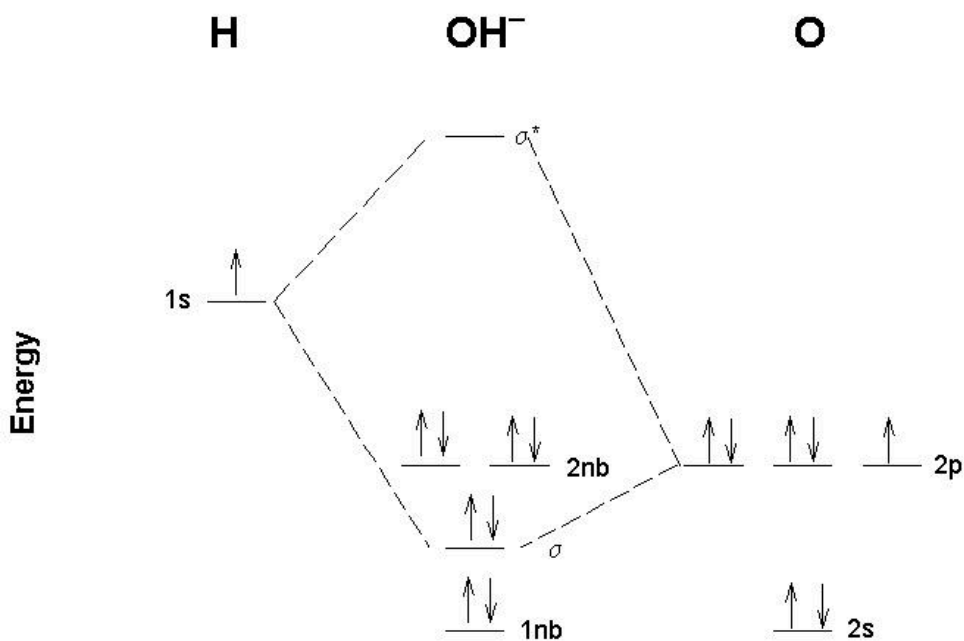
**+1 point for saying that melting temperature is higher**

**+1 point for correct explanation**

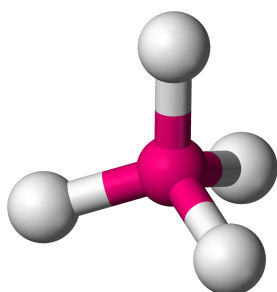
**Problem #7: (10 points)**

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.

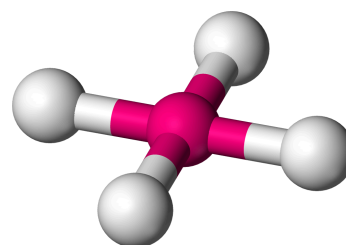
For example, the molecular orbital diagram for  $\text{OH}^-$  is shown.



You know that methane ( $\text{CH}_4$ ) has tetrahedral geometry, but what if it actually had square-planar geometry instead?



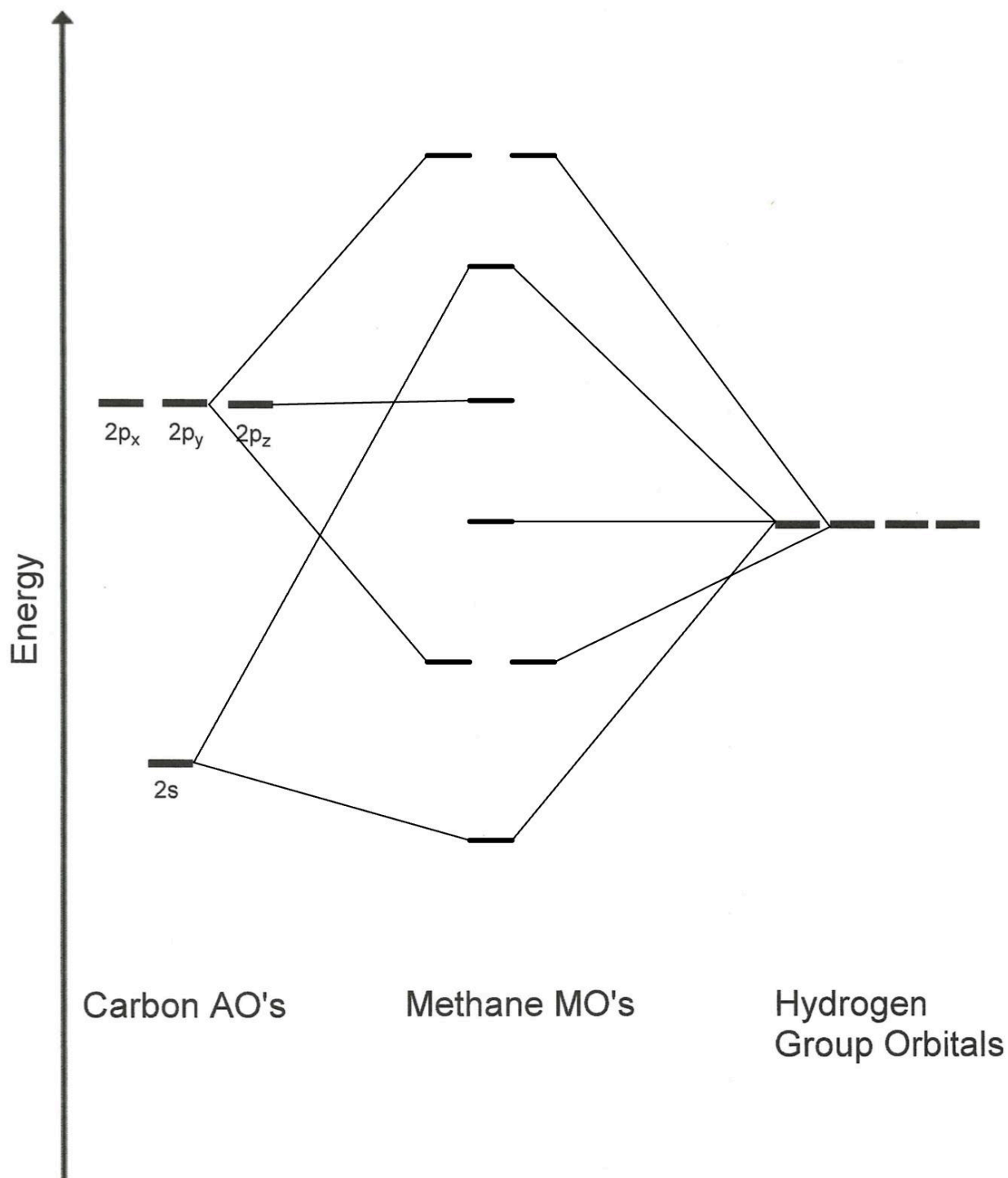
**Tetrahedral**



**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)



+0.5 points for correct Carbon 2s orbital

+0.5 points for correct Carbon 2p orbitals

+0.5 points for correct Hydrogen Group orbitals

+1.5 points for correct Methane MO's

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

$$\frac{1}{2} \left( \frac{\text{\#bonding electrons} - \text{\#antibonding electrons}}{\text{\# of bonds}} \right) =$$
$$\left(\frac{1}{2}\right)\left(\frac{6}{4}\right) = \frac{3}{4}$$

**+2 points for correct bond order**

- 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)

A square-planar geometry for methane would lead to the bond order of each C-H bond being  $\frac{3}{4}$  compared to a bond order of 1 for tetrahedral C-H. A higher bond order means stronger and more stable bond that is overall lower in energy. A tetrahedral shape allows for the maximum symmetry between the orbitals of C and H, which leads to a maximum orbital overlapping, allowing for a stronger bond and a larger bond order of 1.

**+1 point for identifying that the bond order of each C-H bond in a square-planar geometry is less than that in a tetrahedral geometry**

**+1 point for saying that a higher bond order means a stronger and a more stable bond**

**+1 point for identifying that a tetrahedral shape allows for the maximum symmetry between the orbitals of C and H.**

**+1 point for saying that the maximum symmetry leads to optimized overlap**

**+1 point for saying that the optimized overlap leads to stronger bonds and a larger bond order of 1 for each C-H bond.**