

Final Examination

Do all questions. You may use a calculator, a ruler, character tables and molecular models; no additional material may be used. Answer all questions on the test - if more space is required, use the back of the page and indicate that your answer is not complete. Equations that you may want to use are found on the last page with the periodic table.

The exam is out of 200 point - use your time wisely.

Question #1 [15]

(a) Balance the following equation (put a number in front of each compound): [4]



(b) What is the difference in energy between the ground state and the third excited state of He(+1)?[4]

(c) What is the ground state electron configuration of selenium?[1]

(d) For a given value of n , why are ns orbitals always more stable than np orbitals?[2]

(e) Provide two reasons why Hund's rule must be used to determine the ground state electron configuration.[4]

Question #2 [25]

(a) Draw, as carefully as you can the following orbitals: $3p_x$, $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{z^2}$. Be sure to show the axes and the relative phases (with + or - signs) of ψ . [4]

(b) Draw, as carefully as you can graphs of the radial function $R(r)$ for the orbitals: $4d_{xy}$ and $3s$. [4]

(c) Construct a **Walsh diagram** and use it to explain why H_3^+ has a triangular structure (D_{3h}) instead of a linear arrangement (D_{4h}). Draw and label the MO's for each structure. Explain why the orbital energy levels change the way that they do in your diagram as the angle at the central H atom varies from 180° to 60° . [12]

(d) With a drawing to specify the orientation of the hybrid orbitals, write appropriate LCAO's for a set of sp^3 hybrid orbitals. [5]

Question #3 [25]

(a) **What** is the trend in first ionization enthalpies for the group 17 elements (use " $>$ ", " $<$ " or " \cdot ")? *Note that the heavier elements missing from the periodic table are I and At.* [2]

(b) Explain what is meant by "the d-block contraction". Provide an example of an effect caused by "the d-block contraction". [4]

(c) **What** is the trend in first ionization enthalpies for the elements of the second period (describe in a sentence or two and **draw an approximate plot of ionization energy vs. element**)?[4]

(d) **Explain** the general trend in first ionization enthalpies for the elements of the second period and explain all the anomalies in the trend. [9]

- (e) Which of the following would you expect to have the smallest radius: boron, aluminum, silicon or carbon? Why? (Briefly - one sentence) [2]
- (f) Which of the elements in (e) has the highest effective nuclear charge? (You don't have to calculate it) [2]
- (g) Lead (Pb, the heaviest element in group 14) generally forms compounds in the +2 oxidation state instead of the +4. Suggest a reason for this behaviour. [2]

Question #4 [35]

- (a) Draw valence MO diagrams for the heteronuclear diatomic compounds BF and HF. The ordering of the orbitals in BF is similar to that of O₂. Be sure to label everything correctly. [14]
- (b) What is the most significant difference between the two diagrams that you have drawn in part (a)? [2]
- (c) Using your diagram from part (a), what bond orders would be predicted for BF, BF⁺, BF⁻. [3]
- (d) Draw pictures of the HOMO and the LUMO for BF. [4]
- (e) HF reacts with the H⁺ to give a cation with the formula [H₂F]⁺. Based on your MO diagram in part (a), what would be the Lewis structure of [H₂F]⁺? [2]
- (f) HF reacts with the F⁻ to give an anion with the formula [HF₂]⁻. Based on your MO diagram in part (a), what would be the Lewis structure of [HF₂]⁻? [2]
- (g) Construct a simple MO diagram for the sigma bonding in [HF₂]⁻. Use only the ns atomic orbitals on each atom to build your MO's! What is the bond order of each bond? [8]

Question #5 [20]

- (a) Use an appropriate Born-Haber cycle to estimate the electron attachment enthalpy for the formation of O²⁻(g) from O⁻¹(g) using the following data (all in kJ/mol): [7]

$$\text{Na}_{(s)} \rightarrow \text{Na}_{(g)} \quad \Delta H_{\text{vap}} = 108$$

$$\text{O}_{2(g)} \rightarrow 2 \text{O}_{(g)} \quad \Delta H_{\text{d}} = 497$$

$$\text{O}_{(g)} \rightarrow \text{O}_{(g)}^{-} \quad \Delta H_{\text{ea}} = -141$$

$$\text{Na}_{(g)} \rightarrow \text{Na}_{(g)}^{+} \quad \Delta H_{\text{ie}} = 496$$

$$\text{Na}_{(g)}^{+} \rightarrow \text{Na}_{(g)}^{+2} \quad \Delta H_{\text{ie}} = 4562$$

$$\Delta H_{\text{f(Na}_2\text{O)}} = -414$$

$$U_{\theta(\text{Na}_2\text{O)}} = -2527.5$$

- (b) Use the Born-Mayer equation to estimate the lattice energy for NaO using the following data: the radius in Å for Na is 1.91, the radius for Na⁺ is 1.02, the radius for O⁻¹ is 1.72 and the radius for O⁻² is 1.40. The Madelung constant for a rock salt structure is 1.748, the Madelung constant for an anti-fluorite structure is 2.519. [3]

(c) Use the Kapustinskii equation to estimate the lattice energy for NaO using the data in (b). How do the values compare to each other and how do they compare to the value listed for Na₂O in part (a)? [4]

(d) Use the data from (a) and (c) to determine the enthalpy of formation for NaO. Predict the relative stabilities of Na₂O and NaO. [6]

Question #6 [15]

(a) **Draw** a unit cell for a cubic close packed array of anions. **Indicate** as accurately as you can the location of one tetrahedral hole and the location of one octahedral hole. [4]

(b) **What** are the two structures that can be adopted by ZnS? **Explain** the similarities and differences between the two structures. [4]

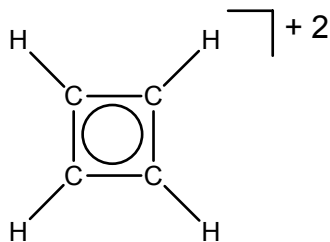
(c) **What** is the maximum radius ratio r_+/r_- for the Rock Salt structure - **draw** a diagram to show how it is derived. [3]

(d) Would the rock salt structure be expected for Al₂S₃ ($r_+(\text{Al}^{3+}) = 0.54 \text{ \AA}$, $r_-(\text{S}^{2-}) = 1.70 \text{ \AA}$)? If not, which of the other simple structures might be observed? [2]

(e) Potassium Iodide crystallizes with the rock salt structure. Should it? ($r_{\text{K}^+} = 1.38 \text{ \AA}$, $r_{\text{I}^-} = 2.20 \text{ \AA}$). [2]

Question #7 [20]

The cyclobutadiene dication, C₄H₄⁺², is a planar aromatic molecule with D_{4h} symmetry.



(a) What is the hybridization of each carbon atom in the molecule drawn above? [2]

(b) **Draw**, as accurately as you can, the four MO's that are used for the π -bonding perpendicular to the molecular plane in C₄H₄⁺². [8]

(c) How would the MO's from part (b) be ordered based on their energies? [4]

(d) What would be the symmetry labels for each of the MO's that you drew in part (b)? [4]

(e) How many electrons would there be in the π -system of C₄H₄⁺²? [2]

Question #8 [35]

(a) Pentaphenylantimony (SbPh₅) has a square-based pyramidal geometry. (a) Assuming a point group of C_{4v}, use the appropriate character table to determine the orbitals on Sb that are used in the σ bonding. Hint: you

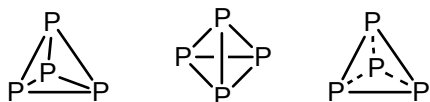
only have to consider the bonds of the SbC_5 fragment. [10]

(b) Comment on the similarities and differences between the orbitals that you have determined and those that are used to make hybrid orbitals in a trigonal bipyramidal molecule. [5]

(c) Determine the point group for each of the following molecules: [10]

SF_4 GeF_5^{-1} XeF_4 XeF_2 $\text{HFC}=\text{CF}_2$ (trifluoroethene)

(d) Determine the number of IR and Raman signals predicted for white phosphorus, P_4 (this is a tetrahedral T_d cluster with nothing at the point, three views of the molecule are shown below). Please note that degenerate modes give rise to only 1 signal per mode. [10]



Question #9 [10]

In the table below insert the correct symbols for the missing elements up to Kr:

BONUS: Identify the number and relative intensities of the signals one would see in the ^{19}F NMR spectra of the compounds listed in Question #8 (c). You can put in on the page beside the point group you have chosen.

Have a great holiday!

Some equations and information you might want to use:

$$U_0 = 1390 * (z_a * z_b / d^0) * A * (1 - (d^* / d^0))$$

$$U_0 = 1210 * (n * z_a * z_b / d^0) * (1 - (d^* / d^0))$$

$$\sin(0E) = \cos(90E) = 0$$

$$\sin(30E) = \cos(60E) = 0.5$$

$$\sin(45E) = \cos(45E) = 0.7071$$

$$\sin(60E) = \cos(30E) = 0.8660$$

$$\sin(90E) = \cos(0E) = 1$$