Question #1 [15]
(a) Use the Bohr equation to determine the electronic energy of the first excited state of B(+4).

(b) What is the difference in energy between the ground state and the third excited state of Be(+3)?

(c) What is the ground state electron configuration of bromine?

(d) What is the Aufbau principle?

(d) What is Hund's rule?

Question #2 [25]
(a) Draw, as carefully as you can the following orbitals: $3p_x$, $3d_{x2-y2}$, $3d_{xy}$, $3d_{z2}$. Be sure to show the axes and the relative phases (with + or - signs) of ψ.

(b) Draw, as carefully as you can graphs of the radial function R(r) for the orbitals: $4p_x$, $3d_{x2-y2}$, $4d_{xy}$, 1s.

(c) Sketch bonding and anti-bonding molecular orbitals that can be obtained from linear combinations of the p_y and the d_{yz} orbitals assuming z is the internuclear axis. Label the orbitals.

(d) With a drawing, show why the molecular orbitals formed by linear combinations of the p_z and the d_{yz} are non-bonding. (Again, take the internuclear axis as z.) Write the equation for the overlap integral for these orbitals.

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

Question #3 [25]
(a) Use Slater's rules to calculate the effective nuclear charge experienced by a valence electron in phosphorus and in sulphur.

(b) Does the result you obtained in part (a) suggest that it would be easier to remove a valence electron from phosphorus or from sulphur? Is this what is observed experimentally? (Yes or No)

(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)?

(d) Explain the general trend in first ionization enthalpies and explain the anomalies in the trend.

(e) Which of the following would you expect to have the smallest covalent radius: oxygen, fluorine, sulphur or chlorine? Why? (Briefly)

(f) Aluminum and gallium have the approximately the same radius in their covalent compounds. Based on your answer to part (e), you might not have predicted this observation. What extra factor(s) help to explain this similarity.

Question #4 [30]
(a) There are two different types of valence MO diagrams for the homonuclear diatomic molecules of the second period (Li_2 to Ne_2). Draw fully labeled diagrams for these two cases and indicate which of the diatomic molecules of the second period are described by each diagram.

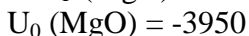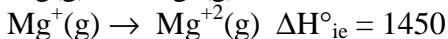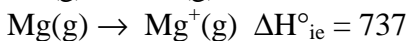(b) Why are the MO's for the diatomic molecules of the second row ordered in these two different ways?
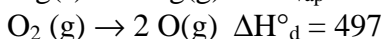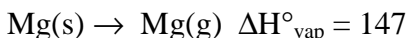
(c) What bond orders are predicted using the diagrams in part (a) for the ions N_2^{+1}, N_2^{-2}. (Hint, the results should be identical for either type of diagram.)

(d) Describe how the diagrams from part (a) should be modified to show the MO energy levels of NO^+, a heteronuclear diatomic ion? (Briefly.)

(e) Draw a Lewis structure for O_2 and using the appropriate molecular orbital energy level diagram drawn above in part (a) determine the following: on which feature(s) of the dioxygen molecule do the two bonding models agree and on which do they differ. Which model agrees most closely with the experimental observations.

Question #5 [25]
(a) Use an appropriate Born-Haber cycle to estimate the total electron attachment enthalpy for the formation of $O^{-2}_{(g)}$ from $O_{(g)}$ using the following data (all in kJ/mol):

$Mg(s) \rightarrow Mg(g)$ $\Delta H°_{vap} = 147$
$O_2 (g) \rightarrow 2 O(g)$ $\Delta H°_d = 497$
$Mg(g) \rightarrow Mg^+(g)$ $\Delta H°_{ie} = 737$
$Mg^+(g) \rightarrow Mg^{+2}(g)$ $\Delta H°_{ie} = 1450$
$\Delta H°_F (MgO) = -602$
$U_0 (MgO) = -3950$

(b) Use the Born-Mayer equation to estimate the lattice energy for Mg_2O using the following data: the radius in Å for Mg is 1.60, the radius for Mg^+ is 1.16, the radius for Mg^{+2} is 0.72 and the radius for O^{-2} is 1.40. The Madelung constant for a rock salt structure is 1.748, the Madelung constant for a fluorite structure is 2.519.

(c) Use the Kapustinskii equation to estimate the lattice energy for Mg_2O using the data in (b). How do the values compare to each other and how do they compare to the value listed for MgO in part (a)?

(d) Use the data from (a) and (c) to determine the enthalpy of formation for Mg_2O. Predict the relative stabilities of Mg_2O and MgO.

Question #6 [15]
(a) Sketch a unit cell for the structure of rock salt (NaCl) and indicate the coordination number around each cation and each anion.

(b) What is the ideal radius ratio r+/r- for the NaCl structure - draw a diagram to show how it is calculated. (derive it if you have the time, note that $\sin(45°) = 0.7071$)

(c) Would the rock salt structure be expected for BeS $(r+(Be^{+2}) = 0.59$ Å, $r-(S^{-2}) = 1.70$ Å)? If not, which of the other simple structures might be observed?

(d) Lithium fluoride crystallizes with the rock salt structure. Should it? $(rLi^+ = 0.90$ Å, rF^- $= 1.19$ Å).

Question #7 [30]
The nitrate anion NO_3^{-1} and sulfur trioxide SO_3 have the same number of valence electrons.

(a) Draw Lewis structures for each of these molecules and indicate the average bond order for the bonds from the central atom to the oxygen atoms.

(b)Use VSEPR theory and VBT to describe the bonding in NO_3^{-1} and SO_3.

(c) Construct an MO diagram for the σ-bonding in NO_3^{-1} (the diagram for SO_3 is essentially identical). For simplicity, make the SALCs from the 2s orbitals on the O atoms.

(d) Construct MO diagrams for the π-bonding in in NO_3^{-1} and SO_3 and indicate the most important difference between the diagrams.   For simplicity, use only the $2p_z$ atomic orbitals on the O atoms to make the SALCs.
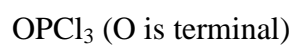
Question #8 [25]
(a) Draw pictures that indicate the location of the different kinds of symmetry elements in a molecule with T_d symmetry.

(b) Determine the point group for each of the following molecules:

XeF_4

SbF_6^{-1}

$SOCl_2$ (O is terminal)

allene

$OPCl_3$ (O is terminal)
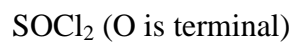
(c) Determine the number of IR and Raman signals predicted for chlorine trifluoride, ClF_3 (the most stable arrangement has C_{2v} symmetry).