Chem 612 – Fall, 2008
Assignment 2

This assignment is due at the beginning of class on Wednesday, September 19th.

1. As we have seen, the bond enthalpies of H–X molecules are greater than the averages of the bond enthalpies of H–H and X–X. Given that $D(\text{H–H}) = 436 \text{ kJ/mol}$, $D(\text{Cl–Cl}) = 242 \text{ kJ/mol}$, $D(\text{Br–Br}) = 193 \text{ kJ/mol}$, and $D(\text{I–I}) = 151 \text{ kJ/mol}$, estimate the bond enthalpies of HCl, HBr, and HI as simple averages of the homonuclear bond enthalpies. Compare the values obtained in this way to the measured values $D(\text{H–Cl}) = 432 \text{ kJ/mol}$, $D(\text{H–Br}) = 366 \text{ kJ/mol}$, and $D(\text{H–I}) = 298 \text{ kJ/mol}$. Calculate the difference between the calculated and observed value in each HX case. Account for the discrepancy in general, and explain the variation in the discrepancies throughout this series.

2. Perform radius ratio calculations to show which alkali halides violate the radius ratio rule.

3. As coordination number increases, the size of the cation hole created by a set of close-packed anions increases. The anion radii for Cl$^-$, Br$^-$, I$^-$ are 181, 194, 220 pm, respectively. Calculate the sizes of the tetrahedral (CN4) and octahedral (CN6) holes created by close packing each of these ions.

4. Draw resonance forms for the following species and estimate the indicated bond order in each case: (a) a BN bond in $\text{B}_3\text{N}_3\text{H}_6$, (b) a CO bond in $\text{HCO}_2^-$, (c) an SO bond in $\text{SO}_3^2-$.

5. Bond distances for free thiocyanate ion, SCN$^-$, have been determined by ab initio calculations to be 167.9 pm for the SC bond and 118.7 pm for the CN bond (G. Baranovic & D. Babic, Spectrochim. Acta Part A. 2004, 60, 1013-1025). Using the Pauli covalent radii given in class, estimate the expected length of the SC bond as a single and a double bond, and the expected length of a CN bond as a single, double, and triple bond. Compare these results to your expectations of relative bond order based on the three principle resonance forms of SCN$^-$. Based on the resonance model and the bond lengths, describe the bond orders in SCN$^-$. Can exact numbers be given for the bond orders in SCN$^-$? Explain.

6. The dipole moment in HBr is 0.827 D and the bond distance is 141.5 pm. Assuming a point-charge model (i.e., ignoring atomic dipoles), calculate the apparent charges on H and Br (the charge distribution). (1 D = $3.336 \times 10^{-30} \text{ C} \cdot \text{m}$, unit charge = $1.602 \times 10^{-19} \text{ C}$).

7. SF$_6$ is non-polar, but SF$_4$ has a dipole moment of 0.632 D. Explain. Although SF$_4$ is polar, its dipole moment is very low. Offer an explanation for this.
8. Write both the valence and complete electronic configurations for each of the following atoms or ions: Br, Tl, Cr, Co$^{2+}$, Sn$^{2+}$. Write both configurations in shell order, grouping all subshells of the same $n$ value together, rather than in aufbau order (the order of filling). For example, the complete configuration of $^{56}$Fe in shell order is $1s^22s^22p^63s^23p^63d^64s^2$, and its valence configuration written in shell order is $3d^64s^2$. Writing configurations in this order is preferred, because it always places the valence electrons at the end.