

Chem 612 – Fall, 2008
Assignment 2 - Solutions

This assignment is due at the beginning of class on Wednesday, September 17th.

- 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.

HX	D_{calc}	D_{obs}	ΔD	$\Delta\chi$
HCl	339	432	93	0.6
HBr	315	366	51	0.5
HI	293	293	5	0

The discrepancy lessens as the difference in electronegativity becomes smaller. This suggests that the greater bond energy in the more polar cases is due to ionic character. Based on Allred-Rochow electronegativities to one decimal place, the bond in HI is nearly nonpolar.

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

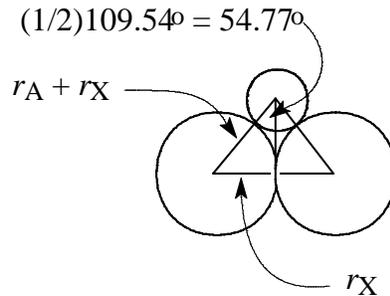
All alkali halides at room temperature have the NaCl structure (CN6), except CsCl, CsBr, and CsI, which have the CsCl structure (CN8). The radius ratio range for CN6 is 0.41-0.73, and the range for CN8 is >0.73 . The following table shows the calculated values of r_+/r_- , using Shannon values for CN6. Those that do not predict the correct structure are indicated in red. (Different conclusions are reached for LiCl, NaF, and KCl, if Pauling values are used.)

	F ⁻	Cl ⁻	Br ⁻	I ⁻
Li ⁺	0.57	0.42	0.39	0.35
Na ⁺	0.77	0.56	0.53	0.46
K ⁺	1.04	0.76	0.71	0.63
Rb ⁺	1.14	0.84	0.78	0.69
Cs ⁺	1.26	0.92	0.86	0.76

- As coordination number increases, the size of the cation hole created by a set of close-packed

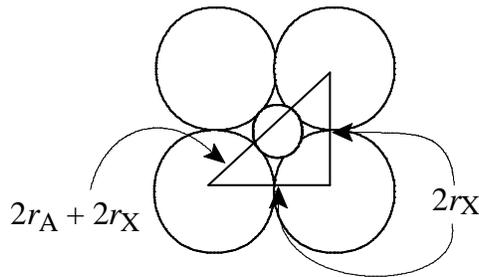
anions increases. The anion radii for Cl^- , Br^- , I^- are 181, 194, 220 pm, respectively. Calculate the sizes of the tetrahedral (CN4) and octahedral (CN6) holes created by close packing each of these ions.

The following diagram pertains to the CN4 tetrahedral case:



Therefore, $\sin 54.77^\circ = \frac{r_X}{r_X + r_A}$, and $r_A = 0.2242r_X$.

The following diagram pertains to the CN6 octahedral case, which can be considered in any one plane of four X^- ions.



Therefore, $r_A = \sqrt{2}r_X - r_X = 0.4142r_X$

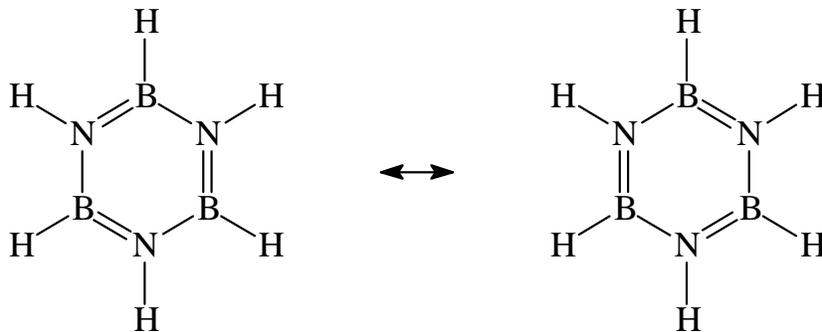
Using these two formulas gives the following values for the radii of the cation holes (pm) for each coordination of each ion.

Anion	r_X	CN4 r_A	CN6 r_A
Cl^-	181	40.6	75.0
Br^-	194	43.5	80.4
I^-	220	49.3	91.1

In all CN4 cases, only the smallest cations (e.g., $\text{Al}^{3+} - 39$ pm) would be able to fit inside the hole made by the anions.

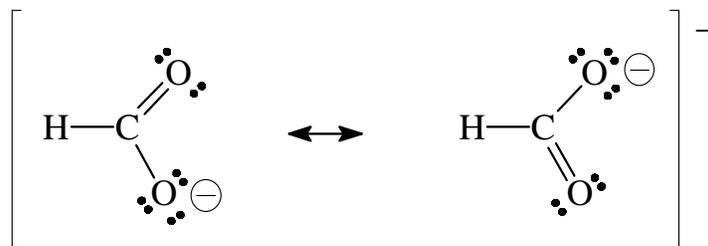
4. Draw resonance forms for the following species and estimate the indicated bond order in each case: (a) a BN bond in $B_3N_3H_6$, (b) a CO bond in HCO_2^- , (c) an SO bond in SO_3^{2-} .

(a)



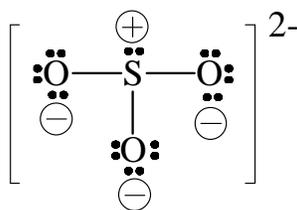
Bond order = $1\frac{1}{2}$

(b)



Bond order = $1\frac{1}{2}$

(c) No resonance forms

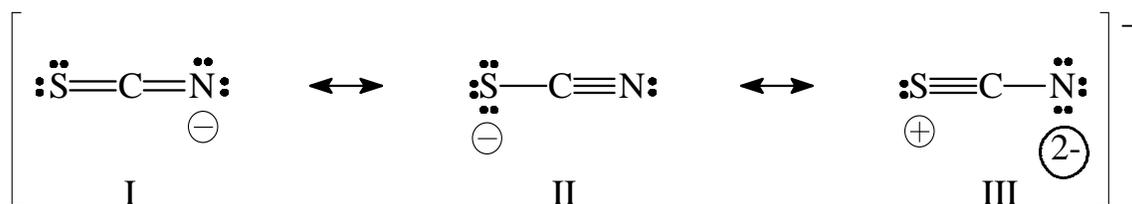


Bond order = 1

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.

Estimated Bond Lengths

S-C	181	C-N	147
S=C	161	C=N	128
		C≡N	115



Form I is most reasonable, based on formal charge assignment giving electronegative nitrogen the negative charge. Form II is somewhat less favored, based on the negative formal charge on S, a less electronegative element. Form III is not reasonable, due to high formal charges and large charge separation. From forms I and II, the SC bond is between a single and double bond, but closer to being double. This agrees with the observed length, which is closer to the calculated double bond length. Likewise, the CN bond is between a double and triple bond, in agreement with the observed bond length. In this case, the observed length appears to be closer to the calculated triple bond. Because the two principal resonance forms are not equally probable, it is not possible to calculate a numerical bond order for either the SC or CN bond.

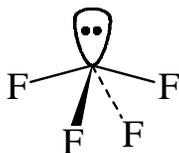
6. The dipole moment in HBr is 0.827 D and the bond distance is 141.5 pm. Assuming a point-charge model (i.e., ignoring atomic dipoles), calculate the apparent charges on H and Br (the charge distribution). (1 D = $3.336 \times 10^{-30} \text{ C}\cdot\text{m}$, unit charge = $1.602 \times 10^{-19} \text{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

$$\mu = (0.827 \text{ D})(3.336 \times 10^{-30} \text{ C}\cdot\text{m/D}) = 2.759 \times 10^{-30} \text{ C}\cdot\text{m}$$

$$\begin{aligned}
 \pm q &= \mu/d = 2.759 \times 10^{-30} \text{ C}\cdot\text{m}/141.5 \times 10^{-12} \text{ m} \\
 &= (1.950 \times 10^{-20} \text{ C})(\text{unit charge}/1.601 \times 10^{-19} \text{ C}) \\
 &= 0.122 \text{ unit charge}
 \end{aligned}$$

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.

SF_6 is octahedral, so all S–F bond polarities cancel one another, making the molecule nonpolar. SF_4 is disphenoid (irregular tetrahedron or “see-saw” shape), based on a trigonal bipyramidal (*tbp*) electron domain structure.



The two S–F bonds formed from the axial positions of the *tbp* are pushed together slightly (173.1°) by repulsions from the lone pair. Being nearly linear, though, they contribute little to the overall molecular polarity. The two S–F bonds formed from the equatorial positions are also pushed together slightly from the ideal 120° angle (101.6°). They are the principal bond contributors to the molecular polarity. The net bond polarity runs along the F–S–F bisector from the S (δ^+) toward the two equatorial F atoms (δ^-). However, the lone pair acts in opposition to this net bond polarity, which accounts for the low overall dipole moment. The net direction of the molecular dipole is uncertain.

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 ${}_{26}\text{Fe}$ in shell order is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$, and its valence configuration written in shell order is $3d^6 4s^2$. Writing configurations in this order is preferred, because it always places the valence electrons at the end.

The valence configuration of each complete configuration is shown in red.

