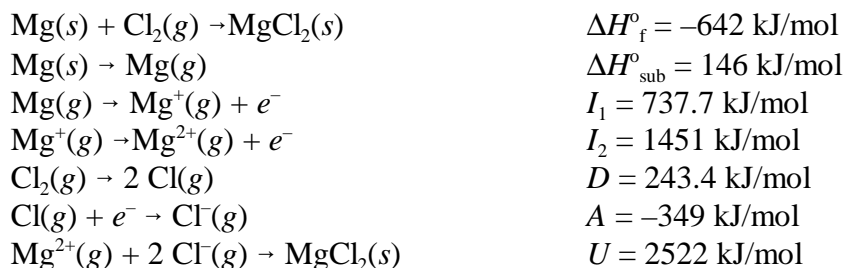


**Chem 612 – Fall, 2008**  
**Assignment 1 - Solutions**

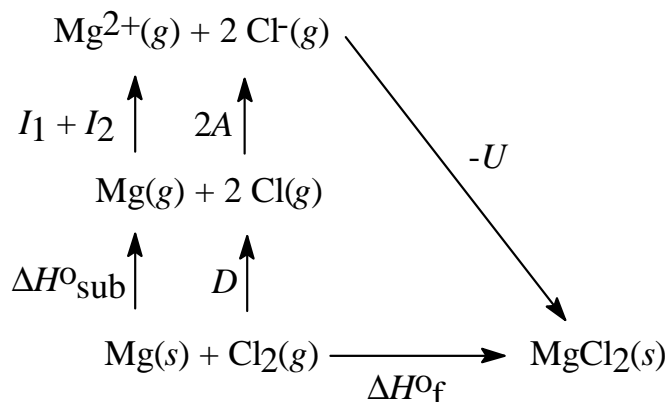
This assignment is due at the beginning of class on Wednesday, September 10, 2008.

1. The standard enthalpy of formation,  $\Delta H^\circ_f$ , is  $-642$  kJ/mol for  $\text{MgCl}_2$ . The enthalpy of sublimation of  $\text{Mg}(s)$ ,  $\Delta H^\circ_{\text{sub}}$ , is  $146$  kJ/mol, and the first and second ionization energies,  $I_1$  and  $I_2$ , of  $\text{Mg}(g)$  are  $737.7$  kJ/mol and  $1451$  kJ/mol, respectively. The dissociation energy of  $\text{Cl}_2$ ,  $D$ , is  $243.4$  kJ/mol, and the electron affinity of  $\text{Cl}(g)$  is  $-349$  kJ/mol. Given these data and additional data below, give answers to the following.

- a. Write thermochemical equations, including state designations, corresponding to all of the data given above and also the lattice energy,  $U$ .



- b. Sketch the Born-Haber cycle for  $\text{MgCl}_2(s)$ , similar to the cycle shown in class for  $\text{NaCl}(s)$ .



- c. Calculate the lattice energy,  $U$ , for  $\text{MgCl}_2(s)$  to verify the value of  $2522$  kJ/mol given in the table shown in class. Show your work.

$$\Delta H^\circ_f = \Delta H^\circ_{\text{sub}} + I_1 + I_2 + D + 2A - U$$

$$U = \Delta H^\circ_{\text{sub}} + I_1 + I_2 + D + 2A - \Delta H^\circ_{\text{sub}} - \Delta H^\circ_f$$

$$= [146 + 737.7 + 1451 + 243.4 + (2)(-349) + 642] \text{kJ/mol} = 2522 \text{ kJ/mol}$$

- d. Explain why the lattice energy of  $\text{MgCl}_2$  is so much greater than that of  $\text{NaCl}$  (787 kJ/mol).

$\text{Mg}^{2+}$  is twice as highly charged and much smaller. Both factors increase the force of attraction between oppositely charged ions, resulting in a much greater potential energy

- e. The values of the lattice energy for  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{SrCl}_2$  are 2522 kJ/mol, 2253 kJ/mol, and 2127 kJ/mol, respectively. Why is this the expected trend?

The cations are progressively larger through the series, increasing the separation between oppositely charged ions. Potential energy decreases with separation of the charges.

- f. The difference in lattice energies between  $\text{MgCl}_2$  and  $\text{CaCl}_2$  is 269 kJ, but the difference between  $\text{CaCl}_2$  and  $\text{SrCl}_2$  is only 126 kJ/mol. Why?

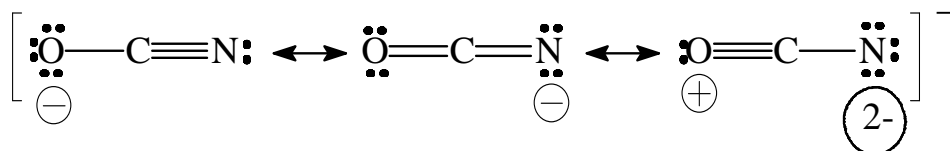
The ionic radii (Shannon CN6 values) are 72 pm, 100 pm, and 110 pm, respectively for  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$ . The lattice energy trend reflects the cation size trend. Both  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  have noble-gas configurations of the type  $ns^2np^6$  ( $n = 2, 3$ ), whereas  $\text{Sr}^{2+}$  has a configuration  $3d^{10}4s^24p^6$ . The size difference between  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  is so much less than between  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , because Ca and Sr are separated by the intervening first transition series, through which sizes decline more gradually owing to poor shielding by  $3d$  electrons. As a result the cation-anion separation in  $\text{SrCl}_2$  is not that much greater than in  $\text{CaCl}_2$ , and the two salts have very similar lattice energies.

2. Difference in electronegativity has sometimes been used to decide if a bond between a pair of atoms is better described as polar covalent or ionic. One often cited criterion is that an electronegativity difference,  $\Delta\chi$ , greater than about 1.6–1.7 marks the beginning of ionic bonds. On this basis, the bond in HF ( $\Delta\chi = 1.9$ ) should be more ionic than that in NaCl ( $\Delta\chi = 1.8$ ). While most chemists would call NaCl ionic, few would do the same for HF. The electron density map of HF indicates a polar covalent bond. But aside from electron density mapping, what properties of HF suggest that it is polar covalent and not ionic? Why is difference in electronegativity an unreliable criterion?

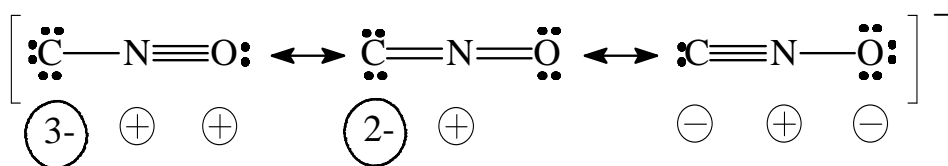
All simple ionic compounds, particularly those composed of monatomic ions, are crystalline solids at room temperature. HF, by contrast, is a gas at room temperature. Moreover, it has a dipole moment ( $\mu = 5.93 \times 10^{-30} \text{ C}\cdot\text{m}$ ), characteristic of a polar covalent molecule. Ionic compounds contain no molecules of the compound, and therefore have no measurable dipole moments. Clearly difference in electronegativity is not a reliable guide to deciding the nature of the bonding between two atoms. The fault lies in assuming that electronegativities are constant from case to case. This is particularly liable to break down in the case of hydrogen. Indeed, as Gillespie and Popelier assert (p. 15), “almost all bonds are polar bonds, whether they are approximately described as covalent or ionic”. “Covalent” and “ionic” cannot be precisely and quantitatively defined, except to note that there are purely covalent bonds (e.g., homonuclear diatomic molecules) but no purely ionic bonds.

3. The cyanate ion,  $\text{OCN}^-$ , forms a number of stable salts, but many fulminates,  $\text{CNO}^-$ , are explosive. (*L. fulmino*, to flash). Draw Lewis structures (including formal charges) for the two anions, and on the basis of these explain the difference in stability.

Cyanate ion can be represented with the following three resonance forms, with the third form being an insignificant contributor:

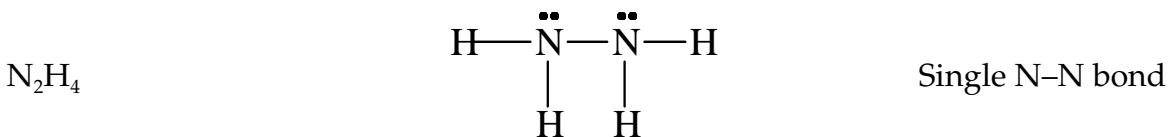


The two principal forms suggest  $\pi$ -delocalization, which stabilizes the molecule. Fulminate ion also has three resonance forms, but only the third is plausible, and even it is less than ideal.

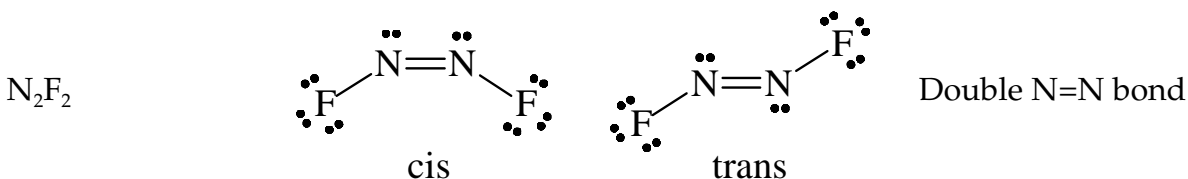


This single plausible form involves extreme charge separation, and it places a positive formal charge on the more electronegative nitrogen and a negative formal charge on the less electronegative carbon.

4. Draw Lewis structures for  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{F}_2$ . What is the N–N bond order in each molecule? Are either capable of having geometrical isomers?



Free rotation about the N–N bond precludes isomers.

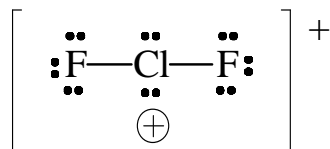


No free rotation about the N–N bond, so there are possible cis and trans isomers.

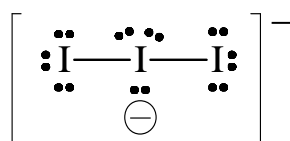
5. Draw Lewis structures, including valence electrons on pendant atoms, for the following molecules and ions. Where appropriate, assign formal charges, but do not draw double bonds or invoke hypervalence solely for the purpose of minimizing formal charges.

$\text{ClF}_2^+$ ,  $\text{I}_3^-$ ,  $\text{ClF}_3$ ,  $\text{IF}_5$ ,  $\text{XeO}_3$ ,  $\text{Cl}_2\text{O}_7$ ,  $\text{SCl}_4$ ,  $\text{B}(\text{OH})_3$ ,  $\text{B}_3\text{N}_3\text{H}_6$  (B and N form a ring),  $\text{Se}_2\text{O}_5^{2-}$ .

$\text{ClF}_2^+$  electron count = Cl (7) + 2F (14) + cation charge (-1) = 20

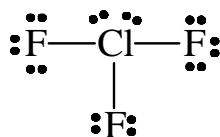


$\text{I}_3^-$  electron count = 3I (21) + anion charge (1) = 22



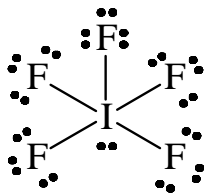
Central I is hypervalent.

$\text{ClF}_3$  electron count = Cl (7) + 3F (21) = 28



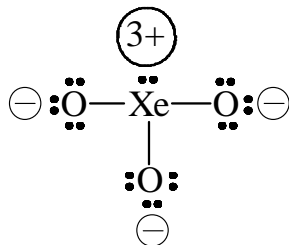
Cl is hypervalent.

$\text{IF}_5$  electron count = I (7) + 5F (35) = 42

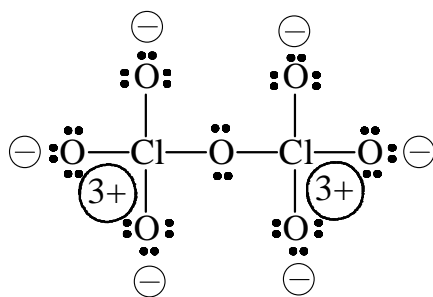


I is hypervalent.

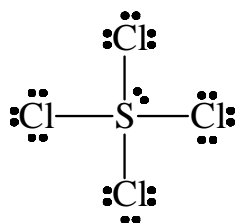
$\text{XeO}_3$  electron count = Xe (8) + 3O (18) = 26



$\text{Cl}_2\text{O}_7$  electron count =  $2\text{Cl} (14) + 7\text{O} (42) = 56$

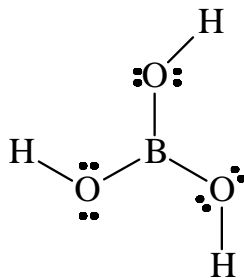


$\text{SCl}_4$  electron count =  $\text{S} (6) + 4\text{Cl} (28) = 34$



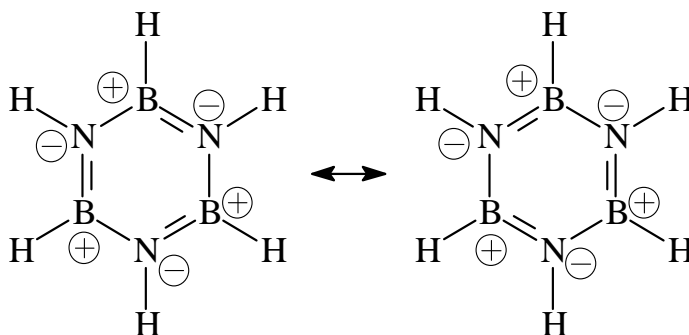
S is hypervalent.

$\text{B}(\text{OH})_3$  electron count =  $\text{B} (3) + 3\text{O} (18) + 3\text{H} (3) = 24$



B is electron deficient.

$\text{B}_3\text{N}_3\text{H}_6$  electron count =  $3\text{B} (9) + 3\text{N} (15) + 6\text{H} (6) = 30$



$\text{Se}_2\text{O}_5^{2-}$  electron count = 2Se (12) + 5O (30) + anion charge (2) = 44

