HW 3
CHEM 362
Answers

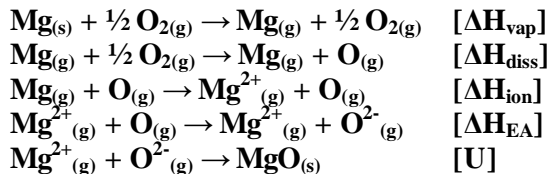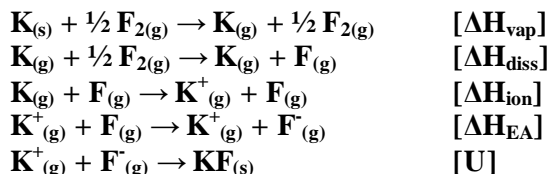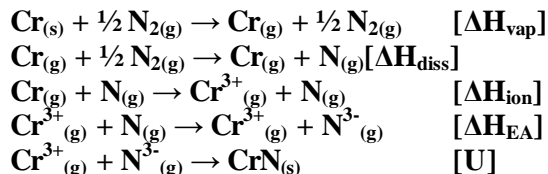Available: Feb. 6, 2008   Due: Feb. 15, 2008

1.   What are the two main contributions to the energy of an ionic solid?

      The contributions to the energy of an ionic solid are: the columbic attraction forces of the cations and and the repulsions of the electron clouds and the nuclei to one another.

2.   What is a Madelung constant? Why can the same Madelung constant be used for seemingly different substances?
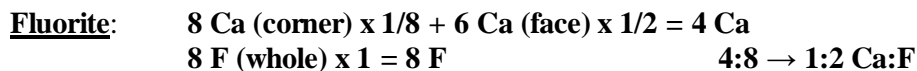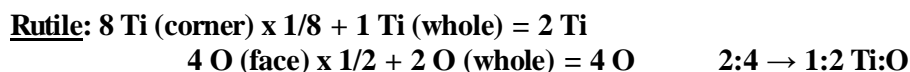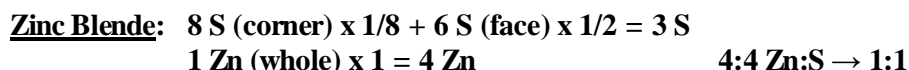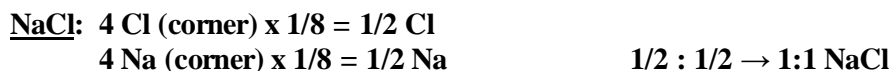
      A Madelung constant is a pseudo-infinite series relating all the charged particles in a lattice with each other. It describes the geometries of all columbic interactions within a lattice. The Madelung constant is determined solely by the geometry of ions in the structure so materials with the same geometries, the same geometric relationship between ions in the lattice can use similar Madelung constants, regardless of the charge on the ions.

3.   Use Figure 4-2 in Cotton as a guide and write out balanced chemical equations for each step in the Born-Haber cycle of CrN, KF and MgO.

$$Cr_{(s)} + ½\,N_{2(g)} \rightarrow Cr_{(g)} + ½\,N_{2(g)} \qquad [\Delta H_{vap}]$$
$$Cr_{(g)} + ½\,N_{2(g)} \rightarrow Cr_{(g)} + N_{(g)} [\Delta H_{diss}]$$
$$Cr_{(g)} + N_{(g)} \rightarrow Cr^{3+}{}_{(g)} + N_{(g)} \qquad [\Delta H_{ion}]$$
$$Cr^{3+}{}_{(g)} + N_{(g)} \rightarrow Cr^{3+}{}_{(g)} + N^{3-}{}_{(g)} \qquad [\Delta H_{EA}]$$
$$Cr^{3+}{}_{(g)} + N^{3-}{}_{(g)} \rightarrow CrN_{(s)} \qquad [U]$$

$$K_{(s)} + ½\,F_{2(g)} \rightarrow K_{(g)} + ½\,F_{2(g)} \qquad [\Delta H_{vap}]$$
$$K_{(g)} + ½\,F_{2(g)} \rightarrow K_{(g)} + F_{(g)} \qquad [\Delta H_{diss}]$$
$$K_{(g)} + F_{(g)} \rightarrow K^{+}{}_{(g)} + F_{(g)} \qquad [\Delta H_{ion}]$$
$$K^{+}{}_{(g)} + F_{(g)} \rightarrow K^{+}{}_{(g)} + F^{-}{}_{(g)} \qquad [\Delta H_{EA}]$$
$$K^{+}{}_{(g)} + F^{-}{}_{(g)} \rightarrow KF_{(s)} \qquad [U]$$

$$Mg_{(s)} + ½\,O_{2(g)} \rightarrow Mg_{(g)} + ½\,O_{2(g)} \qquad [\Delta H_{vap}]$$
$$Mg_{(g)} + ½\,O_{2(g)} \rightarrow Mg_{(g)} + O_{(g)} \qquad [\Delta H_{diss}]$$
$$Mg_{(g)} + O_{(g)} \rightarrow Mg^{2+}{}_{(g)} + O_{(g)} \qquad [\Delta H_{ion}]$$
$$Mg^{2+}{}_{(g)} + O_{(g)} \rightarrow Mg^{2+}{}_{(g)} + O^{2-}{}_{(g)} \qquad [\Delta H_{EA}]$$
$$Mg^{2+}{}_{(g)} + O^{2-}{}_{(g)} \rightarrow MgO_{(s)} \qquad [U]$$

4.   Study the unit cell drawings found in Cotton chapter 4 for NaCl, zinc blende, rutile, CsCl and fluorite. Now by the location of each atom type in the unit cell (corner, edge, face or internal) add up all the contributions from these atoms to show how the empirical formula is arrived at.

Hint: corner atoms are shared by eight unit cells, edges are shared by four unit cells, face atoms are shared by two unit cells and internal atoms belong to only one unit cell.
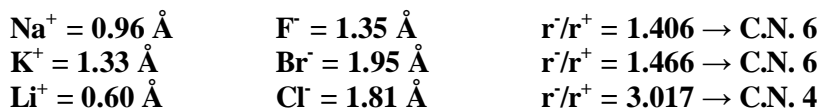
NaCl: **4 Cl (corner) x 1/8 = 1/2 Cl**
4 Na (corner) x 1/8 = 1/2 Na   **1/2 : 1/2 → 1:1 NaCl**

CsCl: **8 Cl (corner) x 1/8 = 1 Cl**
1 Cs (whole) x 1 = 1 Cs   **1:1 Cs:Cl**

Zinc Blende: **8 S (corner) x 1/8 + 6 S (face) x 1/2 = 3 S**
1 Zn (whole) x 1 = 4 Zn   **4:4 Zn:S → 1:1**

Rutile: 8 Ti (corner) x 1/8 + 1 Ti (whole) = 2 Ti
4 O (face) x 1/2 + 2 O (whole) = 4 O   **2:4 → 1:2 Ti:O**

Fluorite: **8 Ca (corner) x 1/8 + 6 Ca (face) x 1/2 = 4 Ca**
8 F (whole) x 1 = 8 F   **4:8 → 1:2 Ca:F**

5.   Lithium fluoride (LiF) adopts the NaCl structure whereas CsI adopts the CsCl structure. Use the radius ratio approach to explain this.

LiF: r^-/r^+ = 1.35/0.60 = 2.25. This ratio falls within the limits of the NaCl structure and has a coordination number of 6. (see table 4-3 on pg 135)

CsI: r^-/r^+ = 2.16/1/69 = 1.28. This ratio falls within the limits of the CsCl structure and has a coordination number of 8. (see table 4-3 on pg 135)

6.   Table 4-3 in Cotton lists the radius ratios r^-/r^+ for perfect packing in structures having coordination numbers of four, six, and eight. In practice, a range of values for these ratios is observed within a series of compounds having the same structure. The typical ranges for the three coordination numbers are (4.44-2.44) for coordination number four; (2.44-1.37) for coordination number six; (1.37 and below) for coordination number eight. with these values in mind, predict coordination numbers for NaF, KBr, and LiCl.
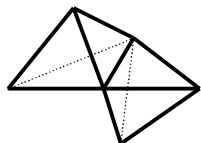
Na^+ = 0.96 Å F^- = 1.35 Å r^-/r^+ = 1.406 → C.N. 6
K^+ = 1.33 Å Br^- = 1.95 Å r^-/r^+ = 1.466 → C.N. 6
Li^+ = 0.60 Å Cl^- = 1.81 Å r^-/r^+ = 3.017 → C.N. 4

7.   Compare the unit cell of zinc blende (pg. 126) with that of diamond (pg. 245). What similarities are there between these two structures?

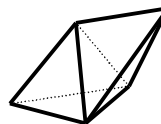**Zinc blende (ZnS) and diamond are structurally identical.**

8. Prepare simple drawings of the following
    a. Two tetrahedra sharing an edge
    b. Two tetrahedra sharing a face
    c. Two octahedra sharing an edge
    d. Two octahedra sharing a face

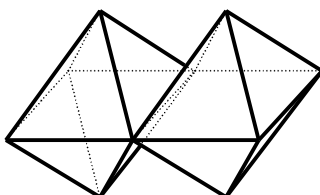   **Note: there are many ways to properly draw these shapes. These are just examples.**
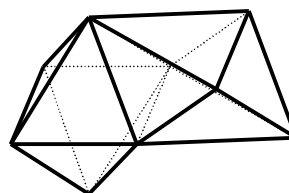   **a. edge sharing tetrahedra   b. face sharing tetrahedra**

   **c. edge sharing octahedral   d. face sharing octahedral**

9. Explain the difference between cubic and hexagonal close packing.

    In cubic close packing the sheets of closed packed spheres are packed three-dimensionally in such a way so that the spheres of layer A fill tetrahedral holes generated by layer B (nestling the two layers together in the most efficient packing) and the spheres of layer C fill octahedral holes generated by layers A and B.

    In hexagonal close packing, the third layer of spheres resides again in the tetrahedral holes generated by layer B, so that there are only two different layers that repeat ABABAB while in ccp there are three layers ABCABCABC. CCP is a more efficient packing arrangement.

10. Why does O^{2-} exist only in ionic lattices?

    O^{2-} cannot exist as a discreet ion in aqueous solutions. They hydrolyze by the following reaction:

    $$O^{2-} + H_2O \rightarrow 2\ OH^-$$
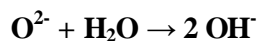
    For instable oxides of the alkaline earths:

    $$CaO + H_2O \rightarrow Ca^{2+} + 2OH^-$$
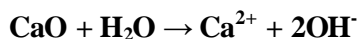
11. List the ways in which OH^- can act as a ligand.
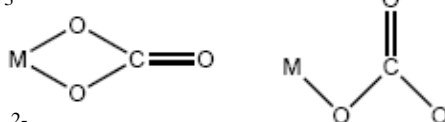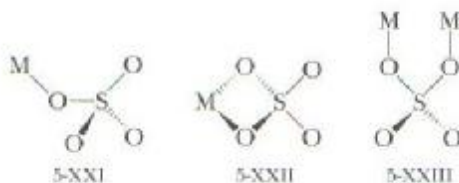
Terminal: **M-OH**

Bridging **Triply Bridging**

12. Many oxoanions can act as ligands in more than one way. Give the ways for:
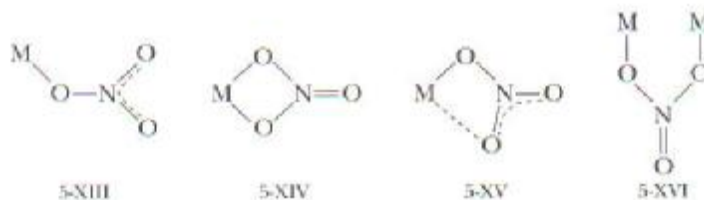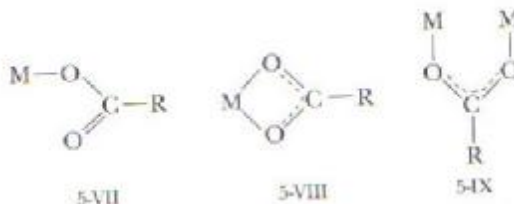
 a. CO_3^{2-}

 b. SO_4^{2-}

 5-XXI 5-XXII 5-XXIII

 c. NO_3^-

 5-XIII 5-XIV 5-XV 5-XVI

 d. $CH_3CO_2^-$

 5-VII 5-VIII 5-IX

13. How are two-dimensional silicate networks built up?

 2D Silicate Networks are built on the sharing of oxygen atoms of SiO_4 in such a way (often hexagonal sheets – see page 156 fig 5-2) that sheets are formed, versus strictly tetrahedral SiO_4 which might lend itself to more 3D networks.

14. What is the composition of zeolites? What are molecular sieves?

 The composition of zeolites can be described with the general formula:

 $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot zH_2O$ where n is the charge of the metal cation, (often K^+, Na^+, or Ca^{2+}) and z is the number of moles of waters of hydration. Zeolites can have very open structures with specific pore sizes. These types of structures with pore sizes designed to trap certain types of molecules are called molecular sieves.

15. What is meant by the terms isopoly and heteropoly anions?

Isopoly ions are complex, transition metal-oxoanions that contain only one type of metal, and oxygen. Heteropoly ions contain 2 or more types of elements (one of them being a transition metal) and oxygen. Both isopoly and heteropoly anions are built by sharing atoms in MO_6 octahedra sharing corners and edges but not faces.

16. Draw Lewis structures of the halate and perhalate anions XO_3^- and XO_4^-.
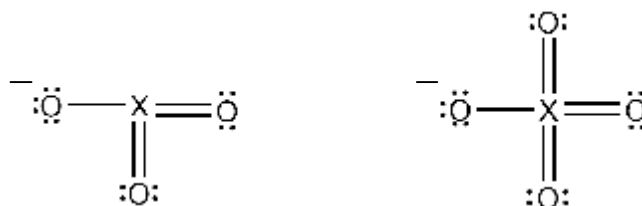
*note formal charge minimization. Also, must have access to orbitals for expanded octet.

17. Titanium ethoxide (empirical formula Ti(OEt)$_4$, where Et ≡ -CH$_2$CH$_3$) is actually a tetramer {Ti(OEt)$_4$}$_4$. Draw a plausible structure for this molecule. Write a balanced equation for its reaction with water.