HW Set 3
Chapter 7

1. CsCl consists of two interpenetrating simple cubic lattices. Both Cs⁺ and Cl⁻ fill cubic holes. CaF₂ consists of a face-centered Ca⁺⁺ lattice combined with a simple cubic lattice of F⁻. The Ca⁺⁺ ions fill cubic holes in the F⁻-lattice, while the F⁻ ions fill Td holes in the Ca⁺⁺ lattice.

2. A unit cell is the motif that, when repeated in three dimensions, gives the full structure of the ionic solid. Since only an integral number of unit cells can be used, the unit cell must contain an integral multiple of the stoichiometry of the formula.

Na⁺: \(8 \times \frac{1}{8} = 1\) corner ion
\(6 \times \frac{1}{2} = 3\) face ions
4 total Na⁺ ions

Cl⁻: 1 center ion
\(12 \times \frac{1}{4} = 3\) edge ions
4 total Cl⁻ ions

The cell contains 4 NaCl formula units.
3. Formula weight of NaCl: 58.45 g/mol

\[
58.45 \text{g} \times \frac{1 \text{mol}}{6.02 \times 10^{23} \text{formula units}} \times 4 \text{formula units} \times 1 \text{unit cell} = 2.167 \text{g}
\]

\[
= 1.792 \times 10^{-22} \text{ cm}^3 \quad \text{(Volume of unit cell)}
\]

\[
(1.792 \times 10^{-22} \text{ cm}^3)^{1/3} = 5.638 \times 10^{-8} \text{ cm}
\]

The edge of the unit cell consists of 2r+ = 2r-

\[
2(107 \text{ pm}) + 2(167 \text{ pm}) = 548 \text{ pm} = 5.48 \times 10^{-8} \text{ cm}
\]

4. 

\[
K(g) \xrightarrow{\Delta H_{IE}} M^+(g)
\]

\[
\Delta H_{Sub} \quad \Delta H_{EA} \quad \Delta H_{dis} \quad \Delta H_{f}
\]

\[
K(s) + \frac{1}{2}F_2(g) \xrightarrow{\Delta H_f} KF(s)
\]

\[
u_0 = \frac{ANZ^+Z^-e^2}{4\pi\varepsilon_0 r_0} \left(1 - \frac{1}{n}\right)
\]

Any equation you use is fine.

A = 1.74756

n: Average for Ne and Ar = 7 + 9 = 8

\[
\frac{7 + 9}{2}
\]
\[ U_0 = (1.74756 \times 10^{23}) (6.02 \times 10^{23}) (1.60218 \times 10^{-19} \text{C})^2 \times (1 - 1) \]
\[ \frac{4\pi}{(8.85419 \times 10^{-12} \text{C}^2 \text{m}^{-1} \text{J}^{-1}) (2.94 \times 10^{-10} \text{m})^5} \]

\[ r_0 = r_{\text{K}^+} + r_{\text{F}^-} = 138 \text{pm} + 117 \text{pm} = 255 \text{pm} \]
\[ 2.71 \times 10^{-10} \text{m} \]

\[ U_0 = -832.7 \text{kJ/mol} \]

\[ \Delta H_{\text{IE}} \text{ for } K = 418.8 \text{kJ/mol} \]

\[ \Delta H_{\text{EA}} \text{ for } F^- = -323.0 \text{kJ/mol} \]

\[ \Delta H_{\text{dis} F} = \frac{1}{2} (154.8 \text{kJ/mol}) = 77.4 \text{kJ/mol} \]

\[ \Delta H_{\text{sub} K} = 89.62 \text{kJ/mol} \]

\[ U_0 = 832 \text{kJ/mol} \]

\[ \Delta H_{\text{IE}} = 418.8 \text{kJ/mol} \]

\[ \Delta H_{\text{EA}} = -323.0 \text{kJ/mol} \]

\[ \Delta H_{\text{dis} F} = 77.4 \text{kJ/mol} \]

\[ \Delta H_{F} = -574.18 \text{kJ/mol} \]

5. \[ \text{F}^- \quad \text{Be}^{2+} \quad \text{F}^- \]

The electrostatic energy consists of 1) the attraction between \text{Be}^{2+} and its 2 neighboring \text{F}^- ions, and 2) the repulsion between the two \text{F}^- ions.
\[ E_c = \frac{2 \cdot Z^+ \cdot Z^- \cdot e^2}{4\pi \varepsilon_0 \cdot r} - \frac{Z^+ \cdot Z^- \cdot e^2}{4\pi \varepsilon_0 \cdot (2r)} \]
attraction \hspace{1cm} repulsion

\[ E_c = (2 - \frac{1}{2}) \frac{Z^+ \cdot Z^- \cdot e^2}{4\pi \varepsilon_0 \cdot r} = \frac{3}{2} \frac{Z^+ \cdot Z^- \cdot e^2}{4\pi \varepsilon_0 \cdot r} \]

- The Madelung constant \( \Lambda = \frac{3}{2} \)

6. a. The lattice energy released by the attraction of the more highly charged ions to each other more than offsets the large ionization energy and electron affinity.

b. Measure the conductivity of the ions in nonaqueous solution. (Can't do it in water because the \( O^2- \) is a strong base and will become \( OH^- \). But acetonitrile or methanol might work.) The greater the conductivity of the solution, the greater the charge on the ions.
<table>
<thead>
<tr>
<th></th>
<th>F^-</th>
<th>Cl^-</th>
<th>Br^-</th>
<th>I^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li^+</td>
<td>119 pm</td>
<td>167 pm</td>
<td>182 pm</td>
<td>206 pm</td>
</tr>
<tr>
<td>CN=4</td>
<td>60 pm</td>
<td>0.50 4 oh/</td>
<td>0.359 Td x</td>
<td>0.330 Td x</td>
</tr>
<tr>
<td>CN=6</td>
<td>79 pm</td>
<td>0.664 0h/</td>
<td>0.473 oh/</td>
<td>0.434 oh/</td>
</tr>
<tr>
<td>CN=8</td>
<td>106 pm</td>
<td>0.891 cubic x</td>
<td>0.635 oh/</td>
<td>0.582 oh/</td>
</tr>
<tr>
<td>Na^+</td>
<td>113 pm</td>
<td>0.95 oh/</td>
<td>0.677 oh/</td>
<td>0.621 oh/</td>
</tr>
<tr>
<td>CN=4</td>
<td>107 pm</td>
<td>0.899 cubic x</td>
<td>0.641 oh/</td>
<td>0.588 oh/</td>
</tr>
<tr>
<td>CN=8</td>
<td>130 pm</td>
<td>0.903 oh/</td>
<td>0.790 cubic x</td>
<td>0.725 oh/</td>
</tr>
<tr>
<td>K^+</td>
<td>CN=4</td>
<td>151 pm</td>
<td>0.788 x cubic</td>
<td>0.904 cubic x</td>
</tr>
<tr>
<td>CN=6</td>
<td>138 pm</td>
<td>0.862 x cubic</td>
<td>0.826 x cubic</td>
<td>0.758 oh/</td>
</tr>
<tr>
<td>CN=8</td>
<td>165 pm</td>
<td>0.701 oh/</td>
<td>0.988 oh/</td>
<td>0.907 oh/</td>
</tr>
<tr>
<td>Rb^+</td>
<td>CN=4</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CN=6</td>
<td>166 pm</td>
<td>0.717 cubic x</td>
<td>0.994 cubic x</td>
<td>0.912 cubic x</td>
</tr>
<tr>
<td>CN=8</td>
<td>164 pm</td>
<td>0.726 oh/</td>
<td>0.982 oh/</td>
<td>0.901 oh/</td>
</tr>
</tbody>
</table>
According to the textbook, many alkali halides share the structure of NaCl. In this lattice, the cation has a coordination number of 6, filling an octahedral hole of the anion. The anion has a coordination number of 6, filling an octahedral hole of the cation. The exceptions appear to be CsCl, CsBr, and CsI, which have the CsCl lattice type. In this lattice, the cation has a coordination number of 8 and fills cubic holes of the chloride lattice. The anion has a coordination number of 8 and fills cubic holes of the sodium lattice.

1. Using a CN of 6 for the cations except Cs in CsCl, CsBr, and CsI, the ionic compounds LiI, NaF, KF, KCl, KBr, RbCl, RbBr, and RbI violate the radius ratio rule.
8. \( \text{LaF}_3 \) \( \text{La}^{3+} + 3\text{F}^- \)

\[
U = 120,200 \, \nu \, Z^+ \, Z^- \, (1 - 34.5) \\
\text{(kJ/mol)} \\
\nu = \text{# of ions per molecule}
\]

\[
\nu = 4
\]

\[
\begin{align*}
\text{r}_{\text{La}^{3+}} &= 117.0 \, \text{pm} \quad (\text{C.N.} = 6) \\
\text{r}_{\text{F}^-} &= 119 \, \text{pm} \quad (\text{C.N.} = 6) \\
\text{r}_{\text{O}} &= 130 \, \text{pm} \quad (\text{C.N.} = 8)
\end{align*}
\]

Use both.

a. \( r_0 = 236 \, \text{pm} \)

\[
U = \frac{120,200 \, (4)(3)(-1) \, (1 - 34.5)}{236.0} = -5215 \, \text{kJ/mol}
\]

b. \( r_0 = 249 \, \text{pm} \)

\[
U = \frac{120,200 \, (4)(3)(-1) \, (1 - 34.5)}{249} = -4990 \, \text{kJ/mol}
\]
9. a. MgC₂O₄

A₂BO₄

A: Cr³⁺  r: 76 pm (CN=6)
B: Mg²⁺  r: 86 pm (CN=6)
This corresponds to the spinel structure.

9. b. K₂MgF₄

A: K⁺  r: 138 pm
B: Mg²⁺  r: 86 pm

Can predict the K₀NiF₄ structure.

10. Diamond is completely covalently bonded in all directions; it consists entirely of σ bonds, and there are no extra electrons to be delocalized.

Graphite consists of stacks of 2-dimensional sheets of C that are aromatic. The delocalization of the π electrons throughout the 2 dimensions makes a good conductor.

11. We know that the more electronegative an atom is, the more tightly it holds its orbitals and therefore the lower they are in energy. Since electronegativity
increases Ga < Ge < As, we expect energy levels to decrease Ga > Ge > As.

12. CdS
Band Gap: 2.485 eV → 2398 kJ/mol
1 eV = 96.5 kJ/mol

\[ \frac{239.8 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ molecules}} = 3.98 \times 10^{-22} \frac{\text{kJ}}{\text{molecule}} \]

\[ 3.98 \times 10^{-22} \text{ kJ} \times 10^3 \text{ J} = 3.98 \times 10^{-19} \text{ J} \]

\[ \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\text{ J s})(2.998 \times 10^{9}\text{ m/s})}{3.88 \times 10^{-19}\text{ J}} \times 10^9 \text{ nm} = 4.99 \text{ nm} \]

Visible region

13. Infrared radiation runs from about 10^4 cm to 10^{-2} cm in wavelength.

\[ E = \frac{hc}{\lambda} \]

\[ E = \frac{6.626 \times 10^{-34}\text{ J s})(2.998 \times 10^{9}\text{ m/s})}{10^{-4}\text{ cm}} \times 100 \text{ cm} = 2 \times 10^{-19} \text{ J} \]

\[ 2 \times 10^{-22} \text{ kJ} \]
\[ E = \frac{6.626 \times 10^{-34} \text{ J.s}}{10^{-2} \text{ cm}} \times 100 \text{ cm} \times \frac{2.998 \times 10^{3} \text{ cm}}{1 \text{ m}} = 2 \times 10^{24} \text{ J} \]

\[ 2 \times 10^{24} \text{ J} \]

For a mole of the compound,

\[ E_1 = (2 \times 10^{-23} \text{ kJ})(6.02 \times 10^{23}) = 120 \text{ kJ/mol} \]

\[ \rightarrow 1.244 \text{ eV} \]

\[ E_2 = (2 \times 10^{-24} \text{ kJ})(6.02 \times 10^{23}) = 1.2 \text{ kJ/mol} \]

\[ \rightarrow 0.0124 \text{ eV} \]

\[ \therefore \text{Si, Ge, } \alpha-\text{Sn, GaSb, InAs, InSb}_{\beta} \text{ would work well} \]

14. \( H_2 \) < \( Xe \) < \( \text{SiCl}_4 \) < \( H_2O \)

- least polarizable
- more e-
- nonpolar
- more e- than \( H_2 \)
- polar
- London dispersion forces
- London dispersion

\( H_2O \) forces
- London dispersion

\( Xe \) forces
- London dispersion

\( \text{SiCl}_4 \) forces
- London dispersion

\( H_2 \) forces
- London dispersion

\( \text{LiI} \) < \( \text{LiF} \) < \( \text{BaO} \) < \( \text{SiO}_2 \)

- both ionic
- \( \text{Ba}^{2+} \) & \( \text{O}^{2-} \)
- extended covalent

- \( \text{F}^- \) smaller than \( \text{I}^- \)
- ionic, higher lattice

\[ \therefore \text{Lattice energy of charge} \]

\[ \text{LiF is greater} \]
15) a. O=O higher bond order

b. C=C should be stronger because the 2p orbitals are more compact and give better overlap than the 3p orbitals.

c. Xe-Xe Only London dispersion (induced dipole-induced dipole forces are involved here, and the larger atoms (with more e-) will be more polarizable.

d. Mg$^{2+}$O$^{2-}$ The coulombic attraction is greater for higher charges

e. Even though Ba$^{2+}$ and Te$^{2-}$ are approximately $r_{Li^+} = 79$ pm $r_F = 117$ pm twice as big as Li$^+$+F$^-$, $r_{Ba^{2+}} = 149$ pm $r_{Te^{2-}} = 207$ pm their higher charge means that they will have the stronger bonding interaction.

For Ba$_2$Te relation to LiF: $E = \frac{(2Z^+)(2Z^-)e^2}{4\pi(2r)\epsilon_0}$

f. The covalent interaction of C=C in diamond is stronger than the ionic interaction of LiF.