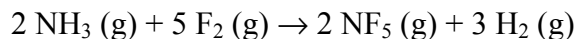


**CHEM 121**  
**Supplemental Questions for Solids and Liquids**

1. Using bond dissociation energies, predict  $\Delta H$  for the reaction shown below. Qualitatively predict whether this reaction is spontaneous (make no calculations! you know  $\Delta H$ , make a reasonable guess at  $\Delta S$  and  $\Delta G$ ). Why doesn't it occur? (hint: Lewis dot structures)



$$\Delta H = 2(3D_{\text{N-H}}) + 5(D_{\text{F-F}}) - 2(5(D_{\text{N-F}})) - 3(D_{\text{H-H}}) \text{ kJ}$$

$$\Delta H = 2(3(391)) + 5(155) - 2(5(283)) - 3(436) \text{ kJ}$$

$$\Delta H = 2346 + 755 - 2930 - 1308 = -1017 \text{ kJ}$$

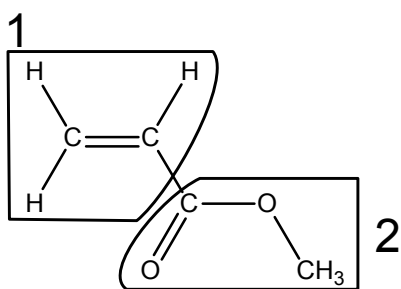
**For this reaction  $\Delta S$  is expected to be negative since 7 moles of gas are converted to 5 moles of gas.**

**Since  $\Delta H$  and  $\Delta S$  are both negative,  $\Delta G$  can be either positive or negative, depending on the temperature. The predicted  $\Delta H$  is relatively large, so it is likely that  $\Delta G$  is negative.**

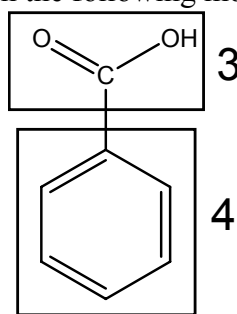
**The reaction can't happen because  $\text{NF}_5$  is not expected to exist because it violates the octet rule on N.**

*This is an example of a chemical reaction that thermodynamics predicts should occur, but does not because there is no pathway that leads from products to reactant (in this case because one of the products does not exist).*

2. Name the indicated functional groups in the following molecules.

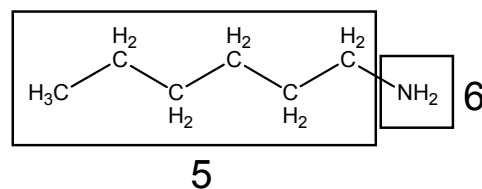


1. **alkene**



2. **ester**

4. **aromatic ring or benzene ring or phenyl group**



3. **carboxylic acid**

5. **alkyl group**

6. **amine (primary amine)**

3. A chemist believes that she has synthesized a compound that has the chemical formula  $\text{C}_6\text{H}_{12}\text{N}_4$ . The density of the compound is  $1.367 \text{ g/cm}^3$  and preliminary X-ray crystallography data show that

it crystallizes in a body-centered cubic unit cell with  $a = 6.984 \text{ \AA}$ . Is it likely that the desired compound has been prepared? The molar mass of a compound with the chemical formula  $\text{C}_6\text{H}_{12}\text{N}_4$  is  $140.19 \text{ g/mole}$ .

$$\rho = \frac{m_{\text{cell}}}{V_{\text{cell}}} = \frac{\left(8\left(\frac{1}{8}\right) + 1(1)\right) \frac{\text{molecules}}{\text{unit cell}} \left(\frac{1 \text{ mole}}{6.0221367 \times 10^{23} \text{ molecules}}\right) (\text{molar mass})}{\left(\frac{(6.984 \times 10^{-8} \text{ cm})^3}{\text{unit cell}}\right)} = 1.367 \frac{\text{g}}{\text{cm}^3}$$

$$\frac{(2 \text{ molecules}) \left(\frac{1 \text{ mole}}{6.0221367 \times 10^{23} \text{ molecules}}\right) (\text{molar mass})}{(6.984 \times 10^{-8} \text{ cm})^3} = 1.367 \frac{\text{g}}{\text{cm}^3}$$

$$\text{molar mass} = \left(1.367 \frac{\text{g}}{\text{cm}^3}\right) (6.984 \times 10^{-8} \text{ cm})^3 \left(\frac{6.0221367 \times 10^{23}}{2 \text{ mole}}\right) = 140.2 \frac{\text{g}}{\text{mole}}$$

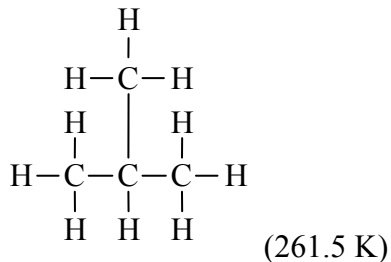
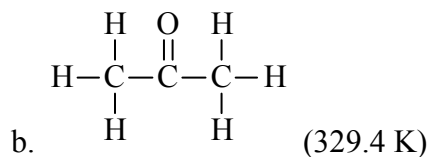
**The molar mass of the compound predicted from the unit cell matches the expected molar mass. Therefore, it is likely, based on the preliminary X-ray data, that the correct compound was synthesized.**

4. Explain the difference in boiling points (shown in parentheses following each compound) for each pair of molecules given below. Discuss the intermolecular interactions that are present in each compound, and how these interactions lead to the different boiling points.

a. HBr (206.2 K) and HCl (188.3 K)

*Both molecules are polar and can have hydrogen bonding between molecules. Since Cl is more electronegative than Br, we expect that HCl is more polar than HBr (electrons in bond are pulled more toward Cl). This would predict that HCl should have the higher boiling point, but it doesn't. Therefore, there must be another cause.*

**Br has more electrons than Cl, so it is more polarizable and has stronger dispersion forces. The stronger dispersion forces in HBr would raise its boiling point, and would account for the observed difference.**

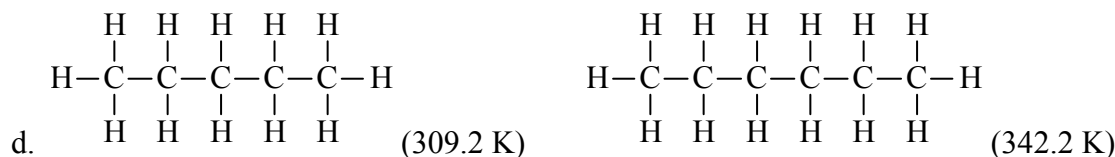


The compound on the left is polar and has strong dipole-dipole interactions between its molecules. The compound on the right is non-polar, which means it only has much weaker dispersion forces between its molecules. Since dipole-dipole interactions are stronger than dispersion forces for molecules of approximately the same mass, the compound on the left has the higher boiling point because it must overcome stronger intermolecular interactions to boil.



Both molecules are polar, but the compound on the left is more polar because the difference in electronegativity between the O and the H is larger than between the C and the O. The more polar the molecule the larger the dipole-dipole interaction, which means more energy must be put in to make the compound boil, so the boiling point is higher.

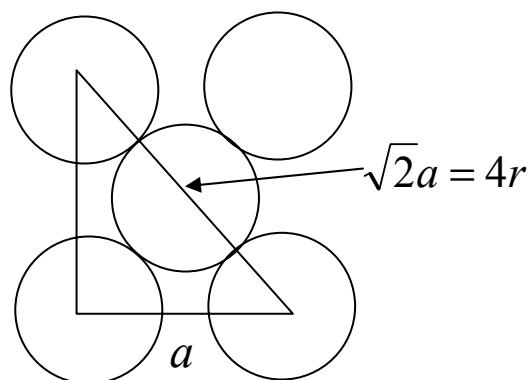
*The dipole-dipole interaction in the compound on the left is called hydrogen bonding. In general, hydrogen bonding is stronger than many dipole-dipole interactions, especially when the hydrogen is attached to an atom that is much more electronegative than H (e. g., O, F). Hydrogen bonding is possible in any molecular compound where H is attached to another atom that is more electronegative than H (e. g., C), but these are much weaker because the dipole moment is much smaller. Therefore, hydrogen bonding between the H attached to C and other electronegative atoms are not important in polar molecules.*



Both molecules are non-polar and the only intermolecular interactions are dispersion forces. The compound on the right is larger, so it has more dispersion forces than the compound on the left. Since it has more dispersion forces to overcome for it to boil, its boiling point is higher.

5. At 141K solid acetylene, C<sub>2</sub>H<sub>2</sub>, has a face-centered cubic unit cell with a = 6.105 Å.

a. Assuming that acetylene is spherical, what is the size of acetylene in Å?



$$\sqrt{2}a = 4r$$

$$\frac{\sqrt{2}a}{4} = r$$

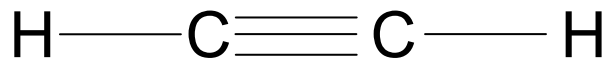
$$r = \frac{\sqrt{2}(6.105\text{Å})}{4} = 2.158_{443}\text{Å}$$

$$d = 2 \cdot r = 2(2.158_{443}\text{Å}) = 4.317\text{Å}$$

**The size of acetylene is 4.317 Å.**

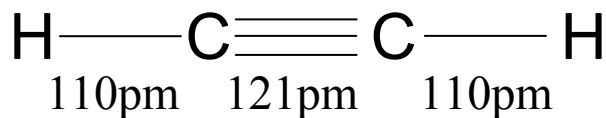
b. Draw the Lewis dot structure of acetylene, and use VSEPR to predict the shape of acetylene.

**Acetylene has (2 x 4 + 2 x 2 = 12 valence electrons). The Lewis dot structure, and the electron-pair geometry, is**



**Acetylene is a linear molecule.**

c. Using the handout of average bond lengths, predict the distance from one hydrogen atom to the other in acetylene.



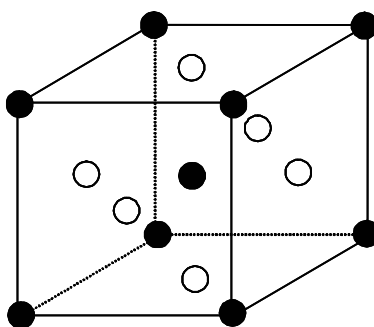
**The total distance from hydrogen to hydrogen in acetylene 341 pm, or 3.41 Å.**

d. From the crystal structure of acetylene at 141K, it can be determined that the hydrogen-hydrogen distance is 3.332 Å. Which method (assuming acetylene is a sphere or using the average bond lengths) gives a more accurate measure of the hydrogen-hydrogen distance? Why is this so? Why don't the average bond lengths give an exact result?

**The average bond lengths give a more accurate hydrogen-hydrogen bond distance. This is because in part a we assumed acetylene is a sphere when it is clearly not (see part b). The average bond lengths do not give an exact result because they are averages calculated from bond distances in many different molecules, each with slightly different bond lengths.**

6. An ionic lattice can be constructed from a body-centered cubic lattice of cations with anions occupying the faces of the cube.

a. Draw this ionic lattice, using ● to represent the cations and ○ to represent the anions.



b. What is the stoichiometry of this lattice (use “C” for the cation and “A” for the anion). Could manganese(III) oxide have this structure?

**There are 8 cations on the corners that count as 1/8 each and one cation in the center, counting as 1, for a total of 2 cations.**

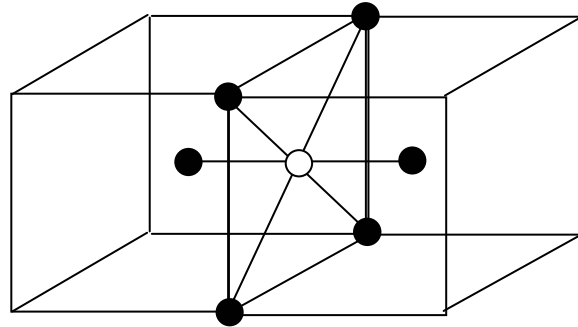
**There are 6 anions on the faces of the cube, each counting as 1/2, for a total of 3 anions.**

**The formula unit is thus, C<sub>2</sub>A<sub>3</sub>.**

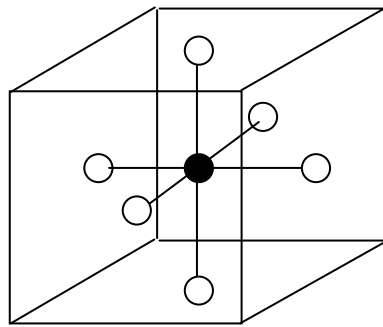
**Manganese(III) oxide, with the chemical formula Mn<sub>2</sub>O<sub>3</sub>, could (at least by its stoichiometry) have this unit cell.**

c. What is the coordination number of the cation? of the anion?

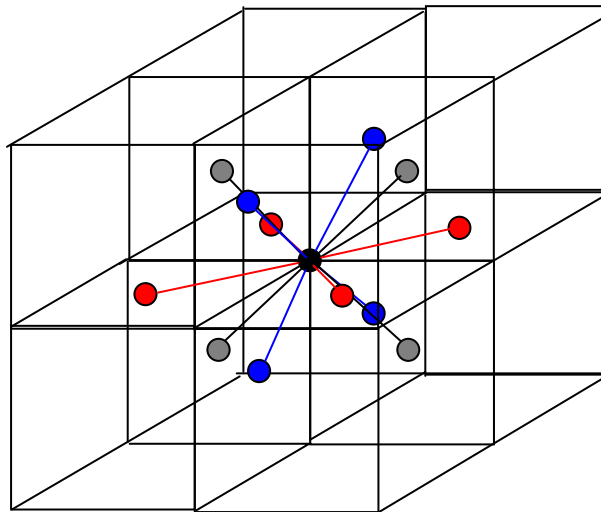
**The anions each have 6 cations around them (four on the corners of the cell, one in the center of the cell, and one in an adjacent unit cell), for a coordination number of 6. See below.**



The cation in the center has 6 anions around it (coordination number of 6), see below.



*The cations in the corners are harder (unintentionally on my part), they have a coordination number of 12 (four nearest neighbors, in three perpendicular planes, shown as red, blue and grey circles in the figure below).*



d. Using  $r_A$  and  $r_C$  for the radius of the anion and the cation, respectively, derive an expression for the radius ratio ( $r_A/r_C$ ) for this cell and evaluate numerically (i. e., your answer will be  $r_A/r_C$  equals some number). Remember that the cations are in a cubic arrangement.

**For the face diagonal (FD)**

$$FD = \sqrt{2}a \quad \text{and} \quad FD = 2(r_A + r_C)$$

which gives

$$\sqrt{2}a = 2(r_A + r_C)$$

$$a = \frac{2}{\sqrt{2}}(r_A + r_C)$$

**For the body diagonal (BD)**

$$BD = \sqrt{3}a \quad \text{and} \quad BD = 4r_C$$

which gives

$$\sqrt{3}a = 4r_C$$

$$a = \frac{4}{\sqrt{3}}r_C$$

Combining the two expressions for  $a$  gives

$$\frac{4}{\sqrt{3}}r_C = \frac{2}{\sqrt{2}}(r_A + r_C)$$

$$\frac{2\sqrt{2}}{\sqrt{3}}r_C = (r_A + r_C)$$

$$\frac{2\sqrt{2}}{\sqrt{3}}r_C - r_C = r_A$$

$$\left(\frac{2\sqrt{2}}{\sqrt{3}} - 1\right)r_C = r_A$$

$$\frac{r_A}{r_C} = \left(\frac{2\sqrt{2}}{\sqrt{3}} - 1\right) = 0.633$$

**The radius ratio of this unit cell is 0.633.**

e. Manganese(III) oxide doesn't really have this structure, but we can use the radius ratios to try to predict its actual structure. Given that the ionic radius of  $O^{2-}$  is 126 pm and the ionic radius of  $Mn^{3+}$  is 79 pm, calculate the radius ratios for  $Mn^{3+}$  and  $O^{2-}$ . Is this compound predicted to crystallize in any of the simple lattices that we've talked about? Briefly explain why or why not.

*First calculate the radius ratios.*

$$\frac{r_{O^{2-}}}{r_{Mn^{3+}}} = \frac{126 \text{ pm}}{79 \text{ pm}} = 1.59 \quad \text{and} \quad \frac{r_{Mn^{3+}}}{r_{O^{2-}}} = \frac{79 \text{ pm}}{126 \text{ pm}} = 0.627$$

**From the radius ratios the maximum coordination number for both ions is 6, and the possible structures are NaCl or rutile. The NaCl structure has a 1:1 ratio of cations to anions, while in rutile it is 1:2. Neither possible structure matches the stoichiometry of  $Mn_2O_3$ , therefore  $Mn_2O_3$  adopts neither of these simple structures. By comparing the stoichiometry of the other simple structures, we can conclude that  $Mn_2O_3$  adopts none of them.**

f. The ionic radius of  $Mn^{3+}$  is 79 pm, while that of  $Mn^{2+}$  is 97 pm. Explain the origin of this difference.

**The effective nuclear charge experienced by the remaining electrons increases as electrons are removed to form the cations. The stronger interaction between the electrons and the nucleus pulls the electrons closer to the nucleus and the ionic radius (a rough measure of the outer most electrons' positions) decreases.**

7. Rutile ( $TiO_2$ ) crystallizes in a tetragonal unit cell. If  $a = 4.5937 \text{ \AA}$  and  $c = 2.9618 \text{ \AA}$ , what is the density of rutile? Given  $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$ .

*To calculate the density we need the mass of the unit cell, for which we need to know how many  $TiO_2$  formula units are in the unit cell, and the cell's volume.*

**From the picture of the unit cell shown in lecture (or the book), there are 8  $Ti^{4+}$  on the corners at 1/8 each and 1  $Ti^{4+}$  in the center counting as 1 for a total of 2  $Ti^{4+}$  in the unit cell, and there are 2  $O^{2-}$  in the cell counting as 1 each and 4  $O^{2-}$  on the faces counting as 1/2 each for a total of 4  $O^{2-}$  in the unit cell.**

**So, there are a total of 2  $TiO_2$  formula units in the unit cell (note the ratio is 2 O for every 1 Ti, as required).**

*Calculating the mass of the unit cell from the formula weight of  $TiO_2$ .*

$$\left( \frac{2 \text{ TiO}_2 \text{ formula units}}{1 \text{ unit cell}} \right) \left( \frac{79.865 \text{ g TiO}_2}{1 \text{ mole TiO}_2 \text{ formula units}} \right) \times \left( \frac{1 \text{ mole TiO}_2 \text{ formula units}}{6.0221367 \times 10^{23} \text{ TiO}_2 \text{ formula units}} \right) = 2.6523_8 \times 10^{-22} \frac{\text{g}}{\text{unit cell}}$$

The volume of the unit cell is

$$V = (4.5937 \times 10^{-10} \text{ m})(4.5937 \times 10^{-10} \text{ m})(2.9618 \times 10^{-10} \text{ m})$$
$$V = (6.2500_1 \times 10^{-29} \text{ m}^3) \left( \frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 6.2500_1 \times 10^{-23} \text{ cm}^3$$

The density is thus,

$$d = \frac{m}{V} = \frac{2.65238 \times 10^{-22} \text{ g}}{6.2500_1 \times 10^{-23} \text{ cm}^3} = 4.2438 \frac{\text{g}}{\text{cm}^3}$$

**The density of rutile is 4.2438 g/cm<sup>3</sup>.**

8a. The density of a solid depends on how the particles are packed together. Of the three Bravais lattices in the cubic crystal system, the face-centered cubic cell is the most dense and primitive cubic cell is the least dense. Qualitatively this makes sense, because a face-centered cubic cell has more particles in it than a primitive cubic cell of the same size. But to quantitate these differences, we must also account for differences in cell volume. In this problem we will derive equations for the density of the three cubic unit cells ( $d_{\text{cell}}$ ) in terms of the density of the atoms ( $d_{\text{atom}}$ ) in the cell. By comparing these we will prove that the primitive cubic cell is the least dense and the face-centered cubic cell is the most dense for atoms of the same size.

The following is a brief outline of the procedure to calculate the density for each unit cell (e. g., you will need do three calculations!).

- 1) Determine  $m_{\text{cell}}$  in terms of  $m_{\text{atom}}$  (i. e.,  $m_{\text{cell}}$  is the dependent variable and  $m_{\text{atom}}$  is the independent variable). Hint: you will need to know how many atoms are in each cell.
- 2) Write an equation for  $V_{\text{cell}}$  in terms of the atomic radius. It may help if you draw the unit cell and from that determine the relationship between the unit cell's length and the atomic radius (like the example we did in class).
- 3) Substitute the expressions of  $m_{\text{cell}}$  and  $V_{\text{cell}}$  into the equation for  $d_{\text{cell}}$  and simplify so that the resulting equation gives the relationship between  $d_{\text{cell}}$  and  $d_{\text{atom}}$ . Evaluate the constants to three significant figures.

To make it easier, please use the following abbreviations in your work.

Parameter	Variable
density of unit cell	$d_{\text{cell}}$
mass of unit cell	$m_{\text{cell}}$
volume of unit cell	$V_{\text{cell}}$
density of atom	$d_{\text{atom}}$
mass of atom	$m_{\text{atom}}$
volume of atom	$V_{\text{atom}}$
atomic radius	$r$

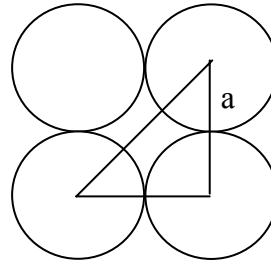
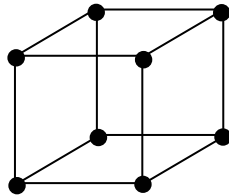
You may find the following relationships useful, but you should be aware that some important equations are not given.

$$d_{cell} = \frac{m_{cell}}{V_{cell}}$$

$$d_{atom} = \frac{m_{atom}}{V_{atom}}$$

$$V_{atom} = \frac{4}{3}\pi r^3$$

**The calculation for the primitive cubic.**



$$m_{cell} = 8\left(\frac{1}{8}\right)m_{atom} = m_{atom}$$

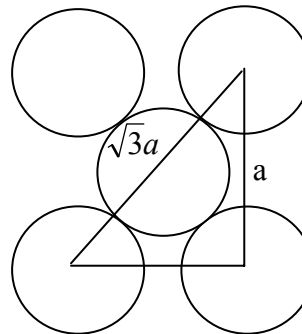
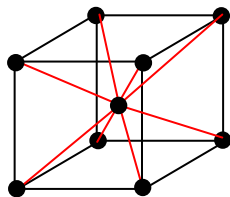
$$V_{atom} = \frac{4}{3}\pi r^3, \text{ so } r^3 = \frac{3V_{atom}}{4\pi} \text{ and with } a = 2r$$

$$d_{cell} = \frac{m_{cell}}{V_{cell}} = \frac{m_{atom}}{a^3} = \frac{m_{atom}}{(2r)^3} = \frac{m_{atom}}{8\left(\frac{3V_{atom}}{4\pi}\right)} = \left(\frac{\pi}{6}\right)\left(\frac{m_{atom}}{V_{atom}}\right) = \left(\frac{\pi}{6}\right)d_{atom}$$

$$d_{cell} = 0.524d_{atom}$$

**The density of the primitive cell is  $0.524d_{atom}$ .**

**The calculation for the body-centered cubic cell.**



$$m_{cell} = \left[8\left(\frac{1}{8}\right) + 1\right]m_{atom} = 2m_{atom}$$

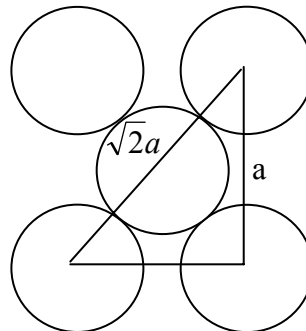
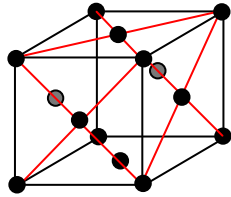
$$r^3 = \frac{3V_{atom}}{4\pi} \text{ with } a = \frac{4r}{\sqrt{3}}$$

$$d_{cell} = \frac{m_{cell}}{V_{cell}} = \frac{2m_{atom}}{a^3} = \frac{2m_{atom}}{\left(\frac{4}{\sqrt{3}}\right)^3 r^3} = \frac{3\sqrt{3}m_{atom}}{32r^3} = \frac{3\sqrt{3}m_{atom}}{32\left(\frac{3V_{atom}}{4\pi}\right)} = \left(\frac{\sqrt{3}\pi}{8}\right)d_{atom}$$

$$d_{cell} = 0.680d_{atom}$$

The density of the body-centered cell is  $0.680d_{\text{atom}}$ .

The calculation for the face-centered cubic cell.



$$m_{\text{cell}} = \left[ 8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) \right] m_{\text{atom}} = 4m_{\text{atom}}$$

$$r^3 = \frac{3V_{\text{atom}}}{4\pi} \quad \text{with} \quad a = \frac{4r}{\sqrt{2}}$$

$$d_{\text{cell}} = \frac{m_{\text{cell}}}{V_{\text{cell}}} = \frac{4m_{\text{atom}}}{a^3} = \frac{4m_{\text{atom}}}{\left(\frac{4}{\sqrt{2}}\right)^3 r^3} = \frac{\sqrt{2}m_{\text{atom}}}{8r^3} = \frac{\sqrt{2}m_{\text{atom}}}{8\left(\frac{3V_{\text{atom}}}{4\pi}\right)} = \left(\frac{\sqrt{2}\pi}{6}\right) d_{\text{atom}}$$

$$d_{\text{cell}} = 0.741d_{\text{atom}}$$

The density of the face-centered cell is  $0.741d_{\text{atom}}$ .

b. Do the results of your calculations agree with our qualitative expectations?

**Yes they do, the face-centered cubic unit cell has the highest density ( $0.741d_{\text{atom}}$ ) and the simple cubic unit cell is the least dense ( $0.524d_{\text{atom}}$ ).**

c. A solid has a body-centered cubic unit cell. The pressure on the solid is increased and the solid undergoes a phase change to another cubic unit cell. The second phase likely has which of the other two unit cells? Explain.

**As the pressure on the solid increases the volume will decrease, which means that the density will increase (assuming that the mass remains the same). Since the effect on the solid as a whole must be reflected in the unit cell, the density of the unit cell must also increase. The body-centered cubic unit cell is predicted to have an intermediate density, so increasing the pressure should cause it to undergo a phase change to a more dense unit cell, which is the face-centered unit cell.**

d. In this discussion we've assumed that the radius of atom remains constant, but this is not required. Write the density of each cell in terms of  $m_{\text{atom}}$  and the atomic radius,  $r$ . Label the density of the primitive cubic cell as  $d_{\text{PC}}$ , that of the body-centered cubic cell as  $d_{\text{BCC}}$  and that of the face-centered cubic cell as  $d_{\text{FCC}}$ . If all three unit cells have the same density (i. e.,  $d_{\text{PC}} = d_{\text{BCC}} = d_{\text{FCC}}$ ) and the same  $m_{\text{atom}}$ , in which of the unit cells will the atomic radius be the largest?

*From part a we have the following:*

$$d_{\text{PC}} = \frac{m_{\text{atom}}}{8r^3} \quad d_{\text{BCC}} = \frac{3\sqrt{3}m_{\text{atom}}}{32r^3} \quad d_{\text{FCC}} = \frac{\sqrt{2}m_{\text{atom}}}{8r^3}$$

*Solving each for  $r^3$  gives*

$$r^3 = \frac{1}{8} \left( \frac{m_{\text{atom}}}{d_{\text{PC}}} \right)$$

$$r^3 = \left( \frac{3\sqrt{3}}{32} \right) \left( \frac{m_{\text{atom}}}{d_{\text{BCC}}} \right)$$

$$r^3 = \left( \frac{\sqrt{2}}{8} \right) \left( \frac{m_{\text{atom}}}{d_{\text{FCC}}} \right)$$

*For simplicity let  $m_{\text{atom}}/d = 1$ , which gives*

**for PC cell,  $r^3 = \frac{1}{8}$**

**for BCC cell,  $r^3 = \left( \frac{3\sqrt{3}}{32} \right)$**

**for FCC cell,  $r^3 = \left( \frac{\sqrt{2}}{8} \right)$**

*Solving for  $r$  gives*

**for PC cell,  $r = 0.500$**

**for BCC cell,  $r = 0.162$**

**for FCC cell,  $r = 0.562$**

**The atomic radius is smallest for the primitive cubic cell and largest for the face-centered cubic cell.**

9. Diamond is a three-dimensional covalent network solid. In diamond each C is covalently bonded to four other C atoms in a tetrahedral geometry. Graphite, the allotrope of C, is also a covalent network, but it has a two-dimensional network consisting of C atoms covalently bonded to three other C atoms in a trigonal planar geometry.

a. Diamond is the hardest substance known, but graphite is quite soft. Explain.

**Diamond has a three dimensional covalent network structure. To scratch it requires moving C atoms or breaking C-C bonds, which are both difficult to do because the C atoms are tied together in three dimensions.**

**Graphite has a two dimensional covalent network structure. While there are strong covalent C-C bonds in planes, there are only weak dispersion interactions between the layers. It is much easier to move the atoms parallel to the planes because they are weakly held in this dimension.**

b. What is the hybridization of the C atoms in diamond? In graphite?

**In diamond the C atoms are  $sp^3$  hybridized and in graphite they are  $sp^2$  hybridized.**

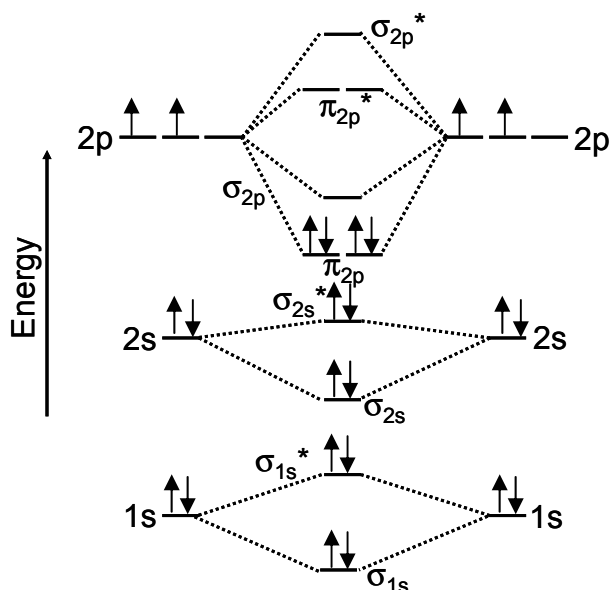
c. Graphite is a semi-conductor, but diamond is an insulator. Explain using band theory. Hint: the answer to part b and the structures of graphite and diamond presented in lecture are important.

**Since diamond is an insulator its band gap must be large, while in graphite it must be relatively small.**

**In diamond all of the orbitals on the C atoms are used to form  $\sigma$  bonds with three other C atoms. Just like the example in class these can be put together to form a large number of bonding and corresponding antibonding molecular orbitals. All of the bonding orbitals only differ slightly in energy (form the valence band), and all of the antibonding orbitals differ only slightly in energy (form the conduction band). Because C-C  $\sigma$  bonds are strong, the  $\sigma$  bonding MOs are at very low energy and the  $\sigma^*$  orbitals are at very high energy. This difference is the band gap in diamond, and it is very large.**

**In graphite there is one p orbital that does not participate in forming the  $\sigma$  bonds between the C atoms. This p orbital can interact with neighboring p orbitals on other C atoms to form a valence band ( $\pi$  bonding orbitals) and a conduction band ( $\pi^*$  orbitals). Since  $\pi$  bonds are weaker than  $\sigma$  bonds (in general), the difference between the  $\pi$  bonding and  $\pi^*$  orbitals (the band gap) is much smaller than in diamond.**

d. When graphite or diamond is vaporized, the ordered structures of the solid state are disrupted and gaseous carbon exists as single C atoms. Experimental evidence suggests that this is true when the pressure is low, or the concentration of C(g) is low. But under conditions of high pressure, or at high C(g) concentrations, gaseous carbon actually exists as C<sub>2</sub>(g). This means that there must be an interaction that holds the C atoms together. Use the MO diagram for C<sub>2</sub>, shown below, to explain the nature of this interaction. Hint: fill in the electrons.



**The bond order for C<sub>2</sub> is 2 (2  $\pi$  bonds). This means that the interaction that holds C atoms together in the gaseous state is covalent bonding.**

e. The van der Waals equation of state describes non-ideal gases in terms of two constants  $a$  and  $b$ . If we were to determine the van der Waals constants for C (g) and compared them to those of Ne (g), which one ( $a$  or  $b$ ) would we expect to show the largest difference between the two species? Why?

**The van der Waals parameter  $b$  is related to size. Since C and Ne are not that much different in size, it is expected that their  $b$  parameters will be similar.**

**Ne is a noble gas, and will have only weak dispersion forces as the only interatomic interaction. C, as was shown in part  $d$ , can have a strong bonding interaction between C atoms, in addition to the dispersion forces. Since the van der Waals  $a$  parameter is measure of the interactions between particles, we expect it to show the biggest difference between the gases.**

10a. Use radius ratios given below to predict the solid state structure of calcium oxide.

$$r_{\text{Ca}^{2+}} = 114 \text{ pm}, r_{\text{O}^{2-}} = 126 \text{ pm}$$

Calculate the radius ratios

$$\frac{r_{\text{Ca}^{2+}}}{r_{\text{O}^{2-}}} = \frac{114 \text{ pm}}{126 \text{ pm}} = 0.905 \qquad \frac{r_{\text{O}^{2-}}}{r_{\text{Ca}^{2+}}} = \frac{126 \text{ pm}}{114 \text{ pm}} = 1.11$$

**This falls between the octahedral and cubic cutoffs. We assume the larger coordination number, and get as the possible lattices CsCl, fluorite and antiferite. The fluorite and antiferite structures do not have the correct 1:1 cation to anion stoichiometry required by CaO's chemical formula, but CsCl does. Therefore, we predict that CaO has the CsCl structure.**

b. Calcium oxide actually has the rock salt structure in the solid state under standard conditions. Use the Born-Landé equation to calculate  $E_{\text{lattice}}$  for calcium oxide.

Start with Born-Landé equation

$$E_{\text{lattice}} = -\frac{NA|z_+||z_-|e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

**Ca<sup>2+</sup> has an [Ar] electronic configuration (n = 9), and that of O<sup>2-</sup> is [Ne] (n = 7). Average the two values to get n = 8.**

**For rock salt structure Madelung constant, A, is 1.7476.**

**The distance between the ions,  $r_0$ , is  $114 + 126 \text{ pm} = 240. \times 10^{-12} \text{ m}$**

Substitute in known quantities.

$$E_{\text{lattice}} = -\frac{(6.022 \times 10^{23})(1.7476)2|2|(1.602 \times 10^{-19})^2}{4\pi(8.854 \times 10^{-12})(240 \times 10^{-12})} \left(1 - \frac{1}{8}\right)$$

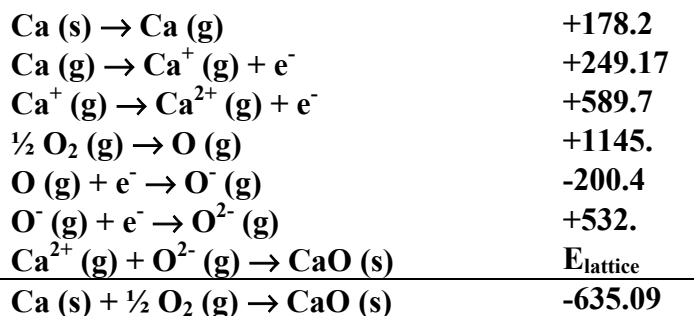
$$E_{\text{lattice}} = -3.54 \times 10^3 \text{ kJ / mole}$$

**The Born-Landé equation predicts  $E_{\text{lattice}}$  for CaO to be  $-3.54 \times 10^3 \text{ kJ/mole}$ .**

c. From the following data, use the Born-Haber cycle to calculate  $E_{\text{lattice}}$  for calcium oxide. Compare these results to your calculated value for  $E_{\text{lattice}}$  from part b; suggest reasons why they may be different. Abbreviations used: IE = ionization energy, EA = electron affinity. The electron affinities are written in the formalism where a positive value means that energy is released when an electron is added.

Parameter	Value (kJ/mole)
IE <sub>1</sub> (Ca)	+589.7
IE <sub>2</sub> (Ca)	+1145.
EA <sub>1</sub> (O)	+200.4
EA <sub>2</sub> (O)	-532.

Parameter	Value (kJ/mole)
$\Delta H_f^0$ (Ca, g)	+178.2
$\Delta H_f^0$ (O, g)	+249.17
$\Delta H_f^0$ (CaO, s)	-635.09



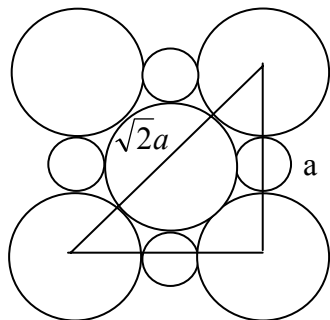
$$-635.09 \text{ kJ/mole} = E_{\text{lattice}} + 2493.67 \text{ kJ/mole}$$

$$E_{\text{lattice}} = -3128.76 \text{ kJ/mole}$$

The  $E_{\text{lattice}}$  for CaO is -3129. kJ/mole.

The value for  $E_{\text{lattice}}$  predicted by the Born-Landé equation and that determined experimentally by the Born-haber cycle are very close. The difference may arise from either covalency, which the Born-Landé equation does not take into account, or the value of  $r_0$  that we used may be incorrect (this is the only parameter in the Born-Landé equation that can possibly have any degree of uncertainty in it, see next question).

d The unit cell of calcium oxide has  $a = 4.8108 \text{ \AA}$  ( $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$ ). Using this, calculate  $r_{\text{Ca}^{2+}}$  and  $r_{\text{O}^{2-}}$ . Compare these values to those given in part a; suggest reasons for any differences.



The following relationships follow from a rock salt lattice:

$$\sqrt{2}a = 4r_{\text{O}^{2-}}$$

$$r_{\text{O}^{2-}} = \frac{\sqrt{2}}{4}a$$

and

$$a = 2r_{\text{Ca}^{2+}} + 2r_{\text{O}^{2-}}$$

Substituting gives

$$a = 2r_{\text{Ca}^{2+}} + \frac{\sqrt{2}}{2}a$$

$$2r_{\text{Ca}^{2+}} = a - \frac{\sqrt{2}}{2}a$$

$$r_{\text{Ca}^{2+}} = \frac{2 - \sqrt{2}}{4}a = \left(\frac{2 - \sqrt{2}}{4}\right)(4.8108 \text{ \AA}) = 0.70452_5 \text{ \AA}$$

and

$$r_{\text{O}^{2-}} = \left(\frac{\sqrt{2}}{4}\right)(4.8108 \text{ \AA}) = 1.7008_7 \text{ \AA}$$

**The ionic radius of  $\text{Ca}^{2+}$  in CaO is 0.70453 Å and the ionic radius of  $\text{O}^{2-}$  is 1.7009 Å**

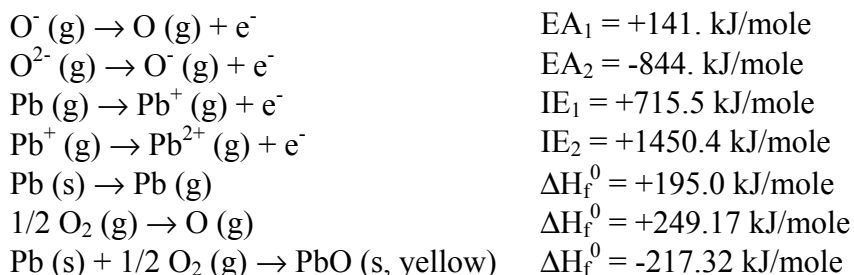
**The calculated ionic radii don't match the ones given in part a because the ones in part a are averages (calculated for many different compounds containing  $\text{Ca}^{2+}$  or  $\text{O}^{2-}$ ). As we've shown the ionic radius depends on the lattice in which the ion is found. It is not unexpected for us to see a range of values.**

11. Qualitatively explain why NaO does not exist.

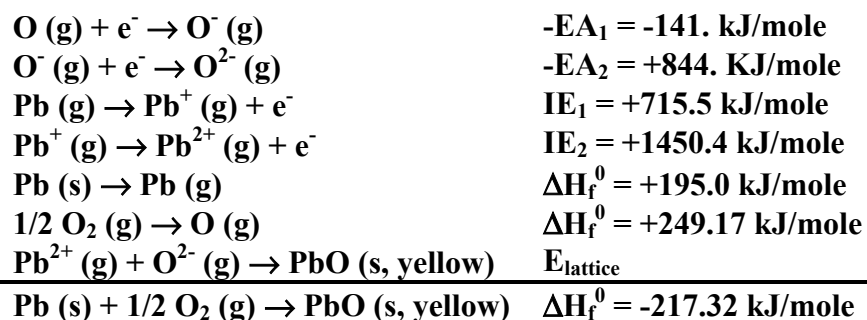
**If NaO is formulated as  $\text{Na}^{2+}$  and  $\text{O}^{2-}$ , then it does not exist because the extremely large  $\text{IE}_2$  of Na cannot be overcome by the increased  $E_{\text{lattice}}$ . This makes  $\Delta H_f^0$  (NaO, s) positive and the formation of the compound energetically unfavorable.**

**If NaO is formulated as  $\text{Na}^+$  and  $\text{O}^-$ , then it does not exist because the increase in  $E_{\text{lattice}}$  upon going to  $\text{O}^{2-}$  more than outweighs the energy required ( $E_{\text{A}_2}$  is negative) to put a second electron on oxygen. The more negative  $E_{\text{lattice}}$  makes  $\Delta H_f^0$  ( $\text{Na}_2\text{O}$ , s) much more negative than  $\Delta H_f^0$  (NaO, s), and so it is energetically favorable to form  $\text{Na}_2\text{O}$ .**

12a. Lead(II) oxide exists in two solid forms; one is yellow and the other is red. Using the data given below calculate the lattice energy for the yellow form of PbO. The electron affinities are written in the formalism where a positive value means that energy is released when an electron is added.



**Need to reverse the electron affinities of O, and add in the  $E_{\text{lattice}}(\text{PbO, yellow})$**



$$\Delta H_f^0(\text{PbO, s, yellow}) = -EA_1(O) + -EA_2(O) + IE_1(Pb) + IE_2(Pb) + \Delta H_f^0(Pb, g) + \Delta H_f^0(O, g) + E_{\text{lattice}}(\text{PbO, yellow})$$

$$E_{\text{lattice}}(\text{PbO, yellow}) = \Delta H_f^0(\text{PbO, s, yellow}) + EA_1(O) + EA_2(O) - IE_1(Pb) - IE_2(Pb) - \Delta H_f^0(Pb, g) - \Delta H_f^0(O, g)$$

$$E_{\text{lattice}}(\text{PbO, yellow}) = -217.32 + ^+141. + -844. - ^+715.5 - ^+1450.4 - ^-195.0 - ^+249.17 \text{ kJ/mole}$$

$$E_{\text{lattice}}(\text{PbO, yellow}) = -3530. \text{ kJ/mole}$$

**The lattice energy of the yellow form of PbO is -3530. kJ/mole.**

b. Place the compounds  $Tl_2O$ ,  $PbO$ ,  $Bi_2O_3$  in order of increasing lattice energy. Rationalize your order.

**In order of increasing lattice energy:  $Tl_2O$ ,  $PbO$ ,  $Bi_2O_3$ .**

**The charge on the metal increases from Tl (+1) to Pb (+2) to Bi (+3) while the charge on the anion ( $O^{2-}$ ) stays the same. The lattice energy depends directly on the charge of the ions.**

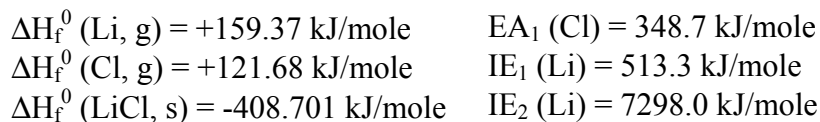
Also there is a small effect due to the size of the ions.  $Tl^+$  is larger than  $Pb^{2+}$ , which is larger than  $Bi^{3+}$ , although this is not a very big difference. Since the lattice energy varies inversely with size, we would expect the smaller ion  $Bi^{3+}$  to have the larger lattice energy.

c.  $\Delta H_f^0$  for the red form of PbO is -218.99 kJ/mole. Which parameter or parameters used in the Born-Haber cycle is or are responsible for the different  $\Delta H_f^0$  for the two forms of PbO? Briefly explain what is different between the yellow and red forms of PbO.

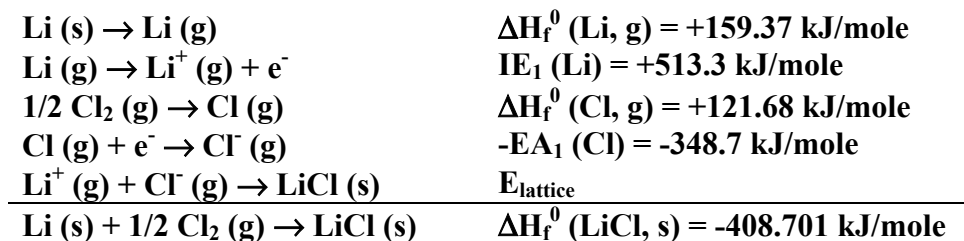
**The only parameter in the Born-Haber cycle that can be different for PbO (s, yellow) and PbO (s, red), other than  $\Delta H_f^0$  for PbO, is the lattice energy. The ionization energies, electron affinities, and all other  $\Delta H_f^0$  are the same.**

**The lattice energy depends on the arrangement of the ions in space and the charges on the ions. Since the charges on the ions are the same in both forms of PbO, we must conclude that the arrangement of the ions in space is different.**

13a. Calculate the lattice energy of LiCl. You are given the following information. The electron affinities are written in the formalism where a positive value means that energy is released when an electron is added.



*The required equations and energies are:*



$$\Delta H_f^0 (\text{LiCl, s}) = \Delta H_f^0 (\text{Li, g}) + IE_1 (\text{Li}) + \Delta H_f^0 (\text{Cl, g}) + -EA_1 (\text{Cl}) + E_{\text{lattice}}$$

$$-408.701 \text{ kJ/mole} = (159.37 + 513.3 + 121.68 - 348.7) \text{ kJ/mole} + E_{\text{lattice}}$$

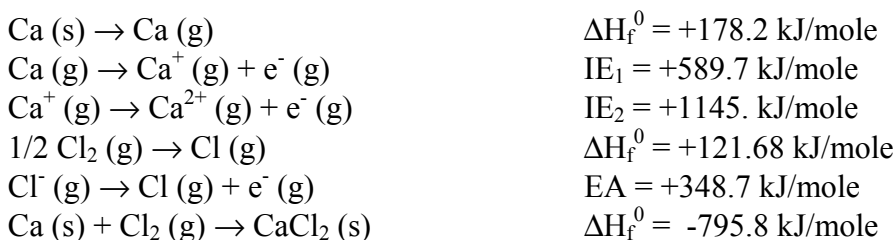
$$-854.4 \text{ kJ/mole} = E_{\text{lattice}}$$

**The lattice energy of LiCl is -854.4 kJ/mole.**

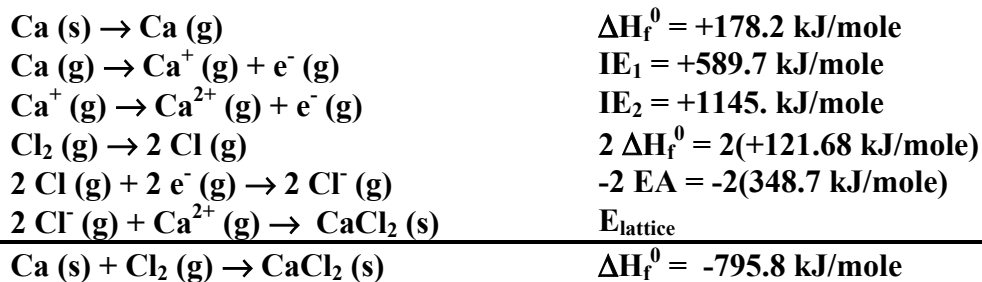
b. Explain why the lattice energy of LiF is much larger (a more negative number) than the lattice energy of LiCl.

**The lattice energy depends on the attractive interaction between the ions, which in turn depends directly on the charge of the ions and inversely on the distance between them. Since the charges are the same in LiF and LiCl, the difference in the lattice energy must be due to the distance between the ions. The  $\text{Li}^+$  is the same in both, therefore the increased lattice energy in LiF must be the result of the smaller size of  $\text{F}^-$  relative to  $\text{Cl}^-$  (remember the periodic trends), which results in a stronger interaction between the ions in LiF.**

14. Using the following data predict the lattice energy ( $E_{\text{lattice}}$ ) for  $\text{CaCl}_2$ . The electron affinities are written in the formalism where a positive value means that energy is released when an electron is added.



*Construct the Born-Haber cycle. Note that one must multiply  $\Delta H_f^0$  (Cl, g) by 2 and the EA (Cl, g) by -2 such that the first five equations plus the definition of  $E_{\text{lattice}}$  sums to  $\Delta H_f^0$  ( $\text{CaCl}_2$ , s).*



*This gives (remembering that we are multiplying by 1 mole in some cases)*

$$(+178.2 \text{ kJ}) + (+589.7 \text{ kJ}) + (+1145 \text{ kJ}) + (+243.36 \text{ kJ}) + (-697.4 \text{ kJ}) + E_{\text{lattice}} = -795.8 \text{ kJ/mole}$$

$$E_{\text{lattice}} = -2255. \text{ kJ/mole}$$

**The lattice energy of  $\text{CaCl}_2$  is -2255. kJ/mole.**

15.  $E_{\text{lattice}}$  for NaCl is -787. kJ/mole. Explain why  $E_{\text{lattice}}$  for  $\text{CaCl}_2$  is so much bigger.

**$E_{\text{lattice}}$  depends on the charge in the same manner as  $E_{\text{ion pair}}$  does. The larger the charges, the greater the interaction between the ions is. So  $E_{\text{lattice}}$  for  $\text{CaCl}_2$  should be larger than  $E_{\text{lattice}}$  for NaCl because  $\text{Ca}^{2+}$  has a higher charge than  $\text{Na}^+$ .**

*Note that to some extent size counteracts the effect of charge, since  $\text{Ca}^{2+}$  is larger than  $\text{Na}^+$ . A comparison of  $E_{\text{lattice}}$  for  $\text{MgCl}_2$  and NaCl would have shown us only the effect of charge on  $E_{\text{lattice}}$  because  $\text{Mg}^{2+}$  and  $\text{Na}^+$  are roughly the same size.*

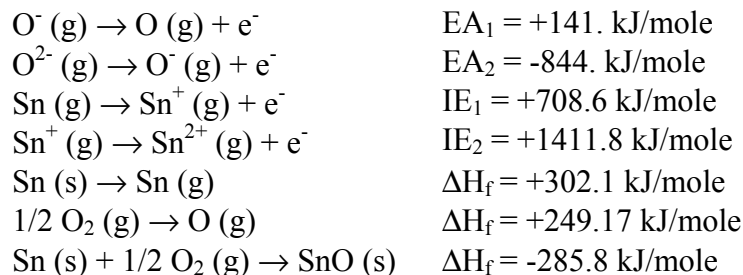
16. Explain the trend shown for the  $E_{\text{lattice}}$  given in the table below.

Compound	$E_{\text{lattice}}$ (kJ/mole)
NaF	-926.
NaCl	-787.
NaBr	-752.
NaI	-705.

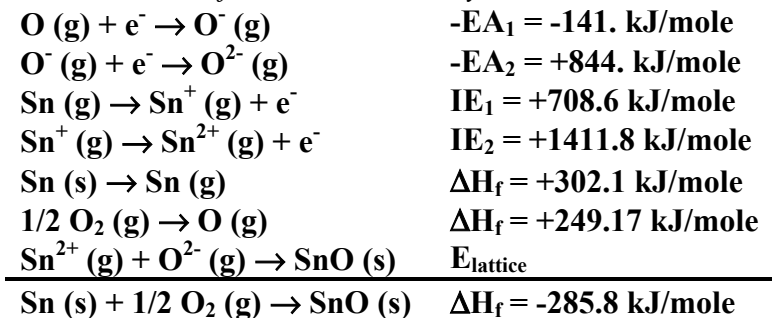
**Descending a group in the periodic table size increases, both for atoms and for ions of the same charge. As size increases the distance between the ions decreases, which in turn decreases the interaction between the two ions.  $\text{F}^-$  is a very small anion and  $\text{I}^-$  is a very large anion, so  $E_{\text{lattice}}$  is larger in NaF than it is in NaI.**

*Note. The electron affinity and ionization energy are not related to  $E_{\text{lattice}}$ .  $E_{\text{lattice}}$  only depends on the interactions between the charged particles in the solid state.  $-EA$  and  $IE$  are how much energy you must put in to form the ions, but have nothing to do with them interacting with each other (this is what  $E_{\text{lattice}}$  is).  $EA$  and  $IE$  do contribute (along with  $E_{\text{lattice}}$ ) to  $\Delta H_f^0$  for an ionic compound, where they can have a profound effect on the overall stability of an ionic compound.*

17a. From the following data calculate  $E_{\text{lattice}}$  for SnO. The electron affinities are written in the formalism where a positive value means that energy is released when an electron is added.



Rearrange given reactions to form Born-Haber cycle.



$$\Delta H_f = -EA_1 + -EA_2 + IE_1 + IE_2 + \Delta H_f(\text{Sn, g}) + \Delta H_f(\text{O, g}) + E_{\text{lattice}}$$

$$-285.8 \text{ kJ} = -141. \text{ kJ} + +844. \text{ kJ} + +708.6 \text{ kJ} + +1411.8 \text{ kJ} + +302.1 \text{ kJ} + +249.17 \text{ kJ} + E_{\text{lattice}}$$

$$E_{\text{lattice}} = -3660. \text{ kJ/mole}$$

**The lattice energy of SnO is -3660. kJ/mole.**

b.  $\Delta H_f$  of SnO is -285.8 kJ/mole and  $\Delta H_f$  of PbO is -217.32 kJ/mole. Comment specifically on how differences in the following contribute to the difference in  $\Delta H_f$  for these two compounds (remember your trends!).

Ionization energies of Sn(g) and Pb(g). IEs for Pb should be smaller than for Sn, because it is lower on the periodic table. All else being equal this would make  $\Delta H_f$  more negative (a larger number absolutely) for PbO, which is not observed.

Electron affinity of O(g). Contributes equally to both  $\Delta H_f$  so does not lead to difference in  $\Delta H_f$  values.

The lattice energy of SnO and PbO.  $E_{\text{lattice}}$  for SnO will be larger (more negative) than for PbO because  $\text{Sn}^{2+}$  is smaller than  $\text{Pb}^{2+}$  ( $E_{\text{lattice}}$  directly depends on charges). A larger (more negative)  $E_{\text{lattice}}$  means  $\Delta H_f$  is more negative (larger absolutely) for SnO, which is observed.

**We may conclude that the difference in  $\Delta H_f$  for PbO and SnO is due to the difference in  $E_{\text{lattice}}$  for the two compounds.**