

Inorganic Chemistry with Doc M.
Fall Semester, 2010
Day 13. Ionic Thrills Part 3.

Name(s):	Element:

Topics:

1. Octahedral and tetrahedral holes and the hcp lattice
2. Occupying the octahedral and tetrahedral holes
3. Lattice energy and the Born-Haber cycle
4. Lattice energies in general

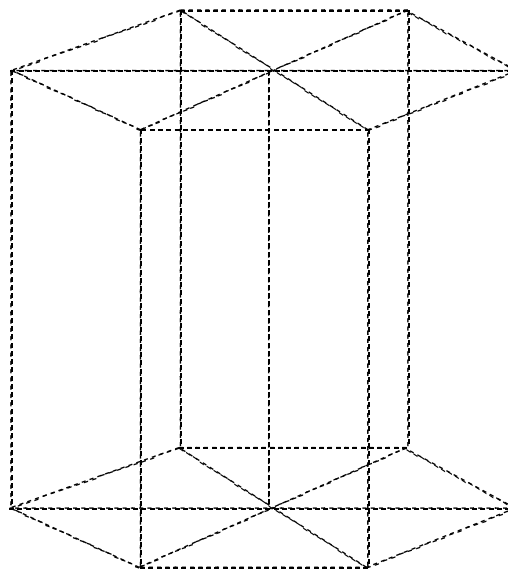
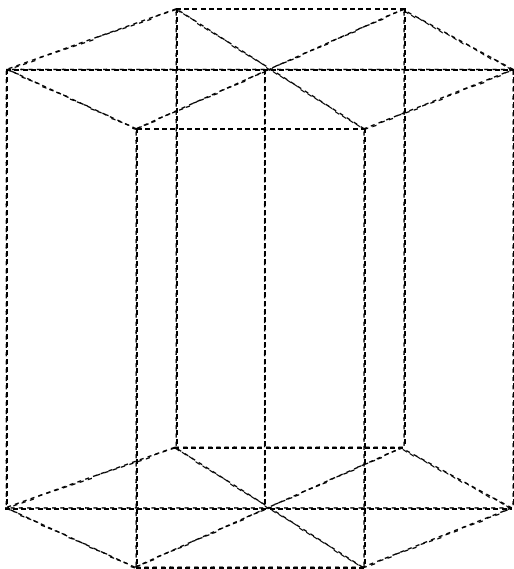
1. Octahedral and tetrahedral holes and the hcp lattice. We've discussed octahedral holes and tetrahedral holes in the context of the fcc lattice in the Day 11 guide. (a) To sum it up, how many spheres and holes are fully contained within each fcc unit cell? This is an important ratio to remember.

Spheres
Octahedral holes
Tetrahedral holes

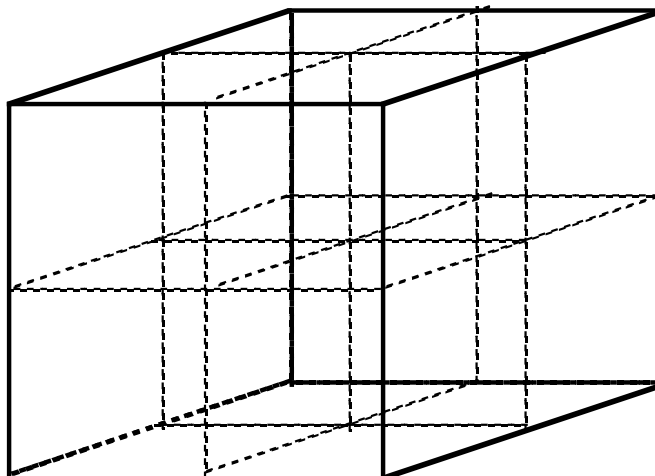
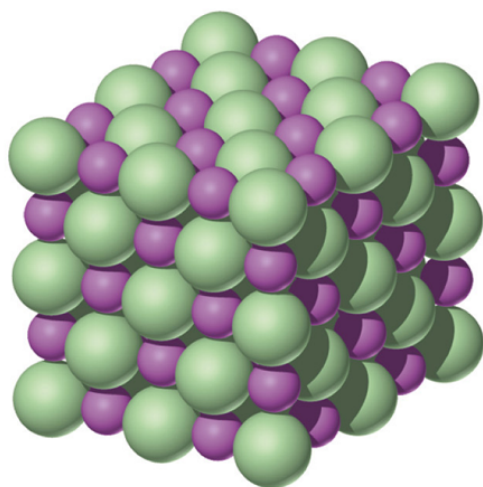
(b) Since we now know that the fcc lattice is equivalent to the close packed lattice ccp, what do you imagine the ratio of spheres : octahedral holes : tetrahedral holes is for hcp structures?

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(c) Mark the octahedral holes (left) and tetrahedral holes (right) *for one unit cell only*:



(c) We are now going to calculate the size of the octahedral and tetrahedral hole. We could do it for *hcp*, but it is easier to visualize for *ccp* = *fcc*. Shown here at left is the NaCl lattice with the sodium cations occupying the **octahedral holes**. Sketch one unit cell featuring the chlorides only.



(c) Remember that the points of contact between any two spheres should be along the line created from corner to face-center to corner. Use geometry to determine e , the edge length in units of r .

(d) Determine the diameter of the hole by subtracting $2r$ from e determined above. What is the diameter of the hole in r units?

(e) What is the **radius ratio**, that is the radius of the hole to the radius of the sphere that formed the hole?

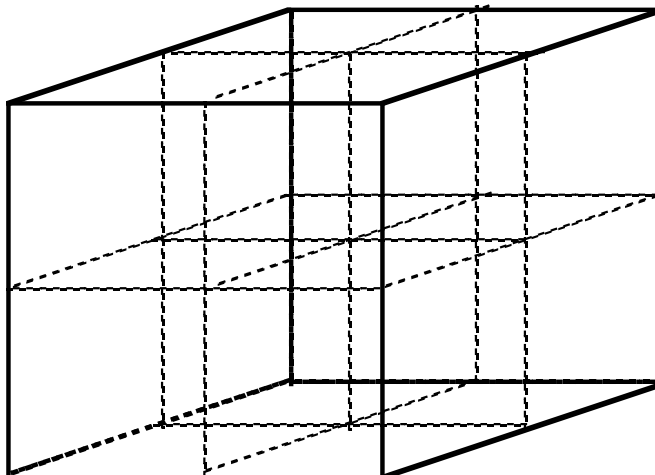
(f) The **radius ratio** determined above is an important number. In instances where the ratio of small ion to large ion is greater than 0.414 (the number you should have gotten in the previous question), there is a tendency for the small ions to occupy the octahedral holes. In cases where the ratio is less than 0.414, the small ions tend to occupy the smaller tetrahedral holes. What hole(s) do(es) the zinc ion(s) occupy in zinc blende? Look up the radius of each ion (coord. number 4) and determine the radius ratio.

(g) The previous paragraph could have provided some confusion: The second sentence seems to suggest that if an ion is too big for a hole that the one it prefers. Hmmmmm? Well, it's true! Stable lattices actually prefer it if the small ions are a little too big for the holes they use. Why might this be so? What do you think?

(h) The smallest holes are the tetrahedral holes. What are some of the smallest of ions and what are their radii? List about five.

(i) Use geometry and/or trigonometry to determine the radius of a tetrahedral hole.

(j) We have learned that in cases where the radius ratio is $r_{\text{small}}/r_{\text{large}} \geq 0.414$ the small ions occupies octahedral holes. Now we will determine the upper limit of the octahedral hole range. A larger hole, called a cubic hole exists at the body-centered position of a simple cubic lattice.



(j) Using the familiar template, determine the radius of a cubic hole in terms of r . You should get $0.732r$.

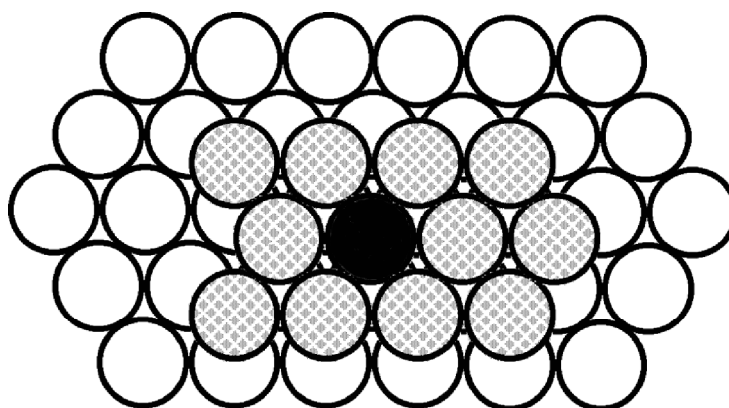
Note that whenever the packing ions are separated from direct contact, we are technically no longer close packed. Furthermore, in the CsCl ionic lattice we are not close packed.

The upper limit of radius ratio is 1.00 since we have defined the radius ratio as $r_{\text{small}}/r_{\text{large}}$.

(l) This sets as the range of radius ratios for the cubic geometry (simple cube lattice of large ions with opposite ions in body centered positions) $0.732 - 1.00$. Using a table of ionic radii, find one example that would fall within that range.

(m) Keep in mind that ratios that are close to the lower limit for cubic, 0.732, may actually turn out to be close-packed (fcc or hcp) with the small ions separating the large ions. That is the situation for NaCl. Determine the radius ratio for NaCl.

(n) The largest type of hole is the cubeoctahedral hole. This is where the cations and anions are the same size, $r_{\text{small}}/r_{\text{large}} = 1.00$. The easiest way to envision the cubeoctahedral hole, is to think of the close-packed array of spheres we were considering earlier on. If we remove one of the spheres (ions) and replace it with one of similar size but opposite charge, it would look like this:



What is the coordination number for the filled in ion in the drawing (don't forget to mentally add the third layer)?

(o) For comparison purposes, what are the coordination numbers for tetrahedral holes, octahedral holes and cubic holes?

2. Occupying the octahedral and tetrahedral holes.

(a) We learned earlier that ZnS has the zinc blende structure, a structure based on the hcp lattice. Another solid form of zinc sulfide, called sphalerite, is also possible. In sphalerite, the sulfides occupy fcc positions and the zinc(II) ions occupy tetrahedral holes. What fraction of the tetrahedral holes are occupied by Zn^{+2} ?

(b) Perovskite contains titanium and calcium cations and oxide anions. The Ca^{+2} ions occupy the corner positions, the titanium ion occupies the body-center position and the oxides occupy all of the face-centered positions of a cubic unit cell. What is the formula of perovskite? (Recall that the body-centered *position* is not the same as a body-centered cubic unit cell!)

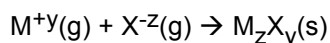
(c) Niobium oxide forms cubic crystals with the oxides occupying all of the edge-centered positions and niobium ions occupying all of the face-centered positions. What is the formula of this oxide of niobium? (Recall that the face-centered *position* is not the same as a face-centered cubic unit cell!)

(d) Rhenium oxide forms cubic crystals with the oxides occupying all of the edge-centered positions and rhenium ions occupying all of the corner positions. What is the formula of this oxide of rhenium?

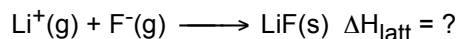
(e) Ag_2HgI_4 is a yellow solid featuring iodide ions in a cubic close packed array (**ccp = fcc**). The Ag^+ and Hg^{+2} ions occupy only tetrahedral holes. What percentage of the tetrahedral holes are occupied?

(f) All of the alkaline earth oxides feature the NaCl lattice? (i) What holes (octahedral or tetrahedral) are occupied and what fraction of these holes is occupied? (ii) What is the relationship between e , the cell edge length and the radii of the ions, r_{cation} and r_{anion} ?

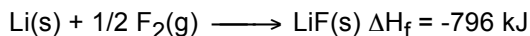
3. Lattice energy and the Born-Haber cycle. The lattice energy is defined as the heat released when one mole of an ionic compound is formed from its gas phase ions:



We'll consider LiF as our example. The lattice energy for LiF is given by:



This is an impossible quantity to measure but it would be a very nice number to know so we can compare lattice energies with one another. Fortunately, Hess's law allows us to calculate the lattice energy for any ionic solid. We do this using the heat of formation for LiF(s) and several other thermodynamic values as needed. The heat of formation of LiF is:



The strategy used to convert the heat of formation into the lattice energy using Hess's Law is summed with these equations and thermodynamic values:

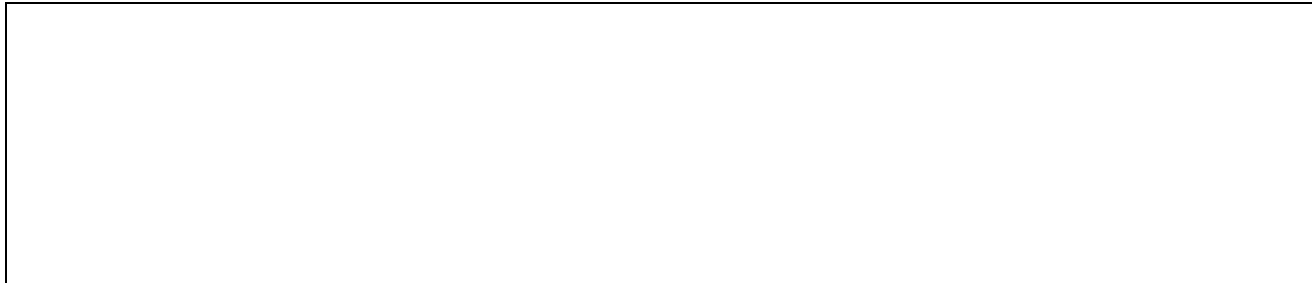
Step 1.	$\text{Li}(s) \longrightarrow \text{Li}(g)$	$\Delta H_{\text{at}} = +161 \text{ kJ}$
Step 2.	$\text{Li}(g) \longrightarrow \text{Li}^+(g) + e^-$	$\Delta H_{\text{ion}} = +531 \text{ kJ}$
Step 3.	$1/2 \text{F}_2(g) \longrightarrow \text{F}(g)$	$\Delta H_{\text{dissociation}} = +79 \text{ kJ}$
Step 4.	$\text{F}(g) + e^- \longrightarrow \text{F}^-(g)$	$\Delta H_{\text{elec aff}} = -328 \text{ kJ}^*$
Step 5.	$\text{Li}^+(g) + \text{F}^-(g) \longrightarrow \text{LiF}(s)$	$\Delta H_{\text{lattice energy}} = ?$
Step 6.	$\text{Li}(s) + 1/2 \text{F}_2(g) \longrightarrow \text{LiF}(s)$	$\Delta H_f = -796 \text{ kJ}$

Step 1 is called a variety of things, including heat of vaporization, atomization, sublimation, etc.

* Step 4. The electron affinity is traditionally defined as the amount of heat *released* when an electron is added. This makes electron affinities *positive* for exothermic processes! Be really careful here! Know that almost all electron affinities are exothermic [Exceptions are Groups 2, 12 (the Zn triad), 18 (the noble gases)]

and nitrogen.] For thermodynamic purposes, the values used here must be used as a negative values for exothermic situations.

This use of Hess's law is called the Born-Haber cycle. Show that the lattice energy works out to be -1239 kJ/mol



(a) Follow the example given for LiF to determine the lattice energy for MgF_2 . Look up all of the thermodynamic values needed.



(b) Use the Born-Haber cycle to determine the lattice energy for NaCl. Look up all of the thermodynamic values needed.



4. Lattice energies in general. The mathematical equation for estimating lattice energy is given by

Coulomb's law: $E_C = q^+q^- / 4\pi r\epsilon$. (a) Look up in our book what each term stands for.

(b) In general, compare the lattice energies of a +1 ion with a -1 ion such as NaCl with a +2 ion with a -2 ion such as MgS.

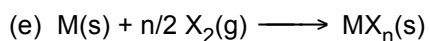
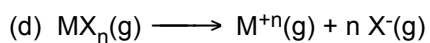
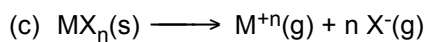
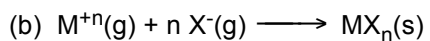
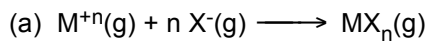
(c) How would solubility be affected by lattice energy?

(d) Recall the solubility rule for phosphate. What is it and how does lattice energy help predict the rule?

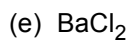
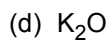
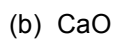
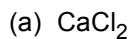
(e) Generally, +1/-1 salts are (soluble/insoluble), and +2/-2 salts are (soluble/insoluble). Find some exceptions to each generalization.

Review for the ACS Final Exam: Solid State

1. Which of the following is an example of lattice energy?



2. Which of the following would exhibit the largest lattice energy?



Answers: B, B