

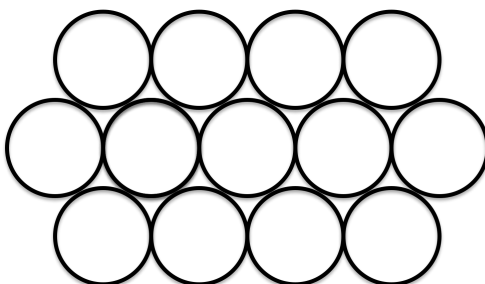
## Inorganic Chemistry with Doc M.

### Day 11. Ionic Thrills Part II.

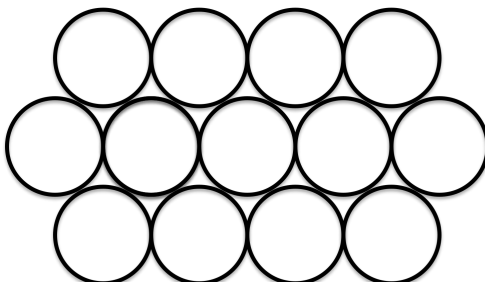
#### Topics:

1. Close packing
2. Holes
3. Hexagonal close packed lattice (hcp)
4. Cubic close packing (ccp)
5. Radius ratio and the radius of octahedral and tetrahedral holes
6. Cubeoctahedral holes
7. Occupying the octahedral and tetrahedral holes
8. Lattice energy and the Born-Haber cycle
9. Lattice energies in general

**1. Close packing** is a term that refers to the most highly efficient packing. In two dimensions, circles can close pack as follows. You may want to build something like this with pennies (or tiddlywinks) so that the next parts are easier.

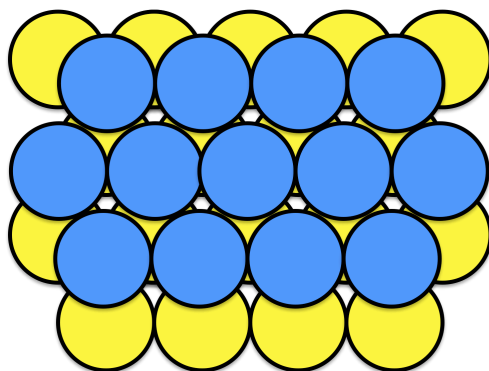


Now we can extend the 2-D circles to what happens for 3-D spheres: the same thing! With spheres, however, additional layers can be added and they do so in quite specific ways in order to maintain close packing: the spheres rest in the divots. Sketch about four close-packed atoms from a second layer on top of this first layer. Shade the second layer atoms. Build a second layer with your pennies or tiddlywinks.

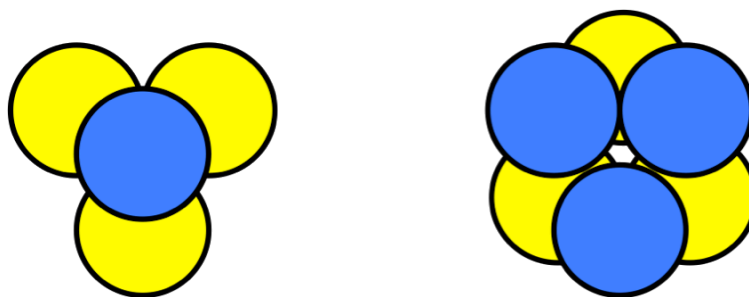


Note that of all the little triangle-shaped holes between the spheres in Layer 1, half of them will be covered with spheres from Layer 2. This brings us to Layer 3! The third layer could either (a) repeat the

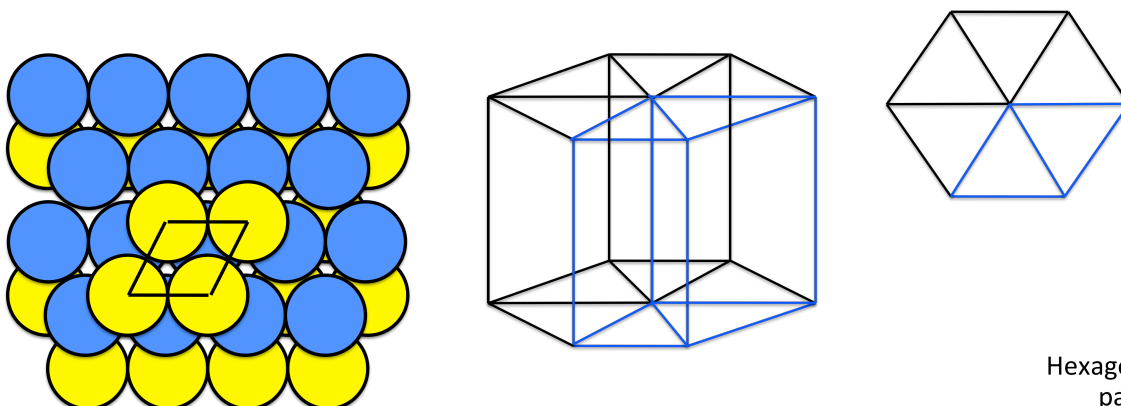
first layer so that the little holes from Layer 1 are still in view or (b) the third row can position itself over the **holes** from Layer 1, creating a third unique layer. When the former happens, the close packed structure is called ABAB, referring to the two layers, A and B. The ABAB layering is more commonly called “hexagonal close packed” or “hcp” When the third layer covers the holes from Layers A and B, the structure is called ABC or “cubic close packed” or simply “ccp.” Locate on this drawing where the third layer would go to create (a) an hcp arrangement or (b) a ccp arrangement.



**2. Holes.** As the second layer is formed, two types of “holes” are created between the two layers – a small hole is created whenever a B-layer atom is placed in the divot of three A-layer atoms as shown in the figure at left. This little hole has four sides and is called a **tetrahedral hole**. A much larger hole is produced when three B-layer atoms cover three A-layer atoms as shown in the figure at right. This hole has six sides to it and is called an **octahedral hole**.

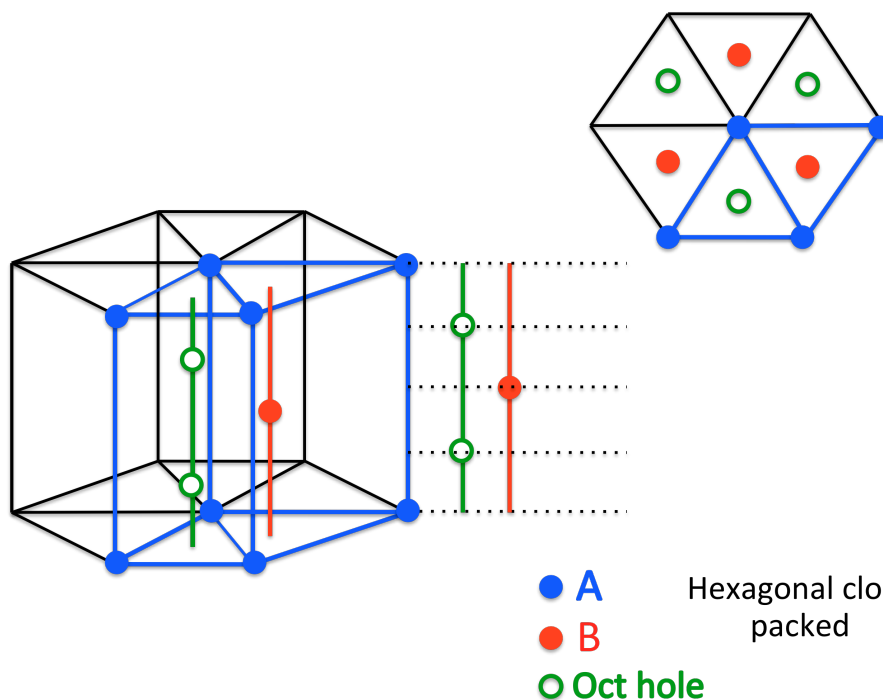


**3. The hexagonal close packed lattice (ABAB, or hcp)** The hexagonal unit cell is formed when the third layer of spheres is an exact repeat of the first layer, hence ABAB. This is shown in leftmost figure below. The middle figure shows a side view of one unit cell (in blue) and its relationship to two other adjacent unit cells. The angles at the corners are  $60^\circ$ ,  $90^\circ$  and  $90^\circ$ . Note: the hexagonal pie-shaped planes are from two A layers. The B layer is between these two layers and is not shown in the two line drawings.



Hexagonal close packed

Now we can add some more detail. In the left drawing below, the location of the B layer atom is shown for the unit cell in red. Note that in the two “prism halves” to each hcp unit cell, there is only one B atom at the very center of one of the prism halves. The relative vertical positions of the B layer is shown in more detail along the side. In the top view shown at right, note that there are three B atoms in alternate prisms – this should be expected as it is the same as the yellow and blue figure from the above. Note also the location of the octahedral holes (green) situated midway between the A-layer and B-layer atoms.



(a) How many octahedral holes are fully contained within each unit cell?

(b) How many B atoms are fully contained within each unit cell?

(c) How many A atoms are fully contained within each unit cell?

(d) What is the ratio of atoms (A and B total) to octahedral holes?

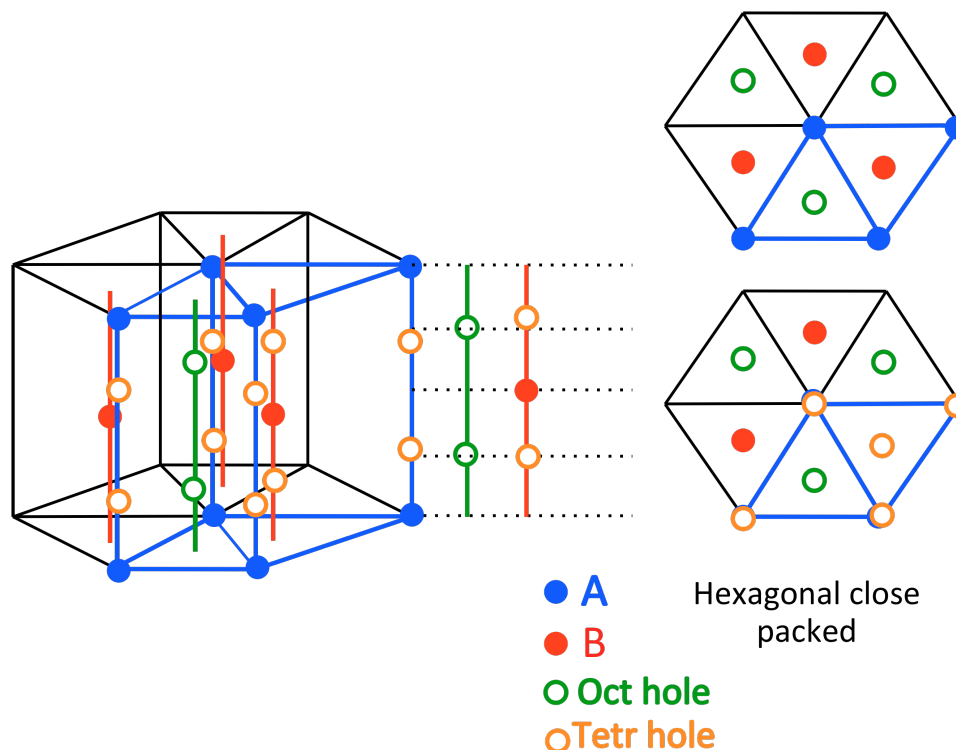
(e) What is the area of the parallelogram, in units of  $r$ , that defines the top and bottom of each unit cell?

(f) What is the vertical length of the unit cell in units of  $r$ ?

(g) What is the volume of the unit cell in units of  $r$ ?



**The tetrahedral holes and the hcp unit cell.** Now we can add the tetrahedral holes. Again, think about the space-filling yellow and blue spheres pictures on the previous page. The location of the tetrahedral holes in the hexagonal close packed unit cell are shown in this drawing:



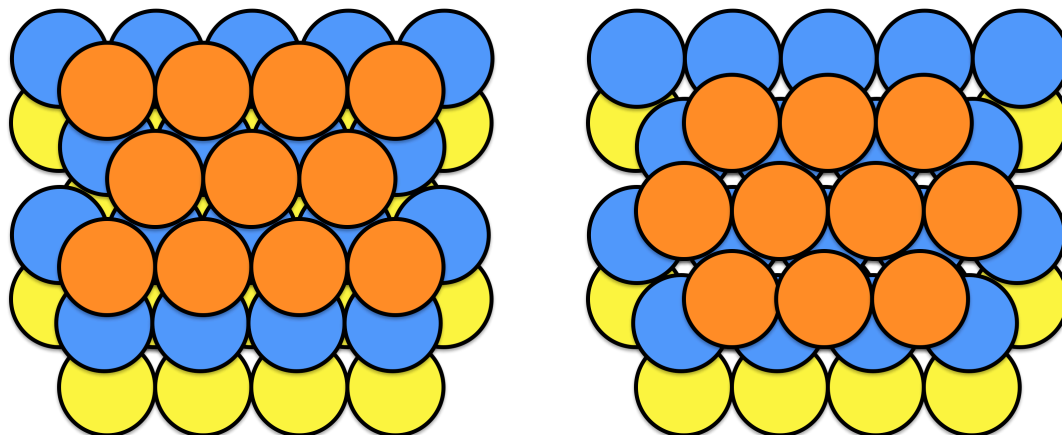
(a) How many tetrahedral holes are fully contained within each unit cell?

(b) What is the ratio of atoms (A and B total) to octahedral holes to tetrahedral holes in the hcp unit cell?

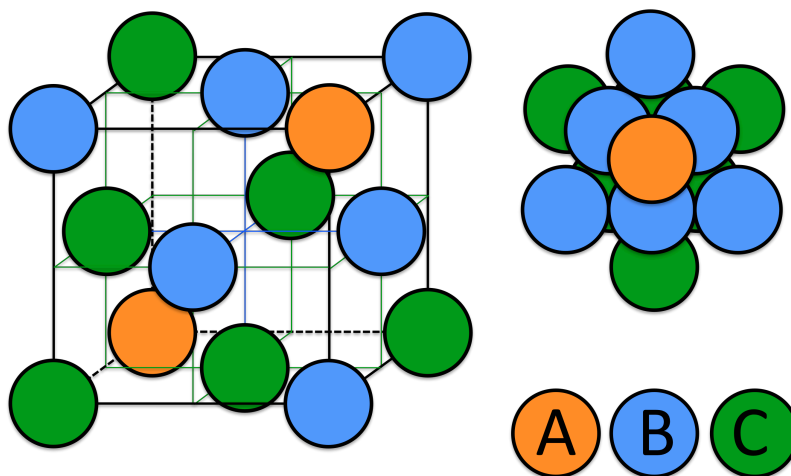
(c) Magnesium, scandium, titanium, cobalt and zinc are just a few examples of elements that exhibit hexagonal close packed structure. Given that the atomic radius of magnesium is 160 pm, calculate the density of magnesium and compare it to the known density given on your colorful and informative periodic table.

**4. The cubic close packed lattice (ccp)** In close packed spheres, there are two distinct ways in which the third layer can be situated, either ABAB (hexagonal close packing) or ABC, also known as **cubic close packing**.

(a) Look at two close-packed lattices and determine which is hcp and which is ccp.



The cubic close packing (ccp) lattice is actually equivalent to the familiar face-centered cubic lattice! This equality can be seen in the following pair of figures. The face-centered unit cell is shown in its traditional cubic view as shown at left. The connection to ABC packing is seen if we view the fcc unit cell from one corner, down through the unit cell to the completely opposite corner as shown in the right figure. The layers are shown in colors for both layers with Layer A being orange, Layer B being shown in blue and Layer C in green:

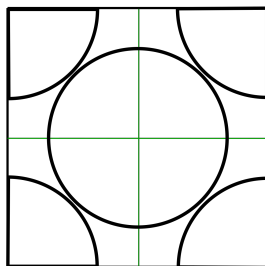


(b) Could body-centered cubic or simple cubic also be examples of close packing? Explain.

(c) Given your answer to (b), if you were to calculate the density for a metal, for example, using simple cube, **bcc** and **fcc** unit cells, would either give a greater density than the other?

(d) Close packed lattices are very important for monatomic elements such as the metals. Why is that so?

**5. Radius ratio and the diameter of the octahedral and tetrahedral holes.** We must now calculate the size of the octahedral and tetrahedral holes. We could do it for **hcp**, but it is easier to visualize for **ccp = fcc** – and the answer will be the same. Shown here is one face of the fcc lattice.



(a) Determine  $e$ , the edge length in units of  $r$ .

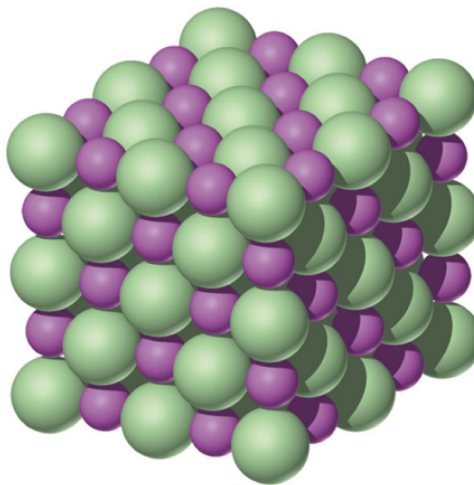
(b) Determine the diameter of the hole by subtracting  $2r$  from  $e$  determined above. What is the diameter of the hole in  $r$  units? What is the radius?

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

(d) In ionic substances, the smaller ions occupy the holes between the larger ions. 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

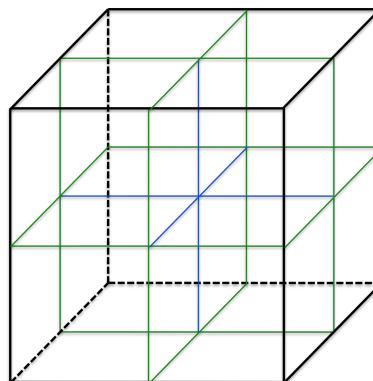
for the small ions to occupy the octahedral holes. In cases where the ratio is less than 0.414, the small ions tend to occupy the smaller tetrahedral holes. What hole(s) do(es) the zinc ion(s) occupy in zinc blende? Look up the radius of each ion (coord. number 4) and determine the radius ratio.

- (e) 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?



- (f) The smallest holes are the tetrahedral holes. Use geometry and/or trigonometry to determine the radius of a tetrahedral hole.

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

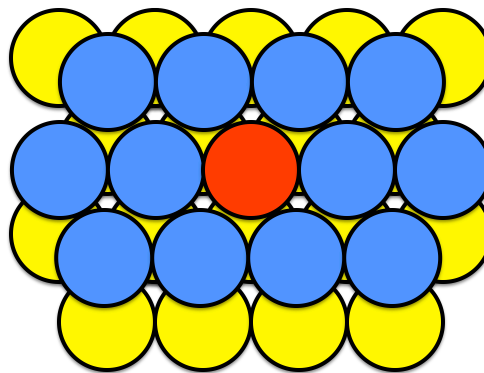


Note that whenever the packing ions are separated from direct contact, we are technically no longer close packed. Furthermore, in the CsCl ionic lattice we are not close packed. The upper limit of radius ratio is 1.00 since we have defined the radius ratio as  $r_{\text{small}}/r_{\text{large}}$ .

- (h) 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.

- (i) 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.

**6. Cubeoctahedral holes.** 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:



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

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

## 7. 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 form a fcc sublattice and the zinc(II) ions occupy tetrahedral holes. What fraction of the tetrahedral holes are occupied by  $\text{Zn}^{+2}$ ?

(b) Perovskite contains titanium and calcium cations and oxide anions. The  $\text{Ca}^{+2}$  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!)

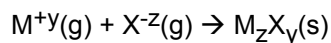
(c) Niobium oxide forms cubic crystals with the oxides occupying all of the edge-centered positions and niobium ions occupying all of the face-centered positions. What is the formula of this oxide of niobium? (Recall that the face-centered *position* is not the same as a face-centered cubic unit cell!)

(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?

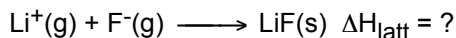
(e)  $\text{Ag}_2\text{HgI}_4$  is a yellow solid featuring iodide ions in a cubic close packed array (**ccp = fcc**). The  $\text{Ag}^+$  and  $\text{Hg}^{+2}$  ions occupy only tetrahedral holes. What percentage of the tetrahedral holes are occupied?

(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,  $r_{\text{cation}}$  and  $r_{\text{anion}}$ ?

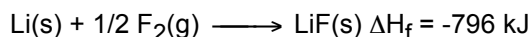
**8. Lattice energy and the Born-Haber cycle.** The lattice energy is defined as the heat released when one mole of an ionic compound is formed from its gas phase ions:



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.	$Li(s) \longrightarrow Li(g)$	$\Delta H_{at} = +161 \text{ kJ}$
Step 2.	$Li(g) \longrightarrow Li^{+}(g) + e^{-}$	$\Delta H_{ion} = +531 \text{ kJ}$
Step 3.	$1/2 F_2(g) \longrightarrow F(g)$	$\Delta H_{dissociation} = +79 \text{ kJ}$
Step 4.	$F(g) + e^{-} \longrightarrow F^{-}(g)$	$\Delta H_{elec \text{ aff}} = -328 \text{ kJ}^*$
Step 5.	$Li^{+}(g) + F^{-}(g) \longrightarrow LiF(s)$	$\Delta H_{lattice \text{ energy}} = ?$
Step 6.	$Li(s) + 1/2 F_2(g) \longrightarrow LiF(s)$	$\Delta H_f = -796 \text{ kJ}$

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  $-1239 \text{ kJ/mol}$

- (a) Follow the example given for LiF to determine the lattice energy for  $\text{MgF}_2$ . 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.

**9. 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?



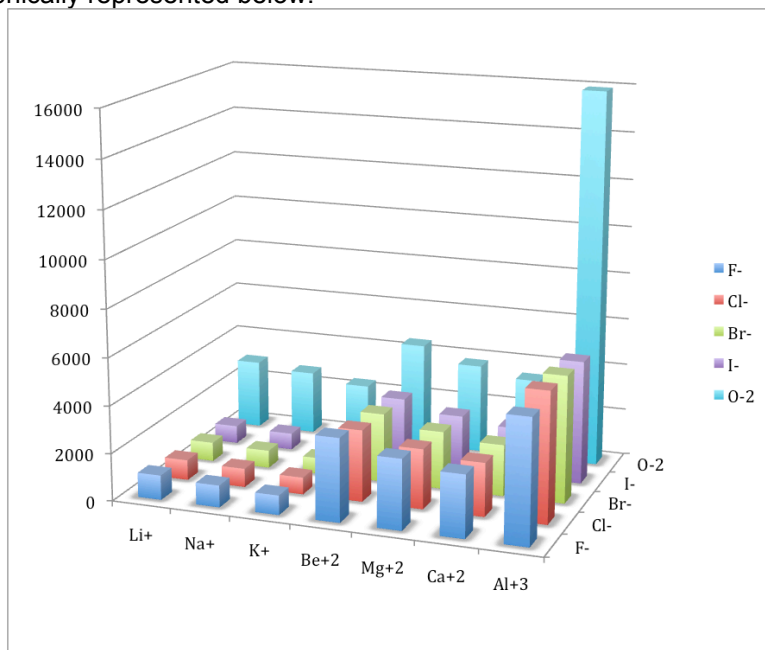
(d) Recall the solubility rule for phosphate. What is it and how does lattice energy help predict the rule?

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

(f) Lattice energies (kJ/mol) This table gives the lattice energy of 35 binary salts. The data shows how the charge on either ion affects the lattice energy.

	<b>F<sup>-</sup></b>	<b>Cl<sup>-</sup></b>	<b>Br<sup>-</sup></b>	<b>I<sup>-</sup></b>	<b>O<sup>-2</sup></b>
<b>Li<sup>+</sup></b>	1036	853	807	757	2925
<b>Na<sup>+</sup></b>	923	787	747	704	2695
<b>K<sup>+</sup></b>	821	715	682	649	2360
<b>Be<sup>+2</sup></b>	3505	3020	2914	2800	4443
<b>Mg<sup>+2</sup></b>	2957	2524	2440	2327	3791
<b>Ca<sup>+2</sup></b>	2630	2258	2176	2074	3401
<b>Al<sup>+3</sup></b>	5215	5492	5361	5218	15916

These data are graphically represented below:



Among just the +1 and -1 salts, why is the lattice energy of LiF the largest?

## Review for the ACS Final Exam: Solid State

- Which of the following best describes the cesium chloride lattice?
  - A face-centered cubic sublattice of one ion with the other ion occupying edge-centered positions.
  - A body-centered cubic sublattice of one ion with the other ion occupying edge-centered positions.
  - A face-centered cubic sublattice of one ion with the other ion occupying body centered positions.
  - A body-centered cubic sublattice of one ion with the other ion occupying edge-centered positions.
  - A primitive cubic sublattice of one ion with the other ion occupying body centered positions.
- Palladium metal has an atomic radius of 137 pm and exists as a cubic close packed solid. What is its density?
  - $\frac{106.4}{(6.02 \times 10^{23} \times (137 \times 10^{-10} \times 4/\sqrt{2})^3)}$
  - $\frac{106.4 \times 4}{(6.02 \times 10^{23} \times (137 \times 10^{-10} \times 2)^3)}$
  - $\frac{106.4 \times 4}{(6.02 \times 10^{23} \times (137 \times 10^{-10} \times 4/\sqrt{2})^3)}$
  - $\frac{106.4 \times 4}{(137 \times 10^{-10} \times 4/\sqrt{2})^3}$
  - $\frac{106.4 \times 2}{(6.02 \times 10^{23} \times (137 \times 10^{-10} \times 4/\sqrt{3})^3)}$
- Which of the following is an example of lattice energy?
  - $M^{+n}(g) + n X^-(g) \longrightarrow MX_n(g)$
  - $M^{+n}(g) + n X^-(g) \longrightarrow MX_n(s)$
  - $MX_n(s) \longrightarrow M^{+n}(g) + n X^-(g)$
  - $MX_n(g) \longrightarrow M^{+n}(g) + n X^-(g)$
  - $M(s) + n/2 X_2(g) \longrightarrow MX_n(s)$
- Which of the following would exhibit the largest lattice energy?
  - $CaCl_2$
  - $CaO$
  - $KCl$
  - $K_2O$
  - $BaCl_2$

Answers: E, C, B, B

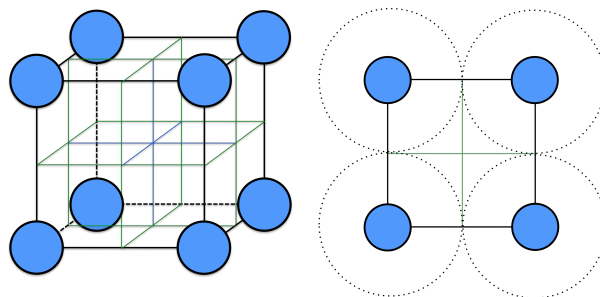
## Answers for Day 10

1. (a) List properties of ionic compounds: high melting, possibly soluble in water, in which case it will conduct electricity, hard but brittle; (b) How would one identify a compound as either ionic or covalent? Formula contains metal cation and non-metal or polyatomic anion, solutions conduct electricity, must be a solid.

### 3. The simple cubic unit cell.

(a) Sketch in the atoms for a **simple cube**.  
Example: polonium

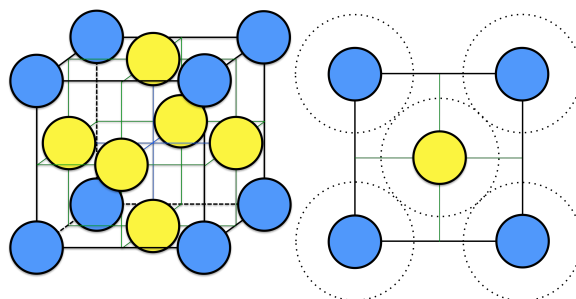
(b) atoms/ions touch along edge; (c) 1 atom is present per unit cell:  $8 \text{ corners} \times \frac{1}{8} = 1$ ; (d)  $e = 2r$ ;  
(e)  $V = e^3 = (2r)^3$ ; (f) percent of the space occupied =  $100\% \times V_{\text{one atom}}/V_{\text{one unit cell}} = 100\% \times (\frac{4}{3} \pi r^3)/(2r)^3 = 52.4\%$



### 4. The face-centered cube

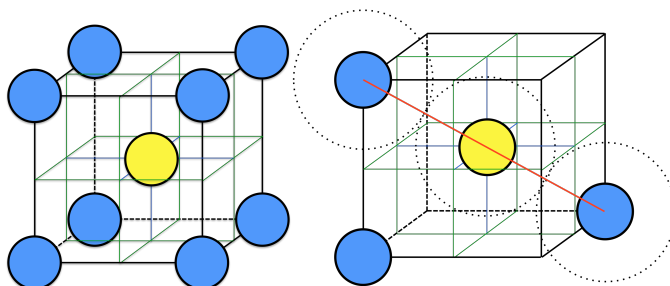
Note that the yellow balls are the face-centered positions and the blue balls are the corners, BUT both yellow and blue are the SAME atom/ion in the fcc. Color is used only to accentuate the two different positions.

(a) see figure above; (b) 4 atoms are present per unit cell:  $8 \text{ corners} \times \frac{1}{8} + 6 \text{ face centers} \times \frac{1}{2} = 4$ ;  
(c)  $4r = 2^{0.5}e$ , therefore  $e = 4r / 2^{0.5}$ ; (d)  $V = e^3 = (4r/2^{0.5})^3$ ;  
(e) percent of the space occupied =  $100\% \times V_{4 \text{ atoms}}/V_{\text{one unit cell}} = 100\% \times (4 \times \frac{4}{3} \pi r^3)/(4r/2^{0.5})^3 = 74.0\%$ ; (f) volume of a calcium unit cell of calcium in  $1.73 \times 10^{-22} \text{ cm}^3$ ;  
(g) density of calcium =  $m_{\text{Ca in one unit cell}}/V_{\text{one unit cell}} = (4 \times 40.08 \text{ g mol}^{-1}/6.02 \times 10^{23})/(1.73 \times 10^{-22} \text{ cm}^3) = 1.54 \text{ g/cm}^3$ , same as the actual density



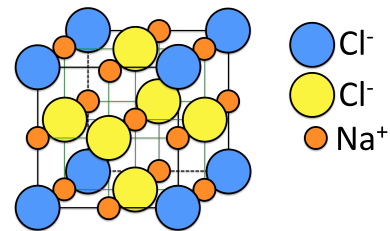
### 5. The body-centered Cube

(a) shown above; (b) Contact occurs along the body diagonal – the body center and the two opposite corners touch in a distance of  $4r$ ; (c) 2 atoms are present per unit cell:  $8 \text{ corners} \times \frac{1}{8} + 1 \text{ body centered entirely within the cell} = 2$ ; (d)  $e = 4r / 3^{0.5}$ ; (e)  $V = e^3 = (4r/3^{0.5})^3$ ; (f) percent of the space occupied =  $100\% \times V_{2 \text{ atoms}}/V_{\text{one unit cell}} = 100\% \times (2 \times \frac{4}{3} \pi r^3)/(4r/3^{0.5})^3 = 68.0\%$



6. The sodium chloride lattice. (a) chlorides are the large spheres and sodium cations are the small ones; (b) fcc; (c) see figure; (d) There are 12 edge-centered positions in the fcc unit cell; (e) Edge-centered positions are only  $\frac{1}{4}$  inside each a particular unit cell. There are  $12 \times \frac{1}{4} = 3$  ions in edge-centered positions within each unit cell; another sodium cation is at the body-centered position.

(g)



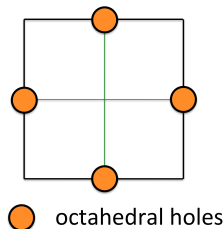
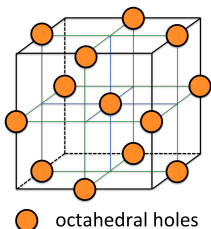
	Corner	Face-centered	Body-centered	Edge-centered
Simple cube	Yes	No	No	No
Face-centered cube	Yes	Yes	No	no
Body-centered cube	Yes	No	Yes	no
NaCl lattice	Yes	Chlorides	Sodium cations	Sodium cations

(h) The ratio of  $\text{Cl}^-$  to  $\text{Na}^+$  in the unit cell is 4:4 or 1:1, same as the formula

(i)  $e = 2 \times 116 \text{ pm} + 2 \times 167 \text{ pm} = 566 \text{ pm}$ ; and the volume is  $1.81 \times 10^{-22} \text{ cm}^3$

(j) density of NaCl =  $m_{\text{NaCl in one unit cell}} / V_{\text{one unit cell}} = (4 \times 58.44 \text{ g mol}^{-1} / 6.02 \times 10^{23}) / (1.81 \times 10^{-22} \text{ cm}^3) = 2.15 \text{ g/cm}^3$ , about the same as the actual density

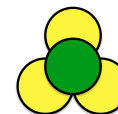
## 7. Octahedral and tetrahedral holes.



(a) There are 8 tetrahedral holes are present within a fcc unit cell;

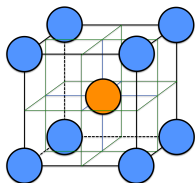
(b) ratio of spheres : octahedral holes : tetrahedral holes fully contained within the fcc unit cell is 4:4:8.

(c) shown at right



(d) Each ion in NaCl has 6 nearest neighbors of opposite charge.

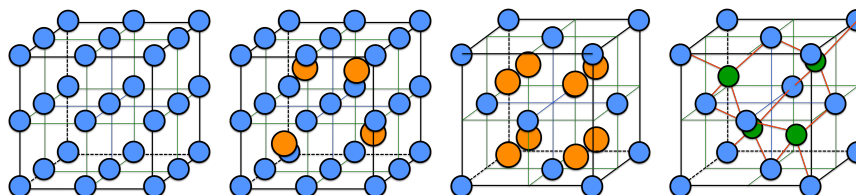
## 8. The cesium chloride lattice. (a)



	Corner	Face-center	Body-center	Edge-center
NaCl	$\text{Cl}^-$	$\text{Cl}^-$	$\text{Na}^+$	$\text{Na}^+$
CsCl	$\text{Cl}^-$		$\text{Cs}^+$	

(c) The  $\text{Cl}^-$  sub-lattice in CsCl is a simple cube; (d) The ratio of  $\text{Cs}^+$  to  $\text{Cl}^-$  is 1:1 in the unit cell, same as its formula; (e) The coordination number for both  $\text{Cs}^+$  and  $\text{Cl}^-$  in the CsCl structure is 8. The coordination number for both  $\text{Na}^+$  and  $\text{Cl}^-$  in the NaCl structure is 6; (f)  $e = 413 \text{ pm}$ ; (g)  $r_{\text{Cl}^-} = 170 \text{ pm}$

**9. The fluorite lattice.** (a-b) pictured below (two left); (c) The coordination number for calcium is 8 and for fluoride is 4; (d) pictured below, third; (e) the same as in (c)



**10. The zinc blende lattice.** (a) fourth figure above; (b) The coordination number for each ion is 4; (c) There are 4  $\text{S}^{2-}$  anions are there per unit cell.

**11. Diamond.** Same as zinc blende but with the green and blue atoms all being carbon.