

Courtesy of G. S. Girolami.

Packing of Spheres

- There are three types of solids: crystalline, quasi-crystalline, and amorphous. We shall be concerned with crystalline solids.
- Crystals are made up by having a repeating array of atoms or ions in three-dimensions.

Cubic and hexagonal close-packing

- If we assume that atoms are hard spheres, then it is reasonable to assume that when they are placed in contact, they will pack in such a way as to get as close as possible to each other. By analogy, when we place marbles into a bag, they tend to adopt an arrangement in which the marbles are in contact. These arrangements are called **close packing**.
- When three or more layers of spheres are placed on top of each other systematically, then there are two possible structures: hexagonal close packing (hcp) and cubic close packing (ccp), illustrated in Figure 1 and Figure 5.2 on page 117 of Housecroft and Sharpe.

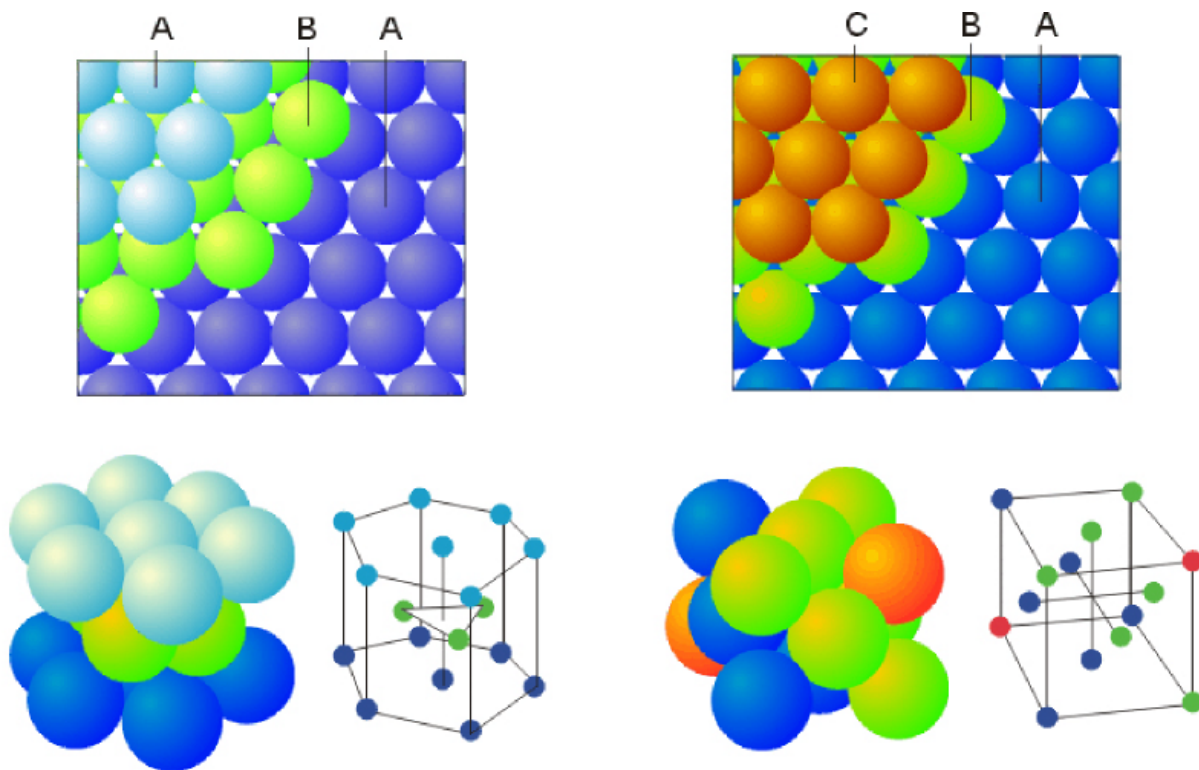


Figure 1: Generation of hcp and ccp Lattices

From Shriver and Atkins, "Inorganic Chemistry", 3rd edition, © W. H. Freeman

- Hexagonal close packing occurs when the third layer of spheres eclipses the first. We call this an ABABAB ... arrangement.
- Cubic close packing occurs when the third layer of spheres does not eclipse the first. We call this an ABCABC ... arrangement.
- Each sphere touches 12 other spheres, so we say the **coordination number** is 12.
- Figure 5.3 of Housecroft and Sharpe illustrates the coordination number of each sphere in the ccp and hcp arrangements.

The unit cell: hexagonal and cubic close-packing

- The simplest portion of a crystal, which contains all the chemical information about that crystal, is called the **unit cell**, which is illustrated in Figure 2.

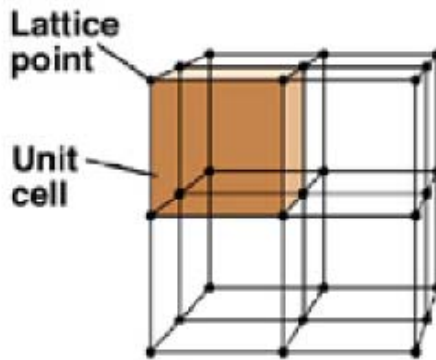


Figure 2: Definition of a Unit Cell for a 3D Lattice.

From Shriver and Atkins, "Inorganic Chemistry", 3rd edition, © W. H. Freeman.

- Cubic close packing results in a **face-centered cubic (fcc)** lattice. The fcc and hcp lattices are shown in Figure 1, Figure 3, and Figure 5.4 on p. 118 of Housecroft and Sharpe.

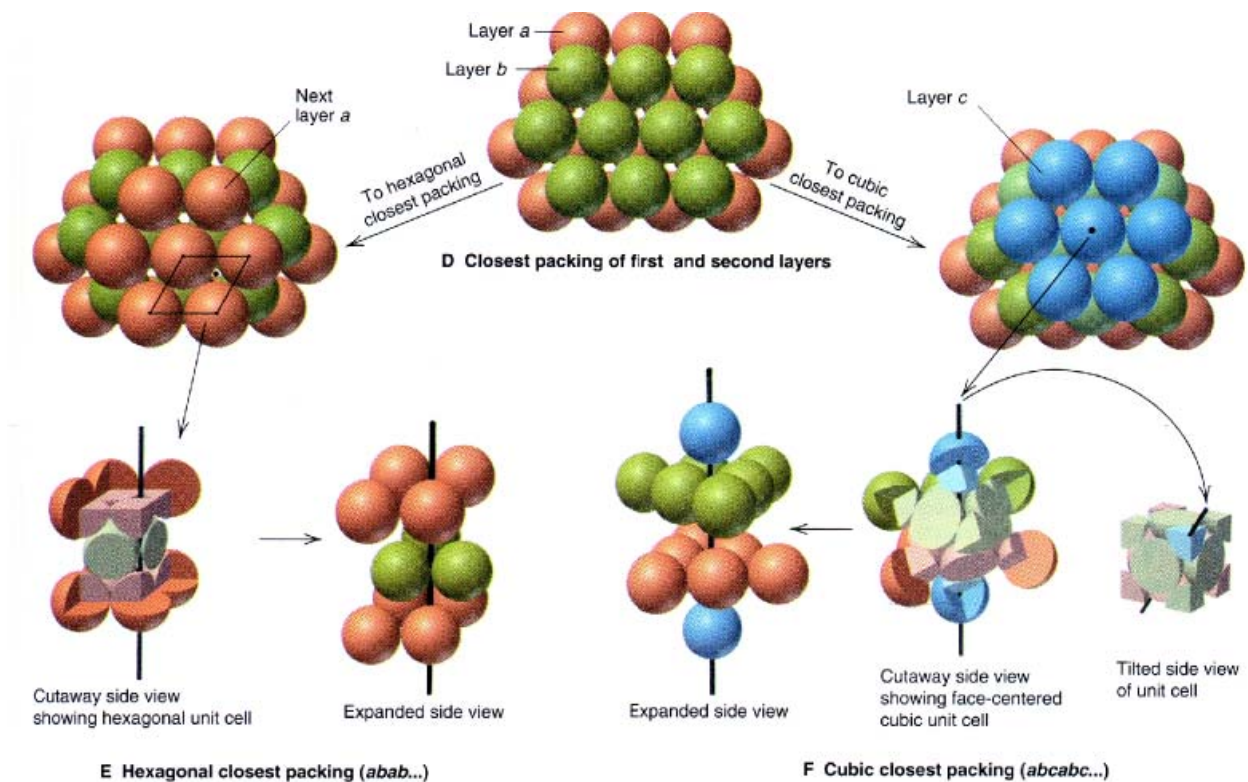


Figure 3: Generation of the hcp and fcc Lattices.

From Silbeberg, "Chemistry: The Molecular Nature of Matter and Change", 2nd edition, © Mosby 2000.

Interstitial holes: hexagonal and cubic close-packing

- When spheres are in a close-packed arrangement, they are located at the corners of an octahedron or a tetrahedron.
- The spaces between the spheres depend on whether the spheres are on the corners of an octahedron or tetrahedron. We call these spaces **tetrahedral** and **octahedral interstitial holes** or **voids**.
- The holes are illustrated in Figure 4 and Figure 5.5 on page 118 of Housecroft and Sharpe.

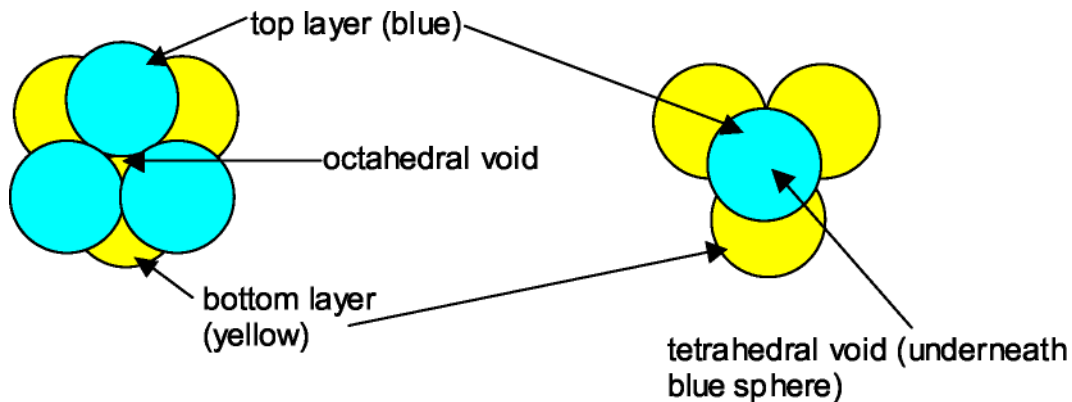


Figure 4: Illustration of Octahedral and Tetrahedral Voids or Holes

Sharing of unit cells

- There are three types of positions in cubic unit cells: corners, faces, and edges, illustrated in Figure 5.

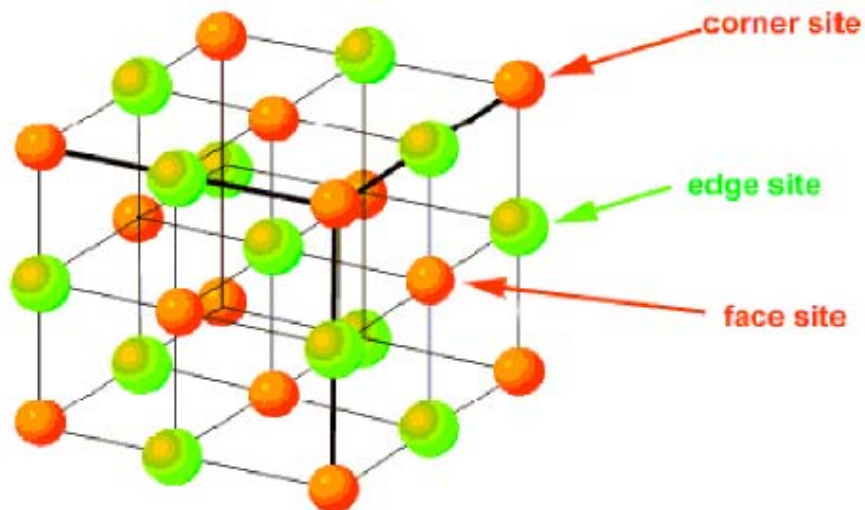


Figure 5: Different Positions in a Cubic Unit Cell

Adapted from Shriver and Atkins, "Inorganic Chemistry", 3rd edition, © W. H. Freeman.

- Eight unit cells share each corner position; two unit cells share each face position; four unit cells share each edge, illustrated in Figure 6.

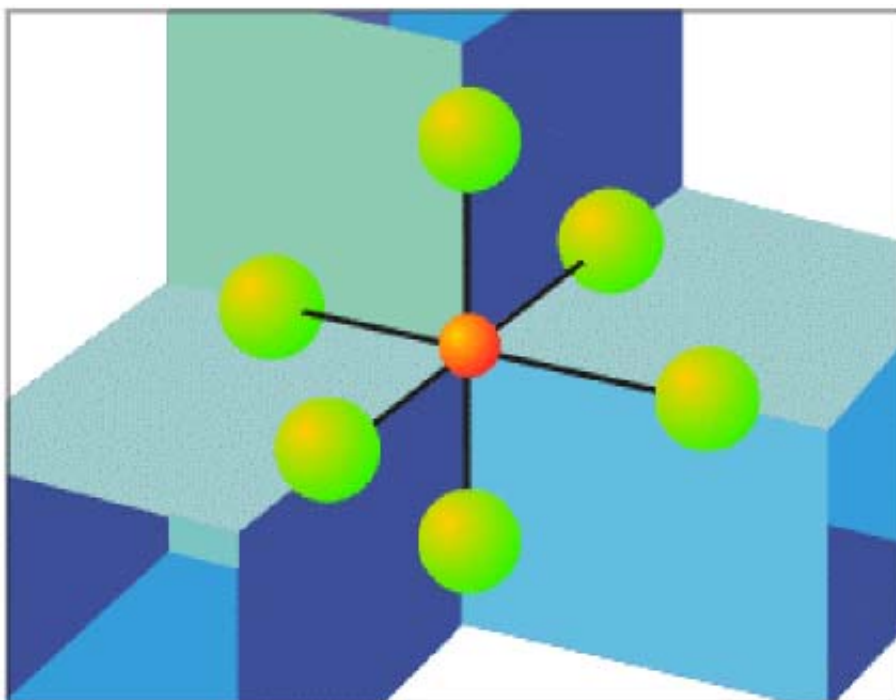


Figure 6: Sharing of Atomic Positions by Neighboring Unit Cells
From Shriver and Atkins, "Inorganic Chemistry", 3rd edition, © W. H. Freeman.

Non-close-packing: simple or primitive cubic and body-centered cubic arrays

- There are 14 possible crystal structures, called Bravais Lattices, which can be classified into 7 different crystal classes, illustrated in Figure 7.
- Each of the seven classifications can be further subdivided into primitive, body-centered, face-centered, and end-centered.
- The crystals are classified in terms of their unit cell length, a , b and c , and the internal angles, α , β and γ .
- It is important to note that the structures we have concerned ourselves with so far contain only one type of atom per unit cell. If there is another type of atom, we get a different unit cell name.

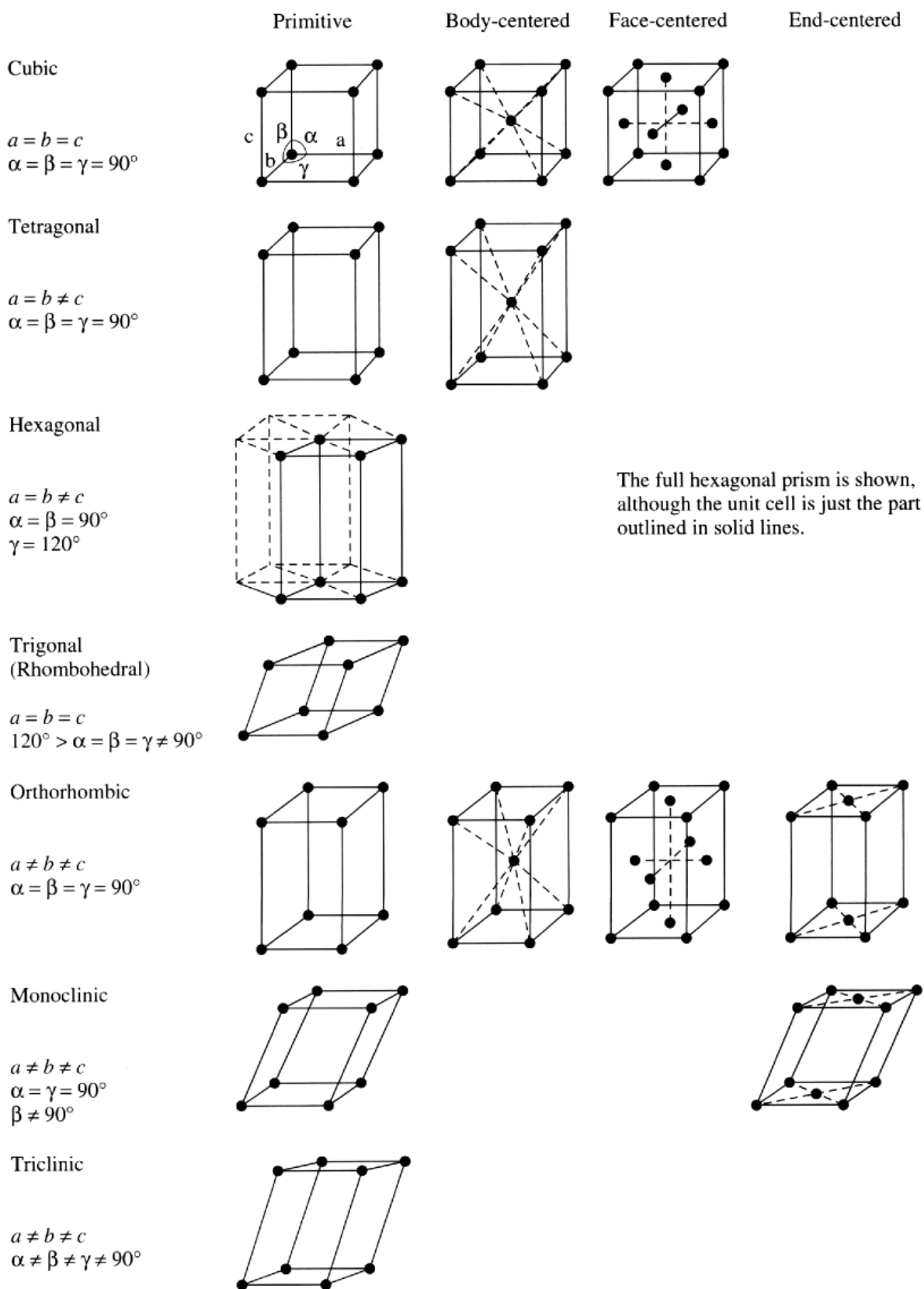


Figure 7: Bravais Lattices

From Miessler and Tarr "Inorganic Chemistry", 2nd edition, © 1999, Prentice Hall.

Cubic

- **Radius Ratio Rules** No matter how closely we pack the atoms or ions into a lattice, there are small holes in between the spheres.

If we know the radius of the packing atom, R , then we can use the Pythagorean Theorem to calculate the radius of the interstitial void.

- **Primitive cubic** is the simplest crystal lattice type.
- Each lattice has one atom at each of the eight corners of the cube.
- Each corner of a cube is shared by eight other cubes: four in one layer, and four in the layer above or below.
- The total number of atoms completely contained in a primitive cubic unit cell is:

$$\begin{aligned} \text{atoms in a simple cubic unit cell} &= 8 \text{ corners/unit cell} \times 1/8 \text{ atom/corner} \\ &= 1 \text{ atom/unit cell} \end{aligned}$$
- We can show that each atom is touched by six others. We say the **coordination number** is six.
- Primitive cubic unit cells are not efficiently packed because 52.4 % of the space is occupied by atoms.

Primitive Cubic Unit Cells

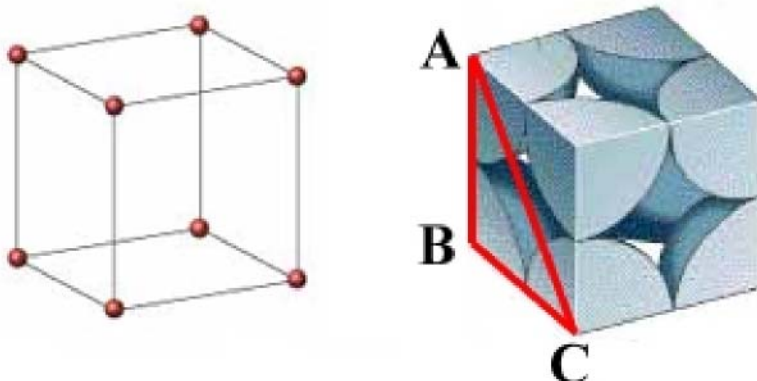


Figure 8: Space Filling Model of a Primitive Cubic Lattice

From Brown, LeMay, and Bursten, "Chemistry: The Central Science", 8th edition, © Prentice Hall.

- In Figure 8 we illustrate the primitive cubic unit cell with space filling models. Notice that the spheres on the edge of the unit cell all touch, but there is a void in the center of the face.
- To calculate the radius of the interstitial void, r , we consider the triangle ABC in Figure 8.
- We call the length of the unit cell a , which is AB and BC in Figure 8. Notice that AB has two packing spheres, each of radius R , touching. This means that $AB = 2R$.
- Now we look at the hypotenuse, AC in Figure 8. Notice that AC contains two packing atom radii, R , and one whole interstitial void. If the interstitial void has *radius* r , then $AC = 2R + 2r$. (The radius of the interstitial void is r . Along AC there is one whole void with radius r , diameter is $2r$.)

Pythagoras tells us that $(AB)^2 + (BC)^2 = (AC)^2$,

so, $a^2 + a^2 = (2R + 2r)^2$.

In other words, $2a^2 = (2R + 2r)^2$.

Taking square roots gives $\sqrt{2} a = 2R + 2r$.

Now we recognize that $a = 2R$, so

$2\sqrt{2} R = 2R + 2r$, and dividing by 2 we get $\sqrt{2} R = R + r$.

Finally, $\sqrt{2} R - R = r$.

And $r/R = \sqrt{2} - 1 = 0.414$.

- It is important to realize that the radius ratio, $r/R = 0.414$, only applies to a primitive cubic lattice.
- The above arguments can be used to calculate many interesting properties of the crystal. For example, if we know the radius of the sphere and the length of the unit cell, then we can calculate the density of the crystal. We can also calculate the percentage of space occupied by the atoms, which is 52.4 % for the above unit cell.

Face-Centered Cubic Unit Cells

- Consider the fcc unit cell illustrated in Figure 9.

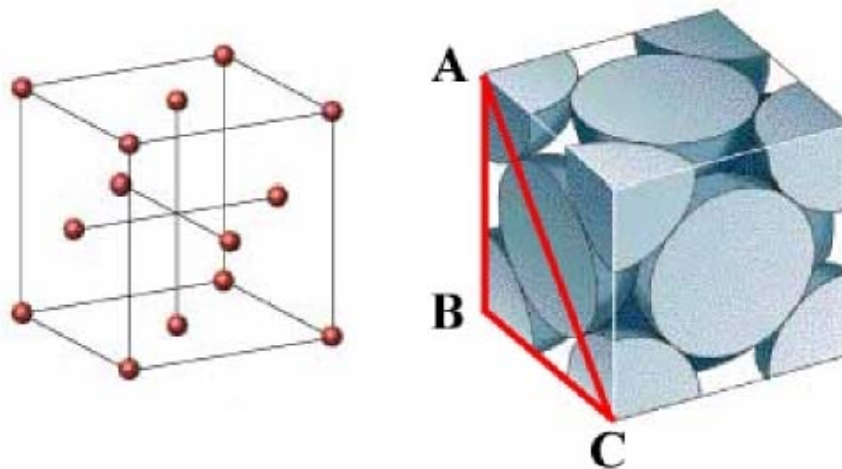


Figure 9: Space Filling Model of an fcc Lattice

Taken from Brown, LeMay, and Bursten, "Chemistry: The Central Science", 8th edition, © Prentice Hall.

- In Figure 9 notice that ABC is again a right triangle, but the void is located along the edges of the unit cell, AB and BC.
- The unit cell length, a , is still AB and BC. However, in Figure 9 $a = (2R + 2r)$. In addition AC is now given by $4R$, since there are four radii of packing atoms along the diagonal. Now we can apply Pythagoras to triangle ABC:

Pythagoras tells us that $(AB)^2 + (BC)^2 = (AC)^2$,

so, $a^2 + a^2 = (4R)^2$.

In other words, $2a^2 = (4R)^2$.

Taking square roots gives $\sqrt{2} a = 4R$.

Now we recognize that $a = 2R + 2r$, so

$\sqrt{2} (2R + 2r) = 4R$, and dividing by 2 we get $\sqrt{2} (R + r) = 2R$.

Finally, $\sqrt{2} R - 2R = -\sqrt{2} r$.

And $r/R = (2 - \sqrt{2})/\sqrt{2} = 0.414$.

- Notice that we get the same radius ratio for a primitive cubic and fcc unit cell. However, the packing efficiency in an fcc unit cell is 74.1 % compared with 52.4 % for the primitive cubic unit cell.

Body-Centered Cubic

- **Body-centered cubic** (bcc) lattices can be formed from a simple cubic lattice by placing a sphere in the center of the unit cell.
- Note that the sphere in the body-center must be identical to the spheres on the corners.
- The bcc unit cell is illustrated in Figure 10.

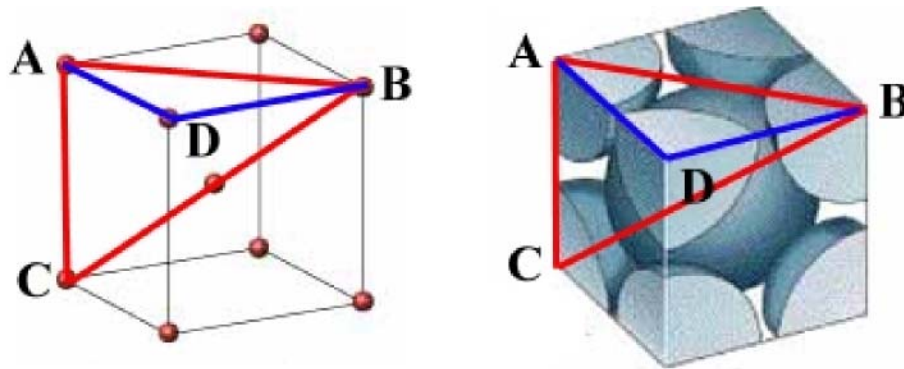


Figure 10: Space Filling Model of a bcc Lattice

Taken from Brown, LeMay, and Bursten, "Chemistry: The Central Science", 8th edition, © Prentice Hall.

- To find the radius ratio for a bcc lattice, first we work with the triangle ABC in Figure 10. Triangle ABC has AC along the edge of the unit cell, equal to a , AB across the face, and BC across the body diagonal (in Figure 10 the body diagonal goes from top right hand position to back left hand position through the center of the cube).
- In triangle ABC we know that $BC = 4R$ because all the spheres touch, and we know that $AC = (2R + 2r)$. However, we do not know how AB is related to a , r , or R . Let us call $AB = l$. In triangle ABD, $AD = BD = a$ and $AB = l$. First we use triangle ABD to give us l in terms of a :

$$(AB)^2 = (AD)^2 + (DB)^2$$

Substituting we get $l^2 = a^2 + a^2$,
So $l^2 = 2a^2$.

- Now that we know l in terms of a , we turn to triangle ABC:

$$(BC)^2 = (AB)^2 + (AC)^2,$$

Substituting we get $(4R)^2 = l^2 + a^2$.
Since $l^2 = 2a^2$, we can write
 $(4R)^2 = 2a^2 + a^2 = 3a^2$.
Knowing that $a = 2R + 2r$, we can write
 $(4R)^2 = 3(2R + 2r)^2$,
 $4R = \sqrt{3} (2R + 2r)$.
Simplifying, we get $2R = \sqrt{3} (R + r)$
And $2R - \sqrt{3} R = \sqrt{3} r$.
Finally we get $r/R = (2 - \sqrt{3})/\sqrt{3} = 0.155$.

Ionic Lattices

- The lattices illustrated above all apply to metallic solids.
- We will assume that the hard sphere model is adequate to describe ionic solids.

Rock salt (NaCl) lattice

- Rock salt structures are appropriate for ions of formula MX. The coordination numbers of M and X must be equal.
- If we take Na^+ ions and place them in an fcc arrangement, and then place Cl^- ions in the spaces between the Na^+ ions, we generate the NaCl structure.
- How many Na^+ cations do we have in the structure? There is one cation at each corner, to give eight corner cations. However, each one of these corner cations is shared by eight unit cells. In addition there is one cation on each face giving a total of six face cations in the unit cell. Each face of the unit cell is shared by two unit cells. This means that there are a total of four cations in the unit cell:

$$\begin{aligned}\text{Cations in NaCl unit cell} &= 8 \text{ corners/unit cell} \times 1/8 \text{ cation/corner} \\ &\quad + 6 \text{ faces/unit cell} \times 1/2 \text{ cation/face} \\ &= 4 \text{ cations/unit cell}\end{aligned}$$

- Since we know that the chemical properties of the crystal must be contained in the unit cell, we need to find homes for eight anions in the unit cell.
- There is one anion on each edge of the unit cell, giving 12 edge anions. Each edge is shared by four unit cells. Thus, there are a total of three anions in the unit cell:

$$\begin{aligned}\text{Anions in NaCl unit cell} &= 12 \text{ edges/unit cell} \times 1/4 \text{ anion/edge} \\ &= 3 \text{ anions/unit cell}\end{aligned}$$

- Where is the missing anion? This anion is in the center of the unit cell, giving the NaCl structure shown in Figure 11.
- Alternatively, we can view the NaCl structure as coming from two intersecting unit cells:

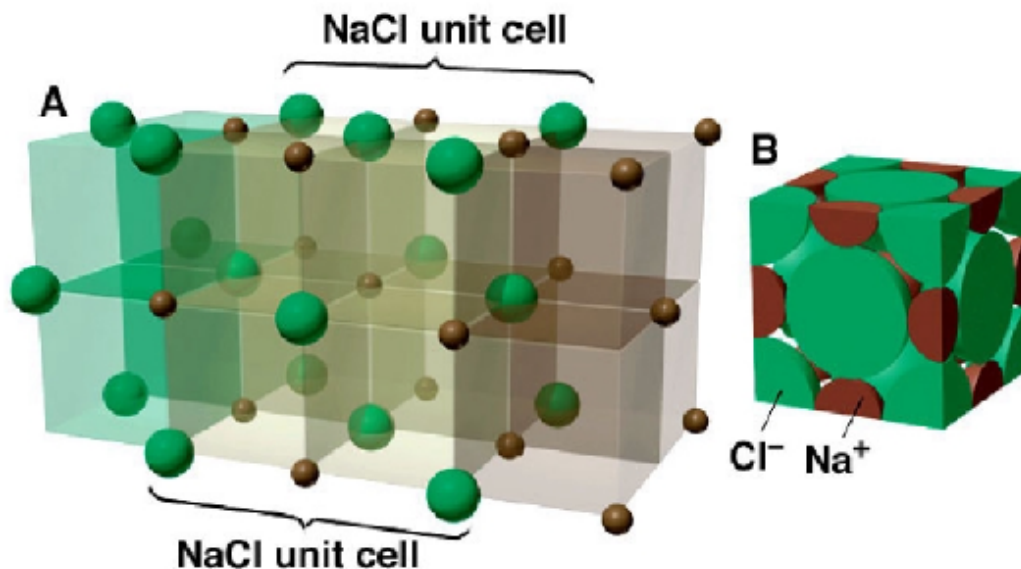


Figure 11: Generation of the NaCl Unit Cell By Intersecting Two fcc Lattices
Taken from Silbeberg, "Chemistry: The Molecular Nature of Matter and Change", © Mosby 1996.

The cesium chloride (CsCl) lattice

- Crystal structures for other ionic compounds can be understood by mixing appropriate units cells.
- We can show that if r is the radius of an atom in a simple cubic lattice, then a sphere of ionic radius $0.73r$ will fit into the center of the lattice.
- If Cs^+ ions pack into a simple cubic lattice, then it is possible for Cl^- , Br^- , or I^- to fit into the body center. The arrangement of Cs^+ and Cl^- results in the CsCl structure.

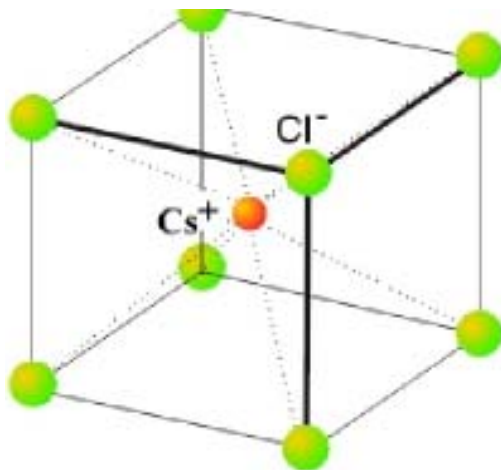


Figure 12: CsCl Lattice

Taken from Shriver and Atkins, "Inorganic Chemistry", 3rd edition, © W. H. Freeman.

- The CsCl lattice can be derived from the intersection of two simple cubes, illustrated in Figure 13 and Figure 5.16 of Housecroft and Sharpe.

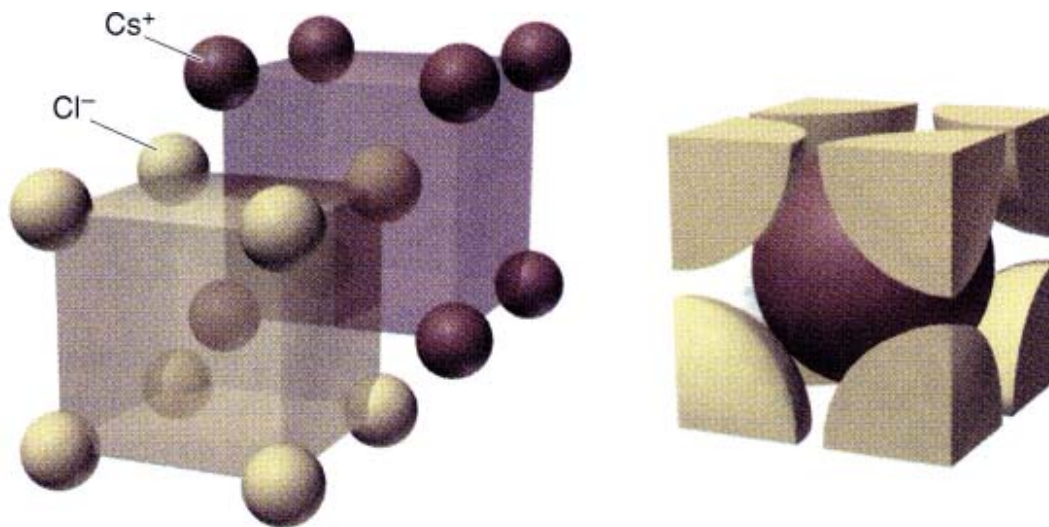


Figure 13: Generation of CsCl Lattice

Taken from Silbeberg, "Chemistry: The Molecular Nature of Matter and Change", © Mosby 1996

- Even though the position in the center of the simple cubic lattice is the "body center", since the sphere in the center is different from the ones on the corners, the lattice cannot be described as a bcc lattice.
- Other examples of lattices that form in the CsCl structure are CsBr, CsI, TlCl, TlBr, TlI, and CsSH.
- At 469°C , CsCl converts into the NaCl structure.

Zinc Blende, ZnS

- In the zinc blende structure we have an fcc arrangements of S^{2-} ions into which the Zn^{2+} pack.
- The zinc ions are also in an fcc lattice that intersects the S^{2-} lattice so that the zinc ions occupy holes in the sulfide fcc lattice:

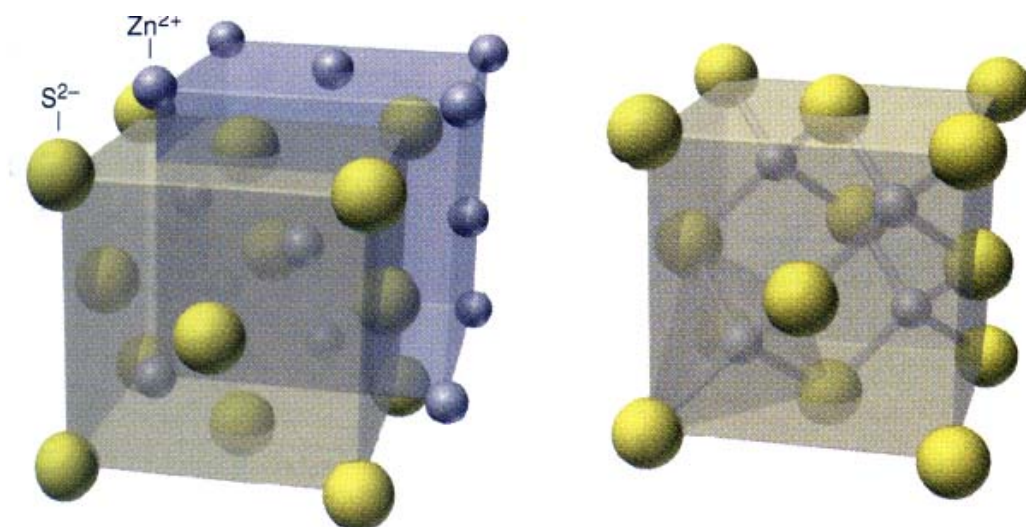


Figure 14: Formation of the Zinc Blende Unit Cell

Taken from Silbeberg, "Chemistry: The Molecular Nature of Matter and Change", © Mosby 1996.

- Stoichiometrically, we require the same number of zinc and sulfide ions in the ZnS unit cell, so half the holes in the sulfide lattice are occupied:

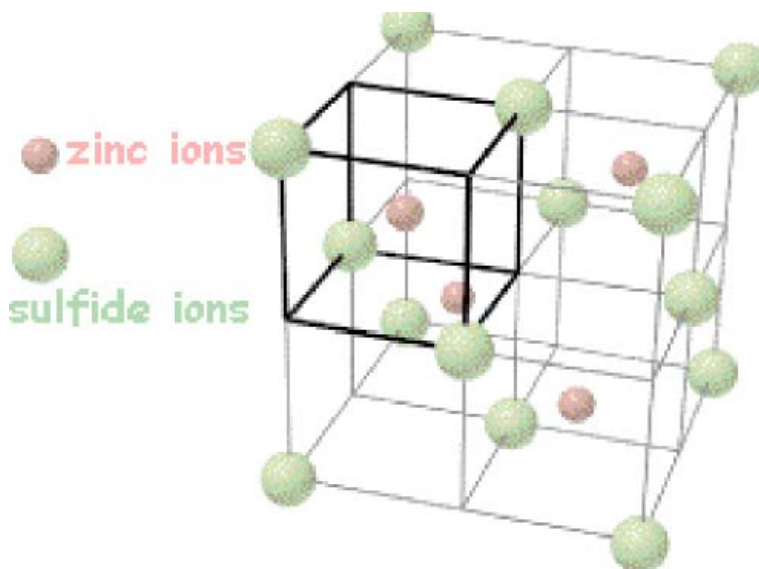


Figure 15: Zinc Blende Unit Cell

Taken from McMurry and Fay, "Chemistry", 2nd edition, © Prentice Hall 1998.

Fluorite, CaF_2

- Fluorite is structurally very similar to zinc blende.
- In ZnS the larger sulfide ions are called packing ions because they are located at the corners of the unit cell. These ions pack the smaller zinc ions into the lattice.
- In the fluorite lattice, the smaller fluoride ions are the packing ions located at the corners of the unit cell, and they pack the larger calcium ions into the holes.

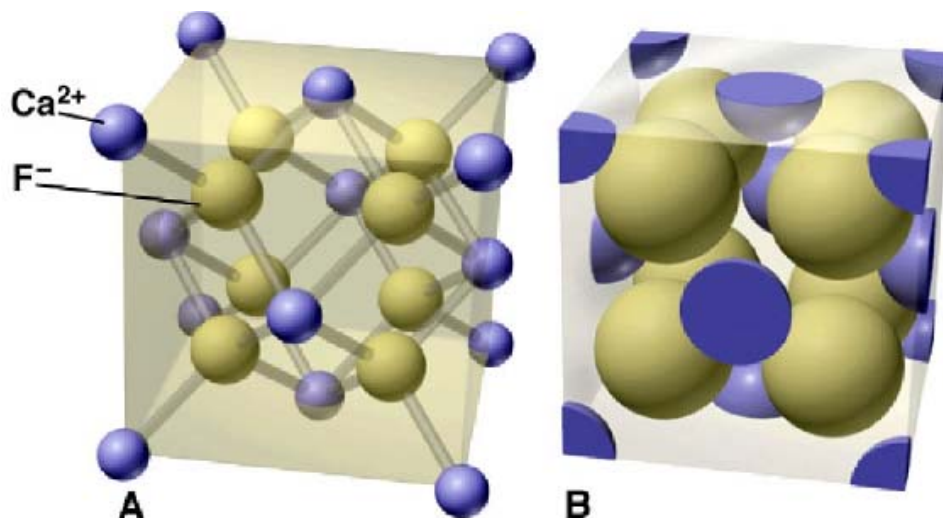


Figure 16: Fluorite Unit Cell

Taken from Silbeberg, "Chemistry: The Molecular Nature of Matter and Change", 2nd edition, © McGraw-Hill, 2000.

- There are many other unit cell types, but the above give a sufficient introduction to the structures encountered in inorganic chemistry.

Ionic Bonding

- So far, we have discussed the structures of solids assuming the solids pack as hard spheres. We need to now investigate the properties of the ionic bond to understand crystal formation.
- There is no sharp boundary between ionic and covalent bonds.
- Purely ionic bonds are best described in terms of an electrostatic (Coulomb's law) model:

$$E = \frac{1}{4\pi\epsilon_0} \frac{q^+ q^-}{r}$$

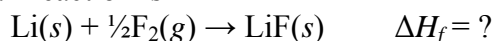
where $4\pi\epsilon_0$ is the permittivity of a vacuum, q is charge, and r is the distance between charges.

- Properties of ionic substances:
 - Low electrical conductivity as solid, but good conductors when molten.
 - High melting point.
 - Hard and brittle.
 - Soluble in polar solvents.
- Ionic substances often exist as 3D crystal lattices.

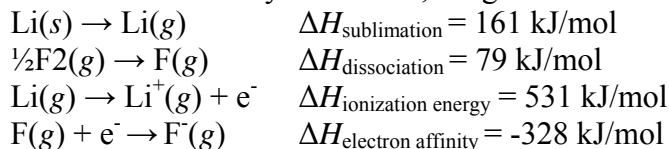
Energetics of Ionic Bond Formation

Lattice Enthalpy

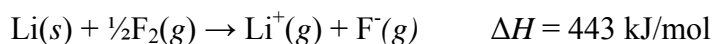
- Let us calculate ΔH_f for the formation of LiF.
- The overall reaction is



- Working from known thermodynamic data, we get



- Note: For the last equation, the enthalpy change is exothermic and therefore carries a negative sign. We note that tables of electron affinities report them as *positive* numbers. You have to adjust for this somewhat confusing practice.
- Using Hess's law, we can sum the above to get the overall reaction:



- Notice that the formation of Li^+ and F^- from their elements is *endothermic*.
- The formation of the solid LiF lattice is highly exothermic. The "missing" enthalpy is called the **lattice enthalpy**.



- (Note: Just as for electron affinities, the lattice enthalpies of ionic solids are always exothermic. Again, however, the lattice enthalpy is usually reported as a positive number.)
- This means that the enthalpy of formation for LiF(s) from its elements in their standard states, ΔH_f , is -796 kJ/mol (obtained by summing the last two equations).

The Madelung Constant

- At first glance the calculation of lattice enthalpy, U , is simple: take every pair of ions and sum the electrostatic energy between them:

$$U = \frac{Z^+ Z^-}{r_0} \left(\frac{e^2}{4\pi\epsilon_0} \right),$$

where Z^+ and Z^- are the ionic charges in electron units, r_0 is the distance between ion centers, e is the charge on the electron (1.602×10^{-19} C), and $4\pi\epsilon_0$ is the permittivity of a vacuum (1.11×10^{-10} C² N⁻¹ m⁻²).

- We can calculate

$$\frac{e^2}{4\pi\epsilon_0} = 2.307 \times 10^{-28} \text{ Jm}$$

- In addition to nearest neighbor interactions, we should also include long-range interactions.
- Consider the NaCl unit cell: for each Na⁺ ion, there are six Cl⁻ ions that are touching it half the unit cell length, a , away. In addition, there are another 12 Cl⁻ ions that are $0.707a$ away. There are even more chloride ions farther away.
- When we use Coulomb's equation, we should consider both the short-range and long-range interactions between Na⁺ and Cl⁻.
- Once we get too far from the Na⁺ ion, the effect of Cl⁻ ions will be negligible.
- When we consider the interactions between Na⁺ and all the Cl⁻ ions up to the point at which the effect of chloride is negligible, we use the **Madelung constant, A**:

$$U = \frac{NAZ^+ Z^-}{r_0} \left(\frac{e^2}{4\pi\epsilon_0} \right),$$

where N is Avogadro's number and A is the Madelung constant.

- Now, we need to take into account repulsion due to close neighbor interactions to get:

$$U = \frac{Z^+ Z^-}{r_0} \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(1 - \frac{\rho}{r_0} \right),$$

where ρ is a constant, usually 30 pm if r_0 is measured in pm.

Example: Calculate the lattice energy for NaCl knowing that the radius of Na^+ is 1.16 Å, the ionic radius of Cl^- is 1.67 Å, and the Madelung constant for NaCl is 1.74756.

Answer: We use equation 5. We know that N (Avogadro's number) is 6.02×10^{23} , $A = 1.74756$, $Z^+ = 1$, $Z^- = 1$, $r_0 = (1.16 + 1.67) \text{ Å} = 2.83 \text{ pm}$, and $\rho = 30 \text{ pm}$. Using the above equation, we get

$$U = \frac{(6.02 \times 10^{23} \text{ mol}^{-1})(1.74756)(1)(1)}{(2.83 \times 10^{-10} \text{ m})} (2.307 \times 10^{-28} \text{ Jm}) \left(1 - \frac{30 \text{ pm}}{283 \text{ pm}}\right)$$

$$= 7.67 \times 10^5 \text{ J/mol}$$

$$= 767 \text{ kJ/mol}$$

The experimental lattice energy for NaCl is 770.3 kJ/mol. (remember that actually the lattice enthalpy is exothermic!).

- Madelung constants are typical of crystal lattice types:

Structure	Examples	Madelung Constant, A
Rock salt	NaCl, LiCl, KBr, RbI, AgCl, AgBr, MgO, CaO, TiO, FeO, NiO, SnAs, UC, ScN	1.74756
Cesium Chloride	CsCl, CaS, TiSb, CsCN, CuZn	1.76267
Zinc Blende	ZnS, CuCl, CdS, HgS, GaP, InAs	1.63806
Wurtzite	ZnS, ZnO, BeO, MnS, AgI, AlN, SiC, NH ₄ F	1.64132
Fluorite	CaF ₂ , UO ₂ , BaCl ₂ , HgF ₂ , PbO ₂	2.51939
Rutile	TiO ₂ , MnO ₂ , SnO ₂ , WO ₂ , MgF ₂ , NiF ₂	2.408

Born-Haber Cycles

- We use Born-Haber cycles (Figure 17) to determine lattice enthalpies.

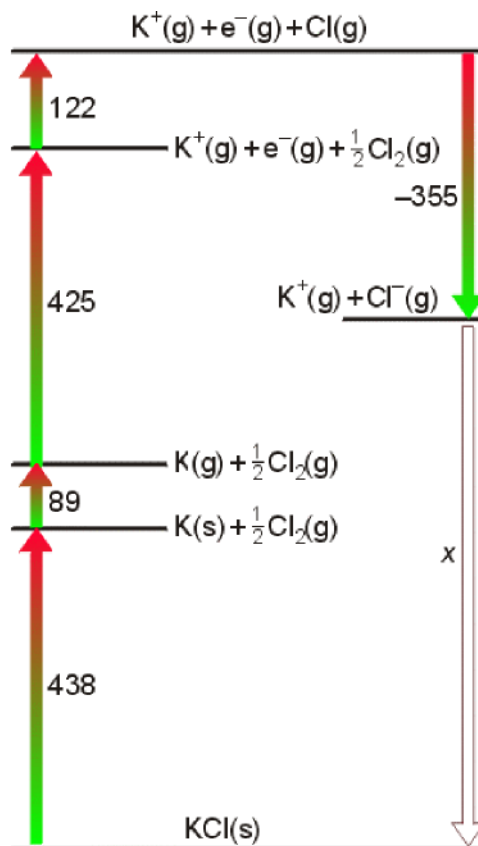


Figure 17: Born-Haber Cycle for KCl

Taken from Shriver and Atkins, "Inorganic Chemistry", 3rd edition, © W. H. Freeman.

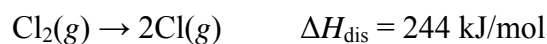
- A Born-Haber cycle is a pictorial representation of the energetics of lattice formation.
- We interpret the data in Figure 17 as follows:
- Beginning with solid potassium and chlorine gas, the change in enthalpy to form gaseous potassium ions is 89 kJ/mol. Notice that 89 kJ/mol is the enthalpy of sublimation for K.



- The ionization enthalpy for potassium is 425 kJ/mol:



- Then, we have to dissociate the chlorine molecules into chlorine atoms:



- Notice that the value for the dissociation of chlorine in the Born-Haber cycle is 122 kJ/mol, which is the enthalpy required for the dissociation of half a mole of Cl₂:



- Finally, we use the electron gain enthalpy, which is the negative of electron affinity, for chlorine:



- The only missing quantity, x in Figure 17, is the lattice enthalpy. Since we know the enthalpy of formation, $\Delta H_f = -438 \text{ kJ/mol}$, we can calculate the lattice enthalpy, x :

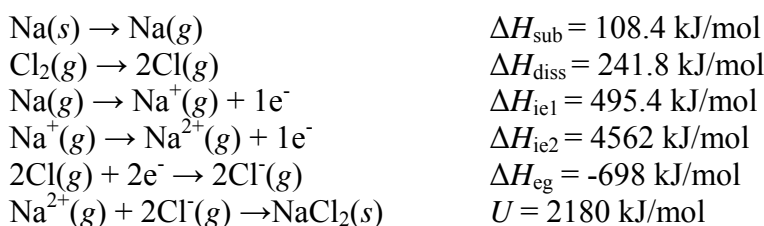
Step	ΔH (kJ/mol)
$\text{K}(s) \rightarrow \text{K}(g)$	89
$\text{K}(g) \rightarrow \text{K}^+(g) + e^-$	425
$\frac{1}{2}\text{Cl}_2(g) \rightarrow \text{Cl}(g)$	122
$\text{Cl}(g) + e^- \rightarrow \text{Cl}^-(g)$	-355
$\text{K}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{KCl}(s)$	-438

From the above and Figure 17: $438 + 89 + 425 + 122 = 355 + x$. So, $x = 719 \text{ kJ/mol} = U_{\text{KCl}}$.

(We have avoided sign problems associated with lattice energies by taking the absolute values of all the enthalpies on the left hand side of the figure and setting them equal the absolute values of the enthalpies on the right hand side of the figure)

The Use of Born-Haber Cycles

- Born-Haber cycles, combined with information obtained using the Madelung constant, provide information about whether or not a compound can exist.
- For example, can NaCl_2 crystallize in the fluorite structure? The knee-jerk response is no, but let us consider the problem in a little more detail.
- To form NaCl_2 we must form Na^{2+} , which is not going to be easy: the ionization energy will be high because we are removing a core electron.
- Since the ionization energy of Na^{2+} is known, it must be possible to form Na^{2+} .
- If we can form Na^{2+} , then NaCl_2 will be stable if we get enough energy back in the formation of the crystal lattice.
- We need to calculate the lattice energy, which is possible with equation 5. Before we can use equation 5, we need to know the lattice structure. The most likely choice is fluorite since CaCl_2 crystallizes in the fluorite structure.
- Using equation 5, we can show $U = 2180 \text{ kJ/mol}$.
- Now we can construct a Born-Haber cycle to calculate the lattice energy for NaCl_2 :



- Now we can calculate ΔH_f :

$$\Delta H_f = \Delta H_{\text{sub}} + \Delta H_{\text{diss}} + \Delta H_{\text{ie1}} + \Delta H_{\text{ie2}} - \Delta H_{\text{eg}} - U$$

(To get the correct sign for ΔH_f we realize that electron gain enthalpy and lattice enthalpy are

both exothermic and everything else is endothermic.)
 $\Delta H_f = 108.4 + 241.8 + 495.4 + 4562 - 698 - 2180$
 $\Delta H_f = 2529.6 \text{ kJ/mol}$

- Notice that this enthalpy of formation is too large for the lattice to exist.
- Thus, we may conclude that the stabilization of the ions in the lattice is not sufficient to overcome the unfavorable second ionization energy of sodium.

Covalent Character of Ionic Bonds

- There is no such thing as a purely ionic or purely covalent bond since most compounds show a mix of covalent and ionic bonding.
- We could look at bonding as covalent and then add some ionic character, or we could look at bonding as ionic with some covalent character. For now, we shall concentrate on the latter.
- Fajans was the first to work on the model that initially assumes bonds are purely ionic and then adds some covalent character to them.
- Fajans considered the effect of a small, highly charged cation on an anion.
- If the anion is large and “soft” enough, then the cation can polarize it. In other words, we visualize the cation penetrating the electron cloud of the anion until it eventually forms a two-electron covalent bond with the anion, Figure 18.

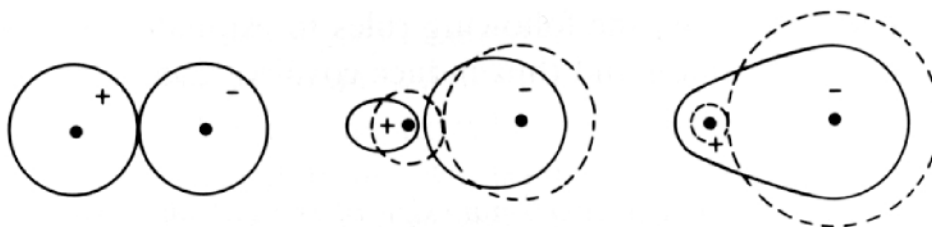


Figure 18: Addition of Covalent Character by Bringing a Small, Highly Charged Cation into the Neighborhood of an Anion

Taken from Huheey, Keiter, and Keiter “Inorganic Chemistry: Principles of Structure and Reactivity”, 4th Edition, Harper Collins, 1993. © Benjamin/Cummings.

- Fajans developed a series of rules that indicate when polarization increases (remember that when polarization increases, the amount of covalent character increases).

1. *Highly charged, small cations* (“hard” cation):

- We can define an *ionic potential*, ϕ , as

$$\phi = Z^+/r,$$

where Z^+ is the charge on the cation and r is the radius in nm.

- As the cation becomes more highly charged and smaller, ϕ increases:

Cation	ϕ (r in nm)
Li ⁺	14
Be ²⁺	48
B ³⁺	120

2. *Highly charged, large anions* (“soft” anions):

- “Softness” is the ease with which we can deform the electron cloud about the anion.
- As charge and size increase, the anion becomes softer. The reason the anion becomes softer is that the electron cloud is less influenced by the nucleus the larger it gets.

3. *Electron Configuration of the Cation:*

- From rule #2, we realize that the less the nucleus influences the electron cloud, the softer the anion.
- Conversely, the less the electrons screen the nuclear charge, the smaller the cation. (Less screening means higher Z^* , which means the outer electron experiences a higher nuclear charge, which means the radius of the ion decreases.) The smaller the cation, the greater its effect on the anion and the greater the degree of covalency.
- We can show that d electrons shield less well than s and p electrons. (See Slater’s rules.)
- If we have two cations of the same charge and the same size, then the one with d electrons will show greater covalency than the one with a noble gas configuration.
- In other words, we expect more covalency with transition metal cations than with alkali and alkaline earth metal ions.