

## **Chapter 4 – Bonding Models in Inorganic Chemistry: 1. Ionic Compounds**

### **The Ionic Bond**

Traditionally, there are two ways of looking at bonding: (1) the interaction between charged species (ionic bonding) and (2) the (roughly) equal sharing of electron density (covalent bonding). As we shall see, these are 2 views of the same ultimate theory. In this chapter, we examine the ionic bond. At this point, it might be helpful to review ionic bonding from your CHM 211 class. It is covered in [Sections 1 and 5 of Chapter 7 in our current book](#).

### **Properties of Ionic Substances**

The first thing to consider is: what is it that distinguishes ionic from molecular compounds? (A word of caution here: Several types of compounds possess covalent bonds. Notably, molecular and covalent network compounds possess only covalent bonds, while ionic compounds frequently possess covalent bonds in polyatomic ions (e.g. nitrate ions).) We begin by examining some of the properties of ionic materials.

- 1) Ionic solids conduct electricity poorly, but when melted or dissolved are good electrical conductors. When molten or in solution, ions are free to move and charge can be transported. In a solid lattice, ions are locked into place so there is no way to move charge.
- 2) Ionic compounds have high melting points. Ionic and covalent bonds are both strong, but unlike covalent bonds, ionic bonds are not directed at only one other atom. Instead all anions, particularly those close by, are attracted to a given cation and *vice versa*. The result is extended arrays of ions that are held together strongly. Thus, in molecules the bonds are all between atoms within that molecule, while in salts the bonds occur between species in adjacent units. The validity of this model can be seen in that most covalent network materials have high melting points. Here the network (e.g. a diamond), requires the breaking of covalent bonds to achieve melting.

3) Ionic compounds tend to be hard and brittle. Again, this arises from ionic interactions.

Let's look at a sodium chloride crystal (Figures: dark grey =  $\text{Na}^+$ ; blue-green =  $\text{Cl}^-$ )

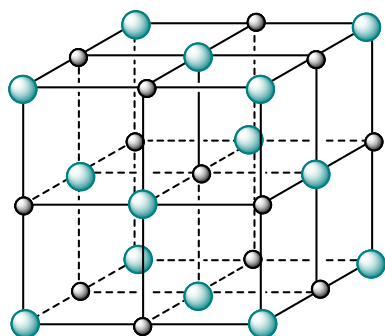


Figure 1

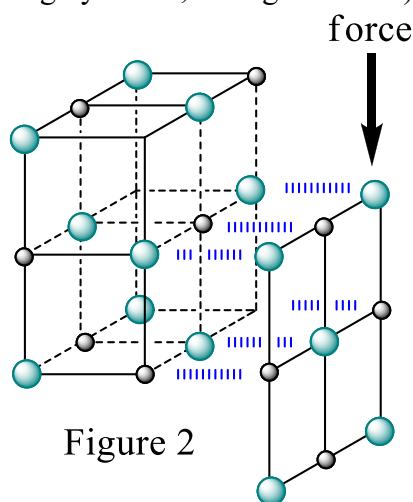


Figure 2

If a mechanical force were to push down on the first plane of ions, what would happen? Each ion moves away from a nearby ion of opposite charge and each moves closer to an ion of the same charge. Thus, simultaneously, attractions decrease and repulsions increase. The result is that it is very difficult to initiate displacement, but once the crystal face shifts one bond length it shears off (Figure 2).

4) Ionic compounds are frequently soluble in solvents with large dielectric constants. These solvents are quite polar and the dipoles are electrostatically attracted to the ions. If the solvation energy is greater than the inter-ion attraction in the crystal, the crystal dissolves. Ionic compounds rarely dissolve in non-polar solvents because the ion-solvent attraction is weak and hence the solvation energy is small.

### **Occurrence of Ionic Bonding**

Ionic bonds tend to occur for the cations of Group IA, IIA, some IIIA elements, and low oxidation states for some other elements (e.g. transition metals,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ ). Elemental anions that engage in ionic bonding are largely limited to the halide ions, some chalcogen anions, and nitride ion. Why? Because the energy cost of the reaction is not very great. A question for you to consider is: why is it a “cost?” Metals in high oxidation states tend to bond covalently. Thus,  $\text{MoCl}_6$  has

considerable covalent character in the Mo-Cl bonds. We will discuss why later in this chapter, but it is reflected in the name of the compound. While formal rules you learned in general chemistry tell you this compound should be named molybdenum(VI) chloride, and that is how it is sold by chemical suppliers, it is almost universally called molybdenum hexachloride (the name for a molecular compound) by chemists.

### **Structures of Crystal Lattices**

The crystal structures of several salts are shown on pages 94-99. You are responsible for being able to draw NaCl and CsCl and being able to recognize rutile (TiO<sub>2</sub>), zinc blend (ZnS), and fluorite (CaF<sub>2</sub>). The University of Liverpool has a very nice [interactive website](#) that shows the different lattice arrangements. Know the coordination numbers for all components of each. The unit cell is the repeating unit of a crystal.

The coordination number of an atom is the number of atoms bound to it. This includes fractional atoms.

A calculation of the number of “molecules” per unit cell follows.

$$\text{e.g. NaCl: } \text{Na}^+: 1(1) + 12(\frac{1}{4}) = 4$$

$$\text{Cl}^-: 8(\frac{1}{8}) + 6(\frac{1}{2}) = 4 \quad \Rightarrow \text{There are 4 NaCl “molecules” per unit cell.}$$

Most crystals of simple inorganic substances are arranged in closest packed arrays. In a closest packed array, the atoms are arranged such that each atom is surrounded by six other atoms/ions in the same plane with 3 each in the planes above and below. An illustration of one sheet of closest packed atoms appears below (Figure 3). There are 2 possible systematic arrangements ABAB ... and ABCABC ... that are most easily seen using models (used on p. 8).

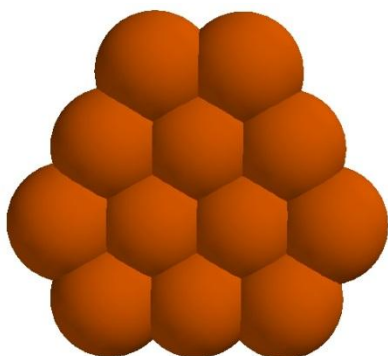


Figure 3

For ionic compounds, the anions are almost always substantially larger than the cations. For example, the chloride ion has a radius *ca.* 50% larger than that of the sodium ion (167 pm vs. 113 pm). This translates to a volume  $2\frac{1}{4}$  times larger. The anions are used for the closest-packed array with the cations filling the holes in the lattice. We'll talk about this more later.

### Lattice Energy

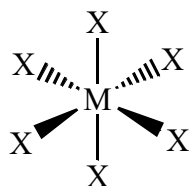
Earlier you were told that all reactions between gas phase atoms that yield ionic compounds do so endothermically. So why do salts form? To answer this question, first consider the question: Why does any compound form? Because, almost always, the products are more stable than the reactants. Is this a contradiction for salts? No. The initial description was of charge transfer in the gas phase not the solid state (which is how salts exist under normal conditions). What makes the solid state so special? To answer this, consider the salt MX which crystallizes in the sodium chloride lattice. The equation that describes the energy of interaction between two ions is:

$$E_c' = \frac{Z^+ Z^- e^2}{4\pi\epsilon_0 r}$$

where  $Z^+$ ,  $Z^-$  = ionic charges,  $e$  = electron charge,  $\epsilon$  = permittivity of a vacuum, and  
 $r$  = separation of the particles

Is this equation reasonable? (i.e. Does it make sense?) Note that  $E_c'$  is always negative (favorable) for ions with opposite charges. It is always positive for ions possessing the same charge. Now each cation is not attracted to just one anion, but all anions near it. It is also repelled by all other cations near it.

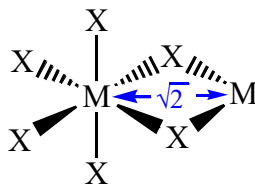
Let's look at NaCl (MX) as an example. In the lattice each  $\text{Na}^+$  ion is surrounded by six chloride ions in an octahedral array:



Each  $\text{Na}^+$  is attracted to those 6  $\text{Cl}^-$  ions, so that the force of attraction felt by  $\text{Na}^+$  is 6 times larger than expected for a single attraction.

$$E_c = E_c' \left( \frac{6}{1} \right) \text{ where } 1 \text{ is arbitrary distance (that is, assume the M-X distance is } 1)$$

However, there is another  $\text{Na}^+$  for each pair of  $\text{Cl}^-$  ions that repels the  $\text{Na}^+$  (total of 12) at a distance of  $\sqrt{2}$  away.



$$\text{Thus, the total attraction is reduced to } E_c = E_c' \left( \frac{6}{1} - \frac{12}{\sqrt{2}} \right).$$

When additional interactions are taken into account, this equation will continue to expand until it eventually forms an infinite series that mathematically converges. The total Coulombic attraction is written:

$$E_c' = \frac{AZ^+Z^-e^2}{4\pi\epsilon_0 r}$$

where A is the Madelung constant

$$A = \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \dots \text{ for the NaCl structure}$$

The Madelung constant is completely geometrical, so there is a different Madelung constant for each crystal type. The total Coulombic attraction, thus, depends on the number of charges, the signs of the charges, the distance of separation between the charges, and the arrangement of those charges in space.

### Repulsive Energy

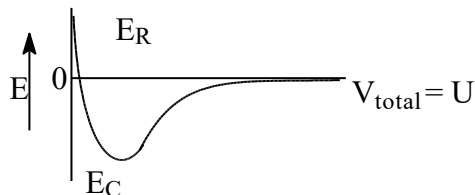
Now the coulombic interaction equation suggests that the attractive energy continually decreases (becomes more favorable) as the particles get closer. However since the ions are not point charges, at very small distances, when core electrons interact, a repulsive energy develops that increases rapidly. The repulsion comes from the interaction of the core electrons of the two ions. This repulsive energy is of the form:

$$E_R = B/r^n \quad \text{where } E_R > 0$$

$$B = \text{constant}$$

$n$  = Born number, related to molecular compressibility

Therefore, the total lattice energy for a mole of compound is:



This is the Born-Landé equation. ( $N$  = Avogadro's number)

$$U = E_C + E_R = \frac{ANZ^+Z^-e^2}{4\pi\epsilon_0 r} + \frac{NB}{r^n}$$

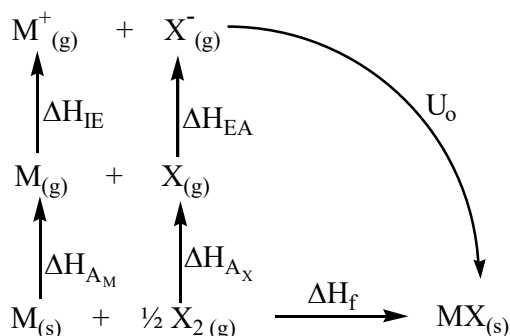
The Born-Landé equation accounts for >95% of the crystal lattice energy. The book solves for the constant  $B$  and the equation simplifies to:

$$U_0 = \frac{ANZ^+Z^-e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right) \quad U_0 = \text{energy minimum, } r_0 = \text{equilibrium distance}$$

These equations account for 90-98% of the total energy of the system, depending on geometry and particular ions. So why cover this, since lattice energies are known for most salts. There are two reasons. First is to demonstrate that the lattice energy is simply a geometric property of the crystal lattice and because it allows us to examine why a particular set of ions crystallizes in one lattice, but not a different one. But to study this, we must first discuss the Born-Haber cycle.

### Born-Haber Cycle

The Born-Haber cycle shown below is drawn somewhat differently from the one in your book (p. 106), but in a similar fashion to the one on p. 104. The first one is drawn to highlight the energetics of the particular reactions, while the one shown below highlights the individual "reactions" that go into the conversion of elements into salts. Pick whichever you feel more comfortable with using because each has its advantages and disadvantages.



$U_o$  = lattice energy

$\Delta H_{IE}$  = ionization energy

$\Delta H_f$  = heat of formation

$\Delta H_{EA}$  = electron affinity

$\Delta H_{A_M}$  = heat of atomization, includes sublimation energy, gaseous bond energies

$\Delta H_{A_X}$  = heat of atomization, includes appropriate terms for the anion

Thus, from Hess' Law:

$$\Delta H_f = \Delta H_{A_M} + \Delta H_{IE} + \Delta H_{A_X} + \Delta H_{EA} + U_o$$

Of these, only the lattice energy,  $U_o$ , cannot be measured. It is calculated from the previous equation. Of the measured terms listed in the Born-Haber cycle,  $\Delta H_{A_M}$ ,  $\Delta H_{A_X}$ , and  $\Delta H_{IE}$  are always energetically unfavorable.  $\Delta H_{IE}$  is very unfavorable and  $\Delta H_{EA}$  can be.  $\Delta H_{EA}$  is favorable for monoanions and unfavorable for all higher anions. Thus for a favorable heat of formation, the lattice energy must be a large negative (favorable) number. Hence, ionic compounds form because of very favorable lattice energies, not because metals “want” to form cations and nonmetals “want” to form anions.

The Born-Haber cycle allows you to predict the stability of a compound before you attempt to prepare it for the first time. Knowing the  $\Delta H_{A_M}$ ,  $\Delta H_{A_X}$ , and  $\Delta H_{IE}$ , and  $\Delta H_{EA}$  for any two substances, and calculating  $U_o$ , allows  $\Delta H_f$  to be estimated for the salt they would form.

For any Madelung constant, from the Born-Landé equation it can be seen that  $U_o$  increases with ionic charge. Thus for any two compounds,  $A^+B^-$  and  $C^{2+}D^{2-}$  with the same structure  $|U_{AB}| < |U_{CD}|$  ( $U_{AB} = \frac{1}{4}U_{CD}$ ).

So why does NaCl form instead of  $NaCl_2$ ? On p.108 the book does this calculation assuming  $NaCl_2$  would have the same structure as  $CaF_2$ . While  $U_{NaCl_2}$  is about 1400 kJ/mol more favorable, this is more than made up for by an increase in the sodium ionization energy (~4000 kJ/mol).

Hence breaking the electronic core more than offsets the increase in lattice energy. This is a principal reason why the chemistry for individual elements is restricted to oxidation numbers available only in their period.

The book works a second example explaining why  $\text{CaF}_2$  is more stable than  $\text{CaF}$ .

*Read the rest of this section on your own.*

*Skip "Some Simplifications and Rules of Thumb"*

### **Size Effects**

**Ionic Radii** - As for all radii, these data come from X-ray crystallography. In crystallography, X-rays bombard a sample and are diffracted by electrons. Because electron density is highest near the core, diffraction is strongest there. The result is a contour map, with the highest regions near the nucleus. (Ironically, this means that electron density is always lowest where the bond is, even for covalent bonds. Is this reasonable?) Ionic radii are determined by calculating the distance from each nucleus to the minimum between the nuclei. For homonuclear diatomic molecules the minimum is halfway between the nuclei.

#### **General trends in ionic radii**

- 1) Radii increase down a group if ionic charge remains constant. (e.g.  $\text{Na}^+$  is larger than  $\text{Li}^+$ .)
- 2) For a given cation, radii decrease as charge increases. ( $\text{Fe}^{2+}$  is larger than  $\text{Fe}^{3+}$ .)
- 3) Radii increase with increasing coordination number, if ionic charge remains constant.
- 4) All other things equal (charge, spin states, etc.), radii decrease left to right across a period.
- 5) Most anions are larger than most cations.  $\text{F}^-$ ,  $\text{O}^{2-}$ ,  $\text{N}^{3-}$  are the primary exceptions with period 6 cations.
- 6) Anions become larger as charge becomes more negative.

### **Polyatomic Ion Sizes** - Skip

### **Efficiency of Packing and Crystal Lattices**

We now return to crystal packing. The book suggests you set out a series of coins to see that the closest packing arrangement is most efficient. You should do this if you can't see that it is in

your mind's eye. There are two “closest packed” arrays and these pack the maximum number of particles into a given volume. Lining the bottom of a box with marbles or balls will yield one layer of a closest packed array. The second layer will always fill the same way, with each marble lying in the gap between three others (forming a trigonal pyramid). The placement of the third layer is what determines the lattice type (it can either be identical to the first layer or shifted.) You may need models to visualize this or the Liverpool [website](#) has a graphic that may help.

The ABAB... pattern is called hexagonal closest packed (hcp) and yields body-centered cubic unit cells. The ABCABC... pattern is called cubic closest packed (ccp) and gives rise to face-centered unit cells. They are in most ways identical and properties of each species crystallizing are responsible for the particular array formed. All metals pack in these arrangements. Both are equally efficient (i.e. have exactly the same number of particles per unit volume) and why some metals pick one and others the other is not understood.

Ionic compounds are a little more difficult to explain. If you place the anions in the major closest packed array positions and the cations in the gaps there are substantial anion-anion repulsions. However, if the cations expand the lattice (i.e. push the anions apart), the basic structural idea still holds (particularly when the anion is much larger than the cation). CsCl is an example of where it is not.

One thing to notice is that there are two different “shaped” holes in the closest packed lattice. Placing one ball on a triangle made by three others creates a gap in the shape of a tetrahedron. Figure 4 shows the triangular shape made by the 3 balls (red) in the base. The blue circle represents the cap. Figure 5 shows the shape of the cavity between the balls.

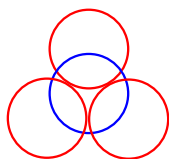


Figure 4

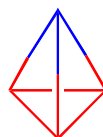


Figure 5

The other shape occurs when two triangles of atoms are nestled on top of one another to yield

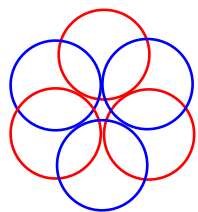


Figure 6

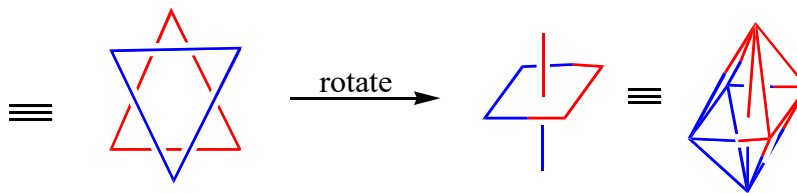


Figure 7

an octahedral hole. This hole is a little larger than the tetrahedral hole. For a salt with larger anions, say iodide: MI, smaller cations will fill tetrahedral holes while larger ones will fill octahedral holes.

**Radius Ratio** - skip (pp. 122 - 127)

### **The Predictive Power of Thermochemical Calculation on Ionic Compounds**

Read on your own. Don't worry about parts we didn't cover.

### **Covalent Character in Predominantly Ionic Bonds**

As we have discussed, while there are purely covalent bonds (homonuclear diatomic), there are no purely ionic bonds. That is, no atom completely lets go of its electrons. Two methods of quantifying this effect are to start off with an ionic bond and then add covalent character, while the other does the reverse. We will first look at the former method.

Start off with a purely ionic bond between two ions. The positive charge of the cation will attract the electrons of the anion causing the anion to deform (or be polarized) in the direction of the cation. This introduces directionality into the bond and that is covalency.

There are some general trends in the ability of cations to polarize and of anions to be polarized.

1. The ability of a cation to polarize an anion increases with increasing charge and decreasing size. In both cases, the charge density on the cation increases. In other words, highly charged small cations distort the electron cloud of anions better than larger, low charged cations.
2. The polarizability of an anion increases with increasing charge and size. In large anions the outer electrons are farther away from the nucleus and shift more easily. Higher charge

causes the size to increase (greater electron-electron repulsions) and provides more electron density to shift.

3. The shielding of core electrons affects the polarizing power of a cation. This effect is smaller than either of the just described effects. Thus for two cations of equal size and charge, the one whose valence electrons shield more poorly will polarize more effectively. This is because the nuclear charge projects further in the case of ion with the poorly shielding electrons.

The effect of polarization is that increasing the extent to which an anion is polarized increases the covalency of its bond.

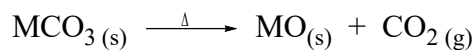
It is also possible to imagine ionic bonding arising from increasing polar covalent bonds, but this is far more difficult because bond strength plays a major role in practice (e.g. consider the series HF-HI).

### **Results of Polarization**

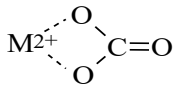
Some effects of increasing the extent of covalency in ionic compounds include:

1. Melting points will decrease. It is true that the cations and anions still attract omnidirectionally, but since the electron clouds can be instantaneously attracted in one direction due to vibrations within the crystal, the bonds can briefly develop covalent type interactions. This weakens the intermolecular forces between those ions and their neighbors and makes melting easier.
2. Solubilities in water will decrease because solvation stability decreases. While increasing charge density causes increased solvation energies, the energy required to separate ions increases more rapidly. Thus, compounds composed of highly charged species are more stable if they remain in a lattice. (You can see this in the solubility rules you learned as freshmen.)
3. Bond lengths vary significantly from predicted values based on ionic radii. One way this is manifested is in decomposition temperatures. Metal carbonates provide an example.

Consider the reaction:



The reaction requires higher temperatures as M becomes larger. e.g. M = Mg (T = 350 °C) vs. M = Ba (T = 1360 °C). Why?



As electron density is pulled towards  $\text{M}^{2+}$ , the C-O bonds weaken and are more easily broken. The bonding in the complex is shown as symmetrical, but consider the possibility of an asymmetry developing in the electron cloud. When this happens one of the M-O bonds strengthens at the expense of the other M-O bond. This makes cleaving the weaker C-O bond easier and lowers the decomposition temperature.

4. This also accounts for the acidity of some metal oxides. In freshman chemistry you learned metal oxides are basic and non-metal oxides are acidic, which is normally the case, but there was an important exception. Do you remember it and did you notice that it was different from the other metal oxides in the list? (If you don't remember use your freshman book or go online and find a few basic metal oxides.)

One oxide was amphoteric, that is neither very acidic nor very basic and that was aluminum oxide. How is it different from the oxides that are basic? The major difference is that the charge on aluminum is +3 versus +1 or +2 on the basic oxides. As the charge on the metal increases the metal oxides can become acidic. In fact,  $\text{CrO}_3$  is about as acidic as  $\text{SO}_3$ . A major reason for this is that the M-O bond becomes much more covalent as the high charge on the metal largely offsets the high electronegativity of the oxygen atom.

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