Pearson

4.5: Ionic Bonding: The Lewis Model and Lattice Energies

As we have seen, ionic compounds are composed of cations (usually a metal) and anions (usually one or more nonmetals) bound together by ionic bonds. The basic unit of an ionic compound is the **formula unit**, the smallest, electrically neutral collection of ions. A formula unit is not a molecule—it does not usually exist as a discrete entity but rather as part of a larger lattice. For example, table salt, an ionic compound with the formula unit NaCl, is composed of Na^+ and Cl^- ions in a one-to-one ratio. In table salt, Na^+ and Cl^- exist in a three-dimensional alternating array. Because ionic bonds are not directional, no one Na^+ ion pairs with a specific Cl^- ion. Rather, as we saw in Figure 4.2, any one Na^+ cation is surrounded by Cl^- anions and vice versa.

> Some ionic compounds, such as K_2NaPO_4, contain more than one type of metal ion.

Although the Lewis model's strength is in modeling covalent bonding, we can also apply it to ionic bonding. To represent ionic bonding, we move electron dots from the Lewis symbol of the metal to the Lewis symbol of the nonmetal, so the metal becomes a cation and the nonmetal becomes an anion. This alone, however, does not account for the stability of ionic substances. To understand that stability, we must account for the formation of a crystalline lattice as a result of the attractions between the cations and anions. In this section of the chapter, we first look at the electron transfer and then examine the formation of the crystalline lattice.

Ionic Bonding and Electron Transfer

Consider potassium and chlorine, which have the following Lewis symbols:

$$\mathrm{K}\cdot \quad :\ddot{\underset{\cdot}{\mathrm{Cl}}}:$$

When these atoms bond, potassium transfers its valence electron (shown here in blue) to chlorine:

$$\mathrm{K}\cdot + :\ddot{\underset{\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{K}^+ + \left[:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:\right]^-$$

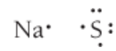
The transfer of the electron gives chlorine an octet (shown as eight dots around chlorine) and leaves potassium without any valence electrons but with an octet in the *previous* principal energy level (which is now its outermost level):

$$\begin{array}{ll} \mathrm{K} & 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 \\ \mathrm{K}^+ & 1s^2 2s^2 2p^6 \underbrace{3s^2 3p^6}_{\text{Octet in previous level}} 4s^0 \end{array}$$

The potassium, having lost an electron, becomes positively charged (a cation), while the chlorine, which has gained an electron, becomes negatively charged (an anion). The Lewis symbol of an anion is usually written within brackets with the charge in the upper right-hand corner, outside the brackets. The positive and negative charges attract one another, resulting in the compound KCl.

We can use the Lewis model to predict the correct chemical formulas for ionic compounds. For the compound that forms between K and Cl, for example, the Lewis model predicts a ratio of one potassium cation to every one chloride anion, KCl. In nature, when we examine the compound formed between potassium and chlorine, we indeed find one potassium ion to every chloride ion.

As another example, consider the ionic compound formed between sodium and sulfur. The Lewis symbols for sodium and sulfur are:



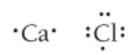
Sodium must lose its one valence electron in order to have an octet (in the previous principal shell), while sulfur must gain two electrons to get an octet. Consequently, the compound that forms between sodium and sulfur requires two sodium atoms to every one sulfur atom—the formula is Na_2S. The two sodium atoms each lose their one valence electron, while the sulfur atom gains two electrons and gets an octet. The Lewis model predicts that the correct chemical formula is Na_2S, exactly what we see in nature.

Example 4.2 Using Lewis Symbols to Predict the Chemical Formula of an Ionic Compound

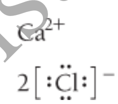
Use the Lewis model to predict the formula for the compound that forms between calcium and chlorine.

SOLUTION

Draw Lewis symbols for calcium and chlorine based on their number of valence electrons, obtained from their group number in the periodic table.



Calcium needs to lose its two valence electrons (to be left with an octet in its previous principal shell), while chlorine only needs to gain one electron to get an octet. Therefore, you must have two chlorine atoms for each calcium atom. The calcium atom loses its two electrons to form Ca^{2+}, and each chlorine atom gains an electron to form Cl^{-}. In this way, both calcium and chlorine attain octets.



Finally, write the formula with subscripts to indicate the number of atoms.

$$CaCl_2$$

FOR PRACTICE 4.2 Use the Lewis model to predict the formula for the compound that forms between magnesium and nitrogen.

Lattice Energy: The Rest of the Story

The formation of an ionic compound from its constituent elements usually gives off quite a bit of energy as heat (the process is exothermic; see Section E.6). For example, when one mole of sodium chloride forms from elemental sodium and chlorine, 411 kJ of heat is evolved in the following violent reaction:

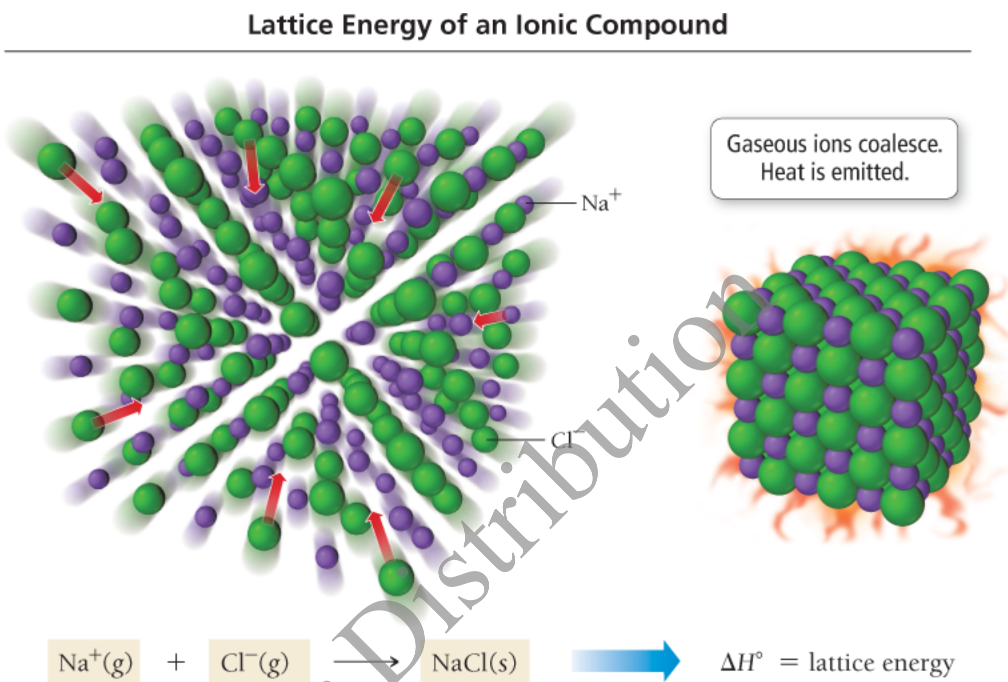
$$Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s)$$

Where does this energy come from? You might think that it comes solely from the tendency of metals to lose electrons and nonmetals to gain electrons—but it does not. In fact, the transfer of an electron from sodium to chlorine—by itself—actually *absorbs* energy. The first ionization energy of sodium is +496 kJ/mol, and the electron affinity of Cl is only −349 kJ/mol. (Recall from Section E.6 that the positive sign indicates the absorption of energy and the negative sign indicates the emission of energy.) Based only on these energies, the reaction should absorb +147 kJ/mol. So why is the reaction so *exothermic*?

The answer lies in the **lattice energy**—the energy associated with the formation of a crystalline lattice of alternating cations and anions from the gaseous ions. Since the sodium ions are positively charged and the chlorine ions are negatively charged, the potential energy decreases—as described by Coulomb's law—when these ions come together to form a lattice. That energy is emitted as heat when the lattice forms, as illustrated in Figure 4.5. The exact value of the lattice energy, however, is not simple to determine because it involves a large number of interactions among many charged particles in a lattice. The easiest way to calculate lattice energy is with the *Born–Haber cycle*, which we will discuss in Section 9.11.

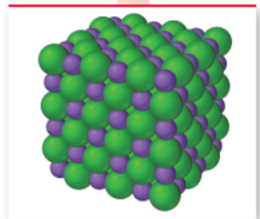
Figure 4.5 Lattice Energy

The lattice energy of an ionic compound is the energy associated with the formation of a crystalline lattice of the compound from the gaseous ions.



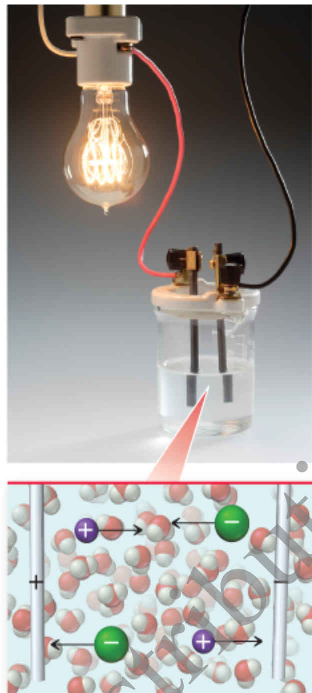
Ionic Bonding: Models and Reality

In this section, we applied the Lewis model to ionic bonding. The value of a model lies in how well it accounts for what we see in nature (through experiments). Does this ionic bonding model explain the properties of ionic compounds, including their high melting and boiling points, their tendency *not to conduct* electricity as solids, and their tendency *to conduct* electricity when dissolved in water?



$NaCl(s)$

Solid sodium chloride does not conduct electricity.



$NaCl(aq)$

When sodium chloride dissolves in water, the resulting solution contains mobile ions that can create an electric current.

We model an ionic solid as a lattice of individual ions held together by coulombic forces that are not directional (which means that, as we move away from the center of an ion, the forces are equally strong in all directions). To melt the solid, these forces must be overcome, which requires a significant amount of heat. Therefore, our model accounts for the high melting points of ionic solids. In the model, electrons transfer from the metal to the nonmetal, but the transferred electrons remain localized on one atom. In other words, our model does not include any free electrons that might conduct electricity (the movement or flow of electrons in response to an electric potential, or voltage, is electrical current). In addition, the ions themselves are fixed in place; therefore, our model accounts for the nonconductivity of ionic solids. When our idealized ionic solid dissolves in water, however, the cations and anions dissociate, forming free ions in solution. These ions can move in response to electrical forces, creating an electrical current. Thus, our model predicts that solutions of ionic compounds conduct electricity (which in fact they do).

Conceptual Connection 4.3 **Melting Points of Ionic Solids**

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