Skills to Develop

- To describe the characteristics of ionic bonding.
- To describe quantitatively the energetic factors involved in the formation of an ionic bond.

**Ions** are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** are negatively charged. Ions form when atoms gain or lose valence electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged. **Ionic bonding** is the attraction between positively- and negatively-charged ions. These oppositely charged ions attract each other to form ionic networks, or **lattices**. Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

The properties of ionic compounds follow from the orderly crystal lattice arrangement of tightly bonded charged particles that make them up. Ionic compounds tend to have high melting and boiling points, because the attraction between ions in the lattice is very strong. Moving ions out of the lattice disrupts the structure, so ionic compounds tend to be brittle rather than malleable. Ionic compounds do not conduct electricity in the solid state because ions are not free to move around the lattice; however, when ionic compounds are dissolved, they may **dissociate** into individual ions which move freely through the solution and therefore conduct electricity well.

### Generating Ionic Bonds

Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding. In the overall ionic compound, positive and negative charges must be balanced, because electrons cannot be created or destroyed, only transferred. Thus, the total number of electrons lost by the cationic species must equal the total number of electrons gained by the anionic species.

Ionic compounds are held together by electrostatic forces, which are described in classical physics by **Coulomb's Law**. According to this law, the energy of the electrostatic attraction ($\langle E \rangle$) between two charged particles is proportional to the magnitude of the charges ($\langle Q_1 \rangle$ and $\langle Q_2 \rangle$) and inversely proportional to the internuclear distance between the particles ($\langle r \rangle$):

\[
\langle E \rangle \propto \dfrac{\langle Q_1 \rangle \langle Q_2 \rangle}{\langle r \rangle} \quad \langle Q_1 \rangle \langle Q_2 \rangle \langle r \rangle = \text{constant} \tag{Eq1a}
\]

The energy of attraction ($\langle E \rangle$) is a type of **potential energy**, since it is based on the position of the charged particles relative to each other. If the two particles have opposite charges (as in ionic compounds), the value of $\langle E \rangle$ will be negative, meaning that energy is **released** by bringing the particles together—that is, the particles naturally **attract** each other. According to Coulomb’s Law, the larger the magnitude of the charges on each particle, the stronger the attraction will be. So, for example, Mg$^{2+}$ and O$^{2-}$ will have a stronger attraction than Na$^+$ and Cl$^-$, because of the larger charges.
Also, the closer together the charges are, the stronger the attraction. Therefore, smaller ions also form stronger ionic bonds.

In an ionic lattice, many more than two charged particles interact simultaneously, releasing an amount of energy known as the **lattice energy**. The lattice energy is not exactly the same as that predicted by Coulomb's Law, but the same general principles of electrostatic attraction apply. *In an ionic compound, the value of the lattice energy corresponds to the strength of the ionic bonding.*

**Example:** Sodium Chloride

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na$^+$ cation and each Cl atom becomes a Cl$^-$ anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is \(\ce{NaCl}\).

\[
\ce{2Na (s) + Cl2(g) → 2NaCl (s)}
\]

These ions are arranged in solid \(\ce{NaCl}\) in a regular three-dimensional arrangement (or lattice):

*NaCl lattice. (left) 3-D structure and (right) simple 2D slice through lattice. Images used with permission from Wikipedia and Mike Blaber.*

The chlorine has a high affinity for electrons, and the sodium has a low ionization energy. Thus the chlorine gains an electron from the sodium atom. This can be represented using **Lewis dot symbols** showing the valence electrons in each atom (here we will consider one chlorine atom, rather than Cl$_2$):

\[
\text{Na}^+ + \text{Cl}^- \rightarrow \text{Na}^+ + \left[\text{Cl}^-\right]^-
\]

The curved arrow indicates the transfer of the electron from sodium to chlorine to form the Na$^+$ metal ion and the Cl$^-$ chloride ion. Each ion now has full valence shell of eight electrons:

- Na$^+$: 2s$^2$2p$^6$
- Cl$: 3s$^2$3p$^6$
Electron Configuration of Ions

If ionic bonding becomes stronger for compounds with more highly charged ions, why does sodium only lose one electron to form Na\(^+\) rather than, say, Na\(^{2+}\)? The number of electrons transferred between ions depends not only on the energy released in lattice formation but also on the energy required to strip away electrons from one atom and add them to another. In other words, the lattice energy released by ionic compound formation must be balanced against the required ionization energy and electron affinity of forming the ions. Since the Na\(^+\) ion has a noble gas electron configuration, stripping away the next electron from this stable arrangement would require more energy than what is released during lattice formation (Sodium I\(_2\) = 4,560 kJ/mol). Thus, sodium is present in ionic compounds as Na\(^+\) and not Na\(^{2+}\). Likewise, adding an electron to fill a valence shell (and achieve noble gas electron configuration) is exothermic or only slightly endothermic. To add an additional electron into a new subshell requires tremendous energy - more than the lattice energy. Thus, we find Cl\(^-\) in ionic compounds, but not Cl\(^{2-}\). As a general rule, main group elements only form ions with the nearest noble gas electron configuration - otherwise, the lattice energy would not be enough to compensate for the ionization energy / electron affinity.

Typical values of lattice energy can compensate for values as large as I\(_3\) for valence electrons (i.e. can strip away up to 3 valence electrons from cations). Because most transition metals would require the removal of more than 3 electrons to attain a noble gas core, they are not found in ionic compounds with a noble gas core. A transition metal always loses electrons first from the higher 's' subshell, before losing from the underlying 'd' subshell. (The remaining electrons in the unfilled d subshell are the reason for the bright colors observed in many transition metal compounds!) For example, iron ions will not form a noble gas core:

- Fe: [Ar]4s\(^2\)3d\(^6\)
- Fe\(^{2+}\): [Ar] 3d\(^6\)
- Fe\(^{3+}\): [Ar] 3d\(^5\)

Some metal ions can form a pseudo noble gas core (and be colorless), for example:

- Ag: [Kr]5s\(^1\)4d\(^{10}\) Ag\(^+\) [Kr]4d\(^{10}\) Compound: AgCl
- Cd: [Kr]5s\(^2\)4d\(^{10}\) Cd\(^{2+}\) [Kr]4d\(^{10}\) Compound: CdS

Note: The silver and cadmium atoms lost the 5s electrons in achieving the ionic state. Remember that atoms always lost electrons from the subshell with the highest n quantum number first (i.e. 5s before 4d).

When a positive ion is formed from an atom, electrons are always lost first from the subshell with the largest principle quantum number.

Polyatomic Ions

Not all ionic compounds are formed from only two elements. Many polyatomic ions exist, in which two or more atoms are bound together by covalent bonds. They form a stable grouping which carries a charge (positive or negative). The group...
of atoms as a whole acts as a charged species in forming an ionic compound with an oppositely charged ion. Polyatomic ions may be either positive or negative, for example:

- $\text{NH}_4^+$ (ammonium) = cation
- $\text{SO}_4^{2-}$ (sulfate) = anion

The principles of ionic bonding with polyatomic ions are the same as those with monatomic ions. Oppositely charged ions come together to form a crystalline lattice, releasing a lattice energy. Based on the shapes and charges of the polyatomic ions, these compounds may form crystalline lattices with interesting and complex structures.

**Energetics of Ionic Bond Formation**

Ionic bonds are formed when positively and negatively charged ions are attracted by electrostatic forces. Consider a single pair of ions, one cation and one anion. How strong will the force of their attraction be? We can rewrite Coulomb’s Law (Equation \ref{Eq1a}) quantitatively for any two charged particles:

\[
E = k \frac{Q_1 Q_2}{r}
\]

where each ion’s charge is represented by the symbol $(Q)$ and the internuclear distance between the particles is represented by $(r)$. The proportionality constant $k$ is equal to $2.31 \times 10^{-28}$ J·m. This value of $(k)$ includes the charge of a single electron ($1.6022 \times 10^{-19}$ C) for each ion. The equation can also be written using the charge of each ion, expressed in coulombs (C), incorporated in the constant. In this case, the proportionality constant, $k$, equals $8.999 \times 10^9$ J·m/C². In the example given, $Q_1 = +1(1.6022 \times 10^{-19}$ C) and $Q_2 = -1(1.6022 \times 10^{-19}$ C). If $(Q_{-1})$ and $(Q_{-2})$ have opposite signs (as in \(\text{NaCl}\)), for example, where $Q_1$ is $+1$ for Na$^+$ and $Q_2$ is $-1$ for Cl$^-$, then $E$ is negative, which means that energy is released when oppositely charged ions are brought together from an infinite distance to form an isolated ion pair.

Energy is always released when a bond is formed and correspondingly, it always requires energy to break a bond.

As shown by the green curve in the lower half of Figure \(\text{PageIndex(1)}\), the maximum energy would be released when the ions are infinitely close to each other, at $r = 0$. Because ions occupy space and have a structure with the positive nucleus being surrounded by electrons, however, they cannot be infinitely close together. At very short distances, repulsive electron–electron interactions between electrons on adjacent ions become stronger than the attractive interactions between ions with opposite charges, as shown by the red curve in the upper half of Figure \(\text{PageIndex(1)}\). The total energy of the system is a balance between the attractive and repulsive interactions. The purple curve in Figure \(\text{PageIndex(1)}\) shows that the total energy of the system reaches a minimum at $r_0$, the point where the electrostatic repulsions and attractions are exactly balanced. This distance is the same as the experimentally measured bond distance.
Figure \(\PageIndex{1}\): A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous \(\text{Na}^+\) Ion and a Gaseous \(\text{Cl}^-\) Ion. The energy of the system reaches a minimum at a particular distance \((r_0)\) when the attractive and repulsive interactions are balanced.

Consider the energy released when a gaseous \((\text{Na}^+\})\) ion and a gaseous \((\text{Cl}^-\)\) ion are brought together from \(r = \infty\) to \(r = r_0\). Given that the observed gas-phase internuclear distance is 236 pm, the energy change associated with the formation of an ion pair from an \((\text{Na}^+\}_\text{(g)}))\) ion and a \((\text{Cl}^-\}_\text{(g)}))\) ion is as follows:

\[
E = k\frac{Q_1Q_2}{r_0} = (2.31 \times 10^{\text{-28}} \text{ J}\cdot\cancel{m}) \left( \frac{( + 1)( - 1)}{236 \; \cancel{pm} \times 10^{\text{-12}} \cancel{m/pm}} \right) = -9.79 \times 10^{\text{-19}} \text{ J/} \text{ion pair} \tag{Eq2}
\]

The negative value indicates that energy is released. Our convention is that if a chemical process provides energy to the outside world, the energy change is negative. If it requires energy, the energy change is positive. To calculate the energy change in the formation of a mole of \(\text{NaCl}\) pairs, we need to multiply the energy per ion pair by Avogadro’s number:

\[
E = (-9.79 \times 10^{\text{-19}} \text{ J/} \text{ion pair}) \left( 6.022 \times 10^{\text{23}} \text{ ion pair/mol} \right) = -589 \text{ kJ/mol} \tag{Eq3}
\]

This is the energy released when 1 mol of gaseous ion pairs is formed, not when 1 mol of positive and negative ions condenses to form a crystalline lattice. Because of long-range interactions in the lattice structure, this energy does not correspond directly to the lattice energy of the crystalline solid. However, the large negative value indicates that bringing positive and negative ions together is energetically very favorable, whether an ion pair or a crystalline lattice is formed.
Table 1: Lattice energies range from around 700 kJ/mol to 4000 kJ/mol:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>1024</td>
</tr>
<tr>
<td>LiI</td>
<td>744</td>
</tr>
<tr>
<td>NaF</td>
<td>911</td>
</tr>
<tr>
<td>NaCl</td>
<td>788</td>
</tr>
<tr>
<td>NaI</td>
<td>693</td>
</tr>
<tr>
<td>KF</td>
<td>815</td>
</tr>
<tr>
<td>KBr</td>
<td>682</td>
</tr>
<tr>
<td>KI</td>
<td>641</td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>2910</td>
</tr>
<tr>
<td>SrCl$_2$</td>
<td>2130</td>
</tr>
<tr>
<td>MgO</td>
<td>3938</td>
</tr>
</tbody>
</table>

We summarize the important points about ionic bonding:

- At $r_0$, the ions are more stable (have a lower potential energy) than they are at an infinite internuclear distance. When oppositely charged ions are brought together from $r = \infty$ to $r = r_0$, the energy of the system is lowered (energy is released).
- Because of the low potential energy at $r_0$, energy must be added to the system to separate the ions. The amount of energy needed is the bond energy.
- The energy of the system reaches a minimum at a particular internuclear distance (the bond distance).

Example 2: LiF

Calculate the amount of energy released when 1 mol of gaseous Li$^+$F$^-$ ion pairs is formed from the separated ions. The observed internuclear distance in the gas phase is 156 pm.

Given: cation and anion, amount, and internuclear distance

Asked for: energy released from formation of gaseous ion pairs

Strategy:

Substitute the appropriate values into Equation 1 to obtain the energy released in the formation of a single ion pair and then multiply this value by Avogadro’s number to obtain the energy released per mole.
Solution:

Inserting the values for Li$^+$F$^-$ into Equation \(\text{Eq1b}\) (where \(Q_1 = +1, Q_2 = -1,\) and \(r = 156\) pm), we find that the energy associated with the formation of a single pair of Li$^+$F$^-$ ions is

\[
E = k \frac{Q_1 Q_2}{r_0} = \left(2.31 \times 10^{-28} \text{ J} \cdot \cancel{m}\right) \left(\frac{(+1)(-1)}{156\; \text{pm} \times 10^{-12} \cancel{m/pm}}\right) = -1.48 \times 10^{-18} \text{ J}
\]

Then the energy released per mole of Li$^+$F$^-$ ion pairs is

\[
E = \left(-1.48 \times 10^{-18} \text{J/\cancel{ion pair}}\right) \left(6.022 \times 10^{23} \cancel{\text{ion pair/mol}}\right) = -891 \text{ kJ/mol}
\]

Because Li$^+$ and F$^-$ are smaller than Na$^+$ and Cl$^-$ (see Section 7.3), the internuclear distance in LiF is shorter than in NaCl. Consequently, in accordance with Equation \(\text{Eq1b}\), much more energy is released when 1 mol of gaseous Li$^+$F$^-$ ion pairs is formed (−891 kJ/mol) than when 1 mol of gaseous Na$^+$Cl$^-$ ion pairs is formed (−589 kJ/mol).

Exercise \(\PageIndex{2}\): Magnesium oxide

Calculate the amount of energy released when 1 mol of gaseous \(\ce{MgO}\) ion pairs is formed from the separated ions. The internuclear distance in the gas phase is 175 pm.

**Answer**

\(-3180\; \text{kJ/mol} = -3.18 \times 10^3 \text{ kJ/mol}\)

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**Summary**

Ionic compounds are formed when electrons are transferred between atoms or groups of atoms to form charged ions, which then arrange in a crystalline lattice structure due to electrostatic attraction. The formation of ionic compounds are usually extremely exothermic. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance. The total energy of the system is a balance between the repulsive interactions between electrons on adjacent ions and the attractive interactions between ions with opposite charges.

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