

6.3 Describing Chemical Bonding

Warm Up

1. What term do we give to an atom's outer electrons that take part in chemical bonding?

2. Define electronegativity.

3. In which region of the periodic table are elements located that tend to
(a) lose outer electrons most easily during chemical changes?

(b) gain outer electrons most easily during chemical changes?

An Introduction to Chemical Bonding

All matter is composed of atoms, and those individual atoms are far too small to see. From that, it seems reasonable to conclude that matter must be made up of large numbers of atoms connected or bonded together. In this section, we will investigate the nature of the bonds between atoms and how those bonds determine important properties in compounds.

Atoms are electrical species with a negative cloud of electrons surrounding and attracted to a positive nucleus. As you have learned, the electrostatic forces of attraction and repulsion within atoms influence properties such as atomic size, ionization energy, and electronegativity. Those same forces and properties also play a role whenever atoms bond together.

When two atoms approach each other, all of the electrostatic interactions associated with equally and oppositely charged particles occur. The negative electron clouds of the atoms exert repulsive forces on each other, as do the positive nuclei of each atom. This repulsion slows the approaching atoms and converts some of their kinetic energy to potential energy. In addition, each nucleus also begins to attract the approaching atom's outer electron cloud. These attractive forces are most intense in the region of space where the electron clouds "overlap" between the adjacent nuclei. If the attractive forces between the atoms are stronger than the repulsive forces, the two atoms together are in a state of lower energy than when they were apart. Thus, a chemical bond forms between them.

Types of Chemical Bonds

The events described above apply to the formation of all chemical bonds. But recall that we have classified elements as metals and non-metals based on a number of physical and chemical properties that correlate to different positions on the periodic table. These properties and the three possible ways that these two varieties of elements can combine give rise to three different *types* of chemical bonds, which are listed in Table 6.3.1. In this course, we will cover ionic and covalent bonds.

Table 6.3.1 Types of Chemical Bonds

Atoms Involved in Chemical Bond	Type of Chemical Bond
1. metal bonded to non-metal	ionic bond
2. non-metal bonded to non-metal	covalent bond
3. metal bonded to metal	metallic bond

Table 6.3.1 is a simplified summary of chemical bonds because the bonds between atoms in most chemical compounds have varying proportions of both ionic and covalent characteristics. We will begin with clear examples of each type of bond to introduce the concepts involved.

Ionic Bonds

Ionic bonds form between two atoms with large differences in their ionization energies and electronegativities. Recall from Section 6.2 that such combinations typically occur when relatively large metal atoms located on the far left side of the periodic table in groups 1 or 2 combine with smaller non-metal atoms on the far right side of the table belonging to groups 16 or 17.

Look again at the table of electronegativities introduced in section 6.2 (Figure 6.2.6). Imagine a "collision," for example, between an alkali metal atom such as sodium and a halogen atom such as chlorine. These elements are located at opposite ends of the 3rd period of the periodic table and therefore exhibit significant differences in size, ionization energy, and electronegativity.

Compared to an atom of sodium, a chlorine atom is smaller with a higher ionization energy and electronegativity. As a result, when the outer electron clouds of these two atoms encounter each other, sodium's lone valence electron will be closer to chlorine's nucleus than to its own. It will therefore feel a stronger attraction from chlorine's nucleus than from its own. In fact, because the difference in the electronegativities of these two elements is *greater than 1.7*, the probability of finding sodium's outer electron near chlorine's nucleus is so great that the sodium atom can be considered to *transfer* that valence electron to the chlorine atom. Electronegativity difference is often abbreviated as ΔEN .

The large sodium atom, having lost the only electron in its 3rd energy level, is now a much smaller positively charged sodium cation (Na^+). The relatively small chlorine atom, having gained an extra electron, becomes a larger negatively charged chloride anion (Cl^-). These two oppositely charged ions are now bound together by an electrostatic attraction called an **ionic bond**.

An **ionic bond** is the electrostatic attractive force between the oppositely charged ions produced when a metal atom transfers one or more electrons to a non-metal atom.

The electron transfer from sodium to chlorine and the resulting ionic bond is shown in Figure 6.3.1. These diagrams are **Bohr model** diagrams, showing the number of electrons in the shells surrounding the nuclei of the atoms and ions.

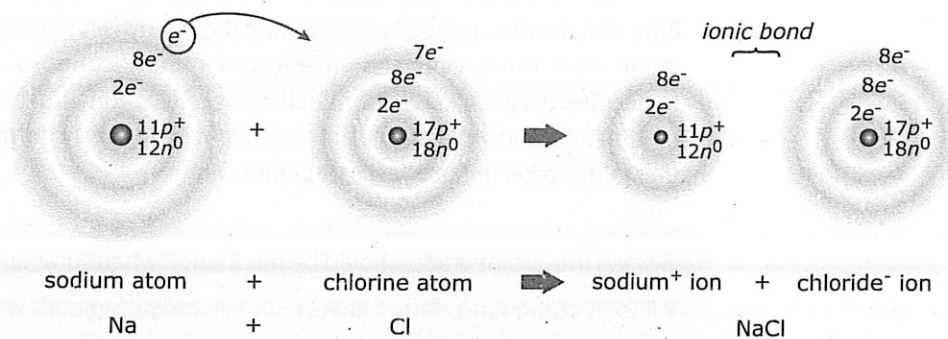


Figure 6.3.1 An electron transfers from sodium atom to a chlorine atom, resulting in the formation of an ionic bond between the ions.

The Ionic Crystal Lattice

Obviously, when any macroscopic sample of chlorine gas and sodium metal react together, countless atoms will transfer electrons to form countless oppositely charged ions. These oppositely charged species being produced in close proximity are drawn together into an ordered, solid, three-dimensional array of cations and anions called a **crystal lattice** (Figure 6.3.2). The smallest whole number cation-to-anion ratio in this structure represents the chemical formula for the ionic compound, in this case, NaCl.

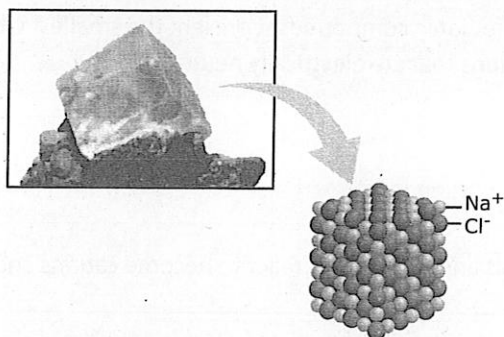


Figure 6.3.2 NaCl crystal lattice

The vast number of interionic forces present in a crystal lattice locks all of the ions into place. This helps explain why all ionic compounds are solids with high melting temperatures (e.g., sodium chloride melts at 801°C.)

Ionic compounds form a number of different crystal structures depending on the relative sizes and ratios of their ions. Those ratios in turn depend on the charges on the ions in the compound.

Recall from section 6.1 that the representative elements in groups 1, 2, 13, 15, 16, and 17 of the periodic table tend to form stable ions by losing or gaining sufficient electrons to become isoelectronic with the nearest noble gas. This results in the common ion charges shown in Table 6.3.2 for those groups.

Table 6.3.2 Common Ion Charges in Groups 1, 2, 13, 15, 16, and 17

Group Number	1	2	13	15	16	17
Most Common Ion Charge	1+	2+	3+	3-	2-	1-

We can think of ionic bond formation as a case of *extremely unequal electron sharing*. Both metal and non-metal nuclei attract the valence electrons between them when their atoms meet. However, the non-metal pulls those electrons so close to its own nucleus that it effectively captures the metal's valence electrons and forms the metal cation and non-metal anion. An accurate analogy might be a grossly mismatched tug-of-war, except that in this case, the smallest competitor wins.

Several important points should be mentioned when summarizing ionic bonding:

1. Ionic compounds form between metals and non-metals whose ΔEN exceed 1.7. They typically form when metals from groups 1 or 2 react with non-metals from groups 16 or 17 of the periodic table.
2. During the formation of an ionic bond, metal atoms will transfer one or more valence electrons to the more electronegative non-metal atoms. This occurs because of the metal's relatively low ionization energies and electronegativities. In the process, metal cations and non-metal anions form and are attracted to each other by ionic bonds.
3. Ionic compounds form structures known as crystal lattices. The vast number of attractive forces present in such lattices account for the high melting temperatures of ionic compounds.
4. The formulas for ionic compounds represent the smallest whole number ratios of cations-to-anions that are electrically neutral.

Quick Check

1. What event occurs when atoms of metals and non-metals react to become cations and anions?

2. Identify the three types of chemical bonds based on the different elements involved.

3. Which chemical families in the periodic table are typically associated with ionic bond formation?

Sample Problem — Ionic Bond Formation

Write formulas for the compounds formed when the following elements combine and justify that the bonds present are ionic by determining the ΔEN in each case.

(a) Ca and Br (b) Al and O (c) Be and O (d) Rb and N (e) Ba and Cl

What to Think about

1. Write the element symbols with their charges and criss-cross the numbers.
2. Reduce formulas to smallest whole number ratios
3. Determine ΔEN values using the table above. Values above 1.7 represent ionic bonds.

How to Do It

- (a) $Ca^{2+} Br^{1-} \rightarrow CaBr_2$ $\Delta EN = 1.8$ (ionic bond)
(b) $Al^{3+} O^{2-} \rightarrow Al_2O_3$ $\Delta EN = 2.0$ (ionic bond)
(c) $Be^{2+} O^{2-} \rightarrow BeO$ $\Delta EN = 2.0$ (ionic bond)
(d) $Rb^{1+} N^{3-} \rightarrow Rb_3N$ $\Delta EN = 2.2$ (ionic bond)
(e) $Ba^{2+} Cl^{1-} \rightarrow BaCl_2$ $\Delta EN = 2.1$ (ionic bond)

Practice Problems — Ionic Compounds

1. Write formulas for the ionic compounds formed when the following elements combine:

(a) Ba and Br

(d) Mg and Cl

(b) Be and O

(e) Fr and F

(c) Sr and N

2. Justify that the bonds in the following compounds are ionic by calculating the ΔEN values for each.

(a) RbF

(c) KBr

(b) $RaCl_2$

(d) Na_2O

3. Write formulas for the ionic compounds formed when the following elements combine. Using the ΔEN values, arrange the compounds in order of the increasing ionic character of the bonds in each compound.

(a) Na and N

(b) Sr and Br

(c) Li and Cl

(d) Cs and F

(e) Rb and O

Covalent Bonds

Now let's look at the formation of a bond between two atoms of the same non-metal element, such as hydrogen (Figure 6.3.3). Obviously, the electronegativities of these or any two identical atoms would be the same.

As mentioned above, bond formation begins with atoms "colliding." As the two hydrogen atoms approach each other, their kinetic energy increases as each electron cloud is attracted to the other's approaching positive nucleus. The two atoms continue moving together until the repulsive forces of the two negative electron clouds and the two positive nuclei slow the atoms and convert their kinetic energy into potential energy.

As the atoms get close to each other, their electron clouds may overlap enough to cause attractive forces to exceed repulsive ones. The two valence electrons will move into the region of space between the adjacent nuclei because this is where they experience the most attractive force from those two centres of positive charge. The two atoms will settle into a position next to each other with the pair of valence electrons in a cloud of negative charge between the two nuclei. As the electron clouds of each hydrogen atom overlap, the two valence electrons experience the maximum attractive force between the two adjacent nuclei. This force of attraction of a pair of valence electrons between two adjacent nuclei constitutes a single **covalent bond**. In our example, the result of this covalent bond is a molecule of hydrogen, H_2

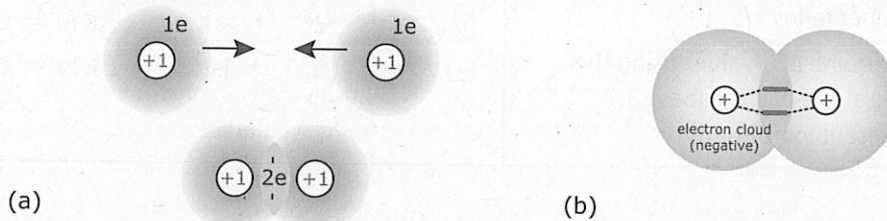


Figure 6.3.3 (a) Two hydrogen atoms collide and two valence electrons move into the space between the nuclei. (b) The valence electrons experience a force of attraction from the two nuclei. This attraction holds the two atoms together to form H_2 .

Because this bond has formed between two atoms of hydrogen, the electronegativity difference associated with the atoms in the bond must be zero. This tells us that, on average, the pair of bonded electrons will spend the majority of their time equidistant between the two hydrogen nuclei. Stated another way, this means that the density of the electron charge cloud is greatest in the region of space halfway between the two adjacent nuclei. This is true whenever two atoms of the same element form covalent bonds. The “equal sharing” of valence electrons is sometimes referred to as a “pure covalent” or non-polar covalent bond.

Although both ionic and covalent bond formation involves only valence electrons, there are several important differences between the two events:

1. Covalent bonds typically form between two non-metal atoms rather than between metal atoms and non-metal atoms.
2. Because no electron transfer occurs and no ions form, all of the species prior to and following covalent bond formation between two atoms are electrically neutral.
3. The force of attraction in a covalent bond is between a pair of electrons and two adjacent positive nuclei, rather than between a cation and an anion as in an ionic bond. Electrons in covalent bonds are *always associated into pairs*.
4. Covalent compounds often exist as independent molecules rather than large crystal structures.

Polar Covalent Bonds

Table 6.3.3 Relationship of ΔEN and Bond Designation

ΔEN	Bond Designation
0	non-polar covalent
< 0.4	mostly covalent
0.4 – 1.7	polar covalent
> 1.7	ionic

We have discussed above the two extreme cases of bonding: complete electron transfer and completely equal electron sharing. Between these extremes are covalent bonds involving *unequal* electron sharing.

When atoms with different electronegativities form covalent bonds, those ΔEN values may be minimal or significant. If ΔEN is less than 0.4, the bonding electrons between the two atoms spend no more of their time nearer one nucleus than the other. Such bonds are designated as being mostly covalent because ΔEN appears to be insignificant. Another way to characterize this is to say that these bonds have very little "ionic character."

However, as ΔEN increases beyond 0.4, the pair of bonding electrons will be drawn closer and closer to the nucleus of the atom with the higher electronegativity. This unequal distribution of electron density will give that end of the bond a partially negative "pole" and the other a partially positive "pole." A bond "dipole" is said to exist and the bond itself is known as a **polar covalent bond**.

As the ΔEN increases and the bonds become more and more polar, we could say that the amount of ionic character in those bonds increases (Table 6.3.3).

Let's look at an example of a polar covalent bond. When a hydrogen atom having an electronegativity of 2.1 bonds to a chlorine atom with an electronegativity of 3.0, the $\Delta EN = 0.9$. The electron density will be concentrated near chlorine giving that end of the bond a partial negative charge and leaving the hydrogen end with a partial positive charge. The bond dipole is said to be in the direction of chlorine and we can designate this polar covalent bond in several ways. Two are shown in Figure 6.3.4. The lower case Greek deltas (δ) indicate that there are slight or *partial* charges associated with each end of the HCl molecule. Note also that more electron density is associated with chlorine. Another depiction of this polar covalent bond simply shows the hydrogen chloride bond as a straight line between the element symbols. Beneath this is an arrow facing in the direction of the highest electron density or the negative end of the bond dipole.

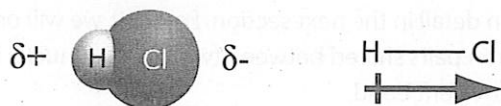


Figure 6.3.4 Polar covalent bond depictions. The bond dipole is in the direction of the chlorine.

Atoms That Form More Than One Bond

So far we have considered the formation of only one bond per atom in two different molecules, namely H_2 and HCl. Notice that hydrogen and chlorine each require a single electron to become isoelectronic with their nearest noble gas. In hydrogen's case, one more electron will complete its first energy level. When chlorine acquires another electron it achieves a stable octet in its valence shell.

In each example, the sharing of a pair of valence electrons, whether equal or not, gives each atom in the bond the benefit of that extra electron in its valence shell. The bond also allows both atoms to have *all of their valence electrons paired*, which is a very stable configuration from a quantum mechanical perspective.

Of course, non-metals sometimes require more than one electron to achieve a stable outer electron shell and have all of their valence electrons paired. Consider several non-metals in groups 14, 15, and 16. To achieve a stable octet containing four electrons pairs in each of their valence shells, carbon requires four electrons, nitrogen needs three, and oxygen needs two.

This tells us that the number of electrons required by an atom to achieve the stable outer electron configuration of the nearest noble gas also represents the number of covalent bonds that the atom must form.

We can use Table 6.3.4 to predict formulas for compounds formed between elements in these families. For example, when phosphorus and chlorine react together, phosphorus requires three electrons to complete its octet, while chlorine requires only one.

Table 6.3.4 Electrons Needed to Achieve a Stable Octet for Non-metals

Periodic Table Group Number	14	15	16	17
Electrons Needed to Achieve Stable Octet	4	3	2	1

The element with the lower electronegativity, in this case phosphorus, normally requires the most electrons and is written first in a chemical formula. Place the number of electrons it requires above its symbol on the right (similar to a charge without the sign). Then do the same for chlorine as follows: $P^3 \quad Cl^1$ Now criss-cross those numbers to give the formula: PCl_3 .

The process is similar to writing ionic formulas except no charges exist and you don't always reduce the formula to the smallest ratio of atoms. This is because a covalent formula does not represent a ratio. Rather, it tells us the actual number of atoms that exist in the molecule. Assume at this point, however, that you *can* reduce covalent formulas unless told otherwise by your teacher.

There are also numerous examples where more than one pair of electrons is shared between the same two atoms. Two pairs of shared valence electrons results in a double covalent bond and three pairs will produce a triple covalent bond. We will discuss multiple bonds in detail in the next section. For now, we will only mention that as the number of electron pairs shared between two adjacent nuclei increases, so does the strength of the covalent bond.

Sample Problem — Covalent Bond Formation

Predict the formulas for the compounds formed when the following elements combine and determine whether the bonds present are non-polar covalent or polar covalent.

- (a) N and F (b) C and H (c) Si and N (d) C and S (e) O and O

What to Think about

- Determine how many electrons each atom requires to complete its valence shell and write that number above the symbol.
- Criss-cross those numbers and reduce ratios if possible (for now).
- Determine the ΔEN for each and classify the bonds present.

How to Do It

- (a) $N^3 F^1 \rightarrow NF_3 \quad \Delta EN = 1.0$ (polar covalent)
 (b) $C^4 H^1 \rightarrow CH_4 \quad \Delta EN = 0.4$ (polar covalent)
 (c) $Si^4 N^3 \rightarrow Si_3 N_4 \quad \Delta EN = 1.2$ (polar covalent)
 (d) $C^4 S^2 \rightarrow CS_2 \quad \Delta EN = 0$ (non-polar covalent)
 (e) $O^2 O^2 \rightarrow O_2 \quad \Delta EN = 0$ (non-polar covalent)

Practice Problems — Comparing Types of Chemical Bonds

- Consider the ΔEN values and pair up the elements Al, Cl, N, and Na to write the formula for the types of compounds identified below. Justify each choice by showing the appropriate ΔEN value next to each formula.
 - A compound with an ionic bond
 - A compound with a polar covalent bond
 - A compound with a non-polar covalent bond
- Calculate the ΔEN values for the bonds in the following compounds. Then arrange the compounds in order from those containing bonds in which the electrons are shared most equally to those in which the electrons are shared most unequally.
 - H_2O
 - PCl_3
 - Cl_4
 - SiO_2
 - AlN
- Complete the following table:

Elements Present	Formula	ΔEN Value	Nature of Bonds	Atom Possessing Greater Electron Density
C and S				
B and Cl				
Al and O				
N and I				
Ca and F				

The Strength of Ionic vs. Covalent Bonds

Remember that ionic compounds are solids at room temperature and have high melting points. This results from the vast number of interionic forces locking all of the ions together in place in the crystal lattice. As mentioned earlier, the common ionic compound NaCl melts at $801^\circ C$.

Covalent compounds, however, usually exist as individual molecules and in any of the three states of matter: solid, liquid, or gas. We shouldn't conclude from this, however, that covalent bonds are any weaker than ionic bonds. Consider, for example, the molecule methane, CH_4 , the main component of natural gas.

Although the melting point of methane ($-182^\circ C$) is very low compared to sodium chloride, this physical property does not reflect the strength of the C – H bonds in methane or indicate that the bonds are weak compared to those in NaCl.

This is because no chemical bonds are broken when methane or any molecular covalent compound melts. Instead, weak intermolecular forces *between* the molecules are overcome. The result is that molecules are separated *from each other* rather than breaking the bonds between the atoms within those molecules.

The energy required to separate the bonded carbon and hydrogen atoms within the molecules from each other is far more than that required to simply pull the molecules apart. In the final section of this chapter, we will discuss the different forces that hold molecules together. Although some of those forces are stronger than others, *none are as strong as chemical bonds.*

Compelling evidence of the strength of covalent bonds can be seen by studying compounds called **network covalent solids**. Rather than consisting of individual molecules, these substances are held together by covalent bonds that extend throughout the entire sample. In the same way that melting an ionic solid requires overcoming all of the attractive forces between the oppositely charged ions in the crystal lattice, melting a network covalent solid involves breaking all of the covalent bonds within what is effectively a giant molecule literally as big as the sample.

Consider quartz, for example, which is a network covalent solid having the formula SiO_2 (Figure 6.3.5). The fact that no separate molecules exist in a quartz crystal means that the melting point is very high: 1550°C . The melting point does reflect the strength of the bonds in the compound. It shows us that covalent bonds can be as strong as ionic bonds.

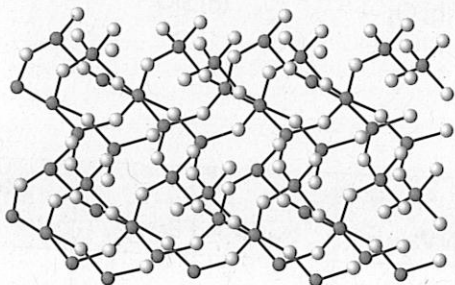


Figure 6.3.5 A quartz crystal