

5.2: Electronegativity and Bond Polarity

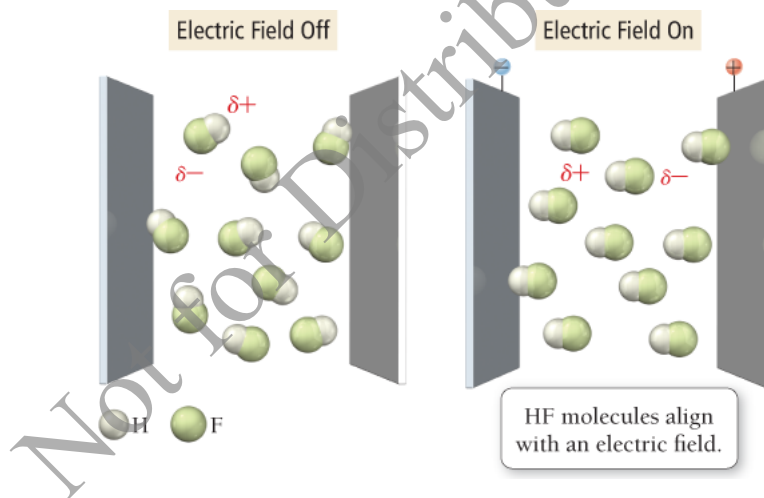
In [Chapter 4](#) we introduced the Lewis model for chemical bonding. In the Lewis model, we represent valence electrons with dots and draw Lewis structures that show how atoms attain octets by sharing electrons with other atoms. The shared electrons are covalent chemical bonds. However, we know from quantum mechanics (introduced in [Chapter 2](#)) that representing electrons with dots, as we do in the Lewis model, is a drastic oversimplification. This does not invalidate the Lewis model—which is an extremely useful theory—but we must recognize and compensate for its inherent limitations. One limitation of representing electrons as dots, and covalent bonds as two dots shared between two atoms, is that the shared electrons always appear to be *equally* shared. Such is not the case. For example, consider the Lewis structure of hydrogen fluoride:



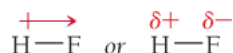
The two shared electron dots sitting between the H and the F atoms appear to be equally shared between hydrogen and fluorine. However, based on laboratory measurements, we know they are not. When HF is put in an electric field, the molecules orient as shown in [Figure 5.1](#).

Figure 5.1 Orientation of Gaseous Hydrogen Fluoride in an Electric Field

Because the hydrogen side of the HF molecule has a slight positive charge and the fluorine side a slight negative charge, the molecules align themselves with an external electric field.



From this observation, we know that the hydrogen side of the molecule must have a slight positive charge and the fluorine side of the molecule must have a slight negative charge. We represent this partial separation of charge as follows:



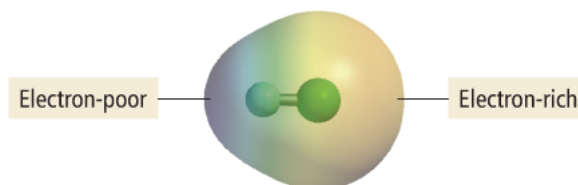
The red arrow above the hydrogen, with a positive sign on the tail, indicates that the left side of the molecule has a partial positive charge and that the right side of the molecule (the side the arrow is pointing *toward*) has a partial negative charge. Similarly, the red $\delta+$ (delta plus) on the H–F structure on the right represents a partial positive charge, and the red $\delta-$ (delta minus) represents a partial negative charge.

Does this make the bond ionic? No. In an ionic bond, the electron is essentially *transferred* from one atom to another. In HF, the electron is *unequally shared*. In other words, even though the Lewis structure of HF portrays

the bonding electrons as residing *between* the two atoms, in reality the electron density is greater on the fluorine atom than on the hydrogen atom (Figure 5.2). The bond is said to be *polar*—having a positive pole and a negative pole. A **polar covalent bond** is intermediate in nature between a pure covalent bond and an ionic bond. In fact, the categories of pure covalent and ionic are really two extremes within a broad continuum. Most covalent bonds between dissimilar atoms are actually *polar covalent*, somewhere between the two extremes.

Figure 5.2 Electrostatic Potential Map for the HF Molecule

Red indicates electron-rich regions, and blue indicates electron-poor regions.



Electronegativity

The ability of an atom to attract electrons to itself in a chemical bond (which results in polar and ionic bonds) is **electronegativity**. We say that fluorine is more *electronegative* than hydrogen because it takes a greater share of the electron density in HF.

Electronegativity was quantified by the American chemist Linus Pauling (1901–1994) in his classic book, *The Nature of the Chemical Bond*. Pauling compared the bond energy—the energy required to break a bond—of a heteronuclear diatomic molecule such as HF with the bond energies of its homonuclear counterparts. In this case, he compared HF with H₂ and F₂. The bond energies of H₂ and F₂ are 436 kJ/mol and 155 kJ/mol, respectively. Pauling reasoned that if the HF bond were purely covalent—that is, if the electrons were shared equally—the bond energy of HF should simply be an average of the bond energies of H₂ and F₂, which would be 296 kJ/mol. However, the bond energy of HF is experimentally measured to be 565 kJ/mol. Pauling suggested that the additional bond energy was due to the *ionic character* of the bond.

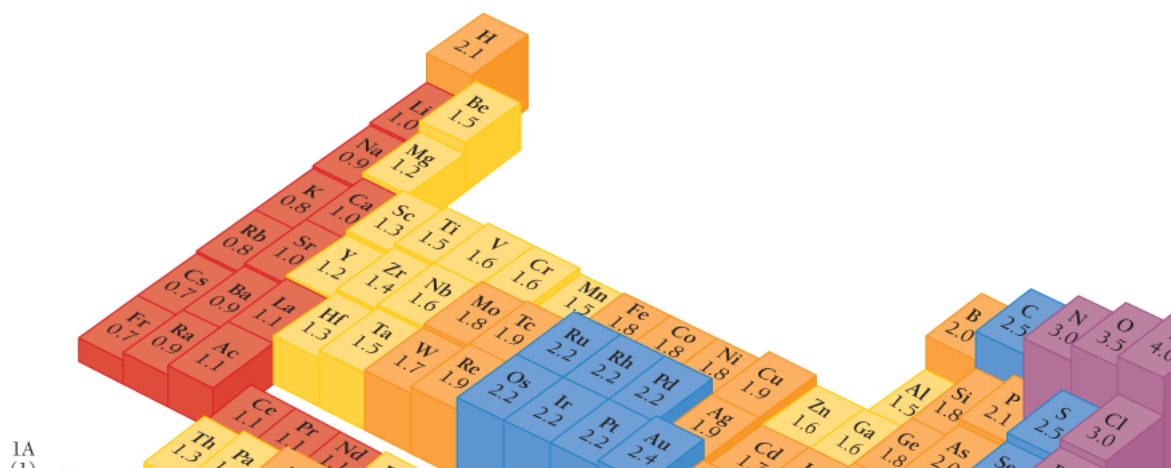
We cover the concept of bond energy in more detail in Section 5.6.

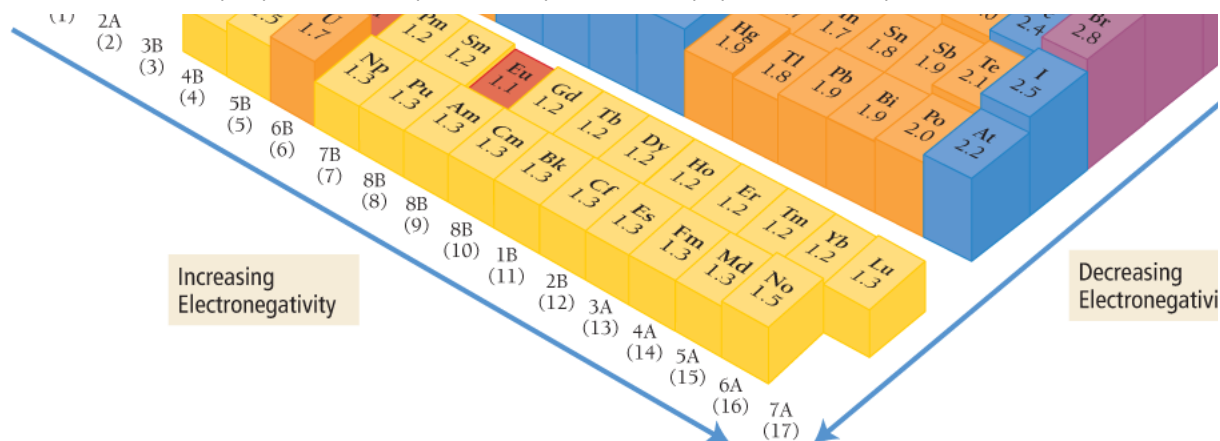
Based on many such comparisons of bond energies, and by arbitrarily assigning an electronegativity of 4.0 to fluorine (the most electronegative element on the periodic table), Pauling developed the electronegativity values shown in Figure 5.3.

Figure 5.3 Electronegativities of the Elements

Electronegativity generally increases as we move across a row in the periodic table and decreases as we move down a column.

Trends in Electronegativity





Pauling's "average" bond energy was actually calculated a little bit differently than the normal average shown in Figure 5.3. He took the square root of the product of the bond energies of the homonuclear counterparts as the "average."

For main-group elements, notice the following periodic trends in electronegativity in Figure 5.3:

- Electronegativity generally increases across a period in the periodic table.
- Electronegativity generally decreases down a column in the periodic table.
- Fluorine is the most electronegative element.
- Francium is the least electronegative element (sometimes called the most *electropositive*).

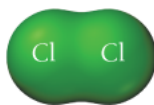
The periodic trends in electronegativity are consistent with other periodic trends we have seen. In general, electronegativity is inversely related to atomic size—the larger the atom, the less ability it has to attract electrons to itself in a chemical bond.

Conceptual Connection 5.1 Periodic Trends in Electronegativity

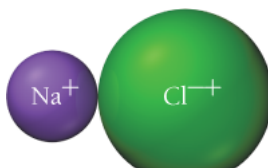
Bond Polarity, Dipole Moment, and Percent Ionic Character

The degree of polarity in a chemical bond depends on the electronegativity difference (sometimes abbreviated ΔEN) between the two bonding atoms. The greater the electronegativity difference, the more polar the bond. If two atoms with identical electronegativities form a covalent bond, they share the electrons equally, and the bond is purely covalent or *nonpolar*.

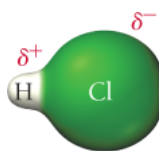
For example, the chlorine molecule, composed of two chlorine atoms (which necessarily have identical electronegativities), has a covalent bond in which electrons are evenly shared.



If there is a large electronegativity difference between the two atoms in a bond, such as normally occurs between a metal and a nonmetal, the electron from the metal is almost completely transferred to the nonmetal, and the bond is ionic. For example, sodium and chlorine form an ionic bond.



If there is an intermediate electronegativity difference between the two atoms, such as between two different nonmetals, then the bond is polar covalent. For example, HCl has a polar covalent bond.

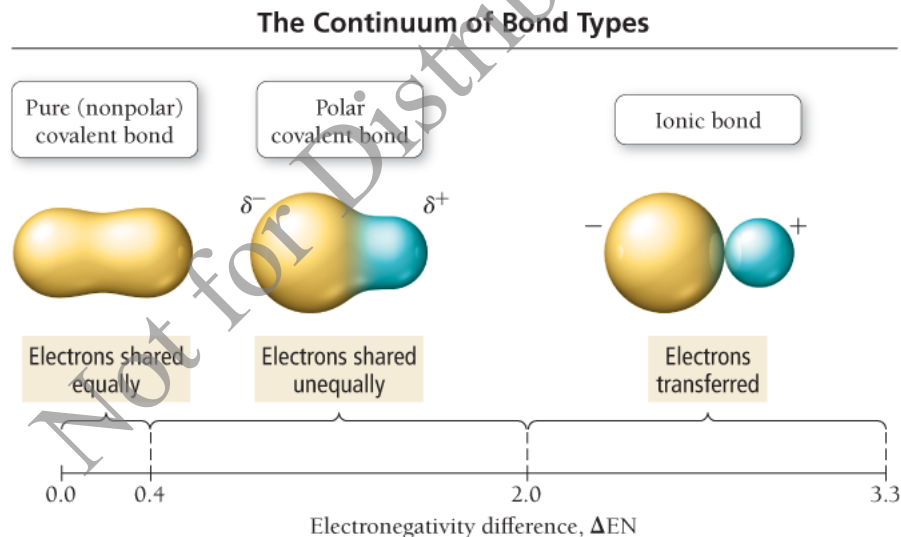


While all attempts to divide the bond polarity continuum into specific regions are necessarily arbitrary, it is helpful to classify bonds as covalent, polar covalent, and ionic, based on the electronegativity difference between the bonding atoms as shown in Table 5.1 and Figure 5.4. The bond between C and H lies at the border between covalent and polar covalent; however, this bond—which is very important in organic chemistry—is normally considered covalent (nonpolar).

Table 5.1 The Effect of Electronegativity Difference on Bond Type

Electronegativity Difference (ΔEN)	Bond Type	Example
Small (0–0.4)	Covalent	Cl_2
Intermediate (0.4–2.0)	Polar covalent	HCl
Large (2.0+)	Ionic	NaCl

Figure 5.4 Electronegativity Difference (ΔEN) and Bond Type



We quantify the polarity of a bond by the size of its dipole moment. A **dipole moment** (μ) occurs anytime there is a separation of positive and negative charge. The magnitude of a dipole moment created by separating two particles of equal but opposite charges of magnitude q by a distance r is given by the equation:

[5.1]

$$\mu = qr$$

We can get a sense for the dipole moment of a completely ionic bond by calculating the dipole moment that results from separating a proton and an electron ($q = 1.6 \times 10^{-19} \text{ C}$) by a distance of $r = 130 \text{ pm}$ (the approximate length of a short chemical bond).

$$\begin{aligned}
 \mu &= qr \\
 &= (1.6 \times 10^{-19} \text{ C}) (130 \times 10^{-12} \text{ m}) \\
 &= 2.1 \times 10^{-29} \text{ C} \cdot \text{m} \\
 &= 6.2 \text{ D}
 \end{aligned}$$

The debye (D) is the unit commonly used for reporting dipole moments ($1 \text{ D} = 3.34 \times 10^{-39} \text{ C} \cdot \text{m}$). Based on this calculation, we would expect the dipole moment of completely ionic bonds with bond lengths close to 130 pm to be about 6 D, and that is in fact the case (the dipole moment for LiF is 6.33 D, as you can see in [Table 5.2](#)). The smaller the magnitude of the charge separation, and the smaller the distance between the charges, the smaller the dipole moment. [Table 5.2](#) lists the dipole moments of several molecules along with the electronegativity differences between their atoms.

Table 5.2 Dipole Moments of Several Molecules in the Gas Phase

Molecule	ΔEN	Dipole Moment (D)
Cl_2	0	0
CIF	1.0	0.88
HF	1.9	1.82
LiF	3.0	6.33

We cover bond lengths in more detail in [Section 5.6](#).

By comparing the *actual* dipole moment of a bond to what the dipole moment would be if the electron were completely transferred from one atom to the other, we can get a sense of the degree to which the electron is transferred (or the degree to which the bond is ionic). The **percent ionic character** is the ratio of a bond's actual dipole moment to the dipole moment it would have if the electron were completely transferred from one atom to the other, multiplied by 100%.

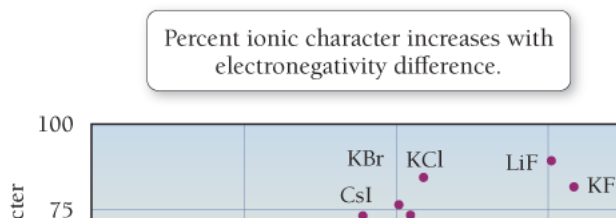
$$\text{percent ionic character} = \frac{\text{measured dipole moment of bond}}{\text{dipole moment if electron were completely transferred}} \times 100\%$$

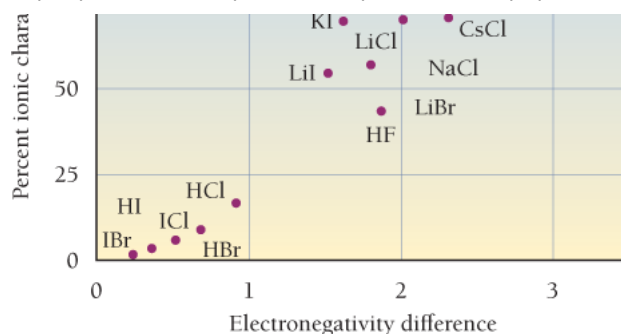
For example, suppose a diatomic molecule with a bond length of 130 pm has a dipole moment of 3.5 D. We previously calculated that separating a proton and an electron by 130 pm results in a dipole moment of 6.2 D. Therefore, the percent ionic character of the bond is 56%:

$$\begin{aligned}
 \text{percent ionic character} &= \frac{3.5 \text{ D}}{6.2 \text{ D}} \times 100\% \\
 &= 56\%
 \end{aligned}$$

A bond in which an electron is completely transferred from one atom to another would have 100% ionic character (although even the most ionic bonds do not reach this ideal). [Figure 5.5](#) shows the percent ionic character of a number of diatomic gaseous molecules plotted against the electronegativity difference between the bonding atoms. As expected, the percent ionic character generally increases as the electronegativity difference increases. However, as we can see, no bond is 100% ionic. In general, bonds with greater than 50% ionic character are referred to as ionic bonds.

Figure 5.5 Percent Ionic Character versus Electronegativity Difference for Some Compounds





Example 5.1 Classifying Bonds as Pure Covalent, Polar Covalent, or Ionic

Is the bond between each pair of atoms covalent, polar covalent, or ionic?

- Sr and F
- N and Cl
- N and O

SOLUTION

- In [Figure 5.3](#), find the electronegativity of Sr (1.0) and of F (4.0). The electronegativity difference (ΔEN) is $\Delta EN = 4.0 - 1.0 = 3.0$. According to [Table 5.1](#), this bond is ionic.
- In [Figure 5.3](#), find the electronegativity of N (3.0) and of Cl (3.0). The electronegativity difference (ΔEN) is $\Delta EN = 3.0 - 3.0 = 0$. According to [Table 5.1](#), this bond is covalent.
- In [Figure 5.3](#), find the electronegativity of N (3.0) and of O (3.5). The electronegativity difference (ΔEN) is $\Delta EN = 3.5 - 3.0 = 0.5$. According to [Table 5.1](#), this bond is polar covalent.

FOR PRACTICE 5.1 Is the bond between each pair of atoms pure covalent, polar covalent, or ionic?

- I and I
- Cs and Br
- P and O

Conceptual Connection 5.2 Percent Ionic Character

Interactive

Not for Distribution

Not for Distribution