Electronegativity and Bond Polarity

4.3

In Section 4.1, you learned about two types of chemical bonding: ionic and covalent. During ionic bonding, 1 or more electrons transfer from a metal atom to a non-metal atom to form negative and positive ions. These ions attract each other. In covalent bonding, neutral atoms share pairs of electrons. In some cases, 2 covalently bonded atoms share electrons equally while, in other cases, 1 of the atoms attracts the shared electron pair more strongly than the other atom. A **non-polar covalent bond** forms when the 2 atoms in a covalent bond share electrons equally. Non-polar covalent bonds usually form between 2 identical atoms, such as in molecular elements like hydrogen, nitrogen, and chlorine. **Polar covalent bonds** form between atoms that attract shared pairs of electrons with different abilities to attract electrons. When you place a sample of hydrogen fluoride gas, HF(g), in an electric field, the molecules orient themselves such that the fluorine end faces the positive pole and the hydrogen end faces the negative pole (**Figure 1**).

non-polar covalent bond a covalent bond in which the electrons are shared equally between atoms

polar covalent bond a covalent bond in which the electrons are not shared equally because 1 atom attracts them more strongly than the other atom

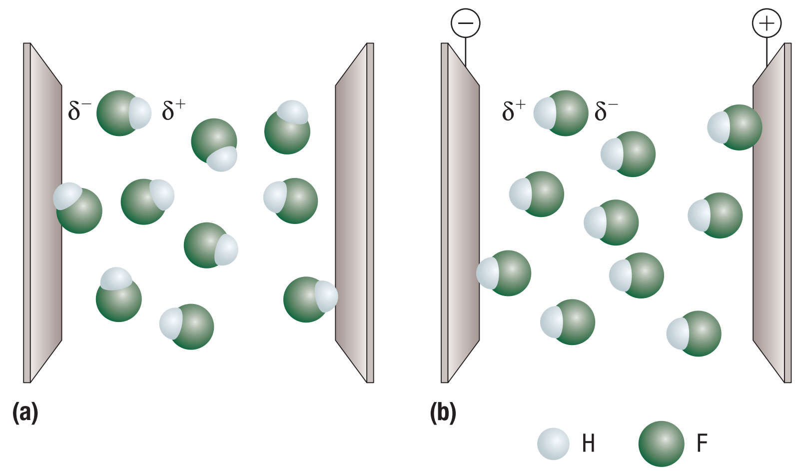

Figure 1 The effect of an electric field on hydrogen fluoride molecules. (a) When no electric field is present, the molecules are randomly oriented. (b) When the field is turned on, the molecules tend to line up with the negative end (fluorine) oriented toward the positive pole and the positive end (hydrogen) oriented toward the negative pole.

This result suggests that in the hydrogen fluoride molecule, the hydrogen and the fluorine atoms share electrons unequally. The symbol δ (lowercase Greek letter delta) represents a partial charge. The hydrogen atom in hydrogen fluoride has a partial positive charge, and the fluorine atom has a partial negative charge:

$$\underset{\delta^+}{\mathrm{H}}-\underset{\delta^-}{\mathrm{F}}$$

You can account for the polarity of the hydrogen fluoride molecule by stating that the fluorine atom has a stronger attraction for the shared electrons than the hydrogen atom does. Similarly, in a water molecule, H_2O, the oxygen atom attracts the shared electrons more strongly than do the hydrogen atoms (**Figure 2**). Bond polarity affects the chemical properties of molecules, so it is useful to quantify the ability of an atom to attract shared electrons.

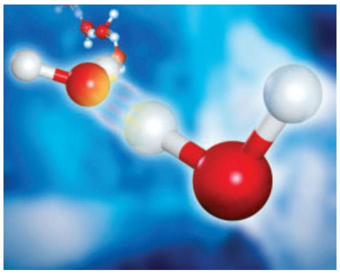

Figure 2 The polarity of the chemical bonds is responsible for some of the unique properties of water.

Electronegativity

electronegativity the ability of an atom in a molecule to attract shared electrons to itself

The **electronegativity** of an atom defines how strongly an atom attracts a pair of electrons it shares with another atom in a covalent bond. Atoms of different elements have different electronegativities.

Consider a hypothetical molecule, HY. If atoms H and Y have identical electronegativities, such as in a hydrogen molecule, H_2, then they share their bonding electrons equally. In general, when the electronegativity difference, ΔEN, between 2 atoms is very small or zero, the covalent bond between them is non-polar. When the electronegativity difference between 2 atoms is relatively large, such as in that of hydrogen fluoride, the covalent bond between them is polar, with a charge distribution as follows:

$$\underset{\delta^{+}}{H}-\underset{\delta^{-}}{Y}$$

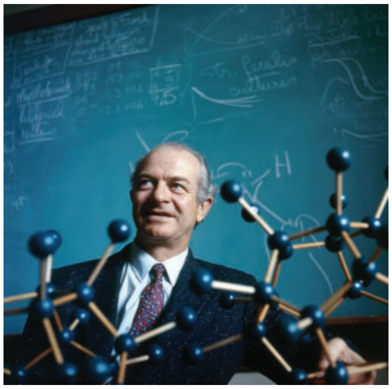

Figure 3 Linus Pauling (1901–1994) won the Nobel Prize in Chemistry for his work on the nature of chemical bonds.

Linus Pauling (**Figure 3**) created a method for determining the electronegativity values of atoms. His table of electronegativity values for all atoms is shown in **Figure 4**. Note that electronegativity generally increases from left to right across a period and decreases going down a group. Electronegativity values range from a high of 4.0 for fluorine (the most electronegative element) to a low of 0.7 for cesium (the least electronegative element). The scale is somewhat arbitrary, and other scientists have proposed slightly different values, based on various assumptions. You may notice that francium also has an electronegativity of 0.7. Due to its high radioactivity, francium is so rare in nature (as little as 20–30 g exists at any given time in Earth's crust) that, for all practical purposes, it is impossible to synthesize and test compounds containing francium. It is possible that francium's electronegativity is even lower than that of cesium.

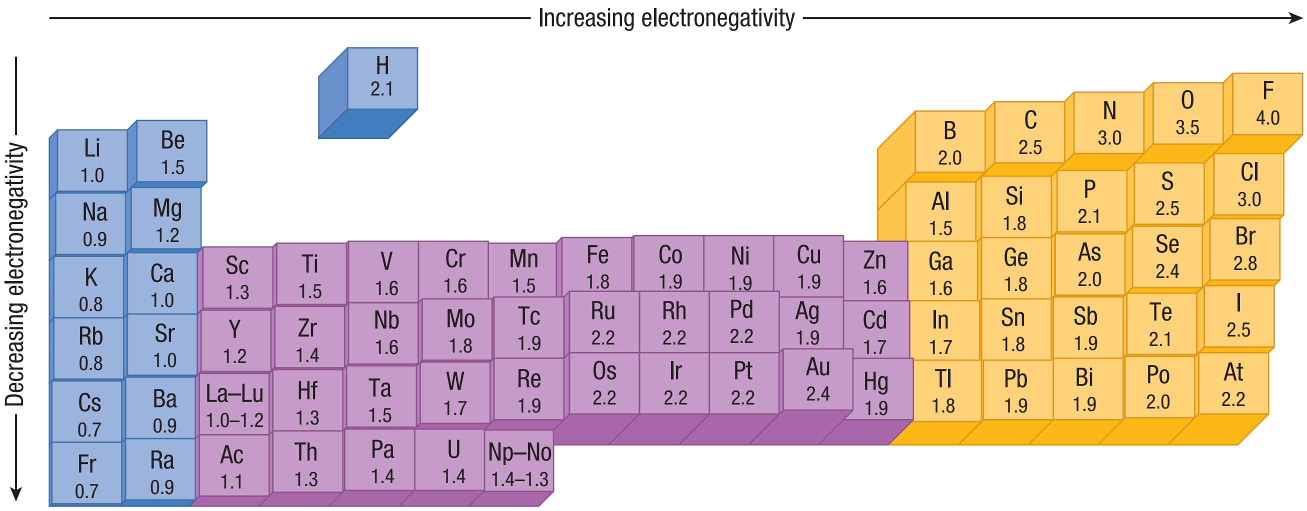

Figure 4 Electronegativity values as determined by Pauling. Electronegativity generally increases across a period and decreases down a group.

You can determine the relative electronegativities of 2 atoms by calculating the difference between their electronegativities. If 2 atoms have an electronegativity difference of less than 0.5, the bond between them is considered non-polar. If the electronegativity difference is 0.5 or greater, the bond is polar. Using Figure 4, you can determine the electronegativity difference for the polar covalent bond in hydrogen chloride, HCl, as follows:

$$\begin{aligned} \Delta EN &= EN_{Cl} - EN_{H} \\ &= 3.0 - 2.1 \\ \Delta EN &= 0.9 \end{aligned}$$

As a general rule, as the electronegativity difference increases, the ionic character of the bond increases. When the difference in electronegativity is greater than 1.7, the chemical bond is considered ionic. A chemical bond that has an electronegativity difference from 0.5 to 1.7 is considered polar covalent (see **Table 1** and **Figure 5**). Labelling bonds as non-polar covalent, polar covalent, or ionic according to these electronegativity difference boundaries is somewhat arbitrary. In reality, with the exception of molecular elements, all bonds are a mixture of covalent and ionic character, which results in the spectrum of values depicted graphically in Figure 5.

UNIT TASK BOOKMARK

As you work on the Unit Task on page 268, think about electronegativity. Does the trend change?

Table 1 Relationship between Electronegativity Difference and Bond Type

ΔEN	Bond type	Character
<0.5	non-polar covalent	covalent
0.5–1.7	polar covalent	covalent and ionic
>1.7	ionic	ionic

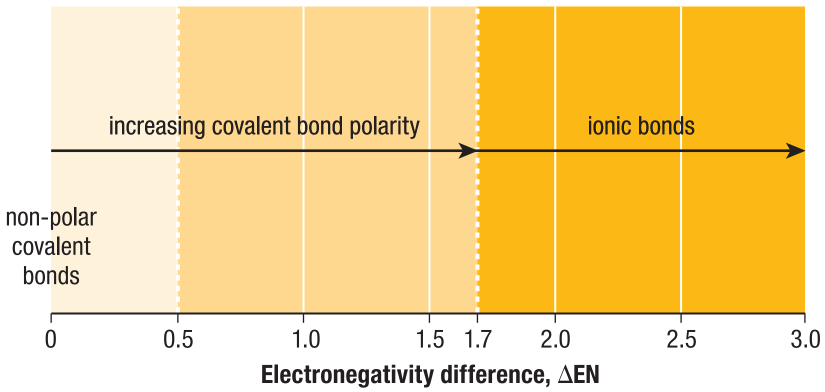

Figure 5 The difference in electronegativity between the atoms involved in bonding determines the character of the chemical bond. A small difference (≤1.7) indicates a covalent or polar covalent bond, and a large difference (>1.7) indicates an ionic bond.

Bond Polarities and Dipoles in Diatomic Molecules

When you place hydrogen fluoride gas in an electric field, the molecules orient themselves in a particular way (Figure 1, page 217)). This occurs because of the charge distribution in the hydrogen fluoride molecule, which has a positive end and a negative end. This separation of charges in a covalent bond is called a **dipole**. **Figure 6** shows the convention for representing a dipole in a diatomic molecule. Notice how an arrow points to the negatively charged end, while the tail of the arrow is in the region of the positively charged end. WEB LINK

dipole a separation of positive and negative charges in a region in space

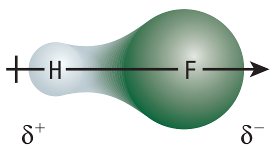

Figure 6 Space-filling view of hydrogen fluoride. The dipole of the hydrogen fluoride molecule is indicated by an arrow. This arrow is drawn so that its head points toward the negative region and its tail to the positive region.

Tutorial 1 Using Electronegativity Values to Predict Bond Polarity

In this Tutorial, you will predict relative bond polarities and the types of bonds based on the electronegativity difference of atoms.

Sample Problem 1: Predicting Relative Bond Polarity

List the following molecules in order of increasing predicted bond polarity: H–H, O–H, Cl–H, S–H, F–H

Solution

Step 1. Using the values in Figure 4, page 218, predict the difference in electronegativity between atoms.

$$\Delta EN_{H-H} = EN_H - EN_H$$
$$= 2.1 - 2.1$$
$$\Delta EN_{H-H} = 0$$
$$\Delta EN_{O-H} = EN_O - EN_H$$
$$= 3.5 - 2.1$$
$$\Delta EN_{O-H} = 1.4$$
$$\Delta EN_{O-H} = EN_{Cl} - EN_H$$
$$= 3.0 - 2.1$$
$$\Delta EN_{Cl-H} = 0.9$$
$$\Delta EN_{S-H} = EN_S - EN_H$$
$$= 2.5 - 2.1$$
$$\Delta EN_{S-H} = 0.4$$
$$\Delta EN_{F-H} = EN_F - EN_H$$
$$= 4.0 - 2.1$$
$$\Delta EN_{F-H} = 1.9$$

Step 2. List the bonds in order of smallest ΔEN to greatest ΔEN.

$\Delta EN_{H-H} = 0$; $\Delta EN_{S-H} = 0.4$; $\Delta EN_{Cl-H} = 0.9$;

$\Delta EN_{O-H} = 1.4$; $\Delta EN_{F-H} = 1.9$

Step 3. According to accepted theory, the polarity of a bond increases as the difference in electronegativity increases. Therefore, the order of these molecules according to their predicted bond polarity, from least to greatest, is

H–H < S–H < Cl–H < O–H < F–H

Sample Problem 2: Predicting the Polarity of a Chemical Bond

Determine the electronegativity difference, and classify the type of bond in the following pairs of atoms:
(a) N–H; (b) P–H; (c) K–Br

Solution

Step 1. Using Figure 4, page 218, predict the difference in electronegativity between atoms.

(a) $\Delta EN_{N-H} = EN_N - EN_H$
$$= 3.0 - 2.1$$
$$\Delta EN_{N-H} = 0.9$$

(b) $\Delta EN_{P-H} = EN_P - EN_H$
$$= 2.1 - 2.1$$
$$\Delta EN_{P-H} = 0$$

(c) $\Delta EN_{K-Br} = EN_{Br} - EN_K$
$$= 2.8 - 0.8$$
$$\Delta EN_{K-Br} = 2.0$$

Step 2. Use Table 1, page 219, to classify the type of bond in each compound.

(a) $\Delta EN_{N-H} = 0.9$

Since $0.5 < \Delta EN < 1.7$, this bond is a polar covalent bond.

(b) $\Delta EN_{P-H} = 0$

Since $\Delta EN < 0.5$, this bond is a non-polar covalent bond.

(c) $\Delta EN_{K-Br} = 2.0$

Since $\Delta EN > 1.7$, this bond is an ionic bond.

Practice

1. Use the electronegativity differences between atoms to classify each of the following bonds as polar covalent, non-polar covalent, or ionic: T/I
   (a) C–F
   (b) P–Cl
   (c) Li–Cl
2. Arrange the bonds in the following sets of atom pairs in order of increasing bond polarity: T/I A
   (a) B–H, H–H, C–H, H–F, O–H, Na–H, Mg–H
   (b) Al–Cl, P–Cl, Li–Cl, Cl–Cl, I–Cl, Rb–Cl
   (c) C–H, C–F, C–Cl, C–O, C–S, C–C

4.3 Review

Summary

- The electronegativity of an atom is the relative ability of the atom to attract shared electrons.
- The polarity of a bond increases as the electronegativity difference increases.
- A diatomic molecule with a polar bond has a region of positive and negative charge, called a dipole.
- The charges in a dipole will orient themselves in an electric field.
- The electronegativity difference, ΔEN, of bonded atoms can be used to predict bond type. The bond will likely be ionic when $\Delta EN > 1.7$, polar covalent when $0.5 \leq \Delta EN \leq 1.7$, and non-polar covalent when $0 < \Delta EN < 0.5$.

Questions

1. Arrange each of the following in order of increasing electronegativity: K/U
   (a) C, N, O
   (b) S, Se, Cl
   (c) Si, Ge, Sn
   (d) Tl, S, Ge
2. If you did not have access to a set of values of the electronegativities of atoms similar to Figure 4, how could you use the periodic table to determine the polarity of a chemical bond? K/U
3. Without using Figure 4 (you can use a periodic table), determine the bond type between each of the following atoms: K/U
   (a) C–O
   (b) F–I
   (c) Li–F
   (d) Ge–Sn
   (e) Al–Cl
4. Without using Figure 4, predict which bond in each of the following groups will be the most polar. Explain your answer. K/U T/I
   (a) C–F, Si–F, Ge–F
   (b) P–Cl or S–Cl
   (c) S–F, S–Cl, S–Br
   (d) Be–Cl, Mg–Cl, Ca–Cl
5. Referring to the electronegativities of the atoms in the bond, describe how the bonds K–Br, C–Br, and Br–Br are different. K/U
6. By indicating the partial positive and partial negative atoms, show the bond polarity for each of the following molecules: K/U C
   (a) O–F
   (b) Br–Br
   (c) C–Br
   (d) C–O
7. For each of the following, state whether the bond polarity is shown correctly. If not, show the bond polarity correctly. K/U T/I C
   (a) $\delta^{+}H{-}Br\delta^{-}$
   (b) $\delta^{+}Cl{-}I\delta^{-}$
   (c) $\delta^{+}Si{-}S\delta^{-}$
   (d) $\delta^{+}F{-}F\delta^{-}$
   (e) $\delta^{+}O{-}P\delta^{-}$
8. (a) Determine the electronegativity difference between C and F.
   (b) What type of bond is the C–F bond?
   (c) When you place molecules of CF_4 in an electric field, the molecules do not display any particular orientation. Explain why. K/U T/I
9. An atom, when bonded to nitrogen, results in a polar covalent bond, with nitrogen having a partial positive charge. K/U T/I
   (a) List all possible atoms that this atom could be.
   (b) Which of the atoms listed in (a) would result in the most polar bond?
   (c) Which atoms, when bonded to nitrogen, would result in a non-polar covalent bond?
10. Predict the type of bond (ionic, non-polar covalent, or polar covalent) that would be expected to form between each pair of atoms: K/U T/I
    (a) Rb and Cl
    (b) S and S
    (c) C and F
    (d) Ba and C
    (e) B and Se
    (f) Cs and Br