Skills to Develop

- Define electronegativity and assess the polarity of covalent bonds

Video \(\PageIndex{1}\): A preview of electronegativity's role in molecular polarity.

Electronegativity Review

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called electronegativity. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure \(\PageIndex{1}\) shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling. In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO\(_2\) do exist, they can only be formed under extreme conditions, and thus they do not fit neatly
Linus Pauling

Linus Pauling is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.

Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a
bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure \(\PageIndex{2}\) shows the relationship between electronegativity difference and bond type.

![Figure \(\PageIndex{2}\): As the electronegativity difference increases between two atoms, the bond becomes more ionic.](image)

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure \(\PageIndex{4}\). This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH\(_3\) a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI\(_2\) have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH\(^-\), NO\(_3^-\), and NH\(_4^+\)), are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO\(_3\), contains the K\(^+\) cation and the polyatomic NO\(_3^-\) anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K\(^+\) and NO\(_3^-\), as well as covalent between the nitrogen and oxygen atoms in NO\(_3^-\).

Example \(\PageIndex{1}\): Electronegativity and Bond Polarity
Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Table A2, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ−:

\[ \text{C–H, C–N, C–O, N–H, O–H, S–H} \]

**Solution**

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ− designation is the more electronegative of the two. Table \( \PageIndex{1} \) shows these bonds in order of increasing polarity.

<table>
<thead>
<tr>
<th>Bond</th>
<th>ΔEN</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H</td>
<td>0.4</td>
</tr>
<tr>
<td>S–H</td>
<td>0.4</td>
</tr>
<tr>
<td>C–N</td>
<td>0.5</td>
</tr>
<tr>
<td>N–H</td>
<td>0.9</td>
</tr>
<tr>
<td>C–O</td>
<td>1.0</td>
</tr>
<tr>
<td>O–H</td>
<td>1.4</td>
</tr>
</tbody>
</table>

**Exercise \( \PageIndex{1} \)**

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure \( \PageIndex{3} \), arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ−.

**Answer**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Electronegativity Difference</th>
<th>Polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>0.0</td>
<td>nonpolar</td>
</tr>
<tr>
<td>C–H</td>
<td>0.4</td>
<td>( \overset{\delta-}{\text{C}} )–\overset{\delta+}{\text{H}} )</td>
</tr>
<tr>
<td>Si–C</td>
<td>0.7</td>
<td>( \overset{\delta+}{\text{Si}} )–\overset{\delta-}{\text{C}} )</td>
</tr>
<tr>
<td>Si–O</td>
<td>1.7</td>
<td>( \overset{\delta+}{\text{Si}} )–\overset{\delta-}{\text{O}} )</td>
</tr>
</tbody>
</table>
Video \( \PageIndex{2} \): Water is a unique polar molecule.
Summary

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**Video \(\PageIndex{3}\):** A review of electronegativity.

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

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**Glossary**

**bond length**

distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

**covalent bond**

bond formed when electrons are shared between atoms

**electronegativity**

tendency of an atom to attract electrons in a bond to itself
**polar covalent bond**
covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

**pure covalent bond**
(also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

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