Learning Objectives

• To define electronegativity and bond polarity
• To calculate the percent ionic character of a covalent polar bond

The electron pairs shared between two atoms are not necessarily shared equally. For example, while the shared electron pairs is shared equally in the covalent bond in \( \text{Cl}_2 \), in \( \text{NaCl} \) the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual \( \text{Na}^+ \) and \( \text{Cl}^- \) ions (ionic bonding). For most covalent substances, their bond character falls between these two extremes. We demonstrated below, the bond polarity is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A nonpolar covalent bond is one in which the electrons are shared equally between two atoms.
- A polar covalent bond is one in which one atom has a greater attraction for the electrons than the other atom. If this relative attraction is great enough, then the bond is an ionic bond.

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table (compare Figure 7.4.2 and Figure 7.4.2). Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called electronegativity (represented by the Greek letter chi, \( \chi \), pronounced “ky” as in “sky”), defined as the relative ability of an atom to attract electrons to itself in a chemical compound. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

Note

Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The greater the value, the greater the attractiveness for electrons.
Electronegativity is a function of: (1) the atom’s *ionization energy* (how strongly the atom holds on to its own electrons) and (2) the atom’s *electron affinity* (how strongly the atom attracts other electrons). Both of these are properties of the *isolated* atom. An element that is will be *highly electronegative* has:

- a large (negative) electron affinity
- a high ionization energy (always endothermic, or positive for neutral atoms)

and will

- attract electrons from other atoms
- resist having its own electrons attracted away.

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**The Pauling Electronegativity Scale**

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901–1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

![Figure 10.3.1: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table](image)

*Figure 10.3.1: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table*

Periodic variations in Pauling’s electronegativity values are illustrated in Figure 10.3.1 and Figure 10.3.2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).
Linus Pauling (1901-1994)

Pauling won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962. When he was nine, Pauling’s father died, and his mother tried to convince him to quit school to support the family. He did not quit school but was denied a high school degree because of his refusal to take a civics class.

Pauling’s method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem (e.g., the Mulliken electronegativity scale).
Electronegativity Differences between Metals and Nonmetals

An element’s electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity ($\chi \geq 2.2$) have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are oxidants). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are reductants). In between the metals and nonmetals, along the heavy diagonal line running from B to At is a group of elements with intermediate electronegativities ($\chi \sim 2.0$). These are the semimetals (or metalloids), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure 10.3.3 shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

**Figure 10.3.3: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements.** (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values ($\geq$ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values ($\leq$ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).

Note

Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

**Example 10.3.1**

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

**Given:** four elements
**Asked for:** order by increasing electronegativity and classification

**Strategy:**

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.

B. Arrange the elements in order of increasing electronegativity.

C. Classify each element as a metal, a nonmetal, or a semimetal according to its location about the diagonal belt of semimetals running from B to At.

**Solution:**

A Electronegativity increases from lower left to upper right in the periodic table (Figure 10.3.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{\text{Cl}} > \chi_{\text{Se}}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. B The overall order is therefore $\chi_{\text{Sr}} < \chi_{\text{Si}} < \chi_{\text{Se}} < \chi_{\text{Cl}}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of semimetals running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a semimetal, and Se and Cl are nonmetals.

**Exercise 10.3.1**

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

**Answer:** Rb < Zr < Ge < N < O; metals (Rb, Zr); semimetal (Ge); nonmetal (N, O)

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**Percent Ionic Character of a Covalent polar bond**

The two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds, which means that electrons are shared unequally between the bonded atoms. Figure 10.3.4 compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (\(\delta\)) is used to indicate that a bonded atom possesses a partial positive charge, indicated by \(\delta^+\), or a partial negative charge, indicated by \(\delta^-\), and a bond between two atoms that possess partial charges is a polar bond.
The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. Electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is nonpolar if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is polarized toward the more electronegative atom. A bond in which the electronegativity of B (χB) is greater than the electronegativity of A (χA), for example, is indicated with the partial negative charge on the more electronegative atom:

\[
\begin{matrix}
\text{less electronegative} & \text{more electronegative} \\
A\; & - & B
\end{matrix}
\tag{10.3.1}
\]

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: \( \Delta \chi = \chi_B - \chi_A \).

To predict the polarity of the bonds in Cl₂, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms.
atoms: $\chi_{\text{Cl}} = 3.16$, $\chi_{\text{H}} = 2.20$, and $\chi_{\text{Na}} = 0.93$ (see Figure 3.3.2). $\text{Cl}_2$ must be nonpolar because the electronegativity difference ($\Delta \chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta \chi$ is 2.23. This high value is typical of an ionic compound ($\Delta \chi \geq 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form $\text{Na}^+$ and $\text{Cl}^-$ ions. In HCl, however, $\Delta \chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

\[
\begin{matrix}
\delta^+ & & \delta^-\\
H & - & Cl
\end{matrix}
\]

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

**Note**

Bond polarity and ionic character increase with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl$_2$, ClF$_5$, and HClO$_4$ would be exactly the same.

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**Dipole Moments as a Measure of Bond Polarity**

The asymmetrical charge distribution in a polar substance such as HCl produces a **dipole moment** where $\langle Qr \rangle$ in meters ($\text{m}$), is abbreviated by the Greek letter mu ($\mu$). The dipole moment is defined as the product of the partial charge $Q$ on the bonded atoms and the distance $r$ between the partial charges:

\[
\mu = Qr \quad \text{(10.3.2)}
\]

where $Q$ is measured in coulombs ($\text{C}$) and $r$ in meters. The unit for dipole moments is the debye ($\text{D}$):

\[
1 \text{ D} = 3.3356 \times 10^{-30} \text{ C} \cdot \text{m} \quad \text{(10.3.3)}
\]

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 10.3.2).
Figure 10.3.5: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 10.3.2. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

\[
Q = \frac{\mu}{r} = 1.109 \, \text{D} \left( \frac{3.3356 \times 10^{-30} \, \text{C} \cdot \text{m}}{1 \, \text{D}} \right) \left( \frac{1}{127.8 \, \text{pm}} \right) \left( \frac{1 \, \text{pm}}{10^{-12} \, \text{m}} \right) = 2.901 \times 10^{-20} \, \text{C}
\tag{10.3.4}
\]

By dividing this calculated value by the charge on a single electron (1.6022 \times 10^{-19} \, \text{C}), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 \, \text{e}^−. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

\[
\frac{2.901 \times 10^{-20} \, \text{C}}{1.6022 \times 10^{-19} \, \text{C}} = 0.1811 \, \text{e}^-
\tag{10.3.5}
\]

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 \times 100), or 82% covalent character.
Instead of writing HCl as

\[
\begin{pmatrix}
\delta^+ & \delta^- \\
H & - & Cl
\end{pmatrix}
\]

we can therefore indicate the charge separation quantitatively as

\[
\begin{pmatrix}
0.18\delta^+ & 0.18\delta^- \\
H & - & Cl
\end{pmatrix}
\]

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine $\chi_H = 2.20; \chi_{Cl} = 3.16, \chi_{Cl} - \chi_{H} = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule. Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:

\[\text{H} \longrightarrow \text{Cl}\]

The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure 10.3.6 shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure 10.3.6 show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 11.
Figure 10.3.6: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms. In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 10.3.2

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

**Given:** chemical species, dipole moment, and internuclear distance

**Asked for:** percent ionic character

**Strategy:**

A Compute the charge on each atom using the information given and Equation 10.3.2.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

**Solution:**

A The charge on each atom is given by

\[
Q = \frac{\mu}{r} = 9.001 \text{ D} \left( \frac{3.3356 \times 10^{-30} \text{ C} \cdot \text{m}}{1 \text{ D}} \right) \left( \frac{1}{236.1 \text{ pm}} \right) \left( \frac{1 \text{ pm}}{10^{-12} \text{ m}} \right) = 1.272 \times 10^{-19} \text{ C}
\]

Thus NaCl behaves as if it had charges of $1.272 \times 10^{-19}$ C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

\[
\% \text{ ionic character} = \left( \frac{1.272 \times 10^{-19} \text{ C}}{1.6022 \times 10^{-19} \text{ C}} \right) \times 100
\]
Exercise 10.3.2

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer: 55.5%

Electrostatic Potential Maps

Electrostatic potential maps convey information about the charge distribution of a molecule because of the properties of the nucleus and nature of electrostatic potential energy. A region of higher than average electrostatic potential energy indicates the presence of a stronger positive charge or a weaker negative charge. Given the positive charge of the nuclei, the higher potential energy value indicates the absence of negative charges (less screening of the nuclei), which would mean that there are fewer electrons in this region. The converse is also true with a low electrostatic potential indicating an abundance of electrons. This property of electrostatic potentials can be extrapolated to molecules as well.

Note: Constructing a Electrostatic Potential Map

The first step involved in creating an electrostatic potential map is collecting a very specific type of data: electrostatic potential energy. An advanced computer program calculates the electrostatic potential energy at a set distance from the nuclei of the molecule. Electrostatic potential energy is fundamentally a measure of the strength of the nearby charges, nuclei, and electrons, at a particular position. To accurately analyze the charge distribution of a molecule, a very large quantity of electrostatic potential energy values must be calculated. The best way to convey this data is to visually represent it, as in an electrostatic potential map. A computer program then imposes the calculated data onto an electron density model of the molecule. To make the electrostatic potential energy data easy to interpret, a color spectrum, with red as the lowest electrostatic potential energy value and blue as the highest, is employed to convey the varying intensities of the electrostatic potential energy values.

The most important thing to consider when analyzing an electrostatic potential map is the charge distribution. The relative
distributions of electrons will allow you to deduce everything you need to know from these maps. Recall the relationship between electrostatic potential and charge distribution. Areas of low potential, red, are characterized by an abundance of electrons. Areas of high potential, blue, are characterized by a relative absence of electrons. Oxygen has a higher electronegativity value than sulfur (Table A2), hence oxygen atoms would have a higher electron density around them than sulfur atoms. Thus the spherical region that corresponds to an oxygen atom would have a red portion on it. Now note that there are two oxygen atoms in sulfur dioxide (Figure 10.3.7). There are two sphere shaped objects that have red regions. These areas correspond to the location of the oxygen atoms. The blue tainted sphere at the top corresponds to the location of the sulfur atom.

![Figure 10.3.7. The electrostatic diagram of Sulfur Dioxide (\(SO_2\)). Which parts of this diagram correlate to the respective atomic components? Red indicates the lowest electrostatic potential energy, and blue indicates the highest electrostatic potential energy. Intermediary colors represent intermediary electrostatic potentials.](image)

**Note**

A high electrostatic potential indicates the relative absence of electrons and a low electrostatic potential indicates an abundance of electrons.

Electrostatic potential maps can also be used to determine the nature of the molecules chemical bond. Consider \((SO_2)\) in Figure 10.3.7, there is a great deal of intermediary potential energy, the non red or blue regions, in this diagram. This indicates that the electronegativity difference is not very great. In a molecule with a great electronegativity difference, charge is very polarized, and there are significant differences in electron density in different regions of the molecule. This great electronegativity difference leads to regions that are almost entirely red and almost entirely blue. Greater regions of intermediary potential, yellow and green, and smaller or no regions of extreme potential, red and blue, are key indicators of a smaller electronegativity difference. Note that the electronegativity difference is a key determinant in the nature of a chemical bond.

**Example 10.3.3**

The following electrostatic potential map of phosphoric acid \((H_3PO_4)\). What regions correspond to atoms of oxygen, hydrogen, and phosphorous respectively?
You do not need to know the molecular structure to answer this question. You do need to know the relative electronegative values of these atoms (Table A4).

- Oxygen has the greatest electronegative value,
- Phosphorous the second most, and
- Hydrogen has the smallest electronegative value.

Simply by knowing this, you can deduce that oxygen would be affiliated with the red region or redish regions of the diagram, and hydrogen would be affiliated with the blue region. Phosphorous would fall in between these two extremes, in the green region.

Here is the molecular diagram of phosphoric acid:

\[ \mu = Qr \tag{10.3.2} \]

**Summary**

- Bond polarity and ionic character increase with an increasing difference in electronegativity.

**Dipole moment**

\[ \mu = Qr \tag{10.3.2} \]

The *electronegativity* (χ) of an element is the relative ability of an atom to attract electrons to itself in a chemical
compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

Compounds with polar covalent bonds have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativities of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a dipole moment, which is the product of the partial charges on the bonded atoms and the distance between them.