5.2.8: Polar Covalent Bonds and Electronegativity

Learning Objectives

- Describe electronegativity and polarity.
- Use electronegativity values to predict bond polarity.

Our discussions of bonding thus far have focused on two types, ionic and covalent. In ionic bonds, like $NaCl$, electrons are *transferred*; 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 Na^+ and Cl^- ions. In covalent bonding, unpaired electrons from individual atoms are *shared* in order to fill the valence shell of each atom. When a covalent bond is formed between the same type of atoms, such as Cl_2, the electrons are *shared equally* between the two. However, when a covalent bond is formed between different types of atoms, the electrons are not necessarily shared equally. In these compounds their bond character falls *between* the two extremes: transferred and shared equally.

Bond Polarity

As demonstrated below, **bond polarity** is a useful concept for describing the sharing of electrons between atoms, within a covalent bond:

- A **nonpolar covalent bond** (Figure $5.2.8.1a$) is one in which the electrons are shared *equally* between two atoms.
- A **polar covalent bond** (Figure $5.2.8.1b$) is one in which one atom has a greater attraction for the electrons than the other atom.
- If the relative attraction of an atom for electrons is great enough, then the bond is an **ionic bond (**Figure $5.2.8.1c$).

Electron density in a polar bond is distributed unevenly and is greater around the atom that attracts the electrons more than the other. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Note that the shaded area around Cl in Figure $5.2.8.1b$ is much larger than it is around H. This imbalance in electron density results in a buildup of *partial negative charge* (designated as δ−) on one side of the bond (Cl) and a *partial positive charge* (designated δ+) on the other side of the bond (H).

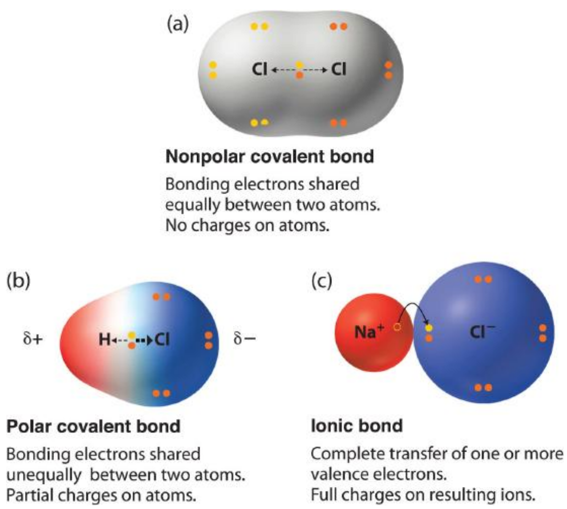


Figure $5.2.8.1$: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Any covalent bond between atoms of different elements is a polar bond, but the degree of polarity varies widely. Some bonds between different elements are only minimally polar, while others are strongly polar. Ionic bonds can be considered the ultimate in polarity, with electrons being transferred rather than shared. To judge the relative polarity of a covalent bond, chemists use electronegativity, which is a relative measure of how strongly an atom attracts electrons when it forms a covalent bond.

Electronegativity

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**, 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.

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 will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always positive for neutral atoms). Thus, it will attract electrons from other atoms and resist having its own electrons attracted away.

> *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.*

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.

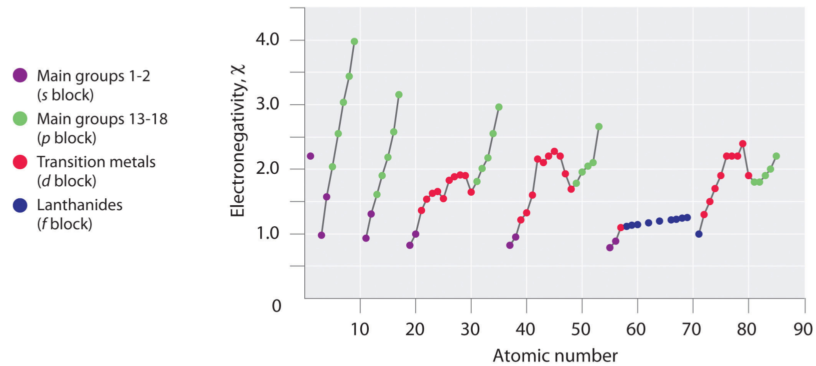


Figure 5.2.8.2: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

The main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

Periodic variations (trends) in Pauling's electronegativity values are illustrated in Figures 5.2.8.2and 5.2.8.3. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine is the most electronegative element and cesium is the least electronegative nonradioactive element. 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).

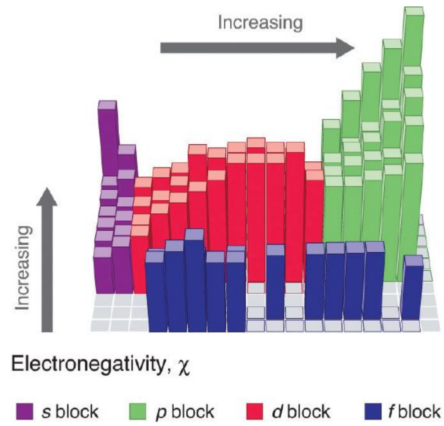


Figure 5.2.8.3: Pauling Electronegativity Values of the *s*-, *p*-, *d*-, and *f*-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (1960).

The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electronegativity increase from bottom to top and left to right.

The polarity of a covalent bond can be judged by determining the difference in the electronegativities of the two atoms making the bond. The greater the difference in electronegativities, the greater the imbalance of electron sharing in the bond. Although there are no hard and fast rules, the general rule, (see Figure 5.2.8.5), is if the difference in electronegativities is less than about 0.4, the bond is considered nonpolar; if the difference is greater than 0.4, the bond is considered polar. If the difference in electronegativities is large enough (generally greater than about 1.8), the resulting compound is considered ionic rather than covalent. An electronegativity difference of zero, of course, indicates a nonpolar covalent bond.

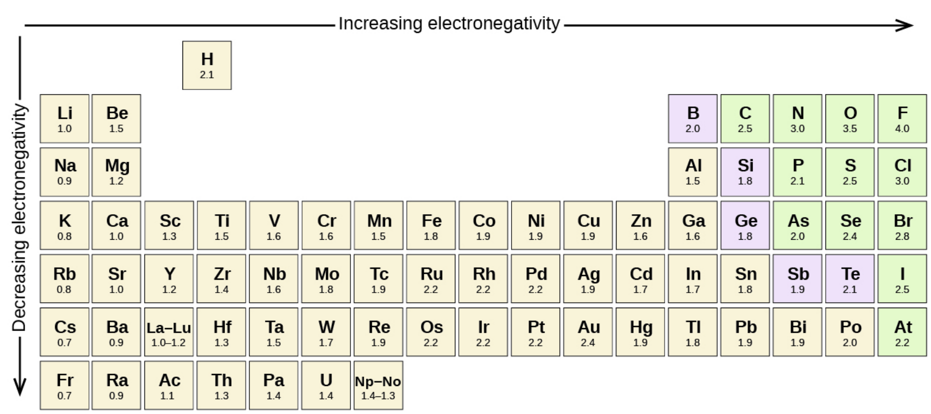
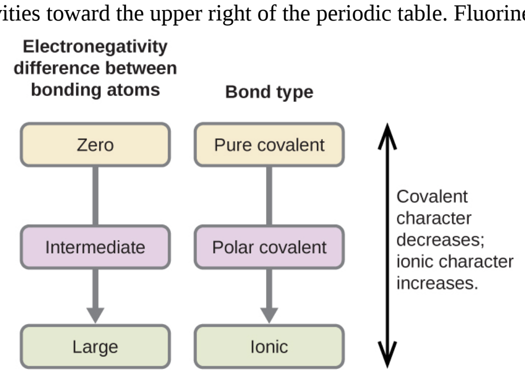


Figure 5.2.8.4 The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table. Fluorine has the highest value (4.0).



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 5.2.8.5: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

Example 5.2.8.1

Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type).

a. C and H
b. H and H
c. Na and Cl
d. O and H

Solution

a. Carbon has an electronegativity of 2.5, while the value for hydrogen is 2.1. The difference is 0.4, which is rather small. The C–H bond is therefore considered nonpolar.
b. Both hydrogen atoms have the same electronegativity value—2.1. The difference is zero, so the bond is nonpolar.
c. Sodium's electronegativity is 0.9, while chlorine's is 3.0. The difference is 2.1, which is rather high, and so sodium and chlorine form an ionic compound.
d. With 2.1 for hydrogen and 3.5 for oxygen, the electronegativity difference is 1.4. We would expect a very polar bond. The sharing of electrons between O and H is unequal with the electrons more strongly drawn towards O.

Exercise 5.2.8.1

Describe the electronegativity (EN) difference between each pair of atoms and the resulting polarity (or bond type).

a. C and O
b. K and Br
c. N and N
d. Cs and F

Answer a:

The EN difference is 1.0 , hence polar. The sharing of electrons between C and O is unequal with the electrons more strongly drawn towards O.

Answer b:

The EN difference is greater than 1.8, hence ionic.

Answer c:

Identical atoms have zero EN difference, hence nonpolar.

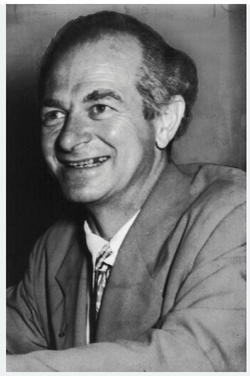
Answer d:

The EN difference is greater than 1.8, hence ionic.

Looking Closer: Linus Pauling

Arguably the most influential chemist of the 20th century, Linus Pauling (1901–94) is the only person to have won two individual (that is, unshared) Nobel Prizes. In the 1930s, Pauling used new mathematical theories to enunciate some fundamental principles of the chemical bond. His 1939 book *The Nature of the Chemical Bond* is one of the most significant books ever published in chemistry.

By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.) He was later awarded the 1962 Nobel Peace Prize for his efforts to ban the testing of nuclear weapons.



Linus Pauling was one of the most influential chemists of the 20th century.

In his later years, Pauling became convinced that large doses of vitamin C would prevent disease, including the common cold. Most clinical research failed to show a connection, but Pauling continued to take large doses daily. He died in 1994, having spent a lifetime establishing a scientific legacy that few will ever equal.
