2.1.2: Electronegativity and the Bonding Continuum

Electronegativity

Electronegativity is the measure of the ability of an atom to attract electrons within a chemical bond. It is related to the electron affinity in the sense that both period properties measure the force by which an electron is attracted to a neutral atom. However, the electron affinity is associated with isolated atoms, that do not make bonds to neighbored atoms, while the electronegativity refers to atoms that are bonded to neighbored atoms. The importance of the electronegativity stems largely from its ability to predict and understand the nature of the bonding between atoms, in particular, covalent, ionic, and metallic bonding.

Pauling Electronegativity Scale

Electronegativity was a concept first developed by Linus Pauling to describe the relative polarity of bonds and molecules. He argued that the electronegativity of an atom could be derived from bond energy differences between homoleptic and heteroleptic bonds (Eq. 1.3.1).

$$\chi(A)-\chi(B) = c\,[(E(A-B) - \{E(A-A)\cdot E(B-B)\}^{1/2}), \text{ eV}].$$

Here E(A-B), E(A-A) and E(B-B) are energies of A-B, A-A and B-B bonds respectively.
c is a constant.

Equation 1.3.1 Electronegativity according to Pauling, eV = electron volts.

For example, the energy required to break the bond in H_2 is 432 kJ mol^{-1}, and for F_2 it is 159 kJ mol^{-1}. However the energy required to break a bond in HF is 565 kJ mol^{-1}, which is much higher than expected just by averaging the energy of the two homonuclear bonds (296 kJ mol^{-1}). Pauling argued that the difference could be assigned to electrostatic attractions between the F and H “ends” of the molecule whereby the F end has more electron density and the H end has less electron density. The greater the difference between the average energy of the homoleptic bonds and the heteroleptic bonds, the greater the electronegativity difference between the atoms, and the greater the polarity of the heteroleptic bond.

First, Pauling used the arithmetic means of the heteroleptic bond energies, later he used the geometric means, because he found empirically that it worked better (Equation 1.3.1). The geometric mean of the homoleptic bond energies is the square root of the product of the homoleptic bond energies. This method only provided electronegativity differences. He therefore needed to define a reference atom with an arbitrarily defined electronegativity value, and then determine the electronegativity values of all other atoms relative to that value. He chose the most electronegative atom, the fluorine atom, as the standard and assigned a value of 4.0. The values of all other atoms vary between 0.7 (Fr) and 3.44 (O), and are shown in the periodic table on the below (Fig. 1.3.6).

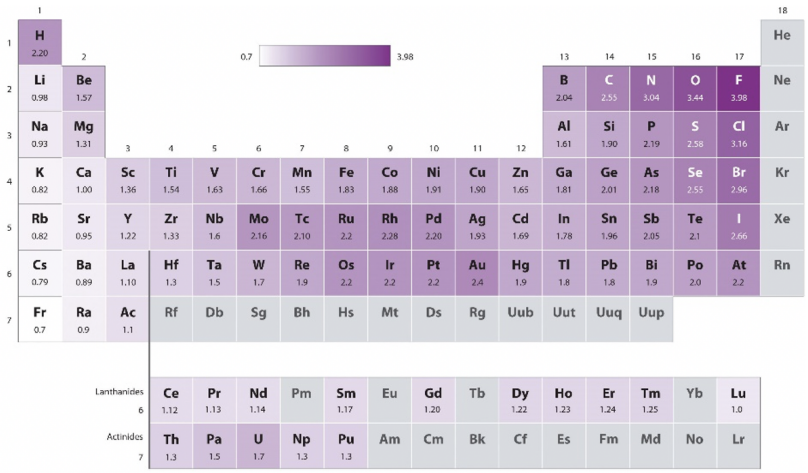

Figure 1.3.6 Periodic trends of electronegativity (Attribution: Chemlibretexts https://chem.libretexts.org/@api/dek...jpg?revision=1 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

What are the periodic trends? One can see that within a period the electronegativity values of the main group elements strictly increase with the group number. Note though that the noble gases do not have a Pauling electronegativity because, with few exceptions, noble gases do not make compounds and thus no bond energies are available for them. We can also see that for main group elements the electronegativity strictly decreases down a group. This makes the fluorine the most electronegative atom, and

the cesium the least electronegative atom. Cesium has an electronegativity value of 0.7. We ignore the radioactive francium here. For the d-block, the trends are less strict, but there is a tendency of electronegativity increase from group 3 to group 11. All group 12 elements have smaller electronegativities compared to their neighbored group 11 elements. What about trends within a group? In group 3 to group 5 there is a small decrease in electronegativity down a group. For group 6 and 9, the period 5 elements have higher values than their neighbored elements in period 4 and 6. For group 10 to 12 the electronegativity increases down a group. The d-block element with the highest electronegativity is the gold, it has a value of 2.4. Note that this is similar to the electronegativity of non-metals such as I, S, and P. For these reasons, sometimes gold can behave like a non-metal in compounds with very low electronegativity. For example, there is the compound cesium auride (CsAu) which is a transparent, ionic crystalline compound due to the high electronegativity difference between cesium and gold. The f-block elements generally have low electronegativity.

Allred-Rochow Electronegativity Scale

The Pauling electronegativity scale is derived from empirical data on bond energies. It works very well in practice and it is up to date the most used electronegativity scale. However, it does not to relate electronegativity to other periodic properties, and the quantum-mechanical model of the atoms. One electronegativity scale that addresses this short-coming the Allred-Rochow scale. It relates the electronegativity to the Coulomb force that acts on an electron on the surface of an atom. The Coulomb force is proportional to the effective nuclear charge Z* and inverse proportional to the atomic radius square. Z^*/r^2 is multiplied with a factor of 3590 and a value of 0.744 is added to this term. These numbers are empirically chosen so that the values of the Allred-Rochow scale become comparable to the Pauling scale.

$$\text{Allred-Rochow: } \chi = [0.744+3590 \cdot Z^*/r^2]$$

Here Z^* is effective nuclear charge and r is atomic radius.

Equation 1.3.2 Allred-Rochow definition of electronegativity

Mulliken Electronegativity Scale

Another frequently used scale is the Mulliken electronegativity scale. The Mulliken scale relates the electronegativity to the sum of the first ionization energy IE and the first electron affinity EA. We would intuitively agree that the ability of an atom to attract electrons within a chemical bond is the higher, the harder it is to remove an electron from an isolated atom, and the easier it is to add an electron to an isolated atom. The numbers 0.118 and -0.207 are empirically chosen to make comparisons to the Pauling scale possible. The Mulliken scale is related to the Allred-Rochow scale in the sense that you can explain ionization energies and electron affinities of atoms with the concept of the effective nuclear charge.

$$\text{Mulliken: } \chi = [0.118 \cdot (IE+EA)-0.207]$$

Here IE is ionization energy and EA is electron affinity of an atom

Equation 1.3.3 Mulliken definition of electronegativity

Allen Electronegativity Scale

Another electronegativity scale has been developed by Leland C. Allen. It designed for main group elements in particular. It argues that the electronegativity is proportional to the average energy of the s and p valence electrons in the atom. This electronegativity concept also has a relationship to that of Allred-Rochow, because orbital energies can be calculated from the effective nuclear charge.

$$\text{Allen: } \chi = [(me_p+ne_s)/(m+n)]$$

Here e_p is the energy of p-electrons and e_s is the energy of s-electrons; m and n are populations of p- and s-orbitals respectively.

Equation 1.3.4 Leland C. Allen definition of electronegativity

Overall, you can see that the electronegativity scales are inter-related, they say essentially the same, but present electronegativity from a somewhat different perspective.

Electronegativity of the Elements and Chemical Bonding

One of the most powerful attributes of electronegativity is that it can predict what type of chemical bond is to expect in elements and compounds. Let us first look at the bonding between elements.

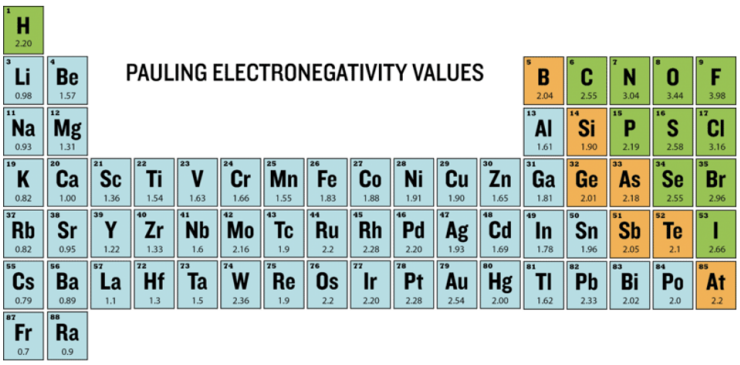

Figure 1.3.7 Pauling electronegativity values for the elements (Attribution: Ck12.org https://www.ck12.org/flx/show/default/image/user%3Ack12editor/20141124141684723269001l_ab8840393ea93a2a7c9fc01e395da3b2-20141124141684756943010 7.png https://creativecommons.org/licenses/by-nc/3.0/legalcode)

In the depicted periodic table (Figure 1.3.7) you can see the type of chemical bonding between atoms indicated by different colors. There is metallic bonding in metals, indicated by the color blue. In metallic bonds the electrons are shared between atoms but are delocalized over many atoms in the metal. The green color indicates covalent bonding seen in non-metals. In covalent bonding the electrons are shared, but localized in between typically two atoms. Metalloids have chemical bonding with a mix of covalent and metallic character shown in orange. There is electron-sharing with a moderate degree of delocalization. The Pauling electronegativity values of the elements are written underneath the element symbols.

Can we relate the electronegativity values to the chemical bonding in the elements? We can clearly see that elements with high electronegativity values significantly above 2.0, the non-metals, tend to make covalent bonds in between them. All metalloids with a hybrid covalent-metallic character, have intermediate electronegativity around 2.0. Most metals have low electronegativity values below 2.0 except noble metals like Pt and Au. Overall, we can say that there is a clear relationship between the bonding type in an element and its electronegativity. Now let us see if electronegativity can also predict chemical bonding in compounds.

Ketelaar's Triangle

The ability of electronegativity to predict the bonding type in compounds can be understood by Ketelaar's triangle, named after J.A.A. Ketelaar.

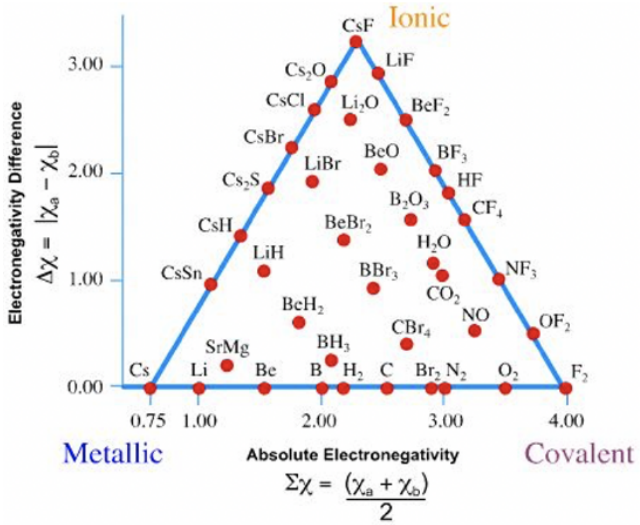

Figure 1.3.8 Ketelaar's Triangle (Attribution: Chemlibretexts https://chem.libretexts.org/@api/dek...jpg?revision=2 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

You can see that Ketelaar's triangle has three corners (Figure 1.3.8). Two of the corners are occupied by the elements F and Cs, and the third corner is occupied by CsF. All elements are located on the horizontal edge of the triangle, and there many compound indicated by dots either on the two other edges or within the triangle. There are no compounds or elements outside of the triangle. How can we understand this triangle and what does it say about the relationship between bonding character and electronegativity? To understand this, look at the two axes. The horizontal x-axis represents the average electronegativity of the atoms in an element

or a compound. The vertical y-axis represents the electronegativity difference between the atoms in the elements or the compound. For elements the electronegativity difference between the atoms is zero, because in an element all atoms are of the same type. Therefore, all the elements lie on the horizontally oriented edge of the triangle. Because Cs is the element with the lowest electronegativity, it lies furthest to the left on this edge. Fluorine is the element with the highest electronegativity, and thus lies the furthest on the right side. The other elements are in located in between the cesium and the fluorine on the edge. The higher the electronegativity of the elements, the further right their position on this edge of the triangle.

For compounds, the electronegativity difference between atoms is never exactly zero, therefore all compounds are located above the horizontal edge of the triangle. The compound with the highest electronegativity difference is the CsF. Its average electronegativity is the sum the electronegativity of Cs and F divided by 2: Therefore, CsF defines the third corner of the triangle. All other compounds must lie on the edges or within the triangle. All cesium compounds are located on the edge between the Cs and CsF, and all the fluorine compounds are located on the edge between CsF and F2. The compounds of all other elements are inside the triangle. The position of the compound on or in the triangle defines its bonding character. The closer the position of the compound toward the Cs corner, the more metallic, the closer the position is to the F2 corner, the more covalent, and the closer it is to the CsF corner, the more ionic. For example Li_2O is located close to CsF, and the bonding would be predominantly ionic, although there is also a small degree of covalent and metallic bonding. In contrast to that, SrMg has mostly metallic bonding, a little bit of covalent bonding, and even less ionic bonding. The bonding situation in LiH is in between metallic and ionic, with a little bit of covalent bonding character mixed in. Note that a 100% ionic bond is not possible because the electronegativity difference is finite, and thus there must always be a certain degree of electron sharing. In contrast to that, a 100% covalent bond is possible because electrons can be equally shared between two atoms when the electronegativity difference is zero.

The take home message is that in compounds and elements there is usually a mix of bonding types, and not a single bonding type, even through one bonding type may strongly dominate. The concept of electronegativity, and Ketelaar's triangle in particular, is extremely helpful to predict to which degree the three bonding types are present in a substance.
