Electronegativity

Skills to Develop

- Describe and explain the periodic trend for electronegativity
- Discuss the significance of electronegativity

Electronegativity is a measure of how much an atom attracts electrons. For instance, a more electronegative atom will be easily reduced, while a less electronegative atom will be easily oxidized. In covalent bonds, more electronegative atoms "pull harder" on the bonding electrons, so the shared electrons may spend more than half their time with the more electronegative atom, giving it a partial negative charge. (For example, O in water has a partial negative charge because it is more electronegative than H.) This will also influence the bond dipole moment.

How do we Define Electronegativity?

One way we can define electronegativity is by saying it is proportional to the sum of ionization energy and electron affinity. If it's hard to take electrons away, and easy to add electrons, the electronegativity is big.

$$EN = constant \times (IE + EA) \tag{1}$$

We choose the constant so that F has EN=4, and then use the same constant for all other elements.

However, electron affinities are not known exactly for most elements, so the first definition (the Mulliken definition, we'll talk more about Mulliken in the next section) is limited. Pauling proposed a different definition, which gives similar results but uses easier measurements.

Pauling's electronegativity scale is based on ionic resonance energies. Consider 2 diatomic molecules A_2 and B_2. We can measure the bond energy of each. We can also describe the bonding using resonance between a covalent structure, A—A and ionic structures $[A^+][A^-]$. If we make the molecule AB, what is its bond energy? In this case, because A isn't the same as B, one of the ionic resonance structures will be more important, and contribute to increased resonance stabilization. We can model the bond in AB using resonance between the covalent and ionic structures, A—B, $[A^+][B^-]$, and $[A^-][B^+]$. We can guess that the pure covalent A—B bond strength is the average of the A—A and B—B covalent bonds, because this depends on factors like distance between the nuclei and repulsion between the electrons. The extra resonance energy from increased stability of one of the ionic structures should make the A—B bond energy bigger than the average of the A—A and B—B bonds, and this is observed. (Convince yourself using the data in the previous section.) The bigger the difference between the elements, the more stable the ionic structure becomes, and the greater the resonance energy is. The difference between the average of the A—A and B—B bonds and the experimental A—B bond energy is used as the basis of Pauling's electronegativity scale.

Predicting Relative Electronegativities

It pretty much follows the same pattern you would expect based on ionization energy and electron affinity. Thus, in general, electronegativity is big in the upper right of the periodic table and decreases down and to the left. It's good to know that H's electronegativity is between B and C. (Even though H is written on the far left of the periodic table, it is sort of in between an alkali metal and a halogen.)

Look at EN for yourself!

Go to Ptable's electron affinity page. See the general trend (bigger up and right) with some relatively high electronegativities among the heavy transition metals, like gold, as well.

An illustration of the general trend for electronegativity throughout the periodic table.

Using Electronegativity

We can use electronegativity as a convenient way to predict the polarization of covalent bonds (in other words, how ionic they are). At the extreme, we can use it to predict whether compounds are covalent or ionic, which suggests also that it correlates roughly with metallic or non-metallic character. We can also use it to predict good Lewis structures, which usually have the negative formal charges on the more electronegative atoms. (If you follow this rule consistently, you'll predict much more ionic bonding than you might expect, which is actually consistent with more sophisticated models.)

The Pauling definition of electronegativity leads us to the conclusion that "combination of elements" reactions should always or nearly always be exothermic if only single bonds are present in the products and reactants. For N_2 and O_2 the multiple bond energy is greater than 2 times or 3 times the single bond energy. For this reason, compounds between N and O and elements of similar electronegativity like Cl might have positive heats of formation, meaning that they can exothermically decompose to the elements. Many reactive compounds that decompose to form elemental gases, such as explosives and bleaches, are compounds of Cl, N, and O.

Outside Links

- CrashCourse Chemistry: Polar and Non-Polar Molecules (11 min)
- Khan Academy: electronegativity (12 min)

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