

How did Linus PAULING come up with values of "electronegativities" for the elements?

(J. Encarnación. March 2006)

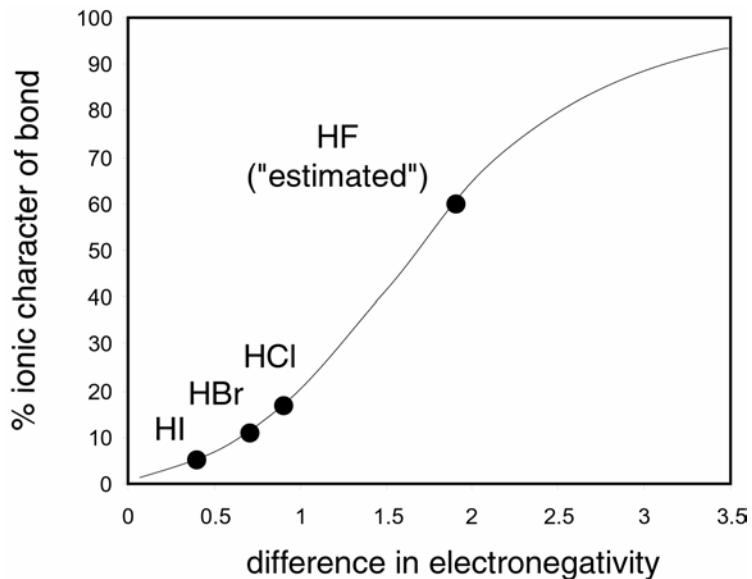
Based on reading Linus Pauling's original book "*The Nature of the Chemical Bond and the Structure of Molecules and Crystals*" published in 1948, here's the answer:

- First, he postulated that bonds between two atoms of the same element are pure or "normal covalent bonds" (for example, O-O, C-C, H-H, etc.). This makes sense: because the atoms have equal electronegativity, neither one will "own" the electron(s) more than the other.
- The strength of the bonds between these atoms can be measured through *thermochemistry* (e.g., measure how much heat is released when H and H combine, or how much heat is needed to break H-H apart). For example, the bond energy for H-H is **103.4 kcal/mol**, and for F-F it is **63.5 kcal/mol**. (**kcal** = kilo calories, a measure of energy; **mol** = moles, a measure of the number of molecules or atoms.)
- Now, if 2 different elements, H and F, say, bond, Pauling proposed that the "normal covalent bond" strength component of their bond is simply the mean or average of the H-H and F-F covalent bonds. So, the H-F bond energy is **83.5 kcal/mol**.
- He then stated that "*the energy of an actual bond between unlike atoms is greater than (or equal to) the energy of a normal covalent bond between these atoms. This additional bond energy is due to the additional ionic character of the bond.*" So, if we actually measure the bond strength of H-F, it will be greater than or equal to 83.5 kcal/mol. Indeed, the measured value is **147.5 kcal/mol**. The difference, which he called Δ between the predicted value of the normal covalent bond (based on the average of the individual bond strengths) and the actual measured value in this case is **64 kcal/mol**.
- So, the magnitude of Δ is a measure of additional bond strength contributed by the ionic character of the bond or, also, proportional to the difference in electronegativity between the two elements since it is the difference in electronegativity that would lead to some ionic character in a bond. ("*...the values of Δ can be used as the basis for the formulation of an extensive scale of electronegativities for the elements.*" -L. Pauling)
- Then, looking at the values of Δ for various element pairs, Pauling noticed that the Δ s were not linear ("not additive" in his words) when comparing two pairs of elements, but the square roots of Δ approximately were. So, he took the square root of all the values. He also converted the Δ values from kcal to e.v. (electron volts) by multiplying by the factor 0.208.
 - So, for example the table below shows delta values as well as the values for the square root of delta times 0.208 for three pairs of elements:

Bond/Element Pair	Δ	0.208*sqrt(Δ)
Si - H	2.1	0.3
Si - F	90	1.97
H - F	64	1.67

The values in column 3 now are the *differences* in electronegativity (EN) between each element pair! (As defined by Pauling.) So, we see that Si must have the lowest electronegativity, with H slightly higher, and F with the highest. That is, if the electronegativity of Si = zero, H must = 0.3, and F = 1.97.

- Then, to have an *absolute* value of electronegativity for each element (instead of just *differences* between elements) an electronegativity of **4.0** was arbitrarily assigned to fluorine (F). So, since the electronegativity of F = 4, H must be 2.3 and Si = 2.0 (rounding to nearest decimal).
- OK, that's basically how electronegativities were determined or assigned. Now, if you check the electronegativity values for F, Si, and H in your textbook and compare them with those above, you will see that they aren't exactly the same, except for F which is, by definition = 4.0. H is given as 2.1 (instead of 2.3) and Si is given as 1.8 (instead of 2.0). Why? Here's where things get a bit obscure. The values in your book are the same values that Pauling has in Table 11-2 ("Electronegativity Values for Some Elements") of his book. Regarding this table, he says "*In constructing Table 11-2 all of the available data have been considered, and the (electronegativity) value which leads to the best general agreement for each atom has been selected.*" (Huh?) Scanning the pages that follow it appears that he basically tweaked the electronegativity values of elements whose known behaviour don't exactly agree with the behaviour that might be predicted by his "untweaked" values.
- So, now you know how Pauling determined or assigned his electronegativities to each element. What about the % ionic character of the bond between two different elements? How did Pauling construct the figure plotting % ionic character vs. difference in electronegativity? (figure 3.10 of your textbook by Nesse; figure 12-1 of Pauling's 1948 book). The degree of ionic character can be determined by *measuring* the *electric dipole moment* of a molecule, HF, say, and comparing it with the *calculated dipole moment* assuming pure ionic character, $\mu = q \times r$, where q is the charge of the ion(s) and r is the interionic separation. Then, $(\text{measured } \mu / \text{predicted } \mu) \times 100\% = \text{percent ionic character}$. (The dipole moment is simply a measure of how strong the charges involved are and how separated they are. In a 100% ionic bond, all the + charge would "belong" to the cation and all the - charge would belong to the anion, so the dipole moment, μ , would be equal to $q \times r$ where r is the separation of the cation and anion---this would be the *calculated* dipole moment for a 100% ionic bond. The *actual* dipole moment is measured experimentally somehow---not sure how, but it can be done.
- It turns out that Pauling had dipole moment data for three atomic pairs/bonds for which he could determine % ionic character using the method above: H-I, H-Br, and H-Cl. *He then plotted the difference in electronegativity between these three pairs (and an "estimated" point for HF) against the % ionic character and fit the curve through just these three points!* (see figure on next page)
- End of story. Cool, eh?



Graph plotting percent ionic character vs. difference in electronegativity for four pairs of bonded elements. The difference in electronegativity is calculated from the negativity values determined by Pauling and given in your book. The percent ionic character was calculated from experimental data on dipole moments (except for HF whose % ionic character was "estimated" by Pauling). The curve is hand drawn by me but can be described by the following formula: $y = 1 - \exp(-0.25 * x^2)$ (Pauling, 1948).