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COMMENTARY

Electronegativity Scales

The concept of electronegativity (EN) is almost as old as chemistry itself. Berzelius classified atoms as electronegative or electropositive. By the turn of the century it was understood that these terms referred to the electron-attracting and -holding power of the atoms. During the twenties the founders of physical-organic chemistry extended the terms to include groups of atoms as well as atoms. There was an approximate ordering of the EN of various atoms and radicals.

In 1932 Pauling made a landmark contribution.[1] He created an empirical scale of EN based on heats of formation or, essentially, bond energies. A number of other scales eventually appeared, such as the widely used Allred–Rochow scale.[2] These scales had two characteristics in common. One was that they were calculated from properties of the free atoms of the elements. The other was that they were tested by seeing if they agreed with the original Pauling scale. Failure to do so would be a serious deficiency.

In 1939, in the first edition of *The Nature of the Chemical Bond*, Pauling gave his meaning of the word electronegativity: "the power of an atom in a molecule to attract electrons to itself." Many would accept this as a definition of the term.

Mulliken presented his scale in 1934;[3] EN = $(I + A)/2$. To match Pauling's scale, I and A were not the ordinary ground-state ionization potentials and electron affinities of the atoms, but the values in some suitable valence state. Like Pauling, Mulliken was primarily interested in the division of bonding electrons between the atoms, or bond polarity.

Important new viewpoints were contained in a paper by Parr and his co-workers in 1978.[4] Using density functional theory, they showed that any chemical system, atom, radical, ion, or molecule, is characterized by a quantity, μ, called the electronic chemical potential. It is constant everywhere in the system and measures the escaping tendency of the electrons in the system. It is a property of equilibrium systems only and, hence, of ground states.

A key property of the electronic chemical potential is that $\mu = (\partial E/\partial N)\upsilon$, where E is the electronic energy, N the number of electrons, and υ the potential of the nuclei. Since a good approximation to the slope of E vs N is $-(I + A)/2$, we have $-\mu \simeq (I + A)/2$, where I and A are now the ground-state values. Because of the close analogy to the Mulliken EN, it was proposed that $(I + A)/2$ be called the absolute EN.[4] The adjective "absolute" was selected because of the near equality to the fundamental property, $-\mu$.

There was a second reason to identify the electronic chemical potential with EN. In 1951 Sanderson had proposed that when two atoms or radicals combined, electrons would flow from the least EN to the most EN, until the two ENs were equalized.[5] This was an assumption, not proven by any theory, but intuitively appealing.

But μ has just this property. If two systems, C and D, are brought into a state of interaction, electron density will flow from one system into the other until a single value, μ_{CD}, exists. This must now be constant everywhere in the combined system. In general, it will be different from the original values, μ_C and μ_D. Hence ENs are equalized in the combining of two different systems.

It is clear that absolute EN differs substantially from Pauling EN. It applies to molecules, ions, and radicals, as well as to atoms. For the latter, it is a property of a free atom in the ground state and not an atom in an excited valence state, suitable for its appearing in a molecule.

As might be expected, applications of the two scales are quite different. The Pauling scale is useful for estimating bond polarities and, to some degree, the strengths of bonds between different atoms. The absolute scale is a measure of the chemical reactivity of an atom, radical, ion, or molecule. A typical application is the estimation of the initial interaction between two such systems.[6]

(1) Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570.

(2) For a useful summary, see: Mullay, J. Electronegativity. In *Structure and Bonding*; Springer-Verlag: New York, 1987; Vol. 66, p 1.

(3) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782.

(4) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801. Earlier work (Pritchard, Sumner, Iczkowski, Margrave) had related EN to $\partial E/\partial N$.

(5) Sanderson, R. T. *Science* **1951**, *114*, 670.

(6) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734; *J. Org. Chem.* **1989**, *54*, 1523.

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The procedure gives the direction of electron flow and an estimate of the initial amount of electron density transferred. This, in turn, is related to energy barriers for reaction and, in some cases, to the strength of the coordinate bond formed. It is not a reliable measure of final bond polarity.

The absolute EN does not conform to the Pauling definition of EN as a property of an atom in a molecule, but the essential idea of EN is that of attracting and holding electrons. There is no compelling reason to restrict this to combined atoms.

The extension of the concept of EN to molecules seems to be a natural and useful step. Donor–acceptor interactions are at the very heart of chemical bonding. The absolute EN is a measure of the intrinsic donor–acceptor character of a species.

There is no inconsistency in the EN of a free atom being different from that of an atom in a valence state. Scales such as Mulliken's and the recently developed spectroscopic scale[7] show that the absolute and Pauling-like scales can be commensurable. Since the applications are so different, it is not a meaningful question to ask which scale is more correct. Each scale is more correct in its own area of use.

The fact that there are two different measures both called EN scales creates considerable opportunity for confusion and misunderstanding. It is the purpose of this commentary to call attention to the difference between the absolute scale and the various Pauling-like scales. Hopefully, this may help to avoid some of the confusion.

(7) Allen, L. C. *J. Am. Chem. Soc.* In press. This scale equates the EN to the average value of the ionization potentials for all the valence-shell electrons of the atom.

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