

The Quantification of Electronegativity: Some Precursors

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ABSTRACT: This paper calls attention to the early work of the American chemists Worth Rodebush and Groves Cartledge, and their anticipations of a quantitative electronegativity scale, which predate the classic 1932 paper of Linus Pauling by several years.

KEYWORDS: History/Philosophy, Atomic Properties/Structure, Periodicity/Periodic Table

Most chemists are under the false impression that the electronegativity concept was first introduced by the American chemist, Linus Pauling, in 1932.¹ However, in a series of historical papers published in this *Journal* it was shown that both the term and the concept predate Pauling by more than a century.^{2,3} These earlier 19th-century electronegativity scales were essentially qualitative in nature, and consequently a weaker claim can still be made that Pauling—if not the originator of the electronegativity concept—was at least the first to provide a fully quantified scale for its measurement. Unfortunately even this weaker claim requires substantial qualification because recent work has uncovered two earlier pre-Pauling attempts to quantify this important chemical concept: two precursors whose subsequent fates illustrate some important lessons about how one goes about successfully developing and marketing a scientific concept.

■ THE V/S SCALE OF WORTH RODEBUSH

The first and earliest of these precursors was due to the American physical chemist, Worth H. Rodebush (1887–1959), who is perhaps best known as the coauthor, along with his doctoral advisor, Wendell Latimer, of the first paper to deal with the concept of the hydrogen bond.⁴ In 1925, seven years before the publication of Pauling's paper, Rodebush published an article in this *Journal* dealing with the Bohr atom and the periodic table in which he made the following passing comment:⁵

If it might be permissible to introduce a qualitative formula into science which is rapidly becoming exact, we might represent the electronegativity as a function of V/S where V is the number of valence electrons and S the number of shells. The basis of this formula is Coulomb's law and I believe that in a few years we shall calculate the energy changes in chemical reactions by means of it.

Ignoring Rodebush's inappropriate description of his equation as "qualitative," which may have been a typographical error for "quantitative" (as an equation must necessarily be), there is little doubt that this interesting suggestion was the result of an explicit attempt on the part of Rodebush to make the electronegativity concept more rigorous, as shown by his comments in an article written for *Science Magazine* the previous year:⁶

I had hoped that we might be able to substitute electron affinity or ionizing potential for the wretched term electronegativity, but these quantities are measured for the gaseous

state and our ordinary chemical properties are concerned with the condensed phases. For instance the electron affinity of the chlorine atom is less than the ionization energy of sodium, so that a chlorine atom should never rob a sodium atom of its electrons, and yet nothing is more certain than that it does so in a solution of sodium chloride.

The historical ambiguity is, of course, that, having suggested this explicit formula for calculating electronegativity values, Rodebush apparently did nothing further with it, though it requires only about five minutes to calculate the resulting electronegativity values for the main-block elements using valence-electron and Bohr-atom shell counts readily available in 1925, as summarized in Figure 1. The resulting values show a 0.92 linear correlation coefficient with the corresponding Pauling electronegativity scale for these elements and a 0.97 correlation coefficient with the corresponding Allred–Rochow scale, results that are essentially identical with the correlation coefficients interrelating the 25 or so modern electronegativity scales.

There are, of course, problems with extending this definition to the transition metals because the valence electrons for these atoms reside in two different shells, though use of an averaged shell number would probably give consistent results. A second problem is that the Rodebush definition gives values for the posttransition elements (Zn, Cd, Hg, Ga, In, Tl) that are too low as it does not take into account the effects of the d-block and f-block insertions on the screening constants for these elements. Likewise it gives values for H and He which are far too small, though it shares this problem with the majority of modern definitions, most of which have to instead make use of the corresponding Pauling values.

Despite these problems, the history of the electronegativity concept would have been quite different if Rodebush had properly developed his suggestion. Having a complete scale in 1925 for even just the main-block elements would have been a considerable advance over what in fact actually happened. Few chemists are aware that in his original paper of 1932 Pauling provided quantitative electronegativity values for only ten non-metallic elements. In the 1939 edition of his famous monograph, *The Nature of the Chemical Bond*, he extended his scale to 33 elements, though he never published the data or calculations on which this extension was based.⁷ Not until 1960, and the

Published: October 17, 2011

	1	2	3	4	5	6	7	8
2	Li (0.50)	Be (1.00)	B (1.50)	C (2.00)	N (2.50)	O (3.00)	F (3.50)	Ne (4.00)
3	Na (0.33)	Mg (0.67)	Al (1.00)	Si (1.33)	P (1.67)	S (2.00)	Cl (2.33)	Ar (2.67)
4	K (0.25)	Ca (0.50)	Ga (0.75)	Ge (1.00)	As (1.25)	Se (1.50)	Br (1.75)	Kr (2.00)
5	Rb (0.20)	Sr (0.40)	In (0.60)	Sn (0.80)	Sb (1.00)	Te (1.20)	I (1.40)	Xe (1.60)
6	Cs (0.17)	Ba (0.33)	Tl (0.50)	Pb (0.67)	Bi (0.83)	Po (1.00)	At (1.17)	Rn (1.33)
7	Fr (0.14)	Ra (0.29)						

Figure 1. Rodebush V/S electronegativity values.

publication of the third edition of his book, did a complete scale finally appear.⁸

In addition, while the Rodebush electronegativity definition is an example of what Ferreira calls a primary definition, meaning one based on fundamental atomic properties and having a clear theoretical justification, the Pauling thermochemical definition is actually an example of a secondary definition, meaning one that is based on an empirical correlation between a macroscopic property of some sort (in this case thermochemical bond energies) and electronegativity and which is, consequently, lacking a clear theoretical justification.⁹

Lastly, it is of interest to note that the Rodebush scale provides, as shown in Figure 1, an unambiguous criterion ($EN > 1.00$) for the zigzag line separating the metals and nonmetals commonly found in introductory textbooks, though it still begs the question of whether this line accurately represents the separation of these two classes of simple substances in the first place.

THE IONIC POTENTIAL SCALE OF GROVES CARTLEDGE

While the V/S scale of Rodebush predated the work of Pauling by seven years, the quantitative scale proposed by the American chemist Groves H. Cartledge (1891–1980) would not appear until 1928 and, thus, predated the work of Pauling by only four years. In addition, a proper understanding of the nature and limitations of Cartledge's work requires some preliminary background.

Younger chemists are often unaware that the early decades of the 20th century saw the development of two alternative approaches to the description of bond polarity. The first of these, owing largely to the American chemist G. N. Lewis, began with an idealized covalent bond and discussed bond polarity as a deviation from this ideal which could be expressed in terms of the relative electronegativity difference between the two bonded atoms.¹⁰ The second approach, due largely to the Polish chemist Kasimir Fajans, began with an idealized ionic bond and discussed bond polarity as a deviation from this ideal which could be expressed in terms of the polarizing ability of the cationic bonding component, on one hand, and the polarizability of the anionic bonding component, on the other.¹¹ The Lewis "covalent/electronegativity" model was subsequently developed by Pauling in the 1930s and became the prevailing paradigm in the United States and Great Britain, whereas, prior to the Second World War at least, the Fajans "ionic/polarization" model was the prevailing paradigm in continental Europe and Russia.

	1	2	3	4	5	6	7	8
2	Li (1.29)	Be (2.54)	B (3.87)	C (5.16)	N (6.71)	O (8.19)	F (10.0)	Ne (NG)
3	Na (1.02)	Mg (1.76)	Al (2.45)	Si (3.13)	P (3.83)	S (4.55)	Cl (5.20)	Ar (NG)
4	K (0.87)	Ca (1.42)	Ga (2.20)	Ge (2.74)	As (3.26)	Se (3.78)	Br (4.24)	Kr (NG)
5	Rb (0.82)	Sr (1.33)	In (1.92)	Sn (2.36)	Sb (2.84)	Te (3.27)	I (3.74)	Xe (NG)
6	Cs (0.77)	Ba (1.21)	Tl (1.78)	Pb (2.18)	Bi (2.60)	Po (3.02)	At (NG)	Rn (NG)
7	Fr (NG)	Ra (1.24)						

Figure 2. Cartledge $\phi^{0.5}$ values (NG means "not given").

The resulting bifurcation of the literature on bond polarity has resulted in most chemists failing to recognize that the various numerical scales of cationic polarizing ability, which have been proposed over time within the context of the Fajans approach, are essentially identical to the various electronegativity scales that have been proposed over time within the context of the Lewis–Pauling approach. Most cations correspond to atomic cores, and because scales of cationic polarizing ability are intended to measure the ability of the cation to attract additional electron density, they can also serve as a crude measure of the ability of an atom's core to retain its valence electrons, as well as to attract additional electrons: in short, they can serve as a measure of an atom's electronegativity.

In 1928 Cartledge proposed a quantitative measure of cation polarizing ability that he called the "ionic potential" (ϕ) and which he defined as the ratio of a cation's net charge to its radius:¹²

$$\phi = (Z/r)_{\text{cation}}$$

In subsequent papers in which he attempted to correlate various properties with the ionic potential, Cartledge came to the conclusion that the square root of the ionic potential ($\phi^{0.5}$) was a more effective parameter.^{13–15} A plot of the numerical values for $\phi^{0.5}$ provided by Cartledge in 1928 for the main-block elements (Figure 2) versus the corresponding Pauling electronegativity values gives a linear correlation coefficient of 0.91, whereas that for the Allred–Rochow scale is 0.96. Once again these are both comparable to the correlation coefficients interrelating various modern definitions and indicate that a $\phi^{0.5}$ scale could also have functioned as a quantitative electronegativity scale had Cartledge chosen to present it as such. Note that, like the Rodebush scale, the Cartledge scale also provides a criterion ($\phi^{0.5} > 3.02$) for the so-called zigzag line separating the metals from the nonmetals.

Of course, neither Rodebush's electronegativity equation nor Cartledge's ionic potential had an impact comparable to Pauling's thermochemical electronegativity scale, though both had the ability to generate a complete set of quantitative electronegativity values several decades before this was finally achieved for the Pauling definition. In the case of Rodebush this negligible impact was due to the simple fact that Rodebush failed to properly develop and publicize his definition, whereas in the case of Cartledge, it illustrates the importance of selecting proper terminology and aligning oneself with the prevailing theoretical paradigm.

A similar fate befell the measure of cation polarizing ability proposed by the Hungarian chemist, Bela Lakatos, almost 30

years after Cartledge.¹⁶ Termed the “effective field strength” by Lakatos, it made use of effective core charges and the Slater screening constants to define the electrostatic force field around the cation:

$$F^* = Z^*e/r^2 = (Z - S)e/r^2$$

The next year the American chemists Eugene Rochow and A. Louis Allred proposed the same definition as a measure of the electronegativities of neutral atoms.¹⁷ While the Allred–Rochow electronegativity definition is now discussed in virtually every inorganic textbook, the Lakatos cationic field strength, like the Cartledge ionic potential, has passed into virtual oblivion.

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ACKNOWLEDGMENT

The author would like to thank Laurent Ouerdane of the University of Pau (UPPA) of Pau, France, for first proposing this question as part of the original “Ask the Historian” column.

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