

When Was Electronegativity First Quantified? I

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Question

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Answer

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). 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 since recent work has uncovered two earlier pre-Pauling attempts to quantify this important chemical concept – attempts whose subsequent fates illustrate some important lessons about how one goes about successfully developing and marketing a scientific concept. Since much of this material has not been published elsewhere, we will take the unusual step of devoting two separate columns to this subject – one for each of these earlier anticipations.

The first and earliest of these precursors was due to the American physical chemist, Worth H. Rodebush (figure 1), who is perhaps best known as the coauthor, along with Wendell Latimer, of the first paper to deal with the concept of the hydrogen bond (3). In 1925, seven years before the publication of Pauling's paper, Rodebush published an article in *The Journal of Chemical Education* dealing with the Bohr atom and the periodic table in which he made the following passing comment (4):

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



Figure 1. Worth Huff Rodebush (1887-1959).

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 typo 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 (5):

Rodebush V/S Electronegativity Values

	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)						

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 the attached table. 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 which 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, since 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 post-transition elements (Zn, Cd, Hg, Ga, In, Tl) which are too low since 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 value.

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 nonmetallic 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 (6). Not until 1960, and the publication of the third edition of his book, did a complete scale finally appear (7).

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 (8).

Lastly, it is of interest to note that the Rodebush scale provides, as shown on the attached table, an unambiguous criterion ($EN > 1.00$) for the zig-zag 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.

Literature Cited

1. L. Pauling, "The Nature of the Chemical Bond: IV. The Energy of Single Bonds and the Relative Electronegativity of Atoms," *J. Am. Chem. Soc.*, **1932**, *54*, 3570-3582.
2. W. B. Jensen, "Electronegativity from Avogadro to Pauling: Part I. Origins of the Electronegativity Concept," *J. Chem. Educ.*, **1996**, *73*, 11-20; "Electronegativity from Avogadro to Pauling: Part II. Late Nineteenth- and Early Twentieth-

Century Developments," *J. Chem. Educ.*, **2003**, *80*, 279-287.

3. W. M. Latimer, W. H. Rodebush, "Polarity and Ionization from the Standpoint of the Lewis Theory of Valence," *J. Am. Chem. Soc.*, **1920**, *42*, 1419-1433.

4. W. H. Rodebush, "Compact Arrangement of the Periodic Table," *J. Chem. Educ.*, **1925**, *2*, 381-383.

5. W. H. Rodebush, "The Subject Matter of a Course in Physical Chemistry," *Science*, **1924**, *59*, 430-433.

6. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press: Ithaca, NY, 1939, p. 58. The same table appears in the second edition of 1948, p. 64.

7. L. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press: Ithaca NY, 1960, p. 93.

8. R. Ferreira, "Electronegativity and Chemical Bonding," *Adv. Chem. Phys.*, **1967**, *13*, 55-84. There have been several attempts to theoretically justify the Pauling scale, but I agree with Ferreira's assessment that they are all lacking in theoretical rigor.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu