

When Was Electronegativity First Quantified? II

William B. Jensen

Department of Chemistry, University of Cincinnati
Cincinnati, OH 45221-0172

Question

When was electronegativity first quantified?

Laurent Ouerdane
University of Pau (UPPA)
Pau, France

Answer

In the first installment of the answer to this question we dealt with the quantitative definition of electronegativity first proposed by the American physical chemist, Worth H. Rodebush, in 1925, which predated the work of Pauling by seven years (1). In this installment we will deal with the quantitative definition given by the American chemist, Groves H. Cartledge (1891-1980), in 1928, which predated the work of Pauling by four years, though a proper understanding of Cartledge's work requires some background context.

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, due 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 (2). The second approach, due largely to the Polish chemist, Kasimir Fajans, began with an idealized ionic bond and discussed bond polarity (figure 1) as a deviation from this ideal which could be expressed in terms of the polarizing ability of the cationic bonding component, on the one hand, and the polarizability of the anionic bonding component, on the other (3). 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.

The resulting bifurcation of the literature on bond polarity has resulted in most chemists failing to recog-

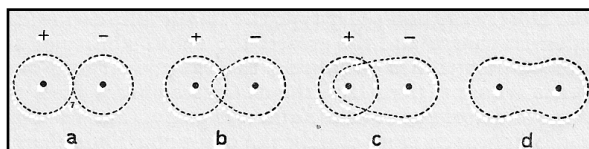


Figure 1. Fajans' concept of the formation of various polar covalent (b and c) and covalent (d) bonds via the progressive polarization of an idealized ionic bond (a) (3).

nize 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 which have been proposed over time within the context of the Lewis-Pauling approach. Most cations correspond to atomic cores and since 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 which he called the "ionic potential" (ϕ) and which he defined as the ratio of a cation's net charge to its radius (4):

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

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 (5-7). A plot of the numerical values for $\phi^{0.5}$ provided by Cartledge in 1928 for the main-block elements (see table) 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 the $\phi^{0.5}$ scale could also have functioned as a quantitative electronegativity scale had Cartledge chosen to present it as such. Note

Cartledge $\phi^{0.5}$ Values (NG = Not Given)

	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)						

that, like the Rodebush scale, the Cartledge scale also provides a criterion ($\phi^{0.5} > 3.02$) for the so-called zig-zag 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 (8). 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 (9). While the Allred-Rochow electronegativity definition is now discussed in virtually every inorganic textbook,

the Lakatos field strength, like the Cartledge ionic potential, has passed into virtual oblivion.

Literature Cited

1. W. B. Jensen, "When Was Electronegativity First Quantified?, Part I," *J. Chem. Educ.*, **2011**, 89, 94-96.
2. Summarized in G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, Chemical Catalog Co: New York, NY, 1923, pp. 83-84.
3. Summarized in K. Fajans, *Radioelements and Isotopes, Chemical Forces and the Optical Properties of Substances*, McGraw-Hill: New York, NY, 1931, Chapters 2-6.
4. G. H. Cartledge, "Studies in the Periodic System: I. The Ionic Potential," *J. Am. Chem. Soc.*, **1928**, 50, 2855-2863.
5. G. H. Cartledge, "Studies in the Periodic System: II. The Ionic Potential and Related Properties," *J. Am. Chem. Soc.*, **1928**, 50, 2863-2872.
6. G. H. Cartledge, "Studies in the Periodic System: III. The Relation Between Ionizing Potentials and Ionic Potentials," *J. Am. Chem. Soc.*, **1930**, 52, 3076-3083.
7. G. H. Cartledge, "The Correlation of Thermochemical Data by the Ionic Potential," *J. Phys. Chem.*, **1951**, 55, 248-256.
8. B. Lakatos, "Ein neuer Weg zum Berechnung des Polaritätsgrades der chemischen Bindung," *Z. Elektrochem.*, **1957**, 61, 944-949.
9. A. L. Allred, E. G. Rochow, "A Scale of Electronegativity Based on Electrostatic Force," *J. Inorg. Nucl.*

THE QUANTIFICATION OF ELECTRONEGATIVITY: PART II

Chem., **1958**, 5, 264-268.

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