Electronegativity from Avogadro to Pauling

Part I: Origins of the Electronegativity Concept

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No concept more thoroughly pervades the fabric of modern chemistry than that of electronegativity and no name is more persistently associated with its origins in the mind of the modern student of chemistry than that of Linus Pauling. Yet, a careful reading of Pauling's original 1932 paper on this subject reveals that, though he proposed a thermochemical method of assigning relative electronegativity values and proceeded to apply it to 10 nonmetallic elements, nowhere in the paper does he offer an explicit definition of the concept (1). Indeed, he proceeds as though the concept is self-evident to his readers, and with good reason; for by the time Pauling proposed his quantification procedure, the electronegativity concept had been a part of chemical thought for nearly 125 years! Yet this early pre-Pauling history seems to have almost completely dropped out of sight, at least as far as the modern textbook and electronegativity literature are concerned.

The intent of this paper is to try to recapture some of this lost history and, in so doing, to remind the modern theorist that those who ignore history always run the risk of repeating it—a cliché, no doubt, but unhappily one that embodies a sizable, albeit depressing, amount of truth. We will approach the subject in three stages. We will begin in Part I with a discussion of the origins of electronegativity as a qualitative concept in the period between 1809 and 1813, followed in Part II by a re-examination of its fate in the period between 1813 and the appearance of Pauling's famous paper in 1932. Finally, in Part III, we will examine Pauling's attempt to quantify the electronegativity concept via a fusion of thermochemical and modern structural data, as well as analyze the problematic role played by quantum mechanics in this process.

Some Prerequisites: Affinity and Chemical Dissimilarity

There are at least two necessary prerequisites for the emergence of a viable electronegativity concept: some kind of crude qualitative understanding of the way in which chemical activity or affinity depends on the similarities or dissimilarities in the chemical character of the reacting substances:

\[ \text{affinity} = f(\text{chemical character}) \] (1)

and a similar approximate understanding of how the electrical properties of materials correlate with that chemical character:

\[ \text{chemical character} = f(\text{electrical properties}) \] (2)

By eliminating the middle term from these relations, one then arrives at the concept of a correlation between chemical activity, on the one hand, and electrical character, on the other:

\[ \text{affinity} = f(\text{electrical properties}) \] (3)

Both of these prerequisites underwent a profound change in the last quarter of the 18th century.

In the case of eq 1, these changes can be illustrated by examining the treatment of chemical affinity found in the 1764 English edition of the book, *Elements of the Theory and Practice of Chemistry*, by the French chemist, Pierre Macquer. First published as two separate works in 1749 and 1751, respectively, this volume was widely used as a text in both European and British universities during the third quarter of the century. In Chapter II, which was entitled "A General View of the Relations or Affinities Between Bodies," Macquer summarized the rules of chemical affinity in the form of seven propositions or laws, the second and third of which read (2):

... it may be laid down as a general rule that all similar substances have an Affinity with each other, and are consequently disposed to unite; as water with water, earth with earth, etc. and

... substances that unite together lose some of their separate properties, and compounds resulting from their union partake of the properties of those substances which serve as their principles.

Yet 25 years later, in the 1789 edition of Antoine Fourcroy's text, *Elements of Chemistry and Natural History*, we encounter a very different story. Organized, like Macquer's earlier volume, around eight (rather than seven) laws of chemical affinity, we now read that affinity or "attraction of composition," as Fourcroy called it, operates not between "similar" substances but, according to Fourcroy's first law, between "bodies of different natures" and that (3):

Figure 1. Antoine-François Fourcroy, 1755–1809 (Oesper Collection).
This first law is invariable, and admits of no exceptions. That two bodies may combine, and form a compound, it is indispensably necessary for them to be different in kind. . . This law holds so invariably, that the attraction of composition is never stronger than when the bodies between which it acts are, in nature, the most essentially different from one another.

and further on we discover, under Fourcroy's sixth law, that the properties of the resulting compound are not an average of those of its components but rather that (3):

Two or more bodies, united by the attraction of composition, form a substance, the properties of which are different from those which each of the bodies possessed.

In short, a minor revolution had occurred in the theory of chemical affinity, and the modern chemist will quickly recognize that Fourcroy's version is much more in accord with the facts of chemistry. Indeed, Fourcroy (Fig. 1) was quite conscious of this change and explicitly contrasted these new laws with the versions formerly held by chemists, indicating that these revisions were a result of an explicit survey of the experimental facts conducted by himself and his mentor, Jean-Baptiste Michel Buechet.

Fourcroy's law relating the strength of chemical affinity to the degree of chemical dissimilarity among the reactants became standard textbook fare and can be found in most texts published prior to the 1860's. Thus, the 1858 edition of David A. Wells' American text, Principles and Applications of Chemistry, listed, like its 15th-century predecessors, seven laws of chemical affinity, the second, third, and fourth of which read (4):

II. It (i.e., chemical affinity) is only exerted between dissimilar substances.

III. Generally speaking, the greater the difference in the properties of bodies, the greater is their tendency to enter into chemical combination. Between bodies of a similar character, the tendency to union is feeble.

IV. Chemical affinity occasioned an entire change in the properties of the substances acted upon.

Our second prerequisite—the establishment of a correlation between the chemical nature of a material and its electrical properties—is likewise a late 18th-century development whose story is well-known and need not be repeated here in detail (5). Beginning with Galvaní's discovery of current electricity in 1786 and proceeding through the work of Volta and that of Nicholson and Carlisle, we need only pause to glance at Humphry Davy's famous Bakerian Lecture of 1806 (6, 7). In section VIII of this lecture, entitled "On the Relations Between the Electrical Energies of Bodies and their Chemical Affinities," Davy hinted at virtually all of the developments that would occur in the next decade. Here he suggested that chemical affinity was due to the close approach of oppositely-charged particles—charges which the particles retained on being separated again—not unlike the coated glass plates of Beccaria which "strongly adhere only to the other when oppositely charged, and retain their charges on being separated;" that the greater the magnitude of these opposite charges or "electrical energies"—as he called them—and the more perfectly matched, the more stable or saturated the resulting compound; that the affinities of bodies could be artificially enhanced, reduced, or even inverted by altering the nature and magnitude of their electrical energies by means of either the voltaic pile or by heating; and lastly, that the relative normal electrical energies or character of substances, and consequently their relative chemical affinities, could be established either by means of contact electrification experiments—that is, by touching together plates made of two dissimilar substances and measuring which became positively electrified and which became negatively electrified—or by measuring the electrical energy required for their decomposition (7).

Allowing combination to depend upon the balance of the natural electrical energies of bodies, it is easy to conceive that a measure may be found of the artificial energies, as to intensity and quantity produced in the common electrical machine, or the voltaic apparatus, capable of destroying this equilibrium; and such a measure would enable us to make a scale of electrical powers corresponding to degrees of affinity.

Origins of the Electronegativity Concept: Avogadro and Oxygenicity

In retrospect, it is puzzling that Macquer was still advocating a correlation between chemical affinity and chemical similarity as late as 1764, since the premiere example of reactivity between dissimilar substances—the neutralization of an acid by a base or alkali—had been the focus of intensive chemical activity throughout the 17th century. Moreover, this work tended to emphasize explicitly the obvious dissimilarity in the properties of the two reactants, the violence of their reaction, and the subsequent total destruction or "neutralization" of their original properties. Thus, Robert Boyle referred to acids and alkalis as "two contrary saline principles" and pictured their reaction as a "conflict between . . . two jarring principles, or, if I may so call them, duellists" (8). Similar statements also can be found in the writing of Lecomte, Mayow, Sylvius, Tuchenuis, and others (9).

The first person to exploit the obvious parallelism between the neutralization of acids and alkalis, on the one hand, and that of opposite electrical charges, on the other, was the Italian physicist, Amedeo Avogadro (Fig. 2), in a paper published in 1809 (10, 11). Inspired by the views of the French chemist, Claude Berthollet, on acidity and affinity, Avogadro suggested that not only were the concepts of acidity and alkalinity purely relative in nature, but also that they should be generalized so as to apply to all chemical interactions, whether involving simple substances or compounds. After first reviewing many of the inconsistencies that had arisen from the use of Lavoisier's more parochial oxygen definition of acidity, Avogadro noted that all of these difficulties could (11):

- . . . be easily explained if one considers acid antagonism and alkaline antagonism as purely relative properties which become something absolute only to the extent that one refers them to an average degree fixed arbitrarily on the scale of acidity and alkalinity. Thus some substance A, which has acid antagonism with respect to substance B, can have alkaline antagonism with respect to a third substance C. Likewise, what we call acids and alkalis in an absolute sense are only substances which have acid and alkaline antagonism with re-
spect to certain bodies whose place on the scale is approximately marked by certain properties, for example, that of not altering blue vegetable colors.

In order to implement this idea, Avogadro further envisioned the placement of all simple substances on a single universal acidity scale, such that each element would display an acid antagonism toward those lower on the scale and an alkaline antagonism toward those higher on the scale (Fig. 3). Oxygen was placed at the head of the scale because one could (II):

- regard oxygen as one of the bodies highest up on the scale of acidity and communicating or allowing by that fact acidity to the majority of substances with which it is combined, but not as exclusively endowed with acidity or the property of giving to its combinations, since there must be other substances placed above the point indicated on the scale of which we have spoken, [i.e., the arbitrary point of neutrality], although less high than oxygen.

In recognition of this fact, Avogadro suggested that the term "oxygencity" be used in place of the term acidity to describe the property in question, the older term being reserved, along with the term alkaline antagonism, to describe only the relative oxygencity values of two interacting substances. The greater the separation between two substances on the oxygencity scale, the greater their acid-base antagonism and the greater their chemical affinity.

However, Avogadro was sufficiently familiar with the work of Berthollet on the modification of affinity by mass action and by changes in state to realize that one could not naively deduce the location of a substance on the oxygencity scale merely on the basis of its observed ability to displace other substances in the course of its chemical reactions. Thus, oxygen, though strongly oxygencic, showed little acidity as a pure substance because, like all gases, its particles were surrounded by highly repulsive caloric envelopes which interfered with the operation of its inherent affinities. Likewise, carbon was also quite oxygencic, a fact which was masked in the pure substance by the necessity of having to overcome the strong affinity of aggregation present in all solids. In short, the true oxygencity of a material was manifested only in a certain state of aggregation, one which offered (II):

- ... too great a cohesion nor too great an elasticity, both of which would prevent substances which are solid and insoluble in water or, likewise, substances which are gaseous and difficult to condense, from manifesting the properties of acids, though possessing the power of acidity to an eminent degree.

Though one could partly infer the true oxygencity of an element from its ability to impart acidity to its compounds, a sounder method was required, and this Avogadro found in Davy’s Bakerian lecture of 1806, since this showed that (II):

- ... there is a close connection between the reciprocal acid and alkaline antagonism and the motive power of electricity in the contact of two bodies in the manner of Volta, the acid taking in this case the negative or recessive electricity and the alkali the positive or vigorous electricity. ... this connection furnishes us at the same time with a simple means of specifying the place that different substances ought to take in the table of which we have spoken and which it would be very difficult to form and complete by consideration of chemical properties only.

In other words, one could determine true relative oxygencity values by means of contact electrification experiments, like those described by Davy, Volta, Pfaff, and others. Thus, the oxygencity scale becomes a manifestation of the ability to assume negative electrification and chemical affinity becomes a function of the degree of electrical separation on the scale or, as Avogadro put it, a function of the reactants’ “electrical heterogeneity” (I):

- It is in effect clear that, according to the indicated correspondence, electrical heterogeneity, by which two bodies become more or less electrified on contact, becomes the measure of the antagonism or chemical affinity between the two bodies.

In modern terms, Avogadro’s universal acidity scale or oxygencity scale was, in all but name, a crude electronegativity scale, and it is of some interest to note that modern solid-state physics provides us, albeit retrospectively, with a theoretical justification for his attempt to measure his scale by means of contact electrification data. According to modern quantum theory (12), the contact or Volta potential (\(\psi_{AB}\)) between two solids is equal to the difference in their work functions (\(\phi\)):

\[
\psi_{AB} = \phi_A - \phi_B
\]  

and reports of empirical linear correlations linking the work function, on the one hand, with various modern electronegativity scales, on the other, have appeared at regular intervals in the solid-state and electrochemical literature (13–18), the earliest being that given by Gordy and Orville Thomas in 1956 (19):

\[
E_N = 0.440 - 0.15
\]  

Elimination of the work function term common to eqs 4 and 5 leads to the logical conclusion voiced by Kapustinikii in 1960, when he wrote (20):

The increase in the values of the contact potentials of many metals with respect to platinum as the standard corresponds to a decrease in the values of their electronegativities... thus, the Volta (or contact) potential series is the same as the electronegativity series.

![Figure 4. Kohlrausch’s parallel-plate apparatus (c. 1853) for the measurement of contact potentials (21).](image-url)
Needless to say, none of these modern writers shows any awareness of the fact that they are rediscovering correlations postulated by Davy and Avogadro more than 185 years ago.

The real difficulty in using contact electrification data to establish an electronegativity scale lies not in the lack of a theoretical basis but rather in the experimental problem of trying to measure accurate and reproducible contact potentials. The standard approach, as it had evolved by the middle of the 19th century, involved forming the substances in question into circular capacitor plates, as shown in the engraving given in Figure 4 of the apparatus used by Kohlrausch in 1853 (21). The plates were first placed in contact to establish a potential difference, which was detected on separation by an electrometer attached to the apparatus (Fig. 5). An opposing voltage was then gradually applied to the plates until the electrometer gave a null reading, at which point the applied voltage was equal but opposite in magnitude to the contact potential. The problem, as Lothar Meyer lamented in 1888, was that (22):

The slightest superficial oxidation of the metals, or the presence of moisture, or of small quantities of impurities in the metals, produces such great changes in their contact electricity that many physicists have denied the existence of contact electricity . . .

The resulting ambiguities gave rise to a protracted debate throughout the 19th and early 20th centuries over both the reality of contact potentials and the validity of their original use by Volta to rationalize the mechanism of his electrochemical cell (23–25).

Obviously, the data on contact electrification available to Avogadro in 1809 was quite meager and, given the above mentioned experimental difficulties, of questionable accuracy. Consequently, he was able to discuss the placement of only a few elements on his oxygenicity scale—nonmetals such as oxygen, sulfur, and carbon having high oxygenic values and metals having low values. Nor did Avogadro immediately undertake an experimental program to further extend his table. This delay meant that by 1811 events began to overtake him. Electrochemical speculations were rapidly becoming the rage and many chemists began to offer half-hearted theories on the probable relationship between chemical affinity, caloric, and light, on the one hand, and the electrical properties of materials, on the other (26).

Origins of Electronegativity: Berzelius and the Theory of Combustion

The eventual victor in this scramble was a young 32-year-old Swedish chemist by the name of Jöns Jakob Berzelius (Fig. 6) (27, 29). In 1811, he published a long article entitled "Essai sur la nomenclature chimique" in Dalméthie’s Journal de Physique in which he outlined his own version of an electrochemical theory of chemical affinity. This was soon translated into both German and English (29). Additional articles appeared in Swedish, German, French, and English between 1811 and 1814, and in 1818 Berzelius inserted an extended account in the third volume of the first edition of his famous Textbook of Chemistry (30). This, in turn, was progressively modified and expanded throughout the five editions of the text which appeared prior to his death in 1848.

Inspired, like Avogadro, by the work of both Berthollet and Davy, as well as by his own experimental work on electrolysis, Berzelius’ model contained many of the same features already found in Avogadro’s 1809 paper—a fact which was not lost on Avogadro, as in 1813 he wrote a short note criticizing Berzelius’ theory in order, as he put it, "to prevent, in my opinion, the false applications that might be made with a system which I regard as belonging to me in its origins" (31). The placement of simple substances on a single universal scale of oxygenicity now becomes in Berzelius’ system a placement on a single universal scale of a property which Berzelius calls "electronegativity", the acid–alkaline antagonism corresponding to the relative positions occupied by any two reactants on this scale now becomes an electronegative–electropositive antagonism and, finally, Avogadro’s arbitrary point of neutrality separating predominantly acidic species from predominantly alkaline species now becomes the dividing line separating predominantly electronegative species from predominantly electropositive species.

All of this might be dismissed as a mere difference in vocabulary but for the fact that there were some significant conceptual differences as well, albeit not necessarily for the better. Though Davy had noted that both chemical and electrical neutralization resulted in the production of heat—an observation that he felt tended to support his theory of their probable identity—he did not speculate on the mechanism involved, and Avogadro did not even raise the subject in his 1809 paper. However, for Berzelius the explanation of heat evolution in chemical reactions was central to his theory. Indeed, in the extended essay which appeared in the various editions of his textbook, Berzelius explicitly presented his electrochemical theory as a new theory of chemical combustion, designed to replace the caloric theory of Lavoisier, just as the latter’s theory had replaced the earlier theory of phlogiston (32).
In Lavoisier's theory, oxygen gas was a compound of the pure element oxygen with caloric and oxidation was a single displacement reaction in which the material being oxidized or displaced was set free part of that combined caloric in the form of heat:

\[ \text{M(s)} + (\text{O} + \text{caloric}) \rightarrow \text{MO(s)} + \text{caloric} \]  

This decrease in combined caloric content was in keeping with the fact that the resulting oxide was usually a solid. In short, heat release or absorption in chemical reactions was associated with the changes in state which accompanied the purely chemical changes. This created problems for the case of exothermic reactions involving the conversion of solids into gases, of which the ignition of gun powder was a prime example. More sophisticated attempts to rationalize these exceptions on the basis of changes in the specific heats of the reactants versus the products also proved futile (33, 34).

Assuming that both caloric and electricity were imponderable fluids, Berzelius based his theory on the proposition that caloric was a compound of negative and positive electricity:

\[ \text{positive fluid} + \text{negative fluid} \leftrightarrow \text{caloric} \]  

Chemical reactants were compounds of the material elements with varying amounts of electrical fluid, and exothermic chemical reactions were double displacement reactions in which the combination of the material elements was accomplished by a simultaneous combination of the displaced electrical fluids to form free caloric or heat.

\[ (\text{A + pos. fl.}) + (\text{B + neg. fl.}) \rightarrow \text{AB + caloric} \]  

Heats of reaction now depended upon the specific electrochemical character of the reactants and not upon changes in state. Chemical affinity was measured by the amount of electrical fluid neutralized or rather converted into caloric. The greater the initial charges on the reactants, the greater their potential for reaction, and the less charge remaining on the products, the greater their stability. By means of the voltaic pile one could either enhance the reactivity of the free reactants by increasing the magnitude of their electrical charges or one could decompose a compound by restoring the charges on its original components. Berzelius further assumed that the postulated relationship between opposite electrical charges and caloric given in eq 7 was reversible. Heating the reactants or products led to dissociation of the added caloric and consequently, in the first case, to an enhancement of the electrical charges of reactants—thus explaining the accelerating effect of heat on chemical reactions—and, in the second case, to a decomposition of the product through a restoration of the original charges on its components.

Though Berzelius' electrochemical model appeared to eliminate the incorrect correlation between changes of state and the exothermicity of a reaction that was required by Lavoisier's caloric model, in actual practice it merely replaced this problem with its own set of equally annoying contradictions. Thus, the premise that association reactions always led to charge neutralization and heat evolution, whereas dissociation reactions required heat absorption in order to restore the initial atomic charges on the separated atoms, meant that the model was unable to explain the existence of both endothermic association reactions and exothermic dissociation reactions. To his credit, not only did Berzelius recognize this problem, he actually listed several contradictory examples of spontaneous exothermic decompositions (35).

Avogadro's use of a single relative scale of oxygenicity implied that acidity and alkalinity were merely excess and defect of the same thing, and thus, by implication, also committed him to a one-fluid model of electricity in which positive and negative charge corresponded to an excess or defect of a single electrical fluid. On the other hand, Berzelius' use of a two-fluid model of electricity to explain the origins of caloric release in chemical reactions, forced him to adopt an overly specific and rather awkward speculative model of atomic charge distributions in order to rationalize the relative nature of electronegativity. Each atom was assumed to contain a characteristic ratio of positive and negative electricity, each of which was concentrated at a pole of the atom—a ratio, because, as we have seen, the absolute quantities could be varied by heating or use of the voltaic pile. This characteristic ratio, which was called the "general polarity" of the species, determined its reactivity; whereas, the particular fluid that dominated the ratio determined the species' "unipolarity," i.e., whether it was predominantly electronegative or electropositive. When two species reacted, they always used those particular poles which maximized charge neutralization and heat evolution, and the remaining charges then redistributed themselves on the molecular poles of the product.

I have attempted to visualize this in Figure 7, where—in the tradition of 18th-century affinity diagrams—I have assigned purely hypothetical charges in order to illustrate the concept. As shown above the top diagram, when two predominately electronegative atoms, such as oxygen and sulfur, reacted, the more electronegative partner (i.e., oxygen) used its dominant negative pole and the less electronegative partner (i.e., sulfur) its subordinate positive pole. This resulted in a product having an even greater unipolarity than that of the two reactants and explained, as Berzelius pointed out, why oxygen and sulfur, which appear to be only weakly acidic as simple substances, produced strongly acidic (i.e., electronegative) oxides upon reacting. Conversely, as shown in the lower diagram, when a predominately electropositive atom, such as sulfur, reacted with a predominately electronegative atom, such as lead, each atom used its dominant pole, and both the unipolarity and general polarity of the product were diminished over that of the reactants. Thus, we see how sulfur, despite its inherent electronegative unipolarity, could act as an electropositive partner relative to oxygen but as an electronegative partner relative to lead.

Note that the oxygen—sulfur example also sustains grave doubts on the often-used argument that Berzelius rejected Avogadro's famous hypothesis (i.e., that simple substances...
contain polyatomic molecules) because his electrochemical theory prohibited bonding between atoms having the same unipolarity and thus, by implication, between identical atoms (10, 36). This, in turn, appears to be based on the even more frequent misconception that Berzelius anticipated the modern ionic model by postulating that chemical bonding was due to electrostatic attractions between oppositely charged atoms (37). As we have seen, nothing could be further from the truth. In Berzelius' model chemical interaction leads to destruction of the charges on the interacting atoms via their combination to form caloric and their escape from the system in the form of heat. Indeed, increasing the charge on the atoms in a compound actually weakens it and leads to its eventual dissociation. In his early papers, Berzelius says nothing about the nature of the force holding atoms together in a molecule after it is formed, though he does suggest that molecular cohesion (i.e., intermolecular forces) might be due to attraction between opposite charges on the adjacent molecules. These he compares to the attraction between the metallic and resinous surfaces in an electrophorus (Fig. 8), in which the apparent charge neutralization is really just a "juxtaposition, and is destroyed again when the surfaces are separated, and each again appears in possession of its original electric state," whereas, chemical affinity, leading to compound formation, is compared to the shorting of a voltaic pile (Fig. 9) with its concomitant evolution of heat and light and the exhaustion of the pile's polarity. In modern terms, Berzelius' association of charge destruction and heat evolution with affinity is a correlation rather than an explanation, in that it makes no attempt to reduce chemical affinity to already-known forces, whether gravitational or electrical, or to the interconversion of various forms of energy, although in later editions of his textbook Berzelius hedged by making vague references to possible hitherto unknown manifestations of atomic electric polarization (38):

The usual electrical phenomena explain quite well the action of substances at greater and smaller distances, their attraction prior to combination, and the fire arising from this combination. But these electrical phenomena give us no information as to the reason for the great force that maintains the combination of the substances after destroying the opposite electrical states. Is this action due to some special force associated with the atoms, like electrical polarization, or is it a property of electricity which is not perceptible in the usual phenomenon?

These observations present us with an interesting problem, as most accounts of the history of electricity claim that both charge conservation and Coulomb's law were well-established theoretical concepts by the end of the 18th century, yet Berzelius' theory ignores both (39). Was Berzelius ignorant of the facts and theories of physics? While a physicist might be willing to accept this answer, as many currently believe it to be equally true of modern-day chemists, I think there are more probable reasons for this neglect. Though Berzelius may not have been familiar with the research literature in physics, he almost certainly had a textbook understanding of it, and this raises the question of whether these two principles were sufficiently highlighted in the textbooks of the period so as to be part and parcel of Berzelius' scientific training. Regrettably, I cannot give a definitive answer to this question as historians of science have largely ignored the study of textbooks. However, my own personal impression is that most textbook accounts of this period tended to focus on the description of apparatus and novel experiments rather than on fundamental laws. A final possibility is that Berzelius was fully aware of both laws but felt that they applied only to static electricity and not to the voltaic electricity which formed the underlying basis of his theory. After all, we need to remind ourselves that, as late as 1832, Faraday felt that it was necessary to establish experimentally the fundamental identity of static, voltaic, and animal electricity before embarking on his own study of electrochemical phenomena.

Even more curious is that fact that Avogadro's concept of a single oxygenic scale, in which the affinity between two elements was directly related to the differences in their oxygenicity values, logically leads to the very conclusion that has been falsely attributed to Berzelius—namely that there can be no chemical affinity between identical atoms. This conclusion, coupled with the fact that Avogadro makes explicit reference to his oxygenicity scale in his famous memoir on molecular weights without commenting on this apparent contradiction, lends support to the arguments of recent historians that Avogadro's postulate of "divisible or fractional molecules" is not identical to its later 19th-century reinterpretation in terms of polyatomic molecules (40, 41).
Some Ahistorical Comparisons

Given this flawed theoretical foundation, just how successful was Berzelius in establishing a viable electronegativity scale? We have already seen that Avogadro's attempt to base his oxygenicity scale solely on contact electrification measurements gave only limited results. Questions about the accuracy and reproducibility of his data aside, the procedure was, in practice, limited only to solids and was ad hoc, because any discrepancies between it and actual chemical behavior could always be rationalized away as being due to the intervention of other changes in aggregation or mass action effects. In 1823 Avogadro again returned to the subject of oxygenicity and attempted to correlate it with the direction of current flow observed on coupling various metal/acid cells, but found that the results depended not only on the nature of the metals but also on the nature and concentration of the acid (42). Beginning in 1816, and to an increasing extent thereafter, Avogadro also began to explore nonelectrochemical correlations with oxygenicity, mostly involving the use of specific heats and various derived quantities which he considered to be measures of a substance's "affinity for caloric." Ultimately this resulted in a correlation between oxygenicity and the relative atomic (i.e., molar) volumes of the elements, and led to the conclusion that strongly oxygenic elements were characterized by small atomic volumes, whereas weakly oxygenic elements had large atomic volumes—a result in keeping with modern views on the relation between electronegativity and atomic size—but again insufficient data prevented the placement of a significant number of elements (43).

In sharp contrast to Avogadro's limited success, Berzelius included a virtually complete list of the relative electronegativities of all the known elements in his textbook, a list which was updated and revised throughout the various editions—the example shown in Figure 10 being from the fourth German edition of 1836 (44). In his early papers, Berzelius had suggested many of the same techniques as Davy and Avogadro for establishing this order, but in his textbook accounts no data or further information is given as to how these final lists were established. By assuming that the unipolarity of an oxide was a direct reflection of the unipolarity of the oxidized element, Berzelius was able to use the results of electrolysis to establish whether an element was predominantly electropositive or electronegative, but since these experiments were purely qualitative they gave no information on relative orders (45). My personal opinion is that these tables were based on Berzelius' extensive knowledge of chemical reactions resulting from the massive analytical work which he undertook in connection with his determination of atomic weights. This would have given him an intimate knowledge of the order in which various elements displaced one another and a feel for the exothermicity of their reactions, though it is curious that he never attempted to make quantitative calorimetric measurements, since this course was logically dictated by his theory and the experimental technique had already been established by Lavoisier and Laplace in the late 18th century. In addition, I suspect he also may have made use of the obvious inverse relationship between metallic character and electronegativity.

This conclusion, if correct, presents us with an unique opportunity, since Berzelius has provided us with a relative electronegativity order that was established purely on the basis of chemical experience and one which is not biased by a knowledge of our modern definitions. Is electronegativity an arbitrary theoretical artifact, as some modern writers have argued, or does it really reflect laboratory experience with actual chemical phenomena (46)? In short, how well does Berzelius' scale compare with our modern scales? I have attempted to assess this by assigning to each element in Berzelius' 1836 list an ordinal number indicating its place in order of increasing electronegativity, the least electronegative element being assigned position one and the most electronegative element the...
highest number, I have extracted the same list of elements from Pauling's thermochemical scale and have assigned ordinal numbers in the same manner. In making my selection, I have used only the main-block elements, because there is still debate about the meaning of electronegativity values for the transition metals. As can be seen from the graph in Figure 11, there is a respectable 0.95 correlation coefficient between the ordinal numbers or relative orders given by Berzelius in 1836 and those given by the most recent data based on Pauling's 1932 definition, the most obvious discrepancy being that for lead. It should be noted that this emphasis on relative order rather than absolute value actually reflects the way in which electronegativity is used in chemistry, since for most purposes the point at issue is not whether the absolute EN value of some element A is 3.42 or 3.36, but rather whether it is or is not more electronegative than some other element B.

In Figure 12 I have made the same comparison for the same set of elements using the relative electronegativity orders given by the modern Allred-Rochow force definition and by Pauling's thermochemical definition. Examination of this graph shows that the degree of correlation as to relative order (not absolute value) between the two most popular modern definitions is identical to that between the scales of Berzelius and Pauling, with lead again being the most blatant discrepancy. Pauling's EN value for lead has long been known to be too high (47). If we normalize it so that it agrees with the Allred-Rochow value, then the correlation between the modern definitions jumps to 0.97 (Fig. 13), and exactly the same thing happens when we normalize Pauling's lead value relative to Berzelius's scale (Fig. 14). This would suggest that, whatever electronegativity really is—and the 30 or more modern definitions currently in the literature still haven't given us a conclusive answer—it really does reflect some intuitive chemical reality—a reality already perceived in its essentials by a master chemist more than 150 years ago.

We already have alluded to the fact that Berzelius' electrochemical model violated both conservation of charge and Coulomb's law, and to Berzelius' own admission that he was unable to account for the nature of intramolecular forces and for the existence of both endothermic association reactions and exothermic decomposition reactions. By suggesting, as we have just done, that Berzelius constructed his electronegativity scale by reversing the functional relationship postulated earlier in eq 3:

\[ \text{electrical character} = f'(\text{chemical affinity}) \]  

that is, by assuming the truth of what he had set out to prove and then working backwards, we have pinpointed the final, and in some ways, the most serious defect in his system. Unlike Avogadro, Berzelius never offered a clear-cut, independent method of measuring electronegativities that would allow for their objective comparison with affinity orders which had, in turn, been independently determined by purely chemical means. Consequently, his approach came perilously close to being little more than a simple relabeling of already existing data and, as such, subject to the same criticism that Wilhelm Ostwald later voiced relative to Davy's earlier electrochemical speculations (48):
It merely permits the expression of already existing facts in another form. Instead of saying that chemical combinations take place according to the measure of an otherwise unknown chemical affinity between substances, this theory says that chemical combinations take place according to the otherwise unknown electrical forces that arise on account of the mutual interactions between substances.

As we will see in Part III, modern electronegativity concepts still are not completely free of this sort of circularity.

The Second Chemical Revolution and the Decline of Electrochemical Dualism

It is well known that Berzelius’ electrochemical theory came under increasingly violent attack in the period 1830–1860, both as a result of its inability to deal with the increasing complexities of organic chemistry and, to a much lesser degree, as a result of its incompatibility with Faraday’s laws of electrolysis (49). On the organic front, this attack was led by the French chemists Jean–Baptiste Dumas, August Laurent, and Charles Gerhardt, and, on the electrochemical front, by Faraday’s close friend, John Frederick Daniell (50, 51). By the 1860’s, as even a superficial survey of the textbook literature clearly shows, the older textbook organization, centered on the laws of chemical affinity and electrochemical dualism, had given way to a new organization based on the emerging concepts of valence and molecular structure. As I have argued in greater detail elsewhere, these changes correspond to what is, in essence, a “second chemical revolution” (52). This second revolution, which roughly spans the period between 1852, when Edward Frankland imperfectly recognized the concept of valence, and 1874, when Jacobus van’t Hoff postulated the tetrahedral carbon atom, gave chemists access to the molecular level of chemical discourse, just as the first chemical revolution, born of Lavoisier and his collaborators in the last quarter of the 18th century, had given them access to the macro or molar level of discourse.

That the demise of electrochemical dualism came about as a result of its inability to deal with the taxonomic problems of organic chemistry, rather than as a result of the fundamental problems outlined in the previous section, is in some ways an excellent illustration of that fact that history does not always follow logic. At a more concrete level, it is also a reflection of the fact that, despite his continual references to the theory of chemical affinity, the theory of electrolysis, and to the theory of chemical combustion, Berzelius’ primary use of his electrochemical theory was in the field of organic chemistry. In other words, his real interest in establishing an electronegativity scale for simple substances was largely motivated by his desire to establish the predominant polarity or unipolarity, and hence the relative acid–base character, of each component in a chemical compound—not unlike a modern-day chemist using electronegativity values as a way of assigning oxidation states—and the resulting implication of this assignment for naming and classifying the compound in question. This limited focus was commented upon by Lothar Meyer in 1888. Referring to Berzelius’ later hints that intramolecular forces also might be due to some hitherto unknown manifestation of electricity, Meyer wrote (53):

Berzelius considered that the electricity contained in the atoms was not only the source of the light and heat which accompanies their combination, but also the cause of their adhering together after combination. His own account of these views acknowledges that this is a contradiction, which he is incapable of solving. This contradiction was scarcely felt, because Berzelius scarcely made any other application of his theory than the division of the elements into electropositive and electronegative, a classification which we still retain. When he attempted further application of his theory he fell into error, e.g.,

in his opposition to Faraday’s law of electrolytic equivalents and Dumas’ theory of substitution . . .

The same point was made in even more explicit terms by Wilhelm Ostwald in 1896 (48):

During the period of time with which we are concerned here the questions discussed above were not raised [i.e., the problems mentioned in the previous section]. Berzelius used his theory exclusively for purposes of chemical systematization. He did not once attempt a theory of electrochemical affinity in the quantitative sense . . . Due to this fact, the later fight against Berzelius’ theory was not conducted in the realm of electrochemistry but in the realm of the downfall of Berzelius’ theory was not a consequence of the above-mentioned incongruities in it. It was because his theory proved incapable of giving a satisfactory explanation of the phenomena of substitution in organic chemistry.

In contrast, Avogadro remained faithful to his original program of developing an oxygenicity scale which could be used to quantify the relative acid–base character and chemical reactivity of substances and continually sought to establish correlations with independently measured electrochemical and thermochemical parameters—not unlike a modern chemist interested in hard–soft acid–base theory and its correlation with modern electronegativity scales and their derivatives. Avogadro’s program was heavily influenced by what historian John Bonner has called the “physicalist tradition” in early 19th-century French chemistry, which was established by Berthelot and Laplace (40). However, as recent biographers have emphasized, Avogadro continued to pursue this program long after it had fallen out of favor (10, 40, 41). After 1820 his papers became too physical and mathematical to attract the attention of most chemists and remained too chemical to attract the attention of most physicists. His inability to construct a complete oxygenicity scale for the simple substances was in part a result of his almost complete reliance on the published experimental data of others and his failure to extend and standardize this data by undertaking an experimental program of his own. His influence was further marginalized by his increasing tendency to publish his papers in such places as the Memoirs of the Royal Academy of Science of Turin, rather than in well-known chemical journals.

As I hope to demonstrate in Part II of this series, what was really rejected in this second chemical revolution was not the concept of electronegativity, but rather Berzelius’ specific model of electronegativity and the compositional and structural implications of dualism—a classification system which Berzelius had inherited from Lavoisier. After 1870 we see an increasing number of attempts to adapt electronegativity to the newer concepts of valence and chemical bonding. Though the older tables of electronegativity are gradually displaced by the periodic table—a classification based instead on valence—we also begin to see discussions of the way in which electronegativity varies across the periodic table. And finally, we see a movement away from the use of contact electrification as a physical supplement to chemical behavior in establishing relative electronegativity values toward the use of heats of reaction—a movement associated more with the discovery of the first law of thermodynamics and the newer thermochimistry of Berthelot and Thomsen than with the older theory of chemical combustion given by Berzelius. By the first decade of the 20th century, this connection between electronegativity and heat evolution is so explicit that Pauling’s 1932 approach seems almost self-evident. Indeed, in the third installment in this series, I hope to show that this restored history clearly demonstrates that it is more logical to view Pauling’s 1932 thermochemical scale as the culmination of the 19th-century concept of electronegativity.
than it is to view it as the harbinger of modern 20th-century definitions, which should clearly be based on our modern knowledge of the electrical structure of atoms and on such concepts as ionization potentials, electron affinities, atomic radii, and effective nuclear charges.

Literature Cited


30. A complete bibliography can be found in Russell, C. A. "The Electrochemical Theory of Berzelius," J. Nat. Pol. Chem. 1813, 35, 38-47, 118-121, 159-166. Only the first two installments of this article deal with electrochemical theory.


35. Different authors have employed different methods to determine the electronic charge of the anode and basic oxides was determined solely by the electrochemical character of the solvated element, Angerov felt that it also depended upon the amount of oxygen present and that, as a consequence, one could not deduce the placement of elements on the electronegativity or oxygenicity scale solely on the basis of the behavior of their oxides.


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