Electronegativity from Avogadro to Pauling: II. Late Nineteenth- and Early Twentieth-Century Developments

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Part I of this series traced the origins of the electronegativity concept in the writings of Amedeo Avogadro and Jöns Jacob Berzelius in the period 1809–1813 *(1)*. Avogadro's approach—based on the concepts of acidity and alkalinity as generalized relative properties, the use of contact or Volta potentials as a measure of relative electronegativity orders, and an awareness of the potential perturbations of mass–action effects in establishing relative affinity orders—was the more sophisticated of the two. However, the less rigorous approach of Berzelius, when coupled with his greater success in establishing a complete table of relative electronegativities for the then known elements and his far more influential reputation among European chemists of the period, soon eclipsed Avogadro's more fundamental contribution.

Unfortunately Berzelius proceeded to tie his version of the electronegativity concept to the oxygen-based, acid–base dualistic system of chemical classification originally introduced by Lavoisier, thereby converting it into a system of "electrochemical dualism". Though this system worked well for simple inorganic compounds and had some initial success when applied to organic chemistry in the period 1820–1839, it began to seriously unravel in the 1840s under the increasing strain of the bewildering array of new organic compounds and reactions being discovered. In a desperate attempt to bring order to the resulting chaos, chemists began to abandon the premises of electrochemical dualism one by one and to try a variety of new organizational schemes. The substitution theory, the unitary theory, the nucleus theory, the old type theory, and the new radical theory followed one another in rapid succession, with the new type theory emerging as the eventual victor in the 1850s *(2)*. This, in turn, was generalized, via the newer concepts of valence and topological bonding in the 1860s, to form "structure theory", which was finally completed in its classical form with the introduction of the tetrahedral carbon atom in 1874. As argued elsewhere, these latter events form the substance of the second chemical revolution of 1855–1875 *(3)*.

In the course of abandoning the electrochemical dualism of Berzelius, chemists tended to abandon the electronegativity concept as well. However, once structure theory began to take on its final form, they came to realize that the electro-negativity concept was in fact independent of the misleading compositional and structural implications of dualism and began to explore ways of reconciling it to the newer concepts of valence and chemical structure. In what follows we will trace this accommodation process as it occurred in four fundamental areas of chemistry in the period 1870–1910 *(4)*:

1. The relationship between electronegativity and classical valence
2. The relationship between electronegativity and the periodic law
3. The relationship between electronegativity and thermochemistry
4. The relationship between electronegativity and the electrical theory of matter

Electronegativity and Classical Valence

An example of the way in which electronegativity was adapted to the newer concepts of valence and chemical structure can be seen by examining the 1870 volume, *A Text-Book of Elementary Chemistry*, by the American chemist George Barker *(5)*. Generally regarded as the first American book to be explicitly based on the new structure theory, Barker's text noted that chemists were now able to determine three different atomic properties: atomic weight, atomic valence, and atomic electronegativity.[1] The first of these, which measured the "quantity of matter" present, allowed chemists to calculate compositional formulas and to quantify chemical reactions. The second, which measured the "quantity of an atom's combining power", allowed chemists to rationalize chemical structure and to predict the number of possible isomers consistent with a given composition. Lastly, the third parameter, which measured the "quality of an atom's combining power", allowed chemists to rationalize differences in chemical reactivity for otherwise isostructural molecules. Barker also included tables of each of the three properties—his table of relative electronegativities (Figure 1) differing from Berzelius's table of 1836 only in the addition of nine new elements (Nb, Ru, In, Tl, La, D, Er, Rb, and Cs) that had been discovered in the interim.[2]

In order to illustrate the manner in which electronegativity allowed chemists to rationalize the reactivity of isostructural or isotypical molecules, Barker used the example of acids, bases, and salts. Within the context of the older dualistic theory, acids corresponded to the oxides of nonmetals or electronegative atoms (e.g., SO_3), whereas bases corresponded to the oxides of metals or electropositive atoms (e.g., K_2O). Salts, in turn, were viewed as additive adducts of the basic oxide and the acidic oxide (e.g., $K_2O{\cdot}SO_3$ or K_2SO_4). Type theory, on the other hand, had adopted the hydrogen theory of acidity first advocated by Humphry Davy earlier in the century. Acids, bases, and salts were all derived by substituting one or more of the hydrogen atoms in water with a suitable monovalent atom or radical (Figure 2).

Since all of these substitutions involved atoms or radicals having identical valence values and all of them were thought to preserve the underlying water structure or type, how was it possible to explain why some of the resulting compounds were acidic, whereas others were basic, and yet still others were neutral in character? The answer, as Barker noted, was that the various atoms and radicals, though having identical valence values, had very different valence qualities or electronegativities *(6)*:

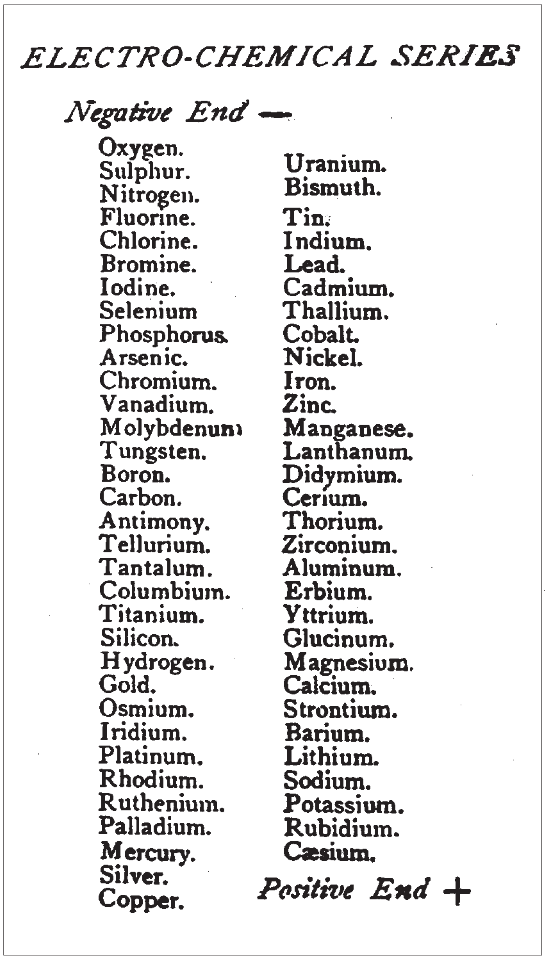
> A molecule of water consists of two atoms of hydrogen linked together by oxygen, thus: H−O−H. By exchanging one of these hydrogen atoms for a negative monad [i.e., monovalent atom or group], an acid, $R^{-}-O-H$, is produced. By a similar exchange for a positive atom, a base $R^{+}-O-H$, is obtained. By replacing both the hydrogen atoms, one by a positive, the other by a negative atom, a salt, $R^{+}-O-R^{-}$, results. Hence these three classes of bodies are said to be formed on the plan of the structure of water; that is, upon the water type.

This example was further elaborated by the American chemist, Josiah Parsons Cooke (Figure 3), in his 1874 book, *The New Chemistry (7).* As indicated by its title, this was also an exposition of the new structure theory, but one intended for the general reader and based on a series of popular public lectures that Cooke had given at the Lowell Institute of Boston in the fall of 1872. Here again Cooke noted that modern structure theory could not explain the distinctive features of acids, bases, and salts without recourse to the electrochemical character or electronegativity of the various atoms and radicals used in deriving these compounds from a single underlying water type *(8)*:

> But the chemists of the new school, in their reaction from dualism, have too much overlooked the electrochemical facts, which are as true now as they ever were. The distinction between positive and negative radicals, based on their electrical relations, is evidently a most fundamental distinction, although, as Berzelius himself showed, a relative and not an absolute one. It is possible to classify the radicals in one or more series in which any member is positive toward all that follow it, and negative toward all that precede it in the same series, and this principle is as true of the compound as it is of the simple radicals. Now, it is in this difference between positive and negative radicals that we shall find the origin of the distinctive features of the acid and the alkali.

Not only did the electronegativity of the substituted radicals explain the difference between a strong acid and a strong alkali, it further implied that these compounds were merely the extremes of a continuum of possible water derivatives or hydrates in which acidity and alkalinity progressively decreased as one moved from the extremes toward the center *(8)*:

> Compare again, the symbols of potassic hydrate and nitric acid as we have now learned to write them—K–O–H and H–O–NO_2 —and seek, by the electrochemical classification to determine what are the electrical relations of the radicals K and NO_2, to which, as I have said, we must refer the distinctive features of these compounds. It will appear that K, the radical of the alkali, is the most



ELECTRO-CHEMICAL SERIES

Negative End −

Oxygen.
Sulphur.
Nitrogen.
Fluorine.
Chlorine.
Bromine.
Iodine.
Selenium
Phosphorus.
Arsenic.
Chromium.
Vanadium.
Molybdenum.
Tungsten.
Boron.
Carbon.
Antimony.
Tellurium.
Tantalum.
Columbium.
Titanium.
Silicon.
Hydrogen.
Gold.
Osmium.
Iridium.
Platinum.
Rhodium.
Ruthenium.
Palladium.
Mercury.
Silver.
Copper.
Uranium.
Bismuth.
Tin.
Indium.
Lead.
Cadmium.
Thallium.
Cobalt.
Nickel.
Iron.
Zinc.
Manganese.
Lanthanum.
Didymium.
Cerium.
Thorium.
Zirconium.
Aluminum.
Erbium.
Yttrium.
Glucinum.
Magnesium.
Calcium.
Strontium.
Barium.
Lithium.
Sodium.
Potassium.
Rubidium.
Cæsium.

Positive End +

Figure 1. Barker's electronegativity series of 1870 *(5)*.

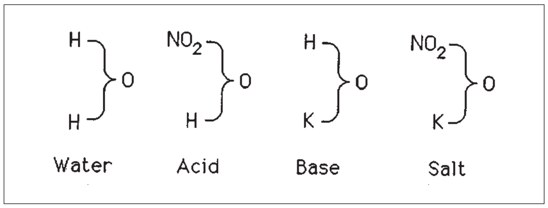


Figure 2. Acids, bases, and salts as substitution products of water.

Figure 3. Josiah Parsons Cooke, 1827–1894 (Oesper Collection).

> highly electropositive, and NO_2, the radical of the acid, one of the most highly electronegative of all known radicals. Moreover, if you will extend your study, and compare in a similar manner the electrical relations of the other well-marked alkaline and acid hydrates, you will find that the radicals of the alkalis are all electropositive, and the radicals of the acids all electronegative, and, further, that the distinctive features of the alkali and acid are the more marked in just the proportion that the position of the radical of the compound, in the electrical classification, is the more extreme. Lastly, those hydrates whose properties are indifferent, and that sometimes act as acids and sometimes as alkalis, will be found to contain radicals occupying an intermediate position in the same classification.

Like Barker, Cooke indicated relative polarities by superimposing positive and negative signs on his chemical formulas (Figure 4). In the case of bivalent oxygen, he also assumed that the two valence poles were of opposite sign, thus making the hydrogen atom in a typical acid electropositive and that in a typical base electronegative—a distinction that explained why the hydrogen in typical acids was easily displaced by electropositive metal atoms whereas the hydrogen in typical bases was not. Cooke likened the generation of the oppositely charged valence poles in oxygen to an induction effect initiated by the substituted radical and further elaborated this theory in later editions of his textbook, *Principles of Chemical Philosophy (9).*

Lest it be objected that the example of acids, bases, and salts is inorganic and not typical of the organic compounds that had led to the rejection of electrochemical dualism in the first place, it should be noted that electronegativity was also slowly seeping back into organic chemistry by the 1870s. Thus in 1875, Vladimir Markovnikov, in his famous memoir on addition across double bonds, noted the role of electronegativity in determining the nature of the resulting product *(10)*:

> When an unsaturated molecule C_nH_mX adds another molecular system YZ at low temperature, the most negative element or group Y combines with the least hydrogenated carbon atom, or with that which is already in direct union with some negative element, but at higher temperatures, it is the element Z which becomes attached to the least hydrogenated carbon, i.e., for the same substances, the reaction takes a path directly opposite to the first.

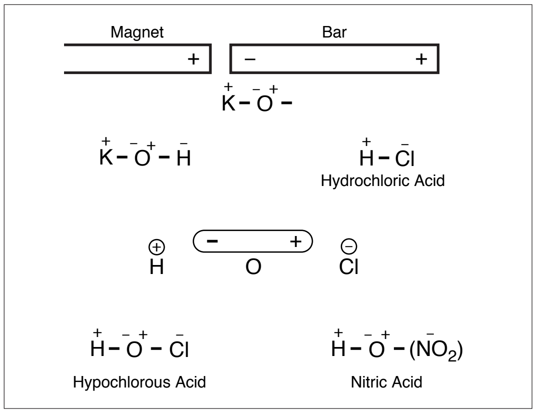


Figure 4. Examples of electrochemical formulas used by Cooke in his 1872 lectures on the "New Chemistry" to illustrate relative polarity or electronegativity *(7).*

About the same time Victor Meyer also began studying the role of negative groups in determining organic reactivity *(11)* and in the 1880s Wilhelm Ostwald observed the effect of negative substituents on the ionic dissociation constants of substituted organic acids *(12).* By 1899 Jacobus van't Hoff saw fit to include a discussion of the question of how the "electro-affinity" or "positive and negative character" of a substituent affected the properties of the parent compound in his *Lectures on Theoretical and Physical Chemistry (13).*

Electronegativity and the Periodic Law

From the time of Lavoisier to the emergence of the valence concept in the late 1850s, classification of the chemical elements was based largely on their metallic character or electronegativity. Beginning in the 1860s, however, chemists began exploring alternative classifications based instead on valence and atomic weight—a trend that culminated in the discovery of the periodic law by the end of the decade. With this event, the earlier electronegativity classifications fell out of favor. Even Cooke—who, as we have seen, strongly championed the use of electronegativity in rationalizing chemical reactivity—felt compelled in the 1891 edition of his textbook to dismiss its utility, in comparison to the periodic law, as a criterion for classifying the chemical elements *(14)*:

> The presence or absence of metallic qualities in elementary substances is for some unknown reason intimately associated with the electrical relations of their atoms—those of the metals being electropositive, with reference, in each case, to the atoms of the opposite class. Indeed, these electrical relations were formally made the chief basis of classification, and in the older works of chemistry, a list of the elementary substances is frequently given, arranged in such an order that each is electropositive to all which precede it, and electronegative to all which follow it in the series. Such a classification, however, does not exhibit the other affinities of the elements, and has little practical value.

Others, however, sought to reconcile the two classifications by pointing out that electronegativity, like atomic (i.e., molar) volume and valence, was also a periodic property. This approach was pioneered by none other than Lothar Meyer (Figure 5), widely regarded as one of the codiscoverers of the periodic law. In the 1888 edition of his book, *Modern Theories of Chemistry*, Meyer summarized the available data relating to the electronegativities of the elements, with special emphasis, like Avogadro before him, on the use of contact potentials *(15).* In the end, however, he concluded that the measurement of such potentials was too unreliable, and that one had to revert, like Berzelius, to the use of chemical evidence instead *(16)*:

> The attempts hitherto made to arrange the elements, as regards their electrical behavior, in a single series ranging from the most positive to the most negative have met with but questionable success. This fact is explained by

> the difficulties attendant on the observation and estimation of contact electricity... If, however, such electrochemical arrangements of the elements are disregarded and their general chemical behavior, which is probably dependent on the former, be considered, then a periodicity is observed coincident with their other physical properties.

Meyer summarized this periodicity not only by appending the labels "electropositive" and "electronegative" to various sections of his famous atomic volume curve, but also by means of a conventional short-form periodic table (Figure 6) in which arrows were used to indicate the direction of increasing electropositive character. To the best of my knowledge, this table is the first known example of a periodic table illustrating the periodicity of electronegativity. The result is a bit confusing for the modern chemist, not only because the absence of numerical electronegativity values necessitated the use of the awkward arrow convention, but also because Meyer's use of a short-form table means that the main-block and transition-block elements have been interleaved. Nevertheless, close inspection of the table and of Meyer's comments shows that most of our modern trends are correctly represented. In general, the electronegativity increases from left to right across a given period. For the most part it also decreases on moving from the top to the bottom of the main-block groups and increases on moving from the top to the bottom of the transition-block groups.

Earlier in his book Meyer had noted that the conventional periodic table could be constructed from his atomic volume–atomic weight curve by cutting the latter into sections at equivalent points and then stacking the sections on top of one another. Where the cuts were made was in fact arbitrary and subject only to the condition that they always correspond to equivalent points on the curve. As it turned out, the points that were most often used happened to correspond to the change from maximum electronegative character (i.e., the halogens) to maximum electropositive character (i.e., the alkali metals) and thus resulted in what Meyer called "electrochemical periods" *(17)*. What Meyer meant by this term is elegantly illustrated by the famous step-pyramid form of the periodic table (Figure 7) proposed by the Danish thermochemist, Jules Thomsen, in 1895 *(18)*. What interests us here are not the pros and cons of this particular form of the table, but rather the labels "Elektropositive Elemente" and "Elektronegative Elemente" that Thomsen attached to the top and bottom of the table to signify the presence of Meyer's electrochemical periods.

A final example is provided by the short-form table (Figure 8) used by the British chemist Sidney Young to illustrate the periodicity of electronegativity in his 1908 monograph on *Stoichiometry (19):*

> The electrochemical character of the elements is roughly indicated by the position of the symbols in the space they occupy, the electropositive elements being placed to the left of the spaces, and the electronegative elements to the right...it is found that the alkali metals as a group are the most electropositive elements, and the halogens the most electronegative, while, of the individual members, cesium is the most electropositive alkali metal and fluorine the most electronegative halogen. Thus in these groups the elements become more positive or less negative as the atomic weights increase; and the same rule is followed by the elements in most of the other groups.

In fact, the latter statement is too broad since Young's table clearly and correctly shows an increase, rather than a decrease, in electronegativity on passing down the Cr, Fe, Ni, Co, Cu, and Zn groups.

Electronegativity and Thermochemistry

As we saw in Part I of this series *(1)*, Berzelius postulated a correlation between charge neutralization and heat evolution in chemical reactions based on the hypothesis that heat or caloric was a compound of a positive and negative electrical fluid. Though this logically implied a similar correlation between heat evolution and electronegativity difference, Berzelius seems to have never exploited this relationship as a possible means of quantifying his electronegativity scale.

With the demise of the caloric theory in the 1840s and the rise of the newer thermochemistry based on the laws of thermodynamics and the kinetic molecular theory, interest in the correlation between enthalpies of reaction and electronegativity appears to have evaporated. I, at least, have been unable to uncover any discussion of this relationship in the

Figure 5. Lothar Meyer, 1830–1895 (Oesper Collection).

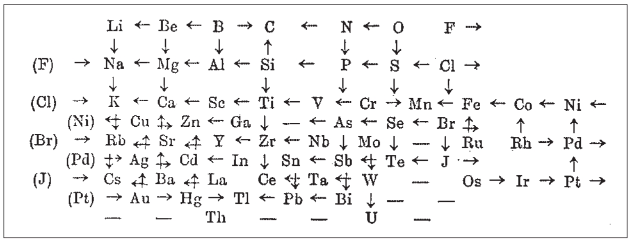


Figure 6. Meyer's table of 1888 illustrating the periodicity of electronegativity *(15)*. The arrows point towards the more electropositive element.

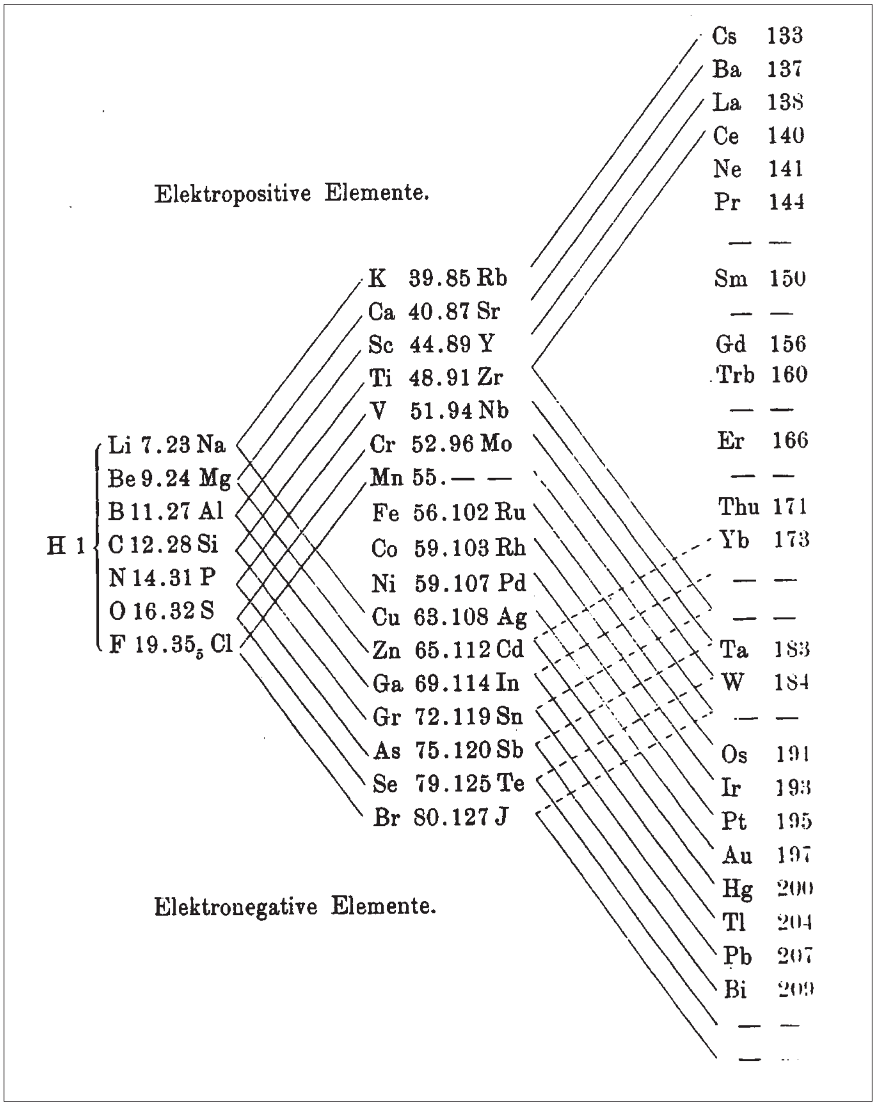
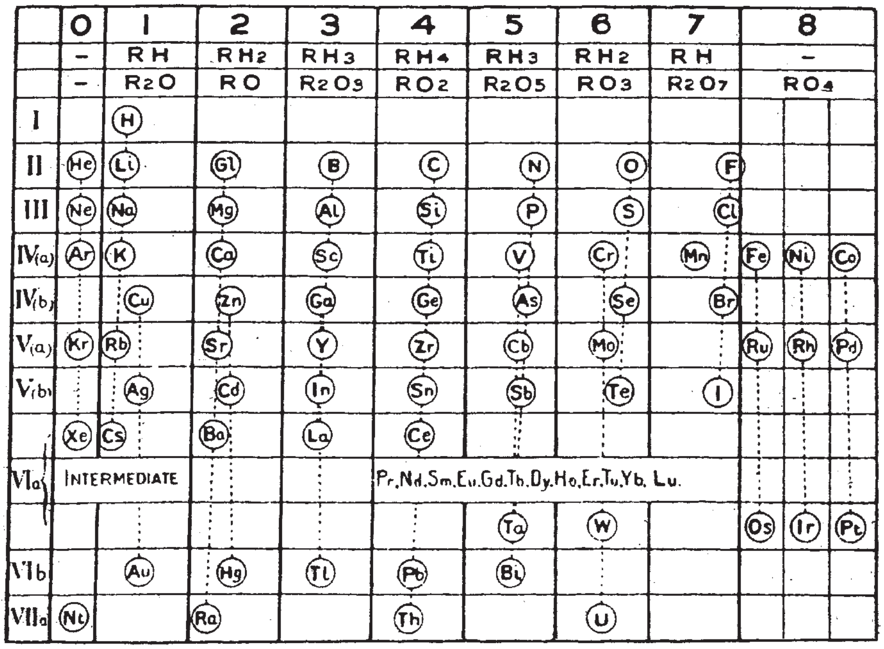


Figure 7. Thomsen's table of 1895 showing the presence of Meyer's "electrochemical periods" *(18).*



	0	1	2	3	4	5	6	7	8		
	–	RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH	–		
	–	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4		
I		H									
II	He	Li	Gl	B	C	N	O	F			
III	Ne	Na	Mg	Al	Si	P	S	Cl			
IV(a)	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co
IV(b)		Cu	Zn	Ga	Ge	As	Se	Br			
V(a)	Kr	Rb	Sr	Y	Zr	Cb	Mo		Ru	Rh	Pd
V(b)		Ag	Cd	In	Sn	Sb	Te	I			
	Xe	Cs	Ba	La	Ce						
VIa	INTERMEDIATE				Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu.						
						Ta	W		Os	Ir	Pt
VIb		Au	Hg	Tl	Pb	Bi					
VIIa	Nt		Ra		Th		U				

Figure 8. Young's table of 1908 illustrating the periodicity of electronegativity *(19):* the further to the right the symbol, the more electronegative the corresponding element.

standard late nineteenth-century monographs on thermochemistry by Berthelot *(20, 21),* Thomsen *(22, 23),* Naumann *(24, 25),* or Pattison Muir *(26),* though, as noted in the previous section, Thomsen made use of the electronegativity concept in his work on periodic law *(18, 27).*

The first person to again draw attention to these correlations appears to have been Jacobus van't Hoff in the third volume of his *Lectures on Theoretical and Physical Chemistry*, first published in 1899. Here van't Hoff presented a graph (Figure 9) contrasting the enthalpies of reaction of chlorine versus sodium with equivalent amounts of sulfur, oxygen, chlorine, iodine, hydrogen, and sodium, and noted that the maximum heat evolution occurred when the electronegativity difference between the two reacting elements was also at a maximum *(28)*:

> ...the contrast which we have seen to exist between sodium and chlorine in the facility for associating with electricity, i.e., for forming ions, reappears in these thermal values, and the evolution of heat in the combination of two elements goes hand and hand with their facility for associating with opposite electrical charges.

A similar correlation was stressed by Robert Cavin and G. D. Lander in the 1907 edition of their advanced textbook, *Systematic Inorganic Chemistry from the Standpoint of the Periodic Law (29)*:

> Generally speaking, the thermal value of a reaction will be greatest when the uniting elements are most widely separated in [electro]chemical character.

Otto Sackur was likewise willing to make a passing reference to these correlations in the 1917 edition of his monograph, *A Text Book of Thermo-Chemistry and Thermodynamics (30)*:

> ...elements at opposite ends of the periodic system combine with great evolution of heat, e.g., the alkalies and the alkaline earths with the halogens and oxygen. In the formation of similar types of compounds, such as oxides, chlorides, sulfides, etc., the heat of formation generally diminishes in the same sequence as the atomic weight increases. It also runs parallel with the tendency to form ions (electroaffinity). The elements that have a strong tendency to form cations (e.g., potassium and sodium), and also those that have a strong tendency to form anions (such as chlorine), give particularly large heats of formation with elements that are opposite to them in electrical character.

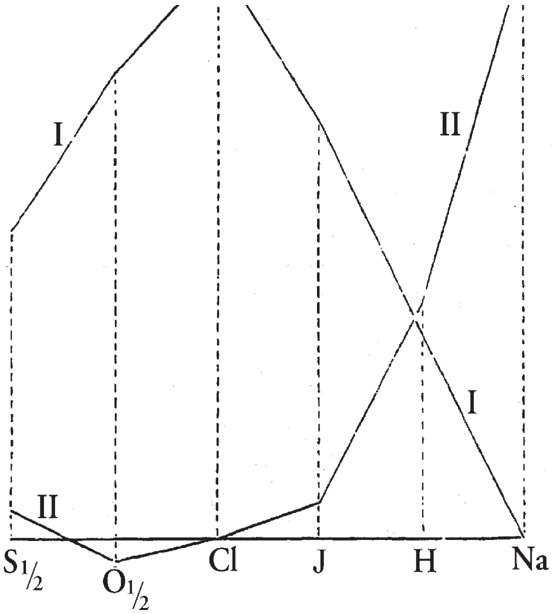


Figure 9. Van't Hoff's graph of the enthalpies of reaction of sodium (curve I) and chlorine (curve II) with equivalent amounts of sulfur, oxygen, chlorine, iodine, hydrogen, and sodium *(13).*

Electronegativity and the Electrical Theory of Matter

As the nineteenth century drew to a close, two events occurred that, although initially causing some confusion, would ultimately lead to a significant refinement of the electronegativity concept. The first of these was the introduction of the ionic theory of dissociation in 1887. As is apparent from the van't Hoff and Sackur quotes, it was now possible to more precisely define electropositive and electronegative character in terms of an atom's "tendency" to form positive and negative ions, respectively. Unfortunately, not everyone was careful to maintain the distinction between the tendency or ease of forming an ion, on the one hand, and the properties of the resulting ion, on the other—a blurring of concepts due, in no small measure, to the continued use of ambiguous terminology, such as "positive and negative element" or "positive and negative character" as synonyms for electronegativity.

Further confusion resulted from the introduction of the "electroaffinity" concept by the German chemists Richard Abegg and Guido Bodländer in 1899 *(31).* This was essentially a measure of what would today be called an aqueous oxidation potential and was interpreted by Abegg and Bodländer as a measure of a given element's tendency to form aqueous ions. Their interest in this parameter centered on its correlation with such properties as the solubility of a given element's salts in water, their degree of ionic dissociation once dissolved, and the tendency of the resulting ions to form complexes with various ligands. Abegg and Bodländer were also aware that—unlike electronegativity, which was presumably an atomic property—the electroaffinity of an element was a complex parameter that was both concentration and temperature dependent.

But these important differences were again ignored by many textbook writers of the period who simply began using the electroaffinity and electronegativity concepts interchangeably. A case in point is the textbook by Cavin and Lander mentioned earlier *(29).* Though there is no evidence that these authors were aware of the earlier work of Avogadro, there are a number of interesting parallelisms. Like Avogadro, these authors postulated a generalized acid–base scale for the elements based on the behavior of their oxides, such that the more acidic its oxide, the more "oxygenic" the element in question. They then compared the order of the elements on their chemical oxygenic scale, not with their positions on the contact electrification scale, as Avogadro had, but rather with their positions on the electroaffinity scale of Abegg and Bodländer. Not surprisingly, they concluded that the two scales did not always coincide—a conclusion that had already been reached by Avogadro and Meyer much earlier when they had also unsuccessfully attempted to use cell potentials to evaluate relative electronegativity orders. Nevertheless, these authors continued to use the electroaffinity concept as a substitute for electronegativity in later editions of their textbook, some appearing as late as the 1940s, and a similar substitution can be found in other early twentieth-century textbooks as well *(32, 33).*

The second event of importance was, of course, the discovery of the electron by J. J. Thomson in 1897. Here the initial source of confusion centered on the question of where the compensating positive charge was located in the atom. Early speculation on this question was heavily influenced by Hermann von Helmholtz's famous Faraday lecture of 1881 *(34).* In this lecture Helmholtz had pointed out that Faraday's laws of electrolysis strongly implied that electricity was particulate in nature. Helmholtz then proceeded to explain chemical valence and bonding using a dualistic theory of electricity in which a neutral atom was composed of equal numbers of mobile positive and negative electrical particles adhering to an underlying central core of Newtonian matter. Both types of electrical particles were capable of being detached from the atom and the creation of positive and negative ions was easily explained in terms of their preferential loss or gain. Within this model, the electronegative and electropositive character of the atom became a measure of an inherent difference in its ability to attract and hold the two types of electrical particles.

Thomson's recently discovered negative electron was quickly identified with Helmholtz's mobile negative particle and it was assumed that a corresponding mobile "positive electron" would also soon be found. The most important advocate of this dualistic interpretation among chemists was the German physical chemist, Walther Nernst, who continued to discuss it as late as 1911 in his highly influential textbook, *Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics*, in a section entitled "Positive and Negative Elements" *(35)*[3]:

> The different elements and radicals have different chemical affinities towards the positive and negative electrons; those that have a strong tendency to combine with the positive electrons form positive groups of elements; similarly negative elements are characterized by their affinity for negative electrons.

Yet others favored a unitary theory of electricity in which only mobile negative particles were capable of being added or detached from the neutral atom and the compensating positive charge was instead assumed to be an inherent part of the underlying core of Newtonian matter. Within the context of this model, ion formation was due to the loss or gain of negative electrons only and electronegativity became a measure of this tendency. The major advocate of this approach was the German physicist, Johannes Stark (Figure 10), who showed remarkable insight in his 1903 monograph, *Die Dissoziierung und Umwandlung chemischer Atome (36)*:

> In a certain sense we have been describing the tendency of the chemical elements to become saturated with respect to negative electrons. And this saturation tendency differs from element to element in keeping with the magnitude of its ionization energy. The greater the force with which a chemical atom holds on to its own electrons, the greater its ionization energy, and in general the greater its saturation tendency for additional negative electrons. By way of example, the ionization energy, as well as the saturation capacity, of a chlorine atom is greater than that of a sodium atom.

Stark also realized that the observed relationship between gaseous ionization energies and ion formation would allow chemists—once these energies were accurately measured—to construct a quantitative electronegativity scale *(36)*:

> Experience has shown that the ionization energy of the metals is smaller than that of hydrogen, and that this, in turn, is smaller than the metalloids [i.e., nonmetals]. If one arranges the chemical elements in an increasing series according to their ionization energies, the so-called electropositive elements will be found at the beginning and the electronegative elements at the end.

It is interesting to note that the dualistic versus the unitary interpretations of Thomson's discovery mirror a similar debate over nature of electricity that occurred within the context of the imponderable fluid theories popular a century earlier—a debate, as we saw in Part I, that was also reflected in Berzelius's choice of a dualistic or two-fluid model versus Avogadro's implicit use of an unitary or one-fluid model of electricity in rationalizing their original interpretations of the electronegativity concept.

Though many physicists and chemists felt that the two models were essentially equivalent *(37),* others argued that not only was the unitary model inherently simpler, it was also more in keeping with the facts of chemistry and physics. Thus, writing in 1905, the British chemist, Geoffrey Martin, after noting the temperature and pressure dependence of metallic versus nonmetallic behavior, observed *(38)*:

> Since the valency bonds of a metal are of an electropositive nature, while the valency bonds of a nonmetal are of an electronegative nature; then, if a metal can be transformed into a nonmetal by simply lowering its tempera-

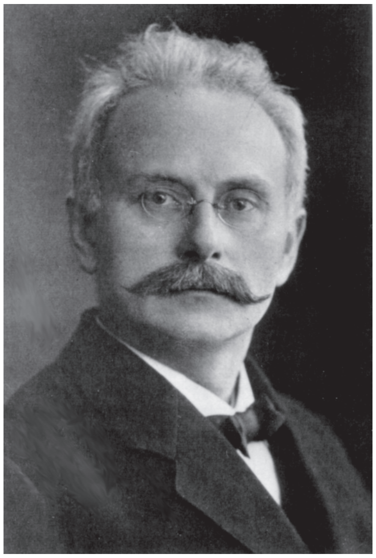


Figure 10. Johannes Stark, 1874–1957 (Oesper Collection).

> ture sufficiently, it follows that the difference between a negative and positive valency lies not in any absolute difference in the nature of the electrons (atoms of electricity), which are supposed to cause the phenomena of valency, but solely in the difference in the stability with which the electrons are held by the atom... Thus we arrive at the generalization that one, and only one, kind of electron causes the phenomena of chemical valence. The electrons can cause an atom to appear either as electropositive or electronegative in nature according as they are feebly or firmly held by the atom.

By 1913 the unitary electron interpretation of electronegativity was sufficiently widespread that Kasimir Fajans could mention it in passing in his famous paper on the beta radioactive decay series without further elaboration or justification *(39)*:

> Electronegative character is defined as the inclination of an atom to split off or take on negative electrons.

Indeed, by the end of the first decade of the twentieth century, chemists and physicists had already begun exploring correlations between the atom's ability to attract or retain valence electrons and such parameters as atomic size. Thus, based on theoretical deductions using J. J. Thomson's well-known charge–cloud model of the atom, the British physicist, Norman Campbell, could write in the 1907 edition of his monograph, *Modern Electrical Theory*, that *(40)*:

> There is one very simple difference in the structure of atoms that will account for the difference in the facility with which atoms lose or gain electrons: it is easily shown that the smaller atom tends to gain electrons at the expense of the larger.

Campbell then proceeded to compare this theoretical conclusion with the experimental facts by using the known periodic trends in both electronegativity and atomic (i.e., molar) volume. Since the latter parameter reflected the true volumes of the component atoms only when the corresponding simple substances were isostructural, Campbell was restricted to intragroup rather than intraperiod comparisons—nevertheless, the facts seemed to support the underlying theory *(40)*:

> It is well known that there is an intimate connection between the valency of the elements and their atomic volume...for the atomic volume of elements of the same chemical group increases with the atomic weight, and an increase in the atomic weight is accompanied by an increase in the "electropositiveness" of the element. Thus, of the alkali metals, the most electropositive is cesium with the heaviest atom, and the least electropositive is lithium with the lightest atom. Of the halogen elements the most electronegative (and least electropositive) is fluorine, the least electronegative is iodine. The nitrogen group offers an even more striking example. The lightest atom, that of nitrogen, is usually electronegative, while the heaviest atom, that of bismuth, is usually electropositive... Since the electropositive elements are those that tend to lose electrons and the electronegative elements are those that tend to gain them, it appears that the smaller element has the greater tendency to acquire electrons and the larger element the greater tendency to lose them. So far then the facts bear out the rule deduced from the structure of our hypothetical atom.

Conclusions

In Part I *(1)* it was noted that nowhere in his 1932 paper on electronegativity did Linus Pauling bother to give an explicit definition of the concept. The reasons for this should now be apparent. By the 1930s the electronegativity concept was more than 120 years old and its most recent reincarnation, in terms of an atom's ability to attract and retain valence electrons, was almost 30 years old. Consequently Pauling could be certain that his readers knew exactly what he meant by the term.

The various themes discussed in this installment form the starting point for the next stage in the evolution of the electronegativity concept— its quantification. The correlation between electronegativity and heat of reaction, suggested by van't Hoff, Caven, Lander, and Sackur, will be pursued by Pauling in his 1932 paper, "The Energies of Single Bonds and the Relative Electronegativities of Atoms" *(41),* whereas the correlation between electronegativity, ionization energy, and "saturation tendency" or electron affinity, discussed by Stark, Martin, and Fajans, will be pursued by Robert Mulliken in his 1934 paper, "A New Electroaffinity Scale" *(42).* The details of these events will form the substance of Part III of this series.

Notes

1. Barker actually used the term "atomic equivalence" rather than valence to describe the quantity of atomic combining power and talked about the relative "positive" and "negative" character of an atom, rather than its electronegativity.
2. Didymium (variously symbolized as D or Di) was later resolved into neodymium (Nd) and praseodymium (Pr) by Auer von Welsbach in 1885.
3. Except for use of the word "electron," this statement is virtually identical to that given by Pattison Muir 27 years earlier based on Helmholtz's original lecture. See Pattison Muir, M. M. *A Treatise on the Principles of Chemistry;* Cambridge University Press: Cambridge, 1884; p 457.

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