

Redefinition of Electronegativity as the Average Valence Electron Energy: The Third Dimension of the Periodic Table

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Abstract: Electronegativity (EN) has been redefined as the average valence electron energy (AVEE) that takes into account all of the s and p electrons in the valence shell for main group elements. This definition confers unambiguous physical meaning on the term electronegativity. EN and AVEE can be used interchangeably, directly relating the parameter to the periodicity of the elements. This paper shows that the EN criterion can be used as an exclusive approach to describing the properties and reactivities of the elements. Various chemical phenomena, such as metallicity, reactivity, type of bonding, and oxidation states, are correlated distinctly to electronegativity. Especially significant is the explanation of the difference in properties of the second row and lower main group elements based exclusively on their electronegativities. This is demonstrated to be a simple and powerful approach that possibly avoids more complicated bonding theories. Electronegativity (in terms of average valence electron energy) qualifies as the third dimension of the periodic table. The purpose of this paper is to effectively address this concept in fundamental chemical education in relation to the periodicity and properties of the elements.

Introduction

The concept of electronegativity (EN), first proposed by Pauling [1], was originally defined as the power of an atom in a molecule to attract electrons to itself. He chose an arbitrary scale for electronegativity based on thermochemical data and assigned EN = 4 to fluorine, the most electronegative element. The values for the other elements are relative to the value for fluorine. Soon after Pauling published his first paper on electronegativity, Mulliken [2] suggested a modified method of treating it by considering both ionization energy (IE) and electron affinity (EA), that is, $EN = 1/2(IE + EA)$. Since then, various EN scales have been proposed [3]. Pauling's scale has been used predominantly in chemistry texts since it was developed. In the last ten years, an alternative treatment of electronegativity has been developed. In his seminal paper [4], Allen proposed that electronegativity be redefined in terms of the average one-electron energy of the valence-shell electrons in ground-state free atoms formulated as

$$EN = (m\varepsilon_p + n\varepsilon_s) / (m + n) \quad (1)$$

where ε_p and ε_s , m and n are the average ionization energies and numbers of p and s electrons in the valence shell, respectively. This quantity is also termed the configuration energy [5] and is synonymous with the average valence electron energy (AVEE) [6], which takes into account all of the s and p electrons in the valence shell. The ionization energies are obtained spectroscopically to high accuracy and found from the National Bureau of Standards atomic energy level tables, and Allen EN values (Figure 1) closely match the widely accepted Pauling and Mulliken scales [4]. This model directly relates electronegativity to the average energy of all valence shell electrons, the central parameter that to a large extent determines the properties and reactivities of the

elements, conferring the term electronegativity with an unambiguous physical meaning. EN and AVEE can be used interchangeably (eq 1), resulting in a unified critical concept that directly connects the periodic table and can be employed as an exclusive approach to the periodic properties of elements, such as metallicity, reactivity, type of bonding, and oxidation states. Traditionally, in most general chemistry textbooks the concept of electronegativity is introduced when discussing the polarity of chemical bonds. The higher the difference in EN values of two chemically bound atoms, the more polar the chemical bond. Because EN is by virtue AVEE, its meaning is no longer limited to the relative tendency of attracting electrons. It has become the third dimension of the periodic table [4]. Recent advances in EN theory have been briefly reviewed in some textbooks [6–8]. The purpose of this paper is to facilitate effectively addressing this conceptual development in relation to the periodicity and properties of the elements in university, general, and inorganic chemistry courses. The remarkable roles that electronegativity plays in determining properties and reactivities are illustrated systematically as they pertain to fundamental chemical education.

Electronegativity, Periodicity, and Metallicity

The chemical properties of an element are ultimately determined by configuration and the energy of its valence-shell electrons. The latter is represented by the redefined electronegativity, that is, the average valence electron energy (eq 1). For main group elements, the similarity of the properties in a given group is related to the same valence-shell electronic configuration as well as to very close EN (AVEE) values. This can be considered as the EN basis of periodicity. For example, Figure 1 shows that all the alkali metals possess a small EN of ~0.66 to 0.91 with a small overall difference of 0.25. They are active metals with similar properties, all

forming monocations in their compounds with nonmetals. Although hydrogen has one valence electron, the same as the alkali metals, its properties are quite different, forming covalent compounds with nonmetals. This discrepancy is due to the much higher EN of hydrogen (2.30), giving rise to its predominant nonmetallic character. All halogens (F, Cl, Br, and I) have seven valence electrons (ns^2np^5) and they exhibit some similar properties; however, F is a much more active nonmetal than Cl, Br, and I, and the properties of the latter three are much closer to each other than to fluorine. This can be explained by comparison of their EN values. Cl, Br, and I have close ENs (2.36–2.87, overall difference of 0.51), accounting for their very similar properties. The difference in the ENs of fluorine (4.19) and chlorine (2.87) is large (1.32), accounting for the substantial difference of fluorine from the other three halogens. For example, fluorine reacts with aqueous alkali giving OF_2 , while the reactions of chlorine, bromine, and iodine lead to the formation of salts of the halogen oxyacids. The EN of fluorine (4.19) is greater than that of oxygen (3.61), but the ENs of chlorine (2.87), bromine (2.69), and iodine (2.36) are smaller than that of oxygen. The same argument can be used to explain the similarities between P (EN = 2.25) and As (EN = 2.21), $\Delta EN = 0.04$ and between S (EN = 2.59) and Se (EN = 2.42), $\Delta EN = 0.17$; however, larger differences in properties are found between N (EN = 3.07) and P (EN = 2.25), $\Delta EN = 0.82$ and between O (EN = 3.61) and S (EN = 2.59), $\Delta EN = 1.02$.

The elements are classified as metals, nonmetals and metalloids. The metallicity has long been fundamentally related to the first ionization energy; however, for the *p*-block elements, both *s* and *p* electrons in the valence shell participate in bonding. Thus, the metallicity would be characterized more precisely by the redefined electronegativity, that is the average valence electron energy. According to the Allen scale (Figure 1), all metals have $EN < 2.0$ and all nonmetals have $EN > 2.3$. In between are the metalloids, B, Si, Ge, As, Sb, and Te, forming a diagonal line with a narrow EN between ca. 1.9 and 2.2. Thus, the classification can be made on the basis of EN values. All metals possess luster, are solids (with the exception of mercury), good conductors for electricity and heat, and many of them react readily with nonmetals. These properties relate to the nature of metallic bonding as described by the “electron-sea” model. The valence electrons possess low average ionization energy, loosely held to the nuclei and moving freely. Thus, the general properties of metals can be correlated with the generally low ENs of the metallic elements. On the other hand, most nonmetals are poor conductors, can have different states at ambient conditions, and react with metals and nonmetals. All these general properties of nonmetals are related to the generally high ENs of nonmetallic elements. The spacings between the *s* and *p* sublevels get larger with increasing EN, resulting in bonding directionality and favoring the formation of covalent bonds [5]. The variation in metallicity moving from one group to another or descending within a group is attributable to the systematic change in EN. The metallic character increases with decreasing EN and the nonmetallic character increases with increasing EN. The substantial differences between B (EN = 2.05) and Al (EN = 1.61) and between C (EN = 2.54) and Sn (EN = 1.82) are well explained by the EN criterion. Hence, the magnitude of EN (in terms of AVEE) is a direct measure of metallicity.

Electronegativity and Reactivity

Because electronegativity has been generalized as the average valence electron energy (eq 1) [4, 5], the difference in electronegativities (ΔEN) of two elements would exert a driving force on their combination and can serve as a unified criterion for predicting the reactivity between them. Qualitatively, in general, a high EN difference relates to a favorable reaction and a low EN difference to an unfavorable one. For example, most noble gases do not readily combine with other elements. One exception to this is the combination of Xe (EN = 2.58) with F (EN = 4.19). This can be explained by considering the relatively low EN of Xe along with the high EN of F, resulting in a large difference, $\Delta EN = 1.61$. The EN differences between Kr and F (1.22) and between Ar and F (0.95) are relatively small and the combinations of fluorine with krypton and argon are known to be less favorable. The EN difference between Xe (2.58) and Cl (2.87) is so small (0.29) that no binary compound has been isolated, although $XeCl_2$ has been identified in a xenon matrix at 20 K [4, 7a]. Hydrogen (EN = 2.30) is more reactive towards nitrogen (EN = 3.07) than towards phosphorus (EN = 2.25), indicated by the difference in the enthalpies of formation of $NH_3(g)$ ($\Delta H_f^0 = -46.2 \text{ kJ mol}^{-1}$) and $PH_3(g)$ ($\Delta H_f^0 = 5.4 \text{ kJ mol}^{-1}$). This is understandable in terms of a larger EN difference (0.77) between N and H relative to ~ 0 between P and H. For interhalogen compounds XY, X and Y being different halogens, the bond energy increases in general (although exceptions exist) as the EN difference of the component atoms increases, for example, IF ($277.8 \text{ kJ mol}^{-1}$), BrF ($249.4 \text{ kJ mol}^{-1}$), ClF ($248.9 \text{ kJ mol}^{-1}$), ICl ($207.9 \text{ kJ mol}^{-1}$), BrCl ($215.9 \text{ kJ mol}^{-1}$), and IBr ($175.3 \text{ kJ mol}^{-1}$) [7b].

Electronegativity plays a key role in determining the reaction site of polyatomic species. For example, to date all the known reactions of unsaturated organic molecules with the linear NO_2^+ ion occur on the central N atom, leading to nitration [9]. However, all the known reactions with the linear sulfur analog, the NS_2^+ ion, occur on the terminal sulfurs [10, 11]. NS_2^+ has been shown to undergo cycloaddition reactions with the $C\equiv N$, $C\equiv C$, and $C=C$ bonds on the two terminal sulfurs giving five-membered rings [10]. NS_2^+ undergoes C–H insertion to benzene forming a sulfur protonated substitution product [$C_6H_5SNSH^+$] (cf., nitration of benzene, which occurs on the central nitrogen of NO_2^+ giving nitrobenzene) [11]. All of the above reactions are electrophilic. The organic substrates function as the electron donors and the cations as the electron acceptors. The difference in reactivity originates from the EN difference between the two elements in each of the binary ions, giving rise to different charge as well as LUMO (the reacting orbital of the cations) distributions [11, 12]. For NO_2^+ , oxygen (EN = 3.61) is more electronegative than nitrogen (EN = 3.07) and the terminal O atoms carry partial negative charge ($\delta = -0.15$) and the central N partial positive charge ($\delta = +1.30$). However, for NS_2^+ , sulfur (EN = 2.59) is less electronegative than nitrogen (EN = 3.07) and the terminal S atoms carry partial positive charge ($\delta = +0.68$) and the central N partial negative charge ($\delta = -0.36$). The less electronegative atom makes a greater contribution to the LUMO and the more electronegative atom makes a smaller contribution [7c]; therefore, the p_π LUMO of NO_2^+ is essentially nitrogen-based (N is less electronegative than O)

H 2.30																	H 2.30	He 4.16
Li 0.91	Be 1.58											B 2.05	C 2.54	N 3.07	O 3.61	F 4.19	Ne 4.79	
Na 0.87	Mg 1.29											Al 1.61	Si 1.92	P 2.25	S 2.59	Cl 2.87	Ar 3.24	
K 0.73	Ca 1.03	Sc 1.2	Ti 1.3	V 1.4	Cr 1.5	Mn 1.6	Fe 1.7	Co 1.8	Ni 1.9	Cu 1.8	Zn 1.6	Ga 1.76	Ge 1.99	As 2.21	Se 2.42	Br 2.69	Kr 2.97	
Rb 0.71	Sr 0.96	Y 1.0	Zr 1.1	Nb 1.3	Mo 1.4	Tc 1.5	Ru 1.7	Rh 1.8	Pd 1.9	Ag 2.0	Cd 1.5	In 1.66	Sn 1.82	Sb 1.98	Te 2.16	I 2.36	Xe 2.58	
Cs 0.66	Ba 0.88											Hg 1.76						

Figure 1. Redefined electronegativities of the elements in the Allen Scale [4].

and the p_π LUMO of NS_2^+ is sulfur-based (S is less electronegative than N). The differences in both the charge and LUMO distributions, which are determined essentially by EN values, account for the observed different reaction sites of the two analogous ions. Although both oxygen and sulfur belong to group VIA, possessing the same valence shell configuration, the contrast in their electronegativities has made the chemistry of these two fundamental polyatomic ions substantially different. All these examples show that electronegativity has the predictive powers of molecular orbital theory.

Electronegativity and Bonding

Electronegativity differences also govern which of the three types of bonding, covalent, metallic or ionic, will occur between atoms [4]. Large EN differences correspond to ionic species, for example, Na_2O ($\Delta\text{EN} = 2.74$), MgO ($\Delta\text{EN} = 2.32$), and Al_2O_3 ($\Delta\text{EN} = 2.00$). Small EN differences correspond to molecular species, for example, SO_2 ($\Delta\text{EN} = 1.02$). In between are the polymeric compounds, for instance, SiO_2 ($\Delta\text{EN} = 1.69$) and P_4O_{10} ($\Delta\text{EN} = 1.36$). Similarly, in contrast to SiO_2 and P_4O_{10} , the oxides of carbon and nitrogen have smaller EN differences (1.07 and 0.54, respectively). They exist as small discrete molecules (e.g., CO_2 and NO_2). The differences between the second and third row elements has been explained effectively by using the EN criterion. The generalized electronegativity in terms of the average valence electron energy (eq 1) has provided an effective and convenient explanation for the hybrid orbital ordering rule (highest to lowest electronegativity): $sp > sp^2 > sp^3$, the greater the percent s character, the larger the EN, simply because $\epsilon_s > \epsilon_p$ for the same valence shell. Therefore, the acidity order of the σ -orbital bound hydrogens ($\text{HC}\equiv\text{CH} > \text{H}_2\text{C}=\text{CH}_2 > \text{H}_3\text{C}-\text{CH}_3$) is well accounted for by the EN criterion.

Electronegativity and Oxidation States

Oxidation states are determined by the number of bonding electron pairs available on an atom. Their differences in various compounds can be effectively correlated to the EN values. This is especially useful when discussing the third row and lower elements as well as halogens. Fluorine is the most electronegative open-shell (incomplete-valence-shell) element. Its only oxidation state in compounds is -1 . The other halogens, Cl, Br, and I, exhibit negative oxidation states (-1) when combining with less electronegative elements and various positive oxidation states, up to $+7$, when combining with more electronegative elements. The highest oxidation state is determined by the electronegativity difference between

the atom under consideration and its adjacent atom [7b]. Generally, the larger the EN difference, the greater the highest oxidation state the central atom can possess. For example, the highest halogen fluorides for Cl (EN = 2.87) and Br (EN = 2.69) are ClF_5 ($\Delta\text{EN} = 1.32$, Cl = $+5$) and BrF_5 ($\Delta\text{EN} = 1.50$, Br = $+5$), respectively. For iodine (EN = 2.36), however, the highest fluoride is IF_7 ($\Delta\text{EN} = 1.83$, I = $+7$), largely because there is a greater electronegativity difference between iodine and fluorine than between Cl or Br and fluorine. Similarly, the highest fluorides of group 5A elements N (EN = 3.07) and P (EN = 2.25) are NF_3 ($\Delta\text{EN} = 1.12$, N = $+3$) and PF_5 ($\Delta\text{EN} = 1.94$, P = $+5$), respectively, again dependent upon electronegativities. The oxidation state of the highest fluoride of S (EN = 2.59), SF_6 ($\Delta\text{EN} = 1.60$, S = $+6$), reaches the number of valence electrons of sulfur; however, OF_2 is the highest fluoride of oxygen with oxidation state of O = $+2$. OF_6 does not exist, largely because of its low EN difference (0.58). In all the above cases, steric effects may also be important because the coordination number to the less electronegative central atom in each case is also related to the size of the central atom. N, P, and S, when combining with less electronegative elements (e.g. H), exhibit negative oxidation states. They exhibit various positive oxidation states when combining with more electronegative elements (e.g. O and F). Hydrogen (EN = 2.30), the least electronegative nonmetal, has only one electron. When combining with more electronegative elements, it functions like alkali metals, exhibiting an oxidation state of $+1$. Because H has one less electron than He, it functions like the halogens, forming hydrides and exhibiting an oxidation state of -1 when combining with less electronegative metals such as sodium (EN = 0.87). The unique properties of hydrogen are largely owed to its EN being between metals and most nonmetals, consistent with its valence shell configuration.

Electronegativity and Acidity

Inorganic oxyacids with the general formula $\text{X}(\text{OH})_m\text{O}_n$ form a large, important group of compounds. Their acidity is directly linked to the electronegativity of X, $\text{p}K_a = 10.5 - 5.0n - \text{EN}$, where K_a is its first dissociation constant [7d]. The higher the EN of X, the more acidic and less basic is the species. This accounts for the order of increase in acidity for the hydroxides of the third period elements: $\text{NaOH} < \text{Mg}(\text{OH})_2 < \text{Al}(\text{OH})_3 < \text{Si}(\text{OH})_4 < \text{H}_3\text{PO}_4$ ($\text{OP}(\text{OH})_3$) $< \text{H}_2\text{SO}_4$ ($\text{O}_2\text{S}(\text{OH})_2$) $< \text{HClO}_4$ (O_3ClOH). Small ENs, such as for X = Na (0.87) and Mg (1.29), correspond to bases, and large ENs, such as for X = P (2.25), S (2.59), and Cl (2.87), correspond to acids. Intermediate ENs, for instance, those of Al (1.61) and Si

(1.92) correspond to amphoteric. For organic carboxylic acids RCOOH, the higher the EN of the R group [7d], the more acidic is the acid. This can be demonstrated by comparison of CH₃COOH (EN_{CH₃} = 2.31, $K_a = 1.8 \times 10^{-5}$) and CF₃COOH (EN_{CF₃} = 3.47, $K_a = 5.0 \times 10^{-1}$) [7d]. These examples demonstrate the importance of EN in the study of acids and bases.

Conclusion

Because electronegativity has been generalized as the average valence electron energy, this quantity has become a central parameter that serves as a general guide for the properties and reactivities of the elements. EN (in terms of AVEE) plays a key role in determining periodicity and thus qualifies as the third dimension of the periodic table as suggested ten years ago [4]. Periodicity of the elements may be understood to a large extent as the consequence of the recurrence (similarity) of EN values with increasing atomic number. The EN criterion is especially useful on a relatively simple basis for accounting for the differences between the second row and lower main group elements that possibly avoids complicated bonding theories, including the controversial d-orbital participation in bonding [7e]. This concept is intuitive and readily understood even by first-year students and sophomores. It is a powerful tool for effectively organizing chemical phenomena. Electronegativity (in terms of AVEE) can be used as an exclusive approach to the periodicity of the elements and should be covered effectively in fundamental chemical education. The periodic table may be

redesigned so that the EN values for various elements are indicated by the use of a continuous spectrum of colors in order to highlight the important role of this quantity in determining the properties of the elements.

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