

chemical principles revisited



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Principles of Electronegativity

Part I. General Nature

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For more than 50 years the concept of electronegativity has been modified, expanded, and debated. It is of great theoretical interest today. However, the practical aspect has greatest potential for promoting chemical understanding in the classroom, for it is now possible not only to correlate the properties of hundreds of compounds with the electronegativities of their elements but also to calculate accurately the energies of polar covalent bonds. Thus students can be provided with valuable insights and understanding of the cause-and-effect relationship between atomic structure and the properties of compounds. They can begin to understand the origin of bond energy and thus the causes and direction of chemical reactions.

This article and one to follow are not intended as a comprehensive review of all that has been proposed. There is no deliberate slighting of any particular contribution, and references 1-7 are provided to suggest some of the more recent work that interested readers may wish to study. As in any growing body of knowledge, there is plenty of room for controversy, and no two workers will agree completely. Some new ideas are included herein that are abundantly supported by convincing evidence, although space is available for only a few illustrative examples. Sources of much additional information will be cited.

The electronegativity of an atom can perhaps least controversially be defined as that property which determines how the bonding electrons will become distributed between it and another atom if the two atoms become connected by a chemical bond. The atoms are recognized as initially equal in electronegativity if they share the bonding electrons evenly. If the electrons are not evenly shared, that atom that acquires more than half share is considered to have had initially a greater electronegativity. From a practical viewpoint, this concept of electronegativity seems to satisfy unambiguously the need to predict the direction and approximate extent of the polarity of a covalent bond, which has been the most common application. For a more thorough understanding, however, we should consider the relation of electronegativity to atomic structure and what happens to it when atoms combine. Furthermore, although various routine attempts to evaluate the electronegativities of transitional elements have been made over many years, the only values reliably applied have been those of the major group elements. Recent work has now produced reasonably reliable

estimates of some of the electronegativities for transitional elements in various oxidation states and for lower-than-normal valence states of major group elements. A summary of the general principles governing the significance and applications of electronegativity follows. The purpose of this paper is to present and discuss such principles in a general way. The second article of this pair will be devoted to greater emphasis on the practical applications.

1. Most atomic properties are a consequence of atomic structure, which in turn must be related to the inherent nature of the component electrons and nuclei. Therefore it is almost inevitable that such properties be related to one another, if only because of their common origin. It should not be surprising that a particular property, here the electronegativity, can be derived from or correlated with a wide variety of other properties, with reasonable agreement among the several results.

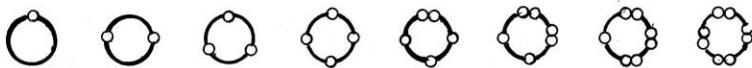
Since electronegativity is a measure of the effectiveness of the nuclear charge as sensed within an outer orbital vacancy, the relationship between atomic structure and electronegativity is quite apparent. It becomes more so when it is realized that the outermost electrons are not very effective in shielding one another from the nuclear charge, and thus permit the *effective nuclear charge* to build up a larger and larger lead as the atomic number increases and the number of outer electrons changes from one to eight. This results in an enforced contraction of the electronic cloud, and the larger effective nuclear charge operative over a shorter radius corresponds to a steadily increasing electronegativity across the period of major group elements. The major effects of increasing the number of outermost electrons across a period of major group elements are summarized in Figure 1. Electronegativity is obviously not merely a number but the logical and inevitable consequence of atomic structure.

2. The best method of evaluating electronegativity remains to be discovered. One successful evaluation may be based on the relative compactness of the electronic clouds that surround atomic nuclei.

It is logical to suppose that any atom unable to hold its own electron cloud compactly around its nucleus (for example, an atom of the alkali metals) may have ample outer space capable of accommodating extra electrons but very little attraction for them. That atom must therefore have low electronegativity. Similarly, any atom capable of holding its own electronic cloud closely and compactly despite the stronger interelectronic repulsions existing within denser clouds (for example, an atom of a halogen) should reason-

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Wherever the atomic structure changes by increasing the number of outermost electrons,

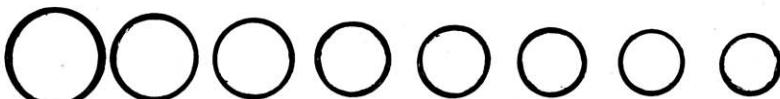


the fraction of the total nuclear charge that can be sensed within an outer orbital (called the effective number charge) is caused to increase:



In turn, this causes three important changes in atomic properties:

(1) The increasing charge pulls the electrons into a more compact cloud of diminished radius:



(2) Greater charge acting over shorter distance corresponds to increasing electronegativity:



(3) It also corresponds to increasing (unweakened) homonuclear bond energy:



Since each atom can form one covalent bond for each half-filled outer orbital it can supply, the changing atomic structure, by increasing the number of electrons in the four outer orbitals, changes the availability of outer half-filled orbitals and thus the covalence:

1—2—3—4—3—2—1—0

Repulsions among bonding electrons and lone pair electrons largely determine bond angles:



All these properties are the logical and inevitable consequences of the changes in atomic structure, as now quantitatively exemplified by the series from Na to Cl:

element	Na	Mg	Al	Si	P	S	Cl
no. outer e's	1	2	3	4	5	6	7
eff. nuclear charge	2.0	2.7	3.4	4.0	4.7	5.3	6.0
covalent radius, pm	154	137	126	117	111	105	99
electronegativity	0.84	1.32	1.71	2.14	2.52	2.96	3.48
B.E., homonuclear (unweakened, kcal)	16.4	42.3	48.2	54.1	60.0	65.9	71.8
covalence	1	2	3	4	3	2	1
bond angle	none	180°	120°	109°	90–109°	90–109°	none

ably be expected to exert a strong attraction for an outside electron, provided it can also provide an outer orbital vacancy to accommodate it. Such an atom must therefore have high electronegativity. For example, the potassium atom holds 19 electrons within a radius of 196 pm, whereas an atom of chlorine holds nearly as many electrons, 17, within a radius of 99.4 pm, only about half that of potassium, and thus within only about one-eighth the volume. The electronegativity of chlorine, 3.475, is nearly eight times that of potassium, 0.445.

It may also be recognized that the natural tendency of any highly electronegative atom is to acquire partial negative charge, which causes expansion of the electronic sphere to a less compact condition. The natural result of partial electron loss by any atom low in electronegativity is contraction of the electronic sphere to a more compact condition.

The "relative compactness" method recognizes that although ideally the relationship between compactness and electronegativity should be quantitative and direct, certain features of the evolution of electronic configurations with increasing atomic number appear to affect compactness without necessarily being related to electronegativity. In particular, clouds on atoms or ions near to argon, atomic number 18, appear significantly lower in average compactness than those near either neon, atomic number 10, or krypton, atomic number 36. For example, an atom of potassium, radius 196 pm, is closer to rubidium, radius 216 pm, than to an atom of sodium, 154 pm, although in number of electrons it is much closer to sodium (19–11) than to rubidium (37). Similarly, chlorine is closer to bromine than to fluorine. The average electronic density of an atom, defined as the average number of electrons per unit volume of the electronic sphere defined by the nonpolar covalent radius, therefore cannot be taken directly as a measure of electronegativity but must be corrected for the change in electronic density with atomic number observed for atoms which do not normally form bonds and is therefore independent of electronegativity. The ratio of the average electronic density of an atom to that of an interpolated hypothetical "noble gas" (M8) atom of equal number is a good measure of relative electronegativity.

Since this development in the early 1950's (8), individual values have been revised from time to time and refined on the basis of better data, newer knowledge, and improved understanding, and finally changed (9) to assign to fluorine, as in most conventional scales, the value 4.000. The justification for this last change was the practi-

Figure 1. Cause (structure) and effect (properties).

cal one of trying to minimize the confusion created by having different numerical evaluations for the same elements. Pauling scale values differ from intermediate values on the relative compactness scale. Future studies may suggest shifting the scale upward or downward for greater convenience or to correspond to a quantitative theoretical standard.

A complete list of electronegativities as of this date is provided in Table 1. Values for major group elements may be seen to exhibit a steady upward trend across each period, as expected on the basis of the steadily increasing effective nuclear charge. An old assumption is that the electronegativity decreases down a major group, but this is not really true and should not be expected. Although aluminum in the third period logically follows magnesium, both having underlying eight-electron shells, the next element of the aluminum group, gallium, does not follow calcium but zinc, owing to the insertion of the first series of transitional elements between calcium and zinc, and both zinc and gallium have underlying 18-electron shells. The significance of this change in electronic type from period 3 to period 4 in the major group elements is that the period 4 elements have smaller and more compact atoms than otherwise expected. Thus gallium atoms have just about the same radius as aluminum atoms (instead of larger) and are more electronegative (instead of less). This trend continues across the period but decreases until no longer in evidence at bromine. Thus the electronegativity tends to alternate down a group instead of steadily diminishing as otherwise expected.

3. Where valence electrons of a major group atom remain unused within a compound, they appear to reduce the initial electronegativity of the atom.

Electronegativities of subnormal oxidation states of major group elements (10) tend to be substantially lower than the normal electronegativity. These elements in their lower oxidation states have bonds to nonmetals that are more polar than expected and hence stronger than expected. This is particularly important in accounting for the properties of compounds exhibiting the "inert pair effect". This is the tendency of M₃ elements to exhibit an oxidation state of I and of M₄ elements to exhibit an oxidation state of II. For example, the partial charge on oxygen in thallium(I) oxide, Tl₂O, is more than twice as negative as it would be if the

electronegativity of thallium(I) were the same as for thallium(III). This causes the (I) oxide to be strongly basic instead of amphoteric or weakly basic as it would otherwise be. This is because the "inert pair" reduces the thallium electronegativity from 2.25 for the (III) state to 0.99 for the (I) state.

An anomaly occurs with lead, in that its bonds to highly electronegative elements appear to favor the (II) state but those to less electronegative elements favor the (IV) state. For example, PbCl₄ tends to decompose readily to PbCl₂ + Cl₂, whereas lead dialkyls are unstable with respect to the tetraalkyls and lead. It seems quite certain that, if the electronegativity of lead were not appreciably lower in the (II) state, PbCl₄ would be favored over PbCl₂. On the other hand, the electronegativity difference between lead (IV) and carbon is much smaller so that the polar component of the Pb-C bond strength is much less significant, and four Pb-C bonds to the same lead atom, plus the formation of metallic lead, are favored over two Pb-C bonds to each of two lead atoms.

The electronegativities of the lower oxidation states as given in Table 1 are not as reliable as those of the normal states because they are based on less accurate thermochemical data. Where all the normal valence electrons may be presumed to be occupied in the bonding, there is as yet no evidence to suggest that electronegativity differs for different oxidation states. For example, the same electronegativity of nitrogen is equally applicable to ammonia and to each of the nitrogen oxides.

4. In the transitional elements, underlying d electrons not involved in the bonding appear to reduce the electronegativity, the 3d electrons having much greater effect than those of 4d and 5d orbitals.

Although numerous attempts to evaluate transitional element electronegativities have been reported, results have not been satisfactory. Recent work, although not as reliable as wished because of uncertainties in the thermochemical data used, has provided approximate electronegativity values for different oxidation states of a number of transitional elements (11). They appear to increase with increasing positive oxidation state of the metal, and much more rapidly in the 3d series than in the heavier elements of the transitional groups. A long-standing puzzle has been the tendency of the

Table 1. Electronegativities and Change with Unit Charge

	S	ΔS_i		S	ΔS_i		S	ΔS_i		S	ΔS_i
H	2.592	2.528	Ti (II)	0.64	1.256	Ni (IV)	3.27	2.839	Mo (IV)	1.40	1.858
Li	0.886	1.468	Ti (III)	1.09	1.639	Ni (V)	3.81	3.065	Mo (V)	1.73	2.065
Be (I)	1.56	1.961	Ti (IV)	1.50	1.923	Cu (II)	1.98	2.209	Mo (VI)	2.20	2.329
Be (II)	1.810	2.112	V (II)	0.69	1.304	Zn	2.223	2.341	Ag (I)	1.826	2.122
B (I)	1.53	1.961	V (III)	1.39	1.851	Ga (I)	0.86	1.456	Cd	1.978	2.208
B (II)	2.19	2.323	V (IV)	1.89	2.158	Ga (III)	2.419	2.442	In (I)	0.71	1.323
B (III)	2.275	2.368	V (V)	2.51	2.487	Ge (IV)	2.618	2.540	In (III)	2.138	2.296
C	2.746	2.602	Cr (II)	1.24	1.748	As	2.816	2.635	Sn (II)	1.49	1.916
N	3.194	2.806	Cr (III)	1.66	2.023	Se	3.014	2.726	Sn (IV)	2.298	2.380
O	3.654	3.001	Cr (IV)	2.29	2.376	Br	3.219	2.817	Sb	2.458	2.461
F	4.000	3.140	Cr (V)	2.83	2.641	Rb	0.312	0.866	Te	2.618	2.540
Na	0.835	1.435	Cr (VI)	3.37	2.882	Sr	0.721	1.333	I	2.778	2.617
Mg	1.318	1.802	Mn (II)	1.66	2.023	Y (II)	0.40	0.993	Cs	0.220	0.736
Al (I)	0.84	1.439	Mn (III)	2.20	2.329	Y (III)	0.65	1.260	Ba	0.683	1.298
Al (II)	1.63	2.004	Mn (IV)	2.74	2.599	Zr (II)	0.52	1.132	W (II)	0.73	1.341
Al (III)	1.714	2.055	Mn (V)	3.28	2.843	Zr (III)	0.79	1.395	W (III)	0.98	1.910
Si (II)	1.99	2.215	Mn (VI)	3.82	3.069	Zr (IV)	0.90	1.489	W (IV)	1.23	1.741
Si (IV)	2.138	2.296	Mn (VII)	4.36(?)	3.278	Nb (II)	0.77	1.378	W (V)	1.48	1.910
P	2.515	2.490	Fe (II)	1.64	2.011	Nb (III)	1.02	1.586	W (VI)	1.67	2.029
S	2.957	2.790	Fe (III)	2.20	2.329	Nb (IV)	1.25	1.755	Hg	2.195	2.326
Cl	3.475	2.927	Co (II)	1.96	2.198	Nb (V)	1.42	1.871	Tl (I)	0.99	1.562
K	0.445	1.047	Co (III)	2.56	2.512	Mo (II)	0.90	1.489	Tl (III)	2.246	2.353
Ca	0.946	1.527	Co (IV)	3.10	2.764	Mo (III)	1.15	1.684	Pb (II)	1.92	2.175
Sc (II)	0.64	1.256	Ni (II)	1.94	2.187				Pb (IV)	2.291	2.376
Sc (III)	1.02	1.586	Ni (III)	2.73	2.594				Bi	2.342	2.403

first member of each transitional group to appear most stable in its lower oxidation states and very unstable in the highest state, whereas the heavier members of each group are very stable in their higher and highest positive states. For example, CrO₃ is a strong oxidizing agent and not very stable; WO₃ is much less oxidizing and more stable. Mn₂O₇ is explosively unstable, whereas rhenium oxidizes in moist air to Re₂O₇, which is not an oxidizing agent.

This puzzle has been fairly well explained by the electronegativity differences. The electronegativity of Cr(VI), 3.37 (Table 1) is much higher than that of W(VI), 1.67. This makes the bonds to oxygen much more polar in the latter, providing much greater stability. (The second paper of this pair explains quantitatively the relationship between bond polarity and strength.) The comparison between manganese and rhenium is very likely similar but cannot be quantified because the electronegativity of rhenium(VII) is not yet known.

5. The pioneering Pauling and Mulliken electronegativities have been improved upon and extended.

Two alternative evaluations that have the distinct advantage of long-time acceptance (1935) are the almost universally adopted Pauling scale (12) and the theoretically more appealing Mulliken scale (13). A different scale is necessary for quantitative accuracy in the light of recent work.

First, consider the original Pauling concept. Pauling recognized differences between homonuclear bonds (between like atoms) and heteronuclear bonds (between unlike atoms), and assumed reasonably that if two diatomic homonuclear molecules interact to form diatomic heteronuclear molecules, the bond energy in the latter should be an average of the two homonuclear bond energies in the original molecules, provided the electrons are also shared evenly in the heteronuclear molecules. He observed that the actual heteronuclear bond energy is always greater than the expected average, and ascribed this to a difference in electronegativity between the two atoms. He assumed that the "excess ionic energy", represented by the difference between the average homonuclear energy and the actual observed heteronuclear bond energy, must be a consequence of uneven sharing of electrons brought about by initial electronegativity differences. He used this extra ionic energy as a basis for evaluating the atomic electronegativities. This approach proved very successful on a qualitative basis but unfortunately could not be reversed to provide a general method of determining bond energy from electronegativity values.

I believe the principal basis for this difficulty lies in the apportionment of the total bond energy between the normal covalent energy (average of the two homonuclear energies) and the ionic energy. Think how or whence a truly covalent bond, in which electrons are evenly shared, derives its energy. It can only be from the constant sharing of the two bonding electrons, during which the bonding electrons on the average are equally attracted by both nuclei. Now, what is meant by "ionic energy"? This can only be a coulombic energy of attraction between unlike charges. This requires unsymmetrical distribution of the charges, since the numbers of negative and positive charges within the system are equal. In a diatomic molecule, somehow the electrons must become unevenly shared. The Pauling concept requires that a coulombic energy derived from uneven sharing must somehow be superimposed upon a system of even sharing. The long-overlooked question is, how can electrons be even a trifle unevenly shared yet simultaneously be exactly evenly shared all the time?

The uneven sharing must *displace* some of the even sharing, not merely add on to it. In other words, no polar covalent bond can be represented accurately as deriving its energy from 100% covalence plus X% ionicity. If the bond has X% ionicity, the covalence must be reduced to (100 - X) percent. Ionic energy cannot add on to covalent energy, but

covalent energy	Pauling ionic energy
covalent energy	ionic energy (theory of polar covalence)

Figure 2. Relative contributions of ionic and covalent energy to the polar bond in HCl.

rather, must displace part of the covalent energy. This means that the apportionment assumed by Pauling weights the ionicity too lightly and the covalence too heavily. For example, the H-H energy is about 104 kcal/mol and the Cl-Cl energy about 58 kcal/mol. Their average is 81 kcal, which Pauling considered the covalent energy, but the actual bond energy is about 103 kcal/mol, the difference being 22 kcal, considered to be the ionic energy. As calculated by more recent methods, the actual maximum covalent energy is only 73.4 kcal/mol, and this is reduced to 61.5 kcal or by about 12 kcal by the ionicity. This, however, substitutes 42 kcal to replace the 12. These differences are represented in Figure 2. *Polarity always increases bond strength because the ionic energy contribution always exceeds that portion of the covalent energy which it replaces.*

A lesser shortcoming in the Pauling concept is the neglect of bond length changes that occur when heteronuclear atoms unite by a polar covalent bond. The bond is usually shorter than the sum of the two nonpolar covalent radii by an amount that becomes more significant with increasing polarity. The experimental homonuclear bond energies correspond to the nonpolar covalent radius and must change if that radius changes, for shorter bonds are stronger. The atom that acquires more than even share of the bonding electrons thereby acquires a partial negative charge that causes it to expand. The other atom is left partially positive and thus contracts. Usually the radial contraction from the nonpolar condition exceeds the radial expansion, causing the sum to be smaller and the bond length to shrink. Accuracy in bond energy calculation must include correction for any difference between the actual bond length and the nonpolar covalent radius sum. For example, in HCl, the nonpolar covalent radius sum is 131.4 pm, to be compared with the experimental bond length of 127.4.

At about the time Pauling was pioneering in this field, Mulliken was suggesting that electronegativity should be an average of the energy required to remove an electron from an atom, as measured as the ionization energy, and the energy released by gain of one electron, as measured as the electron affinity. He specified that these values must correspond to the "valence state", the experimental data being corrected for any promotional energies involved. Probably because of its seemingly simple and straightforward derivation from experimentally determined quantities evaluating easily visualizable processes, the Mulliken concept has always seemed preferable to theoreticians. Recent improvements in the determination of electron affinities to broaden their scope and increase their accuracy have now greatly increased the potential value of Mulliken electronegativities.

Some theoreticians appear convinced that electronegativity is not an atomic property but a property of each particular orbital (14, 15), and the Mulliken concept is especially adaptable to evaluation of "orbital electronegativity". Unfortunately, this idea complicates much and gains little, especially when degrees of hybridization are assigned for convenience. The concept of electronegativity as an *atomic* property has established its utility through extremely widespread and accurate quantitative application.

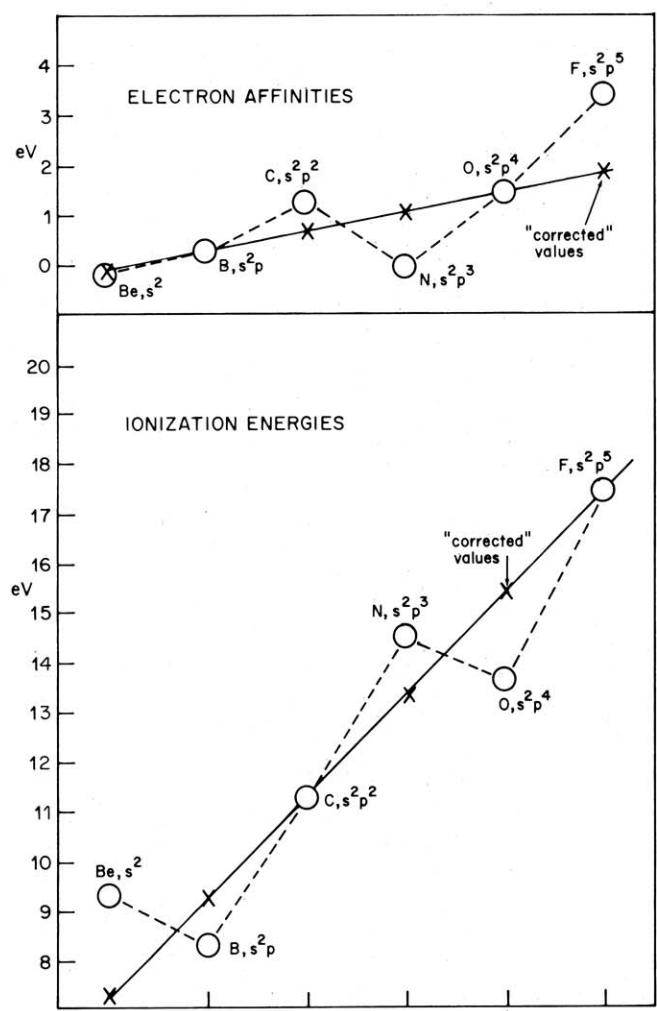


Figure 3. Experimental and corrected ionization energies and electron affinities, period 2.

Unhappily, the Mulliken evaluation of electronegativity is not as straightforward as it seems. One might observe at once that sharing a pair of electrons between two atoms, even unequally, hardly resembles the far more drastic processes of removing an electron to infinity, creating a cation, and bringing in an electron from infinity, creating an anion. Aside from that, however, there is a real problem associated with interactions among electrons that appear unrelated to electronegativity. The electronegativity as evaluated according to the relative compactness concept is a smooth function of the number of outermost electrons, from one to seven, for each period of the periodic table. In contrast, as is well known at least with respect to ionization energy, both it and the electron affinity, as well as their sum or average, are zigzag functions of the number of outermost electrons. Although small contributions may be made by the energy differences between paired and unpaired electrons, the major cause of this zigzagging is believed to be the special stability associated with spherical symmetry in the orbital arrangement of the electrons. Such symmetry is exhibited by the electronic configurations, s^2 , s^2p^3 , and s^2p^6 . Somewhat less energy than otherwise expected must be required for creating such a structure by removing an electron, and more energy than expected is released when such a structure is created by adding an electron. Similarly, destruction of such a structure will require more than expected ionization energy and evolve less than expected electron affinity.

The only ionizations that do neither are of s^2p^2 and s^2p^5 . It seems possible that a linear function connecting these points

could serve as a basis for "correcting" the other ionization energies. Analogously, electron affinities that do not involve creating or disrupting an especially stable configuration are only those involving addition of an electron to s^2p or to s^2p^4 . A line through these points can similarly serve for correcting the other electron affinities. This procedure is illustrated for period 2 in Figure 3. Such correction has been performed, with results summarized in Table 2. Although not determined for "valence states", Mulliken electronegativities when corrected in the described manner do not zigzag. In fact, except for the alkali metal elements, which present special problems, they are approximately a linear function of the relative compactness electronegativities, within each period of major group elements, as shown in the table. Since the creation or destruction of spherical symmetry in the electronic configuration seems quite independent of the electronegativity, the use of the Mulliken concept would appear to require taking these variations into account.

In many instances alternative evaluations of electronegativity have been justified according to how well they agree with Pauling scale values, which casts some doubt on their quantitative validity also.

6. Although the concept of electronegativity was inspired by suspicion of uneven sharing of valence electrons in polar covalent bonds in compounds, it is equally significant (although less useful) in nonpolar bonds.

This is because the homonuclear bond energy, like the electronegativity, as shown in Figure 1, depends on the magnitude of the effective nuclear charge as sensed at the distance of the atomic radius. Electronegativity may be thought of as a coulombic force between the effective nuclear charge and that of an outer electron (1, 2) measured as the ratio of the charge product to the square of the radius. Similarly, the homonuclear bond energy may be considered to be the coulombic energy between the effective nuclear charge and the bonding electrons, assumed to occupy an average position halfway between the two like nuclei, which is measured as the ratio of the charge product to the radius. Although the effective nuclear charge cannot be evaluated precisely, both Sr^2 (where S is the electronegativity) and E_{hr} (where E_h is the homonuclear bond energy) are proportional to the same effective nuclear charge. They must therefore also be proportional to each other. Where C is a proportionality constant for a given period, $E_h = CSr$. Unless E_h is diminished by lone-pair bond weakening (9, 16, 17), it is nearly or exactly linear with the electronegativity-times-radius product, Sr , within each separate period of major group elements.

7. Perhaps the most important feature of electronegativity is what happens to it when atoms initially different combine to form a compound. All atoms become adjusted to the same intermediate electronegativity within the compound.

This, the principle of electronegativity equalization, was originally published in 1951 (18). It attracted interest only very slowly (19) until Parr and co-workers in 1976 (20, 21) and Politzer in 1977 (22) derived it from quantum mechanical concepts. Since then it has found general acceptance among theoretical chemists but still receives little or no attention in most textbooks of general and inorganic chemistry.

A reasonable and easily visualized mechanism by which such equalization may occur can easily be described. For simplicity, consider a diatomic molecule (although the explanation is applicable to molecules of any size or to nonmolecular solids). The initially more electronegative atom will acquire, as the bond forms, more than half share of the bonding electrons. Since both atoms were initially electrically neutral, this implies acquisition by the first atom of a partial negative charge, and leaves the second, initially less electronegative atom with a partial positive charge since it now lacks sufficient electrons to balance its nuclear charge.

Table 2. Mulliken Electronegativity from Corrected Ionization Potentials and Electron Affinities

element	I^a (eV)	I (corr.)	A (eV)	A (corr.)	$I + A$ (corr.)	S (calc)	S^g
Be	9.322	7.16	-0.2 ^d	-0.11	7.05	1.82	1.81
B	8.298	9.21	0.278 ^c	0.28	9.49	2.28	2.28
C	11.260	11.26	1.268 ^b	0.67	11.93	2.74	2.75
N	14.534	13.31	-0.07 ^b	1.06	14.37	3.19	3.19
O	13.618	15.36	1.462 ^b	1.46	16.82	3.65	3.65
F	17.422	17.42	3.399 ^b	1.84	19.26	4.11	4.00
Mg	7.646	4.93	-0.2 ^d	-0.12	4.81	1.30	1.32
Al	5.986	6.54	0.442 ^c	0.43	6.97	1.72	1.71
Si	8.151	8.15	1.385 ^b	0.98	9.13	2.14	2.14
P	10.486	9.76	0.743 ^b	1.53	11.29	2.57	2.52
S	10.360	11.37	2.077 ^b	2.08	13.45	2.99	2.96
Cl	12.967	12.97	3.615 ^b	2.63	15.60	3.41	3.48
Cu	7.726	4.00	1.226	-0.83	3.17	2.02	2.03
Zn	9.394	5.30	-0.49 ^d	-0.26	5.04	2.22	2.22
Ga	5.999	6.60	0.3 ^b	0.31	6.91	2.42	2.42
Ge	7.899	7.90	1.2 ^b	0.88	8.78	2.62	2.62
As	9.81	9.20	0.80 ^b	1.45	10.65	2.82	2.82
Se	9.752	10.50	2.021 ^b	2.02	12.52	3.02	3.01
Br	11.814	11.80	3.364 ^b	2.59	14.39	3.22	3.22
Ag	7.576	4.22	1.303	-0.55	3.67	1.82	1.83
Cd	8.993	5.25	-0.33 ^e	-0.257	4.99	1.98	1.98
In	5.786	6.30	-0.3 ^b	0.3	6.60	2.14	2.14
Sn	7.344	7.34	1.25 ^b	0.857	8.20	2.30	2.30
Sb	8.641	8.38	1.05 ^b	1.417	9.80	2.46	2.46
Te	9.009	9.42	1.971 ^b	1.971	11.39	2.62	2.62
I	10.451	10.46	3.061 ^b	2.528	12.99	2.78	2.78
Hg	10.437	5.93	-0.63 ^e	-0.22	5.71	2.20	2.20
Tl	6.108	6.67	0.3 ^b	0.31	6.98	2.25	2.25
Pb	7.416	7.42	0.37 ^f	0.84	8.26	2.30	2.29
Bi	7.289	8.15	0.95 ^f	1.37	9.52	2.34	2.34

^a Moore C. E. *Ionization Potentials and Ionization Limits from Atomic Spectra*, NSRDS-NBS:34, 1970.^b Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* **1975**, 4, 539.^c Feigerle, C. S.; Corderman, R. R.; Lineberger, W. C. *J. Chem. Phys.* **1981**, 74, 1513.^d Kurtz, H. A.; Jordan, K. D. *J. Phys. B: Atom. Molec. Phys.*, **1981**, 14, 4361.^e Burrow, P. D.; Michejde, J. A.; Comer, J. J. *J. Phys. B: Atom. Molec. Phys.* **1976**, 9, 3225.^f Chamizo, J. A. *J. Chem. Educ.* **1984**, 61, 874.^g Sanderson electronegativity (relative compactness).

Such changes always have a profound influence on the nature of the atom, upsetting the original balance among interelectronic repulsions and attractions between electrons and nucleus.

A partial negative charge means an increase in the average electronic population, which increases the interelectronic repulsions and diminishes the effective nuclear charge. The increase in repulsions causes expansion of the electronic cloud, assisted by the reduction in effective nuclear charge, to a larger radius. The combination of diminished effective nuclear charge and larger distance over which it operates corresponds to a decrease in the electronegativity. One may consider electronegativity as a hunger for electrons, which quite naturally diminishes to the extent that the atom succeeds in acquiring them.

The other atom, left with a deficiency in its electronic cloud, finds repulsions among its electrons reduced and the nucleus less well shielded. Increased effective nuclear charge can pull the fewer electrons in closer and more compactly around the nucleus, causing the radius to become smaller. The combination of increased effective nuclear charge and shorter distance corresponds to an increased electronegativity. Thus the initially more electronegative atom acquires partial negative charge and simultaneously becomes less electronegative, while the initially less electronegative atom acquires partial positive charge and simultaneously becomes more electronegative. These adjustments must cease when the electronegativity has equalized throughout the compound. A thoroughly tested postulate of the principle of electronegativity equalization is that the intermediate electronegativity within the compound is the geometric mean of all the initial atomic electronegativities (8, 23). For example,

the electronegativity of acetyl chloride, CH_3COCl , is the seventh root of the product, $(S_{\text{C}})^2 \times (S_{\text{H}})^3 \times (S_{\text{O}}) \times (S_{\text{Cl}})$:

$$(2.764^2 \times 2.592^3 \times 3.654 \times 3.475)^{1/7} = 2.886$$

Parr (20, 21) points out that electronegativity is the negative of the chemical potential, so the equalization principle corresponds to equalization of chemical potentials in a compound.

Summary Thus Far

An improved electronegativity scale based on the relative compactness of atomic spheres provides electronegativities for the major group elements in normal oxidation states that are believed to be quite accurate. The corresponding values for these elements in subnormal oxidation states and for many of the transitional elements in various oxidation states have also been estimated and are believed usefully informative although less accurate. Where some of the electrons normally used in bonding of the major group atoms are not involved in the bonding, they appear to reduce the electronegativity, causing bonds to more electronegative elements to be more polar and therefore stronger than for the normal valence. This accounts for the properties of compounds exhibiting the "inert pair effect". Similarly, underlying d electrons not used in bonding appear to reduce the electronegativity, 3d being much more effective than 4d and 5d. Thus major differences between the first and heavier members of the transitional groups have been explained. Electronegativity in general is a consequence of incompletely screened nuclear charge effective within stable outer orbital vacancies, which in turn is a function of the atomic structure. Its

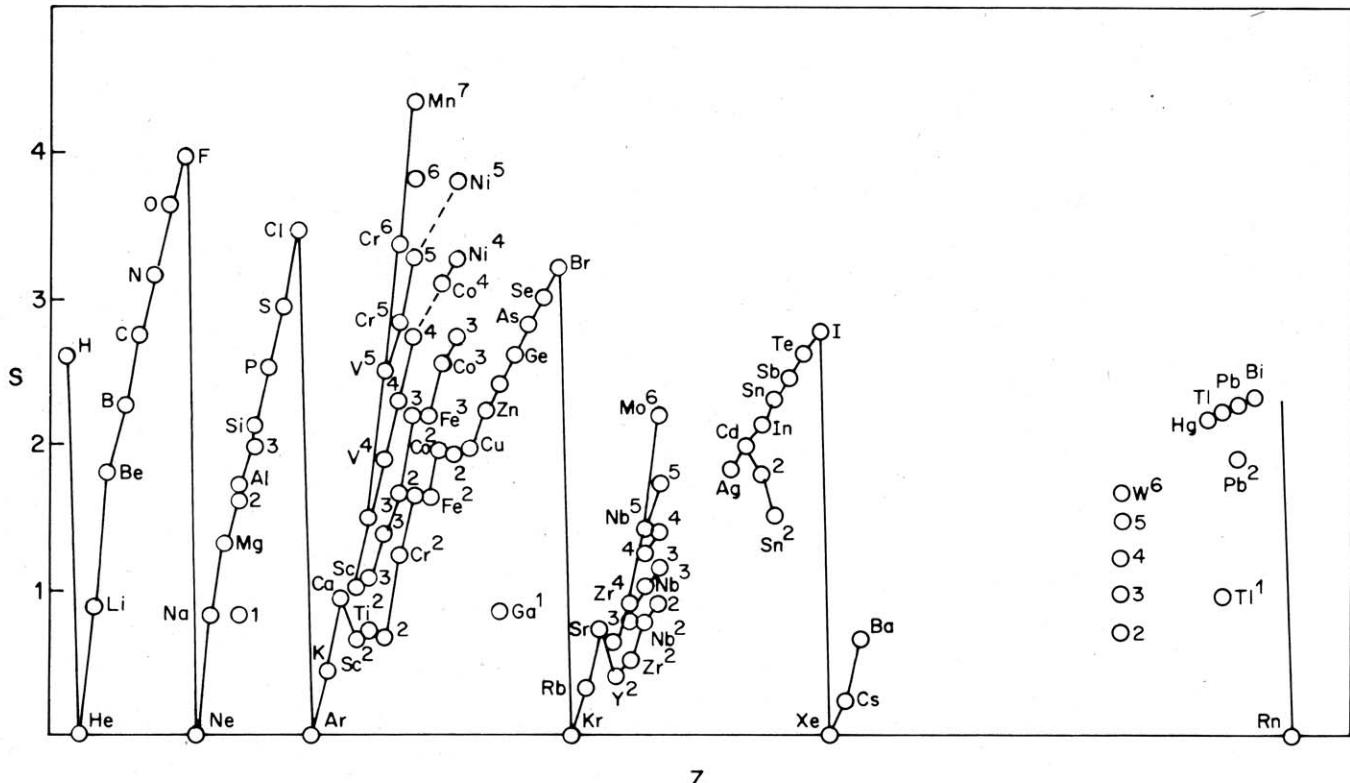


Figure 4. Periodicity of electronegativities. (Note: Oxidation state is indicated by a superscript Arabic numeral.)

equalization when different kinds of atoms unite is easily explained. The periodicity of electronegativity is represented in Figure 4.

The second and concluding paper on this topic will be devoted to the extremely useful applications that have been developed.

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