

A New Method of Determining Electronegativity from Other Atomic Properties

WALTER GORDY

Department of Physics, Duke University, Durham, North Carolina

(Received March 18, 1946)

The relation,

$$x = 0.31 \left(\frac{n+1}{r} \right) + 0.50,$$

where x represents the electronegativity of an atom according to Pauling's revised scale, n the number of electrons in its incompletely filled (valence) shells, and r its single bond covalent radius measured in Angstroms, has been found valid for all elements having x values available for comparison, except for Ag, Au, and Cu. This equation is used to extend the electronegativity scale to include a total of fifty-two elements. A chart is constructed to demonstrate the systematic relation of the values to the periodic table. Beginning with the definition of the electronegativity of a neutral atom in a stable molecule as the potential at a distance r (covalent radius) from its nucleus which is caused by the nuclear charge effective at that distance, a simple theoretical justification is offered for the existence of a linear relation between x and $(n+1)/r$. This relation, like Mulliken's, provides an "absolute" scale of electronegativity values.

INTRODUCTION

RIGID mathematical methods which attempt to express the properties of molecules in terms of the motion of individual electrons are almost hopelessly complicated for any except the simplest type of molecules. For this reason attempts to define and measure over-all properties or lumped constants of the atoms, such as electronegativity or atomic radii, which can be used in approximate but widely applicable calculations, are of great significance.

From thermal data Pauling^{1,2} has established an approximate scale of relative electronegativity values for thirty-three elements. By qualitative theoretical considerations and from a comparison of results with Pauling's relative scale, Mulliken³ has shown that the average of the ionization potential and electron affinity of an atom, $(I+E)/2$, is a measure of its electronegativity. Though it has a somewhat better theoretical basis, Mulliken's method is not as widely applicable as that of Pauling. However, the values that have been determined by his method have served the useful purpose of fixing the origin of the more extensive relative scale of Pauling so that it is no longer arbitrary.

Recently the author⁴ has found an empirical relation, of the form

$$k = aN(x_A x_B / d_{AB}^2)^{\frac{1}{2}} + b,$$

which applies to the bonds of a large number of diatomic and simple polyatomic molecules. In this equation x_A and x_B are the electronegativities of the atoms forming a given bond AB ; N , k , and d_{AB} are the bond order, bond-stretching force constant, and bond length, respectively; and a and b are constants for certain broad classes of molecules. Pauling's values were used to establish the relation, which was then used to determine the electronegativities of several atoms not listed by Pauling and to extend some of his values to an additional place whenever the accuracy of the available data seemed to justify it. By means of a new relation, to be described here, the electronegativity scale is extended further to include a total of fifty-two elements.

ELECTRONEGATIVITY AS A FUNCTION OF ATOMIC RADIUS AND EFFECTIVE NUCLEAR CHARGE

I have examined the possibility of defining the electronegativity of a neutral atom of a stable molecule as the potential, $(Z_{\text{eff}})e/r$, where $(Z_{\text{eff}})e$ is the effective nuclear charge of the atom acting

¹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), p. 64.

² L. Pauling, *J. Am. Chem. Soc.* **54**, 3570 (1932).

³ R. S. Mulliken, *J. Chem. Phys.* **2**, 782 (1934); **3**, 573 (1935).

⁴ W. Gordy, *Phys. Rev.* **69**, 130 (1946); *J. Chem. Phys.*, in press.

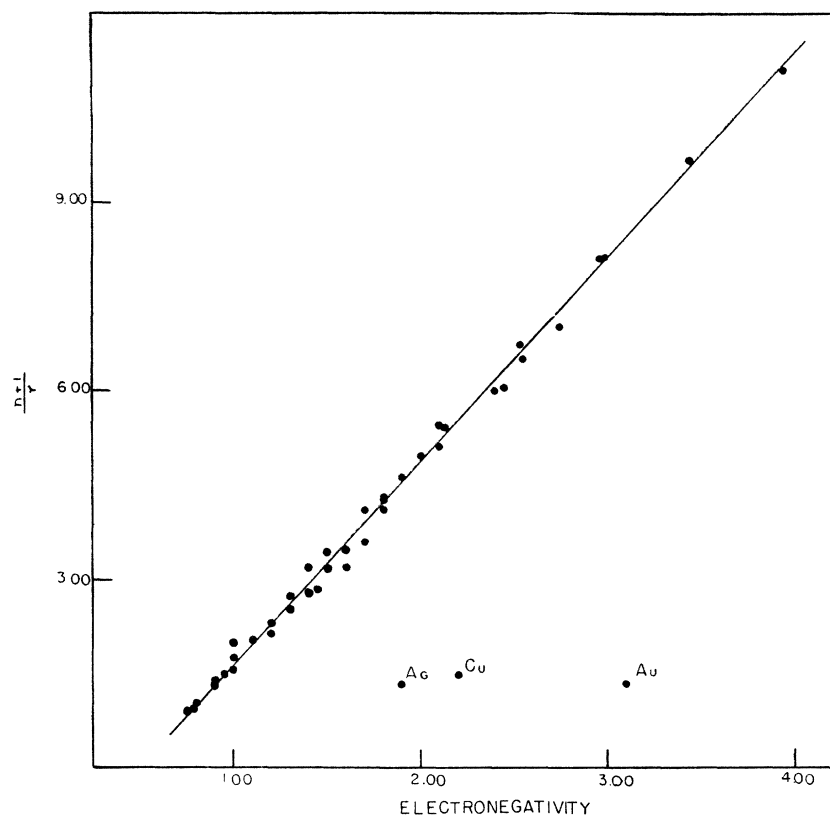


FIG. 1. A plot of electronegativity, x , as a function of $(n+1)/r$, for the elements listed in Table I except those in parentheses.

on a valence electron at a distance from its nucleus equal to its single bond covalent radius r .

If the simplifying assumption is made that all the electrons in the closed shells below the valence shell exert their full screening power, and that the screening constant⁵ of one valence electron for another is 0.5, then,

$$Z_{\text{eff}} = n - 0.5(n-1) = 0.5(n+1),$$

where n represents the number of electrons in the incompletely filled (valence) shells. Similar assumptions⁶ regarding screening constants have been used successfully in atomic spectra for

⁵ Pauling (reference 1, p. 65) uses 0.4 for the screening constant of a valence electron. This value is almost as satisfactory as the one assumed here. Because the same screening constant is used for all the valence electrons the results here are not particularly sensitive to changes in its value.

⁶ A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. van Nostrand Company, New York, 1935), p. 37; L. Pauling and S. Goudsmit, *The Structure of Line Spectra* (McGraw-Hill Book Company, Inc., New York, 1930), Chap. III.

certain non-penetrating orbits. Since the part of the orbit of a valence electron which is effective in forming a covalent bond—which contributes to the effective bonding cloud of an electron pair bond—would probably lie well outside the region of greatest electron density of the inner closed shells, the assumption of complete screening by all except the valence electrons would seem to be justified for the present purpose. It is at least justified for an approximate test of the proposed definition which expresses electronegativity as the potential at a point which is essentially outside the inner closed shell.

Substituting $0.5(n+1)$ for Z_{eff} in the proposed definition of electronegativity, x , gives

$$x = \frac{(Z_{\text{eff}})e}{r} = k \left(\frac{n+1}{r} \right), \quad (1)$$

where k is the constant $0.5e$.

To test this theory, I have plotted x as a function of $(n+1)/r$. Results are shown in

TABLE I. Electronegativities, covalent radii and number of valence electrons.

Atom	Single bond covalent radius r	Valence electrons n	Electro- negativity [†] x	$0.31\left(\frac{n+1}{r}\right)+0.50$
Ag	1.53 ^a	1	1.9	0.91
Al	1.26 ^a	3	1.5	1.48
As	1.21 ^b	5	2.0	2.04
Au	1.50 ^a	1	3.1	0.92
B	0.88 ^b	3	1.9	1.91
Ba	2.17 ^c	2	0.9	0.93
Be	1.06 ^a	2	1.45	1.38
Bi	1.40 ^a	5	1.8	1.83
Br	1.14 ^b	7	2.75	2.68
C	0.77 ^b	4	2.55	2.52
Ca	1.78 ^d	2	1.0	1.03
(Cb)	1.43 ^e	5	(1.8)	1.76
Cd	1.48 ^a	2	1.1	1.13
Cl	0.99 ^b	7	2.97	3.00
(Cr)	1.25 ^e	6	(2.2)	2.24
Cs	2.25 ^e	1	0.75	0.78
Cu	1.35 ^a	1	2.2	0.96
F	0.72 ^e	7	3.95	3.94
Ga	1.26 ^a	3	1.4	1.48
Ge	1.22 ^b	4	1.7	1.77
H	0.37 ^e	1	2.13	2.17
Hg	1.50 ^e	2	1.0	1.12
I	1.33 ^b	7	2.45	2.36
In	1.44 ^a	3	1.4	1.36
K	1.96 ^e	1	0.80	0.82
(La)	1.86 ^c	3	(1.2)	1.17
Li	1.34 ^e	1	0.95	0.96
(Ma)	1.31 ^d	7	(2.4)	2.39
Mg	1.40 ^a	2	1.2	1.16
(Mn)	1.18 ^c	7	(2.6)	2.60
(Mo)	1.36 ^c	6	(2.1)	2.09
N	0.74 ^e	5	2.98	3.01
Na	1.54 ^e	1	0.90	0.90
O	0.73 ^e	6	3.45	3.47
P	1.10 ^b	5	2.1	2.19
Pb	1.46 ^a	4	1.5	1.56
(Po)	1.46 ^d	6	(2.0)	1.98
Rb	2.11 ^e	1	0.78	0.79
S	1.04 ^b	6	2.53	2.58
Sb	1.41 ^b	5	1.8	1.82
Sc	1.61 ^d	3	1.3	1.27
Se	1.17 ^b	6	2.4	2.35
Si	1.17 ^b	4	1.8	1.82
Sn	1.40 ^b	4	1.7	1.61
Sr	1.93 ^d	2	1.0	0.98
Te	1.37 ^b	6	2.1	2.08
Ti	1.45 ^c	4	1.6	1.57
Tl	1.47 ^a	3	1.3	1.34
(V)	1.30 ^e	5	(1.9)	1.93
Y	1.75 ^d	3	1.3	1.21
Zn	1.31 ^a	2	1.2	1.21
Zr	1.58 ^c	4	1.6	1.48

^a L. Pauling, reference 1, p. 167. These values are for tetrahedral covalent radii.

^b L. Pauling, reference 1, p. 154.

^c N. V. Sidgwick, *The Covalent Link in Chemistry* (Cornell University Press, Ithaca, New York, 1933), pp. 83-85.

^d These values are obtained from a smooth curve drawn through points determined by known values for other elements in the same period of the periodic table.

^e V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.* **63**, 37 (1941).

^f These electronegativity values, except those enclosed in parentheses, are taken from Table VIII of the author's paper (*J. Chem. Phys.*, in press). Some are Pauling's values (reference 1), and some were determined by the author (reference 4). Those in parentheses are the rounded off values taken from column 4 of the present table.

Fig. 1. The values* used for x , r , and n are listed in Table I. With the exception of Ag, Au, and Cu the points fall closely along a straight line, the equation of which is

$$x = 0.31\left(\frac{n+1}{r}\right) + 0.50. \quad (\text{II})$$

For comparison with the x values the right-hand side of the equation is evaluated and the results listed in the last column of Table I. In this equation r , the single bond covalent radius, is measured in Angstrom units.

Ag, Au, and Cu are known to form compounds in which they contribute more than one electron to the formation of covalent bonds. Hence the most probable cause of their wide deviation is the assumption of screening constants of unity for all electrons except the one in the final shell. For all other elements the deviations are sufficiently small to be explained by inaccuracies in x and r .

Equation (II) has been used to compute electronegativity values for Cb, Cr, La, Ma, Mn, Mo, Po, and V. These are also listed in Table I, column 3.

Equation (I) defines the electronegativity of an element in an absolute sense rather than in terms of that of some other element. The scale determined by it nevertheless requires a small shift of origin to make its values proportional to those of Mulliken's³ "absolute" scale. This is revealed by the form of Eq. (II), which yields values that are in direct proportion to those of Mulliken.

The electronegativity of a given atom, according to the above theory, would be greater for double or triple bonds—since they have smaller covalent radii—than for single bonds. This assumes that the effects of the decrease in covalent radius are not offset by increased screening factors of the valence electrons.

ELECTRONEGATIVITY CHART

Using the x values given in Table I, column 3,** I have plotted in Fig. 2 electronegativity as a

* Elements included in parentheses are not plotted in this graph. Their electronegativity values, also included in parentheses, were determined from the graph.

** There is one exception. Because Pauling's value for Sn, 1.7, gives a noticeable departure from symmetry in the chart, I have used the value 1.6 given by Eq. (II).

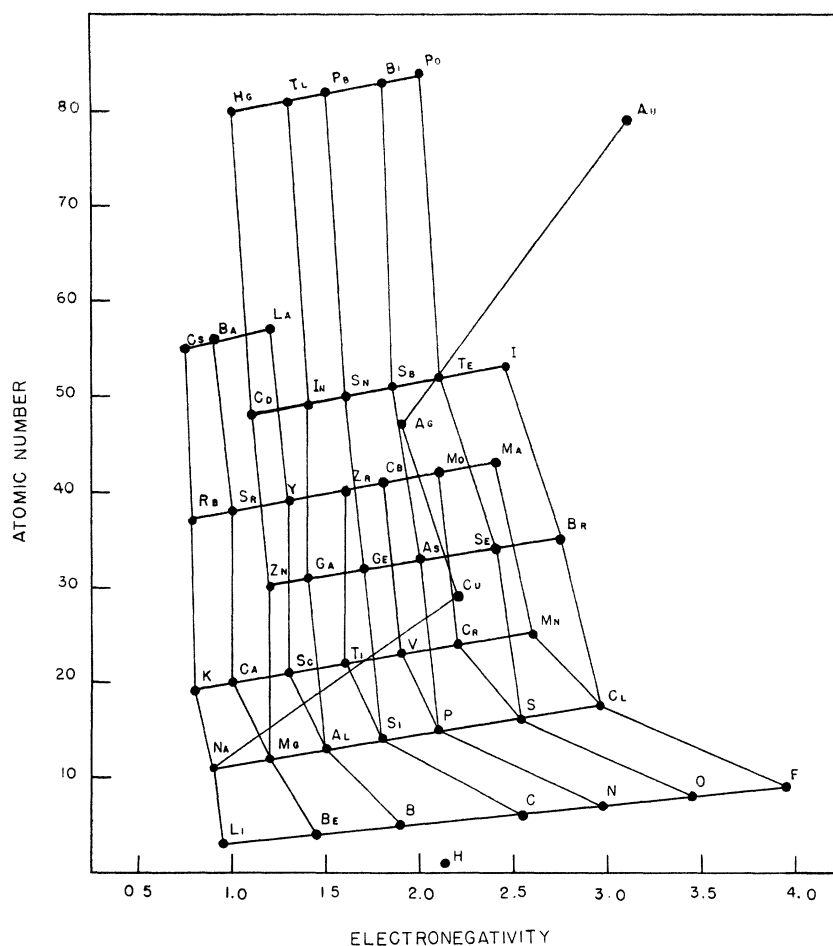


FIG. 2. Electronegativity chart. A plot of electronegativity as a function of atomic number, with lines connecting the elements of the same rows and of the same periods of the periodic table.

function of atomic number. It is seen that, with the exception of Ag, Au, and Cu, the electronegativities for a given period increase in an approximately linear fashion with atomic number—and hence with number of valence electrons—and that there are discrete jumps from period to period.

Pauling⁷ has constructed a scale showing how

⁷L. Pauling, reference 1, p. 65.

electronegativities for the elements of the different periods of the periodic table bear a systematic relation to each other. In Fig. 2 the lines connecting the atoms having the same number of valence electrons show that the additional electronegativity values which I have determined also follow this systematic pattern.

I wish to thank Vida Miller Gordy for her assistance in the preparation of the manuscript.