THE CONCEPT OF ELECTRONEGATIVITY

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I. INTRODUCTION

That qualitative property of an atom which the chemist calls *electronegativity* has been described by Pauling (91) as "the power of an atom in a molecule to attract electrons to itself." It is because electronegativity is concerned with *atoms in molecules* rather than with *atoms in isolation* that its measurement in a precise way is not easy. Unlike the electron affinity of an atom, which is capable both of precise definition and (in principle) of precise measurement, the property of electronegativity is capable of neither. When the chemist says "fluorine is the most electronegative of the elements," a belief is being expressed that the electron distribution in the chemical bond X—F (where X is any other element) more closely resembles that in the ion-pair X^+F^- than in X^-F^+. The *difference* in electronegativity between the atoms X and F might then be regarded as a measure of the degree of *electron transfer* from atom X to atom F on forming the chemical bond between them. But the determination of the precise electron-distribution map of a molecule presents a difficult problem, whether it be addressed to the experimental or to the theoretical chemist, and such information (from which a *quantitative* measure of electronegativity difference between atoms in molecules might be made) is not, in general, avail-

able. (Indeed it is because such precise information is lacking that it becomes profitable to attempt to gain it, albeit crudely, by using a crude measure of electronegativity difference.)

Several methods of measuring electronegativity in a qualitative manner have been proposed, and from the most successful of these it has been possible to construct an electronegativity scale embracing some fifty or more of the elements. The allotment of a single number against each element in the electronegativity scale is, however, barely sufficient for the fullest appreciation of the electronegativity property. It is becoming clear that an atom may exhibit a range of electronegativity, depending upon the range of *valence states* available to it, and in the strictest sense one should speak not of the electronegativity of an atom, but rather of the electronegativity of atomic orbitals. In so far as the electronegativity concept is an offshoot from the conception of the chemical bond, it is natural that it assume a finer structure as the concept of valence bonding develops.

A formal definition of the electronegativity property can be given in the following terms: Consider the bonding between two univalent atoms, A and B, which might be represented, in the most general case, by an admixture of three extreme "structures"—the ionic structures A^+B^- and A^-B^+, and the electron pair or covalent structure A—B. The wave function Ψ has the form

$$\Psi = \gamma_1\psi(A^+B^-) + \gamma_2\psi(A\text{---}B) + \gamma_3\psi(A^-B^+) \tag{1}$$

where the γ's are mixing coefficients. Let us presume that the mixing coefficients can be determined; then if $\gamma_1 > \gamma_3$, there results a formal negative charge associated with B, and we say that B is more electronegative than A. In the special case where $\gamma_1 = \gamma_3$, we say that atoms A and B in the molecule AB are of equal electronegativity. A restatement of the situation expressed in equation 1 is this: let ϕ_A and ϕ_B be *bonding orbitals* of atoms A and B; then if $\gamma_1 \neq \gamma_3$ there is an unequal partition of two electrons between ϕ_A and ϕ_B, in the sense that the more electronegative orbital gains the greater share in the partition. The advantage of this simple restatement is twofold. Firstly, the notion of orbital electronegativity is introduced. Secondly, since the orbitals ϕ_A, ϕ_B will, in general, be hybrids, it leads to an enquiry into the nature of the valence orbitals employed by an atom, and to the dependence of the electronegativity property on the valence state of the atom. Especially notable in this connection is the recent work of Moffitt (76, 77).

II. MEASURES OF ELECTRONEGATIVITY

The mixing coefficients in equation 1 are not observables of experiment, but there are a number of observable physical properties the magnitudes of which depend wholly or in part on the values of the γ's in equation 1 and thus can serve indirectly as bases for the measurement of electronegativity. Malone (72), for example, attempted to correlate bond dipole moments with differences in electronegativity, and the well-known scale of electronegativity of Pauling (90, 91) has its roots in experimental thermochemistry. More recently, Gordy (38, 40) has made use of nuclear quadrupole coupling in molecules as a guide

to the electronegativity property. In this section some of the more successful methods that have been used to measure electronegativity are examined.

A. Pauling's electronegativity scale

Pauling (90) pointed out in 1932, as an empirical fact, that the energy of a bond A—B between atoms A and B is generally *larger* than the additive mean of the energies of the bonds A—A and B—B, and that the enhancement, Δ, in-

TABLE 1

Δ values and electronegativity differences in diatomic molecules

Bond	D(A—B)*	Δ	$0.208\sqrt{\Delta}$	$\lvert x_A - x_B \rvert_P$
Li—H	58.5	−6.9	—	1.1
Na—H	48.2	−12.9	—	1.2
K—H	43.6	−14.6	—	1.3
Rb—H	39.6	−18.2	—	1.3
Cs—H	41.9	−15.6	—	1.4
F—H	135.0	64.2	1.67	1.9
Cl—H	103.1	22.1	0.98	0.9
Br—H	87.4	12.3	0.73	0.7
I—H	71.4	1.24	0.23	0.3
Li—F	136	104	2.12	3.0
Na—F	113	85	1.92	3.1
K—F	119	94	2.02	3.2
Rb—F	119.5	95	2.02	3.2
Cs—F	120	96	2.04	3.3
Cl—F	61.2	13.4	0.76	1.0
Br—F	$\begin{cases} 50.8^{(a)}\dagger \\ 60.5^{(b)} \end{cases}$	$\begin{cases} 9.0^{(a)} \\ 18.7^{(b)} \end{cases}$	$\begin{cases} 0.62^{(a)} \\ 0.90^{(b)} \end{cases}$	1.2
I—F	$\begin{cases} 46.3^{(a)} \\ 66.8^{(b)} \end{cases}$	$\begin{cases} 9.5^{(a)} \\ 30.0^{(b)} \end{cases}$	$\begin{cases} 0.64^{(a)} \\ 1.14^{(b)} \end{cases}$	1.6
Li—Cl	115	73	1.78	2.0
Na—Cl	98	60	1.61	2.1
K—Cl	102	67	1.70	2.2
Rb—Cl	102	67.3	1.71	2.2
Cs—Cl	101.7	67.4	1.71	2.3
Br—Cl	52.2	0.15	0.08	0.2
I—Cl	50.3	3.25	0.37	0.6
Li—Br	102	66	1.69	1.8
Na—Br	87	55	1.54	1.9
K—Br	91.4	62.2	1.64	2.0
Rb—Br	91	62.1	1.64	2.0
Cs—Br	91.4	63	1.65	2.1
I—Br	42.5	1.4	0.25	0.4
Li—I	78.5	47	1.43	1.4
Na—I	69.5	42.5	1.36	1.5
K—I	77.2	53	1.51	1.6
Rb—I	77.2	53.4	1.52	1.6
Cs—I	75.5	52.1	1.50	1.7

* The following D(A—A) values were assumed: $H_2 = 104.2$, $F_2 = 37.5$, $Cl_2 = 58.0$, $Br_2 = 46.1$, $I_2 = 36.1$, $Li_2 = 26.5$, $Na_2 = 18.0$, $K_2 = 12.2$, $Rb_2 = 11.4$, and $Cs_2 = 10.7$ (all in kilocalories per mole).

The D(A—B) values are based on thermochemical data given in *Selected Values of Chemical Thermodynamic Properties*, Circular 500, National Bureau of Standards, Washington, D. C., 1952, and on spectroscopic data given by Gaydon (33); see also Barrow and Caunt (2).

† Alternative values (marked with superscripts (a) and (b)) for the dissociation energies in BrF and IF are given. Gaydon and Durie (27) favor the lower values (a), whilst Slutsky and Bauer (117) have argued for the higher alternatives (b).

TABLE 2

Δ values and electronegativity differences in polyatomic molecules

Molecule	Bond	$\bar{E}^*$ (observed)	Δ	$0.208\sqrt{\Delta}$†	$\lvert x_A - x_B\rvert_P$†
BH₃	B—H	93.3[a]	0.1	0.06	0.1
BF₃	B—F	154.8[a]	95.0	2.03	2.0
BCl₃	B—Cl	108.3[a]	38.4	1.29	1.0
BBr₃	B—Br	90.2[a]	26.1	1.06	0.8
B(CH₃)₃	B—CH₃	89.0[a]	5.2	0.47	0.5
B(OC₂H₅)₃	B—OC₂H₅	119.3[a]	62.2	1.64	1.5
B[N(CH₃)₂]₃	B—N(CH₃)₂	104.3[a]	(38)	(1.24)	1.0
AlCl₃	Al—Cl	100.7[b]	49.8	1.47	1.5
AlBr₃	Al—Br	85.9[b]	40.9	1.33	1.3
AlI₃	Al—I	67.7[b]	27.7	1.09	0.9
Al(CH₃)₃	Al—CH₃	61.6[c]	-3.0	—	1.0
CH₄	C—H	99.5[d]	4.6	0.45	0.4
CF₄	C—F	116.1[e]	54.6	1.54	1.5
CCl₄	C—Cl	78.3[d]	6.5	0.53	0.5
C(CH₃)₄	C—CH₃	85.4[d]	0	0	0
SiH₄	Si—H	78.3[d]	3.7	0.40	0.3
SiF₄	Si—F	133.7[d]	92.4	2.00	2.2
SiCl₄	Si—Cl	87.9[d]	36.4	1.25	1.2
SiBr₄	Si—Br	70.5[d]	25.0	1.04	1.0
SiI₄	Si—I	51.4[d]	10.8	0.68	0.6
Si(CH₃)₄	Si—CH₃	72.3[f]	7.1	0.55	0.7
Si(OC₂H₅)₄	Si—OC₂H₅	91[d]	53	1.51	1.7
GeCl₄	Ge—Cl	81.8[d]	30.5	1.15	1.3
GeBr₄	Ge—Br	65.8[g]	20.5	0.94	1.1
GeI₄	Ge—I	50.4[g]	10.1	0.66	0.8
SnCl₄	Sn—Cl	76.7[d]	30.3	1.14	1.3
SnBr₄	Sn—Br	64.4[d]	24.2	1.02	1.1
NH₃	N—H	93.4[d]	22.0	0.98	0.9
NF₃	N—F	65.4[d]	27.3	1.09	1.0
NCl₃	N—Cl	46.2[d]	-2.2	—	0.0
N(CH₃)₃	N—CH₃	71.3	9.3	0.64	0.5
PH₃	P—H	76.4[d]	0.4	0.13	0.0
PCl₃	P—Cl	76.2[h]	23.3	1.00	0.9
PBr₃	P—Br	61.9[h]	14.9	0.80	0.7
PI₃	P—I	48.9[d]	6.9	0.55	0.3
P(OC₂H₅)₃	P—OC₂H₅	81.7[i]	41.7	1.34	1.4
AsH₃	As—H	58.7[d]	-10.6	—	0.1
AsF₃	As—F	111.7[d]	75.7	1.81	2.0
AsCl₃	As—Cl	73.0[d]	26.8	1.08	1.0
AsBr₃	As—Br	57.6[d]	17.3	0.86	0.8
AsI₃	As—I	42.6[d]	7.3	0.56	0.4
As(OC₂H₅)₃	As—OC₂H₅	64.5[i]	31.2	1.16	1.5
SbCl₃	Sb—Cl	74.3[d]	29.1	1.12	1.2
SbBr₃	Sb—Br	61.3[d]	22.0	0.98	1.0
OH₂	O—H	110.5[d]	41.9	1.35	1.4
OF₂	O—F	45.5[d]	10.2	0.66	0.5
OCl₂	O—Cl	49.4[d]	3.9	0.41	0.5
O(CH₃)₂	O—CH₃	84.2[d]	25.0	1.04	1.0
SH₂	S—H	87.5[d]	3.9	0.41	0.4
S(CH₃)₂	S—CH₃	69.0[d]	-5.2	—	0.0

creases as the atoms A and B become more and more unlike in their electro-negativity property. The specific relationship proposed by Pauling was

$$| x_A - x_B | = 0.208\sqrt{\Delta} \tag{2}$$

where x_A and x_A are the electronegativities of A and B, respectively, and Δ (in kilocalories per mole) is the "extra-ionic energy," given by equation 3.

$$\Delta = D(A\!-\!B) - \frac{1}{2}\Big[D(A\!-\!A) + D(B\!-\!B) \Big] \tag{3}$$

It should be remarked that equations 2 and 3 do not give satisfactory results in all cases. The example of the alkali metal hydrides, for which the Δ values are *negative*, was recognized as a major difficulty by Pauling at the outset, and led him later to his "postulate of the geometric mean," according to which it would be better to replace equation 3 by the amended version:

$$\Delta' = D(A\!-\!B) - \sqrt{D(A\!-\!A)\cdot D(B\!-\!B)} \tag{4}$$

Curiously enough, Pauling does not seem to have made use of equation 4 in deriving his electronegativity scale, and the relationship between $| x_A - x_B |$ and Δ' (i.e., the amendment to equation 2) has not been given by him.

The generally widespread acceptance by chemists of the Pauling scale of electronegativity makes it desirable to examine its empirical basis in some detail. This is done in tables 1 and 2, in which recent extensions in thermochemical and spectroscopic knowledge have been utilized.

Table 1 is restricted to diatomic molecules, for which each of the quantities $D(A\!-\!B)$, $D(A\!-\!A)$, and $D(B\!-\!B)$ is directly observable. The dissociation energies quoted refer to the "standard" temperature (25°C.).

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* The $\bar{E}$ (observed) values are taken or calculated from thermal data given in the following: (a) Skinner and Smith (114); (b) Eley and Watts (28); (c) Long and Norrish (70); (d) National Bureau of Standards Circular 500; (e) Kirkbride and Davidson (61); (f) Tannenbaum (120); (g) Evans and Richards (30); (h) Neale and Williams (87); (i) Chernick and Skinner (13); (j) Charnley, Mortimer, and Skinner (12).

For the calculation of standard single-bond energies, $\bar{E}$(M—M), heats of atomization given in Circular 500 of the National Bureau of Standards were used, except for B = 140.9 (Searcy and Myers (108)), Si = 89.9 and Ge = 89.2 (Baughan (3)), and Sn = 70 (Brewer and Porter (7)). The values $D(N_2)$ = 226 kcal./mole and $D(S_2)$ = 101 kcal./mole (Gaydon (33)) were accepted. The values assumed for $\bar{E}$(M—M) were as follows: B—B = 82.2, Al—Al = 43.8, C—C = 85.6, Si—Si = 45.0, Ge—Ge = 44.6, Sn—Sn = 35.0, N—N = 38.7, P—P = 47.9, As—As = 34.5, Sb—Sb = 32.4, O—O = 33.0, and S—S = 63.0.

The values $\bar{E}$(B—B) and $\bar{E}$(Al—Al) derive from the assumption that the crystalline forms of boron and aluminum are *more* stable than the hypothetical forms of these elements in which each atom is trigonally bonded to its nearest neighbors (cf. graphite), but are less stable than would be the case if the atoms had sufficient electrons to make full use of the s and p orbitals (as in diamond). Hence we conclude $\bar{E}$(B—B) > $\frac{1}{2}\lambda_{sub}$. and < $\frac{2}{3}\lambda_{sub}$. Actually, we assume $\bar{E}$(B—B) ~ $\frac{7}{12}\lambda_{sub}$., and similarly for $\bar{E}$(Al—Al).

† From examination of the final columns in table 2, we note: (i) that rather better agreement between $0.208\sqrt{\Delta}$ and $(x_A - x_B)$ would be given by reducing Pauling's x_F = 4.0 to ca. 3.8 or 3.9, by increasing x_{Ge} = 1.7 to ca. 1.85 or 1.9, and similarly with x_{Sn} (cf. Huggins (50)); (ii) that in those compounds of boron in which it is reasonable to expect some measure of "back-coördination" to the boron atom, the boron atom appears to be more electropositive (x_B ~ 1.7–1.8) than in cases (BH$_3$, B(CH$_3$)$_3$) where "back-coördination" is either not possible or likely to be small (x_B ~ 2.0); (iii) that in Si(CH$_3$)$_4$ the silicon atom appears to be more electronegative (x_{Si} ~ 1.95) than in SiX$_4$ (X = halogen), and compares with the case B(CH$_3$)$_3$; unlike BH$_3$, in SiH$_4$ the data do not suggest the same trend (the thermal data on SiH$_4$ are, however, not well established); (iv) that negative Δ values are shown by Al(CH$_3$)$_3$, NCl$_3$, AsH$_3$, and S(CH$_3$)$_2$. Of these, the former is the least to be expected in view of the appreciable electronegativity difference, $(x_{Al} - x_C)$ ~ 1.0.

The final column of table 1 gives $|x_A - x_B|_P$ values from Pauling's scale. Comparison with the figures in the preceding column (according to equation 2 they should be identical) shows satisfactory agreement for the alkali iodides and the acids hydrogen chloride, hydrogen bromide, and hydrogen iodide. Otherwise, agreement is no better than moderate, and is poor for alkali fluorides and chlorides. Bearing in mind the failure of the method with respect to the alkali hydrides, one can only conclude that the empirical basis for equation 2, at least as far as table 1 is concerned, is unconvincing.

Better support for equation 2 is provided by table 2, in which the data presented refer to bonds in *polyatomic* molecules, all of the type MX_n (where X is an univalent atom) or MR_n (where R is an univalent radical). The *mean* bond energy ($\bar{E}$) in these molecules is defined as $\frac{1}{n}$th the heat of rupture of MX_n into ground-state atoms, or $\frac{1}{n}$th the heat of rupture of MR_n into gaseous M atoms and R radicals. The equations corresponding to equation 3 are:

$$\Delta = \bar{E}(M-X) - \frac{1}{2}\left[\bar{E}(M-M) + D(X-X)\right] \tag{3a}$$

$$\Delta = \bar{E}(M-R) - \frac{1}{2}\left[\bar{E}(M-M) + D(R-R)\right] \tag{3b}$$

$D(R-R)$ is the *dissociation* energy in R_2, and $\bar{E}(M-M)$ the bond-energy term for a single-bonded M—M link. This latter is reasonably well defined in a few elements (e.g., carbon, silicon, germanium, tin, sulfur) but is subject to uncertainty in others and is unknown in the majority of metallic elements. The authors have, with Pauling, identified $\bar{E}(P-P)$ with $\frac{1}{6}$th the heat of atomization of the gaseous P_4 molecule, although the P—P bonding here is of an unusual type (75) and hardly satisfactory for use as a standard. Similar remarks apply to $\bar{E}(As-As)$. Again, the authors follow Pauling to derive $\bar{E}(O-O)$ and $\bar{E}(N-N)$ from the molecules H_2O_2 and N_2H_4, despite the fact that the assumptions in the derivation are difficult to substantiate (111). The values for $\bar{E}(B-B)$ and $\bar{E}(Al-Al)$ are discussed in the notes following table 2, but cannot claim to be well established. It is largely because of the unavailability of $\bar{E}(M-M)$ that the number of elements included in table 2 is comparatively small. Nevertheless, despite these various items of criticism, the weight of empirical evidence in table 2 favoring Pauling's equations is substantial.

In all, Pauling has allotted electronegativity values to thirty-three elements, including hydrogen (for which he arbitrarily adopted $x = 2.1$ units). Of this total, however, only *fourteen* were obtained by the method described, i.e., through equations 2 and 3. Recently, Huggins (50), making use of the considerable accumulation of new and improved thermal data available since the Pauling scale was proposed, has reëvaluated the electronegativities of these same fourteen elements. For the most part, Huggins' amended values agree within ± 0.1 unit with those of Pauling; the largest changes are for antimony

(2.05 given by Huggins; 1.8 given by Pauling) and for germanium and tin (1.9 given by Huggins; 1.7 given by Pauling).

For the majority of elements, however, values of the single-bond energies, $\bar{E}(M—M)$, are unknown, and the Δ values cannot be gained through equations 3 and 3a, so that it is necessary to by-pass equation 3 in order to extend the scale. Pauling does this by supposing that the extra-ionic energy in a compound MX_n may be obtained from the heat of formation $(Q_f = -\Delta H_f^\circ)$ of the compound from its constituent elements in their standard states; e.g., if MX_n is a metal halide, $\Delta = \dfrac{1}{n} Q_f$. Pauling seems prepared, if necessary, to use Q_f values relating to the *solid* state of MX_n in this purely "thermochemical method," and Haïssinsky (44) has argued (some may think unconvincingly) that solid-state Q_f values ought preferably to be employed for most metal halides and oxides.[1] Although the method is admittedly crude (in relation to the definition of extra-ionic energy of equation 3), Pauling justifies its usage on the grounds that the terms it neglects in large measure mutually cancel. Nevertheless, it is perhaps insufficiently realized that the *majority* of Pauling's electronegativity values were derived by the use of this comparatively crude method.

The "thermochemical method" has been applied extensively by Haïssinsky (44, 45) to obtain electronegativity values for a large number of the elements missing from the tabulation of Pauling. They were obtained, in the main, from available thermochemical data on the chlorides, bromides, and iodides of the metals. For those elements showing more than one stable valence (e.g., Sn^{II}, Sn^{IV}), Haïssinsky quotes values which would suggest that an atom becomes more electronegative as its valence increases (see Section C of the Appendix).

One of the earliest attempts to provide a theoretical basis for Pauling's scale was made by Mulliken (83). The problem is, however, a complicated one when examined in detail. It is presented here in a manner similar to that of Warhurst (125).

Consider a bond A—B, in which B is distinctly more electronegative than A. The approximate wave function Ψ describing A—B may be written as

$$\Psi = \gamma_1\psi(A^+B^-) + \gamma_2\psi(A—B) \tag{5}$$

[1] If the heat of formation of a *crystalline* metal chloride, MCl_n, is used to derive

$$\Delta = \frac{1}{n} Q_f$$

and comparison is made with Δ as defined in equation 3, then the assumption being made is that

$$\bar{E}(M—M) = \frac{2}{n}(\lambda_a - \lambda_s)$$

where λ_a = the heat of atomization of the metal and λ_s = the heat of sublimation of MCl_n. In general, one would expect $2\lambda_a/n$ to set an upper limit to $\bar{E}(M—M)$, so that the term $2\lambda_s/n$ may sometimes be advantageously included. But when λ_s is very large—as in some metal fluorides and oxides—it must be doubted if the full value of λ_s should be included.

since γ_3 (equation 1) is in this case small and may be neglected. The functions $\psi(A^+B^-)$ and $\psi(A—B)$ relating to the "pure ionic" structure A^+B^- and the "pure covalent" structure A—B may be represented more fully by equations 6 and 7,

$$\psi(A^+B^-) = \psi_i = \phi_B(1)\phi_B(2) \qquad (6)$$

and

$$\psi(A—B) = \psi_c = \frac{1}{\sqrt{2 + 2S_{AB}^2}} \{\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)\} \qquad (7)$$

in which the ϕ's are atomic orbitals and S_{AB} is the overlap integral $= \int \phi_A(1)\phi_B(1) \, d\tau$. Equation 7 is the Heitler–London function.

The energy of the bond defined by equation 5 may be obtained from

$$E = \int \bar{\Psi} \, \mathcal{H} \, \Psi \, d\tau$$

(where $\mathcal{H}$ is the Hamiltonian operator appropriate to this two-electron system) and may be expressed by

$$E = \left\{ \frac{\begin{array}{c} H_{cc} + H_{ii} - 2S_{ic}H_{ic} \\ - \sqrt{\{(H_{ii} - H_{cc})^2 + 4S_{ic}^2 H_{ic}H_{cc} - 4S_{ic}H_{ic}(H_{cc} + H_{ic}) + 4H_{ic}^2\}} \end{array}}{2(1 - S_{ic}^2)} \right. \qquad (8)$$

where

$$H_{cc} = \int \bar{\psi}_c \mathcal{H}\psi_c \, d\tau = \text{energy of the pure covalent structure,}$$

$$H_{ii} = \int \bar{\psi}_i \mathcal{H}\psi_i \, d\tau = \text{energy of the pure ionic structure,}$$

$$H_{ic} = \int \bar{\psi}_c \mathcal{H}\psi_i \, d\tau = \int \bar{\psi}_i \mathcal{H} \psi_c \, d\tau = \text{the resonance integral, and}$$

$$S_{ic} = \int \bar{\psi}_i \psi_c \, d\tau = \text{the orthogonality integral}$$

A necessary consequence of equation 8 is that E should always be less (i.e., more negative) than both H_{cc} and H_{ii}, so that $(H_{cc} - E)$ is positive in all cases. If now we accept that H_{cc} may be replaced by the additive mean of the single-bonded A—A and B—B energies, we have $(H_{cc} - E) = \Delta$, and the "extra-ionic resonance energy" (i.e., positive Δ values) of Pauling is then explained. But $(H_{cc} - E)$ is itself a rather involved function of the matrix components H_{cc}, H_{ii}, and H_{ic} and of the orthogonality integral S_{ic}, and the manner in which it (and therefore Δ) might be related to $|x_A - x_B|$ has not been determined. Moreover, although Pauling and Sherman (94) from consideration of the ex-

change integrals for one-electron bonds have given theoretical support for the geometric mean rule (equation 4), it has been questioned whether the theoretical basis for it (or for the additive mean rule) is adequate (17). In short, neither equation 2 nor equation 3 can yet be said to have more than empirical foundation.

Recently, Cottrell and Sutton (14) and also Hurley (53) have given a novel interpretation of the origin of Pauling's values that relates these *not* to ionic-covalent resonance at all, but to a reduction in the internuclear repulsion energy in AB molecules relative to the mean of the internuclear repulsion energies in AA and BB. Cottrell and Sutton applied the Heitler–London–Sugiura treatment to a series of model molecules built up from two nuclei (A and B) and two electrons. The nuclear charges, α and β on A and B, were allowed to vary over a range of positive values (greater and less than unity), and α and β were not restricted to the integral values of real molecules. The interesting result was obtained that the calculated dissociation energy of $AB(\alpha,\beta)$ was found in all cases ($\alpha + \beta = 2$, $\alpha \neq \beta$) to be greater than the mean (arithmetic *or* geometric) of the calculated dissociation energies of $AA(\alpha,\alpha)$ and $BB(\beta,\beta)$. Since the wave function used was the simple Heitler–London one, this stabilization in AB molecules has no reference to ionic terms. Examination of the origin of it showed that it was due to a decrease in nuclear repulsion.

Hurley (53) has examined the same type of molecular model as Cottrell and Sutton, but his starting-point was the approximate wave function for the hydrogen molecule proposed by Lennard-Jones and Pople (65), rather than the less exact Heitler–London function. Hurley confirms the general conclusions of Cottrell and Sutton, and adds one significant finding: namely, that in case the mean electronegativity of atoms A and B falls below a certain critical value, the Δ value becomes *negative*. He attributes the failure of the additive mean rule in the alkali hydrides to this latter cause.

The chief objection to this analysis by Cottrell and Sutton is that their two-electron molecular model is entirely artificial and removed from the many-electron diatomic molecule of physical reality. Moreover, the theoretical basis for Mulliken's (82) definition of electronegativity (*vide supra*) is closely allied to ionicity, and not at all to nuclear repulsion forces. Indeed, Hurley admits the failure of the Cottrell and Sutton model to agree with both Pauling's and Mulliken's electronegativity scales simultaneously.

Where the truth lies remains to be determined, but meanwhile the usefulness of Pauling's empirical scale is not to be denied, and its occasional failures are now, perhaps, less mysterious than they at first appeared to be.

B. Mulliken's electronegativity scale

Coulson (18) has expressed the opinion that Mulliken's measure of electronegativity is better and more precise than that of Pauling. Certainly, it rests on a more secure theoretical foundation, and its cognizance of a dependence of the electronegativity property on the orbital characteristics of an atom in a molecule adds a much-needed flexibility to the whole electronegativity concept.

Mulliken's definition, proposed in 1934, is simply

$$\chi_M(A) = \frac{1}{2}(I_A + E_A)$$

where $\chi_M(A)$ is the electroaffinity of atom A, and I_A and E_A are the ionization potential and electron affinity, respectively. However, I_A is not (in general) a physically observable ionization potential of A, but is the "valence-state" ionization potential; similarly E_A is the "valence-state" electron affinity. The qualitative derivation of Mulliken's equation of 1934 has since been more rigorously examined by Mulliken himself (85) and by Moffitt (77). A much abbreviated version of Moffitt's treatment is given here.

Consider a bond A—B in a molecule, in which the bonding orbital of atom A is ϕ_A and that of atom B is ϕ_B. The criterion for equal electronegativity in ϕ_A, ϕ_B is the equality of the mixing coefficients γ_1, γ_3 of equation 1. But in an actual bond the mixing coefficients must so adjust themselves that the energy integral $= \int \Psi \mathcal{K} \bar{\Psi} \, d\tau$ (Ψ is defined in equation 1) is minimal. Moffitt finds that, on minimizing the energy, $\gamma_1 = \gamma_3$ for all values of r(A—B) *if*, and only if,

$$\epsilon(\phi_A) - \frac{1}{2}J(\phi_A; \phi_A) = \epsilon(\phi_B) - \frac{1}{2}J(\phi_B; \phi_B) \tag{9}$$

where $\epsilon(\phi_A)$ is the Hartree–Fock energy of ϕ_A (in the valence state of atom A) and $J(\phi_A; \phi_A)$ is the Coulomb integral. It is possible to show further that $\epsilon(\phi_A) \sim I_A$, and that $\epsilon(\phi_A) - J(\phi_A; \phi_A) \sim E_A$, so that equation 9 reduces to
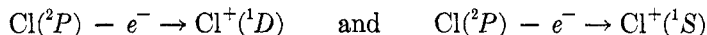
$$\frac{I_A + E_A}{2} = \frac{I_B + E_B}{2} \tag{10}$$

as the basic condition for equality of electronegativity in ϕ_A, ϕ_B. However, the approximations made in translating equation 9 into equation 10 are fairly severe, and there are distinct limitations to the validity of Mulliken's definition.

The quantities I and E of equation 10 refer to the "valence-state" ionization potentials and electron affinities of the orbitals ϕ_A, ϕ_B. The need for, and meaning of, "valence state" in this connection might be shown from two simple examples.

The ground state of the hydrogen chloride molecule is the singlet state, $^1\Sigma^+$. According to equation 1 it may be regarded as built up from the atoms H + Cl, from the ions $H^+ + Cl^-$, and possibly from the ions $H^- + Cl^+$. Now the ground state of Cl^- is ^1S, and this on combination with H^+ can give $^1\Sigma^+$. But the ground state of the positive Cl^+ ion is ^3P, which can only give *triplet* states on combining with H^-, ^1S. The two low-lying *excited* states, ^1D and ^1S, of Cl^+ will give $^1\Sigma^+$ on combination with H^-, and both contribute to the valence state of Cl^+ in which we are interested. Accordingly, the ionization process required is *not* the process
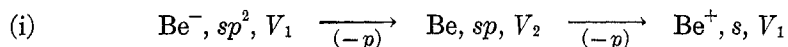
$$Cl(^2P) - e^- \rightarrow Cl^+(^3P)$$
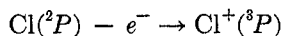
but a suitably weighted mean of the two processes

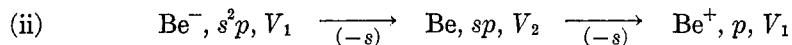$$Cl(^2P) - e^- \rightarrow Cl^+(^1D) \quad \text{and} \quad Cl(^2P) - e^- \rightarrow Cl^+(^1S)$$

The divalent valence state of beryllium provides an example in which the bond orbitals are hybrid in character. The ground state, ^1S, of beryllium is zero-valent, and the divalency of the atom in its chemical compounds is primarily due to the two excited states, ^3P and ^1P, belonging to the configuration sp. The valence state V_2, sp is, in fact, to be regarded as a mixture in the ratio $3:1$ of the states ^3P and ^1P. (The valence state is not, in itself, an *observable* (i.e., stationary) state of the atom, although it can be represented as a mixture of specified stationary states. Moffitt (79) has given a table showing the contribution from each stationary state to each of the valence states arising from the configurations of type $s^m p^n$, where m and n are integers.)

There are two alternative ionization processes of relevance in Be, V_2, sp:

(i) $\qquad$ Be$^-$, sp^2, V_1 $\xrightarrow[(-p)]{}$ Be, sp, V_2 $\xrightarrow[(-p)]{}$ Be$^+$, s, V_1

and

(ii) $\qquad$ Be$^-$, $s^2 p$, V_1 $\xrightarrow[(-s)]{}$ Be, sp, V_2 $\xrightarrow[(-s)]{}$ Be$^+$, p, V_1

The value of $(I + E)/2$ for sequence (i), we might refer to as the p-electronegativity of Be, V_2; similarly, $(I + E)/2$ for sequence (ii), which is numerically very different from that for sequence (i), we refer to as the s-electronegativity. The divalent beryllium atom, however, is believed to make use of *hybrid* orbitals, formed by mixing the s- and p-orbitals equally, so that the proper measure of the electronegativity of beryllium is given by the *mean* of the s- and p-electronegativities.

Despite the formal simplicity of Mulliken's measure of electronegativity, there are difficulties in applying it quantitatively to the majority of elements. The main practical difficulty is the lack of reliable information on electron affinities. Moreover, in the A subgroup and transitional elements of the third (and higher) rows of the Periodic Table, d-orbitals (and f-orbitals) begin to play a major role in the valence descriptions, and the theoretical formulation of the valence-state energies of configurations of the general type $s^m p^n d^q$ ($m \leqslant 2$, $n \leqslant 6$, $q \leqslant 10$; m, n, q are integers)—and of more involved configurations than these—remains for the most part to be given.

A reëvaluation of the Mulliken electronegativities (χ_M) of the elements belonging to the first and second rows of the Periodic Table has been made recently by Skinner and Pritchard (113). The tables of atomic energy levels compiled since 1949 at the National Bureau of Standards by Moore (80) provided the source of empirical spectroscopic data upon which their reëvaluation (and extension) of earlier estimates by Mulliken (and also Hellmann (48)) was based. The authors have, in table 3, extended slightly, and in part modified, the table of χ_M values given by Skinner and Pritchard.

TABLE 3

Electroaffinities of atoms

Atom	Valence	I	E	χ_M	χ_P	χ_P
		e.v.	*e.v.*			
H....................................	s, V_1	13.595	0.747	7.17 s	2.28 s	2.1
Li...................................	s, V_1	5.39	0.54	2.96 s	0.94 s	1.0
Na...................................	s, V_1	5.14	0.74	2.94 s	0.93 s	0.9
Cu...................................	s, V_1	7.72	0.9	4.31 s	1.36 s	—
Be....................................	sp, V_2	5.96	−0.24	2.86 p	0.91	—
	sp, V_2	9.92	2.76	6.34 s	2.01	—
				*4.60**	*1.46**	1.5
Mg..................................	sp, V_2	4.52	0.42	2.47 p	0.78	—
	sp, V_2	8.95	2.82	5.89 s	1.87	—
				*4.18**	*1.32**	1.2
Zn...................................	sp, V_2	4.90	−0.31	2.30 p	0.73	—
	sp, V_2	10.95	3.29	7.12 s	2.26	—
				*4.71**	*1.49**	—
B.....................................	s^2p, V_1	8.30	−0.65	3.83 p	1.22 p	—
	sp^2, V_3	8.53	0.12	4.33 p	1.37	—
	sp^2, V_3	15.15	5.58	10.36 s	3.29	—
				*6.34**	*2.01**	2.0
Al...................................	s^2p, V_1	5.98	−0.05	2.97 p	0.94 p	—
	sp^2, V_3	6.67	1.45	4.06 p	1.29	—
	sp^2, V_3	12.74	5.14	8.94 s	2.84	—
				*5.69**	*1.81**	1.5
C.....................................	s^2p^2, V_2	10.94	0.28	5.61 p	1.78 p	—
	sp^3, V_4	11.42	0.58	6.00 p	1.90	—
	sp^3, V_4	21.43	9.26	15.20 s	4.83	—
				*8.30**	*2.63**	2.5
Si....................................	s^2p^2, V_2	7.94	0.75	4.35 p	1.38 p	—
	sp^3, V_4	8.99	3.02	6.00 p	1.90	—
	sp^3, V_4	17.93	7.53	12.73 s	4.04	—
				*7.68**	*2.44**	1.8
N.....................................	s^2p^3, V_3	13.83	0.85	7.34 p	2.33 p	3.0
	sp^4, V_3	14.49	1.58	8.03 p	2.55	—
	sp^4, V_3	27.5	13.79	20.64 s	6.55	—
P.....................................	s^2p^3, V_3	10.15	1.29	5.72 p	1.81 p	2.1
	sp^4, V_3	11.94	2.42	7.18 p	2.28	—
	sp^4, V_3	(24)	8.60	16.3 s	5.17	—
As....................................	s^2p^3, V_3	9.62	1.37	5.50 p	1.75 p	2.0
	sp^4, V_3	12.24	2.02	7.13 p	2.26	—
	sp^4, V_3	(24)	8.32	(16.2 s)	5.14	—
O.....................................	s^2p^4, V_2	17.28	2.70	9.99 p	3.17 p	3.5
	sp^5, V_2	17.76	4.85	11.30 p	3.59	—
	sp^5, V_2	35.30	19.85	27.57 s	8.75	—
S.....................................	s^2p^4, V_2	12.50	2.70	7.60 p	2.41 p	2.5
Se....................................	s^2p^4, V_2	11.67	2.38	7.02 p	2.23 p	2.4
Te....................................	s^2p^4, V_2	10.6	2.62	6.61 p	2.10 p	2.1
F.....................................	s^2p^5, V_1	20.98	3.65	12.32 p	3.91 p	4.0
Cl....................................	s^2p^5, V_1	15.09	3.82	9.45 p	3.00 p	3.0
Br....................................	s^2p^5, V_1	13.72	3.69	8.70 p	2.76 p	2.8
I.....................................	s^2p^5, V_1	12.61	3.55	8.08 p	2.56 p	2.4

The χ_M values are, with a few exceptions, almost identical with those given earlier by Skinner and Pritchard (113). Additions to the previous list include values for copper, zinc, arsenic, selenium, tellurium, bromine, and iodine.

The valence-state energies were calculated from the formulas of Moffitt (79), using spectroscopic data from Moore (80) and the Landolt-Börnstein *Tabellen* (63); see table 11.

The electron affinities used in preparing table 3 are given in table 10. Although some of the values are provisional, it is unlikely that the error in any given case is seriously in excess of ±1 e.v. Note, however, that an electron affinity is divided by 6.3 in its contribution to χ_P, so that an error of ±1 e.v. in electron affinity brings an error of no more than ±0.16 unit in χ_P.

The χ_M are designated s or p, except for the values marked with asterisks, which apply to hybrid orbitals, i.e., sp in Group II, sp^2 in Group III, and sp^3 in Group IV.

Mulliken referred to the quantities $(I + E)/2$, in which both I and E are measured in *electron volts*, as the "absolute electroaffinities," and empirically correlated his values, χ_M, with Pauling's scale of values by the relation

$$\frac{\chi_M(A) - \chi_M(B)}{2.78} = |x_A - x_B|_P \tag{11}$$

where $\chi_M(A)$ and $\chi_M(B)$ are the electroaffinities of atoms A and B. Skinner and Pritchard suggest that a quantity $\chi_P = \chi_M/3.15$ may be identified satisfactorily with the Pauling electronegativities. The correspondence between the scales of Mulliken and Pauling is shown graphically in figure 1, and in the final columns (under χ_P and x_P) of table 3.

Comparison shows good agreement between the two independent measures of electronegativity for the atoms $H(s)$, $Li(s)$, $Na(s)$, $Be(sp)$, $Mg(sp)$, $B(sp^2)$, $C(sp^3)$, $S(p)$, $Se(p)$, $Te(p)$, $F(p)$, $Cl(p)$, $Br(p)$, and $I(p)$. Agreement is no more than fair for $Al(sp^2)$, $P(p)$, and $As(p)$, and is poor for $Si(sp^3)$, $N(p)$, and $O(p)$. However, close agreement should not be expected unless the orbital description (s, p, etc.) of χ_M is a proper representation of the atom in its compounds, and the poor agreement in the case of χ_P for $N(p)$, for example, is due (at least in part) to the making of an improper comparison, for it is now considered that the nitrogen atom in the trivalent state makes use not of pure p-orbitals but of hybrid orbitals containing a certain amount of s-character (see, e.g., Pople
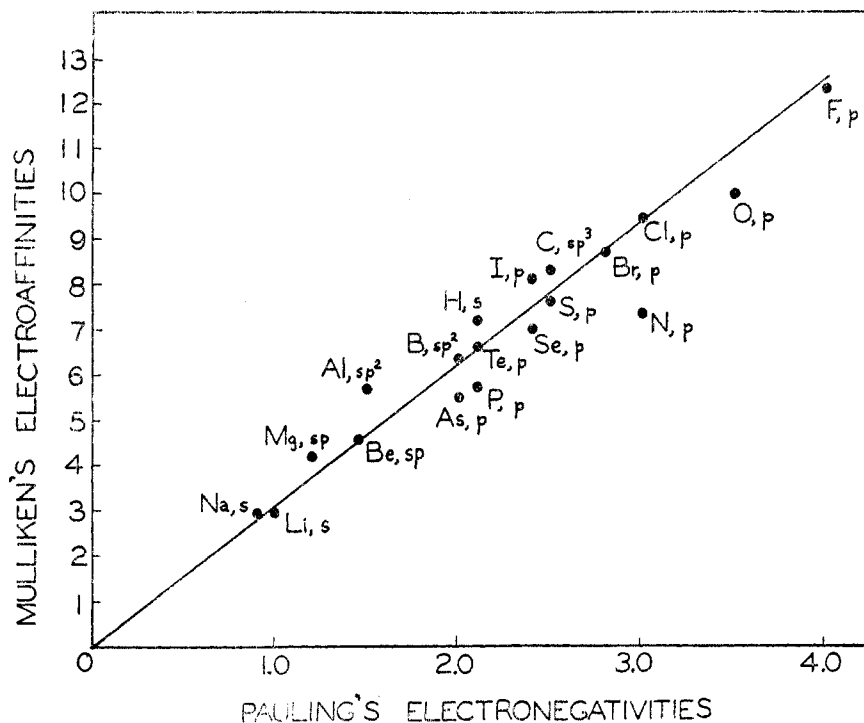

FIG. 1. Correspondence between Mulliken's electroaffinities and Pauling's electro-negativities.

(96)). This type of hybridization has been referred to as "second-order hybridization" by Moffitt (77), and as "isovalent hybridization" by Mulliken (86), and arises from configuration interaction between atomic configurations of equal valence, but differing in numbers of s- and p-electrons: thus, in nitrogen, between s^2p^3, V_3 and sp^4, V_3; in oxygen, between s^2p^4, V_2 and sp^5, V_2. Because of the high values of the s-electronegativities, both in $N(sp^4)$ and in $O(sp^5)$, it would require comparatively little isovalent promotion in these atoms to bring their calculated χ_P into line with the electronegativity values of Pauling.[2]

The removal of an s-electron from an atom is, in general, energetically more difficult than the removal of a p-electron from the same quantum shell, and it is largely because of this that the calculated electronegativity of a hybrid orbital is larger the greater the amount of s-character it contains (*cf.* Walsh (122) and Moffitt (79)). The carbon atom in particular is interesting in this connection, since it can adopt various types of hybridization of differing degrees of s-character. Thus the acidity of acetylene, relative to methane, is understood in terms of the increased electronegativity of carbon in the digonal or sp condition, relative to that of carbon in the tetrahedral or sp^3 condition. Ethylenes and benzene, in which the carbon atom is in the trigonal or sp^2 condition, ought to be less acidic than acetylene, but still acidic relative to methane. Moffitt (79) mentions the hydrogen-exchange reactions occurring upon the solution of certain metallic alkyls in benzene as evidence of acid behavior by benzene.

There is evidence from table 3 suggesting that an atom capable of variable valence exhibits its most electronegative behavior in its (numerically) highest valence state; thus, trivalent boron ($\chi_P = 2.01$) is more electronegative than monovalent boron ($\chi_P = 1.22$), and tetravalent carbon ($\chi_P = 2.63$) more electronegative than divalent carbon ($\chi_P = 1.78$). It is of interest to enquire if this is generally true; if, e.g., $P^V > P^{III}$, $S^{VI} > S^{IV} > S^{II}$, and $Cl^{III} > Cl^I$. Some further comment on this question is given in Section C of the Appendix. Certain of the heavier elements—notably lead, tin, and thallium—which exhibit comparatively high chemical stability in their lower valence states are described by Sidgwick as possessing an "inert pair" of valence electrons. Evidence of a more quantitative nature of such "inertness" is provided, e.g., by the trends in the excitation energies $V_0 \rightarrow V_2$ in the series Be (3.36 e.v.) $\rightarrow$ Zn (4.49 e.v.) $\rightarrow$ Hg (5.56 e.v.) and $V_1 \rightarrow V_3$ in the series B(5.52 e.v.) $\rightarrow$ Ga(5.75 e.v.) $\rightarrow$ Tl(7.31 e.v.) But it may be an additional factor stabilizing the lower valences of the heavier elements that they are decidedly electropositive (relative to their higher valence states) so that many of the bonds formed by them have a high degree of ionic character, and the "extra-ionic resonance" energies are large.[3]

C. Malone's measure of electronegativity

Malone (72) suggested as early as 1933 that there is a rough proportionality between the dipole moment of a bond A—B and the electronegativity difference:

$$\mu_b \sim |x_A - x_B|_P \qquad (12)$$

[2] But see Mulliken (86) for further comment on this point.

[3] Sidgwick (109), referring to the instability of the plumbous alkyls and aryls, remarks: "They show how much less stable divalent lead is in the covalent than in the ionized state."

TABLE 4

Bond dipole moments* and electronegativity

Bond	μ_b	$|x_A - x_B|_P$	Bond	μ_b	$|x_A - x_B|_P$
	Debyes			Debyes	
H—F	1.91[a]	1.9	Cs—F	7.85[d]	3.3
H—Cl	1.03[b]	0.9	K—Cl	10.48[e]	2.2
H—Br	0.78[b]	0.7	K—Br	10.41[e]	2.0
H—I	0.38[b]	0.4	N—H	1.32[c]	0.9
Cl—F	0.88[c]	1.0	P—H	0.34[c]	0.0
Br—F	1.29[c]	1.2	As—H	0.13[c]	0.1
Cl—Br	0.57[c]	0.2	Sb—H	0.07[c]	0.3
Cl—I	0.65[c]	0.5	N—F	0.18[c]	1.0
O—H	1.51[b]	1.4	P—F	0.77[c]	1.9
			As—F	2.13[c]	2.0

* The bond dipole moments are taken or calculated from data given in the following sources: (a) Hannay and Smyth (46); (b) Pauling (91); (c) Gordy *et al.* (40); (d) Honig *et al.* (49); (e) Rabi *et al.* (32, 64).

where μ_b is the bond moment measured in Debyes. Equation 12 applies remarkably well in a few well-known cases (e.g., the hydrogen halides), but fails badly in others, and cannot be accepted as a reliable measure. Some examples, drawn mainly from diatomic molecules and polyatomic molecules of the type MX_3, are given in table 4.

A proportionality between dipole moment and electronegativity difference might be expected in the case where the "pure covalent" function ($\psi(A—B)$ of equation 1) describes a state of *zero* dipole moment. But it seems that this latter condition rarely obtains,[4] so that the net dipole moment is not simply determined by the relative weight (mixing coefficient) of the pure ionic structure in the resonance hybrid.

When written out in detail, the pure covalent function $\psi(A—B)$ needs to specify the atomic orbitals employed both by A and by B in bond formation; in general, these will not be pure s or pure p but hybrids. As Coulson (15) has shown, such hybrids do not possess central symmetry and in consequence have a dipole (the "atomic dipole") which might, in certain cases, be quite large. Furthermore, hybridization of a bonding orbital affects the *non-bonding* ones, with the result that lone-pair electrons may possess markedly asymmetric charge distributions. In an analysis of the dipole moment of the water molecule, Coulson (17) concluded that ionic-covalent resonance accounts for no more than a quarter of the total moment, and that the dominating term is the lone-pair moment. A similar conclusion was reached by Pople (95), who states that "a very considerable contribution (to the dipole moment) arises from the orientation of the lone pairs on the side of the oxygen nucleus remote from the hydrogen nuclei."

Coulson (18) quotes as evidence of the importance of the lone-pair electrons in determining dipole moments a comparison of the molecules NH_3 and NF_3. Since one would expect on electronegativity grounds that the N—F σ-bonds should be distinctly polar, the small moment (0.2 D) of NF_3 would imply a

[4] Mulliken (83) first drew attention to the point that a "pure covalent" bond may nevertheless show a large dipole moment.

large compensating moment from the nitrogen lone-pair electrons (Schomaker and Lu (106)). In NH_3 the N—H σ-bonds are not sufficiently polar to counteract the lone-pair moment, and the net moment remains quite large (1.5 D). In fact, Moffitt (77) has calculated that the electronegativities of the *hybrid* atomic orbitals of nitrogen, oxygen, and hydrogen, *as they occur* in the bonds of NH_3 and OH_2, are almost equal.

Although it is possible that the quantitative calculations have exaggerated the effects of hybridization on dipole moments, they have rather effectively undermined the long-held view that polar characteristics reflect the degree of ionic character. Malone's measure of electronegativity, it seems, must be rejected not solely because of its occasional serious failures; the theoretical basis for it has been questioned, and its successes may be apparent rather than real.

D. Gordy's electronegativity scales

Gordy has proposed three different methods of measuring electronegativity. The first of these (36) is contained in a relation of the form

$$k = aN(x_A x_B/d^2)^{3/4} + b \qquad (13)$$

which was found to hold accurately for a large number of diatomic and simple polyatomic molecules in their ground states.[5] In equation 13 k is the bond-stretching force constant (of a bond A—B), d the bond length, N the bond order, and x_A and x_B are the electronegativities of the bonded atoms. If k is measured in dynes/cm. $\times$ 10^{-5}, and d in Ångström units, a and b have the values 1.67 and 0.30, respectively (except in hydrides and the diatomic alkali metals).

Gordy's equation 13 was arrived at empirically, and no very satisfactory theoretical interpretation of it has been given. The interesting feature is the appearance of the electronegativities as a product,[6] $x_A x_B$, rather than as a difference, $x_A - x_B$. The electronegativity values obtained from equation 13 by Gordy for a number of the elements are listed in table 6.

Gordy's (35) second measure of electronegativity is derived from the relation

$$x = 0.31\left(\frac{n+1}{r}\right) + 0.50 \qquad (14)$$

in which x represents the electronegativity, n is the number of electrons in the valence shell, and r is the single-bond covalent radius of the atom, measured in Ångström units. Gordy has applied equation 14 to obtain an electronegativity

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[5] The average deviation of k (calculated from equation 13, assuming the Pauling values for x_A, x_B) from k (observed) for seventy-one cases was less than 2 per cent.

[6] Guggenheimer (41) has proposed an empirical relationship

$$k = \text{const. } \sqrt{z_A z_B}\ r^{-2.46}$$

in which r = the internuclear separation and z_A, z_B are the numbers of electrons in the valence shells of the bonded atoms A, B. In the first two rows of the Periodic Table (lithium to fluorine; sodium to chlorine) the electronegativities increase more or less regularly with atomic number, so that the products $x_A x_B$ and $z_A z_B$ vary in similar manner to one another.

scale covering a total of fifty-two elements. Where comparison can be made, equation 14 gives x values in good agreement with those of Pauling.

Equation 14 originates from a notion which has the merit of simplicity. In essence, Gordy has identified the electronegativity property of an atom with the *potential, Z^*e/r,* at the covalent boundary of the atom (Z^* is the "effective" nuclear charge of the atom acting on the valence shell at distance r from the nucleus; r is the single-bond covalent radius). Gordy proceeds to derive Z^* on the simplifying assumption that all the electrons in closed shells below the valence shell exert full screening, and that the screening constant of one valence electron for another is 0.5, whence

$$Z^* = n - 0.5(n - 1) = 0.5(n + 1)$$

where n is the number of electrons in the valence shell. From a plot of x_P against $(n + 1)/r$ a straight line, corresponding to equation 14, was obtained. The electronegativity values calculated by Gordy from equation 14 are listed in table 6, and there compared with the values given by other methods.

One objection to equation 14 is that it makes use of an oversimplification with respect to the "effective" nuclear charge, Z^*, and, in consequence, the identity of electroaffinity with atomic electrostatic surface potential is perhaps overstated. Certainly, Gordy chose an unorthodox method of assessing Z^* values, and it is curious that he did not remark upon the effect of calculating Z^* by more conventional methods, e.g., those of Pauling (93) and, in particular, of Slater (116). A reinvestigation of the Gordy assumption, $x \propto Z^*e/r$, with Z^* as from Slater, is given in Section II of the Appendix.

Cottrell and Sutton (14) have derived the approximate relation $x \propto (n + 1)/\sqrt{2}r$, which they find to be particularly good for the elements of the first short period. Their relation, however, originates from entirely different tenets from those of Gordy.

Mention should be made of a formula proposed by Liu (68) some four years before Gordy's equation was published, which is of similar form to equation 14:

$$x = 0.313 \left(\frac{n + 2.6}{r^{2/3}} \right) \qquad (15)$$

Here n and r have the meanings as in equation 14. Liu's equation was established purely empirically.

The third measure associated with Gordy (38) originates from work by Townes and Dailey (121) and is important in that it makes use of information on the electron distribution in molecules that can now be gleaned from radiofrequency spectra. The experimental quantity of value in this connection is known as the "nuclear quadrupole coupling." The nuclei with spins greater than $\frac{1}{2}$ possess electric quadrupole moments which can interact with the electric field due to the electrons and other nuclei in a molecule with an energy of interaction which changes as the orientation of the spin is altered. This quadrupole interaction gives rise to a hyperfine structure in the rotational energy transitions observed in the microwave region ($\nu \sim 25000$ Mc./sec.); alternatively, transitions between individual quadrupole levels may be observed at a

much lower frequency range ($\nu \sim 100$ Mc./sec.). The nuclear quadrupole coupling may be determined from the hyperfine splitting, and gives a measure of the divergence of the potential field (with respect to the bond axis) in the immediate vicinity of a particular nucleus.

The coupling constant is zero for a purely spherical electron distribution about the nucleus, so that all electrons occupying closed shells about the nucleus will not contribute to the hyperfine structure. Electrons in the valence shell which have s-character will not contribute because of the spherical symmetry of s-eigenfunctions. Electrons in d- or higher orbitals have little penetration and cannot influence the nucleus strongly; hence, as Townes and Dailey (121) have concluded, it is the p-electrons in an incomplete valence shell which are mainly responsible for the making of an asymmetric electric field in the vicinity of a nucleus. They proceed from this to suggest that the coupling constant for an atom within a molecule can give valuable information on the nature of the bonding to that particular atom. For example, the coupling constant for a free chlorine atom is -110 Mc./sec., whereas for chlorine in methyl chloride it is -83 Mc./sec. and in sodium chloride it is practically zero. It follows that the electronic environment of the chlorine nucleus in sodium chloride is nearly spherical, a conclusion which is consistent with the idea that there is almost complete charge transfer to form an ion-pair Na^+Cl^-; on the other hand, if the chlorine formed a pure covalent p-bond, the coupling constant would be the same as that for a free atom (this is approximately so in solid Cl_2, which has a coupling constant of -108.5 Mc./sec.). The case of methyl chloride, however, is more difficult to interpret: the magnitude of the coupling constant can be reduced in two ways, either by partial charge transfer, in the sense of $CH_3^+Cl^-$, or by admixture of some s-character in the nature of the bonding orbital. Both of these processes would decrease the asymmetry of the potential field along the bond axis, and it is impossible to distinguish experimentally between them. Nevertheless, it has been shown for a whole series of chlorides that, broadly speaking, the coupling constant decreases as the electronegativity difference increases (69). On the basis of certain assumptions regarding the degree of hybridization in the bonds formed mainly to chlorine and bromine atoms, Gordy (40) suggests a linear relationship between $(1 - U_p)$ and $(x_A - x_B)$, where U_p = the number of unbalanced p-electrons, as determined experimentally. More specifically, he writes

$$(1 - U_p) = \frac{|x_A - x_B|}{2} = \text{degree of ionic character} \qquad (16)$$

Table 5 (taken from Gordy) shows a comparison of observed and theoretical U_p values in chlorides, the theoretical values being based on the assumption of pure p-bonding by the chlorine atom in each case. Gordy points out that a better overall agreement between calculated and observed values of U_p would result from a starting assumption of 5–10 per cent of s-character in the chlorine bonding orbitals in each case.

Dailey (22) favors a slightly different relationship from that proposed by Gordy, in which the degree of ionic character increases slowly at first with

TABLE 5

Comparison of calculated and observed U_p values

Molecule	U_p (theory)	U_p (observed)	Per Cent Ionic Character (equation 16)	Molecule	U_p (theory)	U_p (observed)	Per Cent Ionic Character (equation 16)
Cl₂............	1.00	0.99	0	CF₃Cl............	0.75	0.71	25
BrCl............	0.90	0.94	10	SiH₃Cl............	0.40	0.36	60
ICl............	0.75	0.75	25	SiF₃Cl............	0.40	0.39	60
TlCl............	0.20	0.14	80	GeH₃Cl............	0.35	0.42	65
NaCl............	0	0.01	100	CH₃HgCl........	0.40	0.38	60
CH₃Cl............	0.75	0.69	25				

$| x_A - x_B |$, and then for moderate values of $| x_A - x_B |$ increases more rapidly, finally tailing off to 100 per cent ionic character asymptotically as the electronegativity difference becomes large. The difference between the views of Dailey and those of Gordy arises from differing assessments of the amount of hybridization: thus, for example, in ICl, Gordy assumes pure p-bonding leading to 25 per cent ionic character, whereas Dailey assumes 18 per cent s-character, leading to an ionic contribution of only 9 per cent. This example illustrates the present difficulty—there is as yet no clear way of disentangling the two effects.

It is pertinent at this point to mention another field of study which promises to add further detail to our knowledge of the electron distribution in the chemical bond. All nuclei with non-zero spin have a magnetic moment and, in consequence, give spectra at frequencies of the order of 10 Mc./sec. when placed in magnetic fields of some 5000–10,000 gauss, owing to the reorientation of the nuclear magnetic moment with respect to the direction of the applied magnetic field. However, the magnetic field at the nucleus is not exactly that which is applied to the macroscopic sample because the field interacts slightly with the motions of the electrons in the system; the effect is usually to reduce the effective magnetic field at the nucleus, and hence is often called nuclear magnetic shielding. Thus, for a given nucleus, the magnitude of this shielding effect is related to the electronic environment in which the nucleus is situated. Such studies of electronic environment are best carried out for the nuclei F^{19}, P^{31}, and H^1, which have a spin of $\frac{1}{2}$, so that complicating effects from quadrupole interactions are absent, and to date, most work has been done on fluoride and proton resonances (42, 43, 73, 74). In practice for, let us say, a series of fluorides, the magnetic field required to cause resonance absorption at some fixed frequency is measured; then, using fluorine as a reference substance, the results are expressed as a series of shielding parameters (δ), where δ_F for a given fluoride MF is 1000 times the percentage difference between the field strength required for resonance in MF and that required for F_2. To a first approximation, one might expect the shielding parameters to be related to the amount of electronic charge surrounding the fluorine nucleus, and if the results of Gutowsky and Hoffman (42) for inorganic fluorides are plotted against the electronegativity difference values $(x_M - x_F)_P$, a rough correlation is observed which supports the view of Saika and Slichter (99b) that ionic character is the major factor in determining δ_F values. If this correlation is meaningful, it is interesting to note

that the electronegativity of the halogens apparently increases in the higher valence states (*cf.* page 786 of the Appendix). However, no reasonable correlation is apparent when the proton-shielding parameters (42) for inorganic hydrides are plotted against their respective $(x_M - x_H)_P$ values, suggesting that charge transfer is not the only item affecting the shielding parameters. On the other hand, Shoolery (108a) has measured the δ_{CH_2} values in a series of substituted ethanes, CH_3CH_2X (where $X = H$, SH, I, Br, NH_2, Cl, OH, and $OCOCH_3$), and found that these vary in a linear manner with the Pauling electronegativities of the substituents X.

E. Miscellaneous

This section deals with some other methods of assessing electronegativity that have been proposed but which, in the view of the authors, are rather less acceptable than those described so far.

An extensive scale of values has been given by Bellugue and Daudel (5), based on a modification of Pauling's thermochemical method due to P. and R. Daudel (23). These latter authors consider that the empirical Δ values of Pauling should be related to the difference in electronegativity not of *neutral* atoms, but rather of atoms that already carry partial formal charges, these having arisen by virtue of the ionicity in the bond attendant upon the electronegativity difference. For a binary molecule AB, they replace equation 2 by

$$| x_{A^0} - x_{B^0} | = 0.208\sqrt{\Delta} + m(\zeta_{A^+} + \zeta_{B^-}) \tag{17}$$

where x_{A^0}, x_{B^0} are electronegativities of the neutral atoms, m is the degree of ionic character in the bond AB (*vide supra*), and ζ_{A^+}, ζ_{B^-} measure the change in electronegativity in A and B when they acquire unit positive and unit negative formal charge, respectively.

The advantage of the Daudels' "neutral atom" electronegativities is, the authors claim, that they serve as the starting-point from which the charge distribution and "effective electronegativity difference" may be determined in a polyatomic molecule, e.g., AB_n. They begin by calculating the charge distribution appropriate to the electronegativities x_{A^0}, x_{B^0}; then the influence of the ionicity in changing these "neutral atom" electronegativities is determined; and so on, by an iterative process, until the convergence values are obtained.

Although one may feel that the Daudels have made a useful point in suggesting that the electronegativity of an atom is variable with respect to the atoms to which it is bonded,[7] it is difficult to accept the method that they propose to

[7] The same point is also made by Sanderson (103). In a general way, there seems little doubt that the electronegativity of an atom is variable with respect to its immediate environment. In the chloroform molecule, for example, the electron withdrawal from the carbon atom towards the chlorine atoms apparently increases the electronegativity of the carbon atom with respect to the hydrogen atom sufficiently to render the C—H bond polar enough for the molecules of chloroform to associate to a detectable degree, presumably through hydrogen bonding. Or again, in CF_3I, the increased electronegativity of the carbon atom with respect to the iodine atom renders the iodine atom "positive," so that on hydrolysis (29) the products are CF_3H and KOI rather than CF_3OH and KI.

deal with the problem. In the first place, neither the quantities ζ, nor the degree of ionic character, m (in equation 17), can be measured, other than by very crude ways. But perhaps the main criticism is that equation 17 attempts to add refinement to a starting-point (i.e., equation 2) which is itself no more than approximate and empirical.

Several papers have appeared recently by Sanderson (100, 101, 103), in which he discusses various aspects of electronegativity in relation to a certain quantity termed the "stability ratio." This ratio (SR) is a somewhat curious quantity, defined as the ratio of the "average electron density" in a *real* atom to that in "an *inert* atom having the same number of electrons." The average electron density in a real atom is presumed to be given by dividing the atomic number Z, by the atomic volume, $\frac{4}{3}\pi r^3$, where r is the covalent radius of the atom. The so-called "inert atom" (i.e., the "inert" gas, isoelectronic with the real atom) is, of course, fictional, and to obtain the electron density in it Sanderson interpolates from the calculated electron densities in actual inert gases. The suggestion is that the SR values can be used as a measure of electronegativity.

It is almost impossible to attach real physical meaning to Sanderson's SR values, other than to regard them as a rough measure of the "relative compactness" of atoms. Sanderson has given reasons for correlating SR with electronegativity, but the authors do not find his arguments convincing.

Sanderson (102) has pointed out that the SR values show alternations as one passes from the lighter to the heavier elements in a given group of the Periodic Table; e.g., SR decreases from carbon to silicon, increases from silicon to germanium, and decreases from germanium to tin. From this he concludes that the electronegativities alternate in a similar manner, and he draws attention to a number of interesting chemical "anomalies" in support of this conclusion. However, it seems to the authors of this review that the origin of the alternation in the SR values lies in the alternation in the calculated electron densities of the inert gases, for which Sanderson quotes as follows: helium, 0.61; neon, 1.70; argon, 1.18; krypton, 1.78. Now these latter are ill-defined quantities, since one cannot assign a "radius" to an inert gas[8] with the same degree of confidence that one can assign covalent radii to atoms, so that many of Sanderson's conclusions depend on initial assumptions that are difficult either to refute or to confirm.

It has been suggested by Walsh (123) that the force constants of bonds to hydrogen, i.e., $k_e(A$—$H)$, afford a simple measure of electronegativity. Walsh plots $k_e(A$—$H)$ for a number of diatomic hydrides against the Pauling x_A values and is able to draw a smooth curve through the majority of the points. The point for $A = H$, and to a lesser extent, those for $A = $ Cl, Br, and I, do, how-

[8] Rowlinson (99a), in a recent critical review, gives the following values for the "radii" of the inert gases: He = 1.28, Ne = 1.39, A = 1.71, Kr = 1.80, Xe = 2.0 Å. These radii lead to average electron densities as follows: He = 0.23, Ne = 0.89, A = 0.86, Kr = 1.45, Xe = 1.61. However, since the electron densities in the "active" elements are based on *covalent* radii, comparable electron densities in the inert gases should be based on radii of similar significance, and it is questionable if the "collision radii" are at all relevant.

ever, deviate seriously from his curve. Walsh considers that anomalies may occur when A is of group number more than 4, in that the observed k_e is influenced (in effect, lowered) by repulsions between lone-pair electrons on A and the bonding electrons in A—H. Walsh has noticed empirically that the force constants k_e(A—H) are roughly proportional to the square of the first ionization potential of A, from which he further suggests that ionization potentials in themselves provide a rough measure of electronegativity. This latter suggestion, however, lacks the merit, especially in regard to theoretical content, of the more firmly established relationship of Mulliken, to which it may be compared.

Reference has already been made to the empirical formula of Liu. Two additional empirical formulas, also proposed by Chinese chemists, are given in equations 18 and 19:

$$\left. \begin{array}{ll} x = \dfrac{2.1 \ \sqrt{NZ}}{n^2} & \text{(for 1st and 2nd row elements)} \\[3mm] x = \dfrac{2.1 \ \sqrt{NZ}}{n(n-1)} & \text{(for 3rd and 4th row elements)} \end{array} \right\} \tag{18}$$

$$x = \frac{Z^{2/3}(N + 2.6)}{kn^2} \tag{19}$$

In these equations N is the number of valence shell electrons, Z the atomic number, and n the principal quantum number of the valence group; the constant k in equation 19 has the value 2.1 when $n = 2$, and 2.3 when n is 3, 4, 5, or 6. These equations, due to Sun (119) and Li (66), are about as successful as Liu's equation 15.

F. Comparison of values by different methods

Table 6 contains for the purposes of comparison electronegativity values of the elements as determined by different authors and by different methods. The final column contains the values which the authors of this review have chosen as "best values," bearing in mind that it is unlikely that the electronegativity property of an atom is constant in all circumstances. The values χ_P in column 6 are the same (with a few additional values, given in square brackets) as those of table 3 and are qualified, reference being given to the atomic orbital to which χ_P applies. The bracketed values (which were calculated from less reliable empirical data) should be accepted with reserve.

The agreement between the values given in columns 1 to 5 of table 6 is, on the whole, very fair, with some sharp exceptions (column 5 values for copper, silver, gold, and mercury; column 4 values for gold and mercury). The column 6 values, as has been stated earlier, are in some cases not strictly comparable to those of columns 1 to 5 (e.g., $N(p)$, $O(p)$ and probably also those for arsenic, antimony, sulfur, and selenium); the deviation shown by $Si(sp^3)$ is, perhaps, most difficult to account for.[9]

[9] But see Skinner and Pritchard (113) for some further comment on this, and also page 755.

TABLE 6

Electronegativities of the elements: comparison of values obtained by different authors and by different methods

Atom	Thermochemical		Force Constants	Electric Potential at Covalent Boundary	Electron Affinity and Ionization Potential	"Best" Value
	Pauling	Haïssinsky	Gordy (i)	Gordy (ii)	χ_P	
Ag	—	1.8	1.9	0.91	1.36 s	1.7
Al	1.5		1.5	1.48	1.81 sp^2	1.5
As	2.0		2.0	2.04	1.75 p	2.0
Au^I	—	2.3	3.1	0.92	[1.78 s]	2.1
B	2.0		1.9	1.91	2.01 sp^2	1.8–2.0
Ba	0.9	0.85	0.9	0.93	—	0.9
Be	1.5		1.45	1.38	1.46 sp	1.4–1.5
Bi	—	1.8	1.8	1.83	—	1.8
Br	2.8		2.75	2.68	2.76 p	2.8
C	2.5		2.55	2.52	2.63 sp^3	2.5–2.6
Ca	1.0		1.0	1.03	—	1.0
Cd	—	1.5	1.1	1.13	[1.4 sp]	1.4
Cl	3.0		2.97	3.00	3.00 p	3.0
Co	—	1.7	—	—	—	—
Cs	0.7		0.75	0.78	—	0.7
Cu^I	—	1.8	2.2	0.96	1.36 s	1.7
F	4.0		3.95	3.94	3.91 p	3.9
Ga	—	1.6	1.4	1.48	1.95 sp^2	1.6
Ge	1.7		1.7	1.77	—	1.8–1.9
H	2.1		2.13	2.17	2.28 s	2.1
Hg^{II}	—	1.9	1.0	1.12	1.94 sp	1.9
I	2.5	2.6	2.45	2.36	2.56 p	2.5
In	—	1.6	1.4	1.36	[1.80 sp^2]	1.5
Ir	—	2.1	—	—	—	—
K	0.8		0.80	0.82	0.80 s	0.8
Li	1.0		1.0	0.96	0.94 s	1.0
Mg	1.2		1.2	1.16	1.32 sp	1.2–1.3
N	3.0		3.0	3.01	2.33 p	3.0
Na	0.9		0.9	0.90	0.93 s	0.9
Ni	—	1.7	—	—	—	—
O	3.5		3.45	3.47	3.17 p	3.5
P	2.1		2.1	2.19	1.81 p	2.1
Pb^{IV}	—	1.8	1.5	1.56	—	1.8
Pd	—	2.0	—	—	—	—
Pt	—	2.1	—	—	—	—
Rb	0.8		0.78	0.79	—	0.8
Rh	—	2.1	—	—	—	—
Ru^{III}	—	2.05	—	—	—	—
S	2.5		2.53	2.58	2.41 p	2.5–2.6
Sb	1.8		1.8	1.82	[1.65 p]	1.9
Sc	1.3		—	1.3	—	1.3
Se	2.4	2.3	2.4	2.35	2.23 p	2.4
Si	1.8		1.8	1.82	2.44 sp^3	1.8–1.9
Sn^{IV}	1.7	1.8	1.7	1.61	—	1.8–1.9
Sr	1.0		1.0	0.98	—	1.0
Te	2.1		2.1	2.08	2.10 p	2.1–2.2
Ti	1.6		1.6	1.57	—	1.6
Tl^I	—	1.5	1.3	—	—	1.4
Y	1.3	1.2	—	—	—	1.3
Zn	—	1.5	1.2	1.21	1.49 sp	1.5
Zr	1.6	1.4	1.6	1.48	—	1.5

III. ELECTRONEGATIVITIES OF RADICALS

The concept of electronegativity originally arose out of an attempt to understand the mechanism of a number of simple reactions in organic chemistry, and in this context, it was natural to assign the quality of electronegativity to groups and radicals rather than to individual atoms. The history of the early developments is well known, being associated with such names as Markownikoff, Lucas, Lapworth, and others, and has been discussed in papers by Degering, Gillette, and Schaaf (24, 25) and by Brewster and Floyd (8). However, since the establishment of an electronegativity scale for *atoms*, the tendency has been to discuss the problem of radicals in terms of their constituent atoms rather than as individual entities.

A satisfactory qualitative electronegativity scale for radicals can be set up from a comparison of the reactivities of molecules containing the radicals in question, or from the relative reactivities of the radicals within a particular molecule. For example, the variation of ionization constants of para-substituted benzoic acids may be ascribed to the variation in electronegativity of the substituent; or again, the fate of the two radicals R and R' in the reaction scheme

$$ROR' + 2Na \rightarrow RONa + R'Na \qquad (20)$$

may be discussed in terms of the relative electronegativities of R and R'. A very large amount of data of this kind has been assembled by Hurd (52); unfortunately, the results are most conflicting, and one concludes that other factors besides electronegativity come into play in many cases. In their discussion of this topic the authors of this review have adopted two of the three criteria laid down by Kharasch, Reinmuth, and Mayo (59) to which a satisfactory method for determining relative electronegativities must submit; i.e., it must (1) involve a technique capable of a high degree of quantitative precision and yielding closely reproducible results, and (2) be capable of internal checking and be thoroughly self-consistent. When applied to the available experimental data, these two requirements are extremely rigorous and eliminate all the methods except those based upon the hydrolytic fission of metallic alkyls, such as

$$RHgR' + HCl \rightarrow RH + R'HgCl \qquad (21)$$

and

$$R_2SnR_2' + 2HCl \rightarrow 2RH + R_2'SnCl_2 \qquad (22)$$
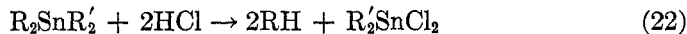
In these reactions the more electronegative of the two radicals turns up predominantly as the hydrocarbon RH, whereas the less electronegative one remains bonded to the metal atom. The validity of this method has been questioned by Adkins (1) on the grounds that there is no equilibrium between products and therefore the ratio of the amounts of products is not a measure of the electronegativity difference between R and R' but is merely an indication of the relative rates of two competitive reactions. The position, however, was convincingly defended by Kharasch, Reinmuth, and Mayo (59); they postu-

lated that in ether and similar solvents the mercury alkyl molecules are weakly ionized as follows

$$RHg^+ + R'^- \rightleftharpoons RHgR' \rightleftharpoons R^- + HgR'^+ \tag{23}$$
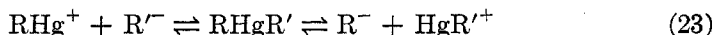
and that when R is considerably more electronegative than R', the concentrations of RHg^+ and R'^- are negligible, accounting for the practically quantitative yield of a single set of reaction products which is obtained upon the addition of hydrochloric acid; when R and R' differ only slightly in electronegativity, there will be a double ionization equilibrium, as shown above, which will, however, lie definitely to the right if R is the more electronegative, leading to the preponderance of RH upon the addition of hydrochloric acid. There seems now little doubt that this thesis is a correct one; the species RHg^+ are known to exist in solution and CH_3HgOH, for example, is a strong base.

The method, which was first used by Kharasch and Marker (57), is limited in its use to saturated or aromatic radicals, but even so a qualitative scale encompassing nearly fifty radicals has been established (6, 55, 56, 57, 58, 60, 88, 127, 128). The scale is shown in table 7, with the most electronegative radical at the top; radicals shown on the right-hand side are those whose positions are known only with respect to certain other radicals and cannot yet be placed in the main sequence.

One might ask to what extent the methods used for atoms can be applied to the quantitative estimation of electronegativities of radicals and whether the results obtained support the sequence shown in table 7? In view of earlier re-

TABLE 7

Relative electronegativities of radicals

1. Cyanide	*a.* Mesityl	$1 > x > 6$
2. α-Thienyl	*b.* $\begin{cases} p\text{-Hydroxyphenyl} \\ p\text{-Aminophenyl} \end{cases}$	$x > 4$
3. *p*-Anisyl		
4. *o*-Anisyl	*c.* β-Naphthyl	$5 > x$
5. α-Naphthyl	*d.* *p*-Diphenyl	$x > 8$
6. *o*-Tolyl	*e.* *p*-Fluorophenyl	$x > 8$
7. *p*-Tolyl	*f.* $(CH_3)_3SiCH_2^-$	$8 > x > 13$
8. Phenyl	*g.* *o*-Bromophenyl	$9 > x$
9. $\begin{cases} m\text{-Fluorophenyl} \\ p\text{-Chlorophenyl} \\ p\text{-Bromophenyl} \end{cases}$	*h.* *m*-Bromophenyl	$g > x$
	i. *p*-CF$_3$-Phenyl	$11 > x$
10. *o*-Chlorophenyl	*j.* *o, m'*-Dichlorophenyl	$11 > x > 18$
11. *m*-Chlorophenyl	*k.* $\begin{cases} \text{Isopropyl} \\ 2\text{-Methylbutyl-}(4) \end{cases}$	$15 > x > 18$
12. *o, o'*-Dichlorophenyl		
13. Methyl	*l.* *sec*-Butyl	$16 > x$
14. Ethyl	*m.* 2,2'-Dimethylbutyl-(3)	$l > x$
15. *n*-Propyl	*n.* $\begin{cases} \text{Cyclohexyl} \\ n\text{-Hexadecyl} \end{cases}$	$18 > x$
16. $\begin{cases} n\text{-Butyl} \\ n\text{-Hexyl} \\ 2,2'\text{-Dimethylbutyl-}(4) \\ 2,2'\text{-Dimethylpentyl-}(5) \end{cases}$		
	o. $\begin{cases} o\text{-Chlorobenzyl} \\ m\text{-Chlorobenzyl} \\ p\text{-Chlorobenzyl} \end{cases}$	$18 > x$
17. *n*-Heptyl		
18. Benzyl	*p.* ω-Phenylethyl	$18 > x$
19. $\begin{cases} tert\text{-Butyl} \\ \text{Neopentyl} \end{cases}$	*q.* Vinyl*	$x > 7$
	r. β-Methylvinyl*	$x > q$
20. Diphenylmethyl	*s.* β-Phenylvinyl*	$x > r$
21. Triphenylmethyl	*t.* Phenylethynyl*	$x > s$
	u. Isopropyl*	$16 > x > 18$
	v. Allyl*	$x = 18$

marks, it is surprising that the use of dipole moments, as suggested by H. C. Brown (9), seems to offer the most encouraging prospect. Expressing the C—Cl bond moment in RCl as the vector sum ($\mu_{RCl} - \mu_{RH}$), he showed that there was a strong correlation between the bond moments and the electronegativities of the radicals derived from equation 21; in fact, he found no discrepancies. The electronegativities (by Brown's method) of a number of radicals which cannot be studied by Kharasch's method have been included in table 7 (they are marked with asterisks).

Absolute electronegativity values, one might hope, could be derived from the application of Pauling's method, but here the prospects are not encouraging. Sufficient thermochemical data are available to make a detailed study of Δ values (which are assembled in table 8) for a number of organic halides. In all cases the behavior of the Δ values for the halides follows quite closely the trend for the hydrogen halides except that a correction term, characteristic of the particular radical R, has to be applied; this correction term presumably has its origins in the differing amounts of conjugation or hyperconjugation, or of non-bonded interactions, in the corresponding R_2 and RX molecules. The variations in Δ in the halides are regular. However, the hydrides present a completely different picture, for the Δ values for RH molecules bear no relation whatsoever to those observed in halide molecules. The hydrides are invariably more stable than can be accounted for in electronegativity terms, possibly owing to hyperconjugation effects. There seems to be a correlation in that the Δ values for the halides (e.g., X = Cl) *decreases* as one passes from the more electropositive radicals to those more electronegative, but the authors are disinclined to attach a lot of significance to this.

A favorable case to which to apply Pauling's method is provided by the mercury alkyls and the alkyl mercuric halides. Here the two R groups are separated by a considerable distance, and non-bonded interactions are probably small; whether or not there is any significant conjugation through the vacant $6p$ orbitals of mercury is not known. Experimentally it is found that $D(R—HgX)$, where X is a halogen, is greater than $D(R—HgR)$ by an amount which correlates well with the electronegativities of both R and X (47, 81, 97), so that the greater the difference between the electronegativities of R and X, the greater is the difference $D(R—HgX) - D(R—HgR)$. By analogy with $A_2 + B_2 \rightarrow 2AB$, we

TABLE 8

Δ *values for RX compounds (in kcal./mole)*

R	X = F	Cl	Br	I	H	R	X = F	Cl	Br	I	H
H................	64.2	22.1	12.3	1.2	0	CH₃CH₂CH₂....	—	11.1	2.4	−6.8	4.8
CH₃CO..........	65.4	20.2	11.4	0.3	0.9	CH₂=CHCH₂..	—	9.8	2.0	−4.2	5.5
C₆H₅CO.........	—	18.0	7.5	−2.2	(0.3)	CH₃..........	—	9.5	2.2	−7.0	7.8
(CH₃)₃C.........	—	16.0	7.6	−3.3	4.4	C₆H₅..........	48	8.8	(1.8)	(−7.4)	1.5
(CH₃)₂CH.......	—	14.9	6.3	−3.4	3.0	CN............	—	5.2	−2.8	−8.2	5.6
C₂H₅............	—	11.6	3.9	−5.0	5.2						

Δ measures the heat evolved in the gaseous redistribution reactions:
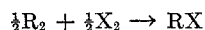
$$\tfrac{1}{2}R_2 + \tfrac{1}{2}X_2 \rightarrow RX$$

TABLE 9

Electronegativity values calculated from the heats of the reactions

$$HgR_2 + HgX_2 \rightarrow 2RHgX + 2\Delta$$

Mercury Alkyl	Reactant			Mean x_R Value
	$HgCl_2$	$HgBr_2$	HgI_2	
Hg(α-thienyl)$_2$	2.73	2.74	—	2.73
Hg(C$_6$H$_5$)$_2$	2.33	2.36	2.46	2.38
Hg(CH$_3$)$_2$	2.12	2.13	2.13	2.13
Hg(C$_2$H$_5$)$_2$	2.03	2.07	2.20	2.10
Hg(n-C$_3$H$_7$)$_2$	2.07	2.09	2.20	2.12
Hg(iso-C$_3$H$_7$)$_2$	2.00	1.90	2.01	1.97

may write for the gas-phase redistribution reaction

$$HgR_2 + HgX_2 \rightarrow 2RHgX + 2\Delta \tag{24}$$
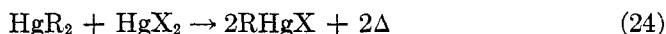
whence

$$\Delta = 23.06(x_X - x_R)(x_{XHg} - x_{RHg}) \tag{25}$$

Plotting the observed Δ values against x_X gives a series of parallel straight lines of slope 0.325×23.06; this means that the quantity $(x_{XHg} - x_{RHg})$ may be effectively taken as a constant, 0.325, whence it is a simple matter to calculate values for x_R as in table 9, using the thermochemical data listed in reference 97 and the values $x_{Cl} = 3.00$, $x_{Br} = 2.76$, and $x_I = 2.56$ in table 3. In view of the uncertainties which are still present in the thermal data (some heats of vaporization are not sufficiently well known), the consistency of the x_R values is satisfactory. Whether or not they can be regarded as true electronegativity values on an equal footing with those for atoms given earlier is another matter. The electronegativity value for an isolated carbon atom hybridized sp^3 is 2.63, and it may seem, by comparison, that the values in table 9 are all too low. But the *trend* in them follows the order given by Kharasch, and the comparatively high values in the case of the two aromatic radicals are consistent with the fact that here sp^2 orbitals are used in bonding.

It is hardly practicable to apply Mulliken's measure to radicals, as so little is known of their electron affinities. Oldham (89) and Hush (54), from studies of the reduction of alkyl mercuric halides at a dropping-mercury electrode, have arrived at the following *provisional* electron affinities: isopropyl $= 0.5$ e.v., ethyl $= 0.9$ e.v., methyl $= 1.1$ e.v., benzyl $= 1.8$ e.v., and allyl $= 2.1$ e.v. The ionization potentials of these radicals have been determined by electron-impact studies by Stevenson (118), who gives the values methyl $= 10.1$ e.v., ethyl $= 8.7$ e.v., isopropyl $= 7.5$ e.v., and by Lossing (71), who gives the values benzyl $= 7.73$ e.v. and allyl $= 8.16$ e.v. The mean $(I + E)$ values thus suggest[10]

[10] The values $(I + E)/6.3$ (*cf.* page 757) are methyl $= 1.78$, allyl $= 1.63$, ethyl $= 1.52$, benzyl $= 1.51$, isopropyl $= 1.27$. The value for methyl is almost the same as the p-electroaffinity for C, s^2p^2, V_2, and might indicate that the methyl radical is planar, in which case the electron capture and ionization processes would be those of a $2p$-electron. These electronegativities of *free* radicals, however, are not strictly to be compared with those of *bound* radicals in molecules. Moreover, it is to be questioned if the observed ionization potential in, for example, isopropyl, in which the electron is removed from a delocalized molecular orbital, is the quantity which is required in the equation $(I + E)/6.3 = \chi_P$.

increasing electronegativity along the sequence isopropyl $\rightarrow$ ethyl $\sim$ benzyl $\rightarrow$ allyl $\rightarrow$ methyl.

Finally, there has recently emerged the possibility that quantitative data for radicals may be obtainable by suitable interpretation of the nuclear magnetic resonance spectra exhibited by organic molecules. Shielding parameters for the fluorine atom (δ_F) have been measured for a large number of substituted fluorobenzenes (43). In the case of the para-substituted fluorides, the variation in the magnitude of δ_F correlates with the order of electronegativity given in table 7; unfortunately, no such agreement is apparent in the ortho and meta compounds, suggesting that other considerations besides electronegativity affect the magnitude of the shielding parameter. The δ_F values for the series CH_3F, CH_2F_2, CHF_3, and CF_4 and the δ_H values for the series CH_4, CH_3F, CH_2F_2, and CHF_3 (73) are consistent with the increasing electronegativity of the methyl radical with successive fluorine substitution; that the CF_3 radical is highly electronegative is borne out by the fact that, apart from fluorine itself, CF_3 is the only other entity sufficiently electronegative (except, perhaps, oxygen) to raise sulfur to its hexavalent state, as in $(CF_3)_2SF_4$ (29).

IV. THE ELECTRONEGATIVITY SCALE: APPLICATIONS

Many of the more common uses to which the scale of electronegativity has been put reflect the methods of measuring electronegativity. Thus, for example, the (unknown) heat of formation of a compound MX_n, or the dipole moment of MX, might be predicted, given that the electronegativities of M and X are reasonably well established (Pauling predicted $\mu = 1.8$ D for the dipole moment of hydrogen fluoride some years before it was measured at 1.9 D). Such obvious functions will not be dealt with here; instead, some of the more indirect usages of the scale will be considered.

A. Percentage ionic character

"It is convenient," Pauling has written, "in discussing types of bonds to be able to make quantitative statements—to say that certain bonds are essentially covalent, with only five or ten per cent of ionic character, others are about equally ionic and covalent, and still others are essentially ionic." Unfortunately, however, the estimation of the percentage ionic character of a bond would now seem to be not a simple matter.

The method that Pauling (91) has used was, nevertheless, a simple one. He assumed, first, that the ionic character in the hydrogen halides may be obtained from their dipole moments; thus, the observed moment in hydrogen chloride of 1.03 D is some 17 per cent of the moment produced by two point charges at a distance apart equal to the internuclear separation in the hydrogen chloride molecule. Similarly, from the moments and distances in hydrogen bromide and hydrogen iodide, the figures are 11 per cent and 5 per cent, respectively, and to these Pauling added an estimate of 60 per cent in hydrogen fluoride. He then proceeded to plot these percentages against the electronegativity differences,

$(x_A - x_B)$, appropriate to each case and derived the equation

$$\text{Per cent ionic character} = 100 \left[1 - e^{-\frac{1}{4}(x_A - x_B)^2}\right] \qquad (26)$$

Later, Hannay and Smyth (46), after their measurement of the dipole moment in hydrogen fluoride, "corrected" Pauling's estimate of 60 per cent ionic character in this molecule to 43 per cent, and amended Pauling's equation 26 to the form:

$$\text{Per cent ionic character} = 16(x_A - x_B) + 3.5(x_A - x_B)^2 \qquad (27)$$

Criticism begins with the initial assumption that the dipole moments can be used as a quantitative guide to ionic character. Recent calculations by Robinson (99) on the nature of the bonding in hydrogen chloride and, in particular, on the significance to be attached to the observed dipole moment, led him to conclude that the moment is a most unsatisfactory guide to ionic character in this case—and indeed is probably a poor guide in the hydrogen halides generally. If one accepts Robinson's conclusions in *toto*, then the whole of Pauling's quantitative measure of ionic character must be discarded, since Robinson attacks the framework of calibration from which Pauling begins. Even if one regards Robinson's calculations as too crude to allow of definite conclusions,[11] it is difficult to overlook the growing body of work which suggests that dipole moment and ionic character do not necessarily stand in direct relationship to one another.

However, it is undoubtedly the case that where $(x_A - x_B)$ is large—as in the alkali halides—the bonding is correctly classified as "essentially ionic," and similarly when $(x_A - x_B)$ is small, the proper classification is "largely covalent", so that it would be incorrect to dismiss equations 26 and 27 as valueless; they are probably serviceable in providing a very *rough* guide to the degree of ionic character. But the existence of these equations has tempted chemists to make use of them in far too literal a manner. Pauling cannot escape censure in this respect; one sentence of his (and there are others no less sweeping) reads: "Beryllium bonds have the following amounts of ionic character: Be—F 79%, Be—O 63%, Be—Cl 44%, Be—Br 35%, Be–I 22%."

Some of the work by French chemists on the subject of electronegativity is marred by an overconfidence in the authenticity of equation 26 or of others similarly derived. Examples which might be cited are a paper by Bellugue and Daudel (5), the starting-point of which is contained in the statement, "Les pourcentages ioniques de IH, BrH, ClH, et FH étant connus *exactement . . .*" (the italics are the authors'), or the use by the Daudels (23) and by Bellugue and Daudel of "diagrammes moleculaires," in which the authors give diagrams purporting to show the detailed charge distributions of various molecules.

A method of estimating charge distribution in molecules has recently been put forward by Sanderson (103), based on a "principle of electronegativity equalization" according to which all the atoms in a molecule tend to adjust towards equal resultant electronegativity by a process of partial charge transfer from atom to atom. Various applications of general chemical interest have been

[11] Schatz (105) has given reasons for doubting the validity of Robinson's conclusions; see also Gordy (39).

described; for example, Sanderson concludes that the resultant positive charge on the boron atom in the series BF_3, $B(CH_3)F_2$, $B(CH_3)_2F$, $B(CH_3)_3$ decreases from 0.67 unit in BF_3 to 0.24 unit in $B(CH_3)_3$, and hence ascribes the diminishing acceptor properties along the series to the diminishing charge on the acceptor atom.

Mention has been made earlier (pages 762–763) of the relations between ionic character and electronegativity difference obtained by Dailey (22) and by Gordy (40) from considerations of nuclear quadrupole coupling data. Both recognize the part played by hybridization as well as by ionicity, so that, in this sense, they do attempt to define the relationship in a more significant way than hitherto. However, it cannot yet be said that these newer relationships are entirely satisfactory.

B. Bond lengths of polar bonds

It has been pointed out by Schomaker and Stevenson (107) that the equilibrium lengths of polar bonds A—B are short by comparison with the sums of the covalent radii, $(r_A + r_B)$. They have proposed a "rule",

$$R = r_A + r_B - \beta \mid x_A - x_B \mid \qquad (28)$$

whereby the length R is predicted to be shortened by an amount proportional to the electronegativity difference between the bonded atoms, β being a constant (empirically, $\beta = 0.09$). In using this rule, one must employ revised radii (107) for hydrogen, fluorine, oxygen, and nitrogen, rather than the radii given by Pauling and Huggins (92) for these atoms.

Although the Schomaker–Stevenson rule gives good agreement with experiment in many instances, there are several examples in which it is not satisfactory (see, e.g., Wells (126), Burawoy (10), and Skinner and Sutton (115)). Gordy (40) has suggested that the rule is improved by assigning the value $\beta = 0.06$ rather than the original $\beta = 0.09$, but the improvement is slight and the performance of the amended version remains erratic. In the amended form, the rule has been applied to double bonds, A=B (37).

Warhurst (124) remarked that the contractions observed in some polar bonds might be ascribed to other causes than ionic-covalent resonance; e.g., contractions due to "back-coördination" in compounds of boron and silicon. But he considers that ionic-covalent resonance *per se* does lead to bond contraction, and quotes the experimental data for twenty-three single bonds in which multiple bond participation can be ruled out, but which are nonetheless short, and moreover in which the magnitude of the bond contraction increases with increase in the ionic resonance energy of the bond. Warhurst (124) and Scanlan and Warhurst (104) have applied a simplified ionic-covalent resonance theory (in which the orthogonality integral was neglected) to the calculation of bond lengths in the hydrogen halides and in some polyatomic molecules of the type MX_n, with results in fair agreement with experiment. One can say, therefore, that both experiment and theory give support to the idea (implicit in the Schomaker–Stevenson rule) that polar bonds are likely to be short.

On the other hand, there are factors other than ionic character which would seem to influence bond lengths; in so far as equation 28 neglects these, it is at fault and oversimplifies the problem. Coulson (16) has drawn attention to the probable variation in the covalent radius of an atom with changes in its hybridization characteristics. Thus, the radius of carbon, e.g., in the digonal condition, is significantly less than that of carbon in its tetrahedral condition. Duchesne (26) considers that the bond lengths in the hydrogen halides (*cf.* Warhurst) may be influenced by hybridization in the halogen-bonding orbitals. Baughan (3), commenting on the failure of the Schomaker–Stevenson rule to predict the bond lengths in CCl_4, CBr_4, and CI_4 (these are all *ca.* 0.06 Å. longer than the rule would require), shows that these "abnormal" bonds can be understood in terms of "non-bonding" repulsions. Recently, Huggins (51) has proposed a relationship between the energy and the length of a bond,

$$R = r_A + r_B - \frac{1}{2} \log \left[\frac{D_{AB}}{\frac{1}{2}(D_{AA} + D_{BB})} \right] \qquad (29)$$

where D_{AB} is the bond energy in AB, and D_{AA}, D_{BB} are the bond energies in AA and BB, respectively. Making use of equations 2 and 3, equation 29 may be recast in the form

$$R = r_A + r_B - \frac{1}{2} \log \left[1 + \frac{23.06(x_A - x_B)^2}{\frac{1}{2}(D_{AA} + D_{BB})} \right] \qquad (30)$$

C. Dissociation energies in polar molecules

Baughan, Evans, and Polanyi (4) have drawn attention to the fact that whereas the bond dissociation energies $D(\text{R—H})$ fall sharply along the series R = methyl, ethyl, isopropyl, *tert*-butyl, the dissociation energies $D(\text{R—X})$, where X = Cl, I, and OH, fall far less sharply, if indeed they fall at all. They have interpreted the fall in $D(\text{R—H})$ in terms of increasing resonance energies in the radicals R, their suggestion, in effect, being that the hyperconjugation energies in the radicals R increase steadily from zero in methyl to several kilocalories per mole in tertiary butyl (see, for a more detailed treatment, Roberts and Skinner (98)). The much reduced fall-off in the RX dissociation energies they ascribe to a compensating additional stabilization in the polar RX molecules (relative to the almost non-polar RH molecules), arising from ionic-covalent resonance in the bonds R—X. Warhurst (125) pointed out that the experimental evidence suggests that the fall-off in $D(\text{R—X})$ is sharper in iodides than in chlorides and amines, and has practically disappeared in the R—OH bonds of alcohols. He concludes that the fall-off diminishes, the more electronegative the atom or group X.

D. Electronegativities and molecular orbital theory

The standard molecular orbital theory (see, e.g., Coulson (20)), is based on the L.C.A.O. approximation, in which the molecular orbitals are built up from atomic orbitals, ϕ_r, ϕ_s, etc., of atoms r, s, etc. The theory introduces two important

quantities, namely α_r, or the Coulomb term

$$\alpha_r = \int \bar{\phi}_r \, \mathfrak{H} \, \phi_r \, d\tau$$

and β_{rs}, or the resonance integral

$$\beta_{rs} = \int \bar{\phi}_r \, \mathfrak{H} \, \phi_s \, d\tau$$

The Coulomb term α_r measures the energy of an electron when confined to the atom r within the molecule. As Coulson and Longuet-Higgins (21) point out, one might expect α_r to be related to the ionization potential of atom r, although it is not necessarily to be identified with it, since the Hamiltonian $\mathfrak{H}$ involves the field from other atoms in the molecule as well as from atom r. But it can be said that the more electronegative the atom r, the larger numerically is α_r likely to be. A detailed examination of the nature of α_r has been given recently by Mulliken (84, 85), and a technique is described whereby α_r may be calculated in given circumstances, but it is not a simple matter to evaluate each of the terms contributing to it. A generally more useful conclusion from Mulliken's analysis is that (in a bond XY) the *difference* $(\alpha_X - \alpha_Y)$ should be proportional to the *difference* in electronegativity of the atoms X and Y (provided that these electronegativities relate to the proper valence states of the bonded atoms). Laforgue (62) and Chalvet and Daudel (11) go a stage further and make the attractive proposal that $(\alpha_X - \alpha_Y)$ can be equated directly with the difference $(x_X - x_Y)_P$, but this represents, one feels, an oversimplification of the problem. Further theoretical developments may clarify the situation which, at present, can hardly be described as in a satisfactory state; meanwhile several authors are making use of relative electronegativity as a basis of approximation to α_r values.

V. CONCLUSIONS

Although twenty years have elapsed since the electronegativity concept was given quantitative expression (mainly through Pauling and Mulliken), it is interesting to remark that the "best" electronegativity scale of today differs but little from those originally put forward. This fact alone might be thought to inspire confidence in the concept as a whole and in the scale of electronegativity in particular. Nevertheless, Moffitt (78) has seen fit to remark upon the "very delicate position in which electronegativity theory now finds itself," whilst Coulson (17) considers that "the concept of electronegativity is beginning to break down."

Now there is no doubt that the theory of ionic-covalent resonance, with which the electronegativity concept has been very closely tied, has, in recent years, been subjected to severe and damaging blows, and, although it would be untrue to say that the theory is discredited, it has diminished in importance, and now suffers, largely owing to overemphasis in the past (19). The effect of this on the electronegativity concept is harmful, not only in theory but also in the very practical sense that some of the uses to which the electronegativity scale has

been put—in particular, the quantitative estimation of the polar characteristics of bonds—must now be regarded as suspect.

The difficulties facing electronegativity theory are not only those which arise from the recognition of an alternative (i.e., to ionic-covalent resonance) way, through the hybridization concept, in which to account for the asymmetric charge distribution in a chemical bond. Indeed, they begin with the initial supposition that electronegativity is an atomic property, which retains its significance within a molecule, despite the profound influence of atoms upon one another under conditions of such close proximity. It is true that this difficulty is lessened if, following Mulliken, we relate electronegativity to the valence state of atoms and speak then of the electronegativity of atomic orbitals. Within the framework of the L.C.A.O. approximation, these atomic-orbital electronegativities may still have relevance in molecules, but their determination requires that the valence states of atoms in molecules be specified completely, and whilst it is possible that this can be done in the case of first-row elements using s, p valence orbitals only, it is a vastly more difficult problem to deal with in the heavier elements.

Let us suppose, however, with Moffitt (78), that it is sufficient, given the specification of the valence state of an atom, to proceed therefrom to a derivation of its electronegativity. We might, for example, calculate the range of electronegativity available to the trivalent nitrogen atom, from the extreme case of pure p-bonding, through various isovalent hybrid orbitals of the general form (as + bp), to trigonal bonding. If now we can, either by calculation or by empirical observation, arrive at a good specification of the valence state of the nitrogen atom *as it exists* in the NH_3 molecule (or in the NF_3 molecule, or in the $N(CH_3)_3$ molecule), then we can evaluate the electronegativity of the nitrogen atom *as it actually is* in the NH_3 molecule (or in the NF_3 molecule, or in the $N(CH_3)_3$ molecule). The crucial point, as Evans (31) has remarked, is that there is the possibility that every molecule must needs be treated as a special case. (Is the valence state of nitrogen the *same* in NH_3, in NF_3, and in $N(CH_3)_3$?)

The electronegativity concept has been useful in the past largely because it denied the need for special treatment of every individual case; thus, the electronegativity of nitrogen was considered well enough defined by a single number. This is now questioned; the geometric arrangement of the valence bonds formed by nitrogen in the molecules pyridine, pyrrole, ammonia, and nitrogen trifluoride is different in each case, and this fact alone is sufficient to raise misgivings that a single electronegativity measure for nitrogen is enough. It seems clear that the further development of the electronegativity theory will attempt to define the *range* of electronegativity open to an atom. There remains the problem of choosing from the range the unique value which the atom achieves in a given molecular environment. Unless some comparatively simple criterion of choice can be found, such as, for example, is provided in case of the carbon atom by the differing spatial arrangements of the bonds formed by the atom in different states of hybridization, the discomforting possibility that Evans has foreseen may become a very real one.

The attempts to refine electronegativity theory are not yet sufficiently complete to enable a verdict to be reached on their efficacy, but one might reasonably expect that a clearer understanding of the electronegativity property will be gained with their further development. Meanwhile, it seems safe to say that the chemist will continue to make use of the "crude" electronegativity theory for some time yet—a practice for which he can hardly be blamed in the absence of an alternative theory of equal generality and in view of (to quote from Coulson again (17)) "the astonishing success which the theory has had in correlating a vast field of chemical knowledge and experience."

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[12] At the Faraday Society Discussion on "Microwave and Radiofrequency Spectroscopy" held at Cambridge on April 4–6, 1955, several papers concerning electronegativity and the electron distribution in chemical bonds were presented; this Discussion took place too late for the authors of this review to make reference to these interesting and important papers.

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VII. APPENDICES

A. Electron affinities of atoms

This subject has been reviewed recently by Pritchard (97), who gives a list of "best" experimental values. Few electron affinities have been measured directly, however, and for most elements the only available information is obtained by some form of extrapolation through ionization potentials. The extrapolation method of Glockler (34) is, perhaps, the best known and easiest to apply in practice. Skinner and Pritchard (113) have remarked that Glockler's method would seem to give values that are too low, and the list of electron affinities which they have proposed for the elements of the first and second rows of the Periodic Table include several that were obtained by a slight upgrading of the Glockler extrapolation values.

The values given in table 10 are taken in part from references 97 and 113 or are obtained by extrapolations similar in type to those described in reference 113. In a few cases where the extrapolations are not easily made (because of uncertainty, or of gaps, in ionization potential data), the values are enclosed in square brackets.

An extensive list of electron affinities values of atoms has been given by Lisitzin (67); these were obtained by an extrapolation method similar to that of Glockler. The values in table 10 for the most part agree with those of Lisitzin within ±0.5 e.v.

TABLE 10

Electron affinities of atoms (in electron volts)

Atom	Electron Affinity	Atom	Electron Affinity	Atom	Electron Affinity	Atom	Electron Affinity	Atom	Electron Affinity
H........	0.747[a]								
Li........	0.54[a]	Na......	0.74[b]	Cu......	0.9[d]	Ag......	1.0[d]	Au......	[2.0]
Be.......	−0.6[b]	Mg......	−0.3[b]	Zn......	−1.2[d]	Cd......	[−1.1]	Hg......	0.8[e]
B........	0.2[b]	Al.......	0.6[b]	Ga......	−0.1[d]	In.......	[0.0]		
C........	1.7[b, a]	Si.......	1.8[c]	Ge......	1.2[d]	Sn......	[1.2]		
N........	0.0[b]	P........	0.8[b]	As......	1.0[d]	Sb......	[1.3]		
O........	2.2[a]	S........	2.4[b]	Se.......	2.0[d, a]	Te......	2.1[d, a]		
F........	3.63[a]	Cl......	3.78[a]	Br......	3.54[a]	I........	3.24[a]		

[a] Pritchard (97).

[b] Skinner and Pritchard (113).

[c] Skinner and Pritchard (113) gave 2.2 e.v. for silicon. The revision here follows the amendment in the ionization potential of phosphorus from 11.0 e.v. to 10.55 e.v. (reference 80, Vol. II). This change brings with it a marked drop in the extrapolated electron affinity of silicon.

[d] Extrapolated from ionization potentials in isoelectronic ions; cf. Skinner and Pritchard (113).

[e] Simons and Seward (110) measured the "apparent electron affinity" of mercury as 1.5 e.v., but this value is not consistent with the small (almost zero) value that is suggested by the Glockler extrapolation method. The value chosen by the authors lies between the two.

TABLE 11

*Energies of valence states**

Valence State	Energy Above Ground State (in electron volts)									
sp, V_2	Li⁻	(1.0)	Na⁻	(1.05)	Cu⁻	(2.25)	Ag⁻	(2.35)	Au⁻	(3.4)
	Be	3.36	Mg	3.12	Zn	4.49	Cd	4.26	Hg	5.56
	B⁺	5.75	Al⁺	5.34	Ga⁺	6.68	In⁺	6.10	Tl⁺	7.67
	C²⁺	8.04	Si²⁺	7.48	Ge²⁺	8.73	Sn²⁺	7.80	—	
sxy, V_3	Be⁻	(2.6)	Mg⁻	(2.3)	Zn⁻	(3.3)	Cd⁻	(3.7)	Hg⁻	(4.6)
	B	5.52	Al	4.65ᵃ	Ga	5.75ᵃ	In	(5.5)	Tl	7.31
	C⁺	8.42	Si⁺	7.06	Ge⁺	8.13	Sn⁺	7.35	Pb⁺	10.0
	N²⁺	11.20	P²⁺	9.26	As²⁺	10.3	Sb²⁺	9.16	—	
sx^2, V_1	Be⁻	(3.0)	Mg⁻	(2.4)	Zn⁻	(3.6)	Cd⁻	(4.3)	Hg⁻	(5.2)
	B	6.58	Al	5.03ᵃ	Ga	6.15ᵃ	In	(6.3)	Tl	8.35ᵇ
	C⁺	10.18	Si⁺	7.74	Ge⁺	8.93	Sn⁺	8.27	Pb⁺	11.47
	N²⁺	13.76	P²⁺	10.33	As²⁺	11.52	Sb²⁺	10.25	—	
	O³⁺	17.28	S³⁺	12.88	Se³⁺	13.96	Te³⁺	12.29	—	
s^2xy, V_2	B⁻	(0.14)	Al⁻	(0.11)	Ga⁻	(0.15)	In⁻	(0.20)	—	
	C	0.32	Si	0.21	Ge	0.31	Sn	0.50	Pb	1.46
	N⁺	0.48	P⁺	0.30	As⁺	0.48	Sb⁺	—	—	
	O²⁺	0.65	S²⁺	0.40	Se²⁺	0.66	Te²⁺	1.11	—	
s^2x^2, V_0	B⁻	(0.85)	Al⁻	(0.65)	Ga⁻	(0.75)	In⁻	(0.7)	—	
	C	1.74	Si	1.16	Ge	1.27	Sn	1.42	Pb	2.99
	N⁺	2.62	P⁺	1.63	As⁺	1.77	Sb⁺	—	—	
	O²⁺	3.46	S²⁺	2.06	Se²⁺	2.25ᵇ	Te²⁺	2.85ᵇ	—	
$sxyz$, V_4	B⁻	(4.7)	Al⁻	(3.8)ᵇ	Ga⁻	4.2ᶜ	—		—	
	C	8.26	Si	6.22ᵇ	Ge	6.8ᶜ	—		—	
	N⁺	11.95	P⁺	8.69ᵇ	As⁺	9.4ᶜ	—		—	
	O²⁺	15.39	S²⁺	10.94ᵇ	Se²⁺	11.4ᶜ	—		—	
	F³⁺	18.84	Cl³⁺	13.24ᵇ	—		—		—	
sx^2y, V_2	B⁻	(5.6)	Al⁻	(3.8)	Ga⁻	(4.2)	—		—	
	C	9.85	Si	(6.6)	Ge	7.16	—		—	
	N⁺	14.18	P⁺	9.40	As⁺	10.05ᵃ	—		—	
	O²⁺	18.36	S²⁺	12.23	Se²⁺	12.70ᵃ	—		—	
s^2xyz, V_3	C⁻	(0.70)	Si⁻	(0.49)	Ge⁻	(0.48)	—		—	
	N	1.19	P	0.70	As	0.67	Sb	0.57	Bi	0.86
	O⁺	1.66	S⁺	0.92	Se⁺	0.84	—		—	
	F²⁺	2.11	Cl²⁺	1.12	Br²⁺	0.98	—		—	
s^2x^2y, V_1	C⁻	(1.74)	Si⁻	(1.26)	Ge⁻	(1.25)	Sn⁻	(1.20)	—	
	N	2.98	P	1.87	As	1.81	Sb	1.68	Bi	2.67
	O⁺	4.17	S⁺	2.44	Se⁺	2.30	Te⁺	(2.15)	—	
	F²⁺	5.31	Cl²⁺	2.97	Br²⁺	2.72	—		—	
sx^2yz, V_3	C⁻	(9.38)	Si⁻	(5.0)	Ge⁻	(3.8)	—		—	
	N	14.23	P	8.01	As	7.62	—		—	
	O⁺	19.17	S⁺	(11.0)	Se⁺	(11.5)ᵇ	—		—	
	F²⁺	24.20	Cl²⁺	(14.0)	—		—		—	
			A²⁺	17.01	—					
sx^2y^2, V_1	O⁺	21.80	S⁺	(12.34)ᵇ	Se⁺	(13.4)ᵇ	—		—	
s^2x^2yz, V_2	N⁻	(0.34)	P⁻	(0.21)	As⁻	(0.30)	Sb⁻	(0.34)	—	
	O	0.50	S	0.30	Se	0.38	Te	0.52	—	
	F⁺	0.66	Cl⁺	0.39	Br⁺	0.49	I⁺	0.71	—	
	Ne²⁺	0.82	A²⁺	0.48	Kr²⁺	0.65	Xe²⁺	0.91	—	

TABLE 11—*Concluded*

Valence State	Energy Above Ground State (in electron volts)				
$s^2x^2y^2$, V_0	N⁻ (1.83) O 2.71 F⁺ 3.58 Ne²⁺ 4.44	P⁻ (1.21) S 1.68 Cl⁺ 2.12 A²⁺ 2.53	As⁻ — Se 1.72 Br⁺ 2.03[b] Kr²⁺ 2.58	Sb⁻ — Te 1.83 I⁺ 2.48 Xe²⁺ 2.96	— —
sx^2y^2z, V_2	N⁻ (12.65) O 17.65 F⁺ 22.76 Ne²⁺ 27.99	P⁻ (6.39) S 9.39 Cl⁺ 12.29 A²⁺ 15.09	As⁻ (6.6) Se (9.5) Br⁺ — Kr²⁺ 15.33	Sb⁻ (4.4) Te (7.3) I⁺ʿ — Xe²⁺ 13.12	— —
$s^2x^2y^2z$, V_1	F 0.02	Cl 0.04	Br 0.15	I 0.31	—
$sp^6, \tfrac{3}{3}V_1$	O⁻ (15.0) F (20.97) Ne⁺ 26.90 Na²⁺ 32.78 Mg³⁺ 38.61	S⁻ (8.0) Cl (10.76) A⁺ 13.48 K²⁺ 16.19 Ca³⁺ 18.89	Se⁻ (8.1) Br (10.83) Kr⁺ 13.51 Rb²⁺ 16.12 Sr³⁺ 18.66	Sb⁻ (5.9) I (8.6) Xe⁺ 11.26 — —	— — —
p^2, V_2	Li⁻ (2.3) Be 7.30 B⁺ 12.37 C²⁺ 17.30	Na⁻ (2.3) Mg 6.87 Al⁺ 11.41 Si²⁺ 15.85	Cu⁻ (5.75) Zn 9.99 Ga⁺ (14.25) Ge²⁺ 18.51 As³⁺ 23.35	Ag⁻ (6.0) Cd 9.41[b] In⁺ 12.87[a] Sn²⁺ 16.27 Sb³⁺ 19.69	— — Tl⁺ 16.15 — —
p^3, V_3	C⁺ 18.13	Si⁺ (16.0)	Ge⁺ (17.5)	—	—
p^4, V_2	N⁺ (27.2) O²⁺ 35.65 F³⁺ (44.1)				
p^5, V_1	O⁺ (39.34) F²⁺ 49.75 Ne³⁺ 60.11 Na⁴⁺ 70.42				

* A superscript a is placed against values calculated from Moffitt's formulas, in which the energy of *one* of the participating spectroscopic states was estimated from trends in the location of identical states in isoelectronic ions. Estimated values (in cm.⁻¹, relative to the ground states) include Al, sp^2, ^2D = 35000; Ga, sp^2, ^2D = 42400; As²⁺, sp^2, ^4P = 66000; As⁺, sp^3, ^1D = 88000; Se²⁺, sp^3, ^1P = 105000; In⁺, p^2, ^1D = 102280.

A superscript b indicates that the value was obtained by the procedure described in reference 113.

The $sxyz$, V_4 states of the third-row elements (marked with a superscript c) were estimated from the location of the sx^2y, V_2 states of these elements. The ^5S states of none of these elements have yet been identified. Calculation by use of the Slater-Condon equations, using the sparse and barely sufficient empirical data that are available, gave the values: Se⁺² = 11.05 e.v., As⁺ = 8.11 e.v., Ge = 7.72 e.v.

B. Energies of valence states

The calculated valence-state excitation energies are listed in table 11, which includes elements from the first and second rows as well as the B subgroup elements of the third and higher rows of the Periodic Table. The values were obtained in the majority of cases by application of the formulas of Moffitt (79). Because of the difference in the methods of calculation some of the values now given differ from those in reference 113, although generally such differences are small. For certain elements the desired spectroscopic data are far from complete, and Moffitt's methods could not be applied directly. The procedure used in these cases is described in the notes following table 11. The blank spaces in the table imply that for the element concerned the required spectroscopic information is lacking. Extrapolated values are enclosed in brackets.

C. Electronegativity and variable valency

Haïssinsky (44) has applied the thermochemical method (page 751) to evaluation of the electronegativities of a number of metals which exhibit more than one stable valence. He finds that the electronegativity of an element apparently increases with increase in its valency:

$$
\begin{cases}
V^{III} & 1.35 \\
V^{IV} & 1.65 \\
V^{V} & \sim 1.8
\end{cases}
\qquad
\begin{cases}
Cr^{II} & 1.5 \\
Cr^{III} & 1.6 \\
Cr^{VI} & \sim 2.1
\end{cases}
\qquad
\begin{cases}
Mn^{II} & 1.4 \\
Mn^{III} & 1.5 \\
Mn^{VII} & \sim 2.3
\end{cases}
$$

$$
\begin{cases}
Cu^{I} & 1.8 \\
Cu^{II} & 2.0
\end{cases}
\qquad
\begin{cases}
Fe^{II} & 1.65 \\
Fe^{III} & 1.8
\end{cases}
\qquad
\begin{cases}
Tl^{I} & 1.5 \\
Tl^{III} & 1.9
\end{cases}
$$

$$
\begin{cases}
Sn^{II} & 1.65 \\
Sn^{IV} & 1.8
\end{cases}
\qquad
\begin{cases}
Pb^{II} & 1.6 \\
Pb^{IV} & 1.8
\end{cases}
\qquad
\begin{cases}
Sb^{III} & 1.8 \\
Sb^{V} & 2.1
\end{cases}
$$

There is a certain amount of evidence that the average bond dissociation energy $\bar{D}(M\text{—}X)$ in a compound MX_n decreases with increase in n (M and X remaining constant). For example, $\bar{D}(Sn\text{—}Cl)$ in $SnCl_2 = 91.3$ kcal./mole, against 76.7 kcal./mole in $SnCl_4$; $\bar{D}(Sn\text{—}Br)$ in $SnBr_2 = 77.6$ kcal./mole, against 64.4 kcal./mole in $SnCl_4$; $D(Cl\text{—}F)$ in ClF $= 60.4$ kcal./mole, against 41.4 kcal./mole in ClF_3; $D(I\text{—}F) = 66.3$ kcal./mole in IF, against 62.2 kcal./mole in IF_5 and 53.9 kcal./mole in IF_7 (117). These trends in $\bar{D}(M\text{—}X)$ would support Haïssinsky's generalization, in that the calculated "extra-ionic energies," Δ, decrease with increasing n in MX_n, if one assumes that $\bar{E}(M\text{—}M)$ is invariant under changes in the valency of M. This latter assumption is, however, a very questionable one. Moreover, other explanations than that of variable electronegativity might be given for the variations (with n) in $\bar{D}(M\text{—}X)$ in molecules of the type MX_n. Skinner (112) has discussed this point in relation to the energies of excitation of an atom M from lower to higher valency states. Slutsky and Bauer (117) suggest that the increase in non-bonded repulsions with increasing n may account for the bond-energy variations in the interhalogen compounds. There is, therefore, reason to doubt the validity of Haïssinsky's application of the thermochemical method to the particular problem under discussion.

Nevertheless, the limited evidence from table 3 bears out Haïssinsky's view, and it has seemed worth while to examine the tetravalency of the Group VI elements, and the trivalency of the halogens, in relation to the Mulliken measure of electronegativity. A detailed treatment of these cases would require an examination of $s^m p^n d^q$ valence states and is not attempted; the examination of tetravalency is limited to the configurations $s^2 p^3 (n+1)s$, and of trivalency to the configurations $s^2 p^4 (n+1)s$ (where $n = 2$ for oxygen and fluorine, $n = 3$ for sulfur and chlorine, and $n = 4$ for selenium and bromine).

The relevant valence-state energies are listed below:

$s^2 p^2 s$, V_3		O^+	23.76	S^+	14.09	Se^+	12.51
$s^2 p^3 s$, V_4		O	10.93	S	7.55	Se	6.92
$s^2 p^3 s$, V_2		F^+	27.35	Cl^+	16.44	Br^+	14.35
		O^-	(2.44)	S^-	(2.9)	Se^-	(2.4)
		F	13.44	Cl	9.39	Br	8.49
$s^2 p^4 s$, V_3		Ne^+	28.18	A^+	17.26	Kr^+	14.74
		Na^{2+}	46.68	K^{2+}	26.48	Rb^{2+}	21.14
		Mg^{3+}	68.98	Ca^{3+}	36.95	Sr^{3+}	28.52
		F^-	(4.03)	Cl^-	(4.15)	Br^-	(4.2)
		Ne	16.68	A	11.63	Kr	10.12
$s^2 p^5 s$, V_2		Na	32.99	K^+	20.28	Rb^+	16.88
		Mg^{2+}	52.96	Ca^{2+}	30.25		
		Al^{3+}	76.71	Sc^{3+}	41.72		

From these values (and data in earlier tables) the excitation energies of the following ionization processes[13] are obtained,

	M = O	M = S	M = Se
M^- (p^3s^2, V_3) → M (p^3s, V_4)	(8.1)	(4.0)	(3.9)
M (p^3s, V_4) → M^+ (p^2, V_3)	4.34	3.73	3.67
M^- (p^4s, V_3) → M (p^3s, V_4)	10.69	7.05	6.52
M (p^3_4, V_4) → M^+ (p^2s, V_3)	26.44	16.90	15.34

	M = F	M = Cl	M = Br
M^- (p^4s^2, V_2) → M (p^4s, V_3)	(9.0)	(4.9)	(2.6)
M (p^4s, V_3) → M^+ (p^4, V_2)	4.64	4.01	3.84
M^- (p^5s, V_2) → M (p^4s, V_3)	13.04	9.02	(7.8)
M (p^4s, V_3) → M^+ (p^3s, V_2)	31.33	20.06	17.70

leading to the electroaffinities below:

O, p^3s, V_4	6.22 s	S, p^3s, V_4	3.87 s	Se, p^3s, V_4	3.78 s
O, p^3s, V_4	18.56 p	S, p^3s, V_4	11.98 p	Se, p^3s, V_4	10.93 p
	15.47[13]		9.95[13]		9.14[13]
F, p^4s, V_3	6.82 s	Cl, p^4s, V_3	4.45 s	Br, p^4s, V_3	3.22 s
F, p^4s, V_3	22.18 p	Cl, p^4s, V_3	14.54 p	Br, p^4s, V_3	12.75 p
	(17.06)[14]		(11.18)[14]		(9.57)[14]

The calculated electroaffinities in each case show a substantial increase over the normal values shown by these elements in their lower valence states; thus, for example, compared with the Pauling electroaffinities we have O^{IV}, χ_P = 4.91 and O^{II}, χ_P = 3.5; S^{IV}, χ_P = 3.16 and S^{II}, χ_P = 2.5; Se^{IV}, χ_P = 2.90 and Se^{II}, χ_P = 2.4; F^{III}, χ_P = (5.42) and F^I, χ_P = 4.0; Cl^{III}, χ_P = (3.55) and Cl^I χ_P = 3.0; Br^{III}, χ_P = (3.04) and Br^I, χ_P = 2.8. It is, of course, true that the electronegativities that we have calculated for these higher valence states are unrealistic, in that the configurations s^2p^3d and $s^2p^3(n+1)p$ and several of the configurations $sp^nd^q(n+q=5)$ contribute to the tetravalency of the Group VI elements as much as, if not more than, the particular configuration $s^2p^3(n+1)s$ examined here, and similarly with respect to the trivalent halogens. The detailed treatment of these higher valences is, however, scarcely practicable at the present time.

D. Gordy's scale (ii)

The relation between electronegativity and surface potential which Gordy makes empirically through equation 14 remains when the effective nuclear charge Z^*e is calculated from rules given by Slater. But now the empirical constants a and b in the formula

$$x = a + b \frac{Z^* e}{r}$$

are not constant for *all* elements but vary from row to row of the Periodic Table. Electronegativities calculated in this way, which are listed in table 12, are about as good as those calculated by Gordy from equation 14.

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[13] There are no empirical data from which the energies of M^- (p^3s^2, V_3) and M^- (p^4s^2, V_2) can be calculated. The authors have assumed that the steps $p^5 \rightarrow p^4s \rightarrow p^3s^2$ require approximately the same energy; similarly, equal energies are ascribed to the steps $p^6 \rightarrow p^5s \rightarrow p^4s^2$.

[14] The hybrid orbitals from p^4s, V_3 are assumed to be trigonal, p^2s.

TABLE 12

Electronegativities calculated from equation 14, using Slater's effective nuclear charges, Z^*

1st row elements: $x = 0.478 \dfrac{Z^*}{r} + 0.50$					2nd row elements: $x = 0.44 \dfrac{Z^*}{r} + 0.28$				
Atom	$r_{cov.}$	Z^*/r	x (calculated)	x_P	Atom	$r_{cov.}$	Z^*/r	x (calculated)	x_P
Li.............	1.336	0.973	0.965	1.0	Na.........	1.54	1.43	0.91	0.9
Be............	(1.00)	1.95	1.43	1.5	Mg.........	(1.38)	2.07	1.19	1.2
B.............	(0.83)	3.13	2.00	2.0	Al.........	1.26	2.78	1.50	1.5
C.............	0.772	4.21	2.51	2.5	Si.........	1.173	3.55	1.84	1.8
N.............	0.74	5.27	3.02	3.0	P..........	1.10	4.36	2.20	2.1
O.............	0.73	6.23	3.48	3.5	S..........	1.04	5.24	2.58	2.5
F.............	0.71	7.32	4.00	4.0	Cl.........	0.994	6.14	2.98	3.0

3rd row elements: $x = 0.42 \dfrac{Z^*}{r} - 0.07$					4th row elements: $x = 0.46 \dfrac{Z^*}{r} - 0.12$				
Atom	$r_{cov.}$	Z^*/r	x (calculated)	x_P	Atom	$r_{cov.}$	Z^*/r	x (calculated)	x_P
Cu.............	1.352	2.74	1.07	—	Ag.........	1.528	2.42	1.11	—
Zn.............	1.309	3.32	1.32	—	Cd..........	1.485	2.93	1.23	—
Ga.............	1.266	3.97	1.60	—	In.........	1.442	3.47	1.48	—
Ge.............	1.223	4.62	1.87	1.8	Sn.........	1.399	4.04	1.74	1.7
As.............	1.21	5.21	2.12	2.0	Sb.........	1.41	4.47	1.93	1.8
Se.............	1.17	5.94	2.42	2.4	Te.........	1.37	5.07	2.21	2.1
Br.............	1.142	6.655	2.73	2.8	I...........	1.333	5.70	2.50	2.5