

## ELECTRONEGATIVITY VALUES FROM THERMOCHEMICAL DATA

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**Abstract**—The electronegativities of sixty-nine elements have been calculated from the most recent thermochemical data. The mean deviation of the calculated electronegativity difference,  $0.208\sqrt{\Delta}$ , from the difference of the average electronegativities is 0.046 units. The trends of electronegativity values within the periodic system are summarized. The transition metal contraction, the lanthanide contraction, and crystal field stabilization are observed to contribute to the relative values of electronegativity.

PAULING's empirical electronegativity scale<sup>(1,2)</sup> based on bond energies has been used to correlate a vast number of chemical and physical properties and has been justified theoretically to some extent.<sup>(3,4,5)</sup> PAULING<sup>(2)</sup> in 1939 proposed electronegativity values for thirty-three elements, HAUSSINSKY<sup>(6)</sup> in 1946 extended the calculations to seventy-three elements (some by extrapolation), and HUGGINS<sup>(7)</sup> in 1953 re-evaluated the electronegativities of seventeen elements. The accumulation of considerable new enthalpy data for elements and compounds not previously included in calculations and the revision of some previously accepted bond energies, including  $E(\text{C—C})$  and  $E(\text{N—N})$ , led to the present recalculation and extension of the electronegativity scale based on thermochemical data. While this work was in progress a revision of PAULING's values appeared.<sup>(8)</sup> In the present recalculation, unlike that of reference 8, the effects of the transition metal contraction and lanthanide contraction are observed; an examination is made of the consistency of the results of Pauling's two methods for evaluating "extra ionic resonance energies"; and accuracy greater than  $\pm 0.1$  electronegativity unit is demonstrated.

### DATA AND CALCULATIONS

PAULING pointed out that the energy,  $E(\text{A—B})$ , of bonds between unlike atoms is usually greater than the average of the energies,  $E(\text{A—A})$  and  $E(\text{B—B})$ , of the homatomic bonds and that the "extra ionic resonance energy,"  $\Delta$ , of the heteratomic bond is related to the difference between the electron-attracting abilities of A and B.

$$\Delta = E(\text{A—B}) - \frac{E(\text{A—A}) + E(\text{B—B})}{2} \quad (1)$$

$$|\chi_{\text{A}} - \chi_{\text{B}}| = 0.208\sqrt{\Delta} \quad (2)$$

<sup>(1)</sup> L. PAULING, *J. Amer. Chem. Soc.* **54**, 3570 (1932).

<sup>(2)</sup> L. PAULING, *Nature of the Chemical Bond*, Chap. 2. Cornell Univ. Press, Ithaca (1939).

<sup>(3)</sup> R. S. MULLIKEN, *J. Chem. Phys.* **3**, 573 (1935).

<sup>(4)</sup> R. G. PEARSON, *J. Chem. Phys.* **17**, 969 (1949).

<sup>(5)</sup> E. WARHURST, *Proc. Roy. Soc. (London)*, **A 207**, 32 (1951).

<sup>(6)</sup> M. HAUSSINSKY, *J. Phys. Radium* **7**, 7 (1946).

<sup>(7)</sup> M. L. HUGGINS, *J. Amer. Chem. Soc.* **75**, 4123 (1953).

<sup>(8)</sup> L. PAULING, *Nature of the Chemical Bond* (3rd Ed.), Chap. 3. Cornell Univ. Press, Ithaca (1960).

Furthermore, it was pointed out that, for many metals,  $E(\text{M—M})$  is unknown and that  $\Delta$  can be calculated approximately from the heat of formation of  $\text{MX}_n$  by

$$\Delta = \frac{-\Delta H_f}{n} \quad (3)$$

The postulate of the arithmetic mean is employed below, since in many cases the postulate of the geometric mean is difficult to apply.<sup>(9)</sup>

In the application of the pair of equations, (1) and (2), sixteen homoatomic and thirty-eight heteratomic bond energies from the recent compilation by COTRELL<sup>(10)</sup> were employed. The average bond energies, not the bond dissociation energies, were used. Calculations involving equations (1) and (2) were made for the elements in Groups IVB to VIIB for which homoatomic, single bond energies are available. All bond energies, except  $E(\text{O—O})$  and  $E(\text{N—N})$ , were obtained from enthalpy data for elements and binary compounds having only one type of bond to avoid making the assumption that the energy of the bond between a particular pair of elements has the same value in different compounds. Thus a few estimates of bond energies, including  $E(\text{C—S})$ , were not used. The energies of the P—P, As—As, and Sb—Sb bonds are assumed to be one-sixth of the dissociation energy, corrected for strain,<sup>(11)</sup> of the respective  $\text{M}_4$  molecules.  $E(\text{C—C})$  and  $E(\text{Sn—Sn})$  are taken as one-half of the heats of atomization<sup>(12)</sup> of diamond and grey tin. The energy of the heteratomic bond,  $E(\text{I—Br})$  tabulated in reference<sup>(10)</sup>, gave an anomalous result and was not employed. The bond energies of Sb—Br, Sb—I, Cl—F, and I—Cl, not reported in reference<sup>(10)</sup> and of I—Br are taken from HUGGINS<sup>(7)</sup>.

The calculations involving the pair of equations, (2) and (3), were made with values of the enthalpy of formation of halides,  $\text{AX}_n$ , in their standard states at 298°A from the elements in their standard states. One hundred and fourteen values were taken from Circular 500 of the National Bureau of Standards.<sup>(12)</sup> Two values,  $\Delta H_{\text{form}}$  of  $\text{CF}_4$  and  $\Delta H_{\text{form}}$  of  $\text{AsCl}_3$ , were taken from COTRELL<sup>(10)</sup> instead of the older and probably inaccurate values in the NBS compilation. Also,  $\Delta H_{\text{form}}$  of  $\text{GeBr}_4$ ,<sup>(13)</sup>  $\Delta H_{\text{form}}$  of  $\text{GeI}_4$ ,<sup>(13)</sup>  $\Delta H_{\text{form}}$  of  $\text{PbCl}_4$ ,<sup>(14)</sup>  $\Delta H_{\text{form}}$  of  $\text{SbCl}_2$ ,<sup>(13)</sup> were not given in the NBS compilation and were taken from other sources.

For small electronegativity differences of the bonded atoms, the ionic character increases steadily with increasing electronegativity difference. However, if  $(\chi_A - \chi_B)$  is large, a further increase in the magnitude of  $(\chi_A - \chi_B)$  will not greatly change the ionic character or the "extra ionic resonance energy."<sup>(4,16,17)</sup> As also done by FINEMAN and DAIGNAULT,<sup>(17)</sup> calculations of  $\Delta$  leading to  $(\chi_A - \chi_B) > 1.8$  were rejected before the construction of the present thermochemical scale of electronegativity. For all potassium, rubidium and cesium halides, thermochemical data predict

<sup>(9)</sup> p. 83 of ref. 8.

<sup>(10)</sup> T. L. COTRELL, *The Strengths of Chemical Bonds* (2nd Ed.), Chap. 8, 10, and 11, Butterworths Scientific Publications, London (1958).

<sup>(11)</sup> (a) L. PAULING, *Nature of Chemical Bond* (3rd Ed.), Chap. 3, Cornell Univ. Press, Ithaca (1960); Ref. 8. (b) W. Moffitt, *Trans. Faraday Soc.* **44**, 987 (1948). (c) Ref. 7.

<sup>(12)</sup> F. D. ROSSINI *et al.* *Selected Values of Chemical Thermodynamic Properties* (Circular 500 of the National Bureau of Standards), U.S. Government Printing Office, Washington, D.C. (1952).

<sup>(13)</sup> D. E. EVANS and R. E. RICHARDS, *J. Chem. Soc.* 1292 (1952).

<sup>(14)</sup> F. YAKULHA, *J. Gen. Chem. U.S.S.R.* (English Translation) **24**, 1677 (1954).

<sup>(15)</sup> L. BREWER, L. A. BROMLEY, P. W. GILLES and N. L. LOFGREN, National Nuclear Energy Series, Div. IV, **19B**, 76 (1960).

<sup>(16)</sup> L. PAULING, *Nature of the Chemical Bond*, p. 61, Cornell Univ. Press, Ithaca (1939).

<sup>(17)</sup> M. A. FINEMANN and R. DAIGNAULT, *J. Inorg. Nucl. Chem.* **10**, 205 (1959).

that  $(\chi_X - \chi_M)$  is greater than 1.8 and values for these three metals were estimated from  $\Delta H_{\text{form}}$  of the iodides in which  $(\chi_X - \chi_M)$  ranges from 1.84 to 1.87. In some cases,  $\Delta$  appeared to be a minus quantity and  $(\chi_A - \chi_B)$  could not be estimated. For example,  $\Delta$  for hydrogen sulphide is  $-16.6$  kcal/mole. The value of 2.53 for the electronegativity of silver in silver fluoride may be anomalous and is not included in Table 2 or in the calculation of the average electronegativity of silver.

In Tables 1 and 2, the electronegativity values for the elements at the left were obtained by assuming the average electronegativity value of the chemically bonded element at the top. Equation (1) gives the values in parentheses, and equation (3) gives the other values. Electronegativity values (not presented here explicitly) for the halogens in compounds with the metals listed in Table 2 were calculated from  $\Delta$  and  $\chi_{M(\text{av.})}$  and used in the determination of the average electronegativities of the halogens. The value of 2.20 for hydrogen was given by HUGGINS<sup>(7)</sup> and was assigned here as the basis of the scale of relative electronegativities. The average electronegativity values are presented in Table 3. The oxidation numbers exhibited by elements in compounds included in these calculations are given in the first row of Table 3. Thus the electronegativity values in this table are for specified oxidation states. Electronegativity values of some elements in other oxidation states were calculated, assuming the average electronegativities of the halogens in Table 3, and are presented in Table 4.

#### DISCUSSION AND RESULTS

A total of 162 computations were made in the evaluation of electronegativities for sixty-nine elements. Electronegativity values for twenty-six elements were assigned on the basis of only one computation; and for the remaining forty-three elements and one hundred and thirty-six computations, the mean deviation of the calculated electronegativity difference,  $0.208\sqrt{\Delta}$ , from the difference of the average electronegativities  $(\chi_A - \chi_B)$  is 0.046 units. In a tabulation of calculated electronegativities published in 1953,<sup>(7)</sup> the mean deviation was 0.062 units for seventeen elements and fifty-four computations. In view of the concept of orbital electronegativity,<sup>(18)</sup> uncertainties in the enthalpy and bond energy data, and the complexity of factors contributing to heats of formation, a mean deviation of 0.046 units is remarkably small. Certainly, each element exhibits a range of electronegativities greater than 0.01.<sup>(18)</sup>

The validity of substituting the approximate equation (3), for equation (1) has been discussed elsewhere.<sup>(2,6,17,18)</sup> PAULING pointed out<sup>(19)</sup> that equation (3) is applicable if the van der Waals stabilization and other factors contributing to the enthalpy have the same magnitude for the elements as for the product. For eighteen bonds,  $\Delta$  was computed by equation (1) and by equation (3), and the results are presented in Table 5. The average values of  $\Delta$  for these eighteen bonds are 21.5 kcal and 22.0 kcal for equations (1) and (3), respectively. The average difference between the two  $\Delta$  values for each bond is 1.9 kcal. Thus the results from equations (1) and (3) are mutually consistent.

Electronegativity values decrease monotonically within the groups, Li-Na-K-Rb-Cs, Be-Mg-Ca-Sr-Ba, Sc-Y-La, N-P-As-Sb-Bi, \* O-S-Se, F-Cl-Br-I. Alternation in electronegativity values is observed in the groups, B-Al-Ga-In-Tl and

\* There is considerable evidence (ALLRED and HENSLEY<sup>(20)</sup>) that the electronegativity of bismuth is considerably higher than the value reported here on the basis of  $\Delta H_{\text{form}}$  of bismuth trichloride.

<sup>(18)</sup> H. O. PRITCHARD and H. A. SKINNER, *Chem. Rev.* **55**, 745 (1955).

<sup>(19)</sup> L. PAULING, *Nature of the Chemical Bond*, p. 63. Cornell Univ. Press, Ithaca (1939).

<sup>(20)</sup> A. L. ALLRED and A. L. HENSLEY, *J. Inorg. Nucl. Chem.* **17**, 43 (1961).

TABLE 1.—CALCULATED ELECTRONEGATIVITIES

	H	C	Si	Ge	Sn	Pb	N	P	As	Sb	Bi	O	S	Se	F	Cl	Br	I
H		(2.11)					(2.07)					(2.11)	(2.17)		(2.31)	(2.18)	(2.22)	(2.42)
C	(2.64)		(2.44)									(1.78)	(1.74)		2.44 (2.44)	2.56 (2.63)	(2.65)	2.08 (1.96)
Si		(2.01)														1.87 (1.92)	1.93 (1.93)	2.08 (1.96)
Ge																1.97 (2.02)	2.02 (2.02)	2.08 (1.98)
Sn																1.96 (2.04)	1.92 (1.93)	
Pb															2.43	2.24		
N	(3.17)											(2.19)			(2.90)	2.08 (2.19)	2.12 (2.20)	2.26
P												(2.22)			(2.22)	2.14 (2.19)	2.13 (2.13)	2.21 (2.16)
As												(2.16)			(2.21)	2.01 (2.04)	2.00 (1.95)	2.08 (1.99)
Sb																2.02		
Bi																		
O	(3.55)		(3.56)					(3.44)	(3.40)	(3.33)					(3.34)	(3.50)		
S	(2.61)		(2.74)													2.38		
Se																(2.55)		
F	(3.87)	4.09 (4.09)				3.88	(4.12)	(3.95)	(3.95)			(4.08)				(3.92)		
Cl	(3.18)	3.15 (3.08)	3.19 (3.14)	3.20 (3.15)	3.16 (3.08)	3.25		3.27 (3.16)	3.20 (3.15)	3.20 (3.17)	3.16	(3.10)	3.36	(3.16)	(3.22)			(3.04)
Br	(2.93)	(2.86)	2.92 (2.93)	2.95 (2.95)	2.99 (2.98)			3.02 (2.94)	3.00 (3.00)	3.00 (3.05)								(2.91)
	(2.44)		2.48 (2.60)	2.59 (2.69)				2.59	2.63 (2.68)	2.63 (2.72)						(2.78)	(2.70)	

TABLE 2.—CALCULATED ELECTRONEGATIVITIES

	Cl	Br	I		Cl	Br	I
Li			0.98	Ti	1.59	1.52	1.51
Na			0.93	Zr	1.39	1.34	1.26
K			0.82	V	1.63		
Rb			0.82	Cr	1.73		1.59
Cs			0.79	Mo	2.18	2.16	2.15
Be	1.53	1.57	1.61	W	2.25	2.31	2.51
Mg		1.32	1.30	Mn	1.58	1.55	1.53
Ca			1.00	Fe	1.83	1.81	1.85
Sr			0.95	Co	1.86	1.85	1.93
Ba			0.89	Ni	1.88	1.87	1.99
Sc	1.37	1.34		Rh	2.28		
Y			1.22	Pd	2.17	2.22	
La			1.10	Ir	2.20		
Ce			1.12	Pt	2.28		
Pr			1.13	Cu	1.98	1.91	1.82
Nd			1.14	Ag	2.01	1.93	1.86
Sm			1.17	Au	2.56	2.51	
Gd			1.20	Zn	1.69	1.65	1.62
Dy			1.22	Cd	1.74	1.68	1.64
Ho			1.23	Hg	2.07	2.01	1.92
Er			1.24	B	1.99	2.08	
Tm			1.25	Al	1.61	1.60	1.62
Lu			1.27	Ga	1.82	1.80	1.80
U	1.40	1.38	1.37	In	1.80	1.77	1.77
Np	1.39	1.36	1.34	Tl	2.06	2.03	
Pu		1.30	1.27				

TABLE 3.—AVERAGE ELECTRONEGATIVES\*

I	II	III	II	II	II	II	II	II	II	I	II	III	IV	III	II	I
H 2.20																
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33		Mo 2.16			Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.66	I 2.66
Cs 0.79	Ba 0.89	La 1.10	Hf 1.10		W 2.36			Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 2.04	Pb 2.33	Bi 2.02		
		Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb	Lu 1.27	
					U 1.38	Np 1.36	Pu 1.28									

\* The oxidation state is specified at the top of each group.

TABLE 4.—ELECTRONEGATIVITIES OF SOME ELEMENTS  
IN DIFFERENT OXIDATION STATES

Mo <sup>II</sup>	2.18	Mo <sup>V</sup>	2.27	Tl <sup>I</sup>	1.62
Mo <sup>III</sup>	2.19	Mo <sup>VI</sup>	2.35	Sn <sup>II</sup>	1.80
Mo <sup>IV</sup>	2.24	Fe <sup>III</sup>	1.96	Pb <sup>II</sup>	1.87

TABLE 5.—VALUES OF  $\Delta$  CALCULATED BY TWO METHODS

	(Eq. 1) (kcal)	(Eq. 3) (kcal)		(Eq. 1) (kcal)	(Eq. 3) (kcal)
CF <sub>4</sub>	54.7	54.5	SnBr <sub>4</sub>	24.0	24.3
CCl <sub>4</sub>	6.5	8.3	PCl <sub>3</sub>	21.8	27.0
SiCl <sub>4</sub>	35.5	38.2	PBr <sub>3</sub>	12.8	15.8
SiBr <sub>4</sub>	24.5	23.8	AsCl <sub>3</sub>	21.8	23.8
SiI <sub>4</sub>	11.5	7.9	AsBr <sub>3</sub>	15.7	15.5
GeCl <sub>4</sub>	29.6	32.5	AsI <sub>3</sub>	5.7	4.6
GeBr <sub>4</sub>	20.5	20.4	SbCl <sub>3</sub>	29.0	30.4
GeI <sub>4</sub>	10.5	7.6	SbBr <sub>3</sub>	23.0	20.7
SnCl <sub>4</sub>	29.1	32.6	SbI <sub>3</sub>	10.0	7.7
			Average:	21.5	22.0

C-Si-Ge-Sn-Pb. Chemical and physical evidence for the alternation in Group IVB has been presented previously.<sup>(21,22,23)</sup> The alternation is explainable in terms of the transition metal contraction and the lanthanide contraction. These contractions lead to a greater force of attraction between the nucleus and the electrons at the covalent boundary of the atom.<sup>(22)</sup> In building up the fourth row of the periodic system, increasing nuclear charge accompanies the filling of the inner 3*d* subshell and causes gallium and germanium to be more compact (although not smaller) than aluminium and silicon. Similarly, in building up the sixth row, increasing nuclear charge is balanced by electrons entering the 4*f* subshell. Thus the elements to the right of hafnium are more compact and more electronegative than the elements in corresponding groups in the fifth row. The effects of the transition metal and lanthanide contractions steadily become less pronounced with increasing group number, IIIB IVB VB VIB VIIIB, due to additional electrons in the ultimate *s* and *p* subshells. In fact, the nitrogen group (VB) marks the transition from alternation to monotonic change of electronegativity.

The electronegativities of the lanthanides increase slightly and steadily with increasing atomic number. This trend with increasing atomic number parallels, as expected, the decrease in basicity of the trihydroxides, the increase in the ease of complex formation, and the decrease of the standard electrode potentials. In the actinide series, the electronegativity increases from plutonium to neptunium to uranium with a corresponding decrease in the standard electrode potentials, Pu: 2.03V, Np: 1.83V and U: 1.80V.<sup>(24)</sup>

The variation of the electronegativities of the elements from calcium to zinc reflects the increase in nuclear charge and the magnitude of the crystal field stabilization

<sup>(21)</sup> R. T. SANDERSON, *J. Amer. Chem. Soc.* **74**, 4792 (1952).

<sup>(22)</sup> A. L. ALLRED and E. G. ROCHOW, *J. Inorg. Nucl. Chem.* **5**, 264 (1958).

<sup>(23)</sup> A. L. ALLRED and E. G. ROCHOW, *J. Inorg. Nucl. Chem.* **5**, 269 (1958).

<sup>(24)</sup> J. J. KATZ and G. T. SEABORG, *The Chemistry of the Actinide Elements*, p. 412, J. Wiley, New York (1957).

energy. In the metal ions in which crystal field stabilization is important, the electronic charge is concentrated in orbitals directed away from ligands; and, therefore, the nuclear charge of the metal is especially effective in attracting electrons from bonded ligands. Thus in the series from calcium to zinc, the relatively low electronegativity values for divalent calcium, manganese, and zinc are explained by the spherically symmetric distribution of charge on the metal ions. The variation of electronegativity in this series is comparable to the variation in the heat of hydration<sup>(25)</sup> of the divalent ions, the lattice energies of the dihalides,<sup>(26)</sup> and the sum of the first and second ionization potentials.<sup>(26)</sup>

Recently, an attempt<sup>(17)</sup> to evaluate electronegativities with a modification of PAULING's equation led to results which differ considerably from those reported here for several metals. The modified equation utilizes data pertaining to two metal halides and does not require the energy of the metal-metal bond. However, the modified equation contains a term having  $(\chi_X - \chi_{X'})$  in the denominator, and a small error in the electronegativity of either of the halogens, X or X', leads to a considerable uncertainty in the calculated electronegativity of the metal. Since each element actually has a small range of electronegativity values instead of an invariant value,<sup>(18)</sup> small uncertainties in the electronegativities of the halogens are expected.

Since PAULING's recent electronegativities are reported to two significant figures, compared with three in the present recalculation, an apparently close agreement of the values in the two scales is expected. However, the value for lead, 2.33, differs considerably from the value of 1.8 reported by PAULING in reference 8. There is considerable evidence for the high electronegativity of lead.<sup>(3)</sup> PAULING's values for zinc, gallium, germanium, and arsenic are surprisingly low and do not reflect the transition metal contraction. For a few other values, there are small discrepancies the origin of which is obscure since in reference 8 there is an incomplete tabulation of the compounds and enthalpy data applied in the calculations.

The scale of electronegativities from thermochemical data in Table 3 can be compared readily with scales of electronegativities obtained from other properties. Several scales of electronegativities are listed in reviews by PRITCHARD and SKINNER<sup>(18)</sup> and by GORDY and THOMAS,<sup>(27)</sup> and a scale of electronegativity based on electrostatic force is presented in reference 22. There is a remarkably close agreement of the values obtained from quite different properties for many elements, and practically all of the disagreements can be traced to the approximate nature of the relations between electronegativities and the properties being observed.

<sup>(25)</sup> L. BREWER, L. A. BROMELY, P. W. GILLES and N. L. LOFGREN, *Chemistry and Metallurgy of Miscellaneous Materials*, p. 165 ff. (Edited by L. L. QUILL) McGraw-Hill, New York (1950).

<sup>(26)</sup> F. BASOLO and R. G. PEARSON, *Mechanisms of Inorganic Reactions*, pp. 66 and 71. Wiley, New York (1958).

<sup>(27)</sup> W. GORDY and W. J. O. THOMAS, *J. Chem. Phys.* **24**, 439 (1956).