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The Electric Moment as a Measure of the Ionic Nature of Covalent Bonds

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(Received January 13, 1933)

The two-electron bond with hydrogen is found to have the following values of $\mu \times 10^{18}$: H−As 0.10; H−P 0.36; H−I 0.38; H−S 0.63; H−Br 0.78; H−Cl 1.03; H−N 1.04; H−O 1.32. These values are believed to give the positions of the elements on an electronegativity scale which is shown to be similar to that prepared by Pauling. The reported moments for inorganic halides as well as the unpublished measurements of A. L. Ferguson and M. G. Malone, giving $\mu = 3.1 \times 10^{-18}$ for $SbCl_3$ and $\mu = 2.4 \times 10^{-18}$ for $SbBr_3$, give fair agreement in most cases with those calculated from the above scale. On the basis of calculated values appreciable moments are predicted for all trihalides of the fifth-group elements except PI_3 and NCl_3 which should give close to a zero moment.

THE idea that the electric moment bears some relation to the ionic quality of the two-electron type of bond has been known for a number of years. It is true that the terms used in describing a bond have been loosely applied, and it is uncertain in some cases just what meaning has been intended. Noyes[1] has clearly described, however, the two-electron bond as potentially polar when it possesses a dipole moment. The qualitative relationship, that atomic bindings between like atoms do not possess moments while those between unlike atoms may do so, is generally known.[2]

The author undertook some six months ago the task of assigning electric moments, derived from the measured moments of molecules to individual bonds. The result of this work was the arrangement of the elements on what Pauling[3] has since called an electronegativity scale. In this early attempt, the scale was built around carbon as a reference. The result was neither as consistent nor as useful as was hoped for.

Certain qualitative regularities did appear, however, among the halides of the fifth-group elements. These will be discussed at more length in light of the fuller knowledge of the subject. The ideas herein involved were of sufficient interest to induce A. L. Ferguson and M. G. Malone to undertake experimental determinations of the electric moments of this group of elements.

It was the belief of the author that any scale which measures the bond differences of atoms should relate to the scale based on electric moments by a constant factor. Attempts to prepare such a scale from independent data were fruitless. At this time the paper of Pauling,[3] giving an electronegativity scale based on thermal data appeared. Since the scale given by Pauling used hydrogen as the point of reference, the author revised his scale to read from the same reference.

The revision of the scale resulted in marked improvement. The factor relating the two scales appeared to be 10^{-18}, but certain difficulties remain. The recent paper by Smallwood,[4] in which a like correlation has been made, induces the author to point out his correlation and certain ways in which it may be applied.

Table I lists the values of the coordinates for the various elements on the two electronegativity scales. The $\Delta^{\frac{1}{2}}$ values are taken from Pauling's[3] paper. He has calculated these values from the increment Δ, of observed bond energy in excess of calculated bond energy. In the latter case, the additivity of the energies of normal covalent bonds has been assumed.

The μ values have been calculated from the observed electric moments of the hydrogen compounds. The moment of the molecule is directly that of the bond in the case of the

[1] W. A. Noyes, J. Am. Chem. Soc. **50**, 2902 (1928).

[2] Ruark and Urey, *Atoms Molecules and Quanta*, McGraw-Hill, 1930; Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford, 1932; Glasstone, *Recent Developments in Physical Chemistry*, Blakiston, 1931.

[3] Linus Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[4] Zeits. f. physik. Chemie **B19**, 242 (1932).

TABLE I. *Coordinates of elements on the two electronegativity scales.*

	$\Delta^{\frac{1}{2}}$	$\mu \times 10^{18}$		$\Delta^{\frac{1}{2}}$	$\mu \times 10^{18}$
H	0.00	0.00	Br	0.75	0.78
As	—	0.10	Cl	0.94	1.03
P	0.10	0.36	N	0.95	1.04
I	0.40	0.38	O	1.40	1.32
C	0.55	—	F	2.00	—
S	0.43	0.63			

hydrogen halides, and since hydrogen is taken as the point of reference the value of the moment fixes the position of the halogen on the electronegativity scale. In the case of oxygen and sulfur the values can be calculated only with a knowledge of the bond angles. The 90° angle taken, places the O−H bond at 1.32 on the scale in good agreement with the value given by Pauling. The position of sulfur at 0.63 is not in accord with the $\Delta^{\frac{1}{2}}$ value of 0.43. Pauling has accepted the tandem structure for S_2Cl_2 in determining the position of sulfur. There is evidence against this structure.[5] Objection has also been raised against the tandem structure for hydrogen peroxide.[6] The value given by Pauling for the O−O bond would be substantially the same, however, if obtained from other sources.

In the case of the fifth-group elements considerable data are obtainable regarding the bond angle.[7] Somewhat arbitrarily the angles 100°, 98°, 96° and 94° have been assumed by the author as the bond angles of N−H, P−H, As−H and Sb−H, respectively. 100° is probably too low for ammonia, but it is nearer the true value than the 90° angle assumed by Smallwood. The decrease in the angles as one proceeds to higher weights is in line with the views of Pauling.[8]

The position of carbon will not be given at this time as it presents difficulties. The substituted halides of methane follow no discernible pattern. Whether the difficulties arise from special proper-

ties of carbon, or from the circumstance that in every polar compound of carbon involving bonds of this type at least three species of atoms are included, is not known, but the latter appears the more probable. To use varying bond angles or induced polarization as an explanation is to defeat the purpose of this report. The electric moment values of the mixed halides of the fifth-group elements would furnish highly desirable information in this connection.

The consistency of the electronegativity scale is indicated by the following moments of molecules calculated from bond moments taken from Table I and the bond angles previously used. The moment of the Sb−H bond has been assumed to be zero in calculating values for the antimony halides.

From several viewpoints, it would be desirable to have electric moment data on the compounds resulting from the reaction of the halides with each other as these offer values for the group moments independent of any bond angle. The $\mu \times 10^{18}$ values calculated for the halides of the fifth group and recorded in Table III also possess

TABLE II. *Comparison of calculated and measured electric moments.*

Molecule	$\mu \times 10^{18}$		Authority
	Calculated	Measured	
SCl_2	0.51	0.56	J. W. S.[9]
PCl_3	0.98	0.8	B. & E.[10]
		0.9	J. W. S.[11]
PBr_3	0.62	0.61	B. & E.
$AsCl_3$	1.44	1.97	B. & E.
$AsBr_3$	1.05	1.66	B. & E.
$SbCl_3$	1.72	3.1	F. & M.[12]
$SbBr_3$	1.31	2.4	F. & M.
SbI_3	0.62	0.4	See reference 13

[5] Matossi and Aderhold, Zeits. f. Physik **68**, 683–95 (1931).

[6] Maass, Can. J. Res. 781 (1932).

[7] L. Pauling, J. Am. Chem. Soc. **53**, 1380 (1931); Wierl, Ann. d. Physik **8**, 521 (1931); Dennison and Uhlenbeck, Phys. Rev. **41**, 313 (1932); D. S. Villars, Chem. Rev. **11**, 369 (1932).

[8] L. Pauling, J. Am. Chem. Soc. **53**, 1380 (1931).

[9] J. W. Smith, Proc. Roy. Soc. **A138**, 154 (1932).

[10] Bergmann and Engels, Zeits. f. physik. Chemie **B13**, 232 (1931).

[11] J. W. Smith, Proc. Roy. Soc. **A136**, 256 (1932).

[12] A. L. Ferguson and M. G. Malone, unpublished measurements.

[13] The value of 0.4×10^{-18} is listed by Smyth (*Dielectric Constant and Molecular Structure*) for SbI_3. He attributes the value to Werner, Zeits. f. physik. Chemie **B4**, 371 (1929). Werner did not measure this compound but quotes the value from Williams, Phys. Zeits. **29**, 684 (1928). Williams and Allgeier, J. Am. Chem. Soc. **49**, 2416 (1927) made an unsuccessful attempt to measure SbI_3 in benzene. The value 0.4×10^{-18} is doubtless too low.

TABLE III. $\mu \times 10^{18}$ *values for the halides of the fifth-group elements.*

	Sb	As	P	N
F_3	≈ 4	≈ 3	≈ 2	≈ 1
Cl_3	1.7	1.44	0.98	0.0
	(3.1)	(2.0)	(0.85)	
Br_3	1.3	1.05	0.62	0.36
	(2.4)	(1.66)	(0.6)	
I_3	0.62	0.43	0.0	0.92
	(0.4)			

considerable interest. Where measured values are known they are given in parentheses just below the calculated values.

In view of the discrepancy between calculated and measured values, the predicted moments may be given only a semi-quantitative significance. That the minimum moment of the iodides is indicated for the phosphorous compound and not the nitrogen, as hasty consideration might have indicated, illustrates a use of the electronegativity scale. Similarly, the moment of the halogen compounds with nitrogen will increase in the order chloride, bromide, iodide instead of decreasing as occurs in the other columns.

The perfection of two independent measures of electronegativity, one based on thermal data and one on dipole moment data, would be of considerable value. Not only would one supplement the other where experimental values were incomplete, but from the complete scales bond angles in polyatomic atoms might be determined. Before this can be done a clearer definition of electronegativity must be given.