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Bond Energies and Polarities[1]

BY MAURICE L. HUGGINS

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New values of electronegativities and non-polar bond energy contributions, for use with Pauling's assumed relationships involving these quantities, have been computed and tested. Using these, the calculated bond energies agree with the experimental values within 2 or 3 kcal./mole, in most cases.

Introduction

One of the most useful of Pauling's contributions to physical chemistry has been his hypothesis[2] that the bond energy (D_{AB}) of a normal single covalent bond can be computed approximately as the sum of a non-polar part ($D_{np,AB}$) and a polar part ($D_{p,AB}$), the former being obtainable additively from constant non-polar bond energy contributions ($D_{np,A}$, $D_{np,B}$) from the two atoms concerned and the latter being proportional to the square of the difference between their "electronegativities" (x_A, x_B)

$$D_{AB} = D_{np,AB} + D_{p,AB}$$

$$D_{np,AB} = D_{np,A} + D_{np,B}$$

$$D_{p,AB} = 23.06(x_A - x_B)^2$$

A set of non-polar bond energy contributions and a set of electronegativities for any group of elements suffice to calculate approximate values of the bond energies for all normal single bonds between these elements.

Pauling's original values of these energy contributions and electronegativities have been revised and extended by him and by others, and various comparisons have been made between electro-negativities computed on the basis of Pauling's assumptions and those computed in other ways. Reference may be made especially to papers by Mulliken,[3] Smyth,[4] Rice,[5] Skinner,[6] Pitzer,[7] Gordy[8] and Sanderson.[9]

In the paper[10] following this, a simple equation will be presented, relating bond lengths (interatomic distances) to bond energies. In order to test this relationship more extensively and to extend its usefulness, it seemed desirable to consider bond-energy values calculated by Pauling's procedure, as well as those deduced more directly from experimental measurements. Although the previously published tables could be used for this purpose, the considerable accumulation of appropriate data since the figures therein were computed made a re-evaluation seem worthwhile. The results of such a re-evaluation are presented in this paper.

Procedure.—Following Pauling, we designate as "bond energies" quantities which are not strictly energies, but contributions of the bonds to the heats of formation of molecules containing them. Except as otherwise noted, the enthalpy data used are from the very valuable compilation of thermodynamic data recently published by the National Bureau of Standards.[11] In line with the convention adopted in this work, the standard temperature, for which the calculations are made, is taken as 25°. The only elements dealt with in this paper are hydrogen and the electronegative elements, from carbon to iodine, in columns 4 to 7, inclusive, of the Periodic Table.

The quantities involving carbon depend on the magnitude assumed for the heat of vaporization of graphite, about which there has been much argument in the literature. Calculations have been made in this work using each of the three values (about 125, 136 and 171 kcal./gram atom at 0°K.) which have been seriously considered in recent years. The general degree of agreement is approximately

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(1) This paper constitutes a revision of some of the material presented in papers at the Atlantic City Meeting of the American Chemical Society on Sept. 22, 1949, and the XIIth International Congress of Pure and Applied Chemistry in New York, N. Y., on Sept. 13, 1951.

(2) L. Pauling, THIS JOURNAL, **54**, 3570 (1932); "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

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

(4) C. P. Smyth, THIS JOURNAL, **60**, 183 (1938).

(5) O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(6) H. A. Skinner, *Trans. Faraday Soc.*, **41**, 645 (1945).

(7) K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948).

(8) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946); *Phys. Rev.*, **69**, 604 (1946).

(9) R. T. Sanderson, THIS JOURNAL, **74**, 272 (1952); *J. Chem. Phys.*, **20**, 535 (1952).

(10) M. L. Huggins, THIS JOURNAL, **75**, 4126 (1953).

(11) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

the same in the three cases. Detailed comparisons are given here (Tables III and IV) only for the intermediate case, the heat of sublimation of graphite being assumed to be 136 kcal./gram atom, since most of the recent pertinent evidence[12-16] favors this value over the others. (The highest value should probably not be considered definitely eliminated, however.[17-21])

The bond energies for bonds involving silicon have been calculated on the somewhat arbitrary assumption that the heat of sublimation of elementary silicon is 100 kcal./gram atom, rather than the NBS value of 88. The latter would require a $D_{np,Si}$ value of 22 or less, which would be out of line with the values for other elements (see Table I). It may be noted in this connection that Bauer and Brunner[22] obtained 94 kcal. for this heat of sublimation, and that Emeleus and Reid[23] found an activation energy of 51 kcal. for the rupture of the Si–Si bond in disilane.

Non-polar bond-energy contributions were first computed from the available bond-energy data for bonds joining two like atoms. For those elements for which there were no data, estimates were made. With the aid of these and the equations given above, electronegativity differences were computed, using all the appropriate data on the energies of bonds between different elements. From these, a set of electronegativities was prepared which would reproduce reasonably well the electronegativity differences. Minor shifts in the values of $D_{np,A}$ and x_A were then made to yield the best over-all agreement, most weight being given to the experimental data which seem to be most reliable. For some of the elements, comparisons between experimental interatomic distances and those calculated by the procedure outlined in the following paper were used to help decide between alternative values.

Bond energies for bonds in substances in the solid state have been used in only a few instances, and then merely to set upper limits, because of the difficulty of estimating the contributions of the interactions between pairs of atoms other than those directly bonded together.

Results and Discussion

The bond-energy contributions and electronegativities so deduced are listed, with previously published values for comparison, in Tables I and II. The degree of agreement with the experimental data is shown in the other two tables. Table III gives the electronegativity values for each atom of each bond, computed from the experimental bond energies and the non-polar bond-energy contributions from Table I, on the assumption that the other atom of the bond has the electronegativity value given in Table II. The few electronegativity values enclosed in parentheses in Table III were computed on the assumption of zero electronegativity difference, for cases in which, contrary to Pauling's basic assumptions, the experimental bond energy is less than the sum of the non-polar bond-energy contributions.

In Table IV the experimental bond energies are compared with those calculated. (Some calculated values, used in the following paper, are included, even though no corresponding experimental values are available.)

TABLE I

NON-POLAR BOND-ENERGY CONTRIBUTIONS, $D_{np,A}$

	H			
Huggins (25°)	52			
Pauling[2] (18°)	51.7			
Rice[5] (room temp.)	51.8			
Skinner[6] (room temp.)	52.05			
Pitzer[7] (0°K.)	51.6			
	C	N	O	F
Huggins	30,[a] 32,[b] 41[c]	16	17	18
Pauling	29.3[a]	11.8	17.45	31.75
Rice	34.6[d]	12.2	17.3	31.8
Skinner	31.2,[a] 34[b], 42.5[c]	21.5	26	31.75
Pitzer	40[c]	18.5	17	25
	Si	P	S	Cl
Huggins	25	25	25	29
Pauling	21.25	9.45	31.9	28.9
Rice				
Skinner	25.5	23.6	26.95	29.05
Pitzer	22.5	26.5	31.5	28.55
	Ge	As	Se	Br
Huggins	20	19	21	23
Pauling	21.25	7.55	28.8	23.05
Rice				23.06
Skinner	17	18.35	20.4	23.15
Pitzer	19.6	19.5	25	22.7
	Sn	Sb	Te	I
Huggins	17	17	17	17
Pauling				18.1
Rice				18.13
Skinner				18.2
Pitzer	17.5	21	24.5	17.8

[a] Based on $\Delta H \approx 126$ kcal./mole for $C_{graph} \rightarrow C_{gas}$. [b] Based on $\Delta H \approx 137$ kcal./mole for $C_{graph} \rightarrow C_{gas}$. [c] Based on $\Delta H \approx 172$ kcal./mole for $C_{graph} \rightarrow C_{gas}$. [d] Assumed.

TABLE II

ELECTRONEGATIVITIES, x_A

	H			
Huggins	2.20			
Pauling[2]	2.1			
Gordy[8]	2.13			
	C	N	O	F
Huggins	2.60	3.05	3.50	3.90
Pauling	2.5	3.0	3.5	4.0
Gordy	2.55	2.98	3.45	3.95
Sanderson[9]	2.68	3.04	3.42	3.66
	Si	P	S	Cl
Huggins	1.90	2.15	2.60	3.15
Pauling	1.8	2.1	2.5	3.0
Gordy	1.8	2.1	2.53	2.97
Sanderson	1.70	2.20	2.74	3.35
	Ge	As	Se	Br
Huggins	1.90	2.10	2.55	2.95
Pauling	1.7	2.0	2.4	2.8
Gordy	1.7	2.0	2.4	2.75
Sanderson				3.22
	Sn	Sb	Te	I
Huggins	1.90	2.05	2.30	2.65
Pauling	1.7	1.8	2.1	2.4
Gordy	1.7	1.8	2.1	2.45
Sanderson				2.89

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TABLE III

CALCULATED ELECTRONEGATIVITIES, x_A

	H	C	N	O	F	Si	P	S	Cl	Ge	As	Se	Br	Sn	Sb	Te	I
H	*2.20*	2.07	2.21	2.16	2.23	2.31	(2.15)	2.16	2.17		(2.10)	(2.50)	2.21			(2.30)	2.33
C	2.73	*2.60*	2.51	2.46	2.53	2.52		2.60	2.54				2.59				(2.65)
N	3.04	3.14	*3.05*		2.90												
O	3.54	3.64		*3.50*	3.24	<3.56			3.54		3.38						
F	3.87	3.97	4.05	4.16	*3.90*	3.91			3.92		3.89		3.88				
Si	1.79	1.98		>1.84	1.89	*1.90*		>1.94	1.89				1.91				1.95
P	(2.20)						*2.15*		2.12				2.12				2.10
S	2.63	(2.60)				<2.56		*2.60*	2.60		2.61		2.59				
Cl	3.18	3.21		3.11	3.13	3.16	3.18	3.15	*3.15*	3.07	3.14	3.13	2.98	3.07	3.11		3.08
Ge									1.98	*1.90*							1.77
As	(2.20)			2.22	2.11			2.09	2.11		*2.10*		2.12				2.13
Se	(2.20)								2.56			*2.55*					
Br	2.94	2.96			2.97	2.94	2.98	2.96	3.12		2.93		*2.95*	2.94	2.98		2.98
Sn									1.98				1.91	*1.90*			
Sb				2.19	2.12				2.04				1.97		*2.05*		1.99
Te	(2.20)															*2.30*	
I	2.52	(2.60)				2.60	2.70		2.72	2.78	2.66		2.62				*2.65*

TABLE IV

BOND ENERGIES, D_{A-B}

Bond	Molecule or crystal	Bond energy Exp.[a]	Calcd.
H–H	H_2	104.2	104
H–C	CH_4	90.8[b]	88
H–N	NH_3	84.3	85
H–O	H_2O	110.6	108
H–F	HF	134.6	137
H–Si	SiH_4	80.8[c]	79
H–P	PH_3	76.4	77
H–S	H_2S	81.3[d]	81
H–Cl	HCl	103.2	102
H–Ge			74
H–As	AsH_3	58.6	71
H–Se	H_2Se	66.0	76
H–Br	HBr	87.5	88
H–Sn			71
H–Sb			70
H–Te	H_2Te	57.4	69
H–I	HI	71.4	74
C–C	Diamond	68[b,e]	64
	C_2H_6	64.5[b,f]	64
C–N	CH_3NH_2	55[b,f,g]	53
	$(CH_3)_2NH$	53[b,f,g]	53
	$C_2H_5NH_2$	56[b,f,g,h]	53
C–O	$(CH_3)_2O$	74[b,f]	68
C–F	CF_4	93.2[b]	89
C–Si	SiC	66[b,e]	68
C–P			62
C–S	$(CH_3)_2S$	52[b,d,f]	57
C–Cl	CCl_4	69.6[b]	68
	$CHCl_3$	70[b,f]	68
	CH_2Cl_2	70[b,f]	68
	CH_3Cl	71[b,f]	68
C–Ge			63
C–As			57
C–Br	CBr_4	58[b]	58
	$CHBr_3$	58[b,f]	58
	CH_2Br_2	57[b,f]	58
	CH_3Br	57[b,f]	58
C–Sn			60
C–I	CHI_3	43[b,f]	49
	CH_2I_2	43[b,f]	49
	CH_3I	43[b,f]	49
N–N	N_2H_4	32[g,j]	32
N–O			37
N–F	NF_3	55.9	51
N–S			46
N–Cl	NCl_3	37[n]	45
O–O	H_2O_2	33[i]	34
O–F	OF_2	45	39
O–Si	SiO_2	106[c,e]	101
O–P			84
O–Cl	Cl_2O	49.5	49
O–As	As_4O_6	74[k]	81
O–Sb	Sb_4O_6	74[k]	82
F–F	F_2	36.6	36
F–Si	SiF_4	136	135
F–P			114
F–Cl	ClF	60.6	60
F–Ge			130
F–As	AsF_3	111.3	112
F–Br	BrF	60.8[l]	62
F–Sb	SbF_3	108[m,n]	114
Si–Si	Si	50[c,e]	50
Si–S	SiS_2	60[c,e]	61
Si–Cl	$SiCl_4$	90[c]	90
Si–Br	$SiBr_4$	73[c]	73
Si–I	SiI_4	53[c]	55
P–P	Normal	51.3[o]	50
P–S			55
P–Cl	PCl_3	78.5	77
P–Br	PBr_3	63.7	63
P–I	PI_3	49[m,n]	48
S–S	S_6	48.4[d,p]	50
	S_8	49.5[d,p]	50
S–Cl	S_2Cl_2	61[d,q]	61
S–As	As_4S_6	50[d,m,n]	50
	As_4S_4	50[d,r]	50
S–Br	S_2Br_2	51[d,m,q]	51
Cl–Cl	Cl_2	58.0	58
Cl–Ge	$GeCl_4$	80[s]	85
Cl–As	$AsCl_3$	73.1	73
Cl–Se	$SeCl_2$	58.1	58
Cl–Br	BrCl	52.2	53
Cl–Sn	$SnCl_4$	77	82
Cl–Sb	$SbCl_3$	74.3	74
Cl–Te			63
Cl–I	ICl	50.3	52
Ge–Ge	Ge	42[e,s]	40
Ge–Br			68
Ge–I	GeI_4	55[e,t]	50
As–As	Normal	38[u]	38
As–Br	$AsBr_3$	58	59
As–I	AsI_3	42[m,n]	43
Se–Se			42
Br–Br	Br_2	46.1	46
Br–Sn	$SnBr_4$	65	65
Br–Sb	$SbBr_3$	62[m]	59
Br–Te			50
Br–I	IBr	42.4	42
Sn–I			47
Sn–Sn	Sn	36[e]	34
Sb–Sb	Normal	35[v]	34
Sb–I	SbI_3	44[m,n]	42
Te–Te			34
I–I	I_2	36.1	34

[a] Except as otherwise indicated, the data are from ref. 11. [b] Based on ΔH_{298} = 137 kcal./mole for C (graphite) → C (gas). [c] Based on ΔH_{298} = 100 kcal./mole for Si(c) → Si(gas). [d] W. H. Evans and D. D. Wagman, *J. Research Natl. Bur. Standards*, **49**, 141 (1952). [e] Crystal; van der Waals energies between non-adjacent atoms neglected. [f] Assuming D_{C-H} = 90.4. [g] Assuming D_{N-H} = 82. [h] Assuming D_{C-C} from C_2H_6. [i] Assuming D_{O-H} from H_2O. [j] D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, THIS JOURNAL, **71**, 2293 (1949). [k] Strain energy and interactions between non-adjacent atoms neglected. [l] L. G. Cole and G. W. Elverum, Jr., *J. Chem. Phys.*, **20**, 1543 (1952). [m] Heat of vaporization estimated. [n] Heat of fusion estimated. [o] From P_4, assuming strain energy per bond = 3.8 kcal.; L. Pauling and M. Simonetta, *J. Chem. Phys.*, **20**, 29 (1952). [p] H. Braune, S. Peter and V. Neveling, *Z. Naturforschung*, **6a**, 32 (1951). [q] Assuming D_{S-S} from S_8. [r] Assuming D_{As-As} from As_4. [s] A. W. Searcy, THIS JOURNAL, **74**, 4789 (1952). [t] W. L. Jolly and W. M. Latimer, *ibid.*, **74**, 5757 (1952). [u] From As_4, estimating strain energy per bond = 3.5 kcal. [v] From Sb_4, estimating strain energy per bond = 3 kcal.

The concordance between the different values in each row of Table III and the close agreement between most of the experimental and calculated values of Table IV show the general applicability of the assumed relationships and constants. The calculated bond energies rarely differ more than 2 or 3 kcal./mole from the experimental values. The larger differences for H_3As, H_2Se and H_2Te are probably due to poor enthalpy data, based on experimental results published in 1888 and earlier. The discrepancies for the simple organic derivatives of sulfur and iodine may be due to error in the assumption that the C–H bond energy is strictly constant. Likewise, the calculation of the N–N bond energy in N_2H_4 on the assumption that the N–H bond energy is the same as in NH_3 is probably unjustified (see Skinner[6]).

ROCHESTER, N. Y.

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Atomic Radii. IV. Dependence of Interatomic Distance on Bond Energy[1]

BY MAURICE L. HUGGINS

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It is shown that most of the departures from strict additivity of radii in normal valence compounds can be attributed to variations in bond energy, D_{AB}. A set of "constant energy radii," r^*_A, has been computed. The simple relationship, $r_{AB} = r^*_A + r^*_B - {}^1/_2 \log D_{AB}$, yields interatomic distances which average within 0.02 Å. of the best experimental values. If experimental bond energies are not available, values computed from electronegativities and non-polar bond-energy contributions (see the preceding paper) can be used, with but little loss of accuracy.

Introduction

The hypothesis of constant additive atomic radii was introduced in 1920 by Bragg.[2] Shortly thereafter the writer showed[3] that the Lewis theory of valence was as applicable to crystals as to molecules and ions and pointed out[4] that the valence electron distributions so obtained enable one to predict, in many cases, whether or not constancy and additivity of radii should exist. Various causes of variability were considered in a qualitative manner. It was shown, nevertheless, that a reasonable degree of constancy and additivity exists in certain classes of structures, the essential requirement being that each atom being considered has a sufficiently similar environment in the different substances being compared. Sets of radii for several such classes were computed, the most extensive being a set of *tetrahedral radii*,[5] computed from and for bonds joining atoms, each having a kernel charge $+n$, tetrahedrally to four others, each with a kernel charge of $8 - n$. In 1934, Pauling and Huggins[6] revised and extended these sets of radii and added a set of *normal valence radii*, differing for only six elements from the tetrahedral radii (see Table I).

The writer has consistently pointed out that one should not expect close correspondence between the experimental interatomic distance and the sum of the appropriate radii from the standard set, if the environment of either or both of the atoms differs much from that of the corresponding atom in the class of substances from which the standard radii were derived. Such departures from additivity are, in fact, often found. They are useful in supplying evidence regarding the dependence of the bond length on various factors.

Many of the more marked departures from additivity have been interpreted[7] as resulting from differences in the "degree of double-bond character." On the other hand, Schomaker and Stevenson[8] attribute these departures to varying degrees of bond polarity. They have published a set of *non-polar radii* ($r_{np,A}$) and proposed the following empirical equation for the calculation of single-bond distances from these radii and Pauling's electronegativities[7,9] (x_A)

$$r_{AB} = r_{np,A} + r_{np,B} - 0.09|x_A - x_B| \qquad (1)$$

Although both of these explanations of departures from additivity seem reasonable and can be used to account for the observed distances in a considerable number of instances, Wells[10] has concluded that the sum total of available evidence is against the general applicability of either.

The present paper reports the results of an attempt to correlate interatomic distances with bond energies in a simple manner for single bonds in normal valence elements and compounds.

Theoretical Background

It is theoretically reasonable and experimentally well established that, other things being equal, the greater the bond energy the shorter is the interatomic distance. The bond energy is minus the sum of the repulsion energy and the (negative) attraction energy, when the molecule is in its lowest energy state, *i.e.*, when the interatomic distance is r_{AB}

$$D_{AB} = -E \text{ when } r = r_{AB} \qquad (2)$$

$$E = E_{rep} + E_{att} \qquad (3)$$

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[1] This is a revision of portions of papers presented on Sept. 22, 1949, at the 116th Meeting of the American Chemical Society in Atlantic City and on Sept. 13, 1951, at the XIIth International Congress of Pure and Applied Chemistry in New York, N. Y. For the three previous papers in this series, see references 4, 5 and 6.

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