leagues Prof. David Herrick and Prof. Paul Engelking along with the instigating influence of William T. Simpson.

Note in Added Proof: Since the submission of this manuscript Prof. Schweig has informed us of additional MO-CI results that are consistent with an NKM interpretation of the spectra of **1** and **2** as well as a number of other related systems. He also reminded us of his first private communication of the calculated CI effect in $\mathbf{1}^+$ in April of 1981. The publication of these results should appear shortly.

Registry No. 1, 502-86-3; **2**, 63238-49-3; **3**, 84694-70-2; 1,1,4,4-tetrafluorobutadiene, 407-70-5.

Electronegativity and Bond Energy

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Abstract: Recognition of quantitative relationships among atomic structure, electronegativity, nonpolar covalent radius, and homonuclear bond energy has permitted a complete revision of electronegativities of all major group elements and a more accurate evaluation of their radii and homonuclear bond energies. The new values have been tested by application to calculating the bond energies in practically all binary compounds of major group elements with halogen, oxygen, sulfur, and positive hydrogen and many other inorganic compounds having more than one kind of bond per molecule. In agreement with the quantitative theory of polar covalence, the calculated energies agree with experimental values within probable limits of experimental error for most of the 304 compounds studied.

Electronegativities of all the active major group elements, including zinc, cadmium, and mercury, have been completely revised on the basis of a study of the interrelationships among atomic structure, nonpolar covalent radius, electronegativity, and homonuclear covalent bond energy. The revised values have been thoroughly tested by application to the calculation of bond energies in more than 300 inorganic compounds containing about 400 kinds of bonds. These compounds, both nonmolecular solids and gaseous molecules, include nearly all of the binary compounds of positive hydrogen, binary halides, oxides, and sulfides of the major group elements for which adequate experimental data are available.[1-7] Also included are 85 compounds each consisting of more than one kind of bond: mixed halides, oxyhalides, hydroxy acids, and a wide variety of miscellaneous compounds. Agreement between calculated and experimental bond energy for most of these compounds is on the average within probable experimental error. Greater differences found for 15% of the compounds studied are believed to result most probably from experimental error in determination of the heats of formation. This paper presents (Table I) the new electronegativity values, together with revised nonpolar covalent radii, homonuclear bond energies, and the electronegativity changes corresponding to the acquisition of unit charge. It also describes the details of revision and discusses the interrelationships among fundamental atomic properties.

Table I. Electronegativities, Covalent Radii, and Homonuclear Bond Energies

element	S	ΔS_i	r_c	E'''	E''	E'
H	2.592	2.528	32.0	104.2		
Li	0.670	1.285	133.6	24.6		
Be	1.810	2.112	88.7	67.6		
B	2.275	2.368	82.2	76.7		
C	2.746	2.602	77.2	85.4		
N	3.194	2.806	73.4	94.9	66.9	38.8
O	3.654	3.001	70.2	104.0	68.8	33.6
F	4.000	3.140	68.1	113.1	76.8	40.5
Na	0.560	1.175	153.9	16.4		
Mg	1.318	1.802	137.3	42.3		
Al	1.714	2.055	125.8	48.2		
Si	2.138	2.296	116.9	54.1		
P	2.515	2.490	110.7	60.0	56.9	53.7
S	2.957	2.700	104.9	65.9	60.4	54.9
Cl	3.475	2.927	99.4	71.8	64.9	58.0
K	0.445	1.047	196.2	13.1		
Ca	0.946	1.527	174	30.8		
Cu	2.033	2.239	133.1	31.3		
Zn	2.223	2.341	129.2	35.8		
Ga	2.419	2.442	125.6	40.3		
Ge	2.618	2.540	122.3	44.8		
As	2.816	2.635	119.4	49.3	45.1	40.9
Se	3.014	2.726	116.7	53.8	46.0	38.2
Br	3.219	2.817	114.2	58.3	52.2	46.1
Rb	0.312	0.877	216	12.4		
Sr	0.721	1.333	191	24.6		
Ag	1.826	2.122	153.3	27.7		
Cd	1.978	2.208	149.3	30.4		
In	2.138	2.296	145.5	33.1		
Sn	2.298	2.380	142.0	35.8		
Sn(II)	1.477	1.908	142.0	35.8		
Sb	2.458	2.461	138.9	38.5	35.8	33.0
Te	2.618	2.540	136.0	41.2	39.2	37.2
I	2.778	2.617	133.3	43.9	40.0	36.1
Cs	0.220	0.736	235	10.8		
Ba	0.651	1.267	198	22.2		
Hg	2.195	2.326	150.0	8.6		
Tl	2.246	2.353	149.0	16.6		
Tl(I)	0.987	1.560	149	16.6		
Pb	2.291	2.376	148	24.2		
Pb(II)	1.900	2.164	148	24.2		
Bi	2.342	2.403	147	32.2		

Polar Covalence. The quantitative theory of polar covalence has been presented in detail elsewhere.[8-11] It will be reviewed very briefly here to emphasize an important aspect of the validity of this work. A polar covalent bond is treated as a blend of the two extremes, nonpolar covalence and complete ionicity. The energy of the nonpolar covalent form, E_c, is simply the geometric mean of the two homonuclear covalent bond energies, corrected for any difference between the actual bond length, R_o, and the

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sum of the nonpolar covalent radii, R_c:

$$E_c = (E_{A\text{-}A}E_{B\text{-}B})^{1/2}(R_c/R_o) \qquad (1)$$

The energy of the ionic form, E_i, is the unit charge product divided by the bond length, adjusted to kcal/mol by the factor 33 200 when the bond length is in pm.

$$E_i = 33\,200/R_o \qquad (2)$$

The actual energy of the polar covalent bond, called the "contributing bond energy" where there are more than one bond in the molecule, is then the weighted sum or blended sum of these two contributions:

$$E = t_cE_c + t_iE_i \qquad (3)$$

where t_c and t_i are the covalent and ionic blending coefficients, the sum of which is 1.000. E is multiplied by an appropriate factor if the bond is multiple (double 1.488, triple 1.787). These equations are appropriately modified for nonmolecular solids.[12]

The blending coefficients are easily evaluated as half the difference between the partial charges on the two atoms. These partial charges are based on the principle of electronegativity equalization and defined as the ratio of the change in electronegativity undergone in forming the compound to the change that would correspond to acquisition of unit charge. The principle of electronegativity equalization, first published[13] in 1951, has been confirmed by quantum mechanics[14,15] and should no longer be difficult to accept. Unfortunately, however, the partial charges themselves have not yet received widespread acceptance, despite their proven value in interpreting chemistry.[16,17] It should therefore be reassuring to realize that the ionic blending coefficient is easily derived entirely independently of any but experimentally verifiable values.[18] From the above equations, the value of t_i is easily determined from the experimental bond energy and the theoretical nonpolar covalent and ionic energies, themselves derived from experimental bond length and covalent radii and homonuclear covalent bond energy, with no dependence on any speculations about partial charge:

$$t_i = \frac{E - E_c}{E_i - E_c} \qquad (4)$$

For example, the experimental atomization energy of solid NaCl is 153.0 kcal/mol, the nonpolar covalent energy, calculated from the experimentally determined homonuclear energies, bond length, and nonpolar covalent radii, is 83.2 kcal/mol, and the ionic energy, calculated from bond length, Madelung constant, and repulsion coefficient, is 181.5 kcal/mol. From these, eq 4 gives $t_i = 0.710$. The electronegativities of Na and Cl (Table I) are 0.560 and 3.475. When the atoms combine, their electronegativities become equalized to the geometric mean, 1.395. The change in Na is from 0.560 to 1.395, or by 0.835. The change for complete loss of an electron, ΔS_i, is 1.175. The partial charge on sodium in NaCl is therefore 1.835/1.175 = 0.711. Similarly, the chlorine has changed from 3.475 to 1.395, or by −2.080. Acquisition of unit charge involves a change of 2.927, so the partial charge on Cl in NaCl is −2.080/2.927 = −0.711. The ionic blending coefficient is here the same, 0.711, in excellent agreement with that calculated from experimental values.

Since there is as yet no direct experimental method of determining the individual contributing bond energies in a compound having more than one kind of bond, eq 4 is not applicable to other than binary compounds. However, when applied to a representative sample of 74 binary compounds, it provides values of t_i agreeing with those calculated from partial charges within an average of only 0.013. Thus partial charges calculated from the principle of electronegativity equalization, and bond energies successfully calculated for hundreds of compounds are mutually supportive.

Table II. Number of Bond Varieties Contained in 304 Inorganic Compounds Studied

H	49	Al	8	Ge	10	Sb	5
Li	10	Si	19	As	5	Te	2
Be	5	P	23	Se	2	I	44
B	64	S	35	Br	55	Cs	10
C	29	Cl	85	Rb	11	Ba	10
N	33	K	10	Sr	10	Hg	4
O	85	Ca	10	Ag	4	Tl	8
F	90	Cu	7	Cd	4	Pb	10
Na	10	Zn	4	In	3	Bi	2
Mg	9	Ga	3	Sn	6		

The average difference between experimental and calculated bond energy in all 304 compounds studied is only 2.6% despite the fact that discrepancies up to 24% are noted and averaged with the others. When the 44 compounds (15% of the total) which exhibit differences of 5% or greater are eliminated from the averaging, the average difference is only 1.2%. It must be kept in mind that atomization energies and therefore bond energies derived from standard heats of formation depend on the accuracy not only of the heats of formation but also of the experimental bond lengths, homonuclear bond energies, and the atomization energies of the individual elements, not all of which are precisely known. For nonmolecular solids, repulsion coefficients must also be known accurately. Consequently, it seems reasonable to assume that the average agreement between experimental bond energies and those calculated according to the theory of polar covalence is within the probable limits of experimental error.

Table II summarizes the kinds of bonds included in this study and clearly demonstrates the wide range of applicability of this theory. The only major group inorganic compounds deliberately omitted from this study, in addition to coordination compounds and more complex solids such as carbonates, sulfates, and so on which have not yet been studied, are (1) compounds of negative hydrogen, in which the experimental bond energies are substantially smaller than those calculated, and (2) binary solids which are only moderately polar in the bonding, for which the usual treatment accorded successfully to highly polar solids appears inappropriate. In compounds of only moderately negative hydrogen, the bond energies appear to correspond rather closely to the nonpolar covalent extreme, suggesting that the expected exceptionally high polarizability of negatively charged hydrogen may in effect nullify the polarity. For the gaseous alkali metal hydrides, the bond energies are well represented by multiplying the calculated total energy by the empirical factor, 0.42. For the same hydrides in solid form, the empirical factor is 0.63. Otherwise, the theory appears remarkably general in its scope. Successful application to nearly 800 organic compounds of all common functional types is reported elsewhere.[19,20]

A single example of bond energy calculation is provided here, as adequately representative of all the calculations in this study. The compound $B_3O_3HCl_2$ consists of a six-membered boron–oxygen ring with an atom of hydrogen attached to one of the atoms of boron and a chlorine atom attached to each of the other two boron atoms. The bond lengths are: BH 111 pm, BO 136 pm, and BCl 175 pm. From Table I, the electronegativity of the molecule is calculated to be the ninth root of the product of all the individual electronegativities, or 2.970. From this the partial charges are calculated to be B 0.293, O −0.228, H 0.150, and Cl −0.173. Their sum over the molecule is of course zero (actually 0.001). The values of t_i are calculated to be 0.072 for BH, 0.261 for BO, and 0.233 for BCl. Having an unoccupied outer orbital in its trivalent state, boron joins to chlorine by the unweakened energy, E''', of the latter and by the half-weakened energy, E'', of oxygen. The geometric mean homonuclear bond energies are then 82.4 for BH (correcting the hydrogen energy for the partial

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change on H), 72.6 for BO, and 74.2 for BCl. The contributing bond energies are calculated as follows: For BH, (0.928)(82.4)(114.2/114 = 76.6; (0.072)(33200)/114 = 21.0; 21.0 + 76.6 = 97.6 kcal/mol. For BO, (0.739)(72.6)(152.4)/136 = 60.1; (0.261)(33200)/136 = 63.7; 63.7 + 60.1 = 123.8; ×6 bonds = 742.8. For BCl (0.767)(74.2)(181.6)/175 = 59.1; (0.233)(33200)/175 = 44.2; 44.2 + 59.1 = 103.3; ×2 bonds = 206.6. Total atomization energy: 97.6 + 742.8 + 206.6 = 1047.0 kcal/mol; extpl. 1044.8.

Revision of Electronegativity, Covalent Radius, and Homonuclear Bond Energy. Revision of the earlier electronegativity values was based on the observation that within each period, they are a linear function of the reciprocal of the radius cubed. (This is expected since they were originally calculated[21] as an inverse function of the volume of an atom, involving r^3.) The lines for the separate periods converge at −0.5 electronegativity and zero radius. Since this suggested revision by adding 0.5 to each electronegativity and since the major application of electronegativities is as relative numbers, it was decided to invite more willing acceptance by adjusting to the more familiar Pauling scale originally based on 4.00 for fluorine. Electronegativities of the halogens have been so thoroughly tested that they were assumed to be strictly reliable, and used as a cornerstone for revision of values for the other elements. The values F 5.75, Cl 4.93, Br 4.53, and I 3.84 were therefore converted by adding 0.5 and multiplying by the factor 0.64, to F 4.000, Cl 3.475, Br 3.219, and I 2.778. Since the product, Sr^3, S being the electronegativity and r the nonpolar covalent radius, is constant for any given period, this allowed adjustment of other values within each period. M1 and M2 elements from calcium on are exceptional and were revised separately.

A critical parameter is of course the nonpolar covalent radius, defined as half the length of a single bond between uncharged like atoms. Accurate experimental evaluation has been possible largely for gaseous diatomic molecules of the M1 and M7 elements and for the diamond type structures of C, Si, Ge, and gray tin. Less accurate radii have been determined for other major group elements. In this work it was found that the function, square root of atomic number divided by the radius cubed $(Z/r^3)^{1/2}$, is linear with the number of outermost electrons, N, within each period. The radii of Table I are consistent with this relationship and used to evaluate Sr^3. It had previously been demonstrated that the change in electronegativity corresponding to acquisition of unit charge can be evaluated as a constant (formerly 2.08) times the square root of the electronegativity. Revision of this constant to 1.57 was accomplished by a study of 74 representative binary compounds.

Finally, the unweakened homonuclear single covalent bond energies as previously evaluated were revised in recognition of their linearity within each period with the number of outermost electrons. The empirical equation, $H''' = 38.75 + 10.7N - 1.6\,nN - 2.75n$, where N is the number of outer electrons and n the principal quantum number, represents the homonuclear energies accurately for elements of the third, fourth, and fifth periods but not the second or sixth. It had previously been noted that within each period the homonuclear bond energy is closely linear with the product of radius times electronegativity. This is also true of all but lithium of the M1 elements and Ca, Sr, and Ba, which do not conform to the previously described relationships but fall on the same straight line when Sr is plotted against E.

The problem of the very important lone pair bond weakening effect[22] (LPBWE) remains to be solved, but satisfactory values of the fully weakened energies were obtained empirically. The fully weakened dissociation energies of the diatomic molecules of the halogens are well-known, and energies for other elements were available from miscellaneous data. The half-weakened energies are then midway between the unweakened and fully weakened energies.

There seems to be no reason to doubt that the exact interrelationships among all these properties and atomic structure will one day be revealed, but it has not yet been possible to relate all the individual periods in a satisfactory way. Nevertheless, the parameters of Table I are proven adequate to permit the accurate calculation of contributing bond energies according to the theory of polar covalence and thus provide valuable insight into the nature of chemical bonds.

In general, if the bond types are known or reasonably predictable, the theory is capable of very satisfactory accuracy in predicting bond energies and heats of formation.

Registry No. H atom, 12385-13-6; Li, 7439-93-2; Be, 7440-41-7; B, 7440-42-8; C, 7440-44-0; N atom, 17778-88-0; O atom, 17778-80-2; F atom, 14762-94-8; Na, 7440-23-5; Mg, 7439-95-4; Al, 7429-90-5; Si, 7440-21-3; P, 7723-14-0; S, 7704-34-9; Cl atom, 22537-15-1; K, 7440-09-7; Ca, 7440-70-2; Cu, 7440-50-8; Zn, 7440-66-6; Ga, 7440-55-3; Ge, 7440-56-4; As, 7440-38-2; Se, 7782-49-2; Br atom, 10097-32-2; Rb, 7440-17-7; Sr, 7440-24-6; Ag, 7440-22-4; Cd, 7440-43-9; In, 7440-74-6; Sn, 7440-31-5; Sb, 7440-36-0; Te, 13494-80-9; I atom, 14362-44-8; Cs, 7440-46-2; Ba, 7440-39-3; Hg, 7439-97-6; Tl, 7440-28-0; Pb, 7439-92-1; Bi, 7440-69-9; tin(2+), 22541-90-8; thallium(1+), 22537-56-0; lead(2+), 14280-50-3.

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