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A New Method for the Estimation of Dissociation Energies and its Application to the Correlation of Core-Electron Binding Energies Obtained from X-ray Photoelectron Spectra

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Abstract. - Dissociation energy is defined here as the energy required to break all the bonds of a species so that the electrons of each bond are divided equally between the atoms of the bond. A method based on electronegativities is devised for estimating the differences in the dissociation energies of pairs of isoelectronic species. Such differences, for appropriately chosen isoelectronic pairs, are closely related to atomic core-electron binding energies obtained from X-ray photoelectron spectra. It is shown that carbon 1s electron binding energies for a variety of carbon compounds correlate reasonably well with the estimated differences in dissociation energies for the carbon compounds and the corresponding isoelectronic nitrogen-containing cations.

Introduction

It has been shown that, when a core electron is removed from an atom in a molecule or ion, the valence electrons adjust as if the nucleur charge of the atom had increased by one unit.[1] Thus a core-electron binding energy is closely related to the energy difference between the species containing the atom and that of the isoelectronic species containing the atom of one higher atomic number. Unfortunately the energy data required for the correlation of binding energies are not always available. Therefore there is a need for a method for estimating the energy differences for pairs of isoelectronic species. The purpose of this research was to devise such a method and to apply it to the correlation of core-electron binding energies.

Differences in energy between pairs of species can be expressed in various ways, which differ in the arbitrary choice of the energy reference level. For example, both differences in the heats of formation from the elements in their standard states and differeneces in the energies of dissociation to atoms are acceptable, although different, measures of the energy differences. We have chosen to estimate differences in the dissociation energies of pairs of isostructural isoelectronic species. For simplicity we have restricted ourselves to gaseous species.

A Method for Estimating Differences in Dissociation Energies

A generalized Definition of Dissociation Energy. - We shall be concerned with pairs of isoelectronic species in which one species differs from the other only by having one of its atoms (the "transmutable" atom) possess an atomic number that differs by ± 1 from that of the corresponding transmutable atom of the other species. (Examples of such pairs are NO_2^-/O_3 and CH_4/NH_4^+). In such pairs of isoelectronic species, at least one species must be an ion. This fact immediately poses a problem that apparently has not previously been resolved - i.e., how do we define the dissociation energy of an ion? When we break the bonds of an ionic species, there is ambiguity in the choice of products. For example, consider the nitrosyl ion, NO^+. We might dissociate this species in either of the following ways.

$$NO^+ \rightarrow N^+ + O$$

$$NO^+ \rightarrow N + O^+$$

We have adopted the following arbitrary (and yet somewhat logical) rule for choosing the atoms and/or monatomic ions into which a species is dissociated: <u>In the dissociation process, the bonding electrons of each bond are divided equally between the atoms of the bond</u>. This procedure is equivalent to dissociation into atoms which bear charges equal to the formal charges[2] of the atoms in the species. Thus we dissociate NO^+ as follows:

$$N\equiv O^+ \rightarrow N + O^+$$

It is interesting to note that, by following the above rule in the case of neutral molecules, we do not always dissociate the molecules in the traditional manner. Thus we dissociate carbon monoxide as shown:

$$^{-}C\equiv O^{+} \rightarrow C^{-} + O^{+}$$

The main justification for this novel method of breaking bonds is the success of its application, to be discussed.

Because we are concerned with differences in dissociation energies, we are concerned only with the energies of the bonds to the transmutable atoms. Thus, for the isoelectronic pair $CH_3CO_2^-/CH_3NO_2$, it is not necessary to be concerned with the C-H bonds; it is sufficient to estimate the energies of the following processes

$$CH_3CO_2^- \rightarrow CH_3 + C + O + O^-$$

$$CH_3NO_2 \rightarrow CH_3 + N^+ + O + O^-$$

The Derivation and Testing of the Method. - Pauling has shown that the energy of a single bond between different atoms may be evaluated as the sum of a covalent contribution and an ionic contribution.[3] The present method for estimating differences in dissociation energies is based on the hypothesis (reached by trial and error) that the covalent contributions to the bonds in a species are equal to those in any isoelectronic species. That is, we equate a difference in dissociation energy to the difference in the sum of the ionic contributions to the bonds. We estimate these contributions using Pauling's relation, involving the electronegativities of the bonded atoms:

$$\Delta E(\text{kcal/mole}) = 23(x_A - x_B)^2 \qquad (1)$$

However, in order to apply equation 1, it is necessary to decide what electronegativities to use for formally-charged atoms. Pauling has suggested[4] that the electronegativity of an atom with a +1 formal charge should be increased by two-thirds of the difference in electronegativity between the atom and the next atom in the periodic table and that the electronegativity of the atom with a -1 formal charge should be similarly decreased. We have found that such adjusted electronegativities may be applied to bond energies, but trial has shown that a factor of one-half works better than two-thirds. The electronegativities that we used are presented in Table I. Most of the values for the neutral atoms are those calculated by Johnson[5] from modern thermodynamic data. The methods used for evaluating the electronegativities of Be, B and F^+ are discussed in Appendix I.

Equation 1 was derived for (and the electronegativities were calculated from data for) molecules with single bonds. Nevertheless we have applied the equation without correction to isoelectronic species having double bonds, triple bonds, and delocalized π bonds. An attempt to account for the extra dissociation energy of bonds having an order greater than one by introducing a multiplicative factor $1 + \underline{c}(\underline{n} - 1)$ (where $\underline{c}$ is a constant and $\underline{n}$ is the bond order) gave no significant improvement in the estimated differences in dissociation energy. We take this result as an indication that the π bond energy is approximately the same in isoelectronic multiply-bonded species.

Table I. Electronegativities Used for the Calculation of Dissociation Energies

Atom	Electronegativity, $(eV)^{1/2}$
H	2.20
Be	1.76
B^-	1.98
B	2.20
C^-	2.33
C	2.45
C^+, N^-	2.80
N	3.15
N^+, O^-	3.40
O	3.65
O^+, F^-	3.82
F	4.00
F^+	4.25
Si	1.95
P	2.20
P^+, S^-	2.47
S	2.75
S^+	3.00
Cl	3.25
Se^-	2.37
Br	3.05

We have observed that a bond energy is enhanced by 242 kcal/mole, on the average, when the atoms have opposite unit formal charges and that it is diminished by that amount when the atoms have the same unit formal charge. For formal charges separated by an intervening atom, we reduce this energy to one-half of 242 kcal/mole,[6] and for adjacent formal charges of ± 1/2, we reduce the energy to one-quarter of 242 kcal/mole.

By applying the rules and empirical observations which we have discussed, we obtain the following equations for estimating the difference[7] in dissociation energy, Δ, for an isoelectronic pair of species.

$$\Delta(\text{kcal/mole}) = \sum_i \Big[23(x_A^2 - x_B^2) + 46(x_B - x_A)x_i\Big] + 242 \sum_j \Big[1/(1 + k)\Big]C_j \qquad (2)$$

$$\Delta(\text{eV}) = \sum_i \Big[(x_A^2 - x_B^2) + 2(x_B - x_A)x_i\Big] + 10.5 \sum \Big[1/(1 + k)\Big] C_j \qquad (3)$$

Here x_A and x_B are the electronegativities of the transmutable atoms A and B (the atomic number of atom A is one less than that of atom B), x_i is the electronegativity of an atom directly bonded to atom A (or B), and C_j is the formal charge of an atom separated by k atoms from A (or B). The sum $\sum_i$ is carried out over the i atoms directly bonded to atom A (or B), and the sum $\sum_j$ is carried out over all the atoms in the species, except atom A (or B).

In Table II, experimental Δ values and Δ values calculated from equation 2 are tabulated for 31 pairs of isoelectronic species. The data are plotted in Figure 1. The fact that the species are almost entirely compounds of elements of the first row of the periodic table is simply a consequence of the availability of relatively accurate data for such species. The fifth column of Table II gives the weights assigned to

Table II. Experimental and Calculated Values of Δ, kcal/mole.

Pair No.	Isoelectronic Pair	Δ_{exp}	Δ_{calc}	wt.
1	BH_4^-/CH_4	- 38	- 2	
2	CH_4/NH_4^+	-117	-126	
3	SiH_4/PH_4^+	- 45	- 1	
4	BF_4^-/CF_4	142	154	
5	CF_4/NF_4^+	189	188	
6	CH_3^-/NH_3	10	- 61	
7	$C_6H_5CH_2^-/C_6H_5NH_2$	25	- 52	
8	NH_3/OH_3^+	-110	-119	
9	PH_3/SH_3^+	- 35	- 45	
10	BH_3/CH_3^+	- 56	- 25	
11	CH_3/NH_3^+	- 88	- 96	
12	NH_2^-/H_2O	- 12	- 80	
13	OH^-/HF	- 25	- 42	
14	HS^-/HCl	- 13	- 24	
15	HSe^-/HBr	- 26	- 16	
16	CO/NO^+	290	283	3
17	C_2^{2-}/CN^-	-198	-258	1
18	CN^-/N_2	11	16	
19	HCN/HCO^+	- 67	- 32	
20	CH_3CN/CH_3CO^+	-104	- 32	
21	BH_3CO/CH_3CO^+	163	125	2
22	CO_2/NO_2^+	78	63	

Table II. (continued)

Pair No.	Isoelectronic Pair	Δ_{exp}	Δ_{calc}	wt.
23	N_2O/NO_2^+	261	240	3
24	OCN^-/N_2O	-194	-211	1
25	N_3^-/N_2O	88	137	1
26	NO_2^-/O_3	-187	-243	1
27	ONF/NF_2^+	- 65	- 22	
28	BF_3/CF_3^+	347	363	3
29	COF_2/CF_3^+	- 88	- 41	
30	CO_3^{2-}/NO_3^-	-322	-411	1
31	$CH_3CO_2^-/CH_3NO_2$	-185	-210	1
32	HCO_3^-/HNO_3	-132	-158	1
33	NO_3^-/NO_2F	69	113	1
34	NO_2F/NOF_2^+	253	234	3
35	NF_2/OF_2^+	202	170	3
36	CN/N_2^+	130	139	2
37	C_2/CN^+	- 46	- 21	
38	NO^-/O_2	60	17	
39	O_2^-/OF	-135	-129	
40	$C_6H_5^-/C_5H_5N$	34	- 22	

the experimental values of Δ in the empirical evaluation of the average energy of the formal charge interaction. The average deviation between the Δ_{exp} and Δ_{calc} values is ±31 kcal/mole. It is believed that many of the discrepancies can be ascribed to inaccuracies in the experimental heats of formation. The heats of formation of most of the anions are based on calculated lattice energies (which are notoriously inaccurate), and the heats of formation of most of the cations are based on ionization potentials (which often have uncertainties of more than 1 eV). We believe that, in view of the uncertainties in the experimental data, it will be difficult to devise a more precise method for calculating Δ values. The sources of the thermodynamic data used in calculating the Δ_{exp} values and examples of the methods of calculating the Δ_{calc} values are given in Appendices II and III, respectively.

The Correlation of Carbon 1s Binding Energies

Equations 2 and 3 are valid for the calculation of Δ only when the transmutable atoms and the atoms to which they are directly bonded have formal charges from ~~of~~ -1, to ~~0, or~~ +1. Therefore Δ_{calc} values can be used to correlate core-electron binding energies only for atoms with formal charges from ~~of~~ -1 ~~and~~ to 0. The only element for which binding energies are known for a reasonably wide selection of compounds wherein the formal charges are in the latter range ~~of the atom is -1 or 0~~ is carbon. In Figure 2 we have plotted carbon 1s binding energies (taken from the data of Nordberg *et al.*[8a], Davis *et al.*,[8b] and Thomas[8c]). *vs.* Δ_{calc} values. The points define a straight line of unit slope.

It should be noted that Δ values are not the same as the E_T values ("thermochemical energies") that we have previously used to correlate binding energies, although, for compounds of a given element, these quantities only differ by a constant amount - viz., the energy corresponding to the different standard states of the elements. In the case of carbon compounds, E_T values are greater than Δ values by 277 kcal/mole, the energy of the following reaction.

$$1/2\ N_2(g) + C(g) \rightarrow N^+(g) + e^-(g) + C(s).$$

The observed linear correlation of the carbon binding energies with the Δ_{calc} values can be explained as follows. The binding energy of gaseous methane is the energy of the following process.

$$CH_4 \rightarrow CH_4^{+*} + e^- \qquad (4)$$

(The asterisk indicates a 1s electron vacancy in the carbon atom.) According to the principle that the chemical behavior of an atomic core is essentially unchanged after the capture of one of its electrons by the nucleus,[1] the following reaction should have $\Delta E = 0$.[9]

$$CH_4^{+*} + N^{5+} \rightarrow NH_4^+ + C^{5+} \qquad (5)$$

Thus the following reaction (the sum of reactions 4 and 5) should still have an energy equal to the binding energy.[10]

$$CH_4 + N^{5+} \rightarrow NH_4^+ + C^{5+} + e^- \qquad (6)$$

We can write similar reactions for the binding energies of other carbon compounds; thus for carbon dioxide we write[10]

$$CO_2 + N^{5+} \rightarrow NO_2^{\ +} + C^{5+} + e^- \qquad (7)$$

The values of Δ for methane and carbon dioxide correspond to the energies of the following processes.

$$CH_4 + N^+ \rightarrow NH_4^{\ +} + C \qquad (8)$$

$$CO_2 + N^+ \rightarrow NO_2^{\ +} + C \qquad (9)$$

It will be noted that reaction 9 minus reaction 8 is the same as reaction 7 minus reaction 6:

$$CO_2 + NH_4^{\ +} \rightarrow NO_2^{\ +} + CH_4$$

Therefore the difference in the Δ values should equal the difference in the binding energies. The same is true for any two carbon compounds, and thus the straight line of unit slope in Figure 2 is explained.

The scatter of the points in Figure 2 is no worse than the scatter in plots of binding energy vs. atomic charge, which also show a linear correlation.[8a,11-13] The fact that binding energy is linearly related to both Δ and atomic charge indicates that Δ and atomic charge must be at least approximately linearly related. This can be shown by comparing equation 2 or 3 with an equation which has been used for calculating atomic charge from electronegativities. In the case of carbon compounds which have no formally-charged atoms, equation 3 reduces to

$$\Delta(\mathrm{eV}) = \Sigma \left[1.9x_i - 5.55\right] \qquad (10)$$

For the same compounds, the atomic charge q can be calculated, according to a procedure due to Pauling,[3,11] by the equation

$$q = \sum\left[1 - e^{-0.25(x_i - 2.5)^2}\right] \tag{11}$$

The sign of the quantity in brackets is determined by the sign of the quantity $x_i - 2.5$. Now in the practical range $1.0 < x_i < 4.0$, the function in brackets is well approximated by the linear function $0.27(x_i - 2.5)$; thus we write

$$q \approx \sum\left[0.27(x_i - 2.5)\right] = \sum\left[0.27x_i - 0.67\right] \tag{12}$$

From equations 10 and 12 it can easily be shown that Δ and q are linearly related:

$$\Delta(\mathrm{eV}) \approx 7.04q - 0.83$$

It should not be concluded from this result that atomic charge is as fundamentally significant a function as Δ (or E_T, the "thermochemical energy"[1]) for correlating core-electron binding energies. It must be remembered that equations 10 and 12 yield very crude approximations for Δ and q, respectively, and that even if Δ and q could be evaluated with high accuracy for a series of compounds, there are theoretical reasons for doubting that either function would correlate perfectly with core-electron binding energies. Thus a correlation with Δ depends on the validity of the approximation that atomic cores of equal charge are chemically equivalent--an approximation that needs thorough testing.

A correlation with q depends on the approximation that the charges of other atoms in the molecule do not influence the binding energy and that the net increase in q after loss of the core electron is independent of the molecular structure.

From the form of equation 10, it is clear that we should expect core binding energies to be equal to an additive function of parameters characteristic of the atoms directly bonded to the atom from which the core electron is ejected. Rather than relying on electronegativities to evaluate these parameters, it is possible to evaluate them empirically by a least-squares treatment of the binding energy data. This was done using the carbon 1s binding energies of Figure 2.[14] The data may be represented by the equation

$$E_B = \sum_i p_i \tag{13}$$

The values of p for the elements follow: H, -0.15; C, 0.55; N, 1.00; O, 2.21; F, 2.84; S, 1.04; Cl, 1.52; Br, 1.33. The binding energies are plotted vs. $\sum_i p_i$ in Figure 3; it can be seen that the correlation is somewhat improved. Probably an empirical treatment of this type, using equation 13, could be used to correlate the binding energies of other elements. An obvious refinement of the method would be to use parameters which are a function of the atoms not directly bonded to the atom which loses the core electron. That is, parameters could be evaluated for groups of atoms.

Appendices

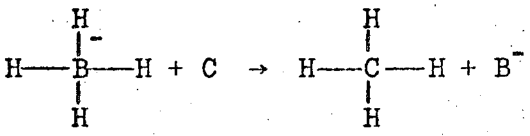
Appendix I. - The electronegativity of beryllium was calculated from the Be-F and Be-Cl bond energies. From the heats of formation of $BeF_2(g)$ (-192.1 kcal/mole),[15] Be(g) (77.9 kcal/mole),[16] and F(g) (18.3 kcal/mole),[3] we calculate E(Be-F) = 153 kcal/mole. From the heats of formation of $BeCl_2(g)$ (-84 kcal/mole)[15] and Cl(g) (29.0 kcal/mole)[3] we calculate E(Be-Cl) = 110 kcal $mole^{-1}$. By interpolation between the values of E(Li-Li) = 26 kcal/mole[3] and E(B-B) = 79 kcal/mole[17], we estimate E(Be-Be) = 52 kcal/mole. By use of the equation $E(A-B) = [E(A-A)\cdot E(B-B)]^{1/2} + 23(x_A - x_B)^2$, the above data yield the values 1.70 and 1.82 for the electronegativity of beryllium; we use the average value, 1.76.

The electronegativity of boron was calculated from the B-H bond energy in BH_3. The latter molecule is one of the few boron compounds not complicated by 3-center bonding and in which the boron has no formal charge. The data, which lead to the electronegativity value 2.20, are the energy of dissociation of diborane into BH_3 groups (ca 36 kcal/mole)[18], ΔH_f° [B(g)] = 135 kcal/mole[16], ΔH_f° [$B_2H_6(g)$] = 5 kcal/mole[19], ΔH_f° [H(g)] = 52.1 kcal/mole[3] and E(B-B) = 79 kcal/mole[17].

The electronegativity of F^+ (4.25) was extrapolated from the electronegativity values for the other first-row elements.

Appendix II. - The heats of formation of monatomic gases were taken from Brewer[16] and Pauling[3]. The following electron affinities were used: EA(B) = 7 kcal/mole[20], EA(C) = 29 kcal/mole[21], EA(N) = - 8 kcal/mole[22], EA(O) = 33.8 kcal/mole[24], EA(S) = 48 kcal/mole[25], and EA(Se) = 49 kcal/mole.[26] Unless otherwise stated, heats of formation of gaseous molecules were taken from Bureau of Standards publications,[27] heats of formation of gaseous cations were obtained by combining the former heats with ionization potentials from Kiser,[28] and the heats of formation of gaseous anions were taken from Waddington.[29] Heats of formation obtained from other sources are given in the following list (the values are in kcal/mole): CF_4(-221)[30], NH_4^+(142)[5], NF_4^+(245)[31], OH_3^+(140)[32,33], CN^-(18)[34], HCO^+(225)[28,30], CH_3CO^+(178)[30], BH_3CO(-28.5)[19,35], NO_2^-(-40)[34], ONF(-16)[30], NF_2^+(280)[37], CF_3^+(119)[28,30], COF_2(-153)[30], CO_3^{2-}(-35)[36], NO_3^-(-81)[29], $CH_3CO_2^-$(-114)[36], HCO_3^-(-177)[36], NO_2F(-19)[30], NOF_2^+(228)[37], NF_2(10)[30], OF_2^+(312)[28,30], CN(105.5)[34], CN^+(430)[34], BH_3(20.5)[18,19], CH_3^+(261)[28,30], SH_3^+(191)[33], CH_3(34)[30], PH_4^+(175)[38], CH_3^-(8)[39,40], $C_6H_5CH_2^-$(24)[39,41], $C_6H_5^-$(29)[39,41], HS^-(-20)[25,30], HSe^-(-5)[42], NO^-(1)[25,27], O_2^-(-10)[25], OF(32)[43], C_5H_5N(34)[44], OH(-33)[25,30]. (By convention, ΔH_f° for the gaseous electron is taken as zero).

Appendix III. - For the isoelectronic pair BH_4^-/CH_4, Δ is the energy of the reaction



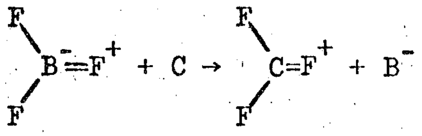
$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{B^-}}}}-H + C \rightarrow H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H + B^-$$

Using equation 2, we calculate

$$\Delta = 4[23(1.98^2 - 2.45^2) + 46(2.45 - 1.98)(2.20)]$$

$$= -2 \text{ kcal/mole.}$$

For the isoelectronic pair BF_3/CF_3^+, Δ is the energy of the reaction

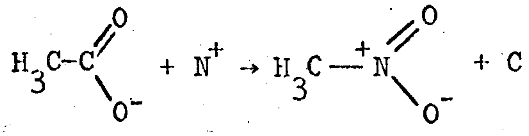


For these and all other resonating species, we write only single valence bond structures. Using equation 2, we calculate

$$\Delta = 3(23)(1.98^2 - 2.45^2) + 46(2.45 - 1.98)\ [4.25 + 2(4.00)] + 242(+1)$$

$$= 363 \text{ kcal/mole.}$$

For the isoelectronic pair $CH_3CO_2^-/CH_3NO_2$, Δ is the energy of the reaction

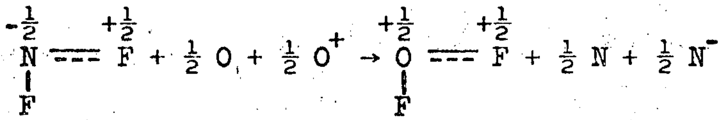


Using equation 2, we calculate

$$\Delta = 3(23)(2.45^2 - 3.40^2) + 46(3.40 - 2.45)(2.45 + 3.40 + 3.65) + 242(-1)$$

$$= -210 \text{ kcal/mole.}$$

For the isoelectronic pair NF_2/OF_2^+, Δ is the energy of the reaction[45]



$$\underset{\displaystyle F}{\overset{-\frac{1}{2}}{N}} \overset{\text{———}}{\text{- - -}} \overset{+\frac{1}{2}}{F} + \tfrac{1}{2}\,O + \tfrac{1}{2}\,O^+ \rightarrow \underset{\displaystyle F}{\overset{+\frac{1}{2}}{O}} \overset{\text{———}}{\text{- - -}} \overset{+\frac{1}{2}}{F} + \tfrac{1}{2}\,N + \tfrac{1}{2}\,N^-$$

By interpolating in Table I for the electronegativities of $N^{-\frac{1}{2}}$, $O^{+\frac{1}{2}}$, and $F^{+\frac{1}{2}}$, and by using equation 2, we calculate

$$\Delta = 2(23)(2.97^2 - 3.73^2) + 46(3.73 - 2.97)(4.12 + 4.00) + 242(+\tfrac{1}{2})$$

$$= 170 \text{ kcal/mole.}$$

For the isoelectronic pair BH_3CO/CH_3CO^+, Δ is the energy of the reaction

$$H_3B^-\text{—}C\equiv O^+ + C \rightarrow H_3C\text{-}C\equiv O^+ + B^-$$

Using equation 2, we calculate

$$\Delta = 4(23)(1.98^2 - 2.45^2) + 46(2.45 - 1.98)[3(2.20) + 2.45] + 242(\tfrac{1}{2})(+1)$$

$$= 125 \text{ kcal/mole.}$$

References

(1) W. L. Jolly and D. N. Hendrickson, J. Am. Chem. Soc., 92, 0000(1970).

(2) Formal charges have their usual meaning only when we have assigned bonds such that each atom (except hydrogen) has, as far as possible, achieved a complete octet of electrons and no more. Formal charges are calculated by assuming that bonding electrons are shared equally by the bonded atoms.

(3) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, Ithaca, N. Y. 1960.

(4) Reference 3, 2nd ed., 1940, pp. 65-66.

(5) D. A. Johnson, "Some Thermodynamic Aspects of Inorganic Chemistry," Cambridge Univ. Press, 1968.

(6) We have used this factor for molecules of various shapes even though it is strictly valid only for a linear array of atoms; the experimental data are too inaccurate to justify the use of a factor which varies with bond angle.

(7) We define Δ as the dissociation energy of the lower atomic number species less that of the higher atomic number species.

(8) (a) R. Nordberg, U. Gelius, P. F. Hedén, J. Hedman, C. Nordling, K. Siegbahn and B. J. Lindberg, paper in Ph. D. dissertation of R. Nordberg, University of Uppsala, 1968; (b) D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas, Lawrence Radiation Laboratory Report UCRL-19515, November, 1969; (c) T. D. Thomas, unpublished results.

(9) This ΔE is probably not exactly zero, and in fact it is unnecessary to assume that it is zero. It is merely necessary to assume that ΔE is constant for all such reactions of carbon and nitrogen compounds so that it will cancel out when energy differences (E_B shifts) are calculated.

(10) As indicated in footnote 9, the energies of reactions 6 and 7 may differ from the binding energies of CH_4 and CO_2, respectively, by a constant which cancels out when the difference in these energies is calculated.

(11) R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Arkiv Kemi*, **28**, 257 (1967).

(12) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johanssen, T. Bergmark, S. Karlsson, I. Lindgren, and B. Lindberg, "ESCA; Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells, Uppsala, 1967.

(13) J. M. Hollander, D. N. Hendrickson and W. L. Jolly, *J. Chem. Phys.*, **49**, 3315 (1968).

(14) Credit is due Leonardo Prizant for carrying out the least-squares treatment.

(15) G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, "Thermodynamics," 2nd ed., McGraw-Hill Book Co., Inc., New York, 1961, p. 683.

(16) L. Brewer, *Science*, **161**, 115 (1968).

(17) S. R. Gunn, L. G. Green and A. I. Von Egidy, *J. Phys. Chem.*, **63**, 1787 (1959).

(18) M. E. Garabedian and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 176 (1964).

(19) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

(20) E. Clementi and A. D. McLean, *Phys. Rev.*, **133**, A419 (1964).

(21) M. L. Selman and L. M. Branscomb, Phys. Rev., 125, 1602 (1962).

(22) We use the average of the values calculated by Clementi and McLean[20] and Öksüz and Sinanoğlu.[23]

(23) I. Öksüz and O. Sinanoğlu, Phys. Rev., 181, 54 (1969).

(24) L. M. Branscomb, D. S. Burch, S. J. Smith and S. Geltman, Phys. Rev., 111, 504 (1958).

(25) R. S. Berry, Chem. Revs., 69, 533 (1969).

(26) R. J. Zollweg, J. Chem. Phys., 50, 4251 (1969).

(27) U. S. National Bureau of Standards Technical Notes 270-1 and 270-2, Gov. Printing Off., Washington, 1965 and 1966; Circular 500, Gov. Printing Off., Washington, 1952.

(28) R. W. Kiser, "Introduction to Mass Spectrometry and its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965.

(29) T. C. Waddington, Adv. Inorg. Chem. and Radiochem., 1, 157 (1959).

(30) S. W. Benson, J. Chem. Education, 42, 502 (1965).

(31) J. N. Wilson, Adv. Chem. Ser., 54, 30 (1965); Chem. Abstr., 65, 4732e.

(32) F. W. Lampe and F. H. Field, Tetrahedron, 7, 189 (1959); also see D. M Bishop, J. Chem. Phys., 43, 4453 (1965).

(33) M. A. Haney and J. L. Franklin, J. Chem. Phys., 50, 2028 (1969).

(34) J. Berkowitz, W. A. Chupka, and T. A. Walter, J. Chem. Phys., 50, 1497 (1969).

(35) A. B. Burg, J. Am. Chem. Soc., 74, 3482 (1952).

(36) M. F. C. Ladd and W. H. Lee, Prog. Solid State Chem., 37 (1964).

(37) V. H. Dibeler and J. A. Walker, Inorg. Chem., 8, 1728 (1969).

(38) T. C. Waddington, Trans. Faraday Soc., 61, 2652 (1965).

(39) D. M. Golden and S. W. Benson, Chem. Revs., 69, 125 (1969).

(40) F. M. Page, Adv. Chem. Series, 36, 68 (1962).

(41) Gaines and F. M. Page, Trans. Faraday Soc., 59, 1266 (1963).

(42) K. B. Yatsimirsky, *J. Gen. Chem. USSR*, *26*, 2655 (1956).

(43) Joint Army-Navy-Air Force JANAF Thermochemical Tables.

(44) K. Li, *J. Phys. Chem.*, *61*, 782 (1957).

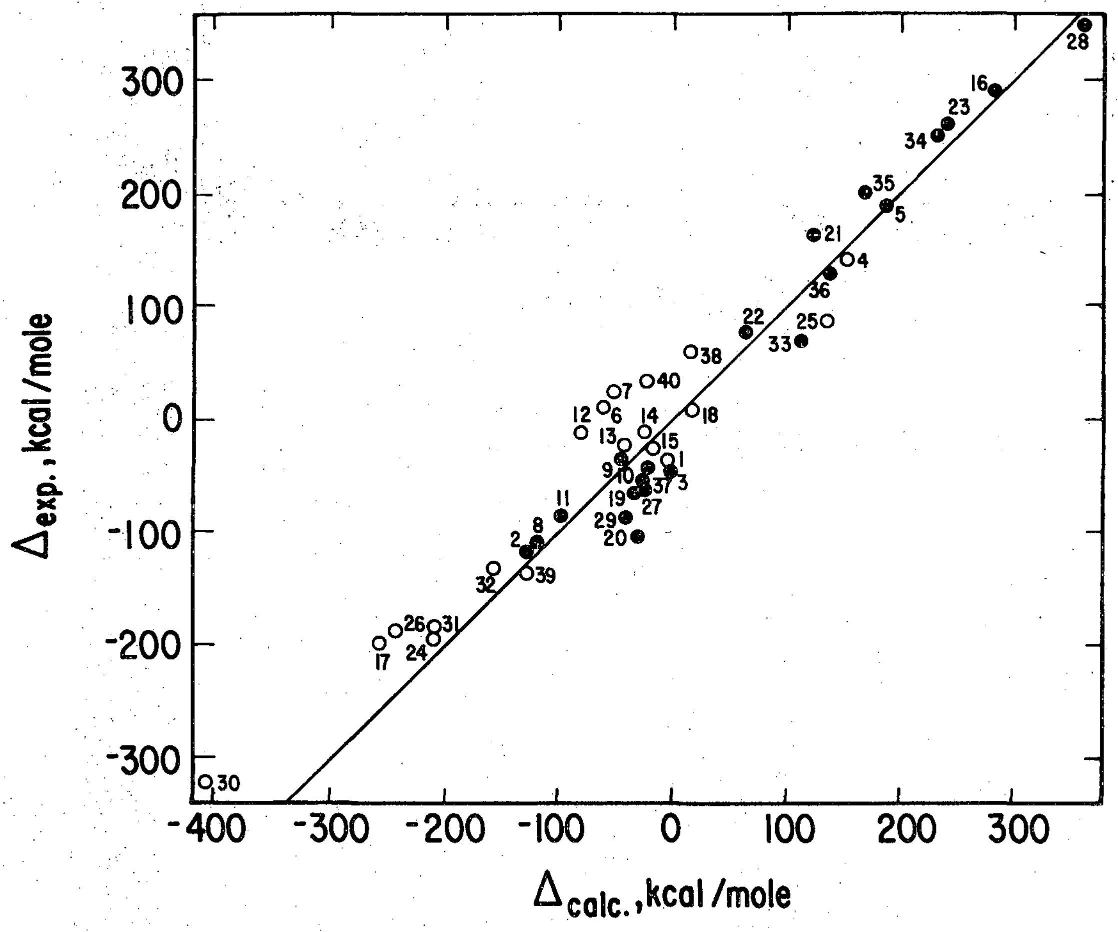
(45) For a method for writing structures for radicals consistent with the octet rule, see J. W. Linnett, "The Electronic Structure of Molecules," Methuen & Co., Ltd., London, 1964.

Figure Captions

Figure 1. Plot of experimental Δ values *vs*. calculated Δ values. Numbers refer to the isoelectronic pairs listed in Table II. Open circles correspond to anion/neutral molecule pairs; solid circles correspond to neutral molecule/cation pairs. The straight line has been drawn through the origin with a slope of unity.

Figure 2. Plot of carbon 1*s* binding energies (relative to methane) *vs*. calculated Δ values. Numbers refer to the following compounds: 1, C_6H_6; 2, C_2H_6; 3, C_2H_4; 4, CH_4; 5, C_2H_2; 6, $CH_3\underset{\sim}{C}H_2NH_2$; 7, CH_3Br; 8, $CH_3\underset{\sim}{C}H_2Cl$; 9, $H\underset{\sim}{C}=N-CH=N-NH$; 10, $CH_3\underset{\sim}{C}H_2OH$; 11, CH_3Cl; 12, CH_3OH; 13, $CH_3\underset{\sim}{C}H_2O(CO)CH_3$; 14, CS_2; 15, CH_2Br_2; 16, HCN; 17, $SC(NH_2)_2$; 18, CH_3F; 19, OCH_2; 20, $(CH_3\underset{\sim}{C}HO)_3$; 21, $O\underset{\sim}{C}(CH_3)_2$; 22, CH_2Cl_2; 23, C_6O_6; 24, C_6F_6; 25, $OC(NH_2)_2$; 26, $CHCl_3$; 27, $CH_3\underset{\sim}{C}OOH$; 28, $H\underset{\sim}{C}(OCH_3)_3$; 29, CCl_4; 30, $O\underset{\sim}{C}(OEt)Cl$; 31, $O\underset{\sim}{C}(OCH_3)_2$; 32, CO_2; 33, $Cl_2F\underset{\sim}{C}CClF_2$; 34, $ClF_2\underset{\sim}{C}CCl_2F$; 35, $F_3\underset{\sim}{C}(CO)CH_3$; 36, CHF_3; 37, OCF_2; 38, CF_4. Data from ref. 8a except for compounds 2, 3, 5, 12, 16, 18, 32, 36, and 38 (ref. 8b), and compounds 1, 7, 11, 22, 26, and 29 (ref. 8c).

Figure 3. Plot of carbon 1*s* binding energies (relative to methane) *vs*. $\sum_i p_i$. Significance of numbers indicated in caption of Fig. 2.



XBL 6910-5916

Fig. 1

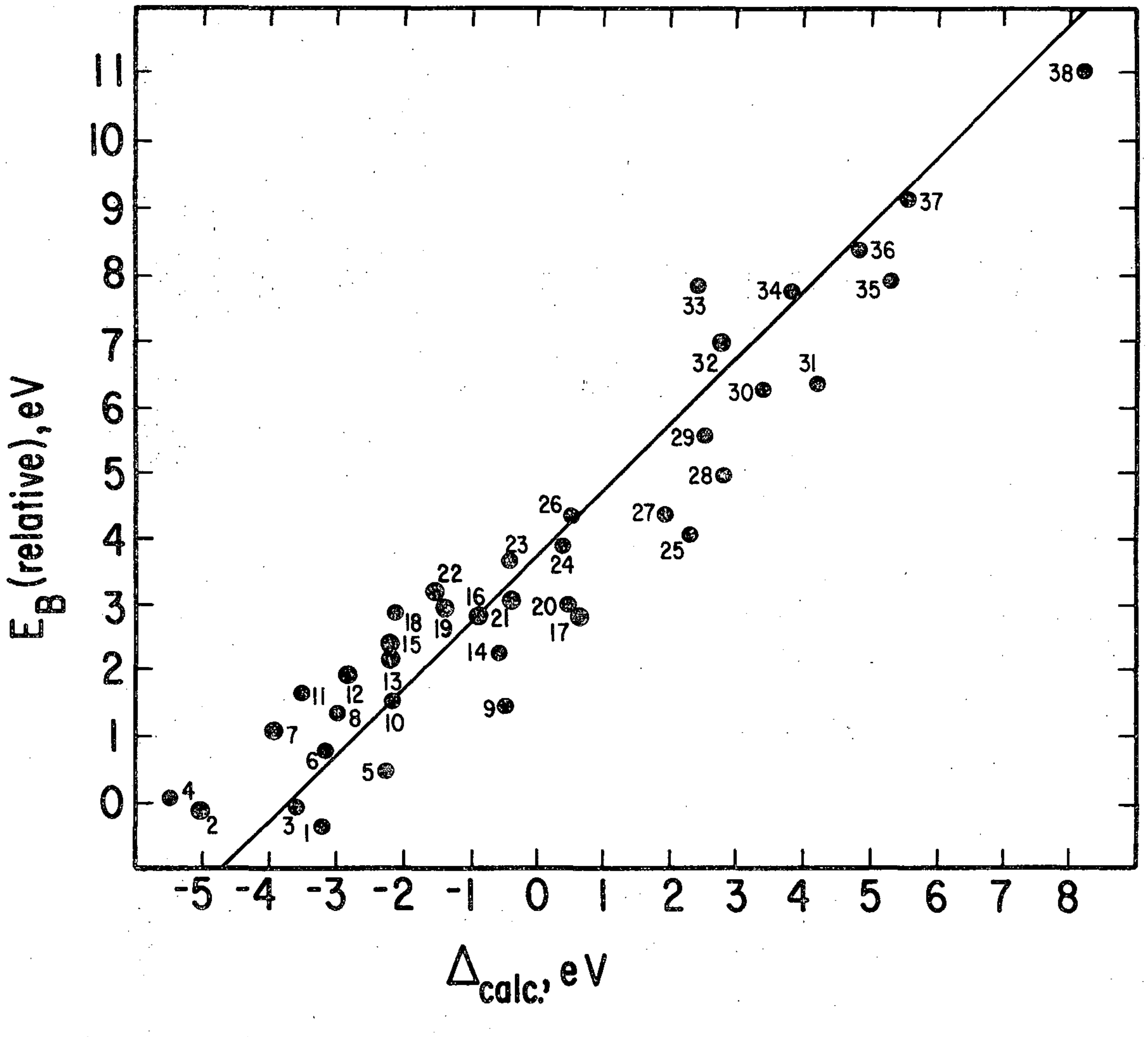


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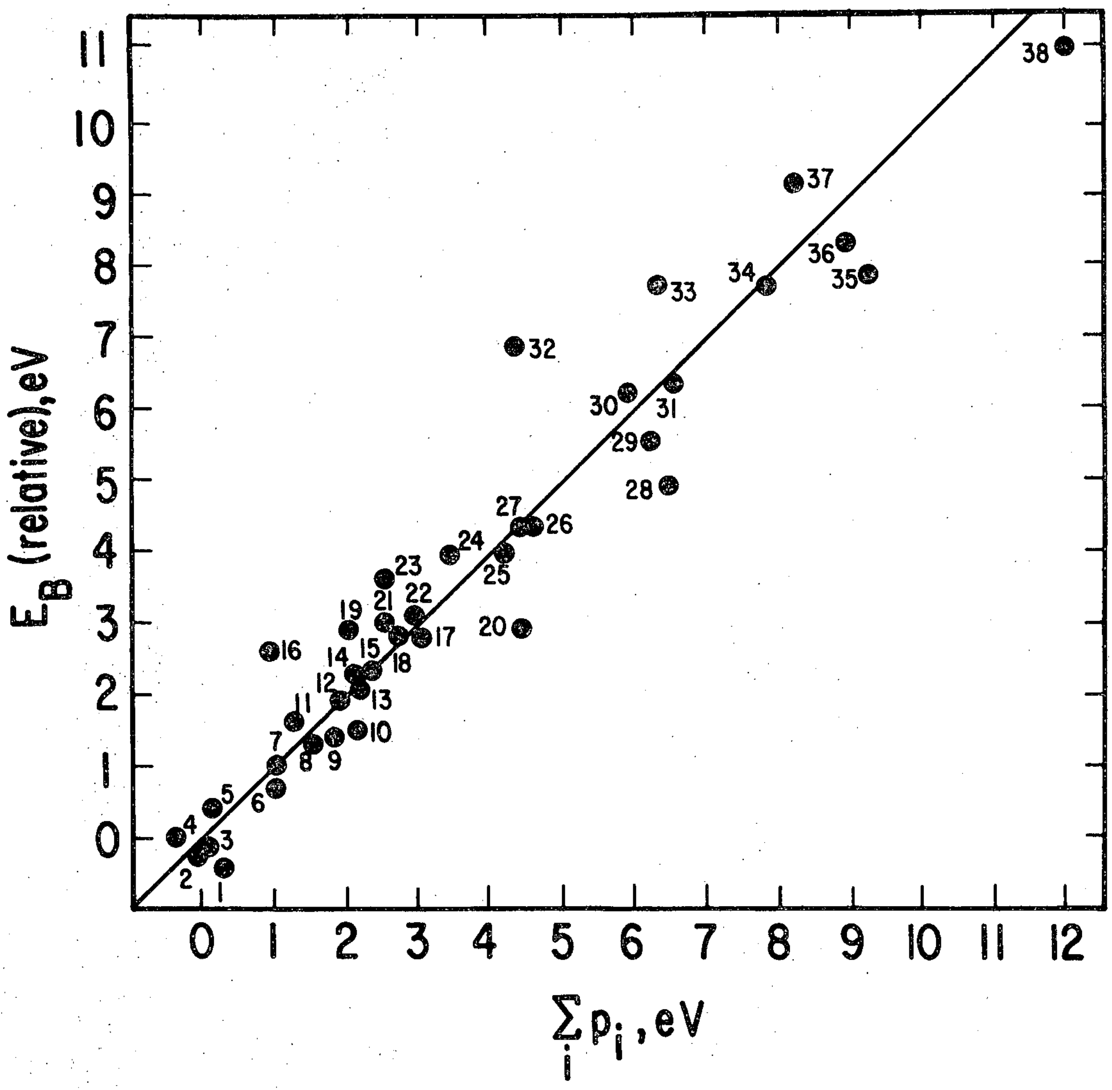
Fig. 2



XBL 6910-5914

Fig. 3

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