TABLE IV
EXPERIMENTAL AND CALCULATED DISSOCIATION HEATS FOR ADDUCTS EXPECTED TO BE ABNORMALLY WEAK

Acid	Base	ΔH, kcal/mol Exptl	ΔH, kcal/mol Calcd	Ref[a]
F^+	F^-	356	431.7	
OH^+	OH^-	311	341.5	
OH^+	NH_2^-	333	362.2	*b*
NO^+	F^-	185	175.4	*c*
NO^+	OH^-	220	200.0	*c*
H^+	H^-	399	410.0	
NO_2^+	NO_2^-	148	182.2	*b*

[a] See footnote *b*, Table III. [b] See ref *d* and *g*, Table III. [c] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat Bur. Stand.* (*U. S.*), *Tech. Note*, **No. 270-3** (1968).

bases and the rows to various acids) of dissociation heats which can be correlated by eq 1 has the property that all minor determinants of order greater than 2 are zero. This property affords a very convenient method for quickly determining whether or not a given matrix of heats can be satisfactorily correlated by eq 1.

All the parameters in Tables I and II are positive except the E_A value for atomic oxygen. Two questions arise regarding this fact. (1) By a suitable choice of the arbitrarily fixed parameters, can all the parameters be made positive? (2) What is the significance of a negative parameter? It can be shown that, for our set of parameters, the answer to the first question is no. An infinite number of sets of parameters giving an equally good fit can be derived by application of the transformation equations

$$E_A' = aE_A + bC_A$$
$$C_A' = cE_A + dC_A$$
$$E_B' = (dE_B - cC_B)[1/(ad - bc)]$$
$$C_B' = (aC_B - bE_B)[1/(ad - bc)]$$

where $ad - bc \neq 0$. If we specify that $E_A' > 0$, $E_B' > 0$, $C_A' > 0$, and $C_B' > 0$ for all the species in the set and that $E_A < 0$ for one particular acid, it can be shown that one of the following two relations must hold for the species

$$\frac{C_B}{E_B} > -\frac{E_A}{C_A}$$
$$\frac{C_A(X)}{|E_A(X)|} > \frac{E_B}{C_B}$$

where $C_A(X)$ and $E_A(X)$ refer to the particular acid. If neither of these relations holds for all the species, the parameters cannot all be positive. Such is the case for our data.

The second question, regarding the significance of the negative parameters, is more difficult to answer. A negative E_A value probably is acceptable whenever it is to be combined with a positive E_B value, but we doubt that combination of a negative E_A value with a negative E_B value is meaningful. Probably it is impossible to apply eq 1 to both ion–ion and neutral–neutral acid–base adducts with a common set of parameters. This limitation of eq 1 may be a consequence of the fact that in ion–ion adducts the ionic contribution to bonding is a "no-bond" contribution (*e.g.*, Na^+Cl^-) and the nonionic contribution is covalent (*e.g.*, Na–Cl), whereas in neutral–neutral adducts the ionic contribution is covalent (*e.g.*, $H_3N^+{-}B^-Cl_3$) and the nonionic contribution is a "no-bond" contribution (*e.g.*, $H_3N\ BCl_3$).

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E and *C* Parameters for Ionic Interactions

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In this article we report an extension of our *E* and *C* equation, used to correlate enthalpies of interaction of neutral acids and bases to ionic Lewis acid–base reactions of the type $M^+(g) + X^-(g) \rightarrow MX(g)$. E_A, E_B, C_A, and C_B parameters are reported for the ions and the trends in these values are reasonable in terms of the earlier qualitative suggestions of the meaning of these parameters. In some instances, new insights into the important factors affecting bond energies are provided. The C_AC_B products give reasonable estimates of the covalent bond energy contributions to the M–X bond. Parameters are evaluated from 93 enthalpies and can be used to predict and correlate the enthalpies for over 180 interactions. Deviations between predicted and calculated enthalpies are observed for systems with substantial contributions to the measured enthalpies from lone pair–lone pair repulsions or π bonding.

Introduction

We have spent considerable effort correlating enthalpies of neutral donor–acceptor interactions and in this regard have introduced a four-parameter equation (eq 1) which successfully calculates enthalpies for a wide variety of adducts.[1,2] Soon after our initial success, we realized that the Lewis acid–base reactions which are described by eq 2 and which can be calculated from literature data should be amenable to a similar treatment. Of special interest to us was the fact that these enthalpies would have no contributions from condensed phases or solvation effects. The enthalpies for this reaction can be calculated for any compound MX for

$$-\Delta H = E_AE_B + C_AC_B \qquad (1)$$

$$M^+(g) + X^-(g) = M^{\delta+}X^{\delta-}(g) \qquad (2)$$

(1) R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, **87**, 3571 (1965).
(2) R. S. Drago, G. C. Vogel, and T. E. Needham, *ibid.*, **94**, 6014 (1972).

which the enthalpy of dissociation is known and for which the ionization energy of M, IP(M), is known and the electron affinity of X, EA(X), is known; *i.e.*, the following processes can be combined to produce the enthalpy for eq 2

$$\begin{array}{ll} M(g) \longrightarrow M^+(g) + e^-(g) & IP(M) \\ X^-(g) \longrightarrow X(g) + e^- & EA(X) \\ MX(g) \longrightarrow M(g) + X(g) & D_{MX} \end{array}$$

The enthalpy for eq 2 is given by substituting the appropriate quantities (signs included with exothermic electron affinities defined as positive) into eq 3. In

$$-\Delta H = IP(M) - EA(X) + D_{MX} \qquad (3)$$

short order, an excellent fit of the data was obtained, but the report of the fit has been delayed while effort has been directed toward seeking a model which is consistent with the data. In previous work on neutral molecule acid–base adducts,[1] it was proposed that the C_AC_B product was equal to the covalent bond energy and the trends observed for the *E* and *C* parameters were very satisfying in terms of the model. It was felt that a similar interpretation should be applicable for suitable ion parameters. The initial fit we obtained on the ions gave C_AC_B products that were not reasonable for such an interpretation.

In the course of deciding which model provides a satisfactory fit and interpretation, it should be noted that, while the experimental enthalpies are large, a considerable portion of the energy is owed to an ionization potential which is in general known to good accuracy and that the experimental error is largely found in the reported dissociation energies, which are of the order of 90 kcal. The parameters should be evaluated on the basis of the per cent error compared not to the total heat but to the dissociation energy.

This article reports a fit of the data which is reasonable in view of the error in the experimental enthalpies and which is consistent with many of our qualitative explanations of the important factors contributing to bond strength. Some different ideas involving intermolecular interactions on cerrain systems result.

Calculations

The basic program used previously to correlate the neutral molecule data was employed and has been described in detail.[2] In this section further constraints imposed on this solution are described and justification for them will appear in the Discussion.

For several homonuclear diatomic molecules and certain other symmetrical molecules (CH_3CH_3), we attempted to fit the *CC* product to the dissociation energy *D*

$$C_{X^+}C_{X^-} = D_{X_2} \qquad (4)$$

For unsymmetrical molecules derived from the symmetrical molecules to which eq 4 applied, we attempted to fit the *CC* product to the geometric mean of the dissociation energies of the reactant species as in

$$C_{M^+}C_{X^-} = \sqrt{D_{M_2}D_{X_2}} \qquad (5)$$

For certain systems (*vide infra*), a best fit of eq 6 was

$$C_{M^+}C_{X^-} = C_{X^+}C_{M^-} \qquad (6)$$

also required. In general, restrictions were placed on the system as long as agreement between the calculated and experimental enthalpies was not seriously impaired when compared to experimental error. We shall subsequently show all of these restrictions logically follow from only one assumption, *i.e.*, eq 4.

Systems of the type MX when M^+ is a metal ion, an alkyl cation, or a halonium ion (except F^+) and where X^- is Cl^-, Br^-, I^-, CN^-, or an alkyl anion were incorporated into eq 4 and 5. Biphenyl was also included under eq 4 with a weighting factor of 3.000. Systems involving CN^- were assigned weighting factors of 4.000. All other systems were assigned weighting factors of 2.000 except Br_2 and I_2 which were assigned 1.000 and Cl_2, $C_3H_7CH_3$, CH_3CH_3, $C_2H_5CH_3$, $CH_3C_2H_5$, and $C_2H_5C_2H_5$ which were assigned 1.414. Higher weights (smaller weighting factor) were given to eq 5 and 6 for those systems in which it was felt that the energies were very accurate and lone-pair repulsions were not important factors. Equation 5 was not used for OH^- and NH_2^- because of the possible existence of lone-pair repulsions contributing to the measured dissociation energies.

The cations starred in Table I were involved in an additional added constraint. We attempted to fit all of these systems to the equality $C_{M^+}C_{X^-} = C_{M^-}C_{X^+}$. The weighting factors for these interactions were 3.000 except for those which included OH^+ or $C_6H_5^+$ where 4.000 was assigned and those involving CN^+ which were assigned 6.000. For any combinations of these latter systems in the same equation, *e.g.*, $C_{C_6H_5^+}C_{OH^-} = C_{OH^+}C_{C_6H_5^-}$, the sum of the weight of the two ions was assigned (*e.g.*, the above system was weighted as 8.000). Two standards[2] had to be selected as can be shown since any matrix which transforms to another solution and maintains the C_AC_B product constant must be a diagonal matrix.

In deciding the weighing factors to use, the following general scheme was used: (1) if the expected experimental error was 1 kcal, 0.500 or 1.000 was used; (2) if the expected experimental error was 1–3 kcal, 1.414 was used; (3) if the expected experimental error was 4–10 kcal, 1.732 or 2.000 was used; (4) if a system was expected to deviate from the model, a weighting factor of from 2.000 to 4.000 was used, depending on the individual case. Those systems to which point 4 above applies are now discussed.

Certain systems were weighted less when there was ambiguity regarding which electron the measured IP or EA referred to, *e.g.*, cyanogen or phenyl radicals. These considerations lead to a weighting factor of 3.000 for the enthalpies of reactions of K^+, I^+, CH_3^+, and Na^+ with CN^-. C_2N_2 was given a weighting factor of 4.000 since here carbon–carbon π bonding might be expected to be important. For the same reason when $C_{M^+}C_{CN^-}$ products were fit, the weighting factor was given as 4.000. Similar considerations applied to $C_6H_5^+$, $C_6H_5^-$, and NO^+ ions where in each case the weighting factor used was 4.000. The EA for NO_2 is in doubt[3] and 2.15 eV was used. All enthalpies involving NO_2^- were assigned weighting factors of 4.000. The enthalpies of IOH and BrOH are known to be poor[4] and were assigned weighting factors of 4.000. The possibility of lone-pair repulsions in H_2O_2, F_2, and N_2H_4 led to weighting factors of 4.000.

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(3) J. Berkowitz, W. A. Chupka, and D. Gutman, *J. Chem. Phys.*, **55**, 2733 (1971).

(4) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

TABLE I

E AND *C* PARAMETERS FOR IONS

Acid Parameters

Acid	E_A (conditional) (marginal)[a]	C_A (conditional) (marginal)[a]
*CH_3^+	62.1 (*b*) (*b*)	7.30 (*b*) (*b*)
*$C_2H_5^+$	51.49 (0.47) (1.06)	7.05 (0.11) (0.27)
$C_3H_7^+$	48.93 (0.52) (1.24)	7.08 (0.13) (0.32)
*$C_6H_5^+$	57.08 (1.95) (3.08)	7.77 (0.36) (0.60)
Li^+	45.04 (0.73) (1.67)	4.11 (0.18) (0.40)
Na^+	39.84 (0.68) (1.50)	3.27 (0.16) (0.34)
K^+	36.49 (0.68) (1.48)	2.66 (0.16) (0.34)
Rb^+	35.83 (0.82) (1.64)	2.63 (0.20) (0.38)
Cs^+	34.28 (0.80) (1.63)	2.63 (0.20) (0.38)
*HO^+ [c]	82.87 (1.63) (3.07)	6.59 (0.63) (0.73)
*NH_2^+	72.20 (1.19) (2.25)	6.61 (8.40) (0.58)
Cu^+	52.61 (1.40) (2.32)	5.29 (0.29) (0.48)
Ag^+	49.12 (1.14) (1.91)	4.96 (0.25) (0.41)
Al^+	52.18 (0.84) (1.78)	4.84 (0.20) (0.41)
In^+	45.84 (0.69) (1.66)	3.77 (0.17) (0.40)
Tl^+	46.34 (0.77) (1.69)	3.04 (0.19) (0.39)
NO^+ [c]	50.73 (2.57) (55.39)	3.81 (0.69) (14.9)
*Cl^+	88.16 (0.56) (2.13)	5.86 (0.14) (0.40)
*Br^+	78.8 (0.52) (1.72)	5.21 (0.13) (0.32)
*I^+	68.72 (0.44) (1.45)	4.57 (0.12) (0.29)
*CN^+ [c]	101.5 (4.64) (7.20)	9.08 (0.48) (0.71)
*F^+ [c]	109.9 (1.61) (2.83)	6.33 (0.26) (0.46)

Base Parameters

Base	E_B (conditional) (marginal)[a]	C_B (conditional) (marginal)[a]
F^-	2.94 (0.02) (0.08)	10.38 (0.22) (0.68)
Cl^-	2.47 (0.01) (0.05)	9.66 (0.13) (0.39)
Br^-	2.47 (0.01) (0.05)	8.59 (0.14) (0.37)
I^-	2.46 (0.02) (0.05)	7.50 (0.15) (0.35)
CH_3^-	3.24 (0.04) (0.06)	12.07 (0.21) (0.43)
$C_2H_5^-$	3.29 (0.05) (0.07)	11.66 (0.27) (0.43)
CN^-	2.43 (0.06) (0.11)	14.93 (0.54) (0.90)
OH^-	3.10 (0.03) (0.11)	11.32 (0.28) (0.94)
NH_2^-	3.38 (0.03) (0.10)	11.04 (0.26) (0.83)
$C_6H_5^-$ [c]	2.80 (0.11) (0.17)	12.86 (0.61) (0.99)
NO_2^- [c]	2.68 (0.10) (0.64)	9.97 (0.85) (5.24)

[a] The significance of these error estimates is discussed in ref 2. [b] These parameters were fixed as standards. [c] These parameters are regarded as tentative.

Lone-pair repulsions might be expected to be important in Cl_2. Using 62.1 kcal/mol instead of 57.1 had no effect on the fit, however, so the experimental value was used. The weighting factor given was 1.414. The weighting factor used for the geometric means was 2.000 and the fit is probably better than should be expected in view of experimental error. The weighting factors used for OH^+, $C_6H_5^+$, and CN^+ were 4.000, 4.000, and 6.000, respectively, for the fit of the equality as in eq 6 for similar reasons as discussed above for the 1:1 adducts. Certain acids were involved in very few reactions. According to the model to be proposed, $E_{X^+}E_{X^-} = IP(X) - EA(X)$ for symmetrical molecules, *e.g.*, N_2H_4. In an effort better to determine the *E* and *C* parameters for ions with limited enthalpy data, *EE* products calculated from the above equation were included in the fit and assigned weighting factors of 2.000 for F_2, H_2O_2, N_2H_4, Cl_2, Br_2, and I_2.

Our computer program found the best set of parameters to minimize the deviations in calculated and experimental values for eq 1, 5, and 6.

Discussion

Description of the Model.—It was shown previously that a one-term equation is not sufficient to correlate enthalpies of adduct formation for neutral Lewis acid–base interactions but that a two-term four-parameter equation works quite well. On attempting a blanket fit of all literature data on ionic interactions of the general forms

$$M^+(g) + X^-(g) \longrightarrow M^{\delta+}X^{\delta-}(g) \qquad (7)$$

and

$$M^-(g) + X^+(g) \longrightarrow M^{\delta+}X^{\delta-}(g) \qquad (8)$$

a good fit was obtained with the same four-parameter, two-term equation. We were unable to find a satisfactory interpretation of the C_AC_B and E_AE_B products which was consistent with previous work[1,2] on the neutral adducts.

Though it is difficult to determine the relative magnitudes of the covalent and the ionic contributions to a given bond energy, it has long proven useful to consider bonding in these terms. One ascribes the bond energy between two symmetrical fragments to a covalent bond energy as in the bond in Cl–Cl. When there exists an unequal charge distribution, there is also a contribution from ionic bonding as in Na–Cl.

The total enthalpy of the reaction corresponding to eq 7 or 8 can be divided into two parts, associated with the steps shown in eq 9 and 10. We are ascribing the

$$M^+ + X^- \longrightarrow M^{\delta+} + X^{\delta-} \text{ or } M^- + X^+ \longrightarrow M^{\delta+} + X^{\delta-} \qquad (9)$$

$$M^{\delta+} + X^{\delta-} \longrightarrow M^{\delta+}X^{\delta-} \qquad (10)$$

difference in the energy of eq 7 and 8 for the same M and X to step 9. Accordingly, the covalent bond energy contribution is contained in step 10 (along with some ionic energy) and thus is the same for eq 7 and 8. The first step is clearly devoid of any covalent contributions because the acid and base are at infinite separation and consequently all of the energy in the first step will be included in $E_{M^+}E_{X^-}$. The second step will have contributions from both $E_{M^+}E_{X^-}$ and $C_{M^+}C_{X^-}$. On applying this model to available data, the enthalpies for interactions in which more than one electron was transferred were not fit well.

When NH_2^+ is interacting with chloride, some frac-

TABLE II

SYSTEMS WHICH ARE EXCEPTIONS TO THE CORRELATION

		Enthalpy, kcal mol^{-1}				Enthalpy, kcal mol^{-1}	
Acid	Base	Calcd	Exptl	Acid	Base	Calcd	Exptl
$C_6H_5^+$	OH^-	265	273	NH_2^+	I^-	228	248
$C_6H_5^+$	NH_2^-	279	286	NH_2^+	Br^-	235	245
Cl^+	CN^-	302	319	I^+	CH_3^-	278	271
Br^+	CN^-	270	282	Br^+	$C_2H_5^-$	320	319
I^+	CN^-	235	247	Br^+	$C_6H_5^-$	288	294
Cl^+	F^-	320	280	I^+	Cl^-	213	208
Cl^+	OH^-	340	322	Br^+	I^-	233	244
HO^+	OH^-	332	313	Cl^+	CH_3^-	356	358
NH_2^+	CH_3^-	314	316	Cl^+	NH_2^-	363	343

tion of an electron is transferred to NH_2^+. Similarly, when I^- reacts with K^+, I^- releases some fraction of an electron to K^+. The $E_{NH_2^+}$ and E_{I^-} parameters that account for the energy of these respective transfers do not account for the *EE* product when I^- is the base and NH_2^+ the acid in which case more than one electron is transferred. Table II contains this and several other interactions listed at the end of the table in which the expected polarity of the product suggests more than a one-electron transfer. We cannot expect a reliable prediction of the enthalpies for this kind of system with our parameters. Some systems in Table III in which

TABLE III

ACID-BASE PAIRS, EXPERIMENTAL AND CALCULATED ENTHALPIES

		Enthalpy, kcal mol^{-1}			
Acid	Base	Calcd	Exptl[a]	Wt factor	Ref
CH_3^+	F^-	258.1	254	1.414	*b*
$C_2H_5^+$	F^-	224.4	220	1.414	*b*
$C_3H_7^+$	F^-	217.1	213	1.414	*b*
Li^+	F^-	174.9	181	1.732	
Na^+	F^-	150.9	152	1.732	
K^+	F^-	134.8	137	1.414	
Rb^+	F^-	132.5	136	1.732	
Cs^+	F^-	128.0	133	1.414	
Al^+	F^-	203.5	216	1.414	
In^+	F^-	173.7	176	1.414	
Tl^+	F^-	167.6	165	1.414	
F^+	F^-	388.3	358	4.000	
CH_3^+	Cl^-	223.6	227	1.000	*b*
$C_2H_5^+$	Cl^-	195.1	193	1.414	*b*
$C_3H_7^+$	Cl^-	189.0	186	1.414	*b*
$C_6H_5^+$	Cl^-	215.8	213	4.000	*b*
Li^+	Cl^-	150.8	154	1.414	
Na^+	Cl^-	129.8	133	1.414	
K^+	Cl^-	115.7	117	1.414	
Rb^+	Cl^-	113.7	115	1.414	
Cs^+	Cl^-	109.9	112	1.414	
NH_2^+	Cl^-	241.9	240	1.732	*b*
Cu^+	Cl^-	180.8	178	1.732	
Ag^+	Cl^-	169.0	166	1.732	
Al^+	Cl^-	175.4	172	1.414	
In^+	Cl^-	149.4	154	1.414	
Tl^+	Cl^-	143.6	146	1.414	
NO^+	Cl^-	161.9	162	4.000	*b*
Cl^+	Cl^-	274.0	274	0.500	
Br^+	Cl^-	244.7	241	1.414	
I^+	Cl^-	213.5	208	1.000	
F^+	Cl^-	332.0	376	4.000	
CH_3^+	Br^-	215.9	218	1.000	*b*
$C_2H_5^+$	Br^-	187.6	185	1.414	*b*
$C_3H_7^+$	Br^-	181.5	178	1.414	*b*
$C_6H_5^+$	Br^-	207.6	206	4.000	*b*
Li^+	Br^-	146.4	147	1.414	
Na^+	Br^-	126.4	128	1.414	
K^+	Br^-	112.9	113	1.414	
Rb^+	Br^-	111.0	110	1.414	
Co^+	Br^-	107.2	106	1.732	
Cu^+	Br^-	175.2	178	1.732	
Ag^+	Br^-	163.8	166	1.732	
Al^+	Br^-	170.3	164	1.732	
In^+	Br^-	145.4	147	1.414	
Tl^+	Br^-	140.4	141	1.414	
NO^+	Br^-	157.9	158	4.000	*b*
Br^+	Br^-	239.3	240	0.500	
I^+	Br^-	208.8	205	1.000	
CH_3^+	I^-	207.8	211	1.000	*b*
$C_2H_5^+$	I^-	179.8	177	1.414	*b*
$C_3H_7^+$	I^-	243.9	170	1.414	*b*
$C_6H_5^+$	I^-	198.9	203	4.000	*b*
Li^+	I^-	141.8	135	1.414	
Na^+	I^-	122.7	117	1.414	
K^+	I^-	109.9	107	1.414	
Rb^+	I^-	108.0	105	1.414	
Cs^+	I^-	104.2	97	1.414	
Ag^+	I^-	158.2	159	1.732	
Al^+	I^-	164.9	154	1.732	
In^+	I^-	141.2	139	1.414	
Tl^+	I^-	137.0	137	1.414	
I^+	I^-	203.6	206	0.500	
CH_3^+	OH^-	275.4	276	1.414	*b*
$C_2H_5^+$	OH^-	239.7	244	1.414	*b*
$C_3H_7^+$	OH^-	232.0	237	1.414	*b*
Li^+	OH^-	186.3	184	1.732	*c*
Na^+	OH^-	160.7	162	1.414	*b, e*
K^+	OH^-	143.4	144	1.732	*b, c*
HO^+	OH^-	331.9	313	4.000	*b*
In^+	OH^-	184.9	177	1.732	*c*
Br^+	OH^-	303.7	287	4.000	*b*
I^+	OH^-	265.0	255	4.000	*b*
CH_3^+	NH_2^-	290.7	288	1.000	*b, h*
$C_2H_5^+$	NH_2^-	252.1	255	1.414	*b, h*
$C_3H_7^+$	NH_2^-	243.6	248	1.414	*b, h*
NH_2^+	NH_2^-	317.2	318	4.000	*d, h*
I^+	NH_2^-	282.9	280	2.000	*b, h*
CH_3^+	CH_3^-	289.3	288	1.000	*f*
$C_2H_5^+$	CH_3^-	251.9	253	1.414	*f*
$C_3H_7^+$	CH_3^-	243.9	246	1.414	*f*
CH_3^+	$C_2H_5^-$	289.2	288	1.414	*f*
$C_2H_5^+$	$C_2H_5^-$	251.5	253	1.414	*f*
CH_3^+	$C_6H_5^-$	268.0	268	4.000	*b*
$C_2H_5^+$	$C_6H_5^-$	235.1	233	4.000	*b*
$C_6H_5^+$	$C_6H_5^-$	260.0	262	4.000	*b*
CH_3^+	CN^-	260.1	256	3.000	*b, g*
Na^+	CN^-	145.8	139	3.000	*e, g*
K^+	CN^-	128.5	121	3.000	*e, g*
I^+	CN^-	235.4	247	3.000	*b, g*
CN^+	CN^-	382.6	383	4.000	*b, g*
CH_3^+	NO_2^-	239.5	240	4.000	*b, i*
$C_2H_5^+$	NO_2^-	208.5	210	4.000	*b, i*
$C_6H_5^+$	NO_2^-	230.7	229	4.000	*b, i*
NO^+	NO_2^-	174.2	174	4.000	*b, i*

[a] Unless otherwise noted, the dissociation energy is taken from A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed, Chapman and Hall, London, 1968; the electron affinity is taken from R. S. Berry, *Chem. Rev.*, **69,** 533 (1969); and all ionization potentials are taken from J. L. Franklin, *et al.*, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," Report NSRDS-NBS26, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1969. [b] Bond energies and heats of formation from ref 4. [c] Bond energies and heats of formation from V. I. Vedeneyev, *et al.*, "Bond Energies, Ionization Potentials and Electron Affinities," E. Arnold, London, 1966. [d] Bond energies from S. W. Benson, D. M. Spokes, and D. M. Golden, *Chem. Eng. News*, 31 (Nov 23, 1970). [e] Heats of formation from "JANAF Thermochemical Tables, First Addendum," PB168 370-1, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., Aug 1966. [f] Electron affinities from F. M. Page, *Advan. Chem. Ser.*, **No. 36,** 68 (1962). [g] Heats of formation and electron affinities from ref 3. [h] Electron affinity from J. Beauchamp, private communication. [i] Electron affinities from J. Berkowitz, W. A. Chupka, and T. A. Walker, *J. Chem. Phys.*, **50,** 1497 (1969).

the bond is significantly of "reverse polarity" work surprisingly well. More data are necessary before any reliable interpretation can be offered.

Our inability to fit systems in which more than one electron is transferred is reasonable when one considers that the VSIP or electron affinity of an acid (which we have placed in the *EE* term) might be fairly well approximated by a straight-line function over the region $\delta = 0.8+$ to $\delta = 0$ but certainly is not over the region $\delta = 0.8+$ to $\delta = 0.8-$. Consequently, we eliminated from the enthalpy fit (eq 1) those interactions in which the polarity of the final molecule would require that more than one electron is transferred in the interaction, *e.g.*, $Cl^+ + I^-$, etc. Even though this rationalizes the inability to fit the enthalpy of systems where more than one electron is transferred, the covalency in the bond should be independent of our inability to predict the *EE* product. The covalency in the bond is the same if the molecule is formed from M^+X^- or from M^-X^+. Therefore

$$C_{M^+}C_{X^-} = C_{M^-}C_{X^+} \qquad (11)$$

if we assume that the *CC* product gives the covalent bond energy. This assumption that we can represent the covalent bond energy contribution by the product C_AC_B is the basic assumption involved in placing this model on the system. Accepting this proposal, we can derive the geometric mean relationship, GMR, suggested by Pauling for determining electronegativities. Given eq 11 and the facts that

$$\Delta H_D(M_2) = C_{M^+}C_{M^-} \qquad (12)$$

$$\Delta H_D(X_2) = C_{X^+}C_{X^-} \qquad (13)$$

we can substitute expressions for M^- and X^+ from eq 12 and 13, respectively, into eq 11, leading to

$$C_{M^+}C_{X^-} = \frac{\Delta H_D(M_2)}{C_{M^+}}\,\frac{\Delta H_D(X_2)}{C_{X^-}}$$

Rearrangement gives the GMR

$$C_{M^+}C_{M^-} = \sqrt{\Delta H_D(M_2)\Delta H_D(X_2)}$$

Thus, in addition to fitting the parameters to eq 11, we can calculate *CC* products for all interactions in which ΔH_{M_2} and ΔH_{X_2} are known.

When a fit of the data was attempted including all the interactions in Table III and those of eq 5, plus data involving HX molecules and eq 6, the fit was poor. The literature reports[5] considerable difficulty in reproducing covalent bond distances for X–H molecules using half the H_2 bond distance. Although the atoms come very close together in H_2, it appears that an unusually large nuclear repulsion term makes the measured dissociation energy lower than it would be from other bonding considerations. We tried to eliminate this problem by only requiring the proton *E* and *C* parameters to obey eq 6, in effect allowing the data to find a "virtual" dissociation energy that works for H_2. A poor fit was obtained in which many HX systems missed the experimental data by 10 kcal mol^{-1}. An HX system is unique in that there are no core electrons on the proton as there are on every other nucleus in the correlation. One potential difficulty which is attributable to the absence of core electrons is a nonlinear variation in the electron affinity of the proton with the extent of electron transfer.

The enthalpy of dissociation of H_2O_2 is also a source of difficulty,[5] because it is thought to be low from lone pair–lone pair repulsions. This would be a case comparable to the existence of steric effects in the neutral molecule system and we would not expect accurately to predict this enthalpy. The F_2, ClOH, and ClF molecules were eliminated for the same reason. Thus we excluded the above molecules, H^+, and H^- from the data set.

We were interested in determining the error introduced into the fit of the ionic interactions by imposing eq 4–6. Even though covalency must be the same for M^+X^- and M^-X^+, our C_AC_B parameters may not be able to account for this empirically. Accordingly, we lowered the weight given to eq 4–6 in the fit. A significant improvement in the prediction of enthalpies for the 1:1 interactions was not obvious relative to experimental error in the data. Thus, even though eq 4–6 are very restrictive, they appear to be consistent with the data.

Other Models Attempted.—As discussed earlier, our initial results gave a good fit for the data, but the numbers were not meaningful in terms of our previous model for the *E* and *C* equation. It was thought that this was a result of our having chosen one of the infinite solutions[2] (parameter sets) for the minimum we had found and that we only had to find a way to choose the set with parameters that would lend themselves to interpretation. In view of the success we had had with the neutral molecule adducts and the reasonable trends found for *CC* and *EE* products in this system, we decided to lock in on an ion solution *via* ion–molecule interactions, holding the neutral molecule parameters fixed. We felt if we could determine four suitable ion parameters from ion–molecule heats where we held the parameters for the neutrals fixed and solved for the ion parameters, we could then fix these ion parameters and lock in on a good set of ion parameters. Unfortunately, the paucity of ion–molecule data severely limited our work. A few proton affinities that were applicable had been reported.[6] From these E_{H^+} and C_{H^+} were found to be a 133.1 and 21.0, respectively, based on the fixed neutral base parameters. An estimated heat of Cl^- and $(CH_3)_3SnCl$ from a J_{Sn-H} *vs.* ΔH relation[7] was used along with the enthalpy of interaction of the proton with Cl^- to solve for the Cl^- parameters. These four parameters are not sufficient to define a new set, however.[2] We tried to estimate E_{Br^-} from E_{Cl^-} on the assumption that the ratio of their *E*'s was inverse to the ratio of their ionic radii. We were encouraged by the fit that was found because the trends in the *E* and *C* parameters seemed reasonable and especially because, fortuitously, the *E*'s for I^- and F^- came out almost exactly to what would have been predicted by the ratioing procedure. Thus encouraged, we tried various estimates of the radii but were unable to obtain *CC* products for the ionic interactions consistent with expected covalency contributions (*e.g.*, C_AC_B for KCl was 60 kcal mol^{-1} compared to a dissociation energy of 100 kcal mol^{-1}). We reasoned that the enthalpy for $(CH_3)_3SnCl + Cl^-$ had contributions from ion-pairing interactions and was thus not a true ion–molecule en-

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[5] See, for example, K. B. Harvey and G. B. Porter, "Introduction to Physical Inorganic Chemistry," Addison-Wesley, Reading, Mass., 1965.

[6] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969).

[7] T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 5730 (1966).

thalpy and complications with the proton (*vide infra*) negates use of the proton affinities.

Our search for ion–molecule enthalpies led us to some methyl cation affinities measured by Holtz, *et al.*[8] The methyl cation affinities for a series of amines enabled us to obtain *E* and *C* numbers for CH_3^+. The CH_3^+ and H^+ numbers would be enough to determine one set of parameters from the infinite number possible. The methyl cation affinities for ammonia, methylamine, and dimethylamine predict $E_{CH_3^+} = 62.1$ and $C_{CH_3^+} = 7.30$. When the ion system was solved, it was found, however, that the new *E* and *C* parameters obtained included some negative numbers and did not show reasonable trends.

Recognizing that there was no guarantee that the parameters for the neutral molecules were perfectly predicting covalency, we decided to seek some constraints to place on the ions by themselves, and if a solution was found which gave a good breakup into ionic and covalent energy, then perhaps in turn we could use this solution to carry out a slight transformation on the neutral parameters to an even more meaningful set.

We next tried to impose restrictions on the *CC* products of the ions by setting the *CC* product of diatomic molecules and certain symmetrical molecules like ethane equal to the dissociation energy. This defines the bond energy as equal to the covalent energy for these cases. The molecule H_2 was not included because of complications with the dissociation energy. No restrictions were placed on the C_AC_B products of unsymmetrical molecules (*e.g.*, no equations like (5) and (6) were used). Thus, H^+ and H^- were only required to fit enthalpy data and a good fit was obtained. We then showed that there was no transformation of the neutral set which would be consistent with the model placed on the ions that allowed for all positive numbers. This observation, coupled with some recent proton affinity data[8] which indicated that there was no set of *E* and *C* numbers for the proton which would predict proton affinities with the neutral bases in our correlation, caused us to abandon this approach and intensify our search for meaning and internal consistency in the ion system alone. Any connection between the two schemes must await more ion–molecule enthalpy data. On the basis of our inability to fit proton data with the *E* and *C* equation toward neutral donors and our inability to incorporate the proton into the model reported here, data other than proton affinities will be required to test the connection of the two scales. Moreover, the proton is an exception to our correlation and we cannot reliably predict proton affinities.

Utilization and Interpretation of the Parameters.—The most obvious use of the parameters reported here is to predict enthalpies of reactions that have not been measured. Some 93 interactions were included in the fit and the resulting parameters permit the calculation of over 180 enthalpies. It should be emphasized that interactions in which more than one electron is transferred cannot be reliably predicted with our parameters. The reliability of the predicted enthalpies is obtained from the calculated variances and covariances as described previously.[2] In most cases, the expected uncertainty is 6 kcal mol^{-1} or less indicating that considerable confidence can be placed in the enthalpies predicted. Larger errors are obtained with the parameters that we have indicated are tentative. A sampling of the predicted enthalpies and corresponding errors are listed in Table IV.

TABLE IV
SOME PREDICTIONS OF ENTHALPIES AND POTENTIAL ERROR

Acid	Base	Predicted enthalpy, kcal mol^{-1}	Possible error, kcal mol^{-1}	Acid	Base	Predicted enthalpy, kcal mol^{-1}	Possible error, kcal mol^{-1}
Li^+	CH_3^-	195	3	NO^+	OH^-	201	10
Li^+	NH_2^-	198	3	Cl^+	F^-	320	4
Rb^+	$C_2H_5^-$	148	3	Cl^+	CN^-	302	8
Rb^+	CN^-	126	4	Tl^+	CH_3^-	187	3
Rb^+	$C_6H_5^-$	134	5	Tl^+	OH^-	178	3
NH_2^+	F^-	281	5	$C_6H_5^+$	F^-	248	7
NH_2^+	NO_2^-	260	14	$C_6H_5^+$	OH^-	265	7
Ag^+	OH^-	209	4	$C_6H_5^+$	NH_2^-	279	8
Ag^+	NH_2^-	221	4				

Several inferences concerning factors affecting bond energies can be obtained by comparing calculated and experimental enthalpies on various systems. For example, systems in which the anion is expected to π bond to the phenyl ring (*e.g.*, OH^- and NH_2^-) were not included in the data used to evaluate the parameters for these ions. Thus, the parameters are expected to predict the σ contribution to bond energy and it is interesting to note that the predicted enthalpy for the reaction of OH^- and NH_2^- with $C_6H_5^+$ underestimates the experimentally determined value as can be seen from Table II, though the differences in the calculated and experimental enthalpies are at the limits of the expected standard deviations in the predicted enthalpies for NH_2. The most interesting aspect of the results on both of these systems is the very small amount of stabilization of the carbon–heteroatom bond from π-bonding effects. The π-bond stabilization is considerably greater in ClCN, BrCN, and ICN. The calculated numbers show the expected decrease in π-bond stabilization as the atom bonded to carbon increases in size.

In contrast to the behavior described above, the predicted enthalpies for H_2O_2, ClOH, and ClF exceed the experimental values. It is felt that lone pair–lone pair repulsions are destabilizing the bonds in these cases. This repulsion is similar to steric effects in the neutral molecule system and adducts in which this exists are exceptions to the correlation also. The enthalpy of forming fluorine, hydrogen peroxide, and hydrazine were included in the data set but given low weight because of potential lone-pair repulsions. Even with this low weight, the enthalpy for hydrazine was fit well leading us to believe that lone-pair repulsions are not important here. This is not unexpected, since the lone pairs can attain a position trans to each other. The $C_{HO^+}C_{OH^-}$ product is calculated to be 74.6 compared to a dissociation energy of 52 kcal mol^{-1}, suggesting lone-pair repulsion destabilization of about 20 kcal mol^{-1}. This result is only approximate because HO^+ enters the correlation only *via* H_2O_2, the *EE* product of H_2O_2 and eq 6 leading to uncertainty in its value. The difficulty is illustrated by the fact that the extent of the deviation depends upon the weighting factor assigned

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(8) D. Holtz, *et al.*, *J. Amer. Chem. Soc.*, **92**, 7484 (1970), and private communications.

to the H_2O_2 enthalpy. The 20 kcal mol^{-1} value is reasonable and the value of C_{OH^-} is consistent with the other C_B values. The "virtual" dissociation energy of 74.6 kcal mol^{-1} determines the C_AC_B products through eq 6 for MOH systems.

For similar reasons, the parameters for F^+ are to be regarded as tentative. Even though $F^+ + Cl^-$ is a more than one-electron transfer system, it was included in the fit because of the paucity of data involving F^+. As in the case of hydrogen peroxide, for F_2 the calculated enthalpy is much larger than the observed. The anomalous behavior of fluorine in a series of trends noted for the halogens has been thoroughly treated recently by Politzer.[9] The anomaly was reported to occur in free-atom properties and for both ionic and covalent fluorides. He concluded that the anomaly was an inherent property of the fluorine atom arising from electron–electron repulsions within the valence electrons in compact orbitals around an individual fluorine nucleus. Our F^+ parameters are too poorly defined to comment rigorously on this problem, but if they are correct, they would suggest considerable lone pair–lone pair repulsions in F_2. Any effect which is a property of the atom should be reflected in the magnitude of our parameters. The trend in the parameters for the halides is monotonic, but the difference between F^- and Cl^- is less than the other differences, in accord with Politzer's observations.

The interpretation of the parameters in Table I is of interest. In view of the model imposed on the system, a straightforward interpretation of the *EE* product is not possible, but the *CC* products should provide an estimate of covalency. The trends in most of the parameters are consistent with qualitative ideas about covalent bonding. In this connection, it is interesting to note the decrease in the C_B values in the series $F^- > Cl^- > Br^- > I^-$. The trend in polarizability which is related to the size of the ion is known to increase in the series. One interpretation of the trend is that the larger atoms have more diffuse orbitals and form weaker bonds than smaller atoms because the former are less able to localize the bonding electrons between the participant nuclei. This explanation is not a new one and has been employed in the past to account for the inert-pair effect.[10] Although the polarizability effect is real, the orbital diffuseness is more important and our results suggest I^- forms weaker covalent bonds than does Cl^-. The approximately constant values of the E_B numbers for Cl^-, Br^-, and I^- require that the trend in adduct enthalpies will always be the same as the trend in the C_B (in the absence of π-bonding and steric effects) for these halides. In this connection, it is of interest to point out that the HX compounds show the same trend even though the proton cannot be included in the correlation. To test this observation, it would be most interesting to have a very large, low-valent metal ion in the correlation with very different *E* and *C* numbers than are presently included. In this connection, it is significant that even toward CH_3Hg^+, which is one of Pearson's reference soft acids,[11] the heat of dissociation of the chloride is greater than that of the iodide.

On interpreting the meaning of the *E* and *C* parameters, careful attention should be paid to the way this model divides up the energy of interaction (see eq 9 and 10). The *C* numbers reported refer to the ions by virtue of our breakup of the *CC* products by fixing the *E* and *C* parameters using the methyl cation affinities. A transformation matrix is available which maintains the integrity of the fit and the *CC* product and converts the $C_M{}^+$ and $C_M{}^-$ parameters to new parameters that are equal. The transformation matrix for accomplishing this is

$$\begin{bmatrix} 0.777 & 0 \\ 0 & 1.286 \end{bmatrix} \begin{bmatrix} C_{M^-} \\ C_{M^+} \end{bmatrix} = \begin{bmatrix} C_M \\ C_M \end{bmatrix}$$

We would interpret these new parameters as *C* parameters for the atoms. The existence of a transformation which preserves the *CC* product is consistent with our definition that the covalent contribution to the bonding is the same regardless of whether the product is formed from atoms M^+X^- or M^-X^+.

It should be emphasized that the model we have imposed on our system simply amounts to defining the covalent bond energy as the dissociation energy in a homonuclear diatomic molecule and making *only one assumption*, namely, that the covalency can be represented by a product function, $C_M{}^+C_X{}^-$, as was done for neutral adducts. With this, we have derived a set of relationships similar to those employed by Pauling to derive his electronegativity scale[11]

$$D = \sqrt{D_{M_2}D_{X_2}} + 23(X_M - X_X)^2$$

Since $C_MC_X = \sqrt{D_{M_2}D_{X_2}}$, we need only subtract our $C_M{}^+C_X{}^-$ products from the measured dissociation energy to get the ionic resonance energy which Pauling has fitted to an expression involving electronegativities X_M and X_X. In view of the excellent agreement of our *CC* products with the GMR which Pauling indicates is the preferred way of obtaining electronegativities, our results would be the same. There could be substantial differences with the results obtained using the covalent bond additivity postulate. We considered recalculating the electronegativities of fluorine or hydroxyl, but the results would be of questionable value because of the dependence of our *CC* products for these examples on our selection of the weighting factors. Since we could not find a "virtual" dissociation energy for H_2 that would work in our correlation, we are led to conclude that a single electronegativity for hydrogen cannot be defined. The extension of our parameters in this regard is obvious, but we have not proceeded any further in view of the questionable significance of a quantitative electronegativity scale and the relative ease with which one could obtain this data from our reported parameters if so desired.

We have assumed that the covalent bond energy of a homonuclear diatomic or symmetrical molecule is the dissociation energy. With that definition and eq 6, the geometric mean rule is derived. The reported fit requires only a best fit of eq 6 instead of a fixed constraint. This is because the dissociation energy for certain symmetrical systems may contain contributions other than from covalent bonding (*e.g.*, abnormal electron–electron repulsions).

Ideally, a statistical test could be performed to decide whether the added constraints generated by eq 5

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(9) P. Politzer, *J. Amer. Chem. Soc.*, **91**, 6235 (1969).

(10) R. S. Drago, *J. Phys. Chem.*, **62**, 353 (1958).

(11) R. G. Pearson, *Chem. Commun.*, 65 (1968); *J. Chem. Educ.*, **45**, 581, 643 (1968).

and 6 are valid or can be rejected at the level of accuracy of our enthalpy data. The *R* factor ratio test[12] is well suited to do this for a linear problem. Generally, it is assumed that it gives reliable results for a nonlinear problem as well. A test comparing our reported parameters and a set of parameters obtained from a best fit of the enthalpy data with the minimum four parameters fixed was carried out. A large value was obtained for *R*, but the nonlinearity of our problem is thought to make the test of questionable value. The deviations between calculated and experimental values are within the error believed present in almost every enthalpy. A similar set of parameters and an excellent *R* factor ratio could be obtained by forcing eq 6 to hold rigorously and changing the weight of eq 5 to 20.

The results given here are encouraging in that they suggest a physical model may well apply to the empirical equation but, of course, do not constitute proof of that model. The model could not be derived from a fit of the enthalpies of interaction alone but had to be imposed on the system. This is in part due to the fact that no systems exist in our data in which reversals in acid strength occur when the base is varied or *vice versa*.

A shortcoming of the electronegativity concept, discussed by Pearson,[11] involves the inability of the equation

$$\Delta H = 46(X_C - X_A)(X_B - X_D) \qquad (14)$$

to predict enthalpies for several reactions like $LiF(g) + CsI(g) \rightarrow LiI(g) + CsF(g)$. Equation 14 predicts an enthalpy of -21 kcal mol^{-1} compared to an experimental value of $+10$ kcal mol^{-1}. Using our *E* and *C* parameters to evaluate the enthalpies of each compound, we predict an enthalpy of $+9$ kcal mol^{-1}. The excellent agreement is in part fortuitous because we anticipate larger errors than this in our ability to predict the individual enthalpies. In view of the discussion above indicating the similarity in our approach and that of Pauling, it appears that the difference must be attributed to error introduced in Pauling's attempted breakup of the ionic resonance energy, Δ, into electronegativity parameters using $\Delta = 24(X_A - X_B)^2$.

As pointed out in our earlier work[2] on the neutral donors and acceptors, softness is given by the *C*/*E* ratio and all the information about strength is lost in the ratio. In the ion system reported here, the *E* parameters are more complex and softness cannot be inferred from this ratio. We can, however, ask the question, "What percentage of the total enthalpy results from covalent bonding (as predicted by our *CC* products)?" For K^+ reacting with the halides, the percentages are 20.1, 22.0, 20.3, and 18.7% for F^-, Cl^-, Br^-, and I^-, respectively. For CH_3^+, the corresponding values are 29.8, 31.0, 28.8, and 25.9%, respectively. (Fluoride is anomalous in these trends because of its anomalous electron affinity.[9]) However, there is no evidence that the softer base I^- is interacting in a more covalent fashion with the softer acid CH_3^+ than it is with K^+ relative to Cl^-.

When one asks the question, "What percentage of the total dissociation energy comes from covalency?", a different result is obtained. Toward potassium, we find 23.6, 25.4, 25.4, and 25.2% for F^-, Cl^-, Br^-, and I^-. Toward methyl, the values are 70.2, 83.9, 89.6, and 97.7%. This trend results not because there is more covalency in CH_3I than in CH_3Cl as indicated by our *CC* product but because there is less contribution to the dissociation energy from ionic contributions in the former. Contrary to the rule that hard prefers hard and soft prefers soft, we find that both the dissociation energy and ionic adduct formation energy of CuCl and AgCl are greater than those of the respective iodides.

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[12] W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964.