

because of the difficulty of the permeation experiment. The E_a values decrease with increasing alkyl chain lengths of the coating amphiphile in the temperature region above T_c . This suggests that NaCl permeates through the fluid, though hydrophobic, bilayer matrix if the alkyl chain is short. However, if the alkyl chain is long, the permeation through the hydrophobic matrix becomes difficult and NaCl permeates through defective pores (smaller E_a), instead.

The extent of permeability gap near T_c also depends on the alkyl chain length of the coating amphiphiles (Table II). The shorter $2C_{18}N^+2C_1$ bilayers gave smaller permeability gaps near T_c .

It is interesting that the permeability is varied by a factor of 7.4 by temperature change of less than 5 °C in the $2C_{18}N^+2C_1$ -coated capsules. The permeability change is reversibly controlled as shown in Figure 6. When a $2C_{18}N^+2C_1$ -coated capsule was immersed alternately in distilled water at 40 and 45 °C, slow and fast leakage of NaCl was repeated at 40 °C (below T_c) and at 45 °C (above T_c), respectively. This indicates that the bilayer coat acts as a kind of thermo-valve.

Conclusion

Although nylon capsule membranes are simply semipermeable, the permeability of water-soluble substances such as NaCl can reversibly control the use of the phase transition of the coating bilayer in the case of dialkyl amphiphile-coated capsules. The

bilayer-coated capsule membrane has advantages of both polymer membrane and bilayer vesicle: a large inner aqueous phase, a physically strong wall against osmotic pressure, and bilayer characteristics.

By choosing other synthetic amphiphiles, we can easily prepare new, signal-receptive capsule membranes that respond to stimuli from outside, such as pH change, photoirradiation,⁴¹ metal ion interaction,⁴² and so on. These capsules should be useful for biological and industrial uses.

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Registry No. NaCl, 7647-14-5; *N*-dodecyl-*N,N*-dimethyl-1-dodecanaminium bromide, 3282-73-3; *N,N*-dimethyl-*N*-tetradecyl-1-tetradecanaminium bromide, 68105-02-2; *N*-hexadecyl-*N,N*-dimethyl-1-hexadecanaminium bromide, 70755-47-4; *N,N*-dimethyl-*N*-octadecyl-1-octadecanaminium bromide, 3700-67-2.

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Theory of the Chemical Bond. 6. Accurate Relationship between Bond Energies and Electronegativity Differences

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Abstract: A new formula relating bond energies, D_{AB} , to bond polarities, f , is deduced. The formula has the form $D_{AB} = (1-f)\bar{D}_{AB} + 252(f/R_e)$, where R_e is the equilibrium bond length and $\bar{D}_{AB} = (D_{AA} + D_{BB})/2$ is the arithmetic average of bond energies D_{AA} and D_{BB} . For a random sampling of bonds, predicted bond energies are found to vary from measured ones by an average of about 3%. The formula is used in conjunction with the observation $f/R_e \approx 2i/3$, where $i = 1 - \exp(-\Delta X^2/4)$ corresponds to Pauling's approximation to ionic character, to deduce the relationship $D_{AB} = \bar{D}_{AB} + K(1 - \exp(-30\Delta X^2/K))$, where $K = 103$, ΔX represents electronegativity differences $X_A - X_B$, and \bar{D}_{AB} equals the geometric average $(D_{AA}D_{BB})^{1/2}$. This relationship is shown to yield accurate bond energy estimates for both ionic and covalent bonds. A comparison with Pauling's formula $D_{AB} = \bar{D}_{AB} + 30\Delta X^2$ is given. It is shown that for a representative sampling of bonds the new formula predicts bond energies with an average error of 2.6%. The corresponding error associated with Pauling's equation is 43.6%. Ramifications regarding a more accurate electronegativity scale are discussed.

I. Introduction

In the first paper¹ in this series,¹⁻⁴ a quantum mechanical technique called implicit perturbation theory was used to derive an accurate model relating bond dipole moment curves to three principal effects: charge transfer; charge polarization; and charge collision.⁵ The leading term in this model is the charge-transfer term, fR , where f is the effective charge transferred in the curve-crossing region during bond formation and R is the internuclear spacing. This charge is approximately related to partial charges q_A and q_B by the equation

$$f = (q_A - q_B)/2 \quad (1)$$

For single bonds, f varies from one (ionic) to zero (covalent). The effective charge f is an accurate measure of asymmetry in bond charge distributions. To obtain f we utilize the equation (derived in paper 2)²

$$f = \frac{5}{9} \frac{\mu_c}{R_e} + \frac{4}{9} \mu_c' + \frac{1}{18} \mu_c'' \quad (2)$$

where μ_c^k is the k th derivative of the dipole moment curve, μ_c , evaluated at R_e .

Measurements of f indicate a highly regular and systematic variation throughout the periodic table. This is clearly illustrated in Figure 2 of ref 4. Since f is a direct measure of charge transfer occurring in bonds and since, by definition, charge transfer is directly related to electronegativity differences, f would seem to be a natural parameter on which to base an electronegativity scale.

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That indeed turns out to be the case as is shown in this paper.

One of the most frequently quoted electronegativity tables is that constructed by Pauling.⁶ He uses as a basis for his thermochemical table the empirical relationship

$$D_{AB} = \bar{D}_{AB} + 30\Delta X^2 \quad (3)$$

This equation relates bond energies, D_{AB} , to the geometric average of component bond energies,

$$D_{AB} = (D_{AA}D_{BB})^{1/2} \quad (4)$$

and to electronegativity differences $\Delta X = X_A - X_B$. Equation 3 yields reasonably accurate estimates of covalent bond energies. However, it fares badly when applied to ionic bonds. Estimated ionic bond energies can be in error by as much as 190%.

Obviously, a more accurate relationship is desirable. In section II we obtain one which relates D_{AB} to $(1-f)\bar{D}_{AB}$ and f/R_c . This equation is used in turn, in conjunction with the empirical observation $f/R_c \approx 2i/3 = 2/3(1 - \exp(\Delta X^2/4))$, to deduce a new relationship between D_{AB} , \bar{D}_{AB} , and ΔX^2 . A comparison with Pauling's bond energy estimates is given in section III. The equation deduced in this paper is found to be clearly superior, especially when applied to ionic bonds. The ramifications regarding a more accurate thermochemical electronegativity scale are discussed in section IV.

II. Bond Energy Formula

We can obtain an appropriate form for a bond energy-electronegativity relationship, valid for both ionic and covalent bonds, by applying some simple quantum mechanical theory to model the interaction potential between two atoms A and B. Let $|\psi_{ion}\rangle$ represent the state corresponding to the interaction between ions A^+ and B^- with interaction energy E_{ion} such that

$$H|\psi_{ion}\rangle = E_{ion}|\psi_{ion}\rangle \quad (5)$$

with $\langle\psi_{ion}|\psi_{ion}\rangle = 1$, and let $|\psi\rangle$ represent the total normalized bond wave function. If we define a normalized covalent function by the projection

$$|\psi_{cov}\rangle = \frac{(1 - |\psi_{ion}\rangle\langle\psi_{ion}|)|\psi\rangle}{[\langle\psi|(1 - |\psi_{ion}\rangle\langle\psi_{ion}|)|\psi\rangle]^{1/2}} \quad (6)$$

we can write, without approximation,

$$|\psi\rangle = C_1|\psi_{cov}\rangle + C_2|\psi_{ion}\rangle \quad (7)$$

where $C_1 = \langle\psi|\psi_{cov}\rangle$ and $C_2 = \langle\psi|\psi_{ion}\rangle$. By construction $\langle\psi_{cov}|\psi_{ion}\rangle = 0$ and $C_1^2 + C_2^2 = 1$. If we now evaluate the expectation value

$$E = \langle\psi|H|\psi\rangle \quad (8)$$

we obtain

$$E = C_1^2 E_{cov} + C_2^2 E_{ion} \quad (9)$$

where $E_{cov} = \langle\psi_{cov}|H|\psi_{cov}\rangle$ and $E_{ion} = \langle\psi_{ion}|H|\psi_{ion}\rangle$. We can express C_1^2 and C_2^2 in terms of known quantities by computing the expectation value of the dipole moment operator $\mu = \mu_E + \mu_n$ where $\mu_E = -\sum_i r_i$ and $\mu_n = \sum_\alpha Z_\alpha R_\alpha$ with i summed over all electrons and α over all nuclei. Substituting for $|\psi\rangle$ in the equation

$$\langle\mu\rangle = \langle\psi|\mu|\psi\rangle \quad (10)$$

and letting $r_i = R_c + (r_i - R_c)$ and $R_\alpha = R_c + (R_\alpha - R_c)$, where R_c is the vector from an arbitrary origin to the center of the bond, we find,

$$\langle\mu\rangle = [(Z_A + Z_B) - \sum_{i=1}^N \langle\psi|\psi\rangle]R_c + C_1^2 \langle\psi_{cov}|\mu_c|\psi_{cov}\rangle + 2C_1C_2 \langle\psi_{cov}|\mu_c|\psi_{ion}\rangle + C_2^2 \langle\psi_{ion}|\mu_c|\psi_{ion}\rangle \quad (11)$$

where

$$\mu_c = \frac{(Z_A - Z_B)}{2}R - \sum_i (r_i - R_c) \quad (12)$$

The first term on the right of eq 11 vanishes for neutral bonds.

The second and third terms can be neglected since these reduce approximately to sums over bonding electrons of integrals containing the product $(r_i - R_c)\psi_{cov}$ and either $r_i - R_c$ or ψ_{cov} is small over the whole range of integration. Thus

$$\langle\mu\rangle = C_2^2 \langle\psi_{ion}|\mu_c|\psi_{ion}\rangle \quad (13)$$

Following the method given in paper 1 we can show that

$$\langle\psi_{ion}|\mu_c|\psi_{ion}\rangle = R \left(1 - \frac{\alpha_A + \alpha_B}{R^3} + Ke^{\gamma R} \right) \quad (14)$$

where α_A and α_B are effective ionic polarizabilities and K and γ are constants related to atomic volume. Similarly, as shown in paper 1, if we ignore covalent terms, we can write

$$\langle\mu\rangle \approx fR \left(1 - \frac{\alpha_A + \alpha_B}{R^3} + Ke^{\gamma R} \right) \quad (15)$$

Comparing eq 13, 14, and 15, we see that $C_2^2 = f$. Since $\langle\psi|\psi\rangle = C_1^2 + C_2^2 = 1$, it follows that $C_1^2 = 1 - f$. If we now replace, in eq 9, E by $-D_{AB} + E_{CT}(f)$, E_{cov} by $-D_{cov}$, and E_{ion} by $-D_{ion}$ we can write

$$D_{AB} = (1-f)D_{cov} + fD_{ion} - E_{CT}(f) \quad (16)$$

where $E_{CT}(f)$ is the energy associated with partial charge transfer. Except for the very good approximation $C_2^2 \approx f$, eq 16 is formally an exact equation.

We now introduce several approximations. We first set

$$D_{cov} = \bar{D}_{AB} \quad (17)$$

where \bar{D}_{AB} is the average covalent bond energy $(D_{AA} + D_{BB})/2$. We next approximate D_{ion} by the Rittner potential^{7,8} representing the interaction between polarizable charge spheres

$$D_{ion} = \frac{1}{R_c} \left(1 + \frac{\alpha_A + \alpha_B}{R_c^3} - ke^{-\delta R_c} \right) \quad (18)$$

where α_A and α_B are polarizabilities and k and δ are constants characterizing short-range repulsive forces. Finally, we let

$$E_{CT}(f) = E_A(f) + E_B(-f) \quad (19)$$

where the function $E_A(q)$ represents the energy of atom A as a function of charge q (not necessarily integer). This energy is well approximated by the expression^{9,10}

$$E_A = \frac{(IP(A) + EA(A))}{2}q + \frac{(IP(A) - EA(A))}{2}q^2 \quad (20)$$

where $EA(A)$ and $IP(A)$ are the electron affinity and ionization potential, respectively, of atom A.

Let us write eq 16 in the form

$$D_{AB} = (1-f)\bar{D}_{AB} + \frac{f}{R_c} \left[R_c D_{ion} - \frac{R_c E_{CT}}{f} \right] \quad (21)$$

We can partially demonstrate the validity of eq 21 by example, substituting the constants E_{CT} , R_c , and D_{ion} appropriate to LiF. We find

$$D_{AB} = (1-f)\bar{D}_{AB} + 252(f/R_c) \quad (22)$$

Further substitution gives

$$D_{AB} = (1 - 0.84)(31.5) + \frac{(252)(0.84)}{1.56} = 140 \text{ kcal} \quad (23)$$

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Table I. Quantities Relevant to Bond Energy Relationships

mole- cule	D_{AB}^a	\bar{D}_{AB}^b (exptl)	% diff	f/R_e	$2i/3$	Δ^c	D_{AB}^d	% diff
NH	93.4	93.3	0.1	0.13	0.12	177	80.7	13.0
OH	114.7	110.6	3.7	0.25	0.26	185	103.8	3.2
SH	83.2	81.1	2.6	0.04	0.03	148	76.5	9.7
HF	145.0	134.6	7.7	0.40	0.40	187	144.7	7.5
HBr	87.1	87.5	0.5	0.08	0.08	145	80.3	9.2
CSi	75.2	69.3	8.5	0.10	0.08	130	70.5	1.9
CO	88.5	84.0	5.1	0.18	0.22	186	62.2	10.1
CF	102.2	105.3	2.9	0.30	0.28	176	107.1	1.7
AsCl	69.1	68.9	0.3	0.15	0.14	157	66.1	4.0
AsBr	54.8	56.5	3.0	0.10	0.10	162	53.2	5.9
LiF	137.0	137.0	0.0	0.54	0.60	203	238.0	73.7
		av 3.1				av 169		av 12.7

^a Computed with $\bar{D}_{AB} = (1-f)D_{AB} + 252f/R_e$ with $\bar{D}_{AB} = (D_{AA} + D_{BB})/2$. ^b Energies are in kcal/mol. ^c $\Delta = 252 - (D_{AA} + D_{BB})/2$. ^d Energies are in kcal/mol. ^e $\Delta = 252 - R_e\bar{D}_{AB}$. ^f Computed with Pauling's formula $D_{AB} = \bar{D}_{AB} + 30\Delta X^2$ with $\bar{D}_{AB} = (D_{AA}D_{BB})^{1/2}$.

This is in good agreement with the experimental value of 138 kcal.

Similar calculations on several other molecules yield approximately the same result as eq 22. This is demonstrated in Table I where we tabulate $D_{AB}(\text{exptl})$, eq 22, and the percent difference between the two in the second through fourth columns for the bonds listed in the first column. For comparison we list in columns 8 and 9 D_{AB} computed with Pauling's formula $D_{AB} = \bar{D}_{AB} + 30\Delta X^2$ and the percent difference between these values and $D_{AB}(\text{exptl})$. The geometric average is used in Pauling's relationship. The average difference between experimental bond energies and those obtained when eq 22 is used is 3.1%. The corresponding difference associated with Pauling's equation is 12.7%. Equation 22 is remarkable in that it contains no fitting parameters (one if the constant 252 is construed as such) and yet gives bond energy estimates that are more accurate than those obtained with Pauling's equation. The latter requires a fitting parameter associated with each atom (i.e., the electronegativity scale).

To relate eq 22 to Pauling's electronegativity differences we note that Pauling defines a quantity $i = 1 - \exp(-\Delta X^2/4)$ which he equates with ionic character. A comparison of f/R_e and i suggests a strong correlation between these two quantities. This is demonstrated in columns 5 and 6 of Table I where we tabulate f/R_e and $2i/3$ for the bonds in column 1. The two columns are in close agreement, differing by about 0.01 on the average. This suggests that D_{AB} can be related to ΔX by replacing f/R_e by $2i/3$. With such a replacement, eq 22 becomes $D_{AB} = (1-f)\bar{D}_{AB} + 168i$. To utilize this equation we require a method for accurately estimating f for arbitrary bonds. Such a method is developed in another paper.

In this paper we will recast eq 22 into a form similar to that utilized by Pauling to construct his electronegativity scale. We first recombine in the following manner:

$$D_{AB} = \bar{D}_{AB} + (f/R_e)[252 - R_e\bar{D}_{AB}] \quad (24)$$

We next note that the term in square brackets is approximately constant for a series of bonds. This is demonstrated in the seventh column of Table I for the bonds listed in the column. The average percent deviation from the mean, 169, is about 11%. Thus we can write

$$D_{AB} \approx \bar{D}_{AB} + 169(f/R_e) \quad (25)$$

Replacing f/R_e by $2i/3$ gives $D_{AB} \approx \bar{D}_{AB} + 113i$. To increase the accuracy of this equation we add two adjustable parameters. We replace the constant 113 by K and the ionic character by $\tilde{i} = 1 - \exp(-\alpha\Delta X^2)$ with K and α adjustable. Thus

$$D_{AB} = \bar{D}_{AB} + K\tilde{i} \quad (26)$$

To determine K and α we first of all demand that for ΔX small

$$D_{AB} \approx \bar{D}_{AB} + 30\Delta X^2 \quad (27)$$

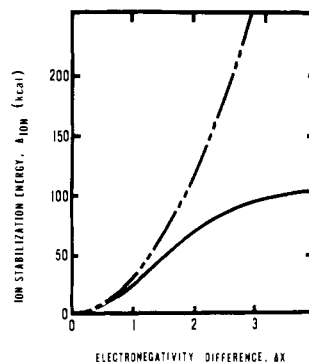


Figure 1. Plot of predicted ion stabilization energies vs. electronegativity differences.

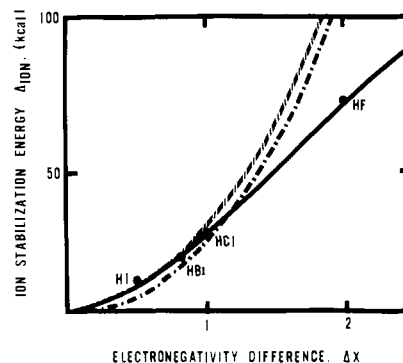


Figure 2. Comparison of fits of Pauling's hydrogen halide data and the proposed bond energy relationship.

This is, of course, Pauling's empirical observation. Second of all we demand that eq 26 give accurate values for highly ionic molecules (i.e., alkali halides). For small ΔX the expansion of $\exp(-\alpha\Delta X^2)$ in \tilde{i} of eq 26 leads to the condition $D_{AB} = \bar{D}_{AB} + K\alpha\Delta X^2$. Thus comparing with eq 27 we see that $K\alpha = 30$. Hence $K\tilde{i}$ becomes $K(1 - \exp(-30\Delta X^2/K))$. We obtain K by minimizing the difference between predicted and experimental alkali halide bond energies. We find $K = 103$. The use of boundary conditions to optimize K and α has resulted in a change in K from 113 to 103 and a change in α from Pauling's 0.25 to 0.29. The two boundary conditions ensure that eq 26 is accurate in both the ionic and covalent limits. The relationship $f/R_e \approx 2i/3$ ensures that it is accurate in between. Our final result is

$$D_{AB} = \bar{D}_{AB} + K(1 - \exp(-30\Delta X^2/K)) \quad (28)$$

In order to be consistent with Pauling we use $\bar{D}_{AB} = (D_{AA}D_{BB})^{1/2}$ in this relationship. The factor 30 in Pauling's equation assumes a geometric average.

III. Comparison of Predicted and Measured Bond Energies

In Figure 1 we plot, as a function of ΔX , the ion stabilization energy, $\Delta_{\text{ion}} = D_{AB} - \bar{D}_{AB}$, computed by using eq 3 and 28. In the region $\Delta X \leq 0.7$, the two curves overlap. Beyond this point, the curve corresponding to Pauling's relationship begins to rise sharply reaching an energy of 480 kcal at $\Delta X = 4$. The curve corresponding to eq 28 rises more slowly reaching, at $\Delta X = 4$, the value of 102.0 kcal. We have made a preliminary determination of electronegativities on the basis of eq 28 by using the bond energy data in Table 3-6 of Pauling's book, "The Nature of the Chemical Bond".⁶ Some differences are evident. For example, our electronegativity value for hydrogen is 2.0 while Pauling's is 2.1. To see the source of this difference consider Figure 2. There we plot measured values of Δ_{ion} for hydrogen halides with three different curves. The solid line corresponds to eq 28. The slanted dashed line represents the short ranged asymptotic form of eq 28. The dashed line represents Pauling's fit to the hydrogen halide data. Pauling's curve should overlap the slanted dashed line since its range of validity is small. The fact that it does not is due to

Table II. Comparison of Experimental and Predicted Bond Energies^a

bond	D_{AB^-} (exptl)	\bar{D}_{AB}	D_{AB^-} (this paper) ^b	% diff	D_{AB^-} (Pauling) ^c	% diff
H-F	134.6	61.7	132.5	1.5	170.0	26.3
H-Cl	103.1	77.7	103.7	0.6	102.0	1.0
H-Br	87.5	69.3	86.8	0.8	84.0	4.0
H-I	71.4	61.3	68.5	4.1	66.1	7.4
Rb-F	116.0	21.3	119.1	2.8	307.2	164.8
Rb-Cl	100.4	26.8	104.6	4.2	172.0	71.3
Rb-Br	90.3	23.8	94.6	3.3	143.8	59.2
Rb-I	76.5	21.1	79.7	4.2	107.8	40.9
Cs-F	119.6	19.6	118.2	1.0	346.0	189.5
Cs-Cl	105.7	24.8	105.7	0.0	170.0	60.8
Cs-Br	96.3	22.1	93.0	3.4	142.1	32.3
Cs-I	82.1	19.5	82.4	0.4	116.7	42.2
Si-H	70.4	66.4	67.6	3.9	69.1	1.8
Si-O	88.1	37.4	91.5	3.9	124.1	40.8
Si-C	69.3	59.3	71.2	2.8	74.0	6.8
O-H	110.6	68.8	113.6	2.7	127.6	15.4
C-H	98.8	93.0	98.9	0.1	97.8	1.0
C-O	84.0	52.5	77.4	7.8	82.5	1.5
			av 2.6		av 43.6	

^a Experimental data from ref 6. Energies are in kcal/mol.

^b Computed with the formula $\bar{D}_{AB} = D_{AB} + K(1 - \exp(-\alpha\Delta X^2))$, with $\alpha = 0.29$, $K = 103$, $\bar{D}_{AB} = (D_{AA}D_{BB})^{1/2}$ and electronegativity differences appropriate to this model. ^c Computed with the formula $D_{AB} = \bar{D}_{AB} + 30\Delta X^2$ and Pauling's electronegativity table.

slightly distorted electronegativity values in the Pauling scale. His electronegativities are chosen to minimize the errors in the predicted stabilization energies of sets like this one. This is done by artificially reducing the electronegativity difference. As a result more accurate electronegativity differences (i.e., more accurate within the framework of more accurate thermochemical models) tend for non-metal bonds to be slightly larger than those given by Pauling's table. We are in the process of constructing a corrected table.

In Table II we tabulate experimental and predicted bond energies and percent differences for a set of molecules whose bonds range from pure ionic to pure covalent. Estimates obtained with Pauling's equation and table differ from measured values by an average of 43.6%. Those obtained with eq 28 and electronegativities appropriate to this model differ by only 2.7%. (For a much larger sampling, the average difference is about 3.4%.)

In Figure 3 we plot predicted and measured values of Δ_{ion} . The solid line corresponds to values predicted by eq 28. The agreement is quite good for both covalent and ionic bonds.

IV. Discussion

Regarding the proposed model several points can be made.

1. Equation 28 correlates electronegativity differences and bond energies better than does the Pauling equation. Thus, it is probably

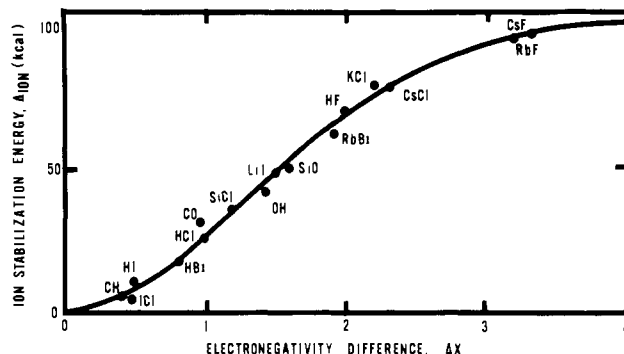


Figure 3. Plot of measured values of ion stabilization energy vs. electronegativity differences. The solid line represents the approximation $\Delta_{ion} = 103(-\exp(-0.29\Delta X^2))$. The electronegativity differences that are used are those appropriate to this model. They tend to be slightly large than corresponding Pauling differences.

a better relationship on which to base a thermochemical electronegativity scale. Pauling's equation tends to slightly underestimate electronegativity differences.

2. In order to estimate the relative covalent and ionic contributions to bond energies we can use the approximate equations

$$D_{e^{cov}} = (1 - f)\bar{D}_{AB} \quad (29)$$

and

$$D_{e^{ion}} = \Delta_{ion} + f\bar{D}_{AB} \quad (30)$$

Thus, for example, f , Δ_{ion} , and \bar{D}_{AB} for CsF are 0.98, 98.6 kcal, and 19.6 kcal, respectively. It follows that $D_{e^{cov}} = 0.392$ kcal and $D_{e^{ion}} = 117.8$ kcal. Similarly f , Δ_{ion} , and \bar{D}_{AB} for CsLi are approximately 0.29, 2.65 kcal, and 18.6 kcal, respectively. Thus $D_{e^{cov}} = 13.0$ kcal and $D_{e^{ion}} = 8.23$ kcal.

3. There is not sufficient bond energy data, similar to that tabulated in Table I, available to construct a complete electronegativity scale. Pauling circumvents this problem by utilizing an arithmetic mean postulate for \bar{D}_{AB} and the empirical formula

$$D_{AB} = \frac{D_{AA} + D_{BB}}{2} + 23\Delta X^2 \quad (31)$$

The analogue of eq 28 which reduces to eq 31 in the limit of small ΔX , and is therefore appropriate for use in conjunction with heat of formation data, is

$$D_{AB} = \frac{D_{AA} + D_{BB}}{2} + K'(1 - \exp(-23\Delta X^2/K')) \quad (32)$$

where $K' = 105$.

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