

On the Electron Affinities of Halogens and the Strength of Ionic Interactions

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A new interpretation is forwarded for the enthalpies of ionic interactions ΔH_{AB} . From observed trends in ΔH_{AB} values for alkalisalt molecules, it is concluded that the electron affinities of halogens are in need of revision.

For an interpretation of bond strengths in simple diatomic heteronuclear molecules several empirical formalisms have been proposed. Pauling's well known bond energy equation¹, whereby the bond energy is split up into ionic and covalent contributions, has led to the concept of electronegativity. The procedure is, however, largely dependent on the value ascribed to the purely hypothetical covalent bonding term, which seems highly problematic.

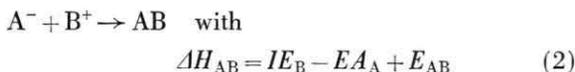
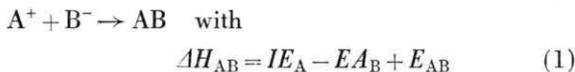
If the so-called ionic-covalent resonance formalism is to be retained, it would be more illustrating to compare the actual energy of a partly ionic bond with the energy of a completely and permanently ionic bond, which, in the usual terminology, is supposed to take part in the resonance-system. Thus, in the case of heteronuclear AB bonds, the energies of the completely ionic bonds A^+B^- and/or A^-B^+ should be known.

A first step in achieving this, consists in considering the enthalpies of ionic interactions



which have recently been shown to fit into the E–C formalism as it was first advanced for the interactions of donor-acceptor interactions².

In general, the following reactions and enthalpies ΔH_{AB} can be considered for AB bonds:



if IE_X and EA_X represent the energy of, respectively, the first and second valence electron of X^- and if E_{AB} is the bond energy.

At first sight, these ΔH_{AB} values are even more complicated than E_{AB} values alone, on which the Pauling procedure was originally applied.

However, the valence electron energy of a pair of ions $A^+ + B^-$ for instance at *infinite* internuclear separation ($r = \infty$), is $IE_B + EA_A$. Now, this is exactly the energy of a permanently 100% ionic bond at *equilibrium* internuclear separation ($r = r_{AB}$) also. In fact, as soon as the ionization energy of a given element A is zero, no electron withdrawal force will be present at the nucleus of A, when this element is involved in bond formation with B. IE_A equal to zero means Z_A (the effective nuclear charge of A) equal to zero and/or r_A (the covalent radius of A) infinite, whence, in first approximation, i. e. neglecting polarization, $r_{AB} \approx r_A + r_B = \infty$, and correspondingly $e^2/r_{AB} = 0$! Therefore, a simple example of a completely and permanently ionic bond is the negative ion B^- , which results from "bonding" between a neutral element B and a free electron³. This has quite important consequences for the interpretation of the ΔH_{AB} values (1) and (2) and the role of E_{AB} therein.

Indeed, ΔH_{AB} values are now seen to represent simply the difference in energy between partly and completely ionic *bonds*. Although it is only formally valid to speak of bonds in the extreme case of X^- , since the internuclear separation is infinite, the present formalism is quite interesting for comparisons of bonds in a particular series.

It is well known for instance that the bonds in alkalisalt molecules are largely ionic in the sense $A^{\delta+}B^{\delta-}$ if A is the alkali and B the halogen, whence these molecules will be used as reference-material for this investigation.

According to the new interpretation to be given to ΔH_{AB} , one should observe the following trends for alkalisalts:

1. in a given series of AB molecules wherein A is constant, $\Delta H_{AB}(1)$ will *decrease* with *increasing* permanent polarity *I* of the AB bond. Increasing polarity in the sense $A^{I+}B^{I-}$ indeed means that the difference between the partly ionic bond AB and the completely ionic bond A^+B^- (or in this case B^-) decreases.
2. in a given series of AB molecules wherein B is constant, $\Delta H_{AB}(2)$ will *increase* with *increasing* permanent polarity *I* of the AB bond. Increasing polarity in the sense $A^{I+}B^{I-}$ now means that the actual bond AB will differ more and more from the ionic structure A^-B^+ (or A^-) with which it is compared.

Table 1 shows some typical examples of "experimental" ΔH_{AB} values in order to illustrate rule 1 and 2 for, respectively, the series LiB and AF.

It is obvious that in obtaining these figures everything depends upon the accuracy of the electron af-

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Table 1. ΔH_{AB} values for some ionic interactions.

Bond ^a	$-\Delta H_{AB}(1)^b$	Bond ^a	$-\Delta H_{AB}(2)^{b,c}$
LiI	135	LiF	525
LiBr	147	NaF	504
LiCl	154	KF	508
LiF	181	RbF	510
		CsF	512

^a bonds arranged in order of increasing polarity.

^b values in Kcal/Mole, taken from Ref. 2 and/or from the sources given therein.

^c EA values for alkali metals taken from Ref. 4 and 5.

finities. Indeed, the bond energies are known with relatively great accuracy and the knowledge of the ionization energies is not even necessary in order to get the ΔH_{AB} trends for a particular AB series.

Thus, the results in Table 1, reveal that

1. in the LiB series, $\Delta H_{AB}(1)$ increases with increasing I -values, completely in disagreement with rule 1 and, that
2. in the AF series (if exception is made for the LiF bond for the time being), $\Delta H_{AB}(2)$ increases with increasing I -values, in agreement with rule 2.

Therefore, if the arguments given above are valid, this paradoxon can only be solved by reconsidering the electron affinities of particular elements.

Recent determinations of EA values for alkali-metals^{4,5} seem to support our earlier statements about the stability of homonuclear bonds⁶. This may be taken as a further justification for the validity of rule 2 and of our present argumentation. Hence, in view of the consistency requirements of the model, it must be concluded that the electron affinity of the halogens should be revised and, that the $\Delta H_{AB}(1)$ values for alkalisalt molecules AB, as they are commonly tabulated, are mutually in-

consistent with the $\Delta H_{AB}(2)$ values for the same bonds!

Refinements in the interpretation of electron affinity values in the way suggested by McMillin and Drago² for hydrogen seem interesting but have not yet been worked out. It appears from the present work that the experimentally determined EA values for halogens might be given a more differentiated interpretation too.

Extension of this procedure to other series of alkalisalt molecules would lead to similar conclusions for EA_X , as already obtained for E_{XX} in earlier work⁷, on account of the relation $EA_X = E_{XX}$ ^{3,6}. This consistently answers the discrepancy observed for LiF in the AF series discussed above, although even the existence of this discrepancy does not affect the conclusion concerning the revision of the EA values for halogens.

This argumentation clearly illustrates the great impact of EA values for explaining chemical bonding, which is not surprising since EA values describe the filling up of a singly occupied valence orbital, which is also a characteristic of ordinary chemical bonding.

Possible alterations in EA values however could greatly affect relationships wherein both EA and IE are involved. This would be the case for the Hinze-Whitehead-Jaffé formalism for electronegativity⁸ in the first place but also for further applications of the ionic approximation to chemical bonding such as, for instance, the interpretation of heteronuclear bond lengths⁹.

Further investigations on these points are under way, although particular attention will be paid to Drago's $E-C$ equation², which is a challenge for any discussion about the nature of electron-pair bond formation in general and about Pearson's HSAB rule¹⁰ in particular.

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