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EMPIRICAL CALCULATIONS OF THE FORCE CONSTANTS, DISSOCIATION ENERGIES AND BOND LENGTHS OF DIATOMIC MOLECULES*

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ABSTRACT

Empirical equations have been derived to calculate the force constant, F, dissociation energy, D, and bond length, R, of diatomic molecules. They are

$$F_{AX} \cong F_{BX}(F_{A_2}/F_{B_2})^{1/2}$$

$$D_{AX} \cong D_{BX}(D_{A_2}/D_{B_2})^{1/2}$$

and

$$R_{AX} \cong R_{BX} + \frac{1}{2}(R_{A_2} - R_{B_2})$$

where the subscripts stand for atoms A, B, X, Y, respectively.

The use of these equations is illustrated with the existing data on the diatomic alkalis, diatomic halogens and alkali halides. Excellent agreement is obtained for these molecules. The relations of the derived equations to the earlier empirical equations are discussed.

I. INTRODUCTION

The molecular properties such as the force constant, dissociation energy and bond length have long been of interest, both experimentally and theoretically. It often turns out that one needs a simple and reliable estimation of these quantities without having to rigorously solve the quantum mechanics involved. This is especially true to the high temperature mass spectrometric studies. Here, evaluation of the thermodynamic data using the third law method requires an estimation of the free energy functions which, in turn, requires a knowledge of the molecular properties such as force constant and bond length. For many molecules of high temperature interest, however, such data are often lacking. Therefore, it is very useful to find empirical relations which correlate the available data in a simple way with physical significance. Among the existing commonly used empirical relations are: for the force constant by Badger (1), Guggenheimer (2), Herschbach and Laurie (3), Somayajulu (4), for the bond energy by Pauling (5), and for the bond length by Schomaker and Stevenson (6). Recently, Hauge and Margrave (7) established some correlations among the force constants and dissociation energies between diatomic oxides and sulfides.

An extensive use of the relations of References 1-6, however, is often limited by the following factors. In order to calculate the force constant, one needs to know the bond length of the molecule; to estimate the bond energy and bond length electronegativities of the component atoms in their valence state are needed which are often lacking. It is, therefore, the purpose of this work to establish some general equations common to these molecular properties and to avoid the limitations inherent in these earlier empirical equations. As will be shown later, the correlations found by Hauge and Margrave are to be expected from the equations derived in this paper.

We start our derivations by assuming that certain relations in common exist among the atoms from the same family in their contributions to the molecular properties of interest. In other words, the change in electronegativity of these atoms from one type of molecule to the other is assumed to be similar. It is through these assumptions equations are derived which relate the molecular properties of heteronuclear diatomics directly to those of the parent homonuclear ones. No explicit values of electronegativity are needed although the equations derived bear some similarity to the mentioned equations (4-6) which include electronegativity.

Section II shows the derivations of our empirical equations, and Section III shows the calculations on the diatomic alkalis, diatomic halogens and alkali halides. The applicability to the other types of molecules and comparisons of these equations to the earlier ones are discussed in Section IV.

II. METHOD

Within the framework of the concept of electronegativity we start with the assumption that atom A retains the same electronegativity among molecules AX, AY and AZ; here X, Y and Z belong to the same family which may or may not be the same to that of A. First, consider the force constant. Assuming a product relation, the above assumption requires a "constant" contribution of $(F^*_{A_2})^{1/2}$ from atom A to the force constants of molecules AX, AY and AZ, with the corresponding ones from the atoms X, Y and Z being $(F_{X_2})^{1/2}$, $(F_{Y_2})^{1/2}$ and $(F_{Z_2})^{1/2}$, respectively. Here F_{X_2} is the force constant of molecule X_2, etc, and $F^*_{A_2}$ is in general different from F_{A_2}, the force constant of molecule A_2, when atom A is not of the same family as X, Y, Z. Our assumption thus has the form

$$F_{AX} \cong (F^*_{A_2} \times F_{X_2})^{1/2} \qquad \text{(A-1)}$$

As an example, consider NaCl and NaBr. Using the data listed in Reference 8b, $F^*_{Na_2}$ is found to be 0.3728 mdyneÅ^{-1} compared with the value of 0.172 mdyneÅ^{-1} for F_{Na_2} (8). The higher value for $F^*_{Na_2}$ implies an increasing contribution of Na in going from Na_2 to NaCl and NaBr in determining the force constants of these molecules. This is expected in view of the change in bonding type from Na_2 to the Na halides. For the molecules composed of atoms from the same family, it is reasonable to assume that atom A has the same contribution in determining the force constants of molecules AB and A_2. This is similar to assuming that the bonding type is very similar in these molecules. For this type of molecules Equation (A-1) thus reduces to

$$F_{AB} \cong (F_{A_2} \times F_{B_2})^{1/2} \qquad \text{(A-1')}$$

For the alkali and halogen series considered here, Equation (A-1') holds to within 2% accuracy (8), as is shown in Table 1, except for the molecules containing flourine atom, which will be discussed later.

Next, consider molecules AX and AY. From Equations (A-1) and (A-1') we have

$$(F_{AX} \times F_{AY})/F_{XY} \cong F^*_{A_2} \qquad (1)$$

With a similar relation for molecules BX and BY, we have the general relation

$$(F_{AX} \times F_{AY})/(F_{BX} \times F_{BY}) \cong F^*_{A_2}/F^*_{B_2} \qquad (2)$$

In the special case where X = Y, Equation (2) becomes

$$F_{AX}/F_{BX} \cong (F^*_{A_2}/F^*_{B_2})^{1/2} \qquad (3)$$

To bring relation like Equation (3) to a more useful form where data are lacking for computing $F^*_{A_2}$, etc, we further assume that

$$F^*_{A_2}/F^*_{B_2} \cong F_{A_2}/F_{B_2} \qquad \text{(A-2)}$$

for A, B being treated toward another family of atoms. In other words, following the earlier assumptions, this is similar to saying that the change in bonding type between A_2 and AX is to the same extent as that between B_2 and BX. Using the data of Reference 8b, we have 1.742 and 1.745 of the ratios F_{Na_2}/F_{K_2} and $F^*_{Na_2}/F^*_{K_2}$, respectively, showing excellent fit with the assumption Equation (A-2). Our empirical equation for the force constant thus has the form

$$F_{AX} \cong F_{BX}(F_{A_2}/F_{B_2})^{1/2} \qquad \text{(FC-1)}$$

Using the same approach similar equations can be derived for the dissociation energy and bond length. Assuming a product relation for the former and an addition one for the latter, these equations have the forms

$$D_{AX} \cong D_{BX}(D_{A_2}/D_{B_2})^{1/2} \qquad \text{(DE-1)}$$

and

$$D_{AB} \cong (D_{A_2} \times D_{B_2})^{1/2} \qquad \text{(A-1')}$$

for the dissociation energy and

$$R_{AX} \cong R_{BX} + \frac{1}{2}(R_{A_2} - R_{B_2}) \qquad \text{(BL-1)}$$

and

$$R_{AB} \cong \frac{1}{2}(R_{A_2} + R_{B_2}) \qquad \text{(A-1')}$$

for the bond length.

These are the equations to be used in our computations. Comparison with the earlier empirical equations will be discussed later.

III. RESULTS

The derived equations are first applied to the diatomic alkalis and halogens, as shown in Tables 1-3. Excellent agreement is obtained with all the observed values using Equations (FC-1), (DE-1) and (BL-1). Also shown in these Tables are the values using the common relation (A-1'). Again, excellent agreement is obtained except for the cases where fluorine atom is involved.

Next, we calculate the properties of alkali halides. Take force constant for example, and the other two properties equally applicable, it is best to find the ratio of F_{AX}/F_{AY} or F_{AX}/F_{BX} and compare with the value $(F_{X_2}/F_{Y_2})^{1/2}$ or $(F_{A_2}/F_{B_2})^{1/2}$, respectively. The results are shown in Tables 4-6. It is seen that through the proper choice of correlations agreement with experiment is very satisfactory for all the alkali halides. Tables 4b and 5b show how the fluorides can be satisfactorily correlated although a nearly constant deviation is noted when the fluorides are correlated in the way shown in Tables 4a, 5a and 6. These deviations, however, can still be made useful for our purposes, as explained later. It is interesting to note that the deviation noted is very similar for the force constant and dissociation energy, being close to 1.44 for both properties.

IV. DISCUSSION

The derived equations of this work have been shown to be very successful to the diatomic alkalis, halogens and alkali halides. No knowledge of the electronegativity is needed for these computations. This, together with the simple relations derived between a heteronuclear molecule and the parent homonuclear diatomic molecules allows estimation of the properties of either type of molecules from the available data of the other. Extension of this work to many other types of diatomic and polyatomic molecules is also successful and will be reported later.

It is recalled that although all the molecules treated in this paper can be satisfactorily correlated, some care is necessary in dealing with the fluorides. This probably implies a rather drastic change in bonding strength between, for example, F_2 and FCl as compared with that between Cl_2 and ClBr. In terms of electronegativity this could be due to the large difference in this quantity between fluorine and other halogen atoms. However, by proper correlations such as that demonstrated in Tables 4b and 5b, this difficulty can be overcome and successful application of our equations achieved.

As mentioned the present equations can be used to estimate heteronuclear molecules from the corresponding homonuclear parent ones. In the cases where information on the latter is lacking a second set of equations in the familar forms can be easily derived from Equations (FC-1), etc, i.e.,

$$F_{AX} \cong F_{BX}(F_{AY}/F_{BY}) \qquad \text{(FC-2)}$$

$$D_{AX} \cong D_{BX}(D_{AY}/D_{BY}) \qquad \text{(DE-2)}$$

and

$$R_{AX} \cong R_{BX} + (R_{AY} - R_{BY}) \qquad \text{(BL-2)}$$

As can be seen from Tables 1-6 these equations work very well for the molecules dealt with here, and can be used wherever necessary.

Our equations are now compared with the earlier ones (1-6). Take the force constant for example, and compare our Equation (FC-1) with that of Somayajulu (4)

$$F_{AB} = (F_{A_2} \cdot F_{B_2})^{1/2} + \Delta$$

Δ being a function of the difference in electronegativity between atoms A and B in their valence states. It is recalled that Equation (FC-1) is derived from the assumption set forth in Equation (A-1) . Comparing Eq. (A-1) with Somayajulu's equation one notices that in our treatment the electronegativity part is absorbed into the term $F^*_{A_2}$. After relating $F^*_{A_2}$ back to F_{A_2} using the assumption (A-2) Equation (FC-1) is derived that relates two heteronuclear molecules through the parent homonuclear ones. It is through these assumptions that no explicit values of electronegativity are needed for our computations. The successful application of the derived equations thus supports our approach here.

Similar auguments also apply to our equations on dissociation energy and bond length when they are compared, respectively, to those of Pauling (5)

$$D_{AB} = (D_{A_2} \cdot D_{B_2})^{1/2} + 30(x_A - x_B)^2$$

and Schomaker and Stevenson (6)

$$R_{AB} = \frac{1}{2}(R_{A_2} + R_{B_2}) - c|x_A - x_B|$$

Here, x's are the electronegativities and c is a function of bond type.

Comparison with the works of Badger (1), Guggenheimer (2), and Herschbach and Laurie (3) reveals further advantages of the present method. Each property can be estimated without having to first estimate another property as in required by these earlier works. In addition, a combined use of the present method with the earlier ones also helps to evaluate the estimated properties. For example, the estimated bond length from the present method can be used in the earlier ones for the force constant, which, in turn, can be compared with the one obtained from the present method using only the data on the force constants from the relevant molecules.

Finally, compare our work with that of Hauge and Margrave (7). These authors found a general empirical relation for the dissociation energies and force constants of diatomic oxides and sulfides

$$(D_{MO}/D_{MS})/(F_{MO}/F_{MS}) \approx \text{constant}$$

where MO and MS stand for the oxides and sulfides, respectively. The ratio has the values of 0.66-0.81 for the molecules investigated with a slight trend noted. Applying our Equations (FC-1) and (DE-1), the above relation takes the form

$$(D_{MO}/D_{MS})/(F_{MO}/F_{MS}) \approx (D_{O_2}/D_{S_2})^{1/2} \cdot (F_{S_2}/F_{O_2})^{1/2}$$

and has a value of 0.70 using the data on D_{O_2}, etc (8,9). The close agreement with experiment thus also provides some physical meaning to the empirical relation found by these workers.

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Table 1. Calculated force constants of diatomic alkalis and halogens.

Mol.	F^{a}_{obs} m dyne $Å^{-1}$	F^{b}_{calc} (A-1') m dyne $Å^{-1}$	F^{b}_{calc} (FC-1) m dyne $Å^{-1}$	Remarks*
LiNa	0.208	0.209	0.208	Standard
LiK		0.1585	0.1574	
LiRb		0.1446	0.1436	
LiCs		0.1327	0.1317	
NaK	0.130	0.1302	0.130	Standard
NaRb	0.121	0.1188	0.1186	
NaCs		0.1089	0.1088	
KRb		0.0899	0.0898	
KCs		0.0824	0.0823	
RbCs	0.0748	0.0752	0.0751	
FCl	4.562	3.837	4.705	
FBr	4.071	3.320	4.071	Standard
FI		2.777	3.404	
ClBr	2.832	2.844	2.832	Standard
ClI	2.383	2.378	2.368	
BrI	2.064	2.058	2.049	

*Those marked "standard" are the molecules used to apply Eq. (FC-1). For example, LiNa for LiK, LiRb and LiCs; FBr for FCl and FI; ClBr for ClI and BrI.

[a] Reference 8.

[b] Values for the homonuclear diatomic molecules needed for computations are from Reference 8.

Table 2. Calculated dissociation energies for the diatomic alkalis and halogens.

Mol.	D^{a}_{obs} Kcal mol^{-1}	D^{b}_{calc} (A-1') Kcal mol^{-1}	D^{b}_{calc} (DE-1) Kcal mol^{-1}	Remarks*
LiNa		21.21		
LiK		17.52		
LiRb		16.76		
LiCs		16.44		
NaK	14.3	14.29	13.69	
NaRb	13.1	13.67	13.1	Standard
NaCs		13.41	12.86	
KRb		11.29	10.82	
KCs		11.08	10.62	
RbCs		10.60	10.16	
FCl	59.0	46.0	59.0	Standard
FBr	55.0	41.0	52.6	
FI		36.3	46.6	
ClBr	51.4	50.9	53.1	
ClI	49.63	45.1	47.0	
BrI	41.91	40.2	41.91	Standard

*See footnote of Table 1 for a similar meaning in applying Eq. (DE-1).

[a] Reference 9

[b] Values for the homonuclear diatomic molecules needed for computations are from Reference 9.

Table 3. Calculated bond lengths for the diatomic halogens.

Mol.	R_{obs}[a] Å	R_{calc}[b] (A-1') Å	R_{calc}[b] (BL-1) Å	Remarks*
FCl	1.628	1.703	1.6081	
FBr	1.7556	1.851	1.7556	Standard
FI		2.042	1.9471	
ClBr	2.138	2.1358	2.1292	
ClI	2.3208	2.3273	2.3208	Standard
BrI		2.4751	2.4682	

*For example, FBr as the standard in applying Eq. (BL-1) for FCl and FI.

[a] Reference 10.

[b] Values for the homonuclear diatomic molecules needed for computations are from Reference 10.

Table 4. Correlations of the force constants among the alkali halides.

a.

Atom M	F_{MF}/F_{MCl} [a]	F_{MCl}/F_{MBr} [a]	F_{MBr}/F_{MI} [a]
Li	1.75	1.18	1.24
Na	1.60	1.15	1.26
K	1.59	1.23	
Rb	1.70		
Cs	1.70		
	$(F_{F_2}/F_{Cl_2})^{1/2}=1.17$	$(F_{Cl_2}/F_{Br_2})^{1/2}=1.16$	$(F_{Br_2}/F_{I_2})^{1/2}=1.20$

b.

Atom X	F_{LiX}/F_{NaX} [a]	F_{NaX}/F_{KX} [a]	F_{KX}/F_{RbX} [a]	F_{RbX}/F_{CsX} [a]
F	1.41	1.29	1.05	1.07
Cl	1.29	1.27	1.13	1.07
Br	1.26	1.37		
I	1.27			
	$(F_{Li_2}/F_{Na_2})^{1/2}=1.22$	$(F_{Na_2}/F_{K_2})^{1/2}=1.32$	$(F_{K_2}/F_{Rb_2})^{1/2}=1.10$	$(F_{Rb_2}/F_{Cs_2})^{1/2}=1.09$

[a] Reference 8.

Table 5. Correlations among the dissociation energies of alkali halides.

a.

Atom M	D_{MF}/D_{MCl}[a]	D_{MCl}/D_{MBr}[a]	D_{MBr}/D_{MI}[a]
Li	1.21	1.12	1.22
Na	1.16	1.11	1.25
K	1.16	1.11	1.16
Rb	1.18	1.11	1.15
Cs	1.17	1.12	1.21
	$(D_{F_2}/D_{Cl_2})^{1/2}=0.81$	$(D_{Cl_2}/D_{Br_2})^{1/2}=1.12$	$(D_{Br_2}/D_{I_2})^{1/2}=1.13$

b.

Atom X	D_{LiX}/D_{NaX}[a]	D_{NaX}/D_{KX}[a]	D_{KX}/D_{RbX}[a]	D_{RbX}/D_{CsX}[a]
F	1.20	0.98	0.98	0.98
Cl	1.15	0.98	0.99	0.97
Br	1.14	0.97	0.99	0.98
I	1.17	0.90	0.98	1.03
	$(D_{Li_2}/D_{Na_2})^{1/2}=1.22$	$(D_{Na_2}/D_{K_2})^{1/2}=1.21$	$(D_{K_2}/D_{Rb_2})^{1/2}=1.05$	$(D_{Rb_2}/D_{Cs_2})^{1/2}=1.02$

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[a] Reference 9.

Table 6. Correlations among the bond lengths of the alkali halides.*

Atom M	$R_{MCl}-R_{MF}$ [a] Å	$R_{MBr}-R_{MCl}$ [a] Å	$R_{MI}-R_{MBr}$ [a] Å
Li	0.49	0.18	0.19
Na	0.43	0.12	0.23
K	0.50	0.16	0.23
Rb	0.51	0.14	0.20
Cs	0.58	0.17	0.23
	$\frac{1}{2}(R_{Cl_2}-R_{F_2})=0.285$	$\frac{1}{2}(R_{Br_2}-R_{Cl_2})=0.1475$	$\frac{1}{2}(R_{I_2}-R_{Br_2})=0.1915$

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[*] Correlations similar to those of Tables 4b and 5b are not made due to insufficient experimental data.

[a] Reference 11.

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