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"Saturation" Effect in Description of Heteropolar Covalent Bonds within Thermochemical Approach

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Abstract—An approach allowing more adequate evaluation of the dissociation energies of strongly polar heteroatomic bonds without knowledge of additional geometrical parameters was developed within the Pauling concept taking into account the "saturation effect."

It was shown [1] that the dissociation energy of a heteropolar covalent bond (E_{AB}) can be described by a sum of two components, one of which is independent of the difference of electronegativities ($\Delta\chi = \chi_{\mathrm{B}} - \chi_{\mathrm{A}}$) and the other is proportional to $\Delta\chi^2$. Within this approach, electronegativity is a decisive parameter determining the capability of a certain atom in a given valence state to hold bonding electrons, whereas $\Delta\chi$ describes the difference in the electron affinity of the interacting atoms. Similar χ values of elements can be easily evaluated not only within the primary thermochemical method from experimental bond energies, but also using ionization, geometrical, and several other approaches (see, e.g., [2]). According to [1], for a single bond, the following ratio is valid:

$$E_{\mathrm{AB}} = \langle E_{\mathrm{AB}} \rangle + \Delta E_i, \qquad (1)$$

where $\langle E_{\mathrm{AB}} \rangle = (E_{\mathrm{AA}} E_{\mathrm{BB}})^{1/2}$ and the ionic correction factor $\Delta_i = 1.30\delta\chi^2$ (eV).

The ionic correction factor ΔE_i in expression (1) appears owing to the fact that the contributions of the Coulomb attraction and charge transfer energy (due to the bond polarization) are always greater than the corresponding weakening of the pure covalent bond [3]. The correctness of the multiplicative approximation $\langle E_{\mathrm{AB}} \rangle$ is confirmed by quantum-chemical estimations of the heteropolar component [3, 4].

In the strict sense, expression (1) can be only used for bonds formed by exchange mechanism in diatomic molecules of low or intermediate polarity (≤35–40%). With further increase in $\Delta\chi$, especially in the case of ionic compounds, this expression becomes inadequate due to overestimation of the calculated ΔE_i values [5]. In some cases, e.g., in Cs–F and Rb–F systems, the deviation between the theoretical and experimental data can exceed experimental E_{AB} itself [6]. This deviation is probably due to the fact that the "saturation" effect, i.e., certain destabilization of the bond as the increase in ΔE decelerates with increasing $\Delta\chi$, was not taken into account [6, 7]. This effect can be explained by the dependence of the ionic increment not only on the difference in the electronegativities, but also on the degree of overlapping of the valence orbitals [2, 8]. As known, the latter decreases with accumulation of opposite effective charges on the dipole edges, which depletes the bonding electron density in the internuclear spacing and increases heteronuclear repulsive interaction.

Various procedure were proposed to correct the Pauling method, using both a new initial function $E_{\mathrm{AB}}(\Delta\chi)$ and more complex calculation procedures with additional parameters (atom size, bond length, polarizability, valence, etc.) [2–4, 6–9]. Among these or other similar modified calculation schemes, there are no universal expressions valid for any range of the bond polarity. Therefore, in this work we attempted to improve the canonical concept [1] within the thermochemical approach taking into account the "saturation" effect. Moreover, in connection with noticeable refinement of the electronegativities of some main group elements [2, 8, 10, 11], it was advisable to check the adequacy of the known analytical expressions of E_{AB}. Since the experimental values at high $\Delta\chi$ correspond to slow increase in $\mathit{\Delta} E_i(\Delta\chi)$, rather than to steeper parabolic dependence, we used as the reference equations those of Matcha (2) [6] and Bratsch (3) [7] to evaluate the "saturation" effect:

$$E_{\mathrm{AB}} = \langle E_{\mathrm{AB}} \rangle + 4.47[1 - \exp(-0.29\,\Delta\chi^2)] \ \text{(eV)}, \qquad (2)$$

$$E_{\mathrm{AB}} = [(r_{\mathrm{A}} + r_{\mathrm{B}})/r_{\mathrm{AB}}]\{\langle E_{\mathrm{AB}} \rangle + 4[1 - \exp(-0.25\,\Delta\chi^2)]\}, \ \text{(eV)}, \qquad (3)$$

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Table 1. Initial parameters

Element	$\chi_{A(B)}$, eV$^{1/2}$	$r_{A(B)} \times 10$, nm	$E_{A(B)}$, eV
H	2.19	0.37	4.52
Li	1.03	1.34	1.14
K	0.83	1.98	0.53
Rb	0.8	2.14	0.51
Cs	0.7	2.33	0.455
B	1.90	0.84	3.08
C	2.47	0.77	3.145
N	2.93	0.74	1.64
O	3.30	0.73	2.58
S	2.65	1.04	2.74
F	3.70	0.71	1.65
Cl	3.13	0.99	2.51
Br	2.96	1.14	2.00
I	2.74	1.33	1.565

where r_A and r_B are the standard covalent radii and r_{AB} is the bond length.

The approaches developed by the above authors were recommended for the most correct description of the bond energy (see, e.g., [2, 12]). In both equations, the approximation ($\Delta E_i \sim i$) substantiated in [6] was used in which the bond ionicity is presented by the known Pauling expression $i = 1 - \exp(-a\Delta\chi^2)$ [1]. As seen, Eq. (2) involves a set of the initial arguments, though the dependence $\Delta E_i = f(\Delta\chi)$ was modified. The distinctive feature of Eq. (3) is that it takes into account the Sanderson geometrical factor [13, 14] in both homeopolar and heteropolar contributions to E_{AB} [7].

When approximating ΔE_i, let us present the ionic valence state as a superposition of singlet and triplet electronic pairs described by asymmetric and symmetric wave functions. In this case, the energy of the heteroatomic bond can be expressed as a matrix element of the perturbation operator $\hat{L} = \hat{L}_A + \hat{L}_B$, where $\hat{L}_A = U_{A2} + U_{12}/2$; $\hat{L}_B = U_{B1} + U_{12}/2$, U_{A2} and U_{B1} are the interaction energies of the first and second valence electrons with the core of the "foreign" atom, and U_{12} is the energy of interelectron interaction. Now, using the known calculation procedure (see, e.g., [6]) the polar contribution to the energy E_{AB} can be presented as follows:

$$\Delta E_i = 2P_{AB}(L_B^{1/2} - L_A^{1/2})^2, \qquad (4)$$

where P_{AB} is the nondiagonal element of the spin-free density matrix plotted on the basis of atomic orbitals.

Putting $P_{AB} = (C/2)^{1/2}$ [15] ($C = 1 - i$), $L_{A(B)} = \chi^2_{A(B)}$ in expression (4), we obtain Eq. (5):

$$E_{AB} = <E_{AB}> + (2C)^{1/2}\Delta\chi^2. \qquad (2)$$

In Eq. (5), the "saturation" effect is taken into account through the degree of the bond covalence $C = \exp(-3p^2)$ [11], which is a single-valued function of the polarity parameter $p = \Delta\chi/\chi_B$ (at $\chi_A < \chi_B$) [17, 18].[1]

To check the adequacy of the approaches in question, we analyzed the typical cases of chemical interactions in diatomic molecules of main group elements (both metals and nonmetals). In our calculations, we used tabulated standard energies of single homoatomic bonds $E_{A(B)}$ [2, 9] and also the data for $\chi_{A(B)}$ [2, 8, 11] and $r_{A(B)}$ [2, 7] (Table 1). The equilibrium bond lengths [2, 7] and the results obtained using the above equations for 45 compounds of various polarities are listed in Table 2.

It was found that the E_{AB} values calculated from Eq. (2) are overestimated at moderately high $\Delta\chi$, and underestimated at $\Delta\chi > 2.3$–2.4. In contrast, the results obtained for ionic compounds using Eq. (3) are greater as compared to experimental data; the results obtained for low-polar bonds better agree with the experimental data. The average relative errors for Eqs. (2) and (3) are similar, 3.9%, which is much less than with any empirical Pauling procedure proposed and tested in [9]. At the same time, Eq. (5) decreases the above error by a factor of 3.5 as compared to the corresponding calculations using Eqs. (2) and (3). Thus, introduction of additional geometrical parameters is unnecessary.

As seen, the dissociation energies calculated using the above approach and Eq. (5), similar to the initial definition [1], are in better agreement with the experimental data for diatomic molecules of both low and high polarity, including covalent bonds of the ionic type. This equation, corresponding to the modern interpretation of the "saturation" effect, expands both the applicability of the electronegativity approach and the range of polarities taken into account, which is of particular importance in the simulation of the intensity of chemical interaction.

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[1] This expression noticeably improves the agreement between the theoretical estimation of the covalence of heteropolar bonds and published data [11].

Table 2. Results obtained using Eqs. (2), (3), and (5) as compared to experimental data

A–B	$r_{A(B)}$ × 10, nm	$E_{A(B)}$, eV			
		Eq. (2)	Eq. (3)	Eq. (5)	experiment
H–C	1.11	3.87	3.97	3.88	$(3.90)^{a,b}$
H–N	1.03	3.38	3.49	3.43	3.42^{a}
H–O	0.96	4.76	5.09	4.88	4.80^{b}
H–S	1.34	3.78	3.94	3.81	$3.81^{b,c}$
H–Cl	1.27	4.38	4.45	4.46	$(4.46)^{a,b}$
H–Br	1.41	3.71	3.81	3.76	$(3.77)^{a,d}$
H–I	1.61	3.03	3.13	3.06	$3.09^{a,d}$
Li–F	1.56	5.27	6.14	5.99	$5.98^{a,d}$
Li–Cl	2.02	4.92	5.03	4.87	$(4.89)^{a,d}$
Li–Br	2.17	4.46	4.49	4.29	4.34^{a}
Li–I	2.39	3.89	3.81	3.64	$(3.63)^{a,b}$
K–Cl	2.67	4.66	4.56	4.48	4.49^{a}
K–Br	2.82	4.30	4.14	3.98	3.96^{a}
K–I	3.05	3.83	3.59	3.40	3.37^{a}
Rb–Cl	2.14	4.67	4.61	4.47	$(4.47)^{a,d}$
Rb–Br	2.94	4.32	4.20	3.98	$(3.98)^{a,d}$
Rb–I	3.18	3.86	3.65	3.40	$(3.41)^{a,b}$
Cs–F	2.34	5.01	5.76	5.61	5.38^{a}
Cs–Cl	2.91	4.73	4.75	4.45	4.54^{b}
Cs–Br	3.07	4.41	4.34	3.97	4.03^{a}
Cs–I	3.32	3.98	3.79	3.41	3.47^{b}
B–H	1.19	3.84	3.87	3.85	3.85^{b}
B–Cl	1.73	4.37	4.27	4.48	4.58^{c}
B–Br	1.87	3.72	3.66	3.79	$3.81^{b,c}$
C–N	1.57	2.54	2.37	2.56	2.60^{a}
C–O	–	3.66	–	3.73	$3.73^{a,d}$
C–S	–	2.98	–	2.98	2.82^{c}
C–Cl	1.65	3.34	3.45	3.39	3.38^{b}
C–Br	1.94	2.81	2.70	2.83	$(2.85)^{a,b}$
C–I	–	2.31	–	2.32	2.27^{a}
N–O	–	2.23	–	2.25	$2.18^{a,d}$
N–Cl	1.68	2.08	2.13	2.09	2.09^{c}
O–F	1.39	2.26	2.29	2.29	$(2.29)^{a,d}$
S–F	1.60	3.35	2.38	3.51	3.55^{a}
S–Cl	2.00	2.91	2.89	2.94	2.87^{a}
S–Br	2.20	2.46	2.42	2.48	2.49^{b}
Cl–O	1.70	2.58	2.60	2.59	$(2.47)^{a,b}$
Cl–F	1.63	2.44	2.45	2.48	2.60^{a}
Br–O	–	2.42	–	2.43	$(2.42)^{a,d}$
Br–F	1.76	2.47	2.45	2.55	2.55^{a}
Br–Cl	2.14	2.28	2.27	2.28	2.27^{b}
I–N	1.96	1.65	1.72	1.65	$1.65^{a,d}$
I–F	1.91	2.65	2.60	2.79	2.82^{a}
I–Cl	2.32	2.17	2.14	2.19	$(2.18)^{b,d}$
I–Br	2.47	1.83	1.82	1.84	$(1.85)^{b,d}$

Note: Data rom ^{a} [2, ^{b} [7], ^{c} [9], and ^{d} [19]; mean values from these sources are given in parentheses.

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