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Bond Energies and Hardness Differences

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An expression for the bond energy between two chemical species, A and B, in terms of the chemical potentials, the hardnesses, and the condensed Fukui functions of the isolated species, and the hardness of the system AB at equilibrium, is derived by dividing the total interaction energy into two contributions, one that corresponds to the charge-transfer process between A and B, at constant external potential, and a second one that corresponds to a reshuffling of the electronic density, at constant chemical potential, and by assuming that the softness of the system AB when A and B are very far apart from each other is equal to the sum of the softnesses of A and B when they are isolated from each other. The calculated bond energies agree rather well with the experimental values and show that the chemical potential difference term is much smaller than the hardness difference term. In addition, an expression for the bond energy only in terms of the chemical potentials and the hardnesses of the isolated species is derived by making use of the arithmetic average principle for the molecular softness. This expression also provides reasonable estimates of the bond energies. Finally, it is shown that, in general, the reaction energy is negative when the sum of the hardnesses of the products is greater than the sum of the hardnesses of the reactants, and it is positive when the opposite occurs, in agreement with the experimental evidence. The overall situation seems to indicate that the bond energy is practically determined by the hardnesses difference, a result that shows that the hardness and softness concepts play a fundamental role in the description of chemical events and that provides strong support for a principle of maximum hardness.

I. Introduction

According to density functional theory,[1] the chemical potential μ, the electronegativity[2] χ, the hardness[3] η, and the softness[4] S of a chemical species are given by

$$\mu = -\chi = (\partial E/\partial N)_v \tag{1}$$

$$\eta = (\partial^2 E/\partial N^2)_v = (\partial \mu/\partial N)_v \quad \text{and} \quad S = 1/\eta = (\partial N/\partial \mu)_v \tag{2}$$

where E is the total electronic energy, N is the total number of electrons, and v is the external potential generated by the nuclei (the factor of 1/2 in the original definition of the global hardness[3] has been omitted here for convenience). These definitions have allowed one to quantify these properties[3,5−8] and have provided a solid theoretical basis to the hard and soft acids and bases (HSAB) principle,[9−16] to the electronegativity equalization principle,[2,17,18] and to the maximum hardness principle.[6,19−22] Thus, through these principles and through the values of the parameters associated with them, it has been possible to understand the behavior of a wide variety of chemical systems under different circumstances.[23]

However, as Pearson has stated,[24] "the recent developments in the hardness concept have not helped greatly in the evaluation of bond energies". The objective of the present work is, precisely, to derive an expression for the interaction energy between two chemical species in terms of the changes in the chemical potential and in the hardness, to show that this expression provides reasonable estimates of bond energies.

II. The Interaction Energy

Let us analyze the bond formation process from the point of view of the changes that take place in the electronic structure of two systems that come into interaction. For this purpose, consider the general case in which A (an atom or a molecule) interacts with B (an atom or a molecule) to form a bond.

$$\mathrm{A} + \rightarrow \mathrm{A{-}B}$$

According to density functional theory,[1] the interaction energy is given by

$$\Delta E_{\text{int}} = E[\rho_{\text{AB}}] - E[\rho^{\circ}_{\text{A}}] - E[\rho^{\circ}_{\text{B}}] + E^{\text{NN}}_{\text{AB}} \tag{3}$$

where $\rho_{\text{AB}}(r)$ is the ground-state electronic density of the system AB at the equilibrium distance (minimum energy), $\rho^{\circ}_{\text{A}}(r)$ and $\rho^{\circ}_{\text{B}}(r)$ are the ground-state electronic densities of the isolated systems, and $E^{\text{NN}}_{\text{AB}}$ is the nuclear−nuclear repulsion energy at the equilibrium distance. The bond energy is equal to $-\Delta E_{\text{int}}$.

In a simple description, chemical binding may be viewed as the result of redistribution and reorganization of electron density among the interacting species. Thus, it has been shown[13] that if the interaction energy is divided into two steps, one may express eq 3 in the form

$$\Delta E_{\text{int}} = \Delta E_v + \Delta E_\mu + E^{\text{NN}}_{\text{AB}} \tag{4}$$

where

$$\Delta E_v = \Delta E^{\text{A}}_v + \Delta E^{\text{B}}_v = E[\rho^{\text{p}}_{\text{A}}] - E[\rho^{\circ}_{\text{A}}] + E[\rho^{\text{p}}_{\text{B}}] - E[^{\circ}_{\text{B}}] \tag{5}$$

and

$$\Delta E_\mu = E[\rho_{\text{AB}}] - E[\rho^{\text{p}}_{\text{AB}}] = E[\rho_{\text{AB}}] - E[\rho^{\text{p}}_{\text{A}}] - E[\rho^{\text{p}}_{\text{B}}] \tag{6}$$

The energy change associated with the first step, ΔE_v, corresponds to the charge transfer process between A and B arising from the chemical potential equalization principle at constant external potential. That is, when A and B are located

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far apart from each other, their chemical potentials, μ_A° and μ_B°, change to reach a common value μ_{AB}^p. Thus, A changes from a state characterized by ρ_A°, N_A°, μ_A°, and external potential v_A°, to a promoted state characterized by ρ_A^p, N_A^p, μ_{AB}^p, and v_A°, and B changes from an state characterized by ρ_B°, N_B°, μ_B°, and v_B°, to a promoted state characterized by ρ_B^p, N_B^p, μ_{AB}^p, and v_B°.

The energy change associated with the second step, ΔE_μ, corresponds to a reshuffling of the electronic density, and it is basically a manifestation of the maximum hardness principle. That is, A and B in their promoted states evolve, as a whole, from a state characterized by $\rho_{AB}^p = \rho_A^p + \rho_B^p$, $N_{AB}^p = N_A^p + N_B^p$, μ_{AB}^p, and v_{AB}^∞ (the external potential generated by the nuclei when the two systems are located very far away from each other), toward the equilibrium state characterized by ρ_{AB}, N_{AB}, μ_{AB}, and v_{AB}^{eq} (the external potential generated by the nuclei when the two systems are located at the equilibrium position), through changes in the electronic density of the global system AB produced by changes in the external potential. Assuming that $\mu_{AB}^p \approx \mu_{AB}$, this step occurs under conditions of constant chemical potential and constant number of electrons, since $N_{AB}^p = N_A^p + N_B^p = N_A^\circ + N_B^\circ = N_{AB}$. In eq 6 it has been assumed that when A and B are very far away from each other, $E[\rho_{AB}^p] = E[\rho_A^p] + E[\rho_B^p]$.

Now, one can show that the energy change due to the charge-transfer process associated with the chemical potential equalization at constant external potential is given by[1,3]

$$\Delta E_v \approx -\frac{1}{2}\frac{(\mu_A^\circ - \mu_A^\circ)^2}{\eta_A^\circ + \eta_B^\circ} \tag{7}$$

where η_A° and η_B° are the hardnesses of the isolated species, and the approximate sign has been introduced because of the assumption $\mu_{AB}^p \approx \mu_{AB}$.

On the other hand, the energy change due to the reshuffling of the electronic density may be estimated from the energy formula[16,20,22]

$$E[\rho] = N_e\mu - \frac{1}{2}N_e^{\,2}\eta + E_{core}[\rho] \tag{8}$$

where $N_e = N - N_c$ represents an effective number of valence electrons, and

$$E_{core}[\rho] = \int dr\ \rho_c(r)\ v(r) + \frac{1}{2}\int\int dr\ dr'\ \rho_c(r)\ \rho_c(r')\frac{\delta^2 F[\rho]}{\delta\rho(r')\ \delta\rho(r)} \tag{9}$$

represents the core contribution to the total electronic energy. The functional $F[\rho]$ is the universal functional of density functional theory, the sum of the electronic kinetic energy functional and the electron−electron repulsion energy functional, $\rho_c(r) = \rho(r) - N_e f(r)$, $f(r) = (\partial\rho(r)/\partial N)_v$ is the Fukui function,[25] and $\rho_c(r)$ integrates to N_c. To derive eq 8, one makes use of the total electronic energy expression $E[\rho] = F[\rho] + \int dr\ \rho(r)\ v(r)$, its associated Euler−Lagrange equation $\mu = \delta F[\rho]/\delta\rho(r) + v(r)$, the properties of the hardness and softness kernels,[1] the second-order functional expansion[26] of $F[\rho]$ in terms of its functional derivatives, and the first-order functional expansion of $\delta F[\rho]/\delta\rho(r)$ in terms of its functional derivatives to obtain an expression in the energy that only contains terms up to second order in the functional derivative of $F[\rho]$.

Since the reshuffling process occurs under conditions of constant chemical potential and constant number of electrons, one finds, using eqs 8 and 9, that

$$\Delta E_\mu = -\frac{1}{2}N_{e_{AB}}^2(\eta_{AB} - \eta_{AB}^p) + (E_{core}[\rho_{AB}] - E_{core}[\rho_{AB}^p]) \tag{10}$$

where η_{AB} is the hardness of the system AB in the equilibrium position, and the quantity η_{AB}^p is the hardness of the system AB when A and B are very far away from each other.

To simplify the term $E_{core}[\rho_{AB}] - E_{core}[\rho_{AB}^p]$, first one may note that since the density functional[1] $F[\rho] = T[\rho] + J[\rho] + E_{xc}[\rho]$, where $T[\rho]$ and $E_{xc}[\rho]$ are the kinetic and the exchange−correlation energy density functionals, and $J[\rho]$ is the classical Coulomb interaction energy density functional, then

$$\frac{\delta^2 F[\rho]}{\delta\rho(r')\ \delta\rho(r)} = \frac{1}{|r - r'|} + \frac{\delta^2 T[\rho]}{\delta\rho(r')\ \delta\rho(r)} + \frac{\delta^2 E_{xc}[\rho]}{\delta\rho(r')\ \delta\rho(r)} \tag{11}$$

Now, by assuming that the core densities of A and B remain unchanged at any distance during the interaction,

$$\rho_{c_{AB}}(r) \approx \rho_{c_A}(r,R_{eq}) + \rho_{c_B}(r,R_{eq}) \tag{12}$$

and

$$\rho_{cAB}^p(r) \approx \rho_{c_A}(r,\infty) + \rho_{c_B}(r,\infty) \tag{13}$$

where R_{eq} means that the sum of the core densities is taken at the equilibrium distance and the ∞ sign means that the sum of the core densities is taken when A and B are very far apart from each other, one finds, using eqs 9 and 11−13 that

$$\begin{aligned} E_{core}[\rho_{AB}] - E_{core}[\rho_{AB}^p] \approx{}& \int\int dr\ dr'\frac{\rho_{c_A}(r,R_{eq})\rho_{c_B}(r',R_{eq})}{|r - r'|} + \\ & \int dr(\rho_{c_A}(r,R_{eq})v_B^\circ(r,R_{eq}) + \rho_{c_B}(r,R_{eq})v_A^\circ(r,R_{eq})) + \\ & \frac{1}{2}\int\int dr\ dr'\ \rho_{c_{AB}}(r)\ \rho_{c_{AB}}(r')\frac{\delta^2(T[\rho_{AB}] + E_{xc}[\rho_{AB}])}{\delta\rho_{AB}(r')\ \delta\rho_{AB}(r)} - \\ & \frac{1}{2}\int\int dr\ dr'\ \rho_{cAB}^p(r)\ \rho_{cAB}^p(r')\frac{\delta^2(T[\rho_{AB}^p] + E_{xc}[\rho_{AB}^p])}{\delta\rho_{AB}^p(r')\ \delta\rho_{AB}^p(r)} \end{aligned} \tag{14}$$

If it is further assumed that the third and the fourth terms on the right-hand side approximately cancel each other and that there is practically no overlap between the core densities of A and B at the equilibrium distance, then

$$E_{core}[\rho_{AB}] - E_{core}[\rho_{AB}^p] \approx -\frac{N_A N_B}{R_{eq}} \tag{15}$$

where it has been considered that $N_e \ll N$. Thus, one can see that if A and B have zero net charge, then the term $E_{core}[\rho_{AB}] - E_{core}[\rho_{AB}^p]$ is approximately equal to the negative of the average nuclear−nuclear repulsion energy.

The quantity η_{AB}^p in eq 10 may be estimated through the expression

$$\eta_{AB}^p = \frac{1}{S_{AB}^p} \approx \frac{1}{S_A^\circ + S_B^\circ} = \frac{\eta_A^\circ\eta_B^\circ}{\eta_A^\circ + \eta_B^\circ} \tag{16}$$

because, in view of eq 2 for the softness, it seems reasonable to assume that the total softness of a system is equal to the sum of the individual components,[12,27−30] when there is practically no overlap between them. Thus, one would expect the total

TABLE 1: Parameters Used in Bond Energy Calculations

atom or radical	μ^a	η^a	$f_{Ai}{}^b$	i^c
H	7.18	12.86	1.000	
Li	3.01	4.78	1.000	
C	6.27	10.00	1.000	
N	7.30	14.46	1.000	
O	7.54	12.16	1.000	
F	10.41	14.02	1.000	
Na	2.85	4.60	1.000	
S	6.22	8.28	1.000	
Cl	8.30	9.36	1.000	
K	2.42	3.84	1.000	
Br	7.59	8.44	1.000	
Rb	2.34	3.70	1.000	
I	6.76	7.38	1.000	
Cs	2.18	3.42	1.000	
CH	5.94[d]	9.40[d]	0.778	C
CN	8.92	10.2	0.824	C
CH_3	4.96	9.74	0.453	C
NH_2	6.07	10.66	0.618	N
OH	7.50	11.34	0.800	O

[a] Experimental values in electronvolts from ref 7, except as indicated. [b] Theoretical values from ref 37. [c] *i* is the atom for which the condensed Fukui function is reported. [d] From ref 29.

softness S^p_{AB} to be roughly equal to $S^p_A + S^p_B$; however, since the global softness is quite insensitive to the number of electrons,[31] one may consider the softness values of the constitutive parts either before or after the charge transfer has occurred, and therefore S^p_{AB} may be estimated from the isolated system values, as indicated in eq 16.

Thus, substituting eqs 7, 10, 15, and 16 in eq 4, one finds that the interaction energy may be expressed in the form

$$\Delta E_{\mathrm{int}} \approx -\frac{1}{2}\frac{(\mu^\circ_A - \mu^\circ_B)^2}{\eta^\circ_A + \eta^\circ_B} - \frac{1}{2}N^2_{e_{AB}}\left(\eta_{AB} - \frac{\eta^\circ_A\eta^\circ_B}{\eta^\circ_A + \eta^\circ_B}\right) \tag{17}$$

Since the bond energy is equal to $-\Delta E_{\mathrm{int}}$, eq 17 provides a formula to estimate bond energies using the chemical potentials and the hardnesses of the isolated species and the hardness of the interacting species at the equilibrium position. It is precisely this quantity that contains the electronic information about the equilibrium geometry.

III. Calculation of Bond Energies

Now, although in order to make use of eq 17 one needs to know the value of the parameter N_e, it seems that $N_e \approx 1$ may provide a good starting point to test this formula, together with the experimental values of the chemical potential and the hardness that may be obtained from the finite differences approximations to the first and second derivatives of eqs 1 and 2,

$$\mu = -(I + A)/2 \quad \text{and} \quad \eta = I - A \tag{18}$$

where *I* is the first ionization potential and *A* is the electron affinity of the reference system (Table 1). Indeed, one can see, in Table 2, that eq 17 with $N_e = 1$, together with the experimental values required in eqs 18, provides reasonable estimates of bond energies, comparable to other estimates that require more experimental information, such as the equilibrium distances, the polarizabilities of the interacting species, or the dissociation energies of the homonuclear species associated with the heteronuclear interaction.[27,32] In Table 2, one can also see the value of N_e that would be required to reproduce the experimental value. Thus, in general, one can see that hydrogen compounds require a value of N_e slightly lower than 1, as could be expected, because for $N_e = 1$, $N_{cH} = N_H - N_e = 0$, and in the absence of core terms, the cancellations that led to eq 17 would not be strictly valid. On the other hand, in compounds where there are double or triple bonds, such as O_2 or N_2, the value of N_e is, in general, greater than the value of N_e for compounds with single bonds, as also could be expected, since in these cases the effective number of valence electrons must increase.

TABLE 2: Molecular Hardness and Bond Energy for Several Diatomic Molecules

molecule	$\eta_{AB}{}^a$	$-\Delta E_v{}^b$	eq 17[c]	eq 21[c]	expt[d]	$N_e{}^e$
H_2	17.40	0.00	126.5	74.1	104.2	0.91
F_2	12.62[f]	0.00	64.7	80.8	37.0[h]	0.76
Cl_2	9.20	0.00	52.1	54.0	57.3[h]	1.05
Br_2	8.00	0.00	43.6	48.7	45.5[h]	1.02
I_2	6.80	0.00	35.9	42.6	35.6[h]	1.00
HF	22.00	4.47	180.8	81.8	135.8	0.86
HCl	16.00	0.65	122.7	63.1	103.3	0.92
HBr	12.54[f]	0.09	85.9	58.9	87.5	1.01
HI	10.60	0.10	68.3	54.2	71.3	1.02
IF	11.64[f]	7.18	85.6	62.9	67.0	0.87
ICl	9.34[f]	1.63	61.7	49.2	50.3	0.90
IBr	7.24[g]	0.50	38.6	45.9	42.4	1.05
LiH	9.74[f]	11.37	83.5	51.6	59.8	0.82
LiF	12.22[f]	33.58	133.4	74.7	136.8	1.02
LiCl	9.40[f]	22.82	94.7	59.3	114.3	1.13
LiBr	8.08[f]	18.30	76.3	53.5	101.9	1.20
LiI	8.78[f]	13.33	81.1	46.8	85.7	1.03
O_2	11.80	0.00	65.9	70.1	119.2	1.34
S_2	7.70	0.00	41.0	47.7	102.4	1.58
N_2	17.80	0.00	121.9	83.4	226.0	1.36
CO	15.80	0.84	119.8	64.1	257.3	1.47
CS	11.46	0.00	79.9	52.2	166.0	1.44

[a] Experimental values in electronvolts from ref 7, except as indicated. [b] Using eq 7, in kcal/mol. [c] With $N_e = 1$, in kcal/mol. [d] Experimental values in kcal/mol from ref 18, except as indicated. [e] Using eq 17 to reproduce the experimental bond energy value. [f] From ref 8. [g] From ref 29. [h] From ref 32.

Now, it is interesting to test eq 17 in the case when A or B, or both, correspond to molecular fragments, because in these cases the interaction occurs through specific atoms of A and B. In this context, it seems reasonable to assume that the interaction energy will be dominated by the local properties[33−35] of the specific atoms when they are placed in the chemical environment provided by molecules A and B, respectively, rather than by the global properties of A and B. This is equivalent to the assumption that only a specific atom of A and a specific atom of B participate in the charge transfer and in the reshuffling steps and that the changes in all the other atoms of A and B can be neglected, which means that one should replace the global softnesses S_A and S_B by the condensed local softnesses $S^\circ_{Ai} = S^\circ_A f^\circ_{Ai}$ and $S^\circ_{Bj} = S^\circ_B f^\circ_{Bj}$, where f°_{Ai} and f°_{Bj} are the condensed Fukui functions[33] of the *i*th atom in A and the *j*th atom in B, respectively, because these values characterize better than the global values the behavior of the site at which the interaction takes place. Thus, since μ_A is the same for all the atoms in A, and μ_B is the same for all the atoms in B, one can express the interaction energy between the *i*th atom of A and the *j*th atom of B in the form

$$\Delta E^{AiBj}_{\mathrm{int}} \approx -\frac{1}{2}\frac{(\mu^\circ_A - \mu^\circ_B)^2}{\eta^\circ_{Ai} + \eta^\circ_{Bj}} - \frac{1}{2}N^2_{e_{AB}}\left(\eta_{AB} - \frac{\eta^\circ_{Ai}\,\eta^\circ_{Bj}}{\eta^\circ_{Ai} + \eta^\circ_{Bj}}\right) \tag{19}$$

where $\eta^\circ_{Ai} = \eta^\circ_A/f^\circ_{Ai}$, $\eta^\circ_{Bj} = \eta^\circ_B/f^\circ_{Bj}$. To derive eq 19 from eq 17 by replacing the global properties by the local properties, one should recall that the condensed local softness is given by the product of the global softness and the condensed Fukui function and that the global softness is the inverse of the global hardness.

TABLE 3: Molecular Hardness and Bond Energy for Several Polyatomic Molecules

molecule	η_{AB}[a]	$-\Delta E_v$[b]	eq 19[c]	eq 21[c]	expt[d]	N_e[e]
CH_3-Cl	15.00	4.17	101.9	79.4	83.0	0.90
CH_3-I	9.40	1.29	46.3	64.6	54.9	1.09
CH_3-OH	15.00[f]	2.09	76.5	100.6	81.2	1.03
CH_3-CN	15.00	5.34	87.7	95.9	87.8	1.00
$H-CN$	16.00	1.38	113.1	74.1	97.2	0.93
CH_3-H	20.60	1.65	146.4	94.4	99.4	0.82
$HO-H$	19.00	0.04	141.4	77.8	110.8	0.89
NH_2-H	16.40	0.47	104.6	85.4	93.4	0.94
$CH-CH$	14.00	0.00	91.8	69.7	189.0	1.44

[a] Experimental values in electronvolts from ref 7, except as indicated. [b] Using eq 7, in kcal/mol. [c] With $N_e = 1$, in kcal/mol. [d] Experimental values in kcal/mol from ref 18. [e] Using eq 19 to reproduce the experimental bond energy value. [f] From ref 8.

Note that eq 19 reduces to eq 17 when $f_{Ai}^\circ = f_{Bj}^\circ = 1$, and therefore, eq 17 may be considered as a particular case of eq 19.

Using the values of the condensed Fukui function given in Table 1, one can see, in Table 3, the bond energies predicted by eq 19 for several cases. Again, the results and the conclusions are quite similar to those found in the diatomic molecules. It is important to note that, in general, the contribution from the first term on the right-hand side of eqs 17 or 19 is almost negligible in comparison with that of the second term, except in those cases in which the chemical potential (electronegativity) difference is very large (see Tables 2 and 3). This situation implies that the bond energy is dominated by the difference between the hardness at the equilibrium position and the hardness of the system when the interacting species are very far apart from each other.

Now, the bond energy given by eq 19 depends on the parameters associated with the isolated systems A and B and on the global hardness of the system AB in the equilibrium position η_{AB}. It would be interesting to express the latter also in terms of the isolated system parameters to obtain an expression for the bond energy just in terms of the properties of the interacting fragments. This may be achieved by making use of the arithmetic average principle for molecular softness[29] that establishes that in the case of a molecule composed by two fragments the softness may be approximated by $S_{AB} \approx {}^1/_2(S_{Ai}^\circ + S_{Bj}^\circ)$; since $\eta_{AB} = 1/S_{AB}$, then

$$\eta_{AB} \approx \frac{2}{S_{Ai}^\circ + S_{Bj}^\circ} = \frac{2\eta_{Ai}^\circ \eta_{Bj}^\circ}{2\eta_{Ai}^\circ + \eta_{Bj}^\circ} \qquad (20)$$

Substituting eq 20 in eq 19, one finds that

$$\Delta E_{int}^{AiBj} \approx -\frac{1}{2}\frac{(\mu_A^\circ - \mu_B^\circ)^2}{\eta_{Ai}^\circ + \eta_{Bj}^\circ} - \frac{1}{2}N_{e_{AB}}^2 \frac{\eta_{Ai}^\circ\,\eta_{Bj}^\circ}{\eta_{Ai}^\circ + \eta_{Bj}^\circ} \qquad (21)$$

which depends only on the properties of the interacting species. The results corresponding to eq 21 are also reported in Tables 2 and 3. One can see that the behavior is quite similar to that corresponding to eqs 17 and 19, although, in general, eqs 17 and 19 provide a better representation of the bond energies, indicating that the information contained in the molecular hardness parameter is very important to take into account the effects of the chemical bonding.

TABLE 4: Calculated Bond Energies in kcal/mol Using the Arithmetic Average Principle and Eq 22 for the Effective Number of Valence Electrons for the Alkaline Halides

molecule	$-\Delta E_v$[a]	eq 21	expt[b]
LiF	33.6	113.4	136.8
LiCl	22.8	91.7	114.3
LiBr	18.3	82.1	101.9
LiI	13.3	70.6	85.7
NaF	35.4	114.3	114.8
NaCl	24.5	93.3	99.0
NaBr	19.9	83.7	88.8
NaI	14.7	72.2	72.2
KF	41.2	114.0	118.1
KCl	30.2	95.8	101.6
KBr	25.1	86.5	91.0
KI	19.4	75.4	77.8
RbF	42.4	113.9	115.7
RbCl	31.4	96.2	100.5
RbBr	26.2	87.0	90.4
RbI	20.3	75.9	76.8
CsF	44.8	113.5	116.2
CsCl	33.8	97.0	101.0
CsBr	28.5	88.0	91.0
CsI	22.4	77.0	75.0

[a] Using eq 7. [b] From ref 18.

It is interesting to note that in the case of highly ionic species the charge-transfer term, ΔE_v, is on the same order of magnitude as the hardness difference term, and also, the effective number of valence electrons is greater than in the case of other single-bond compounds in which $\mu_A \approx \mu_B$. If one considers that N_e represents the effective number of electrons that participate in the interaction, then in addition to the approximate value of 1, corresponding to the bond between the two interacting species, one should also consider the number of electrons transferred from one of the species to the other one, as part of the electrons that participate in the interaction. Since at constant external potential the number of electrons that are transferred is given by[3] $\Delta N_A = -\Delta N_B = (\mu_B - \mu_A)/(\eta_{Bj} + \eta_{Ai})$, then, in this context,

$$N_e \approx 1 + \frac{|\mu_A^\circ - \mu_B^\circ|}{\eta_A^\circ + \eta_B^\circ} \qquad (22)$$

In Table 4, one can see that eq 22, when combined with eq 21, provides a rather good representation of the binding energy in the case of highly ionic compounds. Most of the expressions reported in the literature[27,32] to describe the dissociation energy of highly ionic compounds require, in addition to the electronegativity (chemical potential) and the hardness, information about the bond distance and the dissociation energy of the associated homonuclear species, or the polarizability of the interacting species. It is remarkable that, through the present approach, the dissociation energy of highly ionic molecules may be described only in terms of the chemical potentials and the hardnesses of the interacting species.

In general, the results based on the arithmetic average principle for molecular softness indicate that eq 21 may be very useful to analyze the inherent chemical reactivity of a given species, because it leads to reasonable estimates of the bonding energy, and it also leads to a reasonable description of the tendencies observed within a given family of compounds. Thus eq 21 may provide information about the behavior of the different reactive sites of a chemical species with respect to different reactants, from the knowledge of the properties of the isolated species.

IV. Reaction Energies

The results derived may be applied to the calculation of reaction energies, if a chemical reaction is viewed as a bond breaking and bond formation process, because then one can break down a chemical reaction into several steps, and the energy change associated with each one of these steps may be determined through eq 19. For example, consider the reaction

$$\mathrm{A{-}B + C{-}D \rightarrow A{-}C + B{-}D}$$

in which two bonds are broken and two new bonds are formed. This process may be divided into the following steps

$$\mathrm{A{-}B \rightarrow A + B}$$

$$\mathrm{C{-}D \rightarrow C + D}$$

$$\mathrm{A + C \rightarrow A{-}C}$$

$$\mathrm{B + D \rightarrow B{-}D}$$

and one can apply eq 19 to each one of these steps. Thus, in this case the reaction energy is given by

$$\Delta E_{\mathrm{reac}} = -\frac{1}{2}(N^2_{\mathrm{e_{AC}}}\eta_{\mathrm{AC}} + N^2_{\mathrm{e_{BD}}}\eta_{\mathrm{BD}} - N^2_{\mathrm{e_{AB}}}\eta_{\mathrm{AB}} - N^2_{\mathrm{e_{CD}}}\eta_{\mathrm{CD}}) + \frac{1}{2}\left(N^2_{\mathrm{e_{AC}}}\frac{\eta^\circ_{\mathrm{A}i}\eta^\circ_{\mathrm{C}j}}{\eta^\circ_{\mathrm{A}i} + \eta^\circ_{\mathrm{C}j}} + N^2_{\mathrm{e_{BD}}}\frac{\eta^\circ_{\mathrm{B}i}\eta^\circ_{\mathrm{D}j}}{\eta^\circ_{\mathrm{B}i} + \eta^\circ_{\mathrm{D}j}} - N^2_{\mathrm{e_{AB}}}\frac{\eta^\circ_{\mathrm{A}i}\eta^\circ_{\mathrm{B}j}}{\eta^\circ_{\mathrm{A}i} + \eta^\circ_{\mathrm{B}j}} - N^2_{\mathrm{e_{CD}}}\frac{\eta^\circ_{\mathrm{C}i}\eta^\circ_{\mathrm{D}j}}{\eta^\circ_{\mathrm{C}i} + \eta^\circ_{\mathrm{D}j}}\right) - \frac{1}{2}\left(\frac{(\mu^\circ_{\mathrm{A}} - \mu^\circ_{\mathrm{C}})^2}{\eta^\circ_{\mathrm{A}i} + \eta^\circ_{\mathrm{C}j}} + \frac{(\mu^\circ_{\mathrm{B}} - \mu^\circ_{\mathrm{D}})^2}{\eta^\circ_{\mathrm{B}i} + \eta^\circ_{\mathrm{D}j}} - \frac{(\mu^\circ_{\mathrm{A}} - \mu^\circ_{\mathrm{B}})^2}{\eta^\circ_{\mathrm{A}i} + \eta^\circ_{\mathrm{B}j}} - \frac{(\mu^\circ_{\mathrm{C}} - \mu^\circ_{\mathrm{D}})^2}{\eta^\circ_{\mathrm{C}i} + \eta^\circ_{\mathrm{D}j}}\right) \tag{23}$$

If one assumes that $N_{\mathrm{e}} \approx 1$ in all the interactions, one can show that there will be a great cancellation between the terms that depend on the hardnesses of the A, B, C, and D species and that also there will be a great cancellation between the terms that depend on the chemical potential differences (in addition to the fact that they are rather small in comparison with the hardness dependent terms). Thus, if the second and third terms of eq 23 are neglected, and if $N_{\mathrm{e}} \approx 1$in all the interactions, one finds that

$$\Delta E_{\mathrm{reac}} \approx -\frac{1}{2}(\eta_{\mathrm{AC}} + \eta_{\mathrm{BD}} - \eta_{\mathrm{AB}} - \eta_{\mathrm{CD}}) \tag{24}$$

and therefore, $\Delta E_{\mathrm{reac}} < 0$ if the sum of the hardness of the products is greater than the sum of the hardness of the reactants, and $\Delta E_{\mathrm{reac}} > 0$ if the opposite occurs. These statement is in complete agreement with the experimental evidence that shows that the exchange reactions almost always go in the direction that produces the hardest molecule or the products of highest average hardness.[8,36]

In general, if one assumes that there is a great cancellation between the terms that depend on the hardnesses of the A, B, C, and D species and that also there is a great cancellation between the terms that depend on the chemical potential differences, then, if the second and third terms of eq 23 are neglected, one finds that

$$\Delta E_{\mathrm{reac}} \approx -\frac{1}{2}(N^2_{\mathrm{e_{AC}}}\eta_{\mathrm{AC}} + N^2_{\mathrm{e_{BD}}}\eta_{\mathrm{BD}} - N^2_{\mathrm{e_{AB}}}\eta_{\mathrm{AB}} - N^2_{\mathrm{e_{CD}}}\eta_{\mathrm{CD}}) \tag{25}$$

where the effective number of valence electrons may play a very important role to provide a quantitative description of the reaction energies, and it may also provide the explanation to those cases that cannot be explained through eq 24.

It is important to note that, through the analysis of the difference between the activation energy corresponding to the reaction in the direction of reactants to products and the activation energy corresponding to the reaction in the direction of products to reactants, it has been shown that $\Delta E_{\mathrm{reac}} < 0$ if the sum of the softnesses of the products is lower than the sum of the softnesses of the reactants and $\Delta E_{\mathrm{reac}} > 0$ if the opposite occurs.[30] Thus, one may conclude that, through a bond energy analysis, the arithmetic average of the hardnesses of the reactants and the products determines the sign of the reaction energy, while from a transition-state energy analysis, the harmonic mean of the hardnesses of the reactants and the products determines the sign of the reaction energy. In general, both average values will lead to the same results and provide a strong support to the statement that reactions tend to go in the direction that produces the hardest possible species.

V. Concluding Remarks

The overall situation indicates that eq 19 provides a rather good representation of the bond energies as a function of the chemical potential and the hardness. It is important to note that, in general, the contribution from the first term on the right hand side of eq 19, which has been associated with the charge-transfer process, is almost negligible in comparison with the second term. However, this should not be interpreted as if the charge transfer, in general, is negligible, because the second term in eq 19 may also include some of the charge transfer associated with the bond formation. In this sense, the results indicate only that the change of energy associated with the second step, at constant chemical potential, represents the main contribution to the bond energy.

It is important to mention that Pal, Roy, and Chandra[38] have derived a different expression for the hardness in the separated limit, namely $\eta^{\mathrm{p}}_{\mathrm{AB}} \approx I_{\mathrm{A}} - A_{\mathrm{B}}$. This expression is based on the finite differences expression and on the assumption that in the noninteracting limit the ground state of AB^+ separates into A^+ and B, AB^- separates into A and B^-, and AB separates into A and B. However, there may be other possibilities regarding the separation of the different species that would lead to a different expression. On the other hand, the numerical evidence presented here, and in other works,[12,27−30] seems to indicate that the softness of a system in terms of its constitutive parts is proportional to the sum of the softnesses of the constitutive parts and that the proportionality constant is equal to 1 when the constitutive parts are very far away from each other, and it is approximately equal to 1 over the number of atoms when the chemical bonds between the atoms have been formed.[29] Since both approaches are based on different assumptions, it will be necessary to carry on additional studies to understand them better.

Finally, it should be emphasized that even though the procedure developed here introduces an additional parameter N_{e}, the fact that the value that reproduces the experimental bond energies lies very close to what is expected from the theoretical analysis, $N_{\mathrm{e}} \approx 1$, seems to indicate that, indeed, the main contribution to the bond energy comes from the change in the hardness of the system. A similar result has been obtained in relation with the description of activation energies.[30] All these results show that the hardness and softness concepts play a fundamental role in the description of chemical events and provide strong support for a principle of maximum hardness. However, it will be necessary to carry out additional studies on N_{e}, in order to derive a more accurate expression to predict the bond energies.

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