Chemical Hardness and L. Pauling's Scale of Electronegativity

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The energy of the charge transfer interaction is expressed using absolute electronegativities and hardness parameters. The master equation appears to bind together Pauling and Mulliken scales by the factor $(7/4\pi\varepsilon_0)^{1/2} = 3.174\ \mathrm{V}^{1/2}\,\mathrm{nm}^{1/2}$ electron$^{-1/2}$. An index of charge transfer affinity (CTA) is proposed as possible measure of the tendency to ionic bonding between atoms.

1. Introduction

The problem of chemical electronegativity has been shown by Parr and coworkers to possess a profound theoretical background within the framework of the density functional theory, though traditionally its discussion has been a domain of experimental chemists [1–4]. Theoretical work has illuminated one side of electronegativity, the differential electronegativity function, first proposed by Iczkowski and Margrave [5] and newly formulated as functional derivative $(\delta E(\varrho)/\delta\varrho)_v$, [1]. Chemists, however, have been customarily looking at another side: they need some practical electronegativity indices tabulated first by Pauling [6] and Mulliken [7], then by many followers [8]. A connection between these two images of electronegativity has been proposed by Hinze, Whitehead, and Jaffé [9] and has not been abandoned even after the advent of the density functional theory [10–12]; absolute electronegativity (Mulliken) has been set equal to the differential electronegativity $\chi(q) = \mathrm{d}E(q)/\mathrm{d}q$ at $q = 0$. This limitation has recently been removed in the framework of the "chemical approximation" by introducing the relation $\bar{\chi} = \langle\chi(q)\rangle$; the electronegativity index ($\bar{\chi}$) has been reproduced by a suitable average of the electronegativity function [13, 14]. The differential electronegativity has been given physical meaning by analogy to the classical electrodynamic description and in compliance with Gordy's concept of electronegativity [15]:

$$\chi(q) = q/4\pi\,\varepsilon_0\,r(q)\,.$$

Chemical hardness, which has had a long history of its own, [16, 17], has recently been blended with the density functional theory. Parr and Pearson have introduced an index of absolute hardness, $\frac{1}{2}$(I-EA), [18], Gasques and Ortiz have demonstrated proportionality between the differential hardness $\eta = \mathrm{d}^2E(q)/\mathrm{d}q^2$ and the average of the inverse atomic radial wave function $\langle r^{-1}\rangle$, [19]. Very much in accord with this last finding is the result obtained from the electrodynamical model: $\eta(q) = 1/4\pi\,\varepsilon_0\,r(q)$ [14]; various measures of hardness have then been tabulated [20]. Application of electronegativity and hardness to chemical predictions has been going separate ways so far. It has been known since Pauling's work that the difference in electronegativities of partners can be taken as a guide to bond ionicity. The use of hardness has been limited to qualitative predictions known as Pearson's Hard and Soft Acids and Bases principle (HSAB) [17]. This work is aimed at developing the joint quantitative application of electronegativity and hardness in the area where electronegativity has already proved its usefullness: predicting the bond ionicity.

2. Charge-Transfer Interaction Energy

The interaction energy between two atoms, ions or molecules brought to close contact may be decomposed into several contributions most clearly contained within the multipole expansion. As long as the only process under consideration is the charge transfer, it may be sufficient to write

$$\Delta E_{\mathrm{CT}} = \Delta E_{\mathrm{D}}^{0} + \Delta E_{\mathrm{A}}^{0} + \Delta e_{\mathrm{M}}\,, \qquad (1)$$

where $\Delta E_{\mathrm{D}}^{0}$ and $\Delta E_{\mathrm{A}}^{0}$ are contributions to self energy terms of free atoms due exclusively to the charge

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transfer and Δe_M stands for the charge transfer induced change in interaction energy between the atomic cores D and A; Δe_M has been completely neglected in two important recent studies [10, 22]. The situation may be described by a "Gedankenexperiment": atoms are first brought to a contact at an equilibrium distance R, then the charge transfer occurs and the latter process gives extra energy ΔE_{CT}. Evidently, ΔE_{CT} may be called "ionic" as it does not include other effects than directly charge-dependent ones. If χ^0 and η^0 are the standard differential electronegativity and hardness, respectively, and $\delta > 0$ is the (small) charge exchanged, we have

$$\Delta E_D^0 = \chi_D^0\,\delta + \tfrac{1}{2}\,\eta_D^0\,\delta^2 + \ldots, \tag{2}$$

$$\Delta E_A^0 = -\chi_A^0\,\delta + \tfrac{1}{2}\,\eta_A^0\,\delta^2 + \ldots. \tag{3}$$

Consequently, the interaction term Δe_M should contain the first order charge-to-charge energy as well as the second order induction contribution:

$$\Delta e_M = \frac{\delta}{4\pi\varepsilon_0 R}\,(q_A - q_D - \delta) - \frac{1}{2}\,(\alpha_D + \alpha_A)\left(\frac{\delta}{4\pi\varepsilon_0 R^2}\right)^2. \tag{4}$$

q_D and q_A are the initial charges of the interacting atoms; α_D and α_A are atomic polarizabilities. Eliminating the charge transfer δ by means of the equilibrium condition $\mathrm{d}\,(\Delta E_{CT})/\mathrm{d}\delta = 0$ one obtains

$$\Delta E_{CT} = -\frac{1}{2}\,\frac{\left[(\chi_D^0 - \chi_A^0) + \dfrac{q_A - q_D}{4\pi\varepsilon_0 R}\right]^2}{\eta_D^0 + \eta_A^0 - \dfrac{2}{4\pi\varepsilon_0 R} - \dfrac{\alpha_D + \alpha_A}{(4\pi\varepsilon_0)^2 R^4}}. \tag{5}$$

This expression may be transformed into a meaningful form using identities offered by the chemical approximations $\chi = q/(4\pi\varepsilon_0 r)$, $\eta \cong 1/(4\pi\varepsilon_0 r)$ and $\alpha = 4\pi\varepsilon_0 r^3$, [14]. In addition we assume $R \cong r_D + r_A$, i.e. the atoms in question are placed at a distance given by the sum of their atomic radii. Substitution into (10) yields

$$\Delta E_{CT} = -\frac{1}{8\pi\varepsilon_0 (r_D + r_A)}\,\frac{\left(\dfrac{\chi_D^0}{\eta_A^0} - \dfrac{\chi_A^0}{\eta_D^0}\right)^2}{\left(\dfrac{\eta_A^0}{\eta_D^0} + \dfrac{\eta_D^0}{\eta_A^0}\right) - \boldsymbol{p}}, \tag{6}$$

where $\boldsymbol{p}$ is

$$\boldsymbol{p} = \left(1 + \frac{\eta_D^0}{\eta_A^0}\right)^{-3} + \left(1 + \frac{\eta_A^0}{\eta_D^0}\right)^{-3}. \tag{7}$$

Equation (6) has an interesting and simple form; unfortunately, however, it cannot be applied to any real physical situation as long as the differential electronegativities of the atoms (χ^0) remain unknown. This inconvenience prompts to examine (6) using Mullikens absolute electronegativities $\bar{\chi}$ in place of χ^0. Such a substitution (not identification!) will change the meaning of ΔE_{CT}. Equation (6) represents a real energy change for the infinitely small amount of charge δ exchanged. Since absolute electronegativities were shown to represent an average electronegativity, ΔE_{CT} calculated from $\bar{\chi}$ will also be some average rather than a real energy, and will retain its meaning for considerable charge transfer $|\delta| \leqq 1$. Its negative might be labeled the Charge Transfer Affinity (CTA) of two atoms, using thermodynamical terminology:

$$\mathrm{CTA} = \frac{1}{4\pi\varepsilon_0}\,\frac{1}{2\,(r_D + r_A)}\,\frac{\left(\dfrac{\bar{\chi}_D}{\eta_A} - \dfrac{\bar{\chi}_A}{\eta_D}\right)^2}{\left(\dfrac{\eta_A}{\eta_D} + \dfrac{\eta_D}{\eta_A}\right) - \boldsymbol{p}}. \tag{8}$$

(For the sake of simplicity the superscript degree refering to free atoms was omitted with the hardness.) The CTA should be considered as nothing more than an autonomous index possibly helpful in quantifying the tendency of atoms (ions, molecules) to exchange electrons.

3. Transformation of the Mulliken to Pauling scale

The importance of the CTA can be discovered when (8) is applied to a pair of atoms forming a diatomic molecule. Neglection of the difference in the hardness parameters, $\eta_D \cong \eta_A$, leads to

$$\mathrm{CTA} \cong \tfrac{4}{7}\,\pi\varepsilon_0\,\bar{r}\,(\Delta\bar{\chi}^M)^2, \tag{9}$$

where $\bar{r} = \frac{1}{2}\,(r_D + r_A) \cong r_D \cong r_A$.

When absolute electronegativities $\bar{\chi}^M$ are in volts, atomic radii $\bar{r}$ in nanometers and CTA in electron volts the numerical coefficient in (9) amounts to

$$\tfrac{4}{7}\,\pi\varepsilon_0 = (10.08)^{-1}\ \mathrm{eV}^{-1}\,\mathrm{nm}^{-1}.$$

Hence

$$\mathrm{CTA} \cong \bar{r}\,[\mathrm{nm}]\left(\frac{\Delta\bar{\chi}^M}{3.174}\right)^2\ [\mathrm{eV}]. \tag{10}$$

This latter equation has a very interesting relation to the chemical tradition in electronegativity studies.

The widely accepted coefficient between the Mulliken and Pauling electronegativities is surprisingly close to $\left(\frac{7}{4\pi\varepsilon_0}\right)^{1/2} = 3.174$:

Pritchard and Skinner	3.15	[8],
Hinze and Jaffé	2.98	[23],
Nethercot	2.86	[24].

Thus, the factor 3.174 in (10) may be used to transform the Mulliken ($\bar{\chi}^M$) to Pauling ($\bar{\chi}^P$) electronegativities.

$$\mathrm{CTA} = \bar{r}(\Delta\bar{\chi}^P)^2 = \tfrac{1}{2}(r_D + r_A)(\Delta\bar{\chi}^P)^2. \tag{11}$$

When this equation is applied to bonded atoms, atomic radii may be more conveniently replaced by the interatomic distance R_{DA}, since in many bonds we roughly have $R_{DA} = \frac{1}{2}(r_D + r_A)$, for van der Waals radii. Hence

$$\Delta\bar{\chi}^P = \left(\frac{\mathrm{CTA}\,[\mathrm{eV}]}{R_{DA}\,[\mathrm{nm}]}\right)^{1/2}. \tag{12}$$

This result closely resembles the form of the original Pauling definition

$$\Delta\bar{\chi}^P = (\Delta\,[\mathrm{eV}])^{1/2}, \tag{13}$$

where Δ was originally defined as a difference in dissociation energies (ε):

$$\Delta = \varepsilon_{DA} - \tfrac{1}{2}(\varepsilon_{DD} + \varepsilon_{AA}). \tag{14}$$

It has long been known that numbers of $\Delta^{1/2}$ have served only as a guide to defining $\Delta\bar{\chi}^P$ and neither Pauling nor his successors have ever claimed to identify these quantities [6, 8, 25, 26]. In consequence, contemporary Pauling electronegativities became more or less arbitrary numbers adjusted on the basis of the typical behaviour of an element. Table 1 lists the data of $\Delta\bar{\chi}^P$ and $\Delta^{1/2}$: the mean quadratic deviation between both equals 0.58 for 26 molecules. The deviation calculated for $\Delta\bar{\chi}^P$ and $(\mathrm{CTA}/R)^{1/2}$ in Table 1 is virtually the same, 0.64, which only means that Pauling electronegativity differences are equally well approximated by $\Delta^{1/2}$ as by $(\mathrm{CTA}/R)^{1/2}$. This tends to suggest that the formal relation between the Pauling scale and the charge transfer affinity (11), that has arisen from neglecting the role of hardness, may not be merely accidental. Figure 1 provides an even more convincing argument. The linear relation between $(r_D + r_A)(\Delta\bar{\chi}^P)^2$ and CTA is striking, although its slope is somewhat smaller than required by (11). The alkali halides also show a non-zero intercept, as if some additive excess contribution was included in $\Delta\bar{\chi}^P$ of these highly ionic molecules. When comparing Fig. 1 with Fig. 2, which tests the original Pauling equation (13), one cannot but conclude that

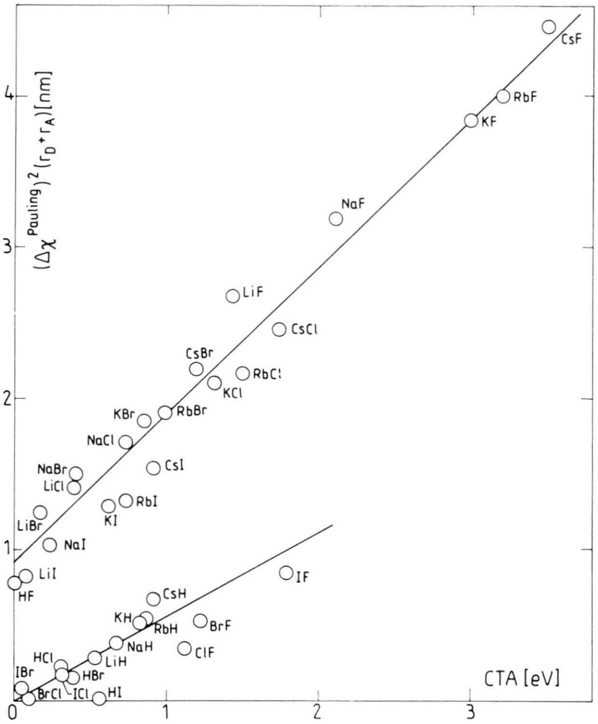

Fig. 1. Experimental test to (11). Charge transfer affinity (CTA) calculated from (8) (see subscript b to Table 1).

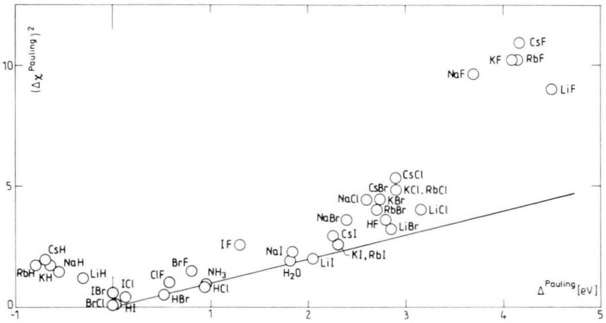

Fig. 2. Experimental test of the Pauling definition (13). Data as in Table 1 and 2.

Table 1. Charge transfer affinity (CTA) for alkali halides and interhalogenes.

Molecule	Bond length R [a] [nm]	Bond dissociation energy [eV] [a]	CTA [b] [eV]	$(\mathrm{CTA}/R)^{1/2}$ $[(\mathrm{eV/nm})^{1/2}]$	$\Delta\bar{\chi}^{\mathrm{P}}$ (Pauling) [c]	$\Delta^{1/2}$ (Pauling) [d]
ClF	0.1628	2.58	1.132	2.64	1.0	0.76
BrF	0.1756	2.58	1.228	2.64	1.2	0.90
IF	0.191	2.88	1.792	3.06	1.6	1.14
BrCl	0.2138	2.23	0.103	0.69	0.2	0.08
ICl	0.2321	2.16	0.325	1.18	0.6	0.37
IBr	0.2485 [e]	1.82	0.060	0.49	0.4	0.25
LiF	0.1547	5.94	1.421	3.03	3.0	2.12
NaF	0.184	4.94	2.114	3.39	3.1	1.92
KF	0.213	5.07	2.956	3.72	3.2	2.02
RbF	0.2266	5.07	3.200	3.76	3.2	2.02
CsF	0.2345	5.20	3.504	3.86	3.3	2.04
LiCl	0.202	4.81	0.399	1.40	2.0	1.78
NaCl	0.2361	4.23	0.740	1.77	2.1	1.61
KCl	0.2667	4.38	1.332	2.23	2.2	1.70
RbCl	0.2787	4.60	1.508	2.33	2.2	1.71
CsCl	0.2906	4.51	1.750	2.45	2.3	1.71
LiBr	0.2170	4.34	0.182	0.92	1.8	1.69
NaBr	0.2502	3.76	0.406	1.27	1.9	1.54
KBr	0.2821	3.92	0.858	1.74	2.0	1.64
RbBr	0.2945	3.99	1.000	1.84	2.0	1.64
CsBr	0.3072	4.31	1.202	1.98	2.1	1.65
LiI	0.2392	3.60	0.085	0.60	1.4	1.43
NaI	0.2712	3.15	0.245	0.95	1.5	1.36
KI	0.3048	3.38	0.617	1.42	1.6	1.51
RbI	0.3177	4.42	0.742	1.52	1.6	1.52
CsI	0.3315	3.46	0.927	1.67	1.7	1.50

[a] Bond lengths and dissociation energies after [21], p. A-32.

[b] Equation (8). For $\bar{\chi}$, the Mulliken-Jaffé valence state electronegativities for appropriate hybridization were employed. Hardness parameters derived from van der Waals radii for alkali metals; from more accurate data of X–X bond distance for other elements ($r_x \cong R_{xx}$). All data from ref. [21].

[c] $\Delta\bar{\chi}^{\mathrm{P}}$ (Pauling) from [8], Tables 1 and 2. – [d] Equation (14); after [8]. – [e] Ref. [27].

at this level of accuracy there is no reason to reject (11) and (12) which offer a formal definition of Pauling electronegativities.

4. Units of Electronegativity

Quantitative indexing of electronegativity has been known since 1932, and electronegativities became almost unanimously accepted by chemists as semiquantitative factors describing properties of atoms. Yet the question of the units has not been definitely answered, even though it has been raised dramatically more than 20 years ago by Iczkowski and Margrave [5]. The lack of harmony is demonstrated by the units of three principal systems:

Pauling:	(energy)$^{1/2}$,
Mulliken:	energy,
Iczkowski and Margrave:	potential.

This leads to most chemists using electronegativity as dimensionless quantity, which is an error to be avoided even in freshman chemistry courses.

The density functional theory leaves no room for ambiguity: volts (potential) are the only acceptable units of electronegativity, very much in accord with Iczkowski and Margrave. Mulliken's absolute electronegativities are readily transformed into volts by taking into account the unit "per electron" implicit for I and EA. The Pauling system, which is a primary concern of this work, is commonly considered as dimensionless, though Pauling's electronegativity should formally be associated with a unit (eV)$^{1/2}$.

Equation (11) and (12) suggest, though, that $(\mathrm{CTA}/R)^{1/2}$ values might equally be accepted as a source of Pauling electronegativities. Then the same scale would be accompanied by the unit (eV/nm)$^{1/2}$. In that case, an elegant way of transforma-

Table 2. Converted Pauling electronegativities (in volts) compared to Mulliken absolute and valence state electronegativities.

Atom	$\left(\frac{7}{4\pi\varepsilon_0}\right)^{1/2}\bar{\chi}^{\mathrm{P}}$ [V] [a]	$\frac{\mathrm{I}+\mathrm{EA}}{2}$ [V] [b]	Mulliken-Jaffé valence state electronegativity [V] [c]
H	6.98	7.17	7.17 s
Li	3.11	3.00	3.10 s
Be	4.98	4.66 [d]	4.78 sp
B	6.47	4.29	6.33 sp^2
C	8.09	6.27	7.98 sp^3
N	9.65	7.27	11.54 sp^3
O	10.92	7.53	15.25 sp^3
F	12.63	10.41	12.18 p
Na	2.95	2.85	2.80 s
Mg	4.16	3.82 [d]	4.09 sp
Al	5.11	3.21	5.47 sp^2
Si	6.03	4.78	7.30 sp^3
P	6.95	5.62	8.90 sp^3
S	8.19	6.22	10.14 sp^3
Cl	10.03	7.31	9.38 p
K	2.60	2.41	2.90 s
Ca	3.17	3.06 [d]	3.30 sp
Cu(I)	6.03	4.48	4.31 s
Zn	5.24	4.70 [d]	4.71 sp
As	6.92	5.29 [d]	8.30 sp^3
Se	8.09	5.89	9.76 sp^3
Br	9.40	7.60	8.40 p
I	8.44	6.76	8.10 p
Rb	2.60	2.34	2.09 s
Ag	6.12	4.44	
Cs	2.51	2.18 [d]	
Ba	2.82	2.61 [d]	
Tl(I)	5.14	3.20 [d]	
Tl(III)	6.47		
Au	8.06	5.8	
Pb(II)	5.93	4.28 [d]	
Pb(IV)	7.40		

[a] Equation (15).
[b] Ref. [18] except where indicated.
[c] Ref. [21].
[d] I and EA from [21].

tion of Pauling electronegativities into volts (SI) may be proposed (9):

$$\Delta\bar{\chi}\,[\mathrm{V}] = \left(\frac{7}{4\pi\varepsilon_0}\right)^{1/2}\Delta\bar{\chi}^{\mathrm{P}} = 3.174\cdot\Delta\bar{\chi}^{\mathrm{P}}. \qquad (15)$$

Such a linear conversion would not touch the chemical nuances contained in the Pauling scale but would endow the numbers with acceptable physical units. One must not require that converted Pauling electronegativities merge with Mulliken absolute values (Table 2). Both systems have to be treated autonomically at least as long as chemists prefer using the electronegativity indices which also include average effects of hardness for most typical chemical situations (Pauling scale).

5. Application of CTA Index

The tentative relation between Pauling electronegativity difference and CTA value introduced as (12) cannot be expected to be accurately fulfilled, for it resulted from the non-trivial simplification of (8). It has been implicitly assumed that neglecting the difference in hardness parameters in (8) will be, at least to some extent, compensated by introducing chemically balanced Pauling values. Since the Pauling electronegativity difference is a crude measure of the ionic part in the bonding energy, one should ask whether the CTA index does not contain a similar information more accurately and a priori accessible from (8). The CTA meets the elementary requirement for the ionic part of the interaction energy, being in all cases smaller than the dissociation energy (Table 1). The variation of the CTA for alkali halides, hydrides and interhalogenes is also in accord with chemical predictions: The CTA span rather broad range between the maximum value for CsF (and IF) and the smallest one for LiI (and IBr), (Table 1). This reproduces qualitatively the variation of either Δ or $\Delta\bar{\chi}$ (Pauling). All these molecules are characterized by considerably high $\Delta\bar{\chi}$, and the role of hardness in (8) appears to be subordinate. For small $\Delta\bar{\chi}$, however, the CTA may be very sensitive to the choice of the hardness parameters, as it is illustrated by the set of hydrogen compounds (Table 3). There is a choice of two possible hardness parameters for hydrogen: either from the van der Waals radius (as for alkali metals) or from the R_{HH} distance in H_2 (as for halogens). Taking the $(\mathrm{CTA}/R)^{1/2} \cong \Delta\bar{\chi}^{\mathrm{P}}$ as a guide, one can see that hydrogen should be considered soft when combined with F, O, N, C. Otherwise, reasonable $(\mathrm{CTA}/R)^{1/2}$ numbers are obtained for the hard hydrogen model. The best values of CTA indicated in Table 3 interestingly compare with the known ionicity of bonds. For 2nd row elements C–F, CTA increases toward fluorine except for oxygene. The overestimated CTA for oxygen comes from the very high valence state electronegativity of O(sp^3), $\chi_v = 15.25$ V. The s-character admixture in the sp^3 bonding hybrid may be too high (pure p orbital would have $\chi_v = 9.65$ V). An appropriate χ_v for CTA

Table 3. Charge transfer affinity (CTA) for hydrogen compounds. Best values of CTA and (CTA/R) are indicated.

Molecule (Bond)	Bond length R [a] [nm]	CTA [b, e] [eV]		$(\mathrm{CTA}/R)^{1/2}$ [e] $[(\mathrm{eV/nm})^{1/2}]$		$\Delta\bar{\chi}^{\mathrm{P}}$ (Pauling) [c]	$\Delta^{1/2}$ (Pauling) [d]
		soft hydrogen	hard hydrogen	soft hydrogen	hard hydrogen		
HF	0.0918	**0.387**	0.010	**2.05**	0.32	1.9	1.67
HCl	0.1274	0.002	**0.310**	0.14	**1.56**	0.9	0.98
HBr	0.1408	0.086	**0.400**	0.61	**1.68**	0.7	0.73
HI	0.1608	0.222	**0.564**	1.17	**1.87**	0.3	0.23
LiH	0.1595	0.301	0.537	1.37	1.83	1.1	–
NaH	0.1887	0.508	0.676	1.64	1.89	1.2	–
KH	0.2244	0.831	0.837	1.92	1.93	1.3	–
RbH	0.2367	0.920	0.876	1.97	1.92	1.3	–
CsH	0.2494	1.038	0.922	2.04	1.92	1.4	–
H_2O (H–O)	0.096	**0.890**	0.003	**3.04**	0.19	1.4	1.35
H_2S (H–S)	0.134	0.004	**0.209**	0.03	**1.25**	0.4	0.41
NH_3 (N–H)	0.101	**0.273**	0.025	**1.64**	0.50	0.9	0.98
PH_3 (P–H)	0.144	0.043	**0.102**	0.55	**0.84**	0	0.13
AsH_3 (As–H)	0.152	0.133	**0.447**	0.87	**1.71**	0.1	–
CH_4 (C–H)	0.109	**0.002**	0.180	**0.13**	1.28	0.4	0.45
C_2H_4 (C–H)	0.109	**0.019**	0.140	**0.42**	1.13	0.4	
C_2H_2 (C–H)	0.109	**0.106**	0.076	**0.99**	0.84	0.4	
SiH_4 (Si–H)	0.148	0.184	**0.480**	1.12	**1.80**	0.3	0.40
GeH_4 (Ge–H)	0.153 [f]	0.142	**0.573**	0.92	**1.93**	0.2	–

[a–d] See footnotes to Table 1. – [e] Soft hydrogen: $\eta = 9.94$ V/e (from van der Waals radius); hard hydrogen: $\eta = 19.4$ V/e (from $r_{\mathrm{H}} = R_{\mathrm{HH}}$). – [f] Ref. [27].

calculation would be 12–13 V, thus indicating some intermediate valence state of oxygen between p and sp^3, as indeed it has been commonly accepted. Passing downwards in the groups increases the CTA of the H–X bond, whereas the dipole moment of hydrogen halides decreases. The CTA might rather reflect the acidity of the H–X bond, which increases in the same direction. The best illustration of that property is the increasing CTA for the C–H bond in methane, ethylene and acetylene.

Though the CTA can hardly be expected to reproduce some real "ionic energy", it might perhaps play a similar role as electronegativity, which has been known to posses the meaning of a quantitative index rather than any real potential, yet it has afforded sensible information for chemist for over 60 years.

6. The Role of Hardness in the Charge Transfer

Using the CTA index as a measure of the charge transfer instead of $\Delta\bar{\chi}^{\mathrm{P}}$ has an interesting advantage by including directly the hardness in (8). Choosing some appropriate hardness parameters may be a subtle problem, but some general predictions are evident.

Equation (8) indicates that increasing the hardness parameters acts in opposite direction to the difference of electronegativities. If $\eta \to \infty$ for at least one partner, CTA $\to 0$ regardeless of the electronegativities of interacting partners. Indeed, hard elements as H, Li, F tend to form covalent rather than ionic bonds even despite the high electronegativity difference. This would suggest that acid-base, hard-hard interactions also lead to small CTA. The Hard and Soft Acids and Bases principle is not contradicted, though: hard-hard acid base interaction may be predominantly electrostatic between ions, but does not necessarily produce significant transfer of charge. A detailed discussion of the HSAB principle will be given separately [28].

Another physically interesting situation is discovered when the $\eta \to 0$ limit is considered, since $\eta = 0$ has been proposed for bulk metals [18]. If $\eta_{\mathrm{A}} = \eta_{\mathrm{D}} = \eta \to 0$, CTA $\sim (\Delta\bar{\chi})^2/\eta^2$ will go to infinity unless the electronegativity difference vanishes. This would produce an extraordinarily high charge transfer affinity between two pieces of different metals, and CTA = 0 when two blocks of the same metal are contacted. The physics of interphase processes between two metals is correctly accounted for by the CTA index.

The condition for zero charge transfer in terms of CTA reads now

$$\bar{\chi}_D \, \eta_D = \bar{\chi}_A \, \eta_A \, . \tag{16}$$

This does not contradict the Sanderson principle, as $\bar{\chi}$ and η are for starting species, not for bonded atoms. Equation (16) provides a neat formal description to the fact that the C−H bond is purely non-ionic despite the ~ 1 V difference in electronegativities of the atoms.

7. Summary

The principal achievement of this work is the derivation of the formula (6) for the charge transfer energy between two atoms, including the variable interaction energy that has been omited by other authors. Practical application of that equation is conditional to introducing absolute electronegativities $\bar{\chi}$, though they have not been claimed to be identical with $\chi^0(0)$. Such an identification has long been known to result from admitting a parabolic energy curve for atoms [29]. Abandoning this assumption has disclosed that the CTA energy must not be considered as any real energy gain. (Therefore, its use to estimate atomic charges is not recommended, even though such a calculation may easily be performed and will frequently give realistic numbers.) Nonetheless, the definition of the CTA has lead to a formal motivation of the Pauling definition, tentatively identified with (12). This derivation hints to the possible origin of discrepancies between the Pauling and Mulliken scales. They are unified by the CTA value which can be reproduced by using either absolute electronegativities and hardness' (8) or, alternatively, using only Pauling electronegativities (11).

From this point of view, Pauling seems to have done an impossibility: $\bar{\chi}^P$ contains implicitly the average effect of hardness. Hence, Pauling and Mulliken indices cannot be equivalent although the scales remain mutually related. This work has for the first time offered an independent factor connecting both systems: $\left(\frac{7}{4\pi\varepsilon_0}\right)^{1/2} = 3.174$; its value is perfectly in accord with statistically determined parameters of experimental correlations.

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[1] R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, J. Chem. Phys. **68,** 3801 (1978).
[2] R. A. Donnelly and R. G. Parr, J. Chem. Phys. **69,** 443 (1978).
[3] R. G. Parr, in: Electron Distribution and the Chemical Bond (P. Coppens and M. B. Hall, eds.). Plenum Publ. Co. 1982.
[4] R. G. Parr, Int. J. Quantum Chem. **26,** 687 (1984).
[5] R. P. Iczkowski and J. L. Margrave, J. Amer. Chem. Soc. **83,** 3547 (1961).
[6] L. Pauling, J. Amer. Chem. Soc. **54,** 3570 (1932).
[7] R. S. Mulliken, J. Chem. Phys. **2,** 782 (1934).
[8] H. O. Pritchard and H. A. Skinner, Chem. Rev. **55,** 745 (1955).
[9] J. Hinze, M. A. Whitehead, and H. H. Jaffé, J. Amer. Chem. Soc. **85,** 148 (1962).
[10] N. K. Ray, L. Samuels, and R. G. Parr, J. Chem. Phys. **70,** 3680 (1979).
[11] S. G. Bratsch, J. Chem. Educ. **62,** 101 (1985), see also references therein.
[12] J. E. Huheey, J. Phys. Chem. **69,** 3284 (1965).
[13] L. Komorowski, Chem. Phys. Lett. **103,** 201 (1983).
[14] L. Komorowski, Chem. Phys. **114,** 55 (1987).
[15] W. Gordy, J. Chem. Phys. **14,** 305 (1946).
[16] R. G. Pearson, J. Amer. Chem. Soc. **85,** 3533 (1963).
[17] R. G. Pearson, J. Chem. Educ. **45,** 581 (1968).
[18] R. G. Parr and R. G. Pearson, J. Amer. Chem. Soc. **105,** 7512 (1983).
[19] J. L. Gasques and E. Ortiz, J. Chem. Phys. **81,** 2741 (1984).
[20] L. Komorowski, Chem. Phys. Lett. **134,** 536 (1987).
[21] J. E. Huheey, Inorganic Chemistry: Principle of Structure and Reactivity. Harper and Row, New York 1983.
[22] R. F. Nalewajski, J. Amer. Chem. Soc. **106,** 944 (1984).
[23] J. Hinze and H. H. Jaffé, J. Amer. Chem. Soc. **84,** 540 (1961).
[24] A. H. Nethercot Jr., Phys. Rev. Lett. **33,** 1088 (1974).
[25] M. L. Huggins, J. Amer. Chem. Soc. **75,** 4123 (1953).
[26] M. Haïssinsky, J. Chim. Phys. **46,** 298 (1949).
[27] Comprehensive Inorganic Chemistry, Vol. 7 (I), Vol. 14 (Ge), Pergamon Press, Oxford 1975.
[28] L. Komorowski, to be published.
[29] L. Komorowski, Chem. Phys. **76,** 31 (1983).