The Covalent Potential: A Simple and Useful Measure of the Valence-State Electronegativity for Correlating Molecular Energetics

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Introduction

Electronegativity (EN) is one of the most basic and oldest concepts in chemistry and is also widely used in physics, biology, and geology.[1,2] Nobel laureate L. Pauling[3-5] was the first person to develop a scale of EN.[6] He defined EN as "the power of an atom in a molecule to attract electrons to itself"[7] and bond polarity as the difference in EN values between two bonded atoms. Pauling's scale is a semiquantitative scale. There are some unexpected exceptions and controversies when it is correlated with some physical and chemical properties. Allen[8] reviewed a thousand-odd texts, review papers, and journal articles which discussed or commented on EN from 1932 to early 1989. A useful summary of Pauling and Pauling-like, nonempirical as well as absolute EN may be found in a recent publication.[2]

Our own interest is in molecular energetics. We have made efforts to correlate heats of formation by means of available scales of atomic and group EN. The scales which are widely used, such as Pauling's, Mulliken's,[9,10] and Allred-Rochow's,[11] do not give correlation to an average of ±1 kcal/mol. Scales which have been less widely used, such as those by Gordy,[12,13] Sanderson,[14-19] Huheey,[20,21] Allen,[22] Zhang,[23] Mullay,[24-26] and Inamoto,[27-29] are not better. The nonempirical and absolute scales,[30-33] such as FSGO,[34] Boyd,[35,36] and Taft,[37,38] have also led to difficulties. Pauling's scale was initially derived from *experimental data on heats of formation or bond energies of diatomic and simple molecules.* The theoretical scales, although very sophisticated, do not help to correlate molecular energetics quantitatively.

A few years ago, while searching for quantitative correlations of heats of formation of polar molecules, we made an accidental but interesting discovery of a little-known EN scale by Yuan.[39,40] A modification of the Yuan scale gave for the first time a quantitative correlation of heats of formation for these polar compounds. It turned out to be a very simple scale and one that has proved applicable to many properties. It has proved to be useful for correlating energetics of both diatomic and polyatomic molecules and to have a reasonable theoretical base.

Yu-Ran Luo's research interests are in the areas of reaction dynamics, kinetics, and the thermochemistry of organic molecules, radicals, and ions. His work has led to a better understanding of homolytic and heterolytic bond dissociation energies and ionization potentials of radicals and molecules. He graduated from China University of Science and Technology in Beijing, China. His Ph.D. studies were at Dalhousie University, Canada. Between 1986 and 1989, he was a postdoctoral associate with Professor S. W. Benson at the University of Southern California. He is currently working with Professor J. L. Holmes at the University of Ottawa.

Sidney W. Benson was born on September 26, 1918, in New York, NY. He earned A.M. and Ph.D. degrees from Harvard University and has held the following posts: Group Leader, Manhattan Project; Chairman, Department of Kinetics and Thermochemistry (SRI); Distinguished Professor of Chemistry, Emeritus, Scientific Co-Director, Loker Hydrocarbon Research Institute. His major interests have been chemical kinetics and thermochemistry with an emphasis on empirical methods for estimation of rate constants and equilibrium constants. Important applications have been in the quantitative modeling of complex chemical systems such as combustion processes, air pollution, tropospheric chemistry, and high-temperature pyrolysis. More general interests have been physical chemistry, solvation, and most recently the thermochemistry of solid salts and the structure of water.

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From Yuan's Scale to Our New Scale of EN

In the mid-1960s, a simple scale of atomic EN was proposed by Yuan.[39] It was defined as

$$X_Y = n_x/r_x \qquad (1)$$

where n_x is the number of valence (s and p) electrons *in atom X*, and r_x is its covalent radius. He then defined a more complex group EN.[40] His group EN is the ratio of the number of effective valence electrons, n_x^*, on the atom X to the effective radius, r_x, of the central atom X in the group. His r_x is determined by Sanderson's method,[41] and n_x^* is given by

$$n_x^* = n_x + 2\sum m \frac{X_A}{X_A + X_B} + P\sum \alpha \frac{X_A - X_B}{X_A + X_B} \qquad (2)$$

where n_x is the number of valence electrons on the free atom X minus the number of electrons taking part in the bonding to B; X_A and X_B are the EN of the atoms A and B, respectively, calculated from eq 1; m and α represent the number of bonded electrons and unbound electrons of atom B, respectively; and P is the propagator of the inductive effect along the chemical bond and was assigned a value $P = 1/2.7$. Yuan's scales of atomic and group EN have never been tested, not even in the original articles.

Because Yuan's scale is not very convenient for groups, such as OH, OCH_3, $CH_2C_6H_5$, etc., we tried to modify it.

A new scale of EN was defined in a first article of ours,[42]

$$V_x = n_x/r_x \qquad (3)$$

where n_x is the number of valence electrons *in the bonding atom in X*, where X represents an atom or group centered on X. In this way, our definition of EN differs from Yuan's although our r_x is the same as his. Note that the concept of group EN becomes unnecessary for our use. This again differs from Yuan's idea and the traditional ones. We do not use the EN of a carbon atom or methyl group. We use instead the EN of a carbon atom with an sp^3, sp^2, or sp hybridization valence state. The EN value of a carbon atom with an sp^3 hybridization valence state is equal to 4/0.771. Here 4 represents four valence electrons of the carbon atom and 0.771 (Å) is the covalent radius of a carbon atom with an sp^3 valence state. The ratio 4/0.771 represents the EN value of bonded carbon atoms with an sp^3 hybridization valence state in alkyl and all carbon-centered groups, such as *tert*-butyl, CH_2COCH_3, CH_2CCH, CH_2CHCH_2, c-C_6H_{11}, and $CH_2C_6H_5$. If we multiply V_x by charge, the units of our scale become energy. For simplicity we omit the charge, which then gives it the dimension of inverse length, of Å^{-1}. By the same reasoning, we may say that the oxygen atom in OH, OCH_3, and other alkoxy groups has the same value of EN, which is 6/0.74. Here 0.74 Å is half of the length of the HO—OH bond, i.e., the covalent radius of the bound oxygen atom.

Many of the initial efforts to relate EN to atomic properties such as the Mulliken EN scale had limited quantitative success because the properties of free atoms such as ionization potential and electron affinity

do not coincide with covalently bound atoms or ions as they exist in molecules or for ions in salts or solvents. The use of valence-state properties taken directly from molecular properties avoids these difficulties and is more in the spirit of Pauling's original use of heats of formation to establish his scale.

EN values of the main group elements have been calculated[43,44] and are shown in Table I. Here the covalent radii are taken from Pauling's paper[45] and more recent data.[46] For halogen and hydrogen atoms, the covalent radii are taken from the single bond lengths measured from homonuclear diatomic molecular spectra.[47] The data we used for the covalent radii are almost the same as those of Huheey,[48] Gordy and Cook,[13] and O'Keeffe and Brese,[96] but differ from those of Sanderson.[49]

The new scale of EN, V_x, was initially called by us "the unshielded core potential of X at the covalent radius of X".[43] In our later work, it has been shortened to "covalent potential".

Molecular Energetics and the Covalent Potential

The covalent potentials have been used to correlate energetics of both diatomic and polyatomic systems. Some interesting examples are presented below.

1. Heats of Formation. We have found[42] a quantitative linear relation between the covalent potential of X and the differences of heats of formation, i.e.,

$$\Delta\Delta_f H°(C(CH_3)_m H_{3-m}X/CH_3X) =$$
$$[0.9 - 1.5m(m-1)] - \frac{m}{0.67 + 0.21m}V_x \qquad (4)$$

where

$$\Delta\Delta_f H°(C(CH_3)_m H_{3-m}X/CH_3X) =$$
$$\Delta_f H°(C(CH_3)_m H_{3-m}X) - \Delta_f H°(CH_3X) \qquad (5)$$

and m is the degree of methyl substitution and represents ethyl, isopropyl, or *tert*-butyl when $m = 1, 2,$ or 3.

Another less precise empirical equation for correlating heats of formation of small size molecules was found shortly after. It is given by[50]

$$\Delta\Delta_f H°(CH_3X/HX)/p =$$
$$-15.8 + 2.58V_x \qquad \text{for H and halogen} \quad (6a)$$

$$\Delta\Delta_f H°(CH_3X/HX)/p =$$
$$-10.2 + 1.81V_x \qquad \text{for polyvalent atoms} \quad (6b)$$

where

$$\Delta\Delta_f H°(CH_3X/HX) = \Delta_f H°(CH_3X) - \Delta_f H°(HX) \qquad (7)$$

and p is the number of hydrogen atoms in the HX molecule. In eqs 5–7, X represents H, F, Cl, Br, I, CH_3, SiH_3, NH_2, OH, and SH.

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Table I
Pauling's Scale (Original and Modified) and V_x for Main Group Elements[a]

	H						
X_P	2.1						
	(1.60)						
V_x	2.70						
	Li	Be	B	C	N	O	F
X_P	1.0	1.5	2.0	2.5	3.0	3.5	4.0
	(0.93)	(1.39)	(1.93)	(2.45)	(2.96)	(3.45)	(4.07)
V_x	0.75	2.08	3.66	5.19	6.67	8.11	9.915
	Na	Mg	Al	Si	P	S	Cl
X_P	0.9	1.2	1.5	1.8	2.1	2.5	3.0
	(0.90)	(1.20)	(1.50)	(1.84)	(2.23)	(2.65)	(3.09)
V_x	0.65	1.54	2.40	3.41	4.55	5.77	7.04
	K	Ca	Ga	Ge	As	Se	Br
X_P	0.8	1.0	1.6	1.8	2.0	2.4	2.8
	(0.85)	(1.07)	(1.49)	(1.79)	(2.11)	(2.43)	(2.77)
V_x	0.51	1.15	2.38	3.27	4.20	5.13	6.13
	Rb	Sr	In	Sn	Sb	Te	I
X_P	0.8	1.0	1.7	1.8	1.9	2.1	2.5
	(0.84)	(1.03)	(1.36)	(1.64)	(1.91)	(2.17)	(2.47)
V_x	0.48	1.05	2.00	2.83	3.63	4.38	5.25
	Cs	Ba	Tl	Pb	Bi	Po	At
X_P	0.7	0.9	1.8	1.8	1.9	2.0	2.4
	(0.82)	(1.02)		(1.56)	(1.80)	(2.05)	(2.27)
V_x	0.43	1.01		2.60	3.29	4.03	4.67
	Fr	Ra					
X_P	0.7	0.8					
	(0.82)	(1.02)					
V_x	0.42	1.00					

[a] The first value under every element is X_P from Pauling's scale;[7] the value in the parentheses is the revised value of Pauling's scale based on eq 27.

Using eq 4, the values of group enthalpy parameters were estimated:[51]

$$\Delta_f H^\circ[C(CH_3)_m XH_{3-m}] =$$
$$0.9 + (m-1)(10.08 - 1.5m) - \frac{mV_x}{0.67 + 0.21m} \quad (8)$$

The three papers not only presented good correlations but also resolved three old problems in the thermochemistry of organic compounds. First, trouble with important exceptions to group additivity[52-55] in compounds such as the fluorocarbons and chlorocarbons with many, very polar bonds has been in part resolved. Second, values of group parameters may now be predicted in the absence of direct data. This could be of great value in extending group additivity to organometallic compounds. Third, heats of formation of alkyl fluorides, SiH_3X, GeH_3X, SnH_3X, PH_2X, AsH_2X, and SeHX can be estimated. This offers a good beginning to the study of the thermochemistry of Si-, Ge-, Sn-, P-, As-, and Se-containing compounds.

It has been found[95] that the X-*tert*-butyl/X-*n*-butyl energy differences are dependent on the EN of the substituent X based on ab initio calculations at the MP3/6-31G** level. The tertiary location for fluoride and alcohol is most stable whereas, in contrast, the normal location for lithium in the alkyllithium molecule is most stable. These results follow very directly[98] from the methods we have developed.

2. Homolytic Bond Energies. A linear relation between the differences in homolytic bond dissociation

energies (BDEs) and the covalent potential has been found.[57] The relation was written as

$$DH^\circ(X-C(CH_3)_m H_{3-m}) =$$
$$DH^\circ(X-CH_3) - m\frac{6.33 + 0.36m - V_x}{0.67 + 0.21m} \quad (9)$$

This equation provides a convenient means[58] of estimating the BDEs of X-R. Equation 9 has revealed three categories of BDEs of X-R bonds as we go from methyl to ethyl to isopropyl to *tert*-butyl for R:

(i) regular order

$$DH^\circ(H-Me) > DH^\circ(H-Et) > DH^\circ(H-i\text{-}Pr) > DH^\circ(H-t\text{-}Bu)$$

(ii) irregular order

$$DH^\circ(HO-Me) < DH^\circ(HO-Et) < DH^\circ(HO-i\text{-}Pr) > DH^\circ(HO-t\text{-}Bu)$$

(iii) reverse order

$$DH^\circ(F-Me) < DH^\circ(F-Et) < DH^\circ(F-i\text{-}Pr) < DH^\circ(F-t\text{-}Bu)$$

It used to be said that

$$DH^\circ(\text{alkyl-X}) \approx DH^\circ(X-C(CH_3)_m H_{3-m}) \quad (10)$$

Luo and Pacey[59] have studied this situation. They have inferred the propagator of the inductive effect of X-C bonds from eq 9. The propagator is expressed as

$$P_{X-C} = \frac{1}{3} + \frac{6.33 + 0.36m - V_x}{42.0(0.67 + 0.21m)} \quad (11)$$

where 42.0 is calculated from the valence-state energy[10] of a carbon atom with sp³ hybridization. Because the concept of the inductive effect is very popular, they have calculated the next-nearest methyl substituent

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effect on the BDEs of X–C bonds using eq 11. The effect has been found to be very small within the present experimental uncertainty (±1 kcal/mol). Thus, the group additivity rule for radicals and eq 10 is acceptable.

BDEs of CH_3CO-, $CN-$, $ONO-$, $i-PrO-$, $ON-$, O_2N-, SiH_3-, GeH_3-, and PH_2-X bonds have also been estimated.[59]

The fission of a bond in a polyatomic molecule may involve significant changes in strain energy. Any empirical model of bond fission energies must treat these explicitly if it is hoped to be quantitative. They are treated in a model proposed for bond fission[84] in alkanes. For the available 21 C–C bonds between alkyls, the average deviation is 0.5 kcal/mol with one maximum deviation of 1.5 kcal/mol.

3. Heterolytic Bond Energies.
In the past 20 years, the growth of information on the thermochemistry of gas-phase ions has been dramatic.[60] We have tried to correlate the energetics of gaseous ions with the covalent potential.

Following the approach used in estimating the homolytic BDEs of alkyl–X bonds, Luo and Pacey[61] have derived an equation similar to eq 9:

$$DH°(X^--alkyl^+) =$$
$$DH°(X^--CH_3^+) - m\frac{f^+(m) - V_x}{0.67 + 0.21m} - f(\gamma^+) \quad (12)$$

or

$$DH°(X^--alkyl^+) = DH°(X^--C^+(CH_3)_mH_{3-m}) - f(\gamma^+)$$
$$(12a)$$

where

$$f^+(m) = 27.91 + 2.38m + 11.07/m \quad (13)$$

$$f(\gamma^+) = 1.4\gamma^+ \text{ kcal/mol} \quad (14)$$

and γ^+ is the total number of carbon atoms at and beyond the γ-position of the formal charge in the cation. $f(\gamma^+)$ is called the γ effect.[61]

The semiquantitative description of heterolytic BDEs of Holmes and Lossing[62] has been quantified very well by Luo and Pacey. The values of $DH°(X^--C^+-(CH_3)_mH_{3-m})$ have been calculated using eq 12. We only need to count the number of carbon atoms at and beyond the γ-position in cations when estimating the heterolytic BDEs of X–alkyl bonds. A special table on $DH°(X^--C^+(CH_3)_mH_{3-m})$ has been available.[61] The average deviation of eq 12a for 30 C–H bonds is 1.3 kcal/mol.

4. Silicon Compounds.
The thermochemistry of silicon compounds is an active topic in organometallic chemistry.[63,64] It has been found that there are equations, similar to eqs 4 and 6,[65–67] for silicon compounds; for example,

$$\Delta\Delta_fH°(SiH_3X/HX)/p = 13.0 - 3.28V_x \quad (15)$$

For $\Delta_fH°$ for silicon compounds, we find two separate correlations, one for atoms like C, H, or Si with no

lone-pair electrons and another for halogens, oxygen, or nitrogen bound to Si and having lone pairs. The so-called "p–d π back-bonding energy", E_{pd}, was determined from these relations. The energy can be expressed as

$$E_{pd} = 22.1 - 0.43V_x \text{ kcal/mol} \quad (16)$$

The estimated back-bonding energies are nearly independent of the covalent potential, the type of bonding, or the donor atom X. This would appear to contradict the popular suggestion[68] that p–d π back-bonding is stronger for the more electronegative atoms.

Using the expressions for silicon compounds, heats of formation of all $Si(CH_3)_mH_{3-m}X$ and SiH_3X compounds have been estimated.[67] The estimated values are in agreement with the observed values[63] within experimental uncertainty, with the sole exception of disilane, Si_2H_6. It is possible that the value from classical combustion calorimetry is in error.

The BDEs of Si–H, Si–C, and Si–Si bonds show no methyl substituent effect.[63,64,69–73] This is very unlike C–H BDEs. Chemists have been puzzled by this problem. Some have commented that "there is hardly any information",[69] and that "the reasons are not yet clear".[70] An answer has been given by Luo and Pacey.[74] Based on refs 50 and 65–67, we obtain

$$\Delta\Delta_fH°(Si(CH_3)_mH_{3-m}X/SiH_3X) =$$
$$\begin{cases} -16.0m + 0.9 \text{ kcal/mol} \\ \quad \text{if } X = H \\ -(15.5m + 9.8) - (0.2 - 1.06)V_x \\ \quad \text{if } X = \text{halogen} \\ -(15.5m - 0.4) - (0.2m - 0.1)V_x \\ \quad \text{if } X = CH_3, SiH_3, OH, SH, \text{ or } NH_2 \end{cases} \quad (17)$$

It has been found that the average replacement enthalpy of a hydrogen atom by a methyl group in methylmonosilanes is about −16.0 (−15.9 to −17.7) kcal/mol.[63,75,76] For the methyldisilanes, the average Me-for-H replacement enthalpy is about −15.3 kcal/mol.[73] The replacement enthalpies have been reproduced very well by eq 17. On the other hand, the heats of formation of the alkylsilyl radicals are also a linear function of m, i.e.,

$$\Delta\Delta_fH°(Si(CH_3)_mH_{3-m}/SiH_3) =$$
$$-0.4 - 15.7m \text{ kcal/mol} \quad (18)$$

Consequently, it is very easy to explain the constancy or uniformity of the BDEs of Si–H, Si–C, and Si–Si bonds, and it is expected that the BDEs of Si–OH and Si–halogen bonds have a stronger dependence on methyl substitution than that for the much less polar Si–H bonds.[74]

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The steric effect on Si-H BDEs also has been expected quantitatively[84] and reproduced well the values observed by Griller's group.[64,69]

From the observed BDEs in main group IV, the differences between $DH°(X-H)$ and $DH°(X-CH_3)$, where $X = CH_3$, SiH_3, and GeH_3, were $14.8 ± 0.3$,[57] $1 ± 1.4$,[63] and about 0 kcal/mol,[97] respectively. These differences can be reproduced using eq 6b and can be written as

$$[DH°(X-H) - DH°(X-CH_3)]/p = 17.0 + 4(1.81V_x - 10.2) \quad (19)$$

Here $p = 4$ for main group IV atoms. On the basis of eq 19, the differences for $X = SnH_3$ and PbH_3 could be -3.2 and -4.9 kcal/mol, both negative! This interesting prediction should be tested experimentally.

5. Ionization Potentials. Ionization potentials (IPs) of atoms and molecules are one of the important energy properties like heats of formation and BDEs. We have described the linear relations between the atomic IPs and the covalent potentials.[44] For rare gas atoms, there is a good relation between the IPs and the reciprocal of atomic radii.[83] DeKock[77] has pointed out that linear correlations were expected according to the absolute EN theory of Parr and Pearson.[32,33]

One of the reviewers has called our attention to an error in copying the IP(F). We used the value 17.967 eV instead of the listed value 17.422 eV. When we used the latter, correct value instead of the incorrect value, the slope and intercept changed to yield the new line (in eV):

$$IP(GVII) = 1.49V_x + 2.60$$

This gives a much improved correlation. The average absolute deviation is now reduced to 0.05 eV while the maximum deviation is reduced to 0.10 eV.

Luo and Pacey[78,79] have studied the IPs of molecules and heats of formation of organic cations. For the values of IPs, the average deviations between estimated and observed values are less than 0.08 eV for 22 hydrocarbons and 0.04 eV for 34 halogen derivatives, respectively. Some interesting relations have been discovered. For example, heats of formation of methyl derivative cations may be reproduced well by means of the following equation:

$$\Delta_f H°(C(CH_3)_m H_{3-m} X^+) = \Delta_f H°(CH_3 X^+) - 1.5m(m + 1.4) - 1.93\frac{(8.21 - m)(m + 0.34)}{n^2} - \frac{m}{0.67 + 0.21m}V_x \quad (20)$$

where the energies are in kilocalories/mole; n is the principal quantum number of the valence electrons of the atom X. As compared with eq 4, the third term in eq 20 is specific for cations.

Luo and Pacey[78] have found linear relations between ΔIP and $1/n^2$. That is,

$$\Delta IP(MeX/RX) = IP(MeX) - IP(RX) = I(m) + S(m)/n^2 \quad (21)$$

where $I(m)$ and $S(m)$ are the intercepts and the slopes, both functions of m.

6. Lewis Acid Strengths. Inorganic crystal structures for over 14 000 coordination environments involving nearly 100 different cations were analyzed by Brown.[80,81] The average coordination number to oxygen observed in a large sample of compounds, N_t, was used to calculate a scale of cation Lewis acid strengths, S_a:

$$S_a = V/N_t \quad (22)$$

where S_a is in valence units (vu), which represents the electron pairs per bond, and V is the oxidation state of the cation.

The values of S_a allow one to predict which Lewis acid will bond to which Lewis bases using the observation that both numerical strengths must be equal. It has been reported that there are linear relations between Brown's scale of Lewis acid strengths and some scales of EN, such as Zhang's[23] and Allred-Rochow's.[11]

We have found that the covalent potential also correlates very well with the intrinsic Lewis acid strengths S_a:[82]

$$S_a = -0.0207 + 0.260V_x \approx V_x/4 \quad (23)$$

The correlation coefficient is 0.9908 for 28 main group elements in their highest oxidation state. This is the highest correlation of more than 20 available scales of EN. The next best fits are Zhang's and Allred-Rochow's scales with coefficients of 0.9839 and 0.9803, respectively.

The correlation of the covalent potential with Lewis acid strengths is encouraging us to quantify the HSAB principle.[33,56]

7. Other Relations. Divalent state stabilization energies (DSSE) for silylenes have been determined by Walsh.[75] The DSSE is defined as the difference of the BDEs:

$$DSSE(SiX_2) = DH°(X_3Si-X) - DH°(X_2Si-X) \quad (24)$$

Walsh has found a linear correlation between the $DSSE(SiX_2)$ of our scale of EN and the covalent potential. The correlation coefficient is 0.9937. Pauling's scale of EN also fits, but the coefficient is lower. Sanderson's scale does not support this correlation.

Activation energies of reactions are among the most important quantities in chemical systems. Our new scale can correlate the ab initio (UMP4sdtq/6-31G*//6-31G*) activation energies for the metal ion (M^+) catalyzed radical reactions:[85] $^3O_2$ (triplet dioxygen) with CH_4. The correlation coefficient is 1.000! We expect that many such correlations will be found.

In an unpublished work,[86] our scale of EN or the covalent potential was used to analyze the lone pair/lone pair interaction energies, E_{ll}. These are repulsive and an important component in relating BDE in single bonds between F, O, and N atoms. The energies may be estimated by the following equation:

$$E_{ll} = 8.35n_{ll} \text{ kcal/mol} \quad (25)$$

where n_{ll} is the number of lone pair/lone pair interactions in the X-Y bond, in which X and Y represent

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oxygen, nitrogen, and fluorine atoms.

Enthalpies of formation of many types of solid salts have been estimated.[87] Hisham and Benson have described the linear relations between the lattice enthalpies of the alkali metal hydrides, halides, and metals and their near-neighbor distances. Linear relations between lattice enthalpies and our new scale of EN of alkali atoms also can be found. These will be discussed in the near future.

Support from the Parr–Pearson Theory. Since the outermost or valence electrons of an atom are directly involved in chemical bonding, the chemical properties of an atom are primarily the properties of the outermost or valence electrons at the bonding (covalent or ionic) distance. Consequently, the covalent potential should be one of the most basic parameters for molecular properties.[82]

Luo and Pacey[88] have found that powerful theoretical support for the covalent potential comes from the absolute electronegativity theory of Parr and Pearson.[32,33] They list four reasons:

(i) The dimension of V_x is energy divided by charge, like EN in Parr and Pearson's theory.

(ii) The value of n_x/r_x is a "global" atomic property, which is consistent with Parr and Pearson's theory.

(iii) The value of n_x/r_x is dependent on the valence state, charge, and ligand number of the central atom. This means it is general, as in Parr and Pearson's theory.

(iv) There are good linear correlations between our V_x and Parr's electronic chemical potential, μ, and the central electrostatic potential, V_Q, at r_μ, for 21 main group elements considered in ref 89. There μ is calculated as the Mulliken EN of a ground-state atom. r_μ is the radial distance at which the total electrostatic potential, $V(r_\mu)$, of a ground-state atom exactly equals its chemical potential, μ. V_Q is defined as Q/r_μ, and Q is the total electronic and nuclear charge inside a sphere of radius r_μ, i.e.,

$$Q = Z - \int_{r=0}^{r_\mu} \rho(r) \, dr \qquad (26)$$

where Z is the nuclear charge of the atom, $\rho(r)$ is the electronic density function, and r is the radial distance.

All of Parr and co-worker's calculations are at the ground state of free atoms, but any atom in a molecule is in its energetically optimum valence state, not in the free ground state. Thus the correlations between V_x and μ and V_Q are not so close as might be wished. We should seek the quantity which describes the property in the valence state. The parameters μ, $V(r_\mu)$, r_μ, and V_Q of atoms in their valence state have been so far too difficult to calculate by absolute EN theory.

Valence-state ionization potentials, electron affinities, and Mulliken EN have been calculated[10] by the semiempirical method of Hinze and Jaffe.[90] According to absolute EN theory, the inherent Mulliken EN scale, X_M, from the valence state, the electronic chemical potential, μ, and Huheey's parameter, a, are all approximately the same.

Luo and Pacey[88] have calculated the correlation coefficient for linear relations between four measures, μ, V_Q, V_x, and X_M, of EN for the 21 main group elements considered in ref 89. Here there are two groups of scales of EN: for the ground state and for the valence state. It is interesting to note that two ground-state measures of EN correlate well with each other and with two valence-state measures. Our V_x and X_M correlate well with each other, but less well between ground-state measures and valence-state measures. This comparison shows that our V_x, the covalent potential, is theoretically reasonable and a good measure of the valence-state EN.

The absolute theory of EN has been criticized by Allen[91] recently, but his criticism is not applicable. The atoms in any molecule are in the valence state rather than in the free ground state, although both may be correlated. The points on the left and right sides in Allen's figure[91] are free atoms and hydride molecules, respectively. The hydrogen atoms in hydrides are in different chemical environments. According to Sanderson's equalization principle and the Parr–Pearson theory, the values obtained from EN tables are regarded as characteristic quantities before the given bond is formed. The values of our V_x in Table I are also such characteristic quantities. Consequently, the chemically identical hydrogen atoms in different chemical environments should have different electronic chemical potentials or EN values. In other words, the points on the right side in Allen's figure will not converge at a single point at the reference line, H_2.

The Covalent Potentials and Pauling's Scale of EN

There have been over 20 available scales of EN since 1932. All scales agree in the essential ordering of the elements in the periodic table. From this view, the periodic table itself may be considered the first, best, and universal table of atomic EN; but one of the goals in developing an EN theory is to correlate quantitatively with knowns and to predict unknowns.

Pauling's scale does not work too well in correlating energetics of polyatomic systems. Its use has caused some controversies between groups, such as Griller's,[92] Arnold's,[93] and Holmes's.[94] These controversies do not arise with our new scale of EN.

From Table I, the range of values of our scale of EN is from 0.42 (Fr) to 9.915 (F), about a factor of 23. The range for Pauling's scale is from 0.7 (Fr) to 4.0 (F). For 36 main group atoms, there is a reasonable correlation between our scale of EN and Pauling's scale:

$$X_P = 0.343 V_x + 0.674 \qquad (27)$$

Revised values of Pauling's scale have also been listed in Table I. Equation 27 is not valid for the first atom in the periodic table, H. The reason for the hydrogen anomaly has been discussed.[43] In our V_x scale, we have used the as covalent radius for the H atom the value obtained from the bond length in H_2, namely, 0.7414 Å. This is consistent with our choice of values for the other univalent and polyvalent elements.

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Drago et al.[99,100] have concluded that it is not possible to calculate bond energies for molecules containing atoms of widely different polarity from electronegativity values. This has generated some needless controversy concerning our own results. From the covalent potential we can correlate $\Delta_f H°$ of molecules $Me_3H_{x-3}CX$ with $\Delta_f H°(CH_3X)$. This together with group additivity makes it possible to predict $\Delta_f H°$ for all alkyl X if we know $\Delta_f H°(CH_3X)$ or with less accuracy $\Delta_f H°(HX)$. If now we know one set of bond strengths we can then calculate all the others. This is a much different problem than just calculating $\Delta_f H°$ or BDE for all compounds using only V_x.

Our exploration of electronegativity has shown that energetic properties of substitutionally related molecules will correlate with EN of the substituent atoms X–M. The correlations are however complex and not simply related to EN. They are influenced by the groups attached to X and M including lone pairs and empty orbitals.

Four factors are needed to estimate quantitatively the $\Delta_f H°$, BDE, and heterolytic BDE of chemical species:

(i) the new scale of EN, V_x; (ii) the degree of methyl substitution on the radical center or the formal charge center, m; (iii) the interaction between radical or formal charge centers and distant atoms, which is called the γ effect;[61,79] (iv) the steric compression relief due to bond cleaving.

This is markedly different from traditional approaches. The basic methods we have used will be extended to unsaturated hydrocarbon derivatives, organometallic, and transition metal containing compounds.

Summary

The covalent potential, V_x, is possibly the simplest and most versatile scale of EN for correlating the energetics of chemical species. V_x is a measure of valence-state EN and appears to describe well the contribution of atoms to molecular properties when proper account is taken of nonbonded interactions. Heats of formation of molecules, radicals, and cations, ionization potentials of molecules, and bond energies of homolysis and heterolysis can be reproduced and estimated well. Our new scale of EN is also a good measure of Lewis acid strengths.

Appendix: Comments on Drago's Commentary[101]

The difference between bond additivity and group additivity behavior involves an enormous difference in data base requirements. It is thus an enormous simplification to be able to predict $\Delta_f H°(R-X)$ from $\Delta_f H°(CH_3-X)$ where R is any saturated alkane. In the sequence Me–H, Et–H, i-Pr–H, t-Bu–H, the values of $\Delta_f H°$ vary nonlinearly from -17.9 to -32.1 kcal, a range of about 14 kcal. In the sequence Me–OH, ..., t-Bu–OH, the nonlinear sequence covers a span of 27 kcal. Clearly, this has to do with interactions between the C–O bond and the adjacent C–H or C–C bonds. The fact that these are quantitatively correlated by V_x, an easily calculated atomic property, is not trivial. The fact that V_x also quantitatively correlates ionization potentials of main group atoms is also of some significance. Drago states that our relations fail in the case of the silanes because we need to make allowances for π–d back bonding. On the contrary, we take this observation as a valuable use of V_x in pointing out a new type of interaction. In the same way, group additivity fails for highly branched compounds, an important phenomenon pointing to the existence of nonbonded steric repulsions.

Drago and co-workers have developed an empirical scheme for estimating $\Delta_f H°$. They have then gone on to make some theoretical generalizations which lead them to conclude that we have not done what in fact we have done. I believe the entire dispute which has arisen may be more semantic than real.

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