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Two Descriptors for Series of Congeneric Molecules

Ray Hefferlin

Physics Department, Southern Adventist University, Collegedale, Tennessee 37315, USA
(*E-mail: hefferln@southern.edu*)

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Abstract. Two quantitative characterizations are compared for series, each of which consists of a central atom or molecule and successively attached functional groups. The vector index component V_2 brings out the periodicity related to the central entity and to the ligands (if they are atoms) or brings out the periodicity related to the substituents (if they are atoms) put into an originating molecule. The Zenkevich parameters also show the periodicity seen in V_2 but are valuable for treating data farther from linearity with respect to the number of attached groups provided that there is not an inflection point. An algebraic comparison shows that it is not possible to derive the vector index components from the Zenkevich parameters or *visa versa* except when the data are exactly linear.

Keywords: Molecular vector index; dyadic data transformations; Zenkevich parameters, congeneric molecules, structurally related molecules, periodicity

INTRODUCTION

In a previous paper,[1] we defined a vector index to characterize molecular series which consist of a central atom (or molecule) and a progressively larger number (n) of identical atomic (or molecular) ligands or which consist of successive substitutions of atoms (or atom groups) into a molecule. The definition is valid for series with a property that varies approximately linearly with n. A significant simplification of the mathematical methods is presented in this paper Zenkevich defines two parameters,[2–4] obtained by iterative use of a simple equation, for the same kinds of molecular series. Both approaches lead to showing that periodicity is evident in those series where atoms take part. We explore the relations between the two components of the vector index and his two parameters.

THEORY AND RESULTS

The Vector Index

Let there be an atom X, whose heat of atomization $\Delta_a H$ is of course zero. Let there be added n ligands Y, where n goes from 0 to a maximum N. Let the data for $\Delta_a H$ be plotted on the y axis of a graph where $n + 1$ (atom plus n ligands) is the x axis. Find the best-fitting trend line that passes through $(x,y) = (1,0)$, as shown in Figure 1. For comparison with previous results, the slope of the least-squares trend line is divided by 10^3 and changed in sign to define V_2. This procedure is a great simplification of that presented in Ref. 1. The vector thus has elements, V_1 and V_2:

$$\boldsymbol{V}(\mathrm{X,Y,}(N+1),\ \Delta_a H) = \begin{pmatrix} \Delta_a H\,(x=0) \\ \text{slope} \pm \text{error} \end{pmatrix} \qquad (1)$$

$\boldsymbol{V}$ at left indicates that the vector concerns X, Y, the maximum number of molecular components, and the property (and phase). If it is desired to use a computer application that can find the error associated with a linear fit, it may be necessary to plot $n + 1$ on the y axis and $\Delta_a H$ on the x axis to do the fitting because most popular applications can only find the error in the vertical direction.

Several comments are in order: (i) It is important to keep in mind that this index refers to a series of molecules, not to a single species. (ii) The method can be generalized to series where the central object or the ligands are molecules, or where atoms or molecules are substituted into an originating molecule, and/or where data for some other property are to be used. In most of these cases the component V_1 is no longer zero. (iii) Once vector indices have been calculated, they can be transformed from one series to another by means of a diagonal matrix (or a dyadic). This transformation

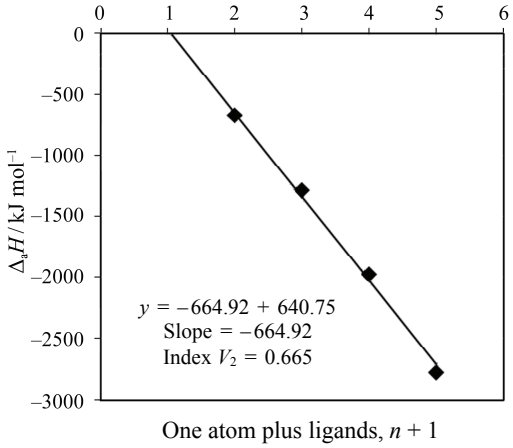

Figure 1. The nearly linear plot for ΔH_a of gas-phase Ti through TiO_4,[5] with a trend line passing through (0,1). The vector index for this series has component $V_1 = 0$ (the horizontal intercept) and $V_2 = 0.665 \pm 0.000$ (the slope of the trend line and its error divided by 10^3, changed in sign, and truncated to three significant figures). The error in V_2 is defined as the average of the differences of the locations of the points from the trend line (in the horizontal direction). The value of V_2 shown in the figure is the lower-left point in Figure 2.

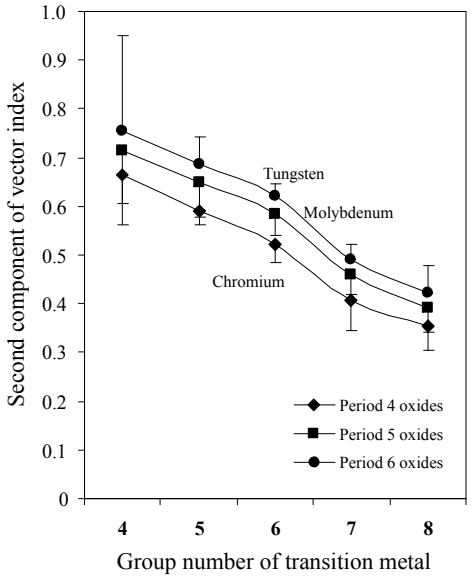

Figure 2. The second elements of the vector indices for $\Delta_a H$ of period 4 to 6, group 4 to 8, transition-metal atoms and their oxides. The central atoms of group 6 are shown. The maximum number of oxygen atom ligands for atoms of any group is the same as the group number. Only the top, bottom, and bottom halves of the error bars are shown from top to bottom.

method is also a simplification compared to that given in Ref. 1. (iv) The second components of vector indices are, when appropriate species are compared, quite periodic as shown by figures in the previous paper and by Figure 2. Inspection of the figure shows that periodicity is present (period 4, 5, and 6 atoms are in that order, and the gap between period 4 and 5 exceeds that between 5 and 6) and shows the location of the inflection point between groups 6 and 7, which is related to the appearance of antibonding f electron orbitals.

The Zenkevich *a* and *b* Parameters

Zenkevich[2-4] has recently studied many series of organic molecules having the characteristics described in the Introduction. One series presented in Table 1 of Ref. 4 consists of unbranched perfluoroalkanes; the first few lines of this table are reproduced here as Table 1, with two additional columns - one enumerating n (the number of added carbon groups) and the other showing the increments in boiling point (t_{bp}/°C) as the groups are added.

Table 1. Boiling points of the first few perfluoroalkanes

Homolog	n	t_{bp}/°C	Increment
CF_4	0	–128.0	-
C_2F_6	1	–78.2	49.8
C_3F_8	2	–36.6	41.6
C_4F_{10}	3	–1.7	34.9

It is clear from the increments that t_{bp}/°C is not linear with respect to the n; however, his plot of $t_{bp}(n+1)$ on $t_{bp}(n)$, or equivalently $t_{bp}(n)$ on $t_{bp}(n-1)$, is strikingly linear. He uses the recursion relation

$$t_{bp}(n) = a\, t_{bp}(n-1) + b \qquad (2)$$

for the successive pairs of data in his complete table (12 molecules) to find overdetermined values for the parameters a and b that can be solved to obtain $a = 0.939 \pm 0.005$ and $b = 33.4 \pm 1.0$. (Starting with $n = 1$ gives smaller errors: $a = 0.946 \pm 0.003$ and $b = 31.7 \pm 0.7$.)[3]

Raw data for $\Delta_a H(n)$ of the same period 4 to 6, group 4 to 8, transition-metal atoms and their oxides were plotted on $\Delta_a H(n-1)$ and it was found that these plots are also hardly distinguishable by eye from being linear. The parameters a and b were found from least-squares trendlines. Figure 3 shows that parameter b displays evidence of the periodicity seen in Figure 2, though not quite as clearly. A plot of the parameter a is chaotic but averages 1.014 ± 0.040, which lacks only 0.007 of agreeing, with touching error bars, to what was stated for 38 out of 56 series of congeneric organic molecules (0.943 ± 0.024).[4]

The parameters a and b for alkali-earth halides each exhibit the first and secondary periodicities of the group-2 atoms and the group-17 atoms. Figure 4

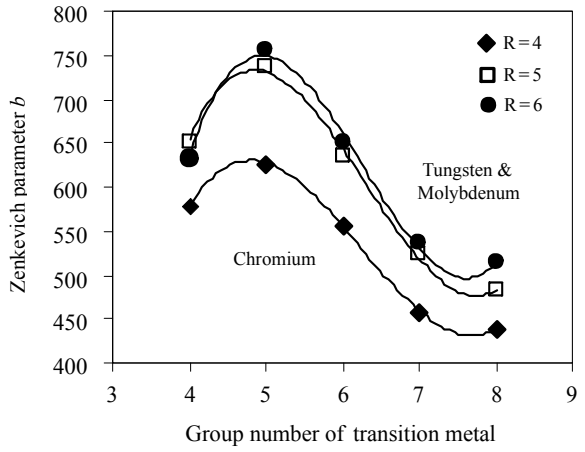

Figure 3. The parameter *b* of period 4 to 6, group 4 to 8, transition-metal atoms and their oxides, and cubic trendlines only for emphasis. The central atoms of group 6 are shown. Evidence for periodicy is seen in the bottom to top sequence of period numbers.

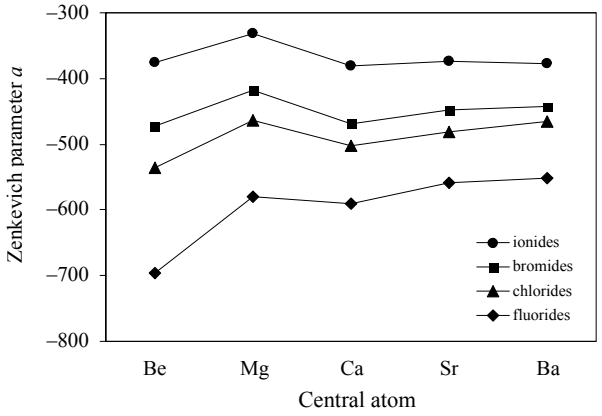

Figure 4. Variation of the magnitudes of the parameter *a*, showing how it changes as the group-2 central atom and the group-17 ligands are changed. The sequence of patterns from bottom (fluorides) to top (iodides) is a manifestation of chemical periodicity. The larger gaps between the fluorides and chlorides, and between bromides and iodides, compared to that between the chlorides and bromides, is a manifestation of secondary periodicity. Within a given pattern, the changes from Be to Mg and from Ca to Sr have more positive slopes than the other segments, which is another evidence of secondary periodicity.

shows one of these, *a*, and it can be compared with the very similar (but upside down) behavior of V_2 shown in Figure 4 of Ref. 1.

The question now arises, can the Zenkevich parameters be derived from the components of the vector index or *visa versa*? Since the vector index is based on a (nearly) linear relationship of t_{bp} on *n*, we assume that for any *n*

$$t_{bp}(n) = \alpha(n) + \beta \tag{3}$$

where α (after multiplication by -10^{-3})[1] and β are the upper and lower components of the vector index. Eq. (3) for a unbranched perfluoroalkane with one less carbon group is

$$t_{bp}(n-1) = \alpha(n-1) + \beta \tag{4}$$

Substituting Eqs. (3) and (4) into Eq. (2) gives

$$\alpha(n) + \beta = a\,[\alpha(n-1) + \beta] + b \tag{5}$$

From the first terms on each side of the equals sign it is clear that $a = 1$. If, going further, Eq. (3) is generalized to a quadratic form in order to take into account the non-linearity of data plotted on n+1 (or n) by writing

$$t_{bp}(n) = \alpha n^2 + \beta n + \gamma \tag{6}$$

then writing same thing with n replaced by n−1, and finally substituting these two into Eq. (2), again it follows that $a = 1$ and also that $b = \alpha$. The first equality correlates, to within a bit more than two of Zenkevich's small error measures, with the average of the 38 *a* values given by him and quoted above (Ref. 3 contains the list of 56 series). The second equality is satisfied only poorly by slopes of the data for various series plotted on *n*.

SUMMARY

The mathematical procedure to obtain vector indices has been very much simplified, and an additional example of how V_2 is periodic (for a collection of transition-metal oxides) has been presented in Figure 1. The procedure has been compared with the excellent work of Zenkevich, which results in two parameters *a* and *b*. These parameters both show periodicity for collections of molecular series in the cases investigated (for 12 transition-metal oxides and especially for 20 group-2 halides). By allowing for a quadratic behavior of the data, it is found that the parameter *a* should equal exactly one and the parameter *b* should correspond to the second component of the vector index. The data for the molecular series investigated by Zenkevich and in this work are not linear; for the majority of organic molecular series that he investigates, *a* is about 0.943. In summary, either procedure may be used to characterize the molecular series, but (i) they cannot be intercompared – the parameter *b* cannot be used to forecast the second (slope-related) component of the vector index, or conversely, V_2 cannot be used to forecast the *b* parameter and (ii) the uncertainties would have much larger error measures for data that have an inflection point when plotted on *n* (such as the boiling points of chlorosubstituted benzenes).

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SAŽETAK

Dva deskriptora za nizove kogeneričkih molekula

Ray Hefferlin

Physics Department, Southern Adventist University, Collegedale, Tennessee 37315, USA

Dvije kvantitativne karakterizacije uspoređene su za nizove molekula od kojih se svaka sastoji od centralnog atoma ili molekule na koje su sljedno spojene funkcionalne grupe. Komponenta V_2 indeksa vektora ispoljava periodičnost povezanu s centralnim entitetom i ligandima (ako su atomi) ili ispoljava periodičnost vezanu uz supstituente (ako su atomi) postavljene unutar izvorne molekule. Zenkevichevi parametri također pokazuju periodičnost viđenu kod V_2 ali su korisni za obradu podataka i izvan područja linearnosti s obzirom na broj dodanih grupa, uz uvjet da nema točke infleksije. Algebarska usporedba pokazuje da nije moguće dobiti komponente indeksa vektora iz Zenkevichevih parametara, ili obratno, osim kada su podaci linearni.