

Letter

Stoichiometric valence *versus* structural valence: conclusions drawn from a study of the influence of polyhedron distortion on bond valence sums

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Abstract. From studies of the influence of polyhedron distortions on bond valence sums (BVS), it is concluded that larger deviations of the BVS values from corresponding values of their classical valence are due to the fact that so far no distinction has been made between the stoichiometric valence derived from chemical analysis and the structural valence derived from structure data.

Introduction

The bond valence model (BVM) is based on Pauling's (1929) electrostatic valence principle which states that the valence V_i of an atom, A_i , of a $[AX_n]$ coordination polyhedron is distributed among its bonds to surrounding atoms, X_j , such that

$$V_i = \sum_j^n s_{ij} \quad (1)$$

According to the equation most widely used, the bond valence s_{ij} is correlated with the length, D_{ij} , of an $A_i - X_j$ bond:

$$s_{ij} = \exp [(r_0 - D_{ij})/b] \quad (2)$$

The bond valence parameter r_0 is considered to be constant for a given type of $A-X$ bond, whereas b is assumed to be equal to 0.37 Å for all types of bonds [Brown, 2002]. For the vast majority of inorganic crystal structures, BVS values calculated with (1) and (2) deviate by less than 0.1 v.u. from the integer stoichiometric valence ($^{\text{stoch}}V$) values of the ions. Sometimes, however, deviations of up to 1 v.u., which cannot be explained by experimental error, have been reported (e.g. Burns, Ewing and Hawthorne, 1997; Krivovichev and Brown, 2001). The

deviations have sometimes been ascribed to inaccuracy of the bond valence parameters (Locock and Burns, 2004). However, elimination of the deviations by adjusting the bond valence parameters may simply shift the given problem to other atoms of a structure (Wang and Liebau, 2005).

Systematic studies of the influence of distortion of coordination polyhedra (CPs) $[A_i(X_j)_n]$ on the difference between calculated BVS values and corresponding classical valences [Wang and Liebau (henceforth abbreviated W & L), 1996a, b; Liebau and Wang, 2004] revealed that these differences are larger in highly distorted CPs. The present authors have calculated r_{0i} values of individual CPs with

$$r_{0i} = b \times \ln \left[\frac{^{\text{stoch}}V_i}{\sum_j \exp(D_{ij}/b)} \right], \quad (3)$$

which is derived from (2) by simple mathematical transformation, in the same way as, for instance, Brese and O'Keeffe [1991] and Brown [2002, p. 227] have done. If (3) is applied to individual $[LX_n]$ polyhedra, where L is a p -block cation with one lone electron pair (LEP), it was shown that calculated r_{0i} values are correlated with distortions of the CPs rather than being constant, as assumed in the present BVM. On the other hand, if r_0 is assumed to be constant for $L-O$ bonds, as for all other bond types, the observed correlation can be interpreted as being due to a variable non-integer valence V_i that was incorrectly fixed to the integer stoichiometric valence during calculation of r_{0i} by equation (3). The non-integer valence will naturally cause substantial deviations of BVS values calculated with tabulated r_0 values derived from the integer stoichiometric valence. In this letter we will discuss the physical meaning of such non-integer atomic valence and its distinction from the stoichiometric valence.

Correlation between r_{0i} and the asphericity parameter Φ_i

To describe distortions of CPs, W & L (1996b) introduced an asphericity parameter Φ_i which has been interpreted as

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a vector pointing from the nucleus of a cation \mathbf{L} to its LEP, the length of which is a measure of the distance of the LEP from the nucleus. A statistical analysis using 1414 $[\text{LO}_n]$, 432 $[\text{LS}_n]$, and 78 $[\text{LSe}_n]$ polyhedra from the literature established that, for a given type of $\mathbf{L}-\mathbf{X}$ bond, r_{0i} can be fitted to

$$r_{0i} = E|\Phi_i| + F \quad (4)$$

(W & L, 1996b). New calculations have now been made with 2084 $[\text{LO}_n]$ polyhedra retrieved from the 2004/2 version of the ICSD using more stringent selection criteria. This new analysis confirms that, if $|\Phi_i|$ increases, i.e. with increasing distortion of the $[\text{LX}_n]$ polyhedra, the r_{0i} values decrease. In addition, the r_{0i} values of $[\text{LX}_n]$ polyhedra whose \mathbf{L} cations belong to the same Group of the Periodic System of Elements (PSE) and which are coordinated by the same type of \mathbf{X} anion, can be fitted to master curves of the form

$$r_{0i} = \exp [p(|\Phi_i| + q)] + t. \quad (5)$$

Figure 1 shows, as an example, the master curve derived from 527 $[\text{LO}_n]$ polyhedra with $\mathbf{L} = \text{P}^{\text{III}}$, As^{III} , Sb^{III} , and Bi^{III} .

Correlation between $(\text{BVS})_i$ and $|\Phi_i|$

For $[\text{LO}_n]$ polyhedra, with \mathbf{L} belonging to the same Period of the PSE, the $(\text{BVS})_i$ values calculated with equations (1) and (2) can be fitted to linear master curves of the form

$$(\text{BVS})_i = \sum_j s_{ij} = A|\Phi_i| + B. \quad (6)$$

The $(\text{BVS})_i$ values are calculated by using tabulated r_0 values (Brese and O'Keeffe, 1991) that are averages of individual r_{0i} values calculated with (3).

In Fig. 2 the correlation is shown for 554 $[\text{LO}_n]$ polyhedra with $\mathbf{L} = \text{Sn}^{\text{II}}$, Sb^{III} , Te^{IV} , and I^{V} as an example. From Figs. 1 and 2 it can be seen that, for reasons that

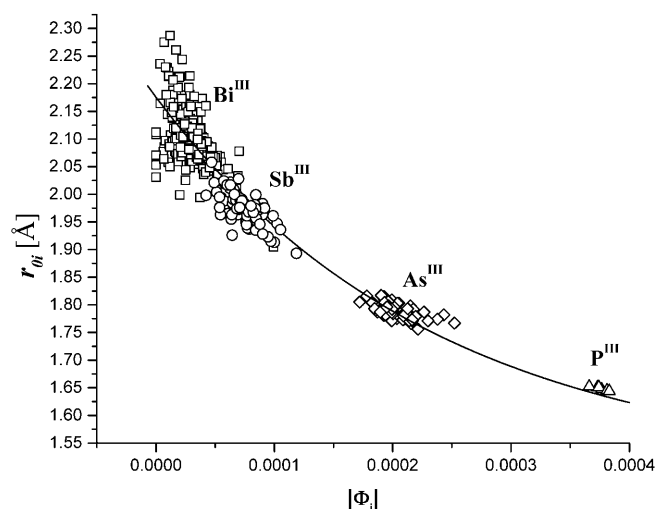


Fig. 1. Correlation between r_{0i} and $|\Phi_i|$ for $[\text{LO}_n]$ polyhedra with $\mathbf{L} = \text{P}^{\text{III}}$ (triangle), As^{III} (diamond), Sb^{III} (circle) and Bi^{III} (square). The data are taken from the ICSD file, release 2004/2.

The fitted master curve is given by $r_{0i} = \exp [-4.25(8) \cdot 10^3 \times |\Phi_i| - 0.392(4)] + 1.5$; $\chi^2 = 0.00116$.

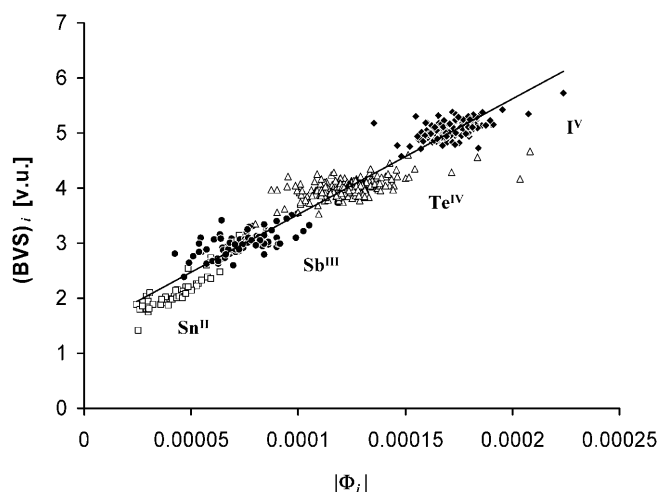


Fig. 2. Correlation between $(\text{BVS})_i$ and $|\Phi_i|$ for $[\text{LO}_n]$ polyhedra with $\mathbf{L} = \text{Sn}^{\text{II}}$ (square), Sb^{III} (circle), Te^{IV} (triangle) and I^{V} (diamond). The data are taken from the ICSD file, release 2004/2.

The fitted master curve is given by $(\text{BVS})_i = 2.10(2) \cdot 10^4 \times |\Phi_i| + 1.42(3)$; $R^2 = 0.946$.

are still not understood, it are the mean values of the data points of each type of $[\text{LO}_n]$ polyhedron rather than the individual r_{0i} and $(\text{BVS})_i$ values that are described by the master curve.

Figure 2 shows that each $\mathbf{L}-\text{O}$ bond type has a linear behaviour similar to that of the master curve, however with different slopes for the different $\mathbf{L}-\text{O}$ types. The master curve clearly shows that the $|\Phi_i|$ values increase as the \mathbf{L} cations change from low-valent to high-valent ions with increasingly higher power of \mathbf{L} to attract anions. This bonding power is reflected by the calculated BVS values. Because $|\Phi_i|$ is considered to be a measure of the separation of the LEP from the atomic nucleus (W & L, 1996b), such correlation is apparently due to different degrees of repulsion between the lone electron pair and the bonding electron pairs. The correlation trend for each $\mathbf{L}-\text{O}$ bond type indicates that, even for the same \mathbf{L} cation, the bonding power increases as $|\Phi_i|$ increases. We consider this bonding power change to be a valence change of \mathbf{L} without changing its stoichiometric valence.

Proposition of the concept of structural valence

From the result of the statistical analyses described above, the conclusion is drawn that the calculated $(\text{BVS})_i$ values reflect the bonding power of cations within a compound. The value of the bonding power of a cation depends on its own bonding requirements and that of its surrounding anions, in particular on their electronegativities. The exact value of this bonding power should be obtained from quantum mechanical methods. Approximate values can be derived by calculating the bond valence sums from structure data, because the bonding power of the cation is contained in the geometric arrangement of the anions surrounding it. For this bonding power, the term *structural valence* and the symbol $\text{struct}V$ are proposed.

The structural valence of an atom is different from its classical stoichiometric valence, $\text{stoich}V$, which is derived

from the stoichiometry of a compound, usually by chemical analysis. The values of $^{\text{stoich}}V$ of an atom are governed by the Group number of the element within the PSE and are, in contrast to the values of $^{\text{struct}}V$, not influenced by the specific structure of a compound.

Both $^{\text{struct}}V$ and $^{\text{stoich}}V$ are measured in valence units (v.u.). Whereas the values of $^{\text{stoich}}V$ are *per definitionem* integer numbers, the values of $^{\text{struct}}V$ are in general non-integer numbers.

For each atom in a compound one value of $^{\text{stoich}}V$ and one value of $^{\text{struct}}V$ have to be assigned. The statistical analysis of the $[\text{LX}_n]$ polyhedra suggests that for undistorted CPs the values of $^{\text{stoich}}V$ and $^{\text{struct}}V$ are numerically equal.

Discussion

Whenever structural data such as bond lengths and bond angles are used to calculate bond valence sums (independent of whether these data were derived from structures of crystalline or non-crystalline materials by diffraction, spectroscopic or other methods), the BVS values are approximations of the structural valences, $^{\text{struct}}V$. In other words, the bond valence model provides information on the bonding power of atoms in a compound. This is in full agreement with Mohri's (2000) suggestion 'that the bond valence sum is the realistic definition of the bonding power' of an atom. The current BVM works successfully for the majority of structures in spite of the fact that no distinction has yet been made between $^{\text{stoich}}V$ and $^{\text{struct}}V$. This suggests that in such structures in which the CPs are undistorted or only slightly distorted, the numerical values of $^{\text{stoich}}V$ and $^{\text{struct}}V$ of the atoms are similar although they have essentially different meanings. In structures with considerably distorted CPs, because of electronic or steric effects, larger deviations of calculated BVS values of an atom from the value of its integer stoichiometric valence are to be expected and the $^{\text{struct}}V$ value is substantially different from the $^{\text{stoich}}V$ value.

Although these conclusions have so far only been drawn from statistical analyses of $[\text{LX}_n]$ polyhedra, where **L** are *p*-block element cations with one LEP, it seems justified to assume that the conclusions are also valid for other $[\text{AX}_n]$ polyhedra where **A** may be cations of *s*-, *p*-, *d*- (transition element), and *f*- (lanthanoides and actinoides) block elements.

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