

On the accurate bond-valence parameters for the
 $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair

Vasyl Sidey

Department of Chemistry and Research Institute
for Physics and Chemistry of Solids, Uzhgorod
National University, Pidgirna Street 46,
Uzhgorod 88000, Ukraine

Correspondence e-mail: vasylsidey@yahoo.com

The improved values of the bond-valence parameters for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair, $r_0 = 1.927 \text{ \AA}$ and $b = 0.446 \text{ \AA}$, have been deduced from the crystal structures of the α and β polymorphs of Sb_2O_3 and from the set of precisely determined complex structures containing $[\text{Sb}^{3+}\text{O}_n]$ coordination shells.

Received 9 January 2010

Accepted 9 March 2010

1. Introduction

The bond-valence model (BVM) in its modern form is a powerful and convenient tool in validating newly determined crystal structures and predicting bond lengths in the structures of known chemical composition and presupposed bond-network topology (Brown, 2002, 2009*b*).

The bond valence (BV) s is defined as part of the 'classical' atomic valence shared with each bond. According to the bond-valence sum (BVS) rule, the oxidation state (atomic valence) V_i can be calculated from the sum of the individual bond valences s_{ij} (where j denotes an atom bonded to i), as given by

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

The valence of a bond (measured in 'valence units', v.u.) is considered to be a unique function of the bond length; the most commonly adopted empirical expressions for the relationship between the bond valences s_{ij} and the bond lengths r_{ij} are

$$s_{ij} = (r_0/r_{ij})^n \quad (2)$$

and

$$s_{ij} = \exp[(r_0 - r_{ij})/b], \quad (3)$$

where r_0 , n and b are the empirically determined parameters for a given ion (atom) pair, r_0 being the length of the conceptual bond of unit valence with $s_{ij} = 1$ (Brown & Shannon, 1973; Brown & Altermatt, 1985). Although both (2) and (3) demonstrate virtually the same performance in approximation of the real (observed) ' s_{ij} versus r_{ij} ' curves (Brown, 2002), (3) is used in almost all recently published works concerning the BVM applications. The b parameter in (3) is commonly taken to be the 'universal constant' equal to 0.37 \AA , and the r_0 parameters have been determined for a large number (~ 1000) of ion pairs, assuming $b = 0.37 \text{ \AA}$ (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991). Hereafter, the BV parameters determined using the 'universal constant' will be referred to as the conventional BV parameters.

In well determined stable ordered crystal structures investigated under ambient conditions, the BVS values calculated for all crystallographically distinct atoms are typically very close to the expected V_i values; large deviations between the

BVS and V_i values can really indicate that the structure is incorrect. It must be noted, however, that applicability and efficiency of the BVM are critically dependent on the *quality* of the BV parameters. High-quality BV parameters are expected to give reasonable BVS values over the *full* range of observed bond lengths and coordination numbers (CNs) of a given ion pair. Furthermore, high-quality BV parameters should accurately reproduce typical interatomic distances r_{ij} observed for a given ion pair in *regular* (or nearly regular) coordination shells¹ with *different* CNs.

In most cases, the performances demonstrated by the conventional BV parameters are reasonably high; but for certain ion pairs (especially for those having a wide range of CNs) close approximations of the real ' s_{ij} versus r_{ij} ' correlations are possible only by *simultaneous* fitting of both r_0 and b (e.g. Krivovichev & Brown, 2001; Locock & Burns, 2004). The unacceptably low performance of the conventional BV parameters reported for such ion pairs can be easily detected by systematic variations of the BVS values calculated for *different* CNs of these ions (Sidey, 2008, 2009b).

In recent BVM literature, a few attempts to improve the poorly determined 'classical' (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) conventional BV parameters for the Sb—O bonds ($r_0 = 1.973$ Å for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair and $r_0 = 1.942$ Å for the $\text{Sb}^{5+}/\text{O}^{2-}$ ion pair) have been undertaken.

Palenik *et al.* (2005) have reported the 'new' conventional BV parameters $r_0 = 1.955$ Å for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair and $r_0 = 1.912$ Å for the $\text{Sb}^{5+}/\text{O}^{2-}$ ion pair. The procedure used by Palenik *et al.* (2005) is equivalent to that described by Brese & O'Keeffe (1991) for direct determination of the conventional BV parameters. This 'traditional' scheme includes:

- (i) selecting the most reliable dataset of bond lengths for a given ion pair;
- (ii) solving (1) for every selected coordination shell by using

$$r_0 = b \ln[V_i / \sum_j \exp(-r_{ij}/b)], \quad (4)$$

where $b = 0.37$ Å;

- (iii) averaging the r_0 values calculated for a given ion pair.

From the crystal structure of Sb_2O_5 (Jansen, 1978, 1979) considered as the 'reference structure' (the definition of this term is given in §4), Sidey *et al.* (2008) have derived $r_0 = 1.908$ Å and $b = 0.409$ Å for the $\text{Sb}^{5+}/\text{O}^{2-}$ ion pair. The mean value of the O— Sb^{5+} bond lengths observed for the two-coordinated O atoms in the structure of Sb_2O_5 (1.908 Å) has been taken as the physically meaningful r_0 parameter for the $\text{Sb}^{5+}/\text{O}^{2-}$ ion pair; and the b parameter has been adjusted to give BVS = 5 v.u. for the Sb^{5+} ions in the structure of Sb_2O_5 .

Sidey (2009a) has obtained $r_0 = 1.924$ Å and $b = 0.47$ Å for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair by least-squares fitting the power-law curve (2) of Brown & Wu (1976) to (3). In this way, the BV parameters were also determined for the $\text{Sn}^{2+}/\text{O}^{2-}$, $\text{Te}^{4+}/\text{O}^{2-}$ and $\text{I}^{5+}/\text{O}^{2-}$ ion pairs (Sidey, 2009a).

¹ For *irregular* coordination shells, the average values of bond valences (s_{ij}) and bond lengths (r_{ij}) do not correspond to each other, in accordance with the distortion theorem (Brown, 2002).

In a very thorough investigation of the Sb—O bonds, Mills *et al.* (2009) have reported $r_0 = 1.925$ Å and $b = 0.455$ Å for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair and $r_0 = 1.904$ Å and $b = 0.430$ Å for the $\text{Sb}^{5+}/\text{O}^{2-}$ ion pair. The statistical procedures used by Mills *et al.* (2009) [*i.e.* minimization of the function $F = \sum (V_i - \text{BVS})^2$ for the set of selected coordination shells] are either equivalent (for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair) or very similar (for the $\text{Sb}^{5+}/\text{O}^{2-}$ ion pair) to that used by Locock & Burns (2004) to determine the BV parameters for the $\text{Ti}^{4+}/\text{O}^{2-}$ ion pair. In the latter case, Mills *et al.* (2009) optimized the BVS values not only on the Sb^{5+} cations but also on the O^{2-} anions of some structures considered as the 'reference structures'.

Comparison (Mills *et al.*, 2009) of the BV parameters reported by different authors for the Sb—O bonds has clearly shown that the BV parameters reported by Mills *et al.* (2009) for the $\text{Sb}^{3+}/\text{O}^{2-}$ and $\text{Sb}^{5+}/\text{O}^{2-}$ ion pairs and by Sidey *et al.* (2008) for the $\text{Sb}^{5+}/\text{O}^{2-}$ ion pair are definitely close to optimum.

The results presented here were obtained in the summer of 2009, when the above article of Mills *et al.* (2009) had not yet been published. Being involved in the systematic investigations of the ternary systems Hg(Pb,Zn)—Sb—O (Sidey *et al.*, 2008, 2010), and being interested in the development of reliable schemes for determining the high-quality BV parameters, the author of the present work decided to derive, as accurately as possible, the BV parameters for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair from the precisely determined crystal structures. The main reason for this work was the fact that the r_0 and b parameters obtained for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair from the corresponding Brown—Wu parameters r_0 and n (Brown & Wu, 1976; Sidey, 2009a) were based on the outdated structural information available in the mid 1970s.

Taking into account the very high performance of the BV parameters reported by Mills *et al.* (2009), the values obtained by the author for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair and reported here cannot be regarded as a significant improvement. Nevertheless, the author believes that the simple original scheme developed and used in the present work could be useful for the crystal chemists wanting to obtain the high-quality BV parameters for some other bond types. Furthermore, discussion on the quality of the BV parameters and on the different calculation schemes proposed for determining these parameters (§§2–4) might be interesting for all scientists working in the field of the BVM.

2. Methodology

2.1. Criteria of quality for the BV parameters

Before starting the calculations of the BV parameters, the criteria of quality of these parameters must be postulated as clearly as possible. The author has set the following criteria (in order of decreasing importance):

- (i) the BVS values calculated from the high-quality BV parameters for *all* the CNs observed for a given ion pair in accurately determined stable ordered structures should be close to V_i (Sidey, 2009b);

(ii) the average BVS value calculated for a statistically representative *set* of selected accurately determined stable ordered structures, $\langle \text{BVS} \rangle_{\text{set}}$, should be close to V_i ,²

(iii) in stable stoichiometric ordered *binary* structures determined accurately and precisely, the average BVS values, $\langle \text{BVS} \rangle_{\text{bin}}$, calculated for cations and/or anions (*i.e.* $\langle \text{BVS} \rangle_{\text{bin}}^{\text{cation}}$ and/or $\langle \text{BVS} \rangle_{\text{bin}}^{\text{anion}}$) should be equal to V_i within the limits of experimental uncertainty (Sidey, 2006; Sidey *et al.*, 2008);

(iv) if a particular electropositive element *A* can form cations with *different* oxidation states [*e.g.* A^{m+} and $A^{(m+n)+}$], the r_0 value determined for the A^{m+}/X ion pair is expected to be *greater* than that determined for the $A^{(m+n)+}/X$ ion pair.

Although all the above criteria are intended primarily for testing the quality of the BV parameters, criteria (ii) and (iii) are also suitable for selecting the ‘reference systems’ for *analytical* determining of the BV parameters (see §4).

Criterion (i) is self-explanatory, and the importance of this criterion for the BVM has been discussed and clearly illustrated in recent articles of the author (Sidey, 2008, 2009*b*). Criterion (i) is the only *obligatory* criterion of the above list, while criteria (ii)–(iv) are definitely less important because of their dependence on criterion (i) and/or their limited applicability.

Criterion (ii) is common for all calculation schemes proposed for determining the BV parameters. Being taken separately, however, criterion (ii) is not sufficient for determining the accurate r_0 and b values because the equality $\langle \text{BVS} \rangle_{\text{set}} \simeq V_i$ can be achieved by underestimation and overestimation of the BVS values calculated for *different* CNs, as observed for some conventional BV parameters (Sidey, 2008, 2009*b*). In other words, if criterion (i) is fulfilled then criterion (ii) is also fulfilled, but not *vice versa*.

Criterion (iii) is based on the strict definition of the term ‘bond valence’ (or ‘bond order’) as the exact fraction (or number) of the Lewis electron pair(s) contributing to the bond (Sidey, 2006; Sidey *et al.*, 2008). In the accurately and precisely determined stable stoichiometric ordered binary structure A_mX_n , the particular s_{ij} values are not known *a priori* (in the general case); but their averaged *sums* calculated for cations and anions of this structure (*i.e.* the $\langle \text{BVS} \rangle_{\text{bin}}^{\text{cation}}$ and $\langle \text{BVS} \rangle_{\text{bin}}^{\text{anion}}$ values) can be safely set equal to the atomic valences expected (*i.e.* to the $\text{cation}V_i$ and $\text{anion}V_i$ values, respectively). Indeed, if the structure is *binary*,³ all the valence electrons (Lewis electron pairs) in this structure are shared exclusively between the *A* and *X* ions and all the *A*–*X* bonds in this structure are not influenced by the additional (‘third-party’) ions. If the binary structure has *stoichiometric* composition, this indicates that *all* the valence electrons of the cations and anions of the structure are involved in the

chemical bonding and form the Lewis electron pairs. If the binary stoichiometric structure is *stable*, this indicates the absence of significant internal strains in the structure. If, at last, the above stable stoichiometric binary structure is *ordered* and *well determined*, this ensures that all the bond lengths in the structure are estimated adequately. The total number of Lewis electron pairs ($^{\text{Lep}}N$) present in the unit cell of the above structure can be easily calculated as the number of cations (anions) present in this unit cell ($^{\text{cation}}N$ or $^{\text{anion}}N$) multiplied by the formal oxidation state (atomic valence) of these cations (anions), *i.e.* $^{\text{Lep}}N = ^{\text{cation}}N \times \text{cation}V_i = ^{\text{anion}}N \times \text{anion}V_i$. Hence, in spite of the possible non-uniform distribution of the Lewis electron pairs in the unit cell of the above structure, their total number ($^{\text{Lep}}N$) is known exactly; this number is equal (by definition) to the total sum of the particular bond valences s_{ij} present in the unit cell ($^{\text{total}}\text{BVS}$). The averaged sums of bond valences calculated for cations and anions present in the unit cell of the above binary structure, $\langle \text{BVS} \rangle_{\text{bin}}^{\text{cation}}$ and $\langle \text{BVS} \rangle_{\text{bin}}^{\text{anion}}$, are equal to $^{\text{total}}\text{BVS}/^{\text{cation}}N = \text{cation}V_i$ and $^{\text{total}}\text{BVS}/^{\text{anion}}N = \text{anion}V_i$, respectively.

In testing the quality of the BV parameters, the $\langle \text{BVS} \rangle_{\text{bin}}$ values must be calculated taking into account the site multiplicity factors for all cations (anions) if crystallographically distinct cations (anions) are present in the unit cell of the aforementioned binary structure; otherwise, the total number of the Lewis electron pairs present in the unit cell of the structure could be estimated improperly.

Taking into account the requirement of the charge balance for nominally *ionic* compounds, the atomic valences of cations ($\text{cation}V_i$) and anions ($\text{anion}V_i$) of the stoichiometric binary structure A_mX_n are strictly related as $m \times \text{cation}V_i = n \times \text{anion}V_i$. Hence, in calculations of the BV parameters based on the binary ‘reference structures’ (see §4), it is sufficient to adjust the r_0 and b values giving $\langle \text{BVS} \rangle_{\text{bin}} = V_i$ only for cations (or only for anions) of the structure. This conclusion can be useful if the ‘reference structure’ selected contains only *one* symmetrically independent cation (or anion).

In spite of the ‘apparent’ correctness of criterion (iii), this criterion must be used with serious caution and sometimes must be relaxed. Thus, for example, the high-symmetry binary structures with *regular* coordination shells (especially, if these structures were determined in a small number of experiments) could be unsuitable for calculating the BV parameters because the experimental errors of determining the particular *A*–*X* bond lengths for such coordination environments are always *multiplied* by a factor of the CN. However, for *irregular* coordination shells, the experimental errors of determining the particular *A*–*X* bond lengths can effectively compensate for each other; and stable ordered binary structures containing such coordination environments can be used successfully as the ‘reference structures’.

Employment of criterion (iv) in testing the quality of the BV parameters is possible only in special cases. If a particular electropositive element *A* can form cations with *different* oxidation states [*e.g.* A^{m+} and $A^{(m+n)+}$], then the A^{m+} –*X* single-bond length is typically *longer* than the $A^{(m+n)+}$ –*X* single-bond length because of the increased interelectronic

² In most cases, the $\langle \text{BVS} \rangle_{\text{set}}$ values can be calculated only for cations (*i.e.* $\langle \text{BVS} \rangle_{\text{set}}^{\text{cation}}$) because coordination environments of anions in the structures of the complex compounds are rarely formed by cations of the same sort.

³ One should not confuse the *binary structures* characterized by cations of one sort and by anions of one sort and the *binary compounds* that may contain ions of the same chemical elements in different oxidation states, as in Fe_3O_4 or $\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_4$.

Table 1

Reliability of the BV parameters obtained for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair in the work of Mills *et al.* (2009) ($r_0 = 1.925 \text{ \AA}$; $b = 0.455 \text{ \AA}$) and here ($r_0 = 1.927 \text{ \AA}$; $b = 0.446 \text{ \AA}$).

Compound	Reference	CN‡	$\text{Sb}^{\text{BVS}}_{\text{str}}$ (v.u.)†	
			Mills <i>et al.</i> (2009)	This work
Binary				
$\alpha\text{-Sb}_2\text{O}_3$	Svensson (1974)	5	3.002 [+0%]	2.993 [−0%]
$\beta\text{-Sb}_2\text{O}_3$	Svensson (1975)	6	3.014 [+0%]	3.007 [+0%]
Average			3.01 (1)	3.00 (1)
Complex				
$\text{Sb}_2(\text{HPO}_3)_3$	Loub & Paulus (1981)	5,6	3.024 [+1%]	3.010 [+0%]
$\text{K}(\text{SbMo}_2\text{O}_8)$	Lii <i>et al.</i> (1990)	7	3.098 [+3%]	3.077 [+3%]
$\text{LiSb}(\text{Mo}_2\text{O}_8)$	Lii & Chueh (1991)	8	3.067 [+2%]	3.045 [+2%]
Sb_2VO_5	Merlino <i>et al.</i> (1989)	6	2.975 [−1%]	2.966 [−1%]
$\text{Sb}_2(\text{MoO}_6)$	Castro <i>et al.</i> (1997)	7	3.049 [+2%]	3.032 [+1%]
ZnSb_2O_4	Gutiérrez Puebla <i>et al.</i> (1982)	6	2.898 [−3%]	2.895 [−4%]
$\text{Cs}_3(\text{SbO}_3)$	Emmerling & Röhr (2001)	3	2.980 [−1%]	2.993 [−0%]
$\text{K}_3(\text{SbO}_3)$	Emmerling & Röhr (2001)	3	3.013 [+0%]	3.027 [+1%]
$\text{K}_2(\text{Al}_2\text{Sb}_2\text{O}_7)$	Hirschle & Röhr (2000a)	3	2.928 [−2%]	2.940 [−2%]
$\text{K}(\text{SbO}_2)$	Hirschle & Röhr (2000b)	4	2.982 [−1%]	2.980 [−1%]
NaSbMoO_5	Wang <i>et al.</i> (2004)	6	3.091 [+3%]	3.081 [+3%]
$\text{Sb}_5\text{O}_6(\text{PO}_4)$	Adair & Cheetham (2000)	4–8	2.965 [−1%]	2.953 [−2%]
Average			3.01(6)	3.00(6)

† The relative $\text{Sb}^{\text{BVS}}_{\text{str}}$ errors calculated as $\{[\text{Sb}^{\text{BVS}}_{\text{str}} - V_i]/V_i\} \times 100\%$ are given in parentheses.

‡ The shortest distance from the central cation to another cation in a given crystal structure was assumed to be the physical limit of the coordination shell under consideration.

repulsion in the lower-charge cation (*e.g.* Batsanov, 1986). As the r_0 values correspond to the lengths of the nominally single bonds (Brown & Shannon, 1973; Brown & Altermatt, 1985), criterion (iv) is expected to be reasonable.

However, as with any other criterion mentioned above, except (i), criterion (iv) should be used cautiously. If the real ‘ s_{ij} versus r_{ij} ’ curve observed for a given ion pair exists only within a rather short s_{ij} range far from $s_{ij} \simeq 1$ v.u., then the r_0 value loses its original physical meaning and plays the role of a purely artificial adjustable parameter. In this case, a reasonably close approximation of the real ‘ s_{ij} versus r_{ij} ’ curve can be achieved using *e.g.* the *monoparametric* ‘conventional’ function $s_{ij} = \exp[(r_0 - r_{ij})/0.37]$ with only *one* adjustable parameter r_0 , which has an artificial value if the actual b value defined by the bond *softness* (Urusov, 1995) is far from 0.37 Å (Sidey, 2009b). Since the ‘real’ r_0 value in the above case is never observed (as for the $\text{Fe}^{6+}/\text{O}^{2-}$ ion pair exclusively showing the $[\text{FeO}_4]$ polyhedra with $s_{ij} \simeq 1.5$ v.u.), the artificial r_0 value is not a serious problem for most of the typical BVM applications. However, criterion (iv) has no validity for such an artificial r_0 value, far removed from the experimental bond lengths. Conversely, if the real ‘ s_{ij} versus r_{ij} ’ curve observed for a given ion pair exists within a *wide* s_{ij} range, including the sub-range corresponding to the coordination shells with $\text{CN} = V_i$ (*i.e.* with $s_{ij} \simeq 1$ v.u.), fulfillment of criterion (i) also means fulfillment of criterion (iv).

The ‘ s_{ij} versus r_{ij} ’ curves observed for the $\text{Sb}^{3+}/\text{O}^{2-}$ and $\text{Sb}^{5+}/\text{O}^{2-}$ ion pairs include the sub-ranges corresponding to the coordination shells with $\text{CN} = V_i$, $[\text{Sb}^{3+}\text{O}_3]$ and $[\text{OSb}_2^{5+}]$ (Sidey *et al.*, 2008; Mills *et al.*, 2009); therefore, criterion (iv) in this study is expected to be fulfilled reasonably well.

2.2. Selecting the structures for calculations

In accordance with criterion (iii), the α and β polymorphs of Sb_2O_3 have been selected as the ‘reference structures’. Both these polymorphs are stable at ambient conditions, and are known in nature as the *minerals* valentinite (α) and senarmonite (β); moreover, their crystal structures have been precisely and accurately determined from single-crystal X-ray diffraction data (Svensson, 1974, 1975). The coordination shells in these structures are not regular, so the experimental errors of determining the particular $\text{Sb}^{3+}-\text{O}$ bond lengths are expected to compensate for each other.

Although no single solution (r_0 ; b) fits the above ‘reference structures’ exactly (see §3), an array of reasonable approximate solutions (r_0 ; b) has been found to exist for b values from ~ 0.40 to ~ 0.60 Å. This array was additionally tested using a set of reliably determined structures, in accordance with criterion (ii). A set of 12 precisely and accurately determined crystal structures containing the $[\text{Sb}^{3+}\text{O}_n]$ coordination shells (see Table 1) was selected from the Inorganic Crystal Structure Database (Belsky *et al.*, 2002) by using the following stringent criteria of selection/rejection:

- (i) since the above ‘reference structures’ were determined with quite high precision and accuracy ($R \leq 0.032$), only the structures investigated at ambient conditions and determined with $R \leq 0.032$ and with reasonably high precision from single-crystal diffraction data were considered for the calculations (methodologically, poorly determined structures cannot be used for careful testing the BV parameters obtained from the precisely and accurately determined structures);
- (ii) since the interatomic distances in the structures with disorder and/or partial occupancies can significantly vary from one particular unit cell to another, such structures were rejected from consideration;
- (iii) in order to exclude the structures with potential but *undetectable* disorder, all the structures with the Sb^{5+} and/or F^- ions were also rejected;
- (iv) at last, in order to exclude the structures with potentially serious steric constraints, the structures with large halide and chalcogenide anions and/or with H_2O molecules were rejected.

2.3. Treatment of the structural data retrieved

After selection of the structures suitable for determining and/or testing the BV parameters for a given ion pair, a researcher must answer the following essential questions: What is the limit of a given coordination environment? What is a single BVS observation to fit the BV parameters against?

The limit of a given coordination environment $[\text{AX}_n]$ is usually taken as the sum of the van der Waals radii of the elements A and X (*e.g.* Krivovichev & Brown, 2001; Locock &

Burns, 2004; Mills *et al.*, 2009). However, as the van der Waals radii (and *any* other set of empirical radii of atoms and ions) have just *approximate* values and cannot be used rigorously, it is methodologically more correct to furnish the limit of a given coordination environment by using a scheme not based on the atomic radii concept. In the present work, the shortest distance from the central cation to another cation in a given crystal structure was assumed to be the physical limit of the coordination shell under consideration. The above plain (and probably the simplest) scheme of determining the limits of coordination shells was successfully used by the author in his previous BVM related works (Sidey, 2006, 2008, 2009a; Sidey *et al.*, 2008); and, in most cases, the limits found in this way were in good agreement with those determined using the van der Waals radii sums.

In works dedicated to calculating BV parameters, the BVS value calculated for *every* selected well determined coordination shell formed by the ion pair of interest is usually considered as an independent observation. If a set of structures selected for determining the BV parameters is large, this consideration can be used with reasonable success. If, however, the set of structures is rather small, as in the present work, this consideration should be revised. Indeed, every crystal structure reported has been determined with unavoidable systematic error(s), and every structure suffers, to some extent, from steric and electronic constraints. Hence, the BV parameters determined from a small number of structures in accordance with the above consideration can be seriously biased towards the errors and constraints present in the structure(s) containing the *largest* number(s) of symmetrically independent coordination shells.

For example, the crystal structure of $\text{Sb}_2(\text{MoO}_6)$ (Castro *et al.*, 1997) considered in this work contains 16 crystallographically distinct coordination environments $[\text{Sb}^{3+}\text{O}_n]$, while most of the remaining structures listed in Table 1 contain only *one* coordination shell of this type. It is clear that the r_0 and b parameters determined from the set of the 12 selected

structures (Table 1) in accordance with the above consideration would be artificially optimized mainly for the structure of $\text{Sb}_2(\text{MoO}_6)$, which is not desirable.

In order to avoid the aforementioned artificial optimization of the BV parameters, the statistical weights of all the structures selected for calculating the BV parameters should be properly equalized. Equalization of these weights can be achieved (and has been attained in the present work) by considering the *average* BVS value calculated from all the coordination shells formed by a given ion pair in the unit cell of a given crystal *structure*, ${}^{\text{cation}}\langle\text{BVS}\rangle_{\text{str}}$ or ${}^{\text{anion}}\langle\text{BVS}\rangle_{\text{str}}$, as a single BVS observation. Thus, the ${}^{\text{Sb}}\langle\text{BVS}\rangle_{\text{set}}$ value has been calculated in the present work not from the BVS values of individual coordination shells $[\text{Sb}^{3+}\text{O}_n]$, but from the ${}^{\text{Sb}}\langle\text{BVS}\rangle_{\text{str}}$ values (see §3).

3. Calculations and results

In the present work, all calculations have been performed by means of simple *ad hoc* programs written in *BASIC*; and all the numeric parameters have been taken with double precision.

As a first step, the ' r_0 versus b ' dependencies have been explored for the α and β polymorphs of Sb_2O_3 . The exact r_0 values have been calculated using (4) for all the b values from 0.20 to 0.80 Å (with the b step of 0.01 Å). A graphical presentation of the ' r_0 versus b ' dependencies found is given in Fig. 1.

One can see that no exact common solution ($r_0; b$) exists for the α and β polymorphs of Sb_2O_3 ; in other words, the two ' r_0 versus b ' curves in Fig. 1 do not intersect each other. However, within the limits of the b value from ~ 0.40 to ~ 0.60 Å, the r_0 values calculated for the α and β polymorphs of Sb_2O_3 are reasonably close to each other: the r_0 differences observed do not exceed 0.005 Å. Hence, virtually *any* solution ($r_0; b$) obtained for the α or β polymorph of Sb_2O_3 at the b value from ~ 0.40 to ~ 0.60 Å satisfies criterion (iii) fairly well; this fact clearly indicates that some additional criteria of quality (see above) must be employed in order to calculate the high-performance BV parameters for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair.

Since criterion (iv) is qualitative rather than quantitative, application of this criterion cannot give the exact or optimum ($r_0; b$) solution *a priori*; but in the present work this criterion has substantially reduced the upper limit of the b value to ~ 0.52 Å [the r_0 values calculated for the α and β polymorphs of Sb_2O_3 at $b \geq 0.52$ Å are significantly *smaller* than ~ 1.91 Å, the value of the r_0 parameter for the $\text{Sb}^{5+}/\text{O}^{2-}$ ion pair (Sidey *et al.*, 2008; Mills *et al.*, 2009)].

Application of criterion (ii) is possible only after *preliminary* calculation of the particular values of BV parameters r_0 and b (otherwise, there is nothing to test by using this criterion). Since the exact common solution ($r_0; b$) does not exist for the α and β polymorphs of Sb_2O_3 (see above), the author decided to obtain and then to test a set of solutions ($r_0; b$) giving ${}^{\text{cation}}\langle\text{BVS}\rangle_{\text{bin}} = {}^{\text{cation}}V_i$ for the Sb^{3+} ions in both these polymorphs *on average* [i.e. the solutions ($r_0; b$) giving

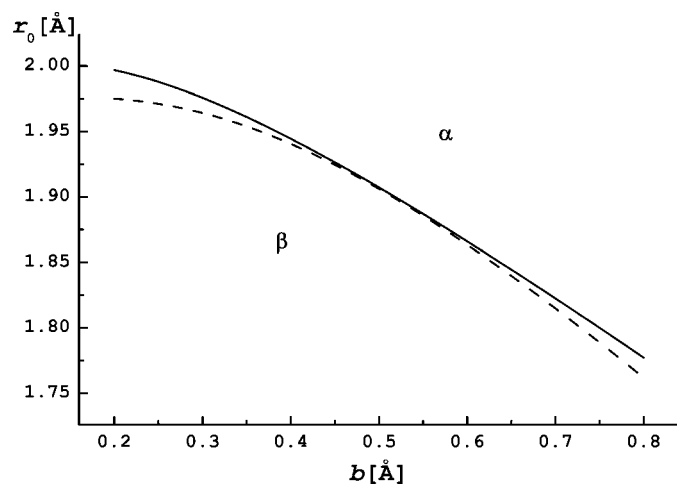


Figure 1
The relations between the ' r_0 versus b ' dependencies for the α (solid line) and β (dashed line) polymorphs of Sb_2O_3 .

$\langle^{Sb}\langle BVS \rangle_{bin}\rangle = 3$ v.u.]. Thus, the *optimum* solution ($r_0; b$) for the Sb^{3+}/O^{2-} ion pair was expected to give *simultaneously* $\langle^{Sb}\langle BVS \rangle_{bin}\rangle = 3$ v.u. and $\langle^{Sb}\langle BVS \rangle_{set} = \langle^{Sb}\langle BVS \rangle_{str}\rangle = 3$ v.u.

For all the b values from 0.40 to 0.52 Å (with the b step of 0.001 Å), the mathematically correct r_0 values giving $\langle^{Sb}\langle BVS \rangle_{bin}\rangle = 3$ v.u. have been calculated using (5) [the modified version of (4)]

$$r_0 = b \ln\{2V_i / [\sum_j \exp(-r_{ij}^\alpha/b) + \sum_j \exp(-r_{ij}^\beta/b)]\}, \quad (5)$$

where r_{ij}^α and r_{ij}^β are the $Sb^{3+}-O$ bond distances in the α and β polymorphs of Sb_2O_3 , respectively.

Then every obtained solution ($r_0; b$) giving $\langle^{Sb}\langle BVS \rangle_{bin}\rangle = 3$ v.u. has been used to calculate the corresponding $\langle^{Sb}\langle BVS \rangle_{str}\rangle$ (or $\langle^{Sb}\langle BVS \rangle_{set}\rangle$) value; it has been established that the *optimum* BV parameters, $r_0 = 1.927$ Å and $b = 0.446$ Å, give $\langle^{Sb}\langle BVS \rangle_{bin}\rangle = 3.000$ v.u. and $\langle^{Sb}\langle BVS \rangle_{set} = \langle^{Sb}\langle BVS \rangle_{str}\rangle = 3.000$ v.u. (with the round-off error of ~ 0.0001 v.u.).

The performance of the BV parameters $r_0 = 1.927$ Å and $b = 0.446$ Å obtained in this work is illustrated in Table 1. One can see that the BV parameters obtained in this work analytically and those obtained statistically in the work of Mills *et al.* (2009) demonstrate nearly equal performances and satisfy all the criteria of quality listed above (see §2.1), including the most important criterion (i). Taking into account the usual experimental uncertainty of crystallographic investigations, the differences between the BVS values calculated from the BV parameters determined here and from those reported by Mills *et al.* (2009) are definitely insignificant.

Nearly the same performance of the above two sets ($r_0; b$) can be easily explained by nearly perfect coincidence of the ' s_{ij} versus r_{ij} ' curves (Fig. 2) defined for the Sb^{3+}/O^{2-} ion pair as $s_{ij} = \exp[(1.927 - r_{ij})/0.446]$ (this work) and as $s_{ij} = \exp[(1.925 - r_{ij})/0.455]$ (Mills *et al.*, 2009) within the full observed r_{ij} range.

4. Discussion

Analysis of the BVM literature has revealed the fact that there are only two methodologically different approaches in determining the high-performance BV parameters r_0 and b (or n) for individual ion pairs: statistical and analytical.

In the *statistical* approach, the BV parameters, r_0 and b (or n), are determined by using non-linear least-squares fitting against the expected BVS (e.g. Brown & Wu, 1976; Locock & Burns, 2004) or s_{ij} (e.g. Brown *et al.*, 1984) values, or by using *linear* least-squares fitting (of r_0 and b) against the expected $\ln(s_{ij})$ values (e.g. Brown, 2009a). In some cases (e.g. when the ion pair of interest has only *one* statistically dominating 'usual' CN), close approximation of the real ' s_{ij} versus r_{ij} ' curve is possible only after introducing much higher statistical weights for coordination shells with 'unusual' CNs (Brown & Shannon, 1973; Brown & Wu, 1976). However, in general, the BV parameters obtained by using the statistical approach are of high quality.

The *analytical* approach of determining the high-performance BV parameters is based on the fact that *two* independent variables [*i.e.* r_0 and b (or n)] can be mathematically

derived from (at least) *two* independent equations concerning these variables. In other words, in order to obtain the BV parameters for a given ion pair analytically, two independent 'reference systems' of this ion pair must be selected, and the solution ($r_0; b$) *common* for both these 'reference systems' must be found.

The term 'reference system' used here denotes:

(i) a real (observed) or imaginary (statistically expected or scientifically predicted) bond length r_{ij} ('reference bond length') for which the s_{ij} value is expected to be known *exactly*;

(ii) a coordination shell ('reference coordination shell') for which the equation $BVS = V_i$ is expected to be obeyed *exactly*;

(iii) a structure ('reference structure') for which the equations $\langle^{cation}\langle BVS \rangle_{str} = \langle^{cation}V_i$ and $\langle^{anion}\langle BVS \rangle_{str} = \langle^{anion}V_i$ are expected to be obeyed *exactly*;

(iv) a set of structures ('reference structure set') for which the equation $\langle^{cation}\langle BVS \rangle_{set} = \langle^{cation}V_i$ (or $\langle^{anion}\langle BVS \rangle_{set} = \langle^{anion}V_i$) is expected to be obeyed *exactly*.

The solution ($r_0; b$) can be found in different ways: mathematically (*i.e.* by solving a system of two independent equations concerning r_0 and b), graphically (*i.e.* by exploring the ' r_0 versus b ' dependencies for the 'reference systems'), by testing the grid-search results *etc.* However, for more convenience and to save time, the 'reference systems' used in calculations of the BV parameters should be as simple as possible. So, if the 'reference structure' contains only *one* symmetrically independent cation (or anion), the coordination shell of this cation (anion) can be considered and treated as the 'reference coordination shell', and there is no reason to calculate the $\langle^{cation}\langle BVS \rangle_{str}$ and/or $\langle^{anion}\langle BVS \rangle_{str}$ values for this structure (see §2.1). Furthermore, if the 'reference coordination shell' [AX_n] is *regular*, the $A-X$ bond length observed in this shell can be considered and treated as the 'reference bond length', so calculation of the BVS value for this shell is redundant (however, as mentioned in §2.1, regular coordination shells should be used cautiously).

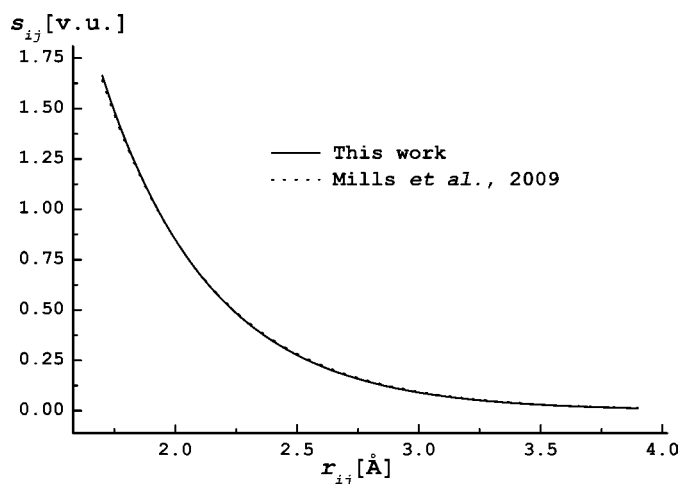


Figure 2
The relations between the ' s_{ij} versus r_{ij} ' curves defined for the Sb^{3+}/O^{2-} ion pair as $s_{ij} = \exp[(1.925 - r_{ij})/0.455]$ (dotted line; Mills *et al.*, 2009) and as $s_{ij} = \exp[(1.927 - r_{ij})/0.446]$ (solid line; this work).

In BVM works, different combinations of the ‘reference systems’ have been successfully used to determine the BV parameters (see below), although the term ‘reference system’ has never been used in those works and its methodological essence has never been discussed at all (to the author’s knowledge).

Krivovichev & Brown (2001) have used the two large ‘reference structure sets’ with the $[\text{PbO}_n]$ and $[\text{OPb}_4]$ coordination shells for determining high-quality BV parameters for the $\text{Pb}^{2+}/\text{O}^{2-}$ ion pair. When calculating the r_0 and b parameters for the $\text{Bi}^{3+}/\text{Br}^-$ ion pair, Sidey (2006) used a combination of the Bi–Br ‘reference bond length’ ($r_{ij} = r_0$) observed in the molecule BiBr_3 and the $[\text{BiBr}_8]$ ‘reference coordination shell’ observed in the crystal structure of $\alpha\text{-BiBr}_3$. To determine the BV parameters for the $\text{Pb}^{2+}/\text{F}^- (\text{Cl}^-, \text{Br}^-, \text{I}^-)$ ion pairs, Hu (2007) has used combinations of the Pb– X ‘reference bond length’ ($r_{ij} = r_0$) observed in the molecule PbX_2 ($X = \text{F}, \text{Cl}, \text{Br}$ and I) and the ‘reference structure set’ with the $[\text{PbX}_n]$ coordination shells. In order to derive the BV parameters for the $\text{Sb}^{5+}/\text{O}^{2-}$ ion pair, Sidey *et al.* (2008) used a combination of the statistically expected ‘reference bond length’ ($r_{ij} = r_0$) observed in the $[\text{OSb}_2^{5+}]$ coordination shells of the crystal structure of Sb_2O_5 and the $[\text{Sb}^{5+}\text{O}_6]$ ‘reference coordination shell’ present in the same structure of Sb_2O_5 . To derive the BV parameters for the $\text{Al}^{3+}/\text{O}^{2-}$ ion pair, Sidey (2008) used the two statistically expected ‘reference bond lengths’ corresponding to the $[\text{AlO}_4]$ and $[\text{AlO}_6]$ coordination shells. In order to derive the BV parameters for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair, in the present work the author has used the two ‘reference structure sets’, one small set of the binary structures of the α and β polymorphs of Sb_2O_3 and one larger set of precisely determined complex structures containing the $[\text{Sb}^{3+}\text{O}_n]$ coordination shells.

In fact, the molecular structures of BiBr_3 , PbF_2 , PbCl_2 , PbBr_2 and PbI_2 , and the crystal structures of $\alpha\text{-BiBr}_3$ and Sb_2O_5 mentioned above can be regarded as the ‘reference structures’; but here the author has used the simplest possible presentations of those structures sufficient for determining the BV parameters (*i.e.* the ‘reference bond lengths’ and the ‘reference coordination shells’).

In spite of the use of *different* combinations of the ‘reference systems’, all the BV parameters determined in the aforementioned BVM work (and here) demonstrate reasonably high performances. This fact clearly indicates that the analytical approach can be successfully employed for determining accurate BV parameters. However, to the author’s knowledge, the r_0 and b values have never been obtained both statistically and analytically for the same ion pair demonstrating a wide s_{ij} range (for such ion pairs, close approximations of the real ‘ s_{ij} versus r_{ij} ’ curves are usually difficult). Therefore, there was no opportunity to test and to compare the results obtained for the same ion pair in the statistical and analytical approaches. In this respect, the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair is probably the first ‘difficult’ ion pair (*i.e.* that having a wide s_{ij} range) for which the high-quality BV parameters have been obtained both statistically (Mills *et al.*, 2009) and analytically (this work). Virtually the same high performance demon-

strated by the BV parameters reported for this ion pair in the article of Mills *et al.* (2009) and by the BV parameters obtained here (Table 1, Fig. 2) indicates that the procedure developed by the author and used in the present work is methodologically adequate.

However, it must be clearly noted that the remarkable similarity of the BV parameters obtained for the $\text{Sb}^{3+}/\text{O}^{2-}$ ion pair statistically (Mills *et al.*, 2009) and analytically (this work) cannot be regarded as evidence for the universality of the calculation scheme proposed here: the criteria of quality of the BV parameters and the rules for selection of the ‘reference systems’ are still to be discussed within the crystallographic and mineralogical community. Nevertheless, if a researcher has found the BV parameters in the literature to be of poor quality, then the calculation scheme proposed in this work should always be considered for determining the high-quality BV parameters.

Finally, it must be stated that, in spite of the power of the statistical approach, the analytical approach of determining the BV parameters should never be ignored in the BVM: while the former approach is able to give the ‘best-fit’ results, the latter approach is a convenient tool for calculation of the BV parameters conforming to a particular chemical theory used for selection of the ‘reference systems’. Comparison of the BV parameters determined in the above approaches for the same ion pairs can result in a number of interesting and scientifically important conclusions. Hence, further development of the analytical approach of determining the BV parameters is expected to become an important BVM branch in the near future.

The author thanks his colleagues and friends, Dr Ruslan Mariychuk and Dr Paul Popovich, for their assistance in the literature search.

References

- Adair, B. A. & Cheetham, A. K. (2000). *J. Solid State Chem.* **155**, 451–454.
- Batsanov, S. S. (1986). *Experimental’nye Osnovy Strukturnoi Khimii* (Experimental Fundamentals of Structural Chemistry). Moscow: Izdatel’stvo Standartov (in Russian).
- Belsky, A., Hellenbrandt, M., Karen, V. L. & Luksch, P. (2002). *Acta Cryst.* **B58**, 364–369.
- Brese, N. E. & O’Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*. IUCr Monograph on Crystallography 12. Oxford University Press.
- Brown, I. D. (2009a). *Acta Cryst.* **B65**, 684–693.
- Brown, I. D. (2009b). *Chem. Rev.* **109**, 6858–6919.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Brown, I. D., Gillespie, R. J., Morgan, K. R., Tun, Z. & Ummat, P. K. (1984). *Inorg. Chem.* **23**, 4506–4508.
- Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* **A29**, 266–282.
- Brown, I. D. & Wu, K. K. (1976). *Acta Cryst.* **B32**, 1957–1959.
- Castro, A., Enjalbert, R. & Galy, J. (1997). *Acta Cryst.* **C53**, 1526–1529.
- Emmerling, F. & Röhr, C. (2001). *Acta Cryst.* **C57**, 1127–1128.
- Gutiérrez Puebla, E., Gutiérrez Rios, E., Monge, A. & Rasines, I. (1982). *Acta Cryst.* **B38**, 2020–2022.
- Hirschle, C. & Röhr, C. (2000a). *Acta Cryst.* **C56**, 5–6.

- Hirschle, C. & Röhr, C. (2000b). *Z. Anorg. Allg. Chem.* **626**, 1305–1312.
- Hu, S.-Z. (2007). *Acta Phys. Chim. Sin.* **23**, 786–789 (in Chinese).
- Jansen, M. (1978). *Angew. Chem.* **90**, 141–142.
- Jansen, M. (1979). *Acta Cryst.* **B35**, 539–542.
- Krivovichev, S. V. & Brown, I. D. (2001). *Z. Kristallogr.* **216**, 245–247.
- Lii, K. H. & Chueh, B. R. (1991). *J. Solid State Chem.* **93**, 503–509.
- Lii, K. H., Chueh, B. R. & Wang, S. L. (1990). *J. Solid State Chem.* **86**, 188–194.
- Locock, A. J. & Burns, P. C. (2004). *Z. Kristallogr.* **219**, 259–266.
- Loub, J. & Paulus, H. (1981). *Acta Cryst.* **B37**, 1106–1107.
- Merlino, S., Orlandi, P., Perchiazzi, N., Basso, R. & Palenzona, A. (1989). *Can. Mineral.* **27**, 625–632.
- Mills, S. J., Christy, A. G., Chen, E. C.-C. & Raudsepp, M. (2009). *Z. Kristallogr.* **224**, 423–431.
- Palenik, R. C., Abboud, K. A. & Palenik, G. J. (2005). *Inorg. Chim. Acta*, **358**, 1034–1040.
- Sidey, V. (2006). *Acta Cryst.* **B62**, 949–951.
- Sidey, V. (2008). *Acta Cryst.* **B64**, 515–518.
- Sidey, V. (2009a). *Acta Cryst.* **B65**, 99–101.
- Sidey, V. (2009b). *Acta Cryst.* **B65**, 401–402.
- Sidey, V. I., Milyan, P. M. & Semrad, O. O. (2010). *J. Alloys Compd.* **490**, 598–601.
- Sidey, V. I., Milyan, P. M., Semrad, O. O. & Solomon, A. M. (2008). *J. Alloys Compd.* **457**, 480–484.
- Svensson, C. (1974). *Acta Cryst.* **B30**, 458–461.
- Svensson, C. (1975). *Acta Cryst.* **B31**, 2016–2018.
- Urusov, V. S. (1995). *Acta Cryst.* **B51**, 641–649.
- Wang, Y., Zhang, H., Huang, C., Sun, Q. & Yu, X. (2004). *Inorg. Chem. Commun.* **7**, 21–23.