

## addenda and errata

## On the correlations between the polyhedron eccentricity parameters and the bond-valence sums for the cations with one lone electron pair. Addendum

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: vasylysidey@yahoo.com

Systematic variations of the bond-valence sums calculated from the poorly determined bond-valence parameters [Sidey (2008), *Acta Cryst.* **B64**, 515–518] have been illustrated using a simple graphical scheme.

Recent discussion on the reliability of the conventional bond-valence (BV) parameters,  $r_0$  and  $b$ , determined using the ‘universal constant’  $b = 0.37 \text{ \AA}$  (Krivovichev & Brown, 2001; Locock & Burns, 2004; Sidey, 2008; Wang & Liebau, 2009) has stimulated writing of this addendum to the earlier communication of the author (Sidey, 2008). The main goal of this addendum is to explain, as simply as possible, the reason for the systematic variations of the bond-valence sums (BVSs) calculated from the poorly determined BV parameters (Sidey, 2008). All the terms, symbols and abbreviations used here correspond to those used in the aforementioned original communication of the author (Sidey, 2008).

The most commonly adopted empirical expression for the relationship between the bond valences  $s_{ij}$  and the bond lengths  $r_{ij}$

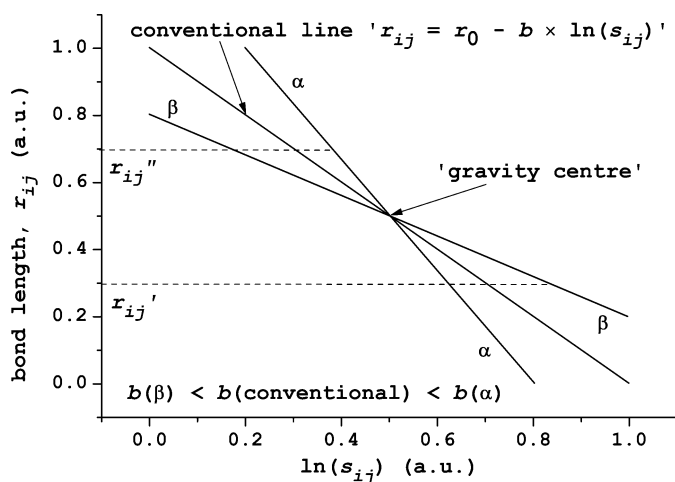


Figure 1

Typical relations between the straight lines  $r_{ij} = r_0 - b \times \ln(s_{ij})$  of different slopes (for simplicity, all the values are given in arbitrary units, a.u.).

(Brown & Altermatt, 1985; Brese & O’Keeffe, 1991) can be rewritten as  $r_{ij} = r_0 - b \times \ln(s_{ij})$ . Hence, every ‘ $s_{ij} - r_{ij}$ ’ curve can be uniquely represented as a straight line  $y = A + Bx$  by using the ‘ $\ln(s_{ij}) - r_{ij}$ ’ coordinate system (Fig. 1). The mathematical slope and the  $y$  intercept of the above straight lines are equal to  $-b$  and  $r_0$ , respectively. The traditional calculation scheme for determining the conventional BV parameters (Brown & Altermatt, 1985; Brese & O’Keeffe, 1991) is based on the rather rough assumption that the mathematical slopes of all ‘ $\ln(s_{ij}) - r_{ij}$ ’ straight lines are equal to  $-0.37 \text{ \AA}$ ; so that all observed ‘ $\ln(s_{ij}) - r_{ij}$ ’ correlations are approximated with the *constant-slope* (conventional) straight lines  $r_{ij} = r_0 - 0.37 \ln(s_{ij})$ . If the real value of the  $b$  constant is not  $0.37 \text{ \AA}$ , then the ‘optimized’ conventional straight line obtained for a given ion pair merely goes through the ‘gravity centre’ datapoint ‘ $\langle \ln(s_{ij}) \rangle - \langle r_{ij} \rangle$ ’ of the whole observed ‘ $\ln(s_{ij}) - r_{ij}$ ’ dataset. As every well-determined coordination shell in the traditional calculation scheme is considered to be an independent ‘observation’ (Brown & Altermatt, 1985; Brese & O’Keeffe, 1991), the coordinates of the above ‘gravity centre’ datapoint observed for a given ion pair are usually close to the ‘ $\ln(s_{ij}) - r_{ij}$ ’ data corresponding to the coordination shells with the most frequently occurring (‘typical’) coordination number(s).

Fig. 1 shows the relations between the straight lines  $r_{ij} = r_0 - b \times \ln(s_{ij})$  of different slopes. The  $\alpha$  and  $\beta$  straight lines represent the idealized hypothetical ‘ $\ln(s_{ij}) - r_{ij}$ ’ correlations with the same ‘gravity centre’ datapoint; the  $\alpha$  line has  $b > b(\text{conventional})$  and the  $\beta$  line has  $b < b(\text{conventional})$ . If the real ‘ $\ln(s_{ij}) - r_{ij}$ ’ correlation is represented by the  $\alpha$  straight line, then the conventional straight line gives overestimated and underestimated  $\ln(s_{ij})$  (and  $s_{ij}$ )<sup>2</sup> values for the shorter ( $r'_{ij}$ ) and longer ( $r''_{ij}$ ) bond lengths, respectively. If the real ‘ $\ln(s_{ij}) - r_{ij}$ ’ correlation is represented by the  $\beta$  straight line, then the conventional straight line gives, in contrast, underestimated and overestimated  $\ln(s_{ij})$  (and  $s_{ij}$ ) values for the shorter ( $r'_{ij}$ ) and longer ( $r''_{ij}$ ) bond lengths, respectively. The two different types of the systematic variations of the  $s_{ij}$  values observed for the  $\alpha$  and  $\beta$  straight lines can be respectively denoted as the  $\alpha$  and  $\beta$  variations.

Using the scheme presented here (Fig. 1), one can easily check the quality of the BV parameters reported for a given ion pair: if these BV parameters show systematic variations of the  $s_{ij}$  (and BVS) values within the short-bond and/or long-bond range(s), then the real ‘ $s_{ij} - r_{ij}$ ’ correlation is approximated poorly. Detecting the type of systematic variations observed for a given ion pair ( $\alpha$ ,  $\beta$ ) can help find the actual value of the  $b$  parameter. It is important to note that overestimating and underestimating the  $s_{ij}$  values calculated for short and long (or *vice versa*) bonds belonging to the same irregular coordination shells can compensate for each other, so that the BVS values obtained for these shells can be quite ‘plausible’; therefore, only *regular* (or nearly regular) shells should be used for checking the quality of the BV parameters.

The performance of the conventional BV parameters reported for a given ion pair is critically dependent: (a) on the real slope of the ‘ $\ln(s_{ij}) - r_{ij}$ ’ correlation and (b) on the range of the observed bond

<sup>1</sup>  $\langle \ln(s_{ij}) \rangle$  and  $\langle r_{ij} \rangle$  denote the mean values for  $\ln(s_{ij})$  and  $r_{ij}$ .

<sup>2</sup> If  $\ln(a) < \ln(b)$ , then  $a < b$ .

lengths  $r_{ij}$ . If the real mathematical slope is close to  $-0.37 \text{ \AA}$  and if the range of observed bond lengths is narrow, then the divergence between the real and conventional straight lines  $r_{ij} = r_0 - b \times \ln(s_{ij})$  is insignificant and, therefore, the conventional BV parameters reported for a given ion pair can be used with reasonable success. Otherwise, these BV parameters can be used successfully only within the  $r_{ij}$  range near to the above ‘gravity centre’ datapoint (Fig. 1),<sup>3</sup> and must be revised. Since the coordinates of the ‘gravity centre’ datapoint observed for a given ion pair,  $\langle \ln(s_{ij}) \rangle$  and  $\langle r_{ij} \rangle$ , are usually close to the ‘ $\ln(s_{ij}) - r_{ij}$ ’ data corresponding to the ‘typical’ coordination shells (see above), even poorly determined conventional BV parameters can give reasonable BVS values in most cases! However, high-quality BV parameters should give reasonable BVS values not only for ‘typical’ coordination shells, but also for less-common shells formed by a given ion pair in ordered, stoichiometric and stable structures determined accurately and investigated under ambient conditions. Unfortunately, this requirement was ignored for a long time and a few theories were developed based on the axiomatic use of

the ‘universal constant’  $b = 0.37 \text{ \AA}$  (e.g. O’Keeffe & Brese, 1991; Wang & Liebau, 2007). In order to be properly validated, *any* BVM related theory (including that of Wang & Liebau, 2007) ought to operate with the BV parameters of the highest possible quality. Most of the conventional BV parameters used by Wang & Liebau (2007) in their theory show the aforementioned systematic  $\alpha$  variations of the BVS values (Sidey, 2008) and, therefore, clearly must be revised.

### References

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<sup>3</sup> Within a small section near to the aforementioned ‘gravity centre’ datapoint, every observed ‘ $\ln(s_{ij}) - r_{ij}$ ’ correlation can be considered as ‘well approximated’.