

Bond-Valence Summation for Borates

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In constructing the table of bond-valence balance for β -HBO₂, Zachariasen [*Acta Cryst.* (1963), **16**, 385–389] makes use of two empirical correlations between bond valence and bond length: one for B–O bonds and one for hydrogen bonds, whose bond valence he apportions to O–H and H···O on the basis of the O–O distance. The root-mean-square deviation Δv_{rms} from the formal anionic charges being taken as the criterion, Zachariasen's curve compares as follows with three analytical functions proposed in the literature: 0.07 v.u. (Zachariasen, 1963); 0.10 [Pauling, *J. Amer. Chem. Soc.* (1947), **69**, 542–553]; 0.09 [Donnay & Allmann, *Amer. Min.* (1970), **55**, 1003–1015; D–A]; 0.10 [Brown & Shannon, *Acta Cryst.* (1973), **A28**, S107]. The D–A curves are then applied to three recently refined borate structures. The resulting Δv_{rms} values [0.08 v.u. for CaB₆O₈(OH)₄·3H₂O, gowerite; 0.04 for K₂B₅O₈OH·2H₂O; 0.07 for Na₂B₄O₆(OH)₂·3H₂O, kernite] show the adequacy of the procedure. Though lacking any obvious theoretical basis, such curves are useful (at their own level of depth) in interpreting structural details through the quantitative application of Pauling's charge-neutrality principle: distorted coordination polyhedra are seen as the expression of the drive toward minimization of Δv_{rms} .

Introduction

Zachariasen (1963) published two curves relating bond valence* to bond length for B–O and O–H···O bonds. No explanation was given of how the curves were obtained, but a reason for their presentation was stated: 'It is useful to interpret structural results for borates in terms of the principle of detailed neutralization of valence first set forth by Pauling (1929) . . . '.

Donnay & Allmann (D–A) (1970) offered a procedure for constructing an analogous curve for any cation–oxygen (or cation–fluorine) pair for a given coordination polyhedron in a known crystal structure. The anionic bond-valence sums so obtained (each one being the sum of the valences of bonds reaching an anion) have proved so reliable that they have been put to many uses (Donnay & Allmann, 1972) besides the original one of locating protons and hydrogen bonds in

structures determined by X-rays. The method, however, has not yet been applied to borates, and it is one of the purposes of this paper to show, for a representative sample of borate structures of mineralogical interest, how these curves work. We shall apply them to gowerite (Konnert, Clark & Christ, 1972), to K₂B₅O₈OH·2H₂O (Marezio, 1969) and to the very accurately known structure of kernite (Cooper, Larsen, Coppens & Giese, 1973).

Furthermore the D–A curves have not yet been compared with the other curves in the literature, and the paper starts with such a comparison. The structure of β -HBO₂ (Zachariasen, 1963) has been chosen as a test case. In addition to Zachariasen's own curves and those of D–A, already mentioned, the following curves are applied: a curve based on the modified Pauling (1947) logarithmic formula that relates bond valence to atomic radius and the curve recently proposed by Brown & Shannon (1972).

Comparison of published curves applied to β -HBO₂

The modified Pauling curve

Pauling (1947) proposed the formula

$$R(v) = R(1) - k \log v, \quad k = 0.300 \quad (1)$$

(rewritten here with v instead of n to designate the bond valence), to be used for metals and alloys. $R(v)$ and $R(1)$ designate *radii* that correspond to the values of the bond valence given between parentheses. By-

* Zachariasen (1963) spoke of the 'bond strength' or 'valence strength', which he symbolized v_{ij} and expressed in 'valence units, v.u.'. His symbol and unit suggested the term 'bond valence', which was proposed by Donnay & Allmann (1970), or 'Pauling-bond valence', previously used by Donnay (1969). Pauling (1949) has used 'bond order' or 'bond number' (Pauling, 1947), originally for metallic compounds. Pauling's 'bond strength' (1929, p. 1017), defined as z/v (formal charge z of the cation divided by its coordination number v) implies an ideal polyhedron, with equal cation–anion bond lengths, and corresponds to the 'ideal bond valence v_i ' of Donnay & Allmann (1970). In case of a distorted polyhedron, it corresponds to the 'mean bond valence \bar{v} '; numerically \bar{v} equals v_i .

ström & Wilhelmi (1951), followed by Evans (1960), modified equation (1) to make it applicable to V-O bonds.

For our purpose, which is to obtain the bond valence of a B-O bond in terms of its length, we add, to each member of (1), the oxygen radius R_O that will make $R_B + R_O$ equal to the B-O bond length L .

We write

$$R_B(v) + R_O = R_B(1) + R_O - k \log v \quad (2)$$

and

$$L(v) = L(1) - k' \log v. \quad (3)$$

R_O varies so little with change in bond valence (Shannon & Prewitt, 1969) that it could be assumed to be constant, in which case the value of k would be the same in (2) as in (1). We do not have to postulate this equality, however, as we will use experimental values of B-O bond lengths (obtained from the β -HBO₂ crystal structure), which will therefore automatically reflect whatever difference in oxygen radii exists. This is the reason why we introduce k' (instead of k) in equation (3).

In equation (3) we first set $v=v'$, then $v=v''$, thus getting two relations, which on subtracting yield a formula from which $L(1)$ has been eliminated,

$$L(v') - L(v'') = k' \log (v''/v'). \quad (4)$$

From the structure under consideration (here, that of β -HBO₂), we obtain the experimental mean bond lengths for $v' = \frac{3}{2}$ and $v'' = 1$, which correspond to tetrahedral boron ^{iv}B and triangular boron ⁱⁱⁱB respectively: $\bar{L}(\frac{3}{2}) = 1.472 \text{ \AA}$ and $\bar{L}(1) = 1.366 \text{ \AA}$. Substituting in (4) yields $k' = 0.85$ (or $1/k' = 1.176$). Equation (3) can now be written, with v as a function of L ,

$$\log v(L) = \frac{1}{k'} [\bar{L}(1) - L], \quad (5)$$

whence

$$v = 10^{1.176(1.366 - L)}. \quad (6)$$

Data for plotting this curve are given in Table 1 (column 1). The curve is slightly concave upwards.

Table 1. Bond lengths $L(\text{\AA})$ corresponding to selected bond valences v for various curves of $v(\text{O-H})$ vs. $L(\text{O-H})$

$v(\text{O-H})$	Pauling (1947) (modified)	Zachariasen (1963)	Donnay-Allmann (1970) (a) For ⁱⁱⁱ B	(b) For ^{iv} B	Brown-Shannon (1973)
1.4 v.u.	1.242 \AA	1.274 \AA	1.207 \AA	1.244 \AA	1.261 \AA
1.3	1.269	1.287	1.240	1.269	1.286
1.2	1.299	1.304	1.277	1.297	1.312
1.1	1.331	1.330	1.319	1.327	1.342
1.0	1.366*	1.365	1.366*	1.362	1.375
0.9	1.405	1.409	1.416	1.401	1.413
0.8	1.448	1.453	1.467	1.447	1.456
0.75	1.472*	(1.475)	1.492	1.472	1.480
0.7	1.498	1.497	1.517	1.498	1.507
0.6	1.554	1.541	1.568	1.551	1.567
0.5	1.621	1.585	1.618	1.605	1.642
0.4	1.704		1.668	1.658	1.739
0.3	1.810		1.719	1.711	1.872

* Experimental, from β -HBO₂.

Table 2. Anionic valence sums calculated by various methods for β -HBO₂*

Anion	Equation (6) Pauling	Empirical correlation Zachariasen	Equation (10) Brown-Shannon	Equations (7), (8) Donnay-Allmann†
O(1)	1.89 v.u.	1.91 v.u.	1.94 v.u.	1.87 v.u.
O(2)	1.92 (1.99)	2.05 (2.00)	2.04 (2.03)	1.99
O(3)	1.91	1.92	1.91	1.94
O(4)	1.98 (2.04)	2.10 (2.05)	2.09 (2.09)	2.03
O(5)H	0.99 (1.00)	1.00 (1.00)	1.03 (1.03)	1.00
H ₂ O(6)	0.42 (0.18)	0.05 (0.14)	0.18 (0.20)	0.17

Equation (6) $10^{1.176(1.366 - L)}$

$\ddagger \Delta v_{\text{rms}}(1)$	0.19	0.07	0.10	0.10	0.09
$\Delta v_{\text{rms}}(2)$		0.10	0.08	0.10	

* Crystal structure by Zachariasen (1963): $P2_1/a$, $Z=12$, all atoms in general position.

† For ⁱⁱⁱB(1): $L=1.367 \text{ \AA}$, $p=2.72$, $v_i=1 \text{ v.u.}$ For ⁱⁱⁱB(2): $L=1.366 \text{ \AA}$, $p=2.71$, $v_i=1 \text{ v.u.}$ For ^{iv}B(3): $L=1.472 \text{ \AA}$, $p=3.70$, $v_i=\frac{3}{2} \text{ v.u.}$

‡ $\Delta v_{\text{rms}}(1)$: hydrogen-bond corrections made by individual curves P, Z, B-S of Fig. 4.

$\Delta v_{\text{rms}}(2)$: hydrogen-bond corrections by L-S curve (Fig. 4).

Note that the value of k' could also be calculated with data taken from the Tables of effective ionic radii (Shannon & Prewitt, 1969). This course will be unavoidable whenever, in the structure at hand, all the cations of a given chemical kind have the same coordination number, yielding only one \bar{L} to use in equation (4). The other \bar{L} needed can be obtained by addition of effective ionic radii, in which the R_O will be the weighted average of the values given in the Tables for the different coordinations of oxygen.

To obtain the modified Pauling equation giving $v(\text{O-H})$ as a function of $L(\text{O-H})$, we make use of two mean bond lengths (obtained by neutron diffraction): $L(1) = 1.006 \text{ \AA}$ and $L(\frac{1}{2}) = 1.225 \text{ \AA}$. We calculate $k' = 0.728$; $1/k' = 1.374$, and write the equation

$$v(\text{O-H}) = 10^{1.374(1.006 - L)}. \quad (6')$$

But this relation, when applied to the O-H bonds in HBO_2 , gives quite unreasonable valences. It has therefore been used to derive a relation between the O-O distance in a hydrogen bond and the bond-valence transfer $v(\text{H} \cdots \text{O})$ from the donor to the acceptor oxygen atom. The derivation follows the procedure used by Brown & Shannon (1973). For a number of pairs of complementary v values, $v(\text{O-H}) = v$ and $v(\text{H} \cdots \text{O}) = 1 - v$, the corresponding bond lengths are calculated by means of equation (6'). For each pair the sum $L(v) + L(1 - v)$ gives the O-O distance, on the assumption of a linear hydrogen bond. The curve (Fig. 4) is then plotted point by point.

The Zachariasen curve for B-O bonds

Zachariasen (1963) published the coordinates of ten points (Table 1, col. 2), from which his empirical curve $v(\text{O-H})$ versus $L(\text{O-H})$ can be drawn (Fig. 1). We note that it passes through points $v = 1$ v.u., $L = 1.365 \text{ \AA}$ and $v = \frac{3}{4}$ v.u., $L = 1.475 \text{ \AA}$. As L increases beyond 1.365 , v is seen to decrease linearly from one to zero where the extrapolated straight line intersects the L axis, at $L = 1.805 \text{ \AA}$. As L decreases from 1.365 \AA , the curve becomes concave upwards.

The curve of $v(\text{H} \cdots \text{O})$ vs. O-O distance (Fig. 4) is also plotted point by point from the data given by Zachariasen (1963, Table 9).

The Donnay-Allmann curves for ${}^{\text{iii}}\text{B-O}$ and ${}^{\text{iv}}\text{B-O}$ bonds in the $\beta\text{-HBO}_2$ crystal structure

The $\beta\text{-HBO}_2$ crystal structure contains two tricoordinated boron atoms, ${}^{\text{iii}}\text{B}(1)$ and ${}^{\text{iii}}\text{B}(2)$, for which the curves are practically identical (see note to Table 2). The curve for tetracoordinated ${}^{\text{iv}}\text{B}(3)$ differs notably from the other two.

Each curve is linear for $\bar{L} \leq L \leq L_{\text{max}}$, where \bar{L} is the mean bond length of the coordinated polyhedron under consideration, for which v equals v_i , the ideal bond valence, and L_{max} is the cut-off value beyond which the bond valence is taken to be zero. L_{max} is obtained graphically as follows. Draw the curve of v vs. effective ionic radius, here a straight line through the two points ($IR = 0.02$, $v = 1$; $IR = 0.12$, $v = \frac{3}{4}$) given by Shannon & Prewitt (1969) for boron, extrapolate it until it intersects the axis of abscissae at $R_{\text{max}}(\text{B}) = 0.42$, then

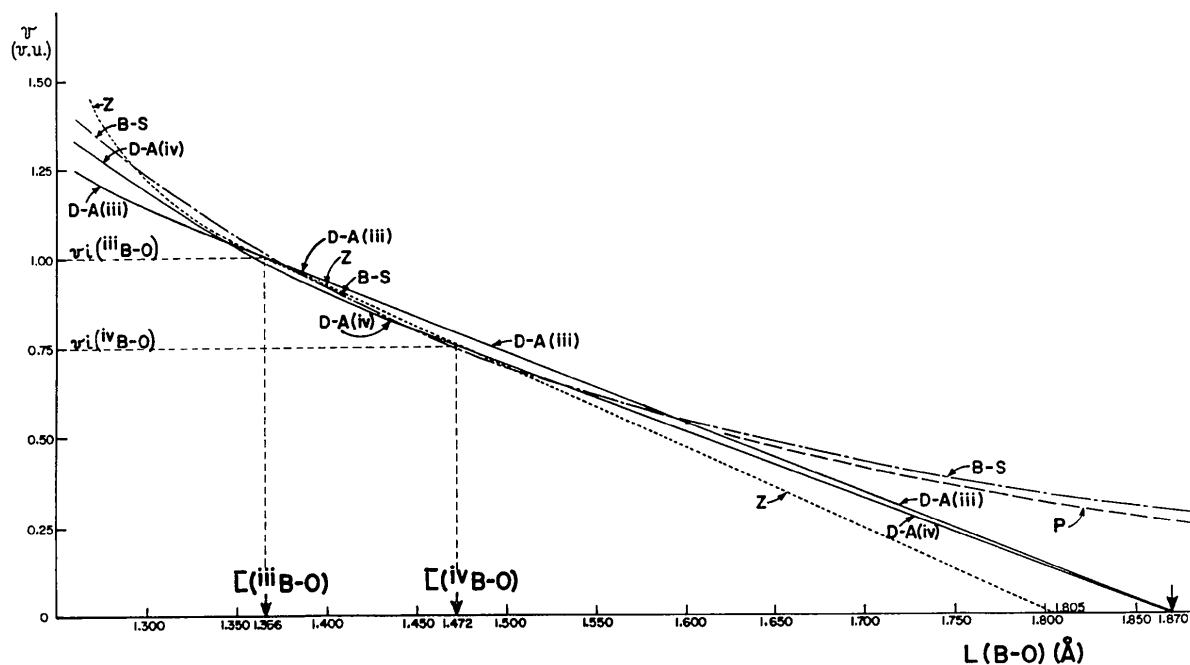


Fig. 1. Curves of bond valence (v.u.) vs. bond length (\AA) for B-O in $\beta\text{-HBO}_2$: P, Pauling (1947) modified; Z, Zachariasen (1963); D-A, Donnay-Allmann (1970); B-S, Brown & Shannon (1972). On this figure the B-S curve obeys the equation $v = (1.370/L)^{4.006}$ of 1972.

likewise find the maximum radius of oxygen $R_{\max}(\text{O}) = 1.45$, and add the two to get the maximum bond length $L_{\max}(\text{B-O}) = 1.87$. The equation of the linear segment is

$$\frac{v}{v_i} = \frac{L_{\max} - L}{L_{\max} - \bar{L}} \quad (7)$$

For $0 < L \leq \bar{L}$ the curve is concave upwards, obeying the equations

$$\frac{v}{v_i} = \left(\frac{\bar{L}}{L}\right)^p \quad (8)$$

with $p = \bar{L}/(L_{\max} - \bar{L})$, so that the linear segment is tangent to the curved segment at $L = \bar{L}$.

Numerical data for plotting the curves for $^{\text{III}}\text{B-O}$ and $^{\text{IV}}\text{B-O}$ are listed in Table 1 (columns 3a and 3b). For $^{\text{III}}\text{B-O}$ equation (8) becomes

$$v = (1.366/L)^{2.71};$$

for $^{\text{IV}}\text{B-O}$, it is

$$v = \left(\frac{3}{4}\right) (1.472/L)^{3.70} = (1.362/L)^{3.70}. \quad (9)$$

Donnay & Allmann obtain the effective fractional charges on non-equivalent oxygen atoms in a linear hydrogen bond from the Lippincott & Schroeder (1955, Fig. 5) curve. This curve also appears on Fig. 4.

The Brown-Shannon curve for B-O bonds

Brown & Shannon (1973) give the following equation,* rewritten in our notation,

$$\frac{v}{v_0} = \left(\frac{1.375}{L}\right)^{3.9}, \quad (10)$$

in which v_0 is chosen as unity and the numerical values are fitted parameters.† The mathematical form of (10) is that of (8). Whereas equation (8) is valid only for $L \leq \bar{L}$ and the values of the constants in it are characteristic of one polyhedron, equation (10) applies over the whole range of L and for any B-O bond, in any coordination, in any crystal structure. Numerical data for plotting the curve are listed in Table 1 (column 4).

The Brown-Shannon treatment of the charge transfer in a hydrogen bond has been explained above, where

* Previously given for Li-O, Be-O and B-O (Brown & Shannon, 1972) as $v = (1.370/L)^{4.006}$.

† It is hard to see why Brown & Shannon considered the constant v_0 at all: in a formula where all the parameters are to be fitted, the v_0 could have been included directly in the constant between parentheses, as in equation (10), where the $v_0 = 1$ can be omitted. They state that v_0 can be chosen arbitrarily, which is of course true. For instance, for $v_0 = \frac{3}{4}$, equation (10) would be written

$$\frac{v}{\left(\frac{3}{4}\right)} = \left(\frac{1.480}{L}\right)^{3.9}$$

[cf. equation (9) in the preceding section]. In Brown & Shannon (1973, Table 1) a great many v_0 values are listed, every one of them a rational number, as the quotient of a formal charge by a coordination number would be.

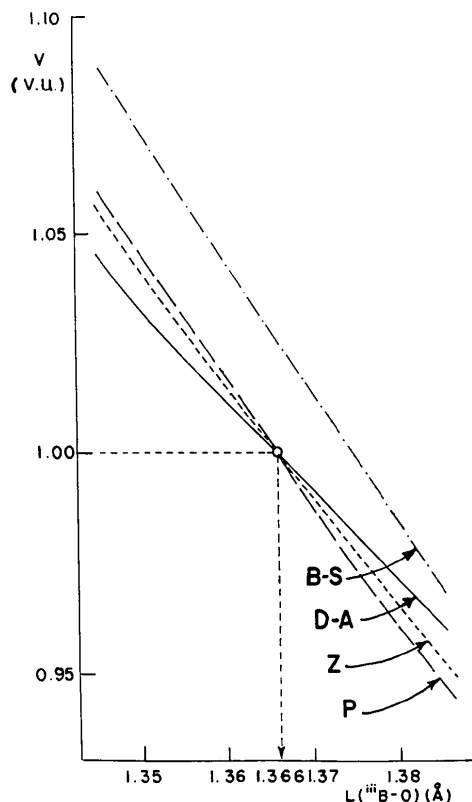


Fig. 2. Enlargement of Fig. 1 in the region applicable to tricoordinated boron, near $L(^{\text{III}}\text{B-O}) = 1.366$, for $1.345 \leq L \leq 1.385$. On Figs. 2 and 3 the B-S curve obeys the equation $v = (1.375/L)^{3.9}$ of 1973.

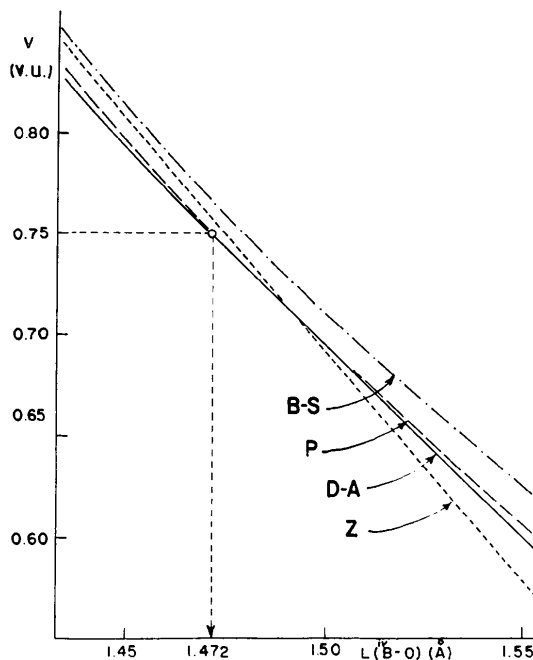


Fig. 3. Enlargement of Fig. 1 in the region applicable to tetracoordinated boron, near $L(^{\text{IV}}\text{B-O}) = 1.472$, for $1.433 \leq L \leq 1.553$.

it was applied to the Pauling procedure. The curve of $v(\text{O-H})$ vs. $L(\text{O-H})$ here obeys the equation

$$v(\text{O-H}) = (0.864/L)^{2.2}. \quad (10')$$

The final curve $v(\text{H}\cdots\text{O})$ vs. O-O distance (Fig. 4) has again been plotted point by point.

Comparison of $v(\text{B-O})$ curves

The general trend of the v vs. $L(\text{B-O})$ curves, drawn over a wide range of $L(\text{B-O})$, $1.250 < L < 1.870$ (Fig. 1), shows the curves close together in the regions where they are actually used, that is, in the neighbourhood of $L(\text{iiiB-O}) = 1.366$ and $L(\text{ivB-O}) = 1.472$, but diverging at both ends. On this figure the Pauling curve has been omitted, except in the region $L > 1.600$, where it lies just below the B-S curve. From $L = 1.250$ to $L = 1.366$, the P curve runs below the Z curve and above the D-A (iii) curve. Near $L = 1.366$ it is above the Z curve, which it crosses at $L = 1.366$ (Fig. 2). It then lies a little above the D-A (iv) curve to $L = 1.472$, where it merges with it; at $L = 1.56$ the two curves separate again (Fig. 3). In the useful regions (Figs. 2 and 3) the B-S curve stays above all the others, which are close together. On the whole, the curves are remarkably similar, a fact that should not occasion surprise since all of them were designed to express empirically observed variations of the bond valence with changes in bond length.

The hydrogen-bond treatment. Comparison of the $v(\text{H}\cdots\text{O})$ curves

The neutron-diffraction data collected by Hamilton & Ibers (1968, Appendix) show that there is no one-to-one relation between the O-O distance and the O-H bond length. By testing, for numerous neutron-refined structures, the valence transfer due to hydrogen bonding, first as a function of O-H and then as a function of O-O, it was found that the O-O distance, combined with the Lippincott & Schroeder (1953) curve, gives better anionic valence sums than does the O-H length.

Zachariasen (1963) treats H as just another cation contributing its share of bond valence to the oxygen atoms to which it is bonded; he gives two curves for bond valence, one in terms of O-H, the other in terms of O-O, but gets the valence transfer from the latter in constructing his bond-valence balance table.

Brown & Shannon (1973) realized that the $v(\text{O-H})$ vs. $L(\text{O-H})$ curve is unusable and have rallied to the use of the O-O distance for determining the charge transfer.

We found that the modified Pauling equation (9) likewise gives a useless curve of $v(\text{O-H})$ vs. $L(\text{O-H})$ and we have derived the corresponding $v(\text{H}\cdots\text{O})$ vs. O-O curve.

The Z curve (Fig. 4) mostly runs above the L-S curve, the P curve below. The B-S curve occupies a central position, cutting across the other three, intersecting the P curve at O-O ~ 2.52 Å, staying very close to the L-S curve for low values of the O-O distance,

crossing it at O-O ~ 2.65 Å and becoming the highest curve at O-O ~ 2.88 .

Comparison of the anionic bond-valence summations

The anionic bond-valence sums are compared (Table 2) by listing them for each of the four methods and showing the root-mean-square deviation Δv_{rms} in each case. On this basis Zachariasen's procedure comes out best ($\Delta v_{\text{rms}} = 0.07$), which was to be expected since Zachariasen's curves were constructed in connexion with this particular crystal structure. If the hydrogen-bond corrections are made according to the L-S curve, the Δv_{rms} increases from 0.07 to 0.08. The Pauling $v(\text{O-H})$ vs. $L(\text{O-H})$ curve, combined with the corresponding P curve for hydrogen-bond correction (Fig. 4), gives $\Delta v_{\text{rms}} = 0.19$; when combined with the L-S curve, it gives $\Delta v_{\text{rms}} = 0.10$. The Brown-Shannon curves (Figs. 2, 3 and 4) give $\Delta v_{\text{rms}} = 0.10$, a result that remains unaltered if the hydrogen-bond corrections are made according to the L-S curve. With $\Delta v_{\text{rms}} = 0.09$ the D-A curves, used in combination with the L-S correction for hydrogen bonds, may have a slight advantage over the modified Pauling and the B-S procedures.

It is fair to remark that, in spite of their analytical similarity, the B-S curve and the D-A curves are essentially different in their very concept: the B-S curve is meant as a universal curve, valid for all the bonds

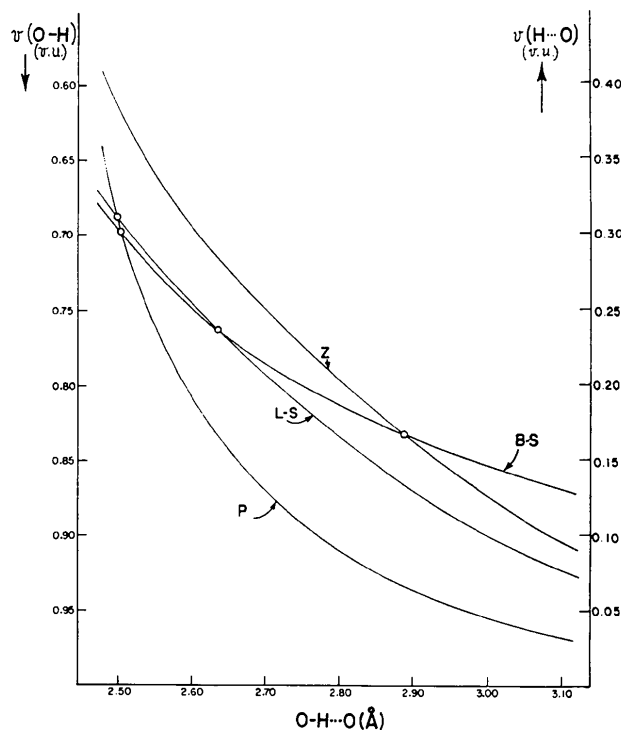


Fig. 4. Curves of bond valences $v(\text{O-H})$ and $v(\text{H}\cdots\text{O})$ vs. O-O distance: L-S, Lippincott & Schroeder (1955); Z, Zachariasen (1963); P, Pauling (1947) modified; B-S, Brown & Shannon (1973).

which one element or a group of elements can make with oxygen for instance, and it corresponds to several D-A curves. The latter are designed to be applied to a

crystal structure that is essentially completed except for proton location, donor-acceptor assignments and ultimate refinement. For a given type of bond, say B-O,

Table 3. Anionic bond-valence sums $\sum_{c,v}$ of $\text{CaB}_6\text{O}_8(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ (gowerite)* showing bond length and bond valence of every bond reaching each anion

Anions	Cations			\sum uncorr.	H-bond correction	\sum corr.	$ \Delta v $	
O(1)	Ca	B(1)	B(4)	1.997 (69)		2.00 (7)	0.00	
	2.730 (16)	1.330 (16)	1.450 (31)					
O(2)	Ca	B(1)	B(2)	1.953 (61)		1.95 (6)	0.05	
	2.470 (11)	1.360 (25)	1.490 (22)					
O(3)	Ca	B(1)	B(3)	2.116 (50)		2.12 (5)	0.12	
	0.243 (3)	0.993 (48)	0.717 (39)					
O(4)	Ca	B(2)	B(3)	2.047 (67)		2.05 (7)	0.05	
	2.540 (17)	1.380 (23)	1.380 (15)					
O(5)	Ca	B(2)	B(5)	1.832 (79)	from O(9)H +0.206	2.04 (8)	0.03	
	0.220 (5)	0.954 (42)	0.942 (27)					
O(6)	Ca	B(2)	B(4)	1.823 (82)	from HO(15)H +0.095	1.92 (8)	0.08	
	2.440 (13)	1.470 (24)	1.330 (25)					
O(7)	Ca	B(3)	B(4)	1.872 (56)		1.87 (6)	0.13	
	0.254 (4)	0.754 (45)	1.039 (50)					
O(8)	Ca	B(4)	B(5)	1.697 (71)	from O(12)H +0.198	1.90 (7)	0.10	
	2.720 (14)	1.340 (24)	1.500 (19)					
O(9)H	Ca	B(5)	B(6)	0.932 (42)	from O(10)H +0.255	0.98 (4)	0.01	
	0.164 (3)	1.019 (47)	0.689 (32)					
O(10)H	Ca	B(6)	B(6)	1.316 (72)	to O(5) -0.206	1.06 (7)	0.06	
	2.420 (17)	1.340 (34)	1.054 (72)					
O(11)H	Ca	B(6)	B(6)	1.096 (56)	to O(9) -0.255	0.88 (6)	0.12	
	0.262 (6)	1.410 (31)	0.913 (56)					
O(12)H	Ca	B(6)	B(6)	1.033 (47)	from HO(13)H +0.210	1.04 (5)	0.04	
	2.660 (17)	1.350 (23)	1.033 (47)					
H ₂ O(13)	Ca	B(6)	B(6)	0.286 (7)	from HO(14)H +0.142	to O(8) -0.198	0.05 (5)	
	0.183 (4)	1.410 (31)	0.913 (56)					
H ₂ O(14)	Ca	B(6)	B(6)	0.03 (3)	to O(15) -0.172	to O(12) -0.210	0.05	
	2.360 (17)	1.340 (34)	1.054 (72)					
H ₂ O(15)	Ca	B(6)	B(6)	0.12 (6)	from HO(15)H +0.176	to O(13) -0.140	0.03	
	0.286 (7)	1.350 (23)	1.033 (47)					
				from HO(13)H +0.172	from O(11)H +0.218	to O(6) -0.095	to O(14) -0.176	0.12
								$\Delta v_{\text{rms}} = 0.08\ddagger$
	Ca	B(1)	B(2)	B(3)	B(4)	B(5)	B(6)	
\bar{L}	2.540	1.357	1.472	1.350	1.467	1.367	1.367	
L_{max}	3.250	1.870	1.870	1.870	1.870	1.870	1.870	
p	3.577	2.643	3.704	2.596	3.646	2.715	2.715	
v_t	2.00/9	3.00/3	3.00/4	3.00/3	3.00/4	3.00/3	3.00/3	
N.F.†	0.990	0.999	0.999	1.000	0.999	0.998	0.999	
$\sum_{\Delta v}$	2.000	3.000	3.000	3.000	3.000	3.000	3.000	

* Crystal structure by Konnert *et al.* (1972).

† N.F. = normalization factor.

‡ We repeated the bond-valence summations with the modified Pauling formula, combined with the L-S curve, and found $\Delta v_{\text{rms}} = 0.09$. The Brown-Shannon curves gave $\Delta v_{\text{rms}} = 0.10$, whether the hydrogen-bond adjustment was based on the B-S curve or on the L-S curve (Fig. 4).

the maximum bond length L_{\max} is determined once and for all and will provide one of the two needed experimental points for any D-A curve. Together with the point (v_i, \bar{L}) provided by one coordination polyhedron, it will yield the curve that is to be used in the vicinity of this particular \bar{L} . Such a curve thus embodies, coming from the structure itself, considerable factual information that intuitively one cannot help feeling should give it the edge (for the structure at hand) over the averaged information gathered from the whole literature.

In the light of the previous remarks, it is clear that the Pauling equation can be used to give either a universal curve or one that applies especially to a given structure. In this paper we have modified it in the latter sense, as we have determined the constant k' from two experimental points drawn from Zachariassen's β -HBO₂ structure. If the two required points were averaged values taken from the Brown-Shannon literature survey, the Pauling curve, as a universal curve, might turn out to be a successful competitor to the B-S universal curve.

One last conclusion: for several purposes all the curves discussed above will prove equally serviceable. Telling an (OH)⁻ or an H₂O from an O²⁻, for instance, does not require much accuracy in the bond-valence sums and any one of the curves gives the answer (see footnote to Table 3).

D-A curves applied to other borates

We shall treat the other three borate structures mentioned above in the order of decreasing value of the residual R .

Gowerite, CaB₆O₈(OH)₄.3H₂O, belongs to space

group $P2_1/a$, $Z=4$, and has all its atoms in general position 4(e). A final R of 9.0% was obtained with extinction correction and anisotropic temperature factors by Konnert *et al.* (1972). From the published coordinates and their σ 's, we calculated the interatomic distances and their σ 's, which are the input data for our valence-sum program. The print-out (Table 3) shows, for each bond, the bond valence under the bond length; it also lists the parameters: \bar{L} , L_{\max} , p , v_i and a normalization factor by which we multiply all bond valences in a given column to set their sum equal to the formal valence of the cation heading the column. The standard deviations following the bond-valence entries are calculated from those of the bond lengths, except for the water molecules, where they are based on the σ 's of the O-O approaches (Table 4). Every anionic valence sum equals the formal charge of the anion to within 3σ or better. We find $\Delta v_{\text{rms}}=0.08$ v.u. There is a change in donor and acceptor relation from the one previously published (Konnert *et al.*, 1972): H₂O(15) donates a hydrogen bond to H₂O(14) and not *vice versa*.

A related but more precisely known structure is that of K₂B₅O₈OH.2H₂O, which crystallizes in $Pna2_1$ with $Z=4$ and all atoms in general position. It was refined by Marezio (1969) to an R of 4.4%. The anionic valence sums and their σ 's (Table 5, left side) show highly satisfactory agreement: the Δv_{rms} is found to be 0.04.

Kernite, Na₂B₄O₆(OH)₂.3H₂O, space group $P2_1/c$, $Z=4$, all atoms in general position, has been used by Cooper *et al.* (1973) for a residual charge determination, for which X-ray data of the highest accuracy were needed. The structure was refined to an R of 3.4%. Professor Coppens provided us with the interatomic distances involving all but the hydrogen atoms, for

Table 4. Oxygen approaches in gowerite

Donor	Acceptor	Distance (Å)	Donor	Acceptor	Distance (Å)
O(10)-H	···O(9)	2.607 (23)	O(12)-H	···O(8)	2.725 (23)
O(11)	O(15)	2.679 (26)	O(15)	O(14)	2.774 (26)
O(13)	O(12)	2.693 (22)	O(13)	O(15)	2.782 (14)
O(9)	O(5)	2.706 (23)	O(14)	O(13)	2.867 (33)
			O(15)	O(6)	3.020 (23)

Table 5. Anionic bond-valence sums $\sum_c v$ before and after H-bond correction

K ₂ B ₅ O ₈ OH.2H ₂ O*			Na ₂ B ₄ O ₆ (OH) ₂ .3H ₂ O (kernite)†		
Anions	\sum uncorr.	\sum corr.	Anions	\sum uncorr.	\sum corr.
O(1)	1.844 (16)	2.00 (2)	O(1)	1.869 (4)	2.04 (0)
O(2)	1.998 (13)	2.00 (1)	O(2)	1.747 (5)	1.97 (1)
O(3)	1.907 (15)	1.99 (2)	O(3)	1.811 (5)	1.97 (1)
O(4)	1.894 (14)	1.99 (1)	O(4)	1.999 (5)	2.00 (1)
O(5)	1.719 (15)	1.91 (2)	O(5)	1.730 (5)	1.87 (1)
O(6)	1.999 (13)	2.00 (1)	O(6)H	1.143 (3)	1.14 (0)
O(7)	2.031 (13)	2.03 (1)	O(7)H	0.973 (3)	0.99 (0)
O(8)H	1.210 (11)	1.02 (1)	H ₂ O(8)	0.196 (0)	0.00 (0)
O(9)	2.027 (15)	2.03 (2)	O(9)	1.913 (5)	1.91 (1)
H ₂ O(10)	0.344 (10)	0.10 (1)	H ₂ O(10)	0.376 (0)	0.08 (0)
H ₂ O(11)	0.140 (10)	0.04 (1)	H ₂ O(11)	0.244 (0)	0.03 (0)

$\Delta v_{\text{rms}}=0.04$ v.u.

$\Delta v_{\text{rms}}=0.07$ v.u.

* Crystal structure by Marezio (1969).

† Crystal structure by Cooper *et al.* (1973).

which the anionic valence sums (Table 5, right side) were calculated. From all the oxygen–oxygen approaches that could possibly be hydrogen bonds, we have chosen the only set that led to satisfactory corrections to the anionic valence sums (Table 5, last column), with $\Delta v_{\text{rms}} = 0.07$ v.u. Only then were the predicted hydrogen bonds checked and confirmed by Cooper *et al.*, who had determined them directly on a Fourier-difference map.

What little theoretical justification there is

If a general equation were available giving the free energy of a crystal in terms of its interatomic distances and other measurable parameters, the terms in such an equation could be expected to bear some relation to the curves we have examined, which relate bond length to bond valence. Pauling (1929), Zachariasen (1931), Brown & Shannon (1973), all begin their discussion with a reference to the Born expression of the lattice energy

$$\phi(L) = \frac{Ae^2}{-L} + \frac{B}{L^n}, \quad (11)$$

which applies to a 100% ionic, alkali halide crystal, and a kind of bonding we now know does not exist. This equation was improved by Born & Mayer (1932) to read

$$\phi(L) = -\frac{Ae^2}{L} - \frac{C}{L^6} + \frac{b_1 b_2}{q} e^{-L/\rho} + \varepsilon, \quad (12)$$

where A is the Madelung constant, L is the shortest interatomic distance (a rational fraction of the cell edge in alkali halide crystals), C is a constant, b_1 and b_2 are constants depending on the ions present, q is equal to 0.345, and ε is the zero-point energy.

For interatomic distances greater than the mean value—a value that will approximate the sum of Shannon & Prewitt's (1969) effective ionic radii—the Coulomb-attraction term, $-Ae^2/L$, should be the most important one, and if the bond valence were proportional to it, we could predict a bond valence inversely proportional to bond length. Zachariasen's empirical B–O curve, instead, is linear from $L = 1.365$ Å to a maximum value $L_{\text{max}} = 1.805$ Å, and so is each D–A curve for $L \leq \bar{L}$.

For interatomic distances smaller than the mean, the repulsion term $\frac{+b_1 b_2}{q} e^{-L/\rho}$ should become dominant and the expression of v would be exponential in L . Pauling's equation is of this form and indeed over the whole range of bond lengths. Brown & Shannon have, for all values of L , one and the same curve which is essentially that used by Zachariasen and Donnay–Allman on the short-bond-length side, one in which the bond valence is proportional to L^{-p} .

In view of the success of these curves for structures with a wide range of bond types, any relation to the terms in the early lattice-energy equations can only be accidental, since these equations were set up for purely

ionic alkali halides. Indeed, Professor C. A. Coulson (private communication, 29 September 1971) has appraised the hope of finding a theoretical basis for the D–A curves as follows: 'I do not see any reasonable chance of proving the truth of any relation of the kind that you use, connecting the bond order (or equivalent) and the interatomic distance. The validity must be that the scheme works'.

Practical value of the curves

How well the scheme works in practice has been demonstrated above, in the case of borate structures, by using the curves of bond valence *v.s.* bond length to calculate the anionic sums that afford a quantitative check of Pauling's rule of local neutralization of charges. This fact being established, the curves can now be confidently applied to solving a variety of problems. Erroneous crystal structures can be detected: Brown & Shannon (1973) have invalidated an early refinement of $\text{Zn}_3(\text{BO}_3)_2$ in Ic , while confirming the refinement in $I2/c$ proposed by Baur & Tillmans (1970). To this example we can add that of B_2O_3 whose structure, determined by the powder method (Berger, 1953), cannot possibly be correct, as its bond-valence summation gives a Δv_{rms} of 0.59 v.u.

The quantitative application of Pauling's rule of local neutrality also permits an interpretation of how various structural details arise. Bond–valence assignments account for the distortion of coordination polyhedra, with a concomitant symmetry loss from the high symmetry of an undistorted triangle ($6m2$ in BO_3) or tetrahedron ($\bar{4}3m$ in BO_4). The effect of the atomic displacements is to minimize the Δv_{rms} of the structure.

The rule stated by Christ (1960), that an oxygen ion not shared by boron coordination polyhedra must belong to a hydroxyl group, is readily understood. The maximum charge received by an unshared oxygen (from ^{11}B) is about one v.u. If the anion were an O^{2-} instead of an $(\text{OH})^-$, it would have to receive additional bonds from metal cations—say, three bonds from ^{11}Ca or six bonds from ^{11}Na —but these cations are not present in sufficient numbers to fulfil such bonding requirements. An illustration is found in kernite (Cooper *et al.*, 1973). The anion O(6) is unshared, its bond length $^{11}\text{B}-\text{O} = 1.383$ Å corresponds to a bond valence of 0.967 v.u. The only two ^{11}Na cations available contribute 0.169 and 0.006 v.u. for actual bond lengths $\text{Na}(1)-\text{O}(6) = 2.392$ and $\text{Na}(2)-\text{O}(6) = 3.106$ Å, corresponding to mean bond lengths $\text{Na}(1)-\text{O} = 2.406$ and $\text{Na}(2)-\text{O} = 2.523$ Å respectively. The anionic sum is 1.14 v.u., and O(6) is part of a hydroxyl group. A somewhat similar situation occurs in $\text{K}_2[\text{B}_5\text{O}_8(\text{OH}) \cdot 2\text{H}_2\text{O}]$ (Marezio, 1969). O(8) belongs to the $^{11}\text{B}(3)$ triangle and is unshared; its B–O bond length (1.379 Å) is greater than the mean (1.369 Å) so that its bond valence is correspondingly reduced (to 0.979 v.u.); the potassium contributions, 0.114 v.u. from $^{39}\text{K}(1)$ and 0.118 v.u. from $^{39}\text{K}(2)$, bring the bond-valence sum to 1.211 v.u.; O(8) is part of a hy-

droxyl group, which transfers most of its excessive positive charge to O(5) *via* a hydrogen bond and leaves the anionic sum at 1.02 v.u.

An oxygen ion that is shared between a ⁱⁱⁱB and ^{iv}B, on the other hand, can receive only about 1.75 v.u. from these two boron ions and will need some additional cationic contribution. A single bond from a ^{vi}Ca, however, would bring in about 0.33 v.u., for a total of ~2.08 v.u.—an excessive positive charge. Driven by the necessity to achieve local neutralization, the oxygen ion will move away from one or both of its bonded boron ions to a distance greater than the mean B–O length for the coordinated triangle or for the tetrahedron or for both. The bond-valence total received from the boron ions will fall below 1.75 v.u., to make the calcium contribution acceptable. The Ca–O bond length itself plays a regulatory role: depending on the B–O distances, the Ca cation will move away from (or toward) the shared anion to reinforce (or counteract) the lowering of the anionic valence sum, and bring about neutrality.

Likewise a tricoordinated oxygen atom ⁱⁱⁱO shared by two boron triangles will form ⁱⁱⁱB–ⁱⁱⁱO bonds much longer than the two mean bond lengths of the BO₃ groups, which will thus be considerably distorted. The third bond reaching ⁱⁱⁱO will be of such a length as to bring the valence sum close to 2. In K₂B₅O₈OH·2H₂O, (Marezio, 1969) for instance, O(9) is bonded to ⁱⁱⁱB(4) and ⁱⁱⁱB(5). Whereas the mean bond lengths in the two triangles are 1.371 and 1.370 Å, the actual bond lengths B(4)–O(9) and B(5)–O(9) are equal to 1.390 and 1.412 Å, with corresponding bond valences of 0.961 and 0.917 v.u. respectively. A ^{viii}K(2)–O(9) bond, 2.688 Å in length, contributes 0.151 v.u. to raise the anionic valence sum from 1.88 to 2.03 v.u.

Finally the importance of hydrogen bonding in the stabilization of crystal structures is dramatically brought out by the effect it exerts on the Δv_{rms} values. Two examples will illustrate the role played by hydrogen bonding in bringing into line valence sums that deviate from the formal anionic charges. For K₂B₅O₈OH·2H₂O the Δv_{rms} value of 0.04 v.u. (Table 5, left side), obtained after hydrogen bonding was taken into account, stood at 0.17 v.u. before the correction was applied. For kernite the drop in the Δv_{rms} value is equally impressive

– from an original 0.20 v.u. to 0.07 v.u. after correction (Table 5, right side). Clearly, without H bonding the bond-valence balance in either case would be so unsatisfactory as to make one wonder about the stability of the structure.

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