

Empirical Parameters for Calculating Cation–Oxygen Bond Valences

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Empirical parameters (R_1 and N) are given for the equation $s = (R/R_1)^{-N}$ relating the cation–oxygen bond length (R) and its bond valence (s) for 84 different cations (67 different elements in various oxidation states). For cation–oxygen bonds not included in this list the following approximate relationship can be used

$$s = \bar{s}(R/\bar{R})^{-(0.6\nu + 2.2)}$$

where \bar{s} and \bar{R} are the average bond valence and bond lengths respectively and ν is a typical coordination number for the cation.

For many years structural mineralogists have found Pauling's concept of bond strength or bond valence a useful tool in evaluating mineral structures. Recently the concept has been refined by the recognition of the close relationship between bond valence and bond length, extending the usefulness of the concept to quantitative discussions of other types of inorganic crystals (Brown, 1974) and permitting the prediction of local variations in bond lengths and angles (Baur, 1972; Brown, 1973).

Several schemes have been proposed for obtaining the correlation between bond valence (s) and bond length (R) (see Allman, 1975) some based on fitting the curves to the environment of individual cations (Donnay & Allmann, 1970; Pyatenko, 1972), others based on the use of universal parameters applicable to all crystals (Brown & Shannon, 1973; Allmann & Donnay, 1974). Two expressions have been proposed

$$s = s_0(R/R_0)^{-N} \quad (1)$$

and

$$R = R_1 - 2k \log s \quad (2)$$

where s_0 , R_0 , N , R_1 , and k are empirical constants. Both equations give similar results over the range of interest (Donnay & Donnay, 1973; Allmann, 1975). The parameter s_0 can be chosen arbitrarily and, if it is chosen to be unity, $R_0 = R_1 =$ length expected for a bond of unit valence, that is

$$s = (R/R_1)^{-N} \quad (3)$$

Since the slope of the curve is given by N or k , these two parameters will be related by

$$N \simeq (\ln 10) \bar{R} / (2k) \quad (4)$$

where \bar{R} is an average observed bond length, *i.e.* the bond length at which the slopes of the two curves are set equal. In practice R_1 can be determined to better

than 0.01 Å, but even in the most favourable cases N and k are known only to within 10% and in some cases they are virtually indeterminate. The value of R_1 will, however, depend critically on the particular value of N or k chosen except when $R_1 \simeq \bar{R}$.

In this paper we report (Table 1) a set of parameters, R_1 and N , for use in equation (3). They cover most of the cation–oxygen bonds for which a sufficient number of suitable structures are available to allow the use of the statistical procedures described by Brown & Shannon (1973). Of the 84 sets of parameters reported, 53 are given for the first time, 10 are revisions of earlier values and 21, taken from earlier papers, are included for completeness. The environments of 936 cations (listed in Table 2)* were included in the present study.

If bond valences are required for bonds not given in Table 1 they can be calculated for a particular structure using a modification of the procedure described by Pyatenko (1972). Pyatenko writes equation (1) in the form

$$s = K/R^N \quad (5)$$

and, assigning an *a priori* value for N (see below), fits K by ensuring that when s is summed over all the bonds formed by the cation it yields the cation valence. A simpler procedure which achieves approximately the same result is to write equation (1) as

$$s = \bar{s}(R/\bar{R})^{-N} \quad (6)$$

where \bar{s} is the average cation–oxygen bond valence (the Pauling bond strength) and \bar{R} the average cation–oxygen bond distance. [If the environment is distorted \bar{R} will be too large by an amount $2k \log(\bar{s}/\bar{s}_g)$ (Allmann, 1975) where \bar{s}_g is the geometric mean of the bond valences in the coordination sphere.]

* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication SUP No. 31563 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester, CH1 1NZ, England.

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Table 1. *Parameters for cation-oxygen bond-valence curves*

Cation (valence)	$R_1(\text{\AA})^{(1)}$	$N^{(1)}$	$n^{(2)}$	Footnote
H(1)	0.87	2.2		(3)
Li(1), Be(2), B(3)	1.378	4.065		(4)
C(4)	1.378	4.065		(5)
Na(1), Mg(2), Al(3), Si(4), P(5), S(6)	1.622	4.290		(4)
S(4)	1.629	4.6	10	(6)
K(1)	2.276	9.1	43	(7)
Ca(2)	1.909	5.4	38	
Sc(3)	1.865	5.4	9	
Ti(4)	1.806	5.2	40	
Ti(3)	(1.789)	(5.2)	2	
V(5)	1.791	5.1	43	
V(4)	1.770	(5.2)	18	
V(3)	(1.762)	(5.2)	4	
Cr(6)	1.787	(5.0)	23	
Cr(5)	(1.769)	(5.2)	3	
Cr(4)	(1.770)	(5.2)	4	
Cr(3)	1.733	(5.2)	7	
Mn(7)	1.780	(5.43)	5	
Mn(4)	(1.774)	(5.2)	3	
Mn(3)	1.769	5.5	9	
Mn(2)	1.798	5.6	34	
Fe(3)	1.780	5.7	48	
Fe(2)	1.764	5.5		(4)
Co(4)	(1.770)	(5.7)	4	
Co(2)	1.727	5.6	29	
Ni(2)	1.680	(5.4)	24	
Cu(2)	1.718	6.0	44	
Zn(2), Ga(3), Ge(4), As(5)	1.746	6.05		(4)
Se(6)	1.775	5.0	15	
Se(4)	1.796	4.0	17	
Rb(1)	2.220	7.0	37	
Sr(2)	2.143	7.0	31	
Y(3)	2.070	7.0	15	
Zr(4)	1.950	6.0	18	
Nb(5)	1.907	5.0	18	
Mo(6)	1.882	6.0	50	(14)
Ag(1)	1.946	7.4	15	
Cd(2)	1.990	7.4	17	
In(3)	1.959	(7.0)	12	
Sn(4)	1.955	8.1	9	
Sn(2)	1.860	4.5		(8)
Sb(5)	1.911	(6.0)	11	
Sb(3)	1.910	4.5		(8)
Te(6)	1.911	(7.0)	11	
Te(4)	1.933	4.5		(8)
I(7)	(1.942)	(5.8)	5	
I(5)	1.967	4.5		(8)
Xe(6)	1.971	4.5		(8)
Cs(1)	2.335	6.6	17	
Ba(2)	2.297	7.0	45	(9)
La(3)	2.167	6.5	5	(10)
Ce(3)	2.160	6.5		(10)
Pr(3)	2.150	6.5	10	(10)
Nd(3)	2.137	6.5		(10)
Pm(3)	2.120	6.5		(10)
Sm(3)	2.107	6.5	8	(10)
Eu(3)	2.090	6.5	3	(10)
Gd(3)	2.077	6.5	9	(10)
Tb(3)	2.065	6.5	1	(10)
Dy(3)	2.053	6.5	2	(10)
Ho(3)	2.041	6.5	3	(10)
Er(3)	2.029	6.5	3	(10)
Tm(3)	2.020	6.5	1	(10)
Yb(3)	2.012	6.5	8	(10)
Lu(3)	2.004	6.5	6	(10)

Table 1 (cont.)

Hf(4)	(1.950)	(6.0)	2	(11)
Ta(5)	(1.907)	(5.0)	4	(12)
W(6)	1.904	6.0	12	
Re(7)	1.910	6.0	7	
Hg(2)	1.983	6.5	7	(13)
Tl(1)	2.100	6.0	9	
Pb(2)	2.044	5.5	18	
Bi(3)	2.010	5.0	7	
U(6)	2.059	4.3	24	

Footnotes

(1) Values of R_1 and N given in parentheses are considered less reliable (uncertainty in $R_1 > 0.01 \text{ \AA}$, in $N > 2$).

(2) n = number of cation environments used in the determination of R_1 and N . Details are given in Table 2 (deposited, see footnote in text).

(3) From Brown & Shannon (1973). This curve can be used in the range $1.7 \leq R \leq 1.9 \text{ \AA}$. A non-analytical curve covering a large range has been given by Brown (1976). Neutron determinations only.

(4) From Brown & Shannon (1973).

(5) These parameters do not work well for organic compounds.

(6) Several SO_3 groups bond to cations through the S atom as well as through the O atoms. In such cases the directionality of the bonds must be taken into account. If the bonds are taken to be directed from the more electronegative to the more electropositive atoms, the valence of S is obtained by adding the valence of those bonds directed towards S ($\text{O} \rightarrow \text{S}$ bonds) and subtracting the valence of those directed away from S ($\text{S} \rightarrow \text{metal}$ bonds).

(7) This exponent is much larger than that given earlier (Brown & Shannon, 1973) or that predicted by equation (8). It is needed to give good sums for compounds in which K is only 4-coordinated. The low sums around $\text{K}_2\text{BaCo}(\text{NO}_2)_6$ (0.69 v.u.) and $\text{K}_2\text{PbCu}(\text{NO}_2)_6$ (0.66 v.u.) arise because K is in a hole whose size is determined by other bonds in the crystal.

(8) From Brown (1974).

(9) Ba frequently gives poor sums particularly in perovskite related crystals in which the environment of Ba is determined by other stronger bonds. In such crystals the other cations may also give poor sums, for example in BaNiTeO_6 the valence sums are Ba: 2.20 v.u., Te: 5.66 v.u., Ni: 1.89 v.u. The effect is related to the tendency of such phases to undergo phase transitions to more distorted structures.

(10) The values of R_1 for the lanthanides have been interpolated between the well determined values.

(11) Based on Zr(4).

(12) Based on Nb(5).

(13) Hg-Hg taken as 1 v.u.

(14) A thorough discussion of the bond order of Mo-O bonds is given by Schröder (1975).

Pyatenko (1972) takes N to increase from 2.5 to 7 with the electronegativity of the cation, that is, N tends to vary *inversely* with the size of the cation. Allmann (1975) finds that for most elements $0.75 < 2k < 1.1 \text{ \AA}$ leading to a value of N (equation 4) given by

$$N \sim 2.6\bar{R}, \quad (7)$$

that is, Allmann finds that N varies *directly* as the size of the cation. Our own results confirm those of Allmann rather than Pyatenko for we find that the values of N in Table 1 can be fitted within ± 1 by the expression

$$N \simeq (0.6\nu + 2.2) \quad (8)$$

where ν is a typical coordination number for the cation.*

Thus in the case of a cation not given in Table 1, the cation-oxygen bond valence can be calculated using

$$s \simeq \bar{s}(R/\bar{R})^{-(0.6\nu + 2.2)} \quad (9)$$

Some parameters for bonds to other anions have been reported by Brown (1974) [Sn(2), Sb(3), Te(4), I(5) and Xe(6) to F] and Hoggins & Steinfink (1975) [Fe(2), Fe(3) to S].

* An effective coordination number around any cation can be defined as the cation valence divided by the largest bond valence. For regular coordination this procedure yields the normal coordination number but for irregular coordination it treats long bonds as making only a partial contribution to the coordination number. Using this definition, equation (8) predicts better than (7) the smaller value of N found for the lower valence states of the main group elements.

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Crystal Structure and Chemical Bonding of Manganese(II) Sulphite Trihydrate

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$\text{MnSO}_3 \cdot 3\text{H}_2\text{O}$ is orthorhombic, $a = 9.72$ (2), $b = 5.63$ (1), $c = 9.53$ (2) Å, $Z = 4$, space group $Pnma$. The structure was solved by the Patterson method and refined by full-matrix least squares to $R = 0.062$. Coordination around Mn atoms is octahedral, the ligands being three oxygen atoms from water molecules and another three from sulphite groups. The anions behave as bridging ligands, linking MnO_6 octahedra together and forming chains parallel to the c unit cell axis. Modifications in SO_3^{2-} geometry are discussed.

Introduction

Several structural studies on metal sulphite compounds have been performed so far. The anion, as was demonstrated in those reports, can behave as a monodentate or as a bridging ligand. In the first case, it generally coordinates through sulphur, sometimes with strong evidence of π -bonding. However, the crystal structure of $(\text{NH}_4)_9\text{Fe}(\text{SO}_3)_6$, where the sulphite group is bonded to the metal atom through an oxygen atom, has recently been reported (Larsson & Niinistö, 1973). As a bridging ligand, the polydentate anion has been found to bind through sulphur and/or oxygen. In this type of compound, polymeric moieties are generally formed.

According to Cruickshank (1961), π -bonding orbitals in sulphur oxy-anions are formed with $3d$ sulphur or-

bitals and $2p$ oxygen orbitals. Robinson (1964) discussed the effect of unshared electrons on sulphur in relation to the S-O bond order, and suggested that the bond order in the SO_3^{2-} ion is only 1.33 (as compared with 1.50 in the sulphate ion) with a lone pair replacing one of the two resonating double bonds in the valence bond formulation. When SO_3^{2-} coordinates through sulphur and its lone pair is engaged in binding to a metal, the effect of the electron pair is reduced and S-O distances should be shorter than found in the free SO_3^{2-} ion. On the other hand, if sulphite coordinates through oxygen, a lengthening of the S-O bond would be expected, since there is a minor availability of $2p$ orbitals for π -bonding. When coordination through sulphur and oxygen occurs, the effects are counteracted and the bonding scheme is obscured.

In order to obtain additional information about the