

- (2) $s_{\max} = 3.0$, $s_{\min} = 0.5$ $r_{\min} = 1.0 \text{ \AA}$, $r_{\max} = 2.5 \text{ \AA}$ $|OX + \Sigma| < \Delta$ (bond valences may have wrong sign, e.g. for CO and CN)
- (3) $s_{\max} = 2 \times \text{MIN}[OX(1), OX(2)]$ $r_{\min} = 1.0 \text{ \AA}$ $|OX - \Sigma| < 0.5$ if central atom is H
 $s_{\min} = 0.15 \times \text{MAX}[OX(1), OX(2)]$ $r_{\max} = 2.0 + 0.075 \times [P(1) + P(2)] \text{ \AA}$ $-0.7 < OX - \Sigma < 0.3$ if central atom is O, S, F or Cl and the structure contains undetermined H atoms (allows for acceptor hydrogen bonds whose lengths cannot be calculated)
- (4) $s_{\max} = 1.5$ $r_{\min} = 1.0 \text{ \AA}$
 $s_{\min} = 0.38 \times OX(CM^*)$ $r_{\max} = 1.4 + 0.1 \times P(CM) + 0.2 \times P(CT) \text{ \AA}$ $|3 - \Sigma| < \Delta$ if central atom is C(+2) (cyanide groups need special treatment).
- Exceptions: if CM^* is C(+2)
 $s_{\max} = 3.6$ $r_{\min} = 1.0 \text{ \AA}$
 $s_{\min} = 0.038 \times OX(C, T)$ $r_{\max} = 3.0 \text{ \AA}$
- (5) $s_{\max} = 2 \times \text{MIN}[OX(1), OX(2)]$ $r_{\min} = 1.0 \text{ \AA}$
 $s_{\min} = 0.15 \times \text{MAX}[OX(1), OX(2)]$ $r_{\max} = 0.9 + 0.2 \times [P(1) + P(2)] \text{ \AA}$
- (6) $r_{\min} = 1.0 \text{ \AA}$
 $r_{\max} = 3.4 \text{ \AA}$

Module (2). Calculation of bonds

If $|s_{\max}| > 0$ and bond-valence parameters are available, set r_{\max} and r_{\min} from s_{\min} and s_{\max} , respectively.

Calculate all distances lying between r_{\min} and r_{\max} .

If either atom is C(+2), N(-1) or N(-2), any interatomic vector closer than 55° to a shorter vector is removed from the bond list. This is necessary to eliminate distances to second neighbours, e.g. metal...O in M-C-O and N(1)...H in N(1)-N(2)-H.

Module (3). Bond calculation check

(i) Calculate the bond valence from the bond lengths using $s = \exp[(r_0 - r)/B]$ based on tabulated values of r_0 and B or, if these are not available, values calculated using the algorithm of Brown & Altermatt (1985).

(ii) Modify the bond valence as follows:

(a) If either atom is H and $s > 0.8$ set $s = 0.8$ v.u. (allows for unrealistically short X-H bonds).

(b) If the terminal atom is a cation change sign of s .

(c) If $OC(\text{terminal}) < OC(\text{central})$ set $s = [OC(t)/OC(c)] \times s$ (allows for cases where the terminal atom is substitutionally disordered).

(iii) Sum the valences of heteroionic bonds around the central atom

$$\Sigma_i = \sum_j s_{ij}(C-A)$$

(homoionic bonds do not contribute to the assigned oxidation number).

Add -0.8 v.u. for each dummy H atom attached to the central atom.

(iv) Check the difference between the oxidation number of the central atom and its bond-valence sum. Let $\Delta = 0.25 + (1.1 - OC)|OX|$ be the permitted tolerance where OC and OX refer to the central atom. (This allows an increase in the tolerance for central atoms that have high oxidation states or low occupation numbers.)

Then agreement is satisfactory if

$$|OX - \Sigma| < \Delta$$

Module (4). Error analysis

If a WARNING or an ERROR is flagged, check:

(i) Does the cell correspond to space-group setting:
 (a) For hexagonal, trigonal and rhombohedral (hexagonal setting) is $\gamma = 120.0^\circ$?

(b) For monoclinic, are the correct two angles 90° for the setting used?
 (ii) Does the number of assigned H atoms correspond to the number of dummy H atoms given? If not, how many H atoms would have to be attached to each anion to give the correct valence sums?

(iii) Is the coordination number of P(+5), S(+6) and Cl(+7) equal to 4?
 (iv) Does any bond exceed its maximum possible valence? i.e. is $s > \text{MIN}[OX(1), OX(2)]$.

(v) Does a halogen anion form no bonds in a structure where H-atom coordinates have not been determined? In this case the anion probably only forms hydrogen bonds.

All of the above tests will print an appropriate diagnostic statement if the error condition is found.

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Bond-Valence Parameters Obtained from a Systematic Analysis of the Inorganic Crystal Structure Database

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Abstract

The parameters needed to calculate bond valences from bond lengths have been determined for 750 atom pairs using the Inorganic Crystal Structure Database. The most accurate 141 are listed and an algorithm is

given which allows the calculation of the remainder as well as the calculation of parameters for over a thousand other bond types. Graphical bond-valence-bond-length correlations are presented for hydrogen bonds.

Determination of bond-valence parameters

The preceding paper (Altermatt & Brown, 1985) describes a program (*SINDBAD*) which determines the chemical connectivity in an inorganic crystal. Essential to the running of this program are the parameters required for calculating the bond valences. Two expressions are commonly used to describe the relationship between the bond length (r) and the bond valence (s)

$$s = (r/r_0)^{-N} \quad (1)$$

and

$$s = \exp [(r_0 - r)/B], \quad (2)$$

where r_0 , N and B are empirically determined parameters, many of which have been tabulated (Brown & Wu, 1976; Brown, 1980).

The bond file produced from the Inorganic Crystal Structure Database (ICSD) (Bergerhoff, Hundt, Sievers & Brown, 1983) by the program *SINDBAD* provides an ideal resource to refine these parameters which are usually determined by fitting equation (3) (relating V_i , the oxidation state of cation i , to s_{ij} , the valence of the bond between the cation i and the anion j) to the environments found around a number of cations (Brown & Shannon, 1973):

$$V_i = \sum_j s_{ij} \quad (3)$$

Reliable values can be found with 10 to 20 cation environments, but the more that are used, the better the resulting parameters.

Equation (2) has a particular advantage over equation (1) because B , unlike N , varies very little from one atom pair to another. By refining B (*i.e.* selecting the value of B that gives the smallest value of σ' described below) it is found that B could rarely be determined to better than 0.05 and that a value of 0.37 was consistent with most or all of the refined values. By assuming this value for B , only one parameter (r_0) remains to be fitted and this can be done exactly for each cation environment by solving the equation

$$V_i = \sum_j s_{ij} = \sum_j \exp \left(\frac{r'_0 - r_{ij}}{B} \right) \quad (4)$$

for r'_0 . A value of r'_0 is calculated for each cation environment in the ICSD in which the ligands are chemically identical and in which there is no disorder. The resultant values are then averaged to give the best value for r_0 for a given ion pair.

The estimated standard deviation (σ') of r'_0 gives a measure of the extent to which the various cation environments give a consistent result. Except for the alkali metals where $\sigma' \sim 0.09 \text{ \AA}$, the standard deviation generally lies in the range 0.01 to 0.05 \AA , giving rise to an estimated standard error (σ_e) in the value

of r_0 that is usually less than 0.01 \AA when more than 10 cation environments are available for a given atom pair. In cases where the number of cation environments warranted, restricting the calculations to structures with crystallographic R factors less than 0.12 generally lowered σ' except for the alkali metals. In these latter cases the large standard deviation represents a real physical variation in cation environment and not merely experimental error.

In total, 750 values of r_0 were determined from 15 371 different cation environments obtained from the ICSD. Table 1 gives the 141 most reliable values of r_0 and includes σ_e , σ' and the number (n) of cation environments used in calculating r_0 . The criterion for inclusion of r_0 in Table 1 is that $\sigma_e \leq 0.01 \text{ \AA}$ and $n \geq 10$.

The results of this analysis were examined for the systematic variation of r_0 with the position of the ions in the Periodic Table. The equation

$$r_0 = r_c + A \times r_a + P - D - F \quad (5)$$

can generally reproduce the well determined values to within about 0.013 \AA (standard deviation) or within about $3\sigma_e$. In this equation r_c and r_a are contributions to r_0 from the cation and anion respectively as given in Table 2 (r_a for oxygen is arbitrarily chosen as zero). The multiplier A is set to 0.8 for transition-metal ions (groups 3–12) with d electrons present, otherwise it is set to 1.0.

P , D and F are corrections required when the cation contains non-bonding p , d and f electrons respectively. The values of D are given in Table 3; the values of P and F are calculated using:

$$P = 0.0175 \times (\text{cation period} - 2)$$

$$F = 0.016 \times \text{number of } f \text{ electrons.}$$

The values of r_0 calculated using this algorithm are not as good as the selected experimental values given in Table 1 but for the remaining 609 (those with $\sigma_e > 0.01 \text{ \AA}$ or $n < 10$) the calculated values are probably as good as or better than those determined experimentally. Furthermore, the program can be used to predict values of r_0 for over a thousand cation-anion combinations whose valence parameters have not yet been determined.

Determining the valence of hydrogen bonds

Hydrogen bonds are of particular interest because of their importance in solid-state chemistry. All distances between 0.95 and 3.2 \AA have been observed for O–H bonds and over a range of this magnitude it would be surprising if any equation as simple as (1) or (2) could give a good fit. Furthermore, the study of hydrogen bonding is complicated by the fact that the H atom itself is often not well located. Both these considerations require that hydrogen bonds be

Table 1. *The bond-valence parameter r_0 for selected bonds*

B has been set to 0.37. An R in the last column indicates that the averaging was restricted to structures with agreement index less than 0.12. Other symbols are defined in the text.

		r_0	σ_e	σ'	n			r_0	σ_e	σ'	n
Ag 1	O -2	1.842 (9)		0.063	48 R	Mg 2	O -2	1.693 (3)		0.040	206 R
Ag 1	S -2	2.119 (7)		0.042	42 R	Mn 2	Cl -1	2.133 (10)		0.037	16
Al 3	Cl -1	2.032 (7)		0.037	30	Mn 2	F -1	1.698 (5)		0.020	17 R
Al 3	F -1	1.545 (2)		0.007	22 R	Mn 2	O -2	1.790 (3)		0.033	173 R
Al 3	O -2	1.651 (2)		0.037	397 R	Mn 3	O -2	1.760 (5)		0.036	51 R
As 3	O -2	1.789 (5)		0.023	24 R	Mn 4	O -2	1.753 (6)		0.020	13 R
As 3	S -2	2.272 (4)		0.022	26 R	Mo 6	O -2	1.907 (2)		0.027	186 R
As 5	F -1	1.620 (10)		0.038	16 R	N 3	O -2	1.361 (9)		0.037	17 R
As 5	O -2	1.767 (3)		0.028	86 R	N 5	O -2	1.432 (2)		0.016	106 R
B 3	F -1	1.281 (3)		0.009	11 R	Na 1	F -1	1.677 (8)		0.089	126
B 3	O -2	1.371 (1)		0.019	436 R	Na 1	O -2	1.803 (3)		0.080	634 R
Ba 2	F -1	2.188 (6)		0.031	30	Na 1	S -2	2.300 (10)		0.056	31 R
Ba 2	O -2	2.285 (4)		0.063	254 R	Nb 5	O -2	1.911 (2)		0.031	228
Ba 2	S -2	2.769 (7)		0.062	88	Nd 3	O -2	2.105 (5)		0.043	80
Be 2	F -1	1.281 (4)		0.019	22 R	Ni 2	F -1	1.596 (5)		0.020	18 R
Be 2	O -2	1.381 (3)		0.019	43 R	Ni 2	O -2	1.654 (4)		0.034	72 R
Bi 3	O -2	2.094 (9)		0.061	52 R	P 5	N -3	1.704 (4)		0.021	30 R
Bi 3	S 2	2.570 (3)		0.015	20 R	P 5	O -2	1.617 (1)		0.017	543 R
C 4	N -3	1.442 (4)		0.017	18	P 5	S -2	2.145 (10)		0.044	21
C 4	O -2	1.390 (2)		0.017	72 R	Pb 2	O -2	2.112 (4)		0.050	174 R
Ca 2	F -1	1.842 (8)		0.031	15 R	Pb 2	S -2	2.541 (6)		0.037	46 R
Ca 2	O -2	1.967 (2)		0.052	450 R	Pb 4	O -2	2.042 (8)		0.036	21
Cd 2	Cl -1	2.212 (9)		0.030	12	Pr 3	O -2	2.138 (10)		0.050	25 R
Cd 2	O -2	1.904 (4)		0.035	93 R	Pr 2	C 2	1.760 (8)		0.036	19
Cd 2	S -2	2.304 (4)		0.014	15 R	Pr 4	O -2	1.879 (10)		0.037	14
Cl 7	O -2	1.632 (5)		0.029	30 R	Rb 1	Cl -1	2.652 (10)		0.052	25 R
Co 2	Cl -1	2.033 (8)		0.026	11 R	Rb 1	O -2	2.263 (9)		0.096	128
Co 2	O -2	1.692 (5)		0.039	65 R	S 2	N -2	1.597 (3)		0.008	11
Co 3	C 2	1.634 (2)		0.007	10	S 2	N -3	1.682 (9)		0.039	17
Cr 3	F -1	1.657 (5)		0.018	16	S 4	N -3	1.762 (5)		0.027	27
Cr 3	O -2	1.724 (4)		0.022	37 R	S 4	O -2	1.644 (9)		0.033	16
Cr 6	O -2	1.794 (2)		0.020	80 R	S 6	O -2	1.624 (1)		0.019	243 R
Cs 1	Cl -1	2.791 (10)		0.071	48 R	Sb 3	F -1	1.883 (7)		0.023	13 R
Cs 1	O -2	2.417 (10)		0.078	60 R	Sb 3	O -2	1.973 (4)		0.026	37 R
Cu 1	I -1	2.108 (10)		0.034	13	Sb 3	S -2	2.474 (5)		0.050	87
Cu 1	S -2	1.898 (3)		0.037	131 R	Sb 5	F -1	1.797 (5)		0.024	24 R
Cu 2	F -1	1.594 (4)		0.020	28 R	Sb 5	O -2	1.942 (8)		0.057	47
Cu 2	O -2	1.679 (2)		0.032	197 R	Sc 3	O -2	1.849 (5)		0.027	34 R
Cu 2	S -2	2.054 (5)		0.018	12	Sc 3	S -2	2.321 (5)		0.017	14
D 1	O -2	0.927 (6)		0.041	51 R	Se 4	O -2	1.811 (5)		0.022	21 R
Dy 3	O -2	2.001 (9)		0.033	14 R	Se 6	O -2	1.788 (2)		0.011	23 R
Er 3	F -1	1.904 (6)		0.018	10	Si 4	C -4	1.883 (1)		0.006	37
Er 3	O -2	1.988 (7)		0.030	20 R	Si 4	N -3	1.724 (3)		0.014	20 R
Eu 2	S -2	2.584 (10)		0.029	10	Si 4	O -2	1.624 (1)		0.018	988 R
Eu 3	O -2	2.074 (5)		0.016	11 R	Si 4	S -2	2.126 (4)		0.013	12 R
Fe 2	O -2	1.734 (3)		0.037	153 R	Sn 2	F -1	1.925 (10)		0.037	16
Fe 3	C 2	1.689 (10)		0.032	11	Sn 4	Cl -1	2.276 (6)		0.018	11
Fe 3	F -1	1.679 (5)		0.028	27	Sn 4	F -1	1.843 (9)		0.032	13
Fe 3	O -2	1.759 (3)		0.038	204 R	Sn 4	O -2	1.905 (8)		0.043	29 R
Fe 3	S -2	2.149 (6)		0.022	13 R	Sn 4	S -2	2.399 (4)		0.020	22 R
Ga 3	O -2	1.730 (3)		0.022	54 R	Sr 2	O -2	2.118 (6)		0.078	192
Ga 3	S -2	2.163 (4)		0.013	13 R	Ta 5	O -2	1.920 (5)		0.044	66 R
Ge 4	O -2	1.748 (2)		0.025	181 R	Tb 3	O -2	2.032 (5)		0.021	17 R
Ge 4	S -2	2.217 (4)		0.020	22 R	Te 4	O -2	1.977 (2)		0.019	60 R
H 1	N -3	0.885 (6)		0.100	243 R	Te 6	O -2	1.917 (8)		0.053	46 R
H 1	O -2	0.882 (3)		0.111	1443 R	Th 4	F -1	2.068 (4)		0.014	11 R
Hg 2	O -2	1.972 (9)		0.060	44 R	Ti 4	O -2	1.815 (4)		0.037	107 R
Hg 2	S -2	2.308 (6)		0.027	20	Ti 1	I -1	2.822 (8)		0.033	19
Ho 3	O -2	2.025 (5)		0.023	21 R	Ti 1	S -2	2.545 (8)		0.057	48
I 5	O -2	2.003 (8)		0.050	36 R	U 4	F -1	2.038 (6)		0.019	11 R
In 3	F -1	1.792 (9)		0.028	11	U 6	O -2	2.075 (6)		0.046	62 R
In 3	O -2	1.902 (8)		0.050	36 R	V 3	O -2	1.743 (5)		0.019	18 R
In 3	S -2	2.370 (3)		0.017	37 R	V 4	O -2	1.784 (6)		0.027	24 R
K 1	Cl -1	2.519 (8)		0.070	72	V 5	O -2	1.803 (3)		0.031	91 R
K 1	F -1	1.992 (7)		0.093	178	W 6	O -2	1.917 (4)		0.040	84 R
K 1	O -2	2.132 (4)		0.092	512	Y 3	O -2	2.019 (9)		0.070	64 R
La 3	O -2	2.172 (5)		0.037	66 R	Yb 3	O -2	1.965 (9)		0.036	16 R
La 3	S -2	2.643 (5)		0.021	20	Zn 2	Cl -1	2.027 (8)		0.025	11
Li 1	F -1	1.360 (6)		0.038	44 R	Zn 2	O -2	1.704 (3)		0.039	148 R
Li 1	O -2	1.466 (3)		0.062	333	Zr 4	F -1	1.846 (7)		0.025	15 R
Mg 2	F -1	1.578 (7)		0.026	15	Zr 4	O -2	1.928 (3)		0.027	63 R

treated specially in any careful analysis of bond valences.

Fig. 1 gives the correlation between bond valence and $H \cdots X$ distance for a variety of anions (X) and is an extension of that given by Brown (1976*b*). It

has been found to give good valences for hydrogen bonds where the donor is O or C but it gives values a little low where the donor is N. In using this graph it is important to remember that since X-ray diffraction locates the centroid of the electron density rather

than the position of the nucleus, the H atom appears to be closer to the donor anion than it actually is. This fact, combined with the large uncertainties in the determination of the H position, make it desirable to move the H atom to a position about 1.0 Å from the donor (0.95 Å for O, 1.10 Å for C, etc.) before using the figure.

Although the position of the H atom is still uncertain even after the shift, the valence of the H...X (acceptor) bond can be well determined because the valence is not sensitive to small uncertainties in bond length. By contrast the (donor) X-H bond valence is extremely sensitive to small uncertainties in distance. Consequently the (donor) X-H valence is best determined by subtracting the sum of the H...X (acceptor) valences from 1.0.

When the position of the H atom is not known and cannot be predicted a different approach is needed. In the case of O-H...O bonds one can use Fig. 2 which shows the correlation between the H...O bond valence and the O-O distance. This graph has been constructed on the assumption that the degree of bending in the hydrogen bond follows the trend

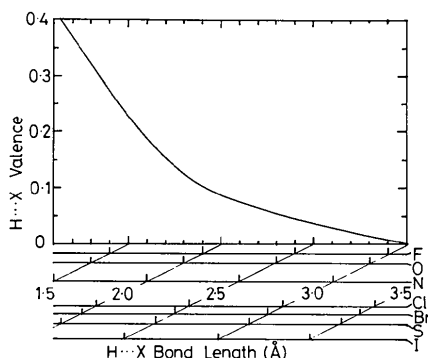


Fig. 1. Bond-valence-bond-length correlation for H...X bonds. The different horizontal scales are to be used depending on the nature of X, e.g. an H...N bond of length 2.5 Å has a valence of 0.08.

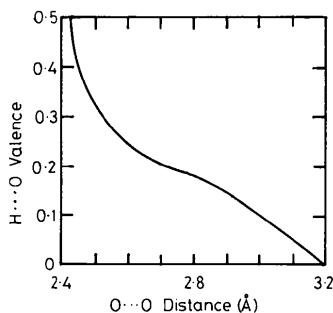


Fig. 2. Bond valence for H...O as a function of O...O distance assuming normal O-H...O bond angles.

Table 2. Values of r_c (Å) and r_a (Å)

(a) Values of r_c							
Group	1	2	3	Period			
1	0.870	1.466	1.802	2.126	2.267	2.438	2.5
2		1.378	1.693	1.967	2.117	2.280	2.4
3				1.849	2.014	2.170	2.07
4				1.814	1.928	1.925	
5				1.804	1.912	1.922	
6				1.794	1.907	1.917	
7				1.790	1.91	1.91	
8				1.760	1.91	1.91	
9				1.685	1.810	1.860	
10				1.794	1.900	1.900	
11				1.895	2.060	2.060	
12				2.084	2.284	2.352	
13		1.371	1.651	1.718	1.902	2.06	
14		1.390	1.624	1.748	1.925	2.042	
15		1.432	1.617	1.760	1.928	2.02	
16		1.43	1.624	1.782	1.926	2.09	
17		1.43	1.632	1.822	1.955	2.09	
18		1.43	1.63	1.94	1.95	2.09	

(b) Values of r_a				
Group	2	3	Period	
14	0.000		4	5
15	0.090	0.300		
16	0.000*	0.490	0.600	0.800
17	-0.110	0.380	0.540	0.801

* Arbitrarily chosen.

Table 3. Correction for non-bonded d electrons

Number of d electrons	D (Å)	Number of d electrons	D (Å)
0	0.0	6	0.033
1	0.020	7	-0.007
2	0.040	8	0.140
3	0.060	9	0.220
4	0.030	10	0.380
5	-0.005		

observed by Brown (1976a). This may not be true in individual cases but the difference will not be large and for many purposes Fig. 2 can give adequate results.

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