Bond valence and bond strength calculations

Pauling: bond strength divided equally between bonds. i.e. undistorted polyhedra

Elaboration: bond strength depends on bond distances, i.e. individual bond-lengths are used. Bond strength calculated individually for each bond are added.
E.g. Brown and Shannon: Empirical bond-strength-bond-length curves for oxides.

Needs empirical ionic radii for each oxidation state, but independent of coordination number.

Another approach:

Bond valence: generalization of bond-order, i.e. assignment of single/double bond.
E.g. O?Keeffe: The bond valence method in crystal chemistry

Needs empirical data for each M-X bond

Using bond-strength-bond-length curves

Relates bond strength to bond length. Several expressions of the form:

Donnay and Allman: $$s = s_0 \left(\frac{\bar{R}}{R} \right)^N$$

s: strength or bond valence of a bond of length R
S_0 : ideal bond strength of the bond of length $\bar{R}$
N: constant different for each cation-anion pair, and sometimes for each cation

Brown and Shannon

$$s = s_0 \left(\frac{R}{R_0} \right)^{-4N}$$

The constant s_0 is chosen, and the constants R_0 and N are determined by fitting to a large number of structures so that the sum of the bond strengths are closest possible to the valence.

In contrast to earlier work, Brown and Shannon use the equation over the whole range of bond strengths. The same curve is used for all bonds between two atomic species. And a large number of structures are included in determining s_0, R_0 and N.

Corrected and uncorrected parameters

?Corrected? for oxygen coordination

Universal bond-strength-bond-lengths parameters, R_1, N_1, for isoelectronic cations can be determined.

(Comparison between results from uncorrected, corrected and universal parameters in table 4.)

Calculated valence sums for V5+ in a number of structures.
Usually within 5%, but significant deviations is observed:

Structural uncertainties?
Second-nearest neighbour effects?
Other effects?

What is the coordination number???

Testing for the correctness of structures

Distinguishing the structure suggestions for $Zn_3(BO_3)_2$

Determining cation distribution

Cation distribution in sanidine, $(Na,K)AlSi_3O_8$
Distribution of Al, Si (Not easy be X-ray diffraction)
Calculate K/Na ratio (not very precise)

Prediction of hydrogen positions

Determining hydrogen positions is not easy from X-ray diffraction.

$MgSO_4$ $4H_2O$: known hydrogen positions

The bond valence method in crystal chemistry
Michael O?Keeffe

Uses the bond-valence concept, i.e. a generalization of bond order

Used for prediction and interpretation of bond lengths

Definition of bond valence:

The valence of a bond between two atoms, *i* and *j* is τ_{ij}. Bond valences are defined so that the sum of all bond valences of the bonds formed by a given atom, *i*, is the atom valency, τ_i.

If Al^{3+} forms four equal bonds, the bond valences are ?.

Correlation between bond length and bond valence:

e.g. Pauling, 1947: $d_{ij} = R_{ij} - b \ln \tau_{ij}$.

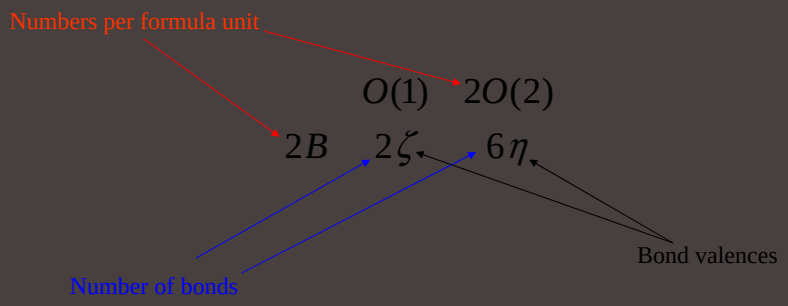
d_{ij} : Bond length
R_{ij}: Length of a single bond ($\tau_{ij} = 1$)
b: constant, ?universal parameter? ~0.37?

Values of Rij can be determined for pairs of atoms, using a variety of coordinations from parameters in experimental crystal structures.

May be used for ?ionic?, ?covalent? and metal-metal bonds.

The Matrix

B_2O_3
High pressure form, B 4-coordinated
$^{iv}B_2{}^{ii}O(1)^{iii}O(2)_2$



Bond valence sums: Horiz: $2\zeta + 6\eta = 2V_B = 6$
Vert: $2\zeta = V_O = 2$ and $6\eta = 2V_O = 4$

B_2O_3, high pressure

	$O(1)$	$2O(2)$
$2B$	2ζ	6η

Bond valence sums: Horiz: $2\zeta + 6\eta = 2V_B = 6$
Vert: $2\zeta = V_O = 2$ and $6\eta = 2V_O = 4$

Solution: $\zeta = 1$
$\eta = 2/3$

$2\zeta + 6\eta = 6$ is the sum of $2\zeta = 2$ and $6\eta = 4$

$R_{BO} = 1.37$?
$d_{ij} = R_{ij} ? b \ln \tau_{ij}$.
B-O(1) = 1.37?
B-O(2) = 1.57?

n cations, m anions: m+n-1 independent valence sums
Bonds from O(1) are equal, and bonds from O(2) are equal (Equal valence rule)

$SrBe_3O_4$

	$O(1)$	$3O(2)$
Sr	3ζ	6η
$2Be(1)$	2ν	6ι
$Be(2)$	4	3κ

5 kinds of bond, valences ζ³#η#ν3#ι3#κ.
But only 5-1=4 independent bond valence sums.
Browns ?equal valences? rule: bonds between equal atoms have almost the same bond valence
In this case: ζ4η#|#ν4ι. (This is the needed extra equation)
Better result when using: $(a-b)/s_{SrO} = (g-d)/s_{BeO}$

More complex:
η-Ga_2O_3
Ga(1)Ga(2)O(1)O(2)O(3)

	$O(1)$	$O(2)$	$O(3)$
$Ga(1)$	ζ	2η	ν
$Ga(2)$	2ι	κ	$\bullet$

6 parameters
5-1=4 equations
3 extra from the equal valence rule

Comparison with use of radii
η-LaOF

LaOF	La - O	La - F
in crystal	2.42	2.60
Bond valence	2.43	2.57
Sum of radii (^{viii}La)	2.54	2.47
Sum of radii (^{vi}La and ^{xii}La)	2.41	2.67

Using the bond valence method

?Verifying crystal structures

?Determining atomic valences and locating atoms:

Ilmenite: $FeTiO_3$
Fe(II)Ti(IV)O_3 or Fe(III)Ti(III)O_3 ?

Hypothesis	V_{Fe}	V_{Ti}
$Fe(II), Ti(IV)$	2.08	3.99
$Fe(III), Ti(III)$	2.22	3.74

Distinguishing O^{2-}, OH^-, F^-
e.g. LaOF

Using the bond valence method

Indications of non-bonded interactions

Example: Al_2O_3 (All oxygen equal, but two Al-O bond lengths)

Two garnets: $Mg_3Al_2Si_3O_{12}$ and $Ca_3Al_2Si_3O_{12}$