Journal of the Arkansas Academy of Science

Volume 71 Article 15

2017

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Recommended Citation

Hardcastle, F. D. and Lykins, R. (2017) "Bond Length and Bond Valence for Tungsten-Oxygen and Tungsten-Sulfur Bonds," *Journal of the Arkansas Academy of Science*: Vol. 71 , Article 15.
DOI: https://doi.org/10.54119/jaas.2017.7120
Available at: https://scholarworks.uark.edu/jaas/vol71/iss1/15

Bond Length and Bond Valence for Tungsten-Oxygen and Tungsten-Sulfur Bonds

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Running Title: Bond Length and Valence for Tungsten-Oxygen and Tungsten-Sulfur Bonds

Abstract

In 1947, Linus Pauling presented an "empirical" dependence of bond valence (*s*, also referred to as bond order) and bond length *R*: $s = \exp(\frac{Ro-R}{b})$, where R_0 is bond length of unit valence and "*b*" is a fitting parameter. Recently, an expression was derived for relating the *b* fitting parameter to theoretically derived atomic orbital exponents. With a method to calculate *b*, both R_0 and atomic orbital exponents can be experimentally determined through optimized fitting for W-O and W-S bonds. In the present study, bond length – valence relationships are found for W-O and W-S chemical bonds using published crystallographic data. The atomic orbital exponent for tungsten was found to be $\zeta_W = 1.534$. Unit valence (single bond) bond lengths were found to be R_o(W-O) = 1.901 Å and R_o(W-S) = 2.307 Å.

Introduction

The oxides and sulfides of tungsten are utilized as catalysts for many industrially important reactions such as green catalytic oxidation processes (Dai *et al.* 2016). Consequently, the molecular structures, bond valences, and oxidation states of the catalytically active species is of importance. A method that has been very successful in relating bond lengths to bond valences (bond orders) and in determining oxidation states is the bond valence method (Brown 2002).

Linus Pauling developed the five basic rules for chemical bonding in 1929 (Pauling 1929). His second rule is the principle of neutrality which states that the principle of local charge neutrality, where the negative charge of each anion is neutralized by the neighboring positive charges of the cations, and the cationic charges are neutralized by neighboring anions. In other words, the total valence of an atom is equal to the sum of the atom's individual bond valences. This is commonly known as the valence sum rule.

In 1947, Pauling published his empirical bond length-bond valence exponential relationship (Pauling 1947).

$$s = \exp\left(\frac{R_o - R}{b}\right) \quad (1)$$

where *s* is bond valence, R_0 is the bond length at unit valence, *R* is bond length associated with *s*, and *b* is a fitting parameter. The range of the values for the fitting parameter "*b*" is anywhere from 0.25 to 0.65 Å. This led to many inconsistencies, hindering chemists from comparing values. As a result, the value 0.37 Å was proposed as a universal constant for the "*b*" parameter (Brown and Altermatt 1985), thereby leaving equation (1) with only one fitting parameter, R_0.

In 2016, Hardcastle derived Pauling's empirical bond length-valence equation using quantum-mechanical considerations. This resulted in an expression for the "*b*" fitting parameter that incorporates the atomic orbital exponents of the bonding atoms (Hardcastle 2016). The "*b*" parameter is now defined as

$$\mathrm{b} = \frac{a_0}{\xi_{ave}} \quad (2)$$

where "*b*" is determined by the Bohr radius, a_0 (0.529 Å), and the average of the atomic orbital exponents of the atoms contributing to the bond. This definition allows the "*b*" parameter to be specific to each type of chemical bond.

In the present study, published crystallographically determined bond lengths for tungsten oxides and sulfides are converted to bond valences using Eqs. (1) and (2), and normalized to the known valence (oxidation state) of the tungsten atom using Pauling's valence sum rule. The R_o and orbital exponent values are numerically optimized to achieve a best-fit to the crystallographic bond distance data.

Methodology

Data for bond lengths of the systems under study were gathered from the Crystallography Open Database

(Grazulis *et al*. 2009). Crystallographic files (cif format) were utilized using the *Mercury 7* program. Bond lengths were recorded into an Excel spreadsheet, then corresponding bond valences were calculated using Eq. (1). Crystallographic bond lengths were recorded to a maximum of 4.5 Å. Bonds outside this range contribute only a negligible amount to an atom's total valence.

All crystallographic data, calculated W-O and W-S bond valences, and calculated tungsten atomic valences are tabulated in a Supplemental File which can be found at http://scholarworks.uark.edu/jaas/.

Results and Discussion

Crystallographic information files (cif files) were collected from the Crystallographic Open Database (Grazulis *et al*. 2009). Single-crystal X-ray diffraction data was collected for tungsten-sulfur (W-S) and tungsten-oxygen (W-O) compounds. Eq. (1) was used to convert published bond lengths to bond valences. Using Pauling's valence sum rule, the total valence of the tungsten was calculated. Then the tungsten atomic orbital exponent and R_0 values were adjusted to minimize the overall error in the spreadsheet.

X-ray diffraction data, was collected for W-O, and W-S bonds lengths. Each environment is represented in Table 1. Data analysis and error minimization led to two formulas one for W-O bonds:

$$s_{W-O} = \exp\left(\frac{1.901 - R}{0.3030}\right) \qquad (3)$$

$$s_{W-S} = \exp\left(\frac{2.307 - R}{0.3027}\right) \qquad (4)$$

The "*b*" values for the W-O and W-S bonds are significantly lower than the assumed universal constant value Brown and Altermatt at 0.37 Å (Brown and Altermatt 1985).

Orbital exponents for oxygen and sulfur have already been determined in previous studies to be ζ_O = 1.959 and ζ_S = 1.962 (Hardcastle 2016). In the present study, the atomic orbital exponent for tungsten was found to be ζ_W = 1.409 using Eq. (2). The bond lengths of unit valence (true single bonds) were found to be R_o(W-O) = 1.901 Å and R_o(W-S) = 2.307 Å.

Table I shows an example from the Supplemental file and also demonstrates how the bond valence method can be used. For the compound O_8W_2Zr (Auray 1995) W-O bond lengths are tabulated in the first column. W-O bond valences (bond orders) are calculated from the bond lengths using Eq. (3), and these are tabulated in the second column. The individual bond valences are added, using Pauling's valences sum rule, to find the total tungsten valence of 6.14 valence units (third column), consistent with the formal oxidation state of 6 for the tungsten cation.

Table 1. W-O Bond Lengths, Calculated Bond Valences, and Calculated W^{6+} Atomic Valence O_8W_2Zr (Auray 1995)

Bond Length (R)	Bond Valence (s)	Total Valence
4.352	0.000307	
1.785	1.4674222	
1.785	1.4674222	
1.785	1.4674222	
3.624	0.0033933	
4.397	0.0002646	
1.736	1.7250002	
4.26	0.0004159	
3.624	0.0033933	
4.397	0.0002646	
3.624	0.0033933	
4.144	0.0006099	
4.26	0.0004159	
4.352	0.000307	
4.397	0.0002646	
4.563	0.000153	
4.26	0.0004159	
4.144	0.0006099	
4.144	0.0006099	
4.352	0.000307	
4.563	0.000153	6.142545

Conclusion

Bond valence—length relationships provide a way to predict validity of proposed crystal structures when used with the valence sum rule. In this study, atomic orbital exponents were used to calculate "*b*" parameters for W-O and W-S bonds: 0.3030 Å and 0.3027 Å, respectively. This parameter was formerly treated as a universal constant. Bond valence—length relationships for W-O and W-S were determined by using published crystallographically determined bond lengths for W-S and W-O chemical bonds. The atomic orbital exponent for tungsten was found to be ζ_W = 1.534. Unit valence (single bond) bond lengths were found to be R_o(W-O) = 1.901 Å and R_o(W-S) = 2.307 Å.

Acknowledgement

The authors gratefully acknowledge Arkansas Tech

https://scholarworks.uark.edu/jaas/vol71/iss1/15
DOI: https://doi.org/10.54119/jaas.2017.7120

University, funding from the Arkansas Tech University Undergraduate Research Grant, and the Arkansas Space Grant Consortium (ASGC).

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