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J. Labrecque
Arkansas Tech University

F. D. Hardcastle
Arkansas Tech University, fhardcastle@atu.edu

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Bond Length and Bond Valence Relationships for Chromium Oxides, Chromium Sulfides, Molybdenum Oxides, and Molybdenum Sulfides

J. Labrecque and F.D. Hardcastle*

Department of Physical Sciences, Arkansas Tech University, Russellville, AR 72801

*Correspondence: fhardcastle@atu.edu

Running Title: Bond Length and Bond Valence Relationships for Oxides and Sulfides of Chromium and Molybdenum

Abstract

Pauling determined an empirical logarithmic dependence of bond order (bond valence), *s*, to bond length, *R*, s = exp(R_0 – R/ b), where R_0 is unit bond length 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 Cr-O, Cr-S, Mo-O, and Mo-S. In the present study, bond length – valence relationships are found for Cr-O, Cr-S, Mo-O, and Mo-S chemical bonds using published crystallographic data. In addition, atomic orbital exponents were found for chromium and molybdenum: ζ_{Cr} = 1.247 and ζ_{Mo} = 1.381. Finally, bond lengths of unit bond valence, or true single bonds, were found using the bond valence model: R_o(Cr-O) = 1.770 Å, R_o(Cr-S) = 2.159 Å, R_o(Mo-O) = 1.893 Å, and R_o(Mo-S) = 2.264 Å.

Introduction

The oxides and sulfides of chromium and molybdenum are utilized as catalysts for many industrially important reactions such as the oxidation of methanol to formaldehyde (Ivanov *et al*, 1998; Klissurski *et al.*, 1993; Weisser and Landa, 1973). Consequently, the molecular structures, bond valences, and oxidation states of the catalytically active species is of keen 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).

In 1947, Linus Pauling developed the following valence sum rule:

$$V_i = \sum_j s_{ij} \tag{1}$$

This relationship states that the total valence (*V*) of an atom will equal the sum of the individual bond valences (s_i) The rule parallels Kirchhoff's law which states the total current at a junction (ie., an atom) is the sum of the individual currents meeting at that point (i.e., the chemical bonds). The valence of different elemental systems can be related to bond lengths using Pauling's empirical relationship:

$$s = \exp\left(\frac{R_o - R}{b}\right) \tag{2}$$

where *s* is the bond valence, sometimes referred to as the bond order, R_0 is the length of a true single bond, R is the length of the individual bond associated with *s*, and *b* is the fitting parameter.

Recently, an equation was derived to calculate the *b* fitting parameter in Eq. (2) from an average of the atomic orbital exponents of the two bonding atoms (Hardcastle 2016):

$$b = \frac{a_o}{(\xi_{ave})} \tag{3}$$

The numerator a_0 is the Bohr radius of a hydrogen atom. The denominator is the average of orbital exponents for the two bonding atoms. Consequently, the bond valence *s* (or, bond order) between any two bonding atoms, given by Eq. (2), exponentially depends on the bond length *R* and the overlap of the electron density which is determined by the average of the orbital exponents (Hardcastle 2016). In this study, published crystallographically determined bond lengths from the oxides and sulfides of chromium and molybdenum are converted to bond valences using Eqs. (2) and (3), and normalized to the known valence (oxidation state) of the chromium or molybdenum atom using Eq. (1). Both, the R_o and Cr/Mo orbital exponent values are optimized to achieve a best-fit to the data.

Methodology

Data for bond lengths of the systems under study were gathered from the Crystallography Open Database (Grazulis *et al*., 2012). 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 Eqs. (2) and (3). The bond valence sum was found using Eq. (1) and the error was determined by comparing to the expected (formal) oxidation state (or valence) of the chromium or molybdenum atom. Both the value of R_o (bond length of unit valence) and the atomic orbital exponent of the Cr or Mo were adjusted to minimize the overall fitting error. 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 bond valences, and calculated Cr or Mo atomic valences are tabulated in a Supplemental File which can be found at http://scholarworks.uark.edu/jaas/.

Results and Discussion

A best fit of 45 compounds and approximately 900 data points (see the Supplemental file) yielded the following bond valence-length relationships for Cr-O, Cr-S, Mo-O, and Mo-S bonds, respectively:

$$s_{Cr-O} = \exp\left(\frac{1.770 - R}{0.3316}\right) \tag{4}$$

$$s_{Cr-S} = \exp\left(\frac{2.159 - R}{0.3308}\right) \tag{5}$$

$$s_{Mo-O} = \exp\left(\frac{1.891 - R}{0.3373}\right) \tag{6}$$

$$s_{Mo-S} = \exp\left(\frac{2.264 - R}{0.3164}\right) \tag{7}$$

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 exponents for chromium and molybdenum were found to be ζ_{Cr} = 1.247 and ζ_{Mo} = 1.381 using Eq. (3). The bond lengths having unit valence (true single bonds) were found to be R_o(Cr-O) = 1.770 Å, R_o(Cr-S) = 2.159 Å, R_o(Mo-O) = 1.893 Å, and R_o(Mo-S) = 2.264 Å.

Table 1 shows an example from the Supplemental file and also demonstrates how the bond valence method can be used. For the compound Li_2MoO_4 (Yip *et al.*, 2010), Mo-O bond lengths are tabulated in the first column. Mo-O bond valences (bond orders) are calculated from the bond lengths using Eq. (6), and these are tabulated in the second column. The individual bond valences are added, using Pauling's valences sum rule Eq. (1), to find the total molybdenum valence of 5.996 valence units (third column), expected to be consistent with the formal oxidation state of 6 for the molybdenum cation.

Table 1: Mo-O Bond Lengths, Calculated Bond Valences, and Calculated Mo^{6+} Atomic Valence in Li_2MoO_4 (Yip *et al.*, 2010)

Bond Length (R)	Bond Valence (s)	Calculated Mo^{6+} Valence
1.759	1.512	
1.766	1.479	
1.769	1.465	
1.770	1.460	
3.316	0.011	
3.700	0.003	
3.712	0.003	5.996

Conclusion

In the present study, Pauling's valence sum rule, Pauling's bond length-valence relationship, a recently derived expression relating a fitting parameter to atomic orbital exponents, and published crystallographic data were used to find bond length – valence relationships for Cr-O, Cr-S, Mo-O, and Mo-S chemical bonds. In addition, atomic orbital exponents were found for chromium and molybdenum: ζ_{Cr} = 1.247 and ζ_{Mo} = 1.381. Finally, bond lengths of unit bond valence, or perfect single bonds, were found using the bond valence model: R_o(Cr-O) = 1.770 Å, R_o(Cr-S) = 2.159 Å, R_o(Mo-O) = 1.893 Å, and R_o(Mo-S) = 2.264 Å.

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