

1 REVISION 1

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3 TITLE: Bond Valence and Bond Energy

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5 Barry R. Bickmore, Owen Craven, Matthew C. F. Wander, Hannah Checketts, Joshua Whitmer,  
6 Christopher Shurtleff, Kiersten Ernstrom, Charles Andros, and Hannah Thompson

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8 Department of Geological Sciences, Brigham Young University, Provo, UT 84602, U.S.A.  
9 E-mail: [barry\\_bickmore@byu.edu](mailto:barry_bickmore@byu.edu)

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12 ABSTRACT

13 The relationship between bond valence and structural energy has never been fully  
14 explored, although a number of predictive models have assumed some simple relationship  
15 between the two. Some of these models relate energy only to bond valence, while others also  
16 take into account other factors, such as bond character. We examined periodic trends in bond  
17 dissociation energies as a function of their ionicity, covalency, and metallicity, defined in terms  
18 of the electronegativity values of the atoms involved. A statistical model was optimized to  
19 describe these trends, allowing us to generate rough bond energy vs. bond valence curves. The  
20 shapes of these curves vary dramatically as a function of bond character, and are strongly  
21 influenced by the lone-pair bond-weakening effect. The curve shapes can be used to rationalize  
22 a number of chemical trends, including the preferred structures of compounds with different  
23 bond types, the prevalence of peroxide and persulfide minerals, preferred bond lengths in oxides,  
24 and the  $pK_a$  values of (hydr)oxy-acids. The last is perhaps the most important, because some  
25 valence-based acidity models are in current use, despite the fact that some aspects of their  
26 rationale are unclear.

## INTRODUCTION

The bond-valence model (BVM) is a standard tool in inorganic chemistry for rationalizing known structures and vetting proposed structures. The fact that the BVM can distinguish between more or less probable structures implies that there must be some systematic relationship between bond valence and structural energy, but the nature of that relationship has proven elusive.

Even so, it is fairly common to simply assume a particular form of the relationship. For example, some schemes for relating energy and stability to bond valence implicitly include the assumption that the energy for a given bond valence is invariant across bond types. The Structure Prediction Diagnostic Software (SPuDS) uses deviations from ideal bond-valence sums to calculate a “global instability index,” which has been successfully used to predict the most stable geometries of compounds with the perovskite structure (Lufaso and Woodward, 2001). Multi-Site Complexation (MUSIC) is a popular type of surface complexation model in which the acidity constants ( $pK_a$  values) for oxide surface groups are fixed using a quantitative structure activity relationship (QSAR) that relates  $pK_a$  values *solely* to deviations from the ideal sums incident to surface oxygen atoms (Hiemstra et al 1996).

Others have challenged the idea that energy cost for a given bond-valence deviation is consistent across bond types. Adams and coworkers (Adams and Rao, 2009; 2014), for example, developed a molecular mechanics force field in which energy cost was assumed to be proportional to the square of bond-valence deviation, but the scaling factors were different between bond types. Wander and Bickmore (2016) created a very accurate, valence-based potential energy model for the Al-Si-H-O system, which required differing, and non-linear bond valence-energy relationships for various bond types. Bickmore and coworkers (2004; 2006a;

1 2006b) showed that the MUSIC model would be more accurate if  $pK_a$  estimates were made by  
2 taking into account both bond character (ionicity vs. covalency) and bond valence  
3 considerations. However, the relationship between  $pK_a$  values and bond character was much  
4 more pronounced for species with low coordination numbers for the central cation.

5 That bond valence cannot be the only consideration for predicting reaction energies  
6 should have been obvious from the start, given that Pauling's (1932) calibration of his  
7 electronegativity scale was based on the fact that single (1.0 v.u.) bonds of different types have  
8 widely disparate dissociation energies. For example, the bond dissociation energy of the  
9 covalently bonded  $F_{2(g)}$  is 158.67 kJ/mol, while more metallically bonded  $Cs_{2(g)}$  has a bond  
10 dissociation energy of 43.919 kJ/mol, and the ionically bonded  $CsF_{(g)}$  has a dissociation energy  
11 of 517.1 kJ/mol. All three of these molecules are held together with a single bond, but their bond  
12 dissociation energies vary by more than a factor of 10 (Wander et al., 2015).

13 We suggest that bond dissociation energies (also called "bond energies") like these  
14 represent the simplest point to begin working out the main features of the relationship between  
15 bond valence and energy. That is, if we can collect examples where both the bond valence and  
16 bond energy are known, we can begin to see if they can be rationalized in terms of periodic  
17 trends related to bond character. Clearly, other considerations (e.g., steric effects and bond angle  
18 strain) affect reaction energies, but simple bond energy additivity schemes have a very long  
19 history, and work well enough that they have often been included in introductory college  
20 chemistry textbooks (Pauling, 1960; Atkins and Jones, 2008). Essentially, dissociation  
21 enthalpies of molecules are distributed among their bonds to obtain individual bond energies for  
22 a given bond type and bond order (valence). It turns out that these individual bond energies are  
23 fairly consistent among species, making it possible to approximate the thermodynamic energy of

1 any compound as the sum of the energies of its constituent bonds. In this way, rough estimates  
2 of reaction energies can be obtained.

3 In this paper, we use previously tabulated bond dissociation energies of molecules and  
4 atomization energies of simple solids to map out the relationship between bond valence, bond  
5 character, and bond energy. We show that the curve shapes, in particular, for plots of bond  
6 dissociation energy vs. bond valence vary dramatically for different types of bonds, and these  
7 shapes are very useful for rationalizing a number of mineralogical/chemical trends. Finally, we  
8 show that the curve shapes may help us solve some long-standing conundrums regarding  
9 valence-based empirical models used to predict acidity.

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## METHODS

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### **Bond Energy**

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Bond energy ( $E_b$ ) was approximated using tabulated experimental bond dissociation  
enthalpy values for molecules, and atomization energies for simple solids (Sanderson, 1976;

1 1983; Gillespie and Popelier, 2001; Luo, 2007; Batsanov and Batsanov, 2012). Bond  
2 dissociation enthalpy data were collected for diatomic molecules, as well as averaged values for  
3 specific bond types, such as C-O single and C=O double bonds, which vary somewhat among  
4 compounds. Atomization energies were collected for simple solids having only one or two types  
5 of atoms and a single bond type. Only compounds in which minimal polyhedral distortion was  
6 present were used, to ensure that all bonds were of approximately the same valence. To obtain  
7 approximate average  $E_b$  values for the solids, we divided atomization energies by the number of  
8 cations per formula unit and the coordination number of the cations.

### 9 **Bond Valence**

10 The bonds for which  $E_b$  values were tabulated were classified according to their bond  
11 valence ( $s_{ij}$ ) values, to form groups with  $s_{ij}$  equal to 0.17 v.u., 0.25 v.u., 0.33 v.u., 0.50 v.u., 0.67  
12 v.u., 0.75 v.u., 1.0 v.u., 2.0 v.u., and 3.0 v.u.

13 The  $s_{ij}$  values for the diatomic molecules were obtained by assuming the valence sum rule  
14 was obeyed. That is, we assumed each atom was valence saturated, and we only chose  
15 molecules with atoms having compatible valences. For example, we used data for the  $\text{NaCl}_{(g)}$ ,  
16  $\text{Na}_2_{(g)}$ , and  $\text{Cl}_2_{(g)}$  molecules, because we could assume a 1.0 v.u. bond in each case, but did not  
17 use data for the  $\text{NaO}_{(g)}$  molecule, because Na is monovalent, while O is divalent. In the case of a  
18 molecule like  $\text{MgO}_{(g)}$ , we assumed a double bond (2.0 v.u.) because both atoms are divalent.  
19 However, in cases where quadrivalent atoms were involved (e.g.,  $\text{Si}_2_{(g)}$ ), a triple bond (3.0 v.u.)  
20 was assumed. (Trends in their  $E_b$  values follow those of triple bonds very closely.)

21 The averaged  $E_b$  values (those for a single type of bond averaged over a number of  
22 species) were tabulated with an associated bond order, so we simply used that bond order as  $s_{ij}$  in  
23 those cases.

1 For the simple solids,  $s_{ij}$  was estimated using the valence sum rule, taking the atomic  
2 valences of the cations divided by their coordination numbers.

### 3 **Bond Character**

4 Bond character (ionicity, covalency, and metallicity) was estimated using the Pauling  
5 electronegativity values of the bonding atoms. To estimate the amount of ionic character in the  
6 bond, we used Equation 1 (Pauling, 1960), where  $I_b$  is the fraction ionic character of the bond  
7 (between 0 and 1), and each  $\chi$  value is the electronegativity of one of the two bonding atoms.

$$8 \quad I_b = 1 - e^{-0.25(\chi_1 - \chi_2)^2} \quad (1)$$

9 An  $I_b$  value of 1 signifies a hypothetical, purely ionic bond, while  $I_b = 0$  denotes a bond with  
10 purely covalent and/or metallic character. The metallic or covalent bond character was estimated  
11 using the average electronegativity of the two bonding atoms ( $\langle\chi\rangle$ ). High average  
12 electronegativity values ( $\langle\chi\rangle \approx 4.0$ ) signify the most covalent bonds, while low average  
13 electronegativity values ( $\langle\chi\rangle \approx 0.7$ ) signify the most metallic bonds. Together, the  $I_b$  and  $\langle\chi\rangle$   
14 values place each bond in a continuum with the most ionic, covalent, and metallic bonds serving  
15 as end members. This is a variation of the quantitative van Arkel-Ketelaar triangle proposed by  
16 Jensen (1995).

### 17 **Periodic Trends**

18 Periodic trends in  $E_b$  were described in three dimensions as a function of  $I_b$  and  $\langle\chi\rangle$ . The  
19 trends were characterized by fitting plane equations to the data. First, the bonds were separated  
20 into groups, according to  $s_{ij}$ . We then used least-squares regression to simultaneously fit a set of  
21 two intersecting planes to predict  $E_b$  values for each  $s_{ij}$  group. (The reason for choosing two

1 planes, rather than some other number, is that this adequately captured the dominant trends.)  
2 The predicted value chosen for each data point corresponded to whichever plane equation gave  
3 the lower  $E_b$  estimate. Given that there were not enough data points in some of the  $s_{ij}$  groups  
4 (especially those with  $s_{ij} < 1$  v.u., obtained from atomization energies) to constrain both planes,  
5 we forced the slopes and intercepts of the plane equations to conform to linear or quadratic  
6 trends with respect to  $s_{ij}$ . Thus, the plane equations for all valence groups were optimized  
7 simultaneously.

8 The resultant plane equations were then used to create hypothetical  $E_b$  vs.  $s_{ij}$  plots for  
9 individual bond types. In addition, we used the plane equations to produce  $E_b$  vs.  $I_b$  plots for  
10 bonds of a given valence, with one of the bonded elements held constant (e.g., 1 v.u. bonds  
11 between O and a range of other elements). The 95% confidence interval for the regression was  
12 calculated using all of the data across all the valence groups.

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## RESULTS AND DISCUSSION

### 15 Trends and Interpolation

16 The predicted  $E_b$  values (kJ/mol) for each  $s_{ij}$  group are described by two plane equations  
17 with the form shown in Eqn. 2. The predicted  $E_b$  value is the lower of the two estimates produced  
18 by the two plane equations. The coefficients of the plane equations derived by the simultaneous  
19 fitting procedure are shown in Table 1. The 95% confidence interval for the regression was  
20  $\pm 190$  kJ/mol for the entire data set, although the low-valence groups ( $s_{ij} < 1$  v.u.) generally  
21 exhibited more scatter.

$$22 \quad E_b = aI_b + b\langle\chi\rangle + c \quad (2)$$

1           The coefficients ( $a$ ,  $b$ , and  $c$ ) in Eqn. 2 were forced to conform to linear or quadratic  
2 equations in  $s$  shown in Eqns. 3-5 for Plane 1 (covalent bonds) and Eqns. 6-8 for Plane 2 (ionic  
3 and metallic bonds). Therefore, the coefficient values shown in Table 1 can be derived from  
4 Eqns. 3-8, as can the coefficient values for any arbitrary value of  $s_{ij}$ .

$$5 \quad a_1 = -136s_{ij}^2 + 657s_{ij} + 11.6 \quad (3)$$

$$6 \quad b_1 = 41.4s_{ij}^2 - 194s_{ij} + 12.1 \quad (4)$$

$$7 \quad c_1 = 592s_{ij} - 23.6 \quad (5)$$

$$8 \quad a_2 = 99.2s_{ij} + 0.904 \quad (6)$$

$$9 \quad b_2 = 294s_{ij} + 14.3 \quad (7)$$

$$10 \quad c_2 = -45.7s_{ij}^2 - 424s_{ij} + 77.0 \quad (8)$$

11           The overall shape of the  $E_b$  distribution is best illustrated by the 1.0 v.u. bonds, which  
12 exhibit the most coverage over the entire range of bond types. Fig. 1a shows a 3D scatter plot  
13 ( $E_b$  vs.  $I_b$  and  $\langle\chi\rangle$ ) of the 1.0 v.u. data (symbols), along with the two planes from Table 1 fitted to  
14 the 1.0 v.u. data, forming a hinged-plane shape. Fig. 1b shows a surface plot of the optimized  
15 planes, providing a more comprehensive view of the general shape of the data distribution. The  
16 main trends in the data can be described as follows. 1) The lowest  $E_b$  single bonds are the most  
17 metallic. 2) Moving toward the most ionic or covalent bonds, the  $E_b$  values rise steeply, but most  
18 steeply toward the most covalent bonds. 3) Along a certain boundary (the hinge between the  
19 planes), the  $E_b$  values begin to go downward toward the covalent limit.



1           The remaining data and fitted planes are shown in Fig. 2a-d. Although some valence  
2 groups exhibit broader coverage of possible bond types than others, and there is considerable  
3 scatter in the data, the hinged-plane model appears to essentially capture the trends in the  $E_b$  data  
4 as a function of bond character.

5           Where data are not available, the model appears to provide reasonable interpolations.  
6 This point is more clearly illustrated in Fig. 3, where  $E_b$  values are plotted vs.  $I_b$  for bonds  
7 involving O in each  $s_{ij}$  group. In  $s_{ij}$  groups for which the most data points exist, the model  
8 predictions clearly mimic the trends, and all the data points are within the 95% confidence limit  
9 of  $\pm 190$  kJ/mol. In the groups for which no data is available for bonds involving O, the  $E_b$   
10 predictions are constrained by other types of bonds, providing plausible estimates. We did not  
11 include any data for M-O triple (3.0 v.u.) bonds, for instance, because O is divalent, so any such  
12 bonds would not meet our selection criteria. However, it is generally agreed that the atoms in  
13  $\text{CO}_{(g)}$  molecules are linked by a triple bond, and this is supported by both  $E_b$  and bond-length  
14 data for C-O single, double, and triple bonds (Glockler, 1958). In any case,  $E_b = 1077$  kJ/mol for  
15  $\text{C}\equiv\text{O}$  triple bonds (Darwent, 1970), which is reasonably close to the model prediction of 1130  
16 kJ/mol. Similarly,  $\text{C}\equiv\text{S}$  triple bonds were not included in our calibration set, but the atoms in  
17  $\text{CS}_{(g)}$  are connected by a  $\text{C}\equiv\text{S}$  triple bond, for which  $E_b = 761$  kJ/mol (Darwent, 1970), close to  
18 our model-estimated value of 693 kJ/mol.

19           The most striking feature of the plots in Figs. 1-3 is the abrupt downturn in the  $E_b$  values  
20 moving toward the covalent limit. Sanderson (1976; 1983) identified this as the lone-pair bond-  
21 weakening effect (hereafter “the lone-pair effect,” for the sake of brevity). As the bonds incident  
22 to an atom become more covalent, non-bonding valence electrons (lone pairs) coalesce to  
23 become more stereoactive, both repelling and weakening the neighboring bonds (Gillespie and

1 Hargittai, 1991; Bickmore et al., 2013; Brown, 2014; 2016). This effect is more pronounced for  
2 low-valence bonds.

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#### 4 **$E_b$ vs. $s_{ij}$ Curves and Chemical Trends**

5 Given the large error estimate for our model, on the one hand, it clearly has limited  
6 usefulness for accurately predicting  $E_b$  for individual bonds. On the other hand, the model does  
7 describe broad trends in  $E_b$  values for bond types across the periodic table, so it is reasonable to  
8 suppose that  $E_b$  vs.  $s_{ij}$  curves generated from the model equations would at least provide  
9 significant insight about the rough shape of the relationship for a given bond type.

10 **Covalent, Ionic, and Metallic Bonds.** If so, the shapes of these curves can be used to  
11 rationalize a number of chemical trends. Fig. 4a, for instance, plots the predicted  $E_b$  vs.  $s_{ij}$  curve  
12 for N-N bonds, which are highly covalent. The most covalent bond types exhibit a concave-  
13 upward shape, which occurs because the lone-pair effect is more effective for lower-valence  
14 bonds. Fig. 4b shows the plot for Ba-O bonds, which are strongly ionic. This relationship is  
15 characterized by a linear increase in bond energy for very low  $s_{ij}$  values ( $< 0.2$  v.u.), followed by  
16 a slope break and a more gently rising, convex upward function at higher  $s_{ij}$  values. Given these  
17 curve shapes, we would expect very covalently bonded compounds to favor fewer, higher- $s_{ij}$   
18 bonds, and very ionically bonded compounds to favor more, lower- $s_{ij}$  bonds. This is, in fact, the  
19 case. The most covalent compounds tend to form molecules held together by single, double, or  
20 triple bonds. In condensed phases, the molecules are held together by Van der Waals forces or  
21 weak hydrogen bonds, resulting in relatively low melting and boiling temperatures. N-N bonds  
22 are an excellent example, because  $N_{2(g)}$  is very stable, is held together by a triple bond, and  
23 condenses only at very low temperatures ( $< 77$  K). Ionic compounds, however, tend to form

1 network solids, held together by a larger number of low- $s_{ij}$  bonds.  $\text{BaO}_{(s)}$ , for example, has  
2 octahedrally coordinated atoms connected by  $\sim 0.33$  v.u. bonds, and the liquid-phase boiling  
3 temperature is 2270 K. Fig. 4c shows the curve for Cu-Cu bonds, which are metallic. The curve  
4 initially goes up at low  $s_{ij}$ , but then flattens and even goes downward at high  $s_{ij}$ . Once again, this  
5 curve shape would favor the formation of a network solid held together by low  $s_{ij}$  bonds, and a  
6 high boiling point. In fact,  $\text{Cu}_{(s)}$  has 12-coordinated atoms, connected by  $\sim 0.17$  v.u. bonds, and  
7 the liquid phase has a boiling point of 2833 K (Straumanis and Yu, 1969; Weir et al., 1971;  
8 Greenwood and Earnshaw, 1997; Haynes, 2016).

9 **Bonds With Oxygen.** The  $E_b$  vs.  $s_{ij}$  curves for oxides are of particular interest for  
10 mineralogists and geochemists (Bunker and Casey, 2016), so they are a good choice to examine  
11 in more detail. Fig. 5a shows the curves for an arbitrary series of M-O bonds (where M is a  
12 cation) with  $0 < I_b < 0.9$ . The most covalent bonds (low  $I_b$ ), once again, have a concave upward  
13 shape, whereas the most ionic bonds linearly increase at low M-O bond valence ( $s_{MO}$ ), and then  
14 above a certain point (the intersection of the two planes) exhibit a convex upward shape. Bonds  
15 with intermediate  $I_b$  values have a concave upward shape at low  $s_{MO}$  (although their curvature is  
16 less than those for the most covalent bonds), and a convex upward shape above the plane  
17 intersection point. The plane intersection point occurs at systematically lower  $s_{MO}$  values the  
18 more ionic the bond. The locations of the intersection points ( $s_{MO,break}$ ) as a function of  $I_b$  are  
19 described by Eqn. 9.

$$20 \quad s_{MO,break} = -8.71I_b^3 + 23.0I_b^2 - 20.8I_b + 6.69 \quad (9)$$

21 The import of these curves can more easily be seen in Fig. 5b, where  $E_b/s_{MO}$  is plotted vs.  
22  $s_{MO}$ . The optimal  $s_{MO}$  value for a given bond type should be where  $E_b/s_{MO}$  is maximized, at least  
23 to the extent that other factors do not come into play. In all cases, there is a local maximum at

1  $s_{MO,break}$ , but extrapolation of our curves to  $s_{MO} = 0$  v.u. would cause  $E_b/s_{MO}$  to go to infinity.  
2 Obviously, this is impossible, because  $s_{MO} = 0$  v.u. would, by definition, have  $E_b = 0$  kJ/mol.  
3 Still, the data we used to calibrate our model included bond valence values as low as 0.17 v.u.,  
4 which is where we have truncated the curves in Figs. 5a and 5b. It appears, therefore, that the  
5 upturn in  $E_b/s_{MO}$  at low  $s_{MO}$  is probably real, even if it cannot be extrapolated with any  
6 confidence to  $s_{MO}$  values lower than 0.17 v.u.

7 For the most ionic bonds shown in Fig. 5b ( $I_b > 0.6$ ), the  $E_b/s_{MO}$  values at  $s_{MO} = 0.17$  v.u.  
8 are higher than those at  $s_{MO,break}$ . We expect, therefore, the optimal  $s_{MO}$  values for these bonds to  
9 be at or lower than  $s_{MO,break}$ , and probably controlled largely by O-O distances.

10 For the most covalent bonds, such as O-O ( $I_b = 0$ ),  $E_b/s_{MO}$  values continue to rise with  
11  $s_{MO}$ , with no slope break until above 3 v.u. In these cases, therefore, we expect the optimal  $s_{MO}$   
12 values to be limited by the bond-valence sums incident to the atoms involved. That is, the bonds  
13 will adopt as high  $s_{MO}$  values as possible, given the valence sum limitations.

14 Clearly, the shapes of the  $E_b/s_{MO}$  vs.  $s_{MO}$  curves in Fig. 5b imply that the optimal  $s_{MO}$   
15 values for bonds involving O should be less than  $s_{MO,break}$  for both the most ionic, and the most  
16 covalent, bonds. However, the shapes of the  $E_b/s_{MO}$  vs.  $s_{MO}$  curves for M-O bonds with  
17 intermediate covalency/ionicity imply that the optimal  $s_{MO}$  values should be very similar to  
18  $s_{MO,break}$ . These implications can be tested by referring to Brown and Skowron's (1990)  
19 definition of "Lewis acid strength" ( $L_A$ ) for cations. The cation valences are divided by their  
20 average observed coordination numbers in oxide crystal structures to obtain  $L_A$ . A cation  $L_A$   
21 value thus has units of v.u., and serves as an expectation value for the valence of bonds between  
22 that cation and O. Brown and Skowron (1990) found that the  $L_A$  values of main-group cations in  
23 their highest oxidation states were highly correlated with cation electronegativity. In Fig. 6, we

1 plot the  $L_A$  values of a number of these cations (Brown, 2002) vs. the  $I_b$  values of the respective  
2 M-O bonds. For comparison, we also plot the calculated  $s_{MO,break}$  values for bonds with a range  
3 of  $I_b$  values, and as expected,  $s_{MO,break}$  is higher than  $L_A$  for the most ionic ( $I_b > 0.77$ ) and covalent  
4 ( $I_b < 0.6$ ) bonds, but closely corresponds to  $L_A$  for intermediate bonds.

5 **Peroxide and Persulfide Minerals.** The curves in Fig. 5 can also readily be used to  
6 explain why, for instance, there are so few peroxide minerals. There are only two known  
7 peroxide minerals, studtite and metastudtite, which are uranyl peroxides that form due to  
8 radiolysis of water (Deliens and Piret, 1983). Peroxides have O-O single bonds, but Fig. 5b  
9 shows that O-O bonds ( $I_b = 0$ ) of 1.0 v.u. have much lower  $E_b/s_{MO}$  values than more ionic M-O  
10 bonds. In fact, O-O bonds cannot begin to compete with the more ionic bonds, except at  $\sim 2.0$   
11 v.u. Therefore, in nature O almost always occurs as zero-valent ( $O_{2(g)}$ ) or as divalent ( $O^{2-}$ ) in  
12 oxides, but almost never as univalent ( $O^{1-}$ ) in peroxides.

13 Some persulfide minerals like pyrite ( $FeS_2$ ) are relatively common, in contrast, and the  $E_b$   
14 vs.  $s_{MS}$  and  $E_b/s_{MS}$  vs.  $s_{MS}$  curves in Figs. 7a and 7b show why that is to be expected.  $E_b/s_{MS}$   
15 values for S-S single bonds ( $I_b = 0$ ,  $s_{MS} = 1.0$  v.u.) are much more competitive with those of more  
16 ionic M-S bonds, than the  $E_b/s_{MS}$  values of O-O single bonds are with those of more ionic M-O  
17 bonds.

18 **(Hydr)oxy-acid Dissociation Constants.** Oxide-water interfacial chemistry is important  
19 in a number of scientific fields, not least the fate and transport of contaminants in subsurface  
20 environments (Stumm, 1992). It is typical to treat the equilibria between oxide surfaces and  
21 aqueous species via surface complexation models (SCMs). These involve equilibrium constants  
22 for reactions between surface functional groups and aqueous species, for which the near-surface  
23 activities of ionic species are corrected from the bulk using various electrostatic models to

1 account for charge build-up at the interface. One pervasive problem with SCMs is that surfaces  
2 usually have a variety of functional groups, the type, number, and spatial distribution of which  
3 cannot easily be characterized. Furthermore, the interfacial charge build-up tends to smear out  
4 the equilibrium response of the different surface functional groups during titration, so that their  
5 response is difficult to differentiate in the macroscopic data. As a result, while SCMs nominally  
6 provide molecular-scale interpretations of titration data, such interpretations are fundamentally  
7 non-unique (Westall and Hohl, 1980)

8 Hiemstra and coworkers (1989; 1996) have developed the Multi-Site Complexation  
9 (MUSIC) model to provide estimates of some of the most influential parameters in SCMs of  
10 oxides, providing more rigid constraints on their molecular-scale interpretations. These  
11 influential parameters include the types and spatial densities of oxide surface functional groups,  
12 and their  $pK_a$  values. The acidity estimates are based on a quantitative structure-activity  
13 relationship (QSAR) that relies solely on the deviation of the oxygen bond valence sums from  
14 the ideal 2.0 v.u. in the conjugate bases of (hydr)oxy-acid solution monomers. The MUSIC  
15 model has been widely used, largely because it has no well-developed competitors, but several  
16 groups have provided some strong criticisms of the model, which are summarized by Bickmore  
17 (2014). The following is a list of criticisms relevant to this discussion.

18 First, the MUSIC acidity QSAR is calibrated on solution monomers in particular  
19 dissociation states, but not others. Because the bond-valence analysis of the monomers employs  
20 idealized geometries, application to multiple acid dissociations of a molecule can result in wildly  
21 inaccurate  $pK_a$  estimates. For example, the QSAR can relatively accurately estimate the  $pK_a$   
22 value for the first acid dissociation of silicic acid ( $\text{Si}(\text{OH})_4$ ), but not the second. Given that the  
23 relationship is subsequently applied to variable-charge surfaces, this is a potential problem. It is

1 worth noting, however, that among the solution monomers this is a critical problem for oxy-acids  
2 like silicic acid, but not so much for hydroxy-acids like  $\text{Fe}^{3+} \cdot 6\text{H}_2\text{O}$  (Bickmore et al., 2004;  
3 2006a; 2006b; Bickmore, 2014). (Here we refer to acids in which  $-\text{OH}$  groups dissociate as oxy-  
4 acids, and those in which  $-\text{OH}_2$  groups dissociate as hydroxy-acids.)

5         Second, when the QSAR has been applied to surfaces, in some cases idealized cation  
6 coordination structures have been employed, but in others polyhedral distortion has been taken  
7 into account using bond lengths from bulk crystal structures. But if these kinds of distortions are  
8 sometimes important, then bond relaxation at solid surfaces should be taken into account, as  
9 well. Bickmore and coworkers (2004; 2006a; 2006b) found that accurate  $\text{p}K_a$  estimates for oxy-  
10 acid solution monomers require bond relaxation to be taken into account across multiple acid  
11 dissociations, and they accomplished this by referring to DFT-calculated gas-phase geometries of  
12 the conjugate bases. However, they also found that idealized geometries, in which all M-O  
13 bonds are assumed to have the same valence, work as well or better than calculated, distorted  
14 structures for the hydroxy-acids.

15         Third, the conceptual foundation of the MUSIC approach is the assumptions that acidity  
16 is related to deviations for ideal valence sums on oxygen atoms, and that a given deviation in v.u.  
17 has the same energy cost across bond types, but both of these assumptions are demonstrably  
18 flawed. Bickmore and coworkers (2006b; 2009) used *ab initio* molecular dynamics simulations  
19 of water and oxy-acids in water to show that, on a time-averaged basis, the valence sums to the  
20 oxygen atoms in these species hover very closely around the ideal value of 2.0 v.u., and we have  
21 already demonstrated here that dissociation energies vary widely as a function of bond type. If  
22 the model is conceptually incorrect, any successes must involve fortuitous cancellation of errors,

1 which raises questions about how well it can be applied to structures significantly different from  
2 those included in the calibration set.

3 Some of these questions were addressed by Bickmore and coworkers (2006a; 2006b),  
4 who optimized Eqn. 10 to relatively accurately estimate “intrinsic” (i.e., corrected for simple  
5 electrostatic effects)  $pK_a$  values across multiple dissociations for (hydr)oxy-acid monomers.

$$6 \quad pK_a = 60.5L_B + \beta I_b + 18.1 \quad (10)$$

7 Here,  $L_B$  is the Lewis base strength of the oxygen atom in the conjugate base, which is based on  
8 the valences of incident M-O and strong H-O bonds,  $I_b$  is the fraction ionic character (Eqn. 1) of  
9 the M-O bond, and  $\beta$  is a unitless parameter that is different for molecules with different  
10 coordination numbers for the central cation. For triangular oxy-acids (e.g., carbonic acid,  
11  $\text{CO}(\text{OH})_2$ ), tetrahedral oxy-acids (e.g., silicic acid,  $\text{Si}(\text{OH})_4$ ), and 6-coordinated hydroxy-acids  
12 (e.g.,  $\text{Fe}^{3+} \cdot 6\text{H}_2\text{O}$ ),  $\beta = 51.6, 20.6,$  and  $5.3,$  respectively.

13 This was an encouraging result, and a clear indication that both bond valence and bond  
14 character must be incorporated in a robust acidity model. Questions remained, however, and it  
15 was not readily apparent how to apply Eqn. 10 to oxide surface functional groups. After  
16 discussing these remaining issues, Bickmore (2014) observed that to solve them, “we need to  
17 better understand the relationship between bond valence and energy.”

18 In fact, the shapes of the estimated  $E_b$  vs.  $s_{MO}$  curves for oxides shown in Fig. 5a can be  
19 used to construct plausible qualitative explanations for the apparent anomalies. For example, the  
20 bond-valence terms in all the QSARs discussed above seem to depend only on the structure of  
21 the conjugate base, rather than some difference between the acid and base structures, whereas the  
22 reaction energy of acid dissociation must, by definition, be due to some difference between the  
23 two systems. Furthermore, the bond-valence sums incident to all the atoms in several oxy-acids



1 and their conjugate bases remain essentially constant, and close to the ideal values, both before  
2 and after dissociation in AIMD simulations (Bickmore et al., 2006b; Bickmore et al., 2009).  
3 Even the total valence of each type of bond (M-O and H-O) remains constant. Therefore, we  
4 posit that differences in acidity among these species might be partially attributable to energy  
5 differences caused by the distortion of the molecule during acid dissociation, coupled with the  
6 relative energetic favorability of the distortion due to the shapes of  $E_b$  vs.  $s_{MO}$  curves (Fig. 5a).  
7 In the regions of the  $E_b$  vs.  $s_{MO}$  curves where  $s_{MO} < s_{MO,break}$ , within which most bonds in  
8 condensed phases are expected, the curvature is concave upward, and increases as the bonds  
9 become more covalent. In the regions where  $s_{MO} > s_{MO,break}$ , the curves become more convex  
10 upward as the bonds become more ionic. Consider a case where there are two 0.5 v.u. bonds  
11 incident to an atom, which then distort to 0.7 and 0.3 v.u. If this region of the  $E_b$  vs.  $s_{MO}$  curve is  
12 a straight line, the average  $E_b$  value for the two bonds would remain unchanged, but a concave  
13 upward curve would result in a higher average  $E_b$ , and a convex upward curve would result in a  
14 lower average  $E_b$ . Supposing the bonds in question mostly form in the region where  $s_{MO} <$   
15  $s_{MO,break}$ , distortions in the molecule due to acid dissociation would be stabilized to the degree the  
16 M-O bonds are covalent. In the region where  $s_{MO} > s_{MO,break}$ , the distortions would be less  
17 destabilized for the more covalent bonds.

18 Differences in acidity would also depend on  $s_{MO}$  and the coordination number of the  
19 central atom, because these would control the region of the  $E_b$  vs.  $s_{MO}$  curves over which the  
20 bond distortions occur, and the degree of distortion required by individual bonds in response to  
21 an acid dissociation event, respectively.

22 Furthermore, this mechanism might also provide an explanation for why Bickmore and  
23 coworkers found that idealized molecular structures could be used for the hydroxy-acid bond-

1 valence calculations, but relaxed structures were required for the oxy-acids. That is, the bonds in  
2 the hydroxy-acids may occur in more linear regions of the curves where there is little energetic  
3 difference between distorted and undistorted forms, and their individual bonds would distort less,  
4 because the coordination numbers of their central atoms are higher than those for the oxy-acids.

5 The shapes of our  $E_b$  vs.  $s_{MO}$  curves, and thus our proposed mechanism for differences in  
6 acidity among (hydr)oxy-acids, are heavily influenced by the lone-pair effect. In fact, our  
7 proposed mechanism is consistent with the findings of Lauvergnat et al. (1996), who used  
8 valence-bond analysis to show that, for  $H_nX$ -H single bonds ( $H_nX = H_2N$  to F), the dissociation  
9 products of the more covalently bonded compounds undergo an electronic reorganization that  
10 stabilizes the  $H_nX^-$  fragments, and thus lowers the dissociation energy compared to what it would  
11 otherwise be, in the absence of the lone-pair effect.

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13

## IMPLICATIONS

14

We conclude with the following implications of our findings.

15

1. Some have assumed a very simple, and usually linear, relationship between bond  
16 energy and bond valence, but this would only approximately be the case in a  
17 limited range of circumstances (ionic bonds with low valence, or over a very  
18 limited range of bond valence and bond character).

19

2. If two similar molecules undergoing the same reaction have similar (e.g., linear)  
20  $E_b$  vs.  $s_{ij}$  dependencies, then it is likely that a purely structural comparison will  
21 produce a reasonable prediction (e.g., comparing bond valences to determine  
22 relative  $pK_a$  values). However, if one has a significantly different magnitude or

1 curvature than the other in the region of reaction, then such a simple comparison  
2 is inadequate.

- 3 3. In general, the *shapes*, as well as the relative magnitudes, of the complex  $E_b$  vs.  
4  $s_{ij}$  curves are predictors of important mineralogical/chemical trends, because  
5 these determine the relative energetic efficiency with which atomic valences can  
6 be satisfied by different combinations of available bond types. However, other  
7 factors, such as repulsion between non-bonded atoms and available valence, also  
8 come into play.
- 9 4. The lone-pair bond-weakening effect is a dominating factor for determining  $E_b$   
10 vs.  $s_{ij}$  curve shapes, but we have found no discussion of the effect in the  
11 mineralogical literature. Certainly this merits a prominent place in any BVM-  
12 based theoretical discussions of mineralogy or structural chemistry (c.f.,  
13 Hawthorne, 2015), because it explains why some types of structures are  
14 uncommon in nature. Brown (2011; 2014; 2016) has recently addressed the steric  
15 effects of non-bonding valence electrons within the framework of his flux theory  
16 of chemical bonding, which is an extension of the ionic model and the BVM. It  
17 should be possible to extend it further to encompass the effects on bond energies  
18 described here.
- 19 5. If QSARs based on bond valence are to be accurate over a broad range of  
20 conditions, other factors, such as bond character, must be taken into account.

## 22 ACKNOWLEDGEMENTS

1 The authors gratefully acknowledge support for this research from the National Science  
2 Foundation (EAR-1424682) and the College of Physical and Mathematical Sciences  
3 undergraduate mentoring program at Brigham Young University. Professor I. D. Brown and an  
4 anonymous reviewer provided very helpful comments on the original manuscript.

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## TABLES

6 **Table 1.** The predicted  $E_b$  values (kJ/mol) for each  $s_{ij}$  group are described by two plane  
7 equations of the form  $E_b = aI_b + b\langle\chi\rangle + c$ . The predicted  $E_b$  value is the lower of the two  
8 estimates produced by the two plane equations. Plane 1 describes the more covalent bonds,  
9 while Plane 2 describes the more ionic and metallic bonds.

$s_{ij}$ (v.u.)	Plane 1			Plane 2		
	$a$	$b$	$c$	$a$	$b$	$c$
0.17	117	-19.0	75.2	17.4	63.3	5.13
0.25	167	-33.7	125	25.7	87.7	-31.7
0.33	216	-47.8	174	34.0	112	-69.3
0.50	306	-74.4	273	50.5	161	-146
0.67	389	-98.6	371	67.0	210	-226
0.75	428	-110	421	75.3	235	-266
1.0	533	-140	569	100	308	-392
2.0	780	-210	1161	199	602	-953
3.0	755	-197	1750	298	895	-1610

10





## FIGURE CAPTIONS

1

2 **Figure 1.** a) 3D scatter plot ( $E_b$  vs.  $I_b$  and  $\langle\chi\rangle$ ) of the 1.0 v.u. data (green symbols), along with  
3 the two planes (green) from Table 1 fitted to the 1.0 v.u. data, forming a hinged-plane shape.  $E_b$   
4 is given in kJ/mol. b) Surface plot of the 1.0 v.u. optimized plane equations. The color scale  
5 represents  $E_b$  in kJ/mol.

6

7 **Figure 2.** Plane fits for the remaining valence groups: a) 0.17 (blue) and 0.33 v.u. (red). b) 0.25  
8 (pink) and 0.5 v.u. (blue). c) 0.67 (red) and 0.75 v.u. (blue). d) 2.0 (blue) and 3.0 v.u. (pink).

9

10 **Figure 3.**  $E_b$  values are plotted vs.  $I_b$  for bonds involving O in each valence group. The markers  
11 represent the actual data, while the lines of the corresponding colors represent the estimates of  
12 the plane equations.

13

14 **Figure 4.**  $E_b$  vs.  $s_{ij}$  curves for various bond types, generated by our hinged-plane model. The  
15 blue-shaded band indicates the 95% confidence interval, and the points represent measured bond  
16 energies. a) N-N ( $I_b = 0$ ,  $\langle\chi\rangle = 3.04$ ). b) Ba-O ( $I_b = 0.80$ ,  $\langle\chi\rangle = 2.17$ ). c) Cu-Cu ( $I_b = 0$ ,  $\langle\chi\rangle =$   
17 1.90).

18

19 **Figure 5.** a)  $E_b$  vs.  $s_{MO}$  and b)  $E_b/s_{MO}$  vs.  $s_{MO}$  curves for M-O bonds in the range  $0 < I_b < 0.9$ ,  
20 where O is in the 0, -1, or -2 oxidation states, and M is a cation or another O atom.

21

1 **Figure 6.** Here the Lewis acidity ( $L_A$ ) values of a number cations (Brown, 2002) vs. the  $I_b$  values  
2 of the respective M-O bonds. For comparison, we also plot the calculated  $s_{MO,break}$  values for  
3 bonds with a range of  $I_b$  values, and as expected,  $s_{MO,break}$  is higher than  $L_A$  for the most ionic ( $I_b$   
4  $> 0.77$ ) and covalent ( $I_b < 0.6$ ) bonds, but closely corresponds to  $L_A$  for intermediate bonds.

5

6 **Figure 7.** a)  $E_b$  vs.  $s_{MS}$  and b)  $E_b/s_{MS}$  vs.  $s_{MS}$  curves for M-S bonds in the range  $0 < I_b < 0.6$ ,  
7 where S is in the 0, -1, or -2 oxidation states, and M is a cation or another S atom.

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