Structure and Acidity in Aqueous Solutions and Oxide–Water Interfaces

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Abstract There have been a number of attempts to relate structural descriptors based on the bond-valence theory to the Brønsted acidity of (hydr)oxyacid monomers and oxide surface functional groups, via simple quantitative structure–activity relationships (QSARs). These models show some promise, but since they have been calibrated solely on monomers, it is difficult to know whether oxide surface functional groups are within their domain of applicability. In fact, there are strong reasons, including direct ab initio computation of equilibrium constants for surface functional groups, for doubting whether acidity QSARs based on the bond-valence theory are yet capable of accurately predicting acidity at the level of individual surface functional groups, despite some apparent successes. For progress to continue, we must further develop the relationship between bond valence and structural energy, so that we will be better able to construct widely applicable models

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Abbreviations

BVT   Bond-valence theory
G   Global instability index
MUSIC   Multisite complexation
QSAR   Quantitative structure–activity relationship
SBE   Solvation, bond strength, and electrostatic model
SCM   Surface complexation model

1   Introduction

Although the bond-valence theory (BVT) is primarily meant to rationalize and predict molecular structures in solids, chemists naturally try to extend structural models to rationalize and predict reactivity. If a model helps us understand why particular equilibrium structures are preferred, for instance, perhaps quantifying the principles underlying the model can help us predict energetic differences between structural states, which are the bases for both thermodynamic and kinetic theory. The BVT is an excellent vehicle for exploring structure–energy relationships, because it is in some respects quantitatively predictive, and boils down complex, multi-body interactions into a single parameter, the bond-valence sum.

In this chapter, I review several attempts to relate bond valence to equilibrium constants for the acid dissociation of (hydr)oxo-monomers and oxide surface functional groups. Rather than exhaustively reviewing the literature on this subject, I have opted to attempt a concise description of the state of the field. For a number of reasons, reaction energetics at individual surface functional groups is particularly difficult to assess, so models capable of estimating equilibrium constants for these reactions are badly needed.

While there have been some successes in this area, however, BVT principles must be applied carefully to these systems. Bond-valence parameters are calibrated on precisely known structures of crystalline solids, for instance, so the application of the BVT to liquids and solid–liquid interfaces, for which less precise structural information is available, may not be straightforward. Furthermore, BVT-based reactivity models usually involve an implicit assumption that, at least for the purpose of predicting particular types of reaction energies, bond lengths are the dominant aspect of the structure. This may, or may not, be the case, depending on the reactions of interest.

It is important, therefore, to address two questions as we discuss various models. (1) How might the BVT-based structural descriptors employed relate to the potential energy surface? (2) What is the model's domain of applicability? That is, when should such models work, and when should they fail?

2 Bond Valence, Energy, and QSARs

The best-developed link between bond valence and energy involves the valence sum rule (Eq. 2 in chapter "Bond Valence Theory"), which is the backbone of the BVT. The valence sum rule predicts that the summed valence of bonds incident to ion i (ΣS_i) should counterbalance its atomic valence (V_i), and in fact, calculated valence sums usually deviate significantly from the ideal only in cases where the structure is strained [1]. It might be possible, therefore, to link deviation from the ideal valence sum (ΔV) with some predictable energy cost. In fact, a number of studies have shown that ΔV or ΔV^2 can be related to a significant part of the structural potential energy. Salinas-Sanchez et al. [2], for example, defined the Global Instability Index (G) for crystals in terms of ΔV, normalized and averaged over all atoms in a crystal formula unit (see Eq. 23 in chapter "Bond Valence Theory"), and showed that it was a good predictor of phase stability. Perez-Mato et al. [3] showed that the G is proportional to energy maps of certain distortion modes in stuffed tridymite-type structures, and in chapter "Bonding at Oxide Surfaces" of this volume, Poeppelmeier and Enterkin show how the G can be modified to correctly predict the relative stability of surface reconstructions. Rappe and coworkers [4, 5] developed a very successful force field for certain oxide materials, in which one of the potential terms is proportional to ΔV. Adams and coworkers [6–9] have developed potentials based on ΔV^2, which they have successfully used with Reverse Monte Carlo methods to investigate diffusion pathways in glasses. (See also chapter "Practical Considerations in Determining Bond Valence Parameters" in this volume.)

These attempts to explicitly relate ΔV to energy are relatively recent, however, and a more common approach has been to create QSARs by finding correlations between reaction energies and structural descriptors based on bond-valence considerations. Although QSARs of many types are common [10], and can under certain circumstances predict reaction energies to within as little as 0.5 kcal/mol [11], they typically suffer from two problems: (1) Whereas reaction energies reflect the difference between two structural states, QSARs are often keyed to "static" aspects of molecular structure – e.g., the number of particular types of functional groups, the electronegativities of particular atoms, dipole moments, polarizability, molecular shape, and molecular volume [11]. (2) The relationships between these static structural descriptors and reaction energies can be complex, and therefore simple QSAR correlations may only be valid under a restricted set of circumstances, in which other important structural factors are held approximately constant. Bond valence has so far been quantitatively related solely to bond length, and it is likely that other structural factors, such as bond directionality and non-bonded interactions, also affect reaction energies.

3 BVT-Based Brønsted Acidity QSARs

Brønsted acid dissociation reactions have the form $HA \leftrightarrow H^+ + A^-$, where HA is the acid and A^- is the conjugate base. Rather than reporting the raw equilibrium constant (K_a), most workers find it convenient to use the negative logarithm (pK_a),

because pK_a is equivalent to the pH at which the acid undergoes 50% dissociation $(a_{HA} = a_{A^-})$.

BVT-based acidity models have so far all been QSARs that relate pK_a values to structural descriptors such as ΔV and Lewis base strength (S_B). Equation 1 is the definition of S_B for a single anion.

$$S_B = \frac{|V|}{N_O} \tag{1}$$

Here, N_O is the average observed coordination number in a large number of oxide crystal structures [1], and the same formula can be used to calculate the Lewis acid strength (S_A) of cations (cf. Eq. 7 in chapter "Bond Valence Theory" of this volume). S_A and S_B take into account both the valence and size of atoms, providing an expectation value for individual bond valences. According to the valence matching rule, the most stable structures are formed when the S_A and S_B values of the cations and anions are similar (see Eq. 9 in chapter "Bond Valence Theory" of this volume).

These structural descriptors were first applied to simple acids, for which pK_a values can easily be determined experimentally. However, the practical reason for this is to predict pK_a values for individual functional groups on large molecules and solid–liquid interfaces, which are much more difficult to determine.

3.1 Simple Acids

Brown [1, 12] related the pK_a values of a number of simple acids to S_B of their conjugate bases via Eq. 2 (cf. Fig. 13 in chapter "Bond Valence Theory").

$$pK_a = 14.3 \ln\left(\frac{S_B}{0.135}\right) \tag{2}$$

For the purpose of predicting oxyacid pK_a values, we take S_B as the expectation value for OH...O bonds incident to the O^{2-} ions in the base from surrounding H_2O molecules. That is, we divide the total expected OH...O bond valence by the expected number of OH...O bonds. For example, in $H_3SiO_4{}^-$, the conjugate base of silicic acid (H_4SiO_4), there is one Si–O bond with an average of 1 v.u. to each of the four O^{2-} ions, and we assume all H–O bonds to be 0.8 v.u. The N_O value for O^{2-} is 4, so that the three OH ligands have two unoccupied bonding sites, while the O^{2-} ligand has three, for a total of nine. However, Brown [1] recommended reducing this to six, because the Si–OH groups do not have enough valence to accept more than a single, weak OH...O bond. The bond valences incident to the OH ligands sum to 1.8 v.u., so that its "unsaturated" (i.e., leftover) valence (V_u) is 0.2 v.u., whereas $V_u = 1$ v.u. for the O^{2-}. The total value of V_u for the molecule is

1.6 v.u., which is divided among the six expected H-bond acceptor sites to obtain $S_b = 0.267$ v.u. Applying Eq. 2, we predict $pK_a = 9.75$, which is close to the measured value of 9.84 [13] (see Table 5 in chapter "Bond Valence Theory" for more examples).

The advantages of this simple relationship are that it can address multiple acid dissociation reactions of the same molecule and be applied to a wide variety of acids. Brown's model proves difficult to apply to individual functional groups on large molecules and surfaces, however, because S_B values are averaged over all the O^{2-} atoms. In addition, the example of silicic acid shows that the rules for counting expected H-bond acceptor sites are somewhat ambiguous. The model may still prove useful for estimating average acidity for these larger systems, but this has not yet been attempted.

Hiemstra et al. [14] attempted to calibrate an acidity QSAR that would be transferable to individual surface functional groups by focusing on individual functional groups in (hydr)oxy-acid monomers. (Hereafter, this will be referred to as the multisite complexation, or MUSIC, method.) In the MUSIC method, pK_a values are related to ΔV of a single O^{2-} ion in the conjugate base via Eq. 3, taking into account Me–O bonds, H–O bonds, and OH...O bonds from the surrounding water molecules.

$$pK_a^{int} = -19.8(\Delta V) \tag{3}$$

Here, pK_a^{int} is the "intrinsic" pK_a value, which is corrected for the electrostatic work of removing H^+ from the base. (An analogous electrostatic correction is done for surfaces.) To calculate ΔV for the O^{2-} ion in $H_3SiO_4^-$, one starts with the N_O value of four for O^{2-} ions in oxides to define the number of expected bonding sites. One of the four expected bonds is the Si–O bond, which is assumed to have the average value of 1.0 v.u. We expect three more bonds to the O^{2-}, which we assume are OH...O bonds of 0.2 v.u. from the surrounding water molecules. This brings the total bond valence incident to the O^{2-} to 1.6 v.u., so that $\Delta V = -0.4$ v.u. Equation 3 predicts $pK_a^{int} = 7.9$ for $H_4SiO_4 \leftrightarrow H^+ + H_3SiO_4^-$, close to the true value of ~8.5 [13]. In cases where the acid is a hydrated cation, the valence of the H–O bond in the hydroxyl group on the base is assumed to be 0.8 v.u. In summary, one tallies the Pauling (average) bond strength of the Me–O bond, 0.8 v.u. for any H–O bonds, and 0.2 v.u. for each addition expected bond, to account for OH...O bonds.

Before we discuss this approach further, it is worth contrasting it to Brown's method. Brown related acidity to the average expected valence of OH...O bonds to the base as a whole, and that expected valence was determined by assuming the valence sum rule holds. Hiemstra and coworkers assumed bond strengths for OH...O bonds to a single O atom on the base, and related acidity to the deviation of the valence sum on that O from the ideal 2 v.u. Thus, a fundamental feature of the MUSIC method is that it assumes the valence sum rule is *not* obeyed.

Several studies by Bickmore and coworkers [13, 15–17] addressed this and other issues with the MUSIC method. They performed a bond-valence analysis of the

output trajectories from ab initio molecular dynamics simulations of liquid water and explicitly hydrated oxo-species, including silicic acid, phosphoric acid, carbonic acid, and their conjugate bases, to show that the valence sum rule is obeyed on a time-averaged basis in such systems. This result does not necessarily imply that the MUSIC method will not work consistently – empirically fitting QSARs may correct systematic errors, after all. But it at least gives notice that the model might be getting the right answers for the wrong reasons, which calls into question its ability to predict outside the calibration set.

Bickmore and coworkers [13] did, in fact, demonstrate that the MUSIC method would not always work outside its calibration set. Equation 3 was calibrated on the pK_a^{int} values for (1) the first acid dissociation of a number of oxyacids (e.g., H_4SiO_4, H_3PO_4, H_2CO_3), and (2) dissociation reactions of hydroxyacids resulting in a neutrally charged base (e.g., $Fe(OH)_2^{+1} \bullet 4H_2O \leftrightarrow H^+ + Fe(OH)_3 \bullet 3H_2O$). The point of doing an electrostatic correction to obtain "intrinsic" pK_a values, however, is to remove the effect of long-range Coulomb interactions, so that only the energy of making and breaking bonds is left to be modeled using bond-valence terms. Thus, it should be possible to predict pK_a^{int} values for multiple dissociations of the same acid. But since ΔV in Eq. 3 is estimated assuming average bond valences for the Me–O bonds, this is impossible. For instance, if all Si–O bonds are taken to be 1.0 v.u., then there should be no difference in pK_a^{int} values for the reactions $H_4SiO_4 \leftrightarrow H^+ + H_3SiO_4^-$ and $H_3SiO_4^- \leftrightarrow H^+ + H_2SiO_4^{2-}$, because ΔV estimates for the Si–O groups on both bases are the same. In fact, the values for these two reactions vary widely (~8.5 and ~10.6, respectively,) and it cannot be the case that the Me–O bond length stays the same throughout such reactions. Curiously, while the pK_a^{int} values through series of acid dissociations vary widely for oxyacids, they are very similar for the hydroxyacids. Therefore, the use of average Me–O bond valences is actually justified for hydroxyacids.

To deal with this problem, one needs to know how the Me–O bond lengths change through multiple acid dissociations, at least in the oxyacids. Detailed structures of aqueous molecules generally cannot be obtained by experiment, unfortunately. Bickmore et al. [13, 15, 16] attempted to address this problem by using density functional theory (DFT) to calculate the Me–O bond lengths of interest for both gas-phase and explicitly hydrated molecules. The purpose of this was to account for progressive bond relaxation as H^+ ions are removed from an acid molecule. They found that they could predict the pK_a^{int} values of successive acid dissociations for a number of (hydr)oxo-monomers within about ±1 log unit, using the following equation.

$$pK_a^{int} = 60.5S_B + \alpha I_b - 18.1 \tag{4}$$

In Eq. 4, S_B for the O^{2-} of interest is derived by subtracting from 2 the calculated Me–O bond valence, and then subtracting another 0.8 v.u. for any H–O bonds
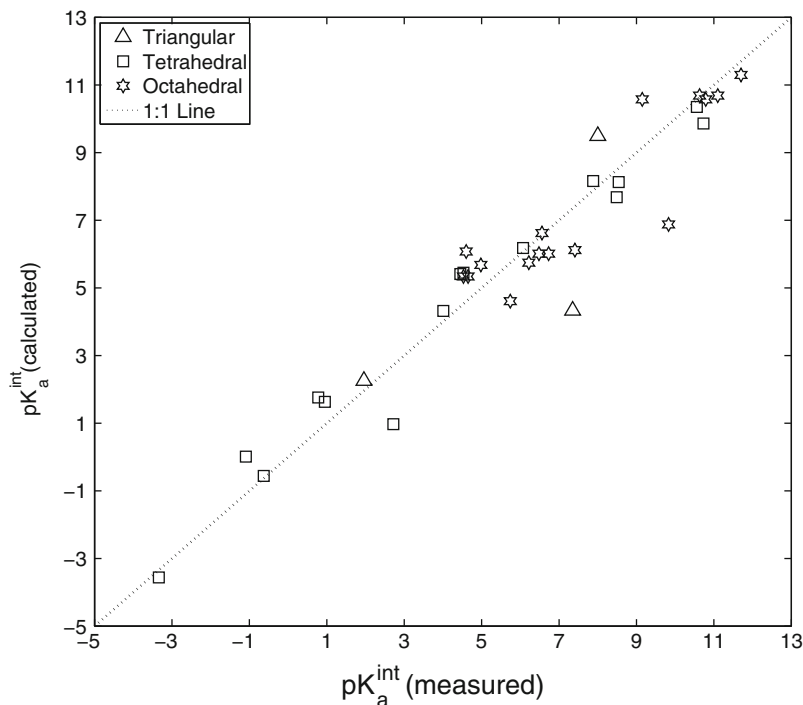
Fig. 1 Predicted (Eq. 4) vs. measured pK_a^{int} values for multiple acid dissociations of a number of (hydr)oxyacids (*triangular*, *tetrahedral*, and *octahedral*) [16]

present. We then divide the result by the number of unclaimed bonding sites. OH…O bonds from the solvent are *not* accounted for, just as in Brown's method [1, 12], so that S_B is an expectation value for the OH…O bonds. The variable I_b is the fraction ionic character of the Me–O bonds, derived from the difference in Pauling electronegativities between Me and O [18], and α is the regression coefficient obtained for the dependence on I_b. It turns out that the value of α is dependent on molecular shape – 5.3 for hexaquo cations (e.g., $Fe^{2+} \cdot 6H_2O$), 20.6 for tetrahedral oxyacids (e.g., H_4SiO_4), and 51.3 for triangular oxyacids (e.g., H_2CO_3). In addition, average (Pauling) bond valences worked better than any derived from calculated bond lengths for the hydroxyacids.

Figure 1 shows the predicted (Eq. 4) vs. measured pK_a^{int} values for a set of tetrahedral oxyacids, triangular oxyacids, and octahedral hydroxyacids. To date, this method is the most chemically accurate BVT-based acidity QSAR for (hydr) oxyacid solution monomers, but in the next section I will show that it is still unclear how successfully any of the methods discussed here can be applied to oxide–water interfaces, although some progress has undeniably been made.

3.2 Surface Functional Groups

The problem with modeling molecular-scale surface acidity is that it is usually impossible to be sure a model is, conceptually, even approximately right. Oxide surfaces can include a number of chemically distinct functional groups, but data on their acidity is often restricted to potentiometric titrations, in which the response of the entire surface is averaged, or data involving the averaged pH response of a single, crystallographically distinct surface, such as measurements of single-surface points of zero charge. Even advanced spectroscopic studies of crystallographically distinct surfaces provide data averaged over the entire surface although there have recently been some interesting attempts to infer the acidity of individual functional groups from such data [19, 20]. The pH response of distinct types of functional groups on aqueous molecules can sometimes be distinguished in a potentiometric titration curve, but surface acidity is significantly affected by the development of surface charge, which is continuously altered as acid–base reactions take place. This smears out the response of individual functional group types, making them indistinguishable from a macroscopic point of view.

Reactions at surface functional groups are typically modeled via surface complexation models (SCMs), which are simply equilibrium chemical models modified to correct for surface electrostatic effects. SCMs model acid–base reactions at surface functional groups via "intrinsic" equilibrium constants and ionic solution species concentrations corrected to account for the electric field around the interface. Thus, the "effective" equilibrium constants account for both chemical and electrostatic effects, and continuously change as surface charging progresses.

There are a number of ways to model the interfacial electric field in SCMs, involving various combinations of a Poisson–Boltzmann distribution and/or one or more parallel-plate capacitors [21]. Originally, modelers treated essentially all the building blocks of an SCM – electrostatic model, site types, site densities, and equilibrium constants – as fitting parameters. It was soon discovered, however, that one could usually fit potentiometric titration data with multiple SCMs that posit widely diverging molecular-scale pictures of the interface [22].

The first attempt to use the BVT to address this deficiency in SCMs was the MUSIC method of Hiemstra and coworkers [14], the point of which is to limit the number of adjustable parameters in SCMs by constraining some of the most important variables. Site types and densities are estimated via crystallographic models and microscopic measurements of the surface area, and surface pK_a^{int} values are estimated via Eq. 3. If we can fit an SCM to titration data with these parameters constrained to empirically or theoretically determined values, we have more confidence that the molecular-scale picture presented by the model is close to the truth.

Dozens of studies have used the MUSIC method to partially parameterize SCMs for various oxide surfaces, so by that measure the method has been very successful. But if the point of the method is to avoid a situation where models successfully explain data based on an inaccurate portrayal of the interface at the molecular scale, we should be careful to examine whether this problem has truly been solved. That is,

does the method work because it provides an accurate molecular-scale picture of the interface, or because there are still enough degrees of freedom in the adjustable model parameters to fit the macroscopic data, no matter whether the microscopic picture is essentially accurate?

There are a number of reasons to question whether the MUSIC method can be consistently successful at estimating surface pK_a^{int} values for oxides, but the most important has to do with how the method is ported to surfaces. We have seen that Eq. 3 was calibrated on the structures of solution monomers, for which averaged (Pauling) Me–O bond valences were assumed. But when Hiemstra et al. [14] applied the method to surfaces, they recommended using unrelaxed Me–O bond lengths from bulk crystal structures. In some cases Hiemstra and coworkers followed this procedure, as with goethite (FeOOH), and in others they used Pauling bond valences, as with gibbsite (Al(OH)$_3$). In fact, the bonds at surfaces often do relax significantly, relative to the bulk solid, but even if we apply Eq. 3 only in cases where surface relaxation is negligible, we have to wonder whether we can expect to use it to consistently obtain accurate pK_a^{int} estimates, when it was calibrated using Pauling Me–O valences.

Another issue with the way the MUSIC method is applied to surfaces has to do with the assignment of O^{2-} coordination numbers. When applied to solution monomers, the method assumes a coordination number of four for an O^{2-} ion in a functional group, so any of the four bonding sites not occupied by Me–O and H–O bonds are assumed to be occupied by OH...O bonds of 0.2 v.u. When applied to surfaces, however, the method instead assumes that O^{2-} ions bonded to one Me (η) have a coordination number of three, those bonded to two Me (μ_2) have a coordination number of three or four, and those bonded to three Me (μ_3) have a coordination number of four. The reason given for this is to account for steric hindrance of H-bonding from the adjacent water molecules, but the modeler decides whether μ_2 groups have a coordination number of three or four. This results in a difference of 0.2 v.u. in ΔV, which translates into a difference of ~4 log units in the calculated pK_a^{int} (Eq. 3). Whereas traditional SCMs have pK_a^{int} values obtained by a computerized optimization algorithm, here modelers must significantly manipulate some of the pK_a^{int} values by hand. In practice, this kind of adjustment has sometimes been applied even more extensively. E.g., Hiemstra et al. [14] had to assume a coordination number of 4 for the silanol (>Si–OH) groups on SiO$_2$ surfaces to obtain an appropriate point of zero charge (pH$_{PZC}$).

Machesky and coworkers have attempted to address some of the aforementioned problems with their seminal work on TiO$_2$ (rutile) and SnO$_2$ (cassiterite) [23–25], which are both dominated by their (110) surfaces. Their approach has been to use Eq. 3 to estimate pK_a^{int}, but to obtain the bond valences via DFT geometry optimizations and both classical and DFT molecular dynamics simulations. They also constrained their SCMs and molecular simulations with potentiometric titration data, single-surface pH$_{PZC}$ determinations, and synchrotron-based spectroscopic data. They were able to successfully reproduce the pH$_{PZC}$ values within ~1.4 log units, which is reasonable, considering all the potential sources of error in the calculated bond lengths.

The ability of the method used by Machesky and coworkers to more or less accurately predict the pH_{PZC} values of these oxides is impressive, and it seems likely that they have gotten at least part of the picture right. But which part? The estimated pH_{PZC} values are derived from the calculated pK_a^{int} values, averaged over the entire surfaces, so it may be that this version of the MUSIC method correctly predicts average behavior, but not the acidity of individual functional groups. In fact, Sprik and coworkers [26, 27] performed ab initio MD simulations of the hydrated rutile (110) surface to directly calculate pK_a^{int} values for the individual functional groups. Whereas their calculated pH_{PZC} value was slightly more accurate than that calculated by Machesky and coworkers, they found that their individual pK_a^{int} values were quite different.

Furthermore, while Machesky and coworkers have addressed the issues raised above regarding the use of Pauling Me–O bond valences and arbitrary numbers and strengths of OH...O bonds, they have not addressed the issue of acidity model calibration. That is, how can we expect to obtain accurate pK_a^{int} estimates by inserting precisely calculated bond lengths into a QSAR calibrated on idealized solution monomer structures with averaged bond lengths?

Once again, Bickmore et al. [13, 15, 16] addressed this issue by calibrating their model (Eq. 4) on calculated solution monomer structures, but at this point it is still unclear how to apply Eq. 4 to surface functional groups, because the dependence of pK_a^{int} on the fraction ionic character of the Me–O bonds (α) was shown to depend on the basic molecular shape. Is there a single α value one can use for all surface functional groups, or does it depend strongly on the specific environment? The answers to these questions depend on the physical meaning of the structural descriptors in the model. Why, for instance, is S_B of the conjugate base such a strong predictor of acidity? Bickmore et al. [16] used ab initio molecular dynamics simulations of several explicitly hydrated oxyacids and their conjugate bases to show that S_B is highly correlated with the valence of the strongest H-bond reaching the O^{2-} from the solvent. They reasoned that stronger H-bonds would make it easier for H^+ ions to jump from solvent molecules to O^{2-} ions on the base. This is undoubtedly true, but as mentioned above, equilibrium constants must somehow be related to a change in energy between the products and reactants, whereas all BVT-based acidity QSARs are related exclusively to the structure of the base.

Casey, Rustad, and coworkers [28–32] brought up yet another issue that must be considered. If all BVT-based acidity QSARs are calibrated on solution monomers, how can we be sure they will correctly predict the acidity of, for instance, bridging (μ_2 or μ_3) oxygens on oxide surfaces? Their research has focused on large oxo-molecules that include such groups, and for which the acidities of the individual functional groups can often be determined with a high degree of confidence via potentiometry, UV–vis spectroscopy, and NMR spectroscopy. Structural analysis and molecular modeling have shown that neither these acidities nor their relative order, can be derived from simple bond-valence considerations, although Casey, Rustad, and coworkers have never analyzed the valence of OH...O bonds incident

to the functional groups, as both Bickmore's and Machesky's groups did. (In one instance, however, Rustad [32] did count OH...O bonds for use in MUSIC calculations.)

Nevertheless, nobody has successfully addressed the criticisms of Casey, Rustad, and coworkers, and their work serves to underscore two glaring facts about this field. First, we need to be doing more work on systems for which we can tell when we have the right answer. Second, we need to know *why* our models work to be confident that they can provide accurate insights into the details of less well understood systems.

4 Outlook

In this chapter, I have described several attempts to predict the Brønsted acidity of oxo-groups on molecules and oxide surfaces based on bond-valence considerations. If I had to choose a metaphor to describe the state of the field, I would say that there is a lot of smoke, but we haven't yet found the fire. Clearly, there have been enough successes to warrant the conclusion that the BVT can be a powerful tool for relating molecular structure to acidity. However, serious doubts have been cast on the ability of any of the BVT-based acidity QSARs so far proposed to consistently make accurate predictions of the acidity of individual functional groups in diverse structural settings.

There are reasons for hope. Sverjensky and Sahai, for instance, published a series of papers [33–37] in which they developed the solvation, bond strength, and electrostatic (SBE) model. The SBE model fairly accurately predicts the surface acidity of a number of simple oxides based on model terms derived from easily obtained characteristics of each solid, including the Pauling bond valence to bond length ratio and the dielectric constant. While this model does not provide molecular-scale information, it has been so successful at explaining the average acid–base reactivity of oxide surfaces that it seems quite plausible that a similar approach might work well at the scale of individual functional groups.

It has become evident that if this is to happen, we need to better understand the relationship between bond valence and energy. A number of attempts to develop this link were mentioned in Sect. 2 of this chapter, but there is still no way of weighing the relative contributions of bond-valence and other structural factors, such as bond angles and non-bonded interactions, to the potential energy surface. Some preliminary work is being done in that area [38], but it is not well developed.

At the beginning of this chapter, I said that we had to pay special attention to two questions when discussing BVT-based acidity models. (1) How might the BVT-based structural descriptors employed relate to the potential energy surface? (2) What is the model's domain of applicability? To date, there are no clear answers to either.

References

1. Brown ID (2002) The chemical bond in inorganic chemistry: the bond valence model. Oxford University Press, New York
2. Salinas-Sanchez A, Garcia-Muñoz JL, Rodriguez-Carvajal J, Saez-Puche R, Martinez JL (1992) Structural characterization of R_2BaCuO_5 (R = Y, Lu, Yb, Tm, Er, Ho, Dy, Gd, Eu and Sm) oxides by X-ray and neutron diffraction. J Solid State Chem 100:201–211
3. Perez-Mato JM, Withers RL, Larsson A-K, Orobengoa D, Liu Y (2009) Distortion modes and related ferroic properties of the stuffed tridymite-type compounds $SrAl_2O_4$ and $BaAl_2O_4$. Phys Rev B79:064111
4. Cooper VR, Grinberg I, Rappe AM (2003) Extending first principles modeling with crystal chemistry: a bond-valence based classical potential. In: Davies PK, Singh DJ (eds) Fundamental physics of ferroelectrics. American Institute of Physics, Melville, New York
5. Shin Y-H, Cooper VR, Grinberg I, Rappe AM (2005) Development of a bond-valence molecular-dynamics model for complex oxides. Phys Rev B 71:054104
6. Adams S (2001) Relationship between bond valence and bond softness of alkali halides and chalcogenides. Acta Crystallogr B 57:278–287
7. Adams S, Moretzki O, Canadell E (2004) Global instability index optimizations for the localization of mobile protons. Solid State Ionics 168:281–290
8. Adams S, Rao RP (2009) Transport pathways for mobile ions in disordered solids from the analysis of energy-scaled bond-valence mismatch landscapes. Phys Chem Chem Phys 11:3210–3216
9. Adams S, Swenson J (2002) Bond valence analysis of transport pathways in RMC models of fast ion conducting glasses. Phys Chem Chem Phys 4:3179–3184
10. Hinchliffe A (2003) Molecular modelling for beginners. Wiley, Chichester
11. Rappé AK, Casewit CJ (1997) Molecular mechanics across chemistry. University Science Books, Sausalito
12. Brown ID (1981) The bond-valence method: an empirical approach to chemical structure and bonding. In: O'Keefe M, Navrotsky A (eds) Structure and bonding in crystals. Academic, New York
13. Bickmore BR, Tadanier CJ, Rosso KM, Monn WD, Eggett DL (2004) Bond-valence methods for pK_a prediction: critical reanalysis and a new approach. Geochim Cosmochim Acta 68:2025–2042
14. Hiemstra T, Venema P, Van Riemsdijk WH (1996) Intrinsic proton affinity of reactive surface groups of metal (hydr)oxides: the bond valence principle. J Colloid Interface Sci 184:680–692
15. Bickmore BR, Rosso KM, Mitchell SC (2006) Is there hope for multisite complexation modeling? In: Lützenkirchen J (ed) Surface complexation modelling. Elsevier, Amsterdam
16. Bickmore BR, Rosso KM, Tadanier CJ, Bylaska EJ, Doud D (2006) Bond-valence methods for pK_a prediction. II. Bond-valence, electrostatic, molecular geometry, and solvation effects. Geochim Cosmochim Acta 70:4057–4071
17. Bickmore BR, Rosso KM, Brown ID, Kerisit S (2009) Bond-valence constraints on liquid water structure. J Phys Chem A 113:1847–1857
18. Pauling L (1960) The nature of the chemical bond. Cornell University Press, Ithaca
19. Catalano JG, Fenter P, Park C (2007) Interfacial water structure on the (012) surface of hematite: ordering and reactivity in comparison with corundum. Geochim Cosmochim Acta 71:5313–5324
20. Sung J, Shen YR, Waychunas GA (2012) The interfacial structure of water/protonated α-Al_2O_3 (11–20) as a function of pH. J Phys Condens Matter 24:124101
21. Kosmulski M (2001) Chemical properties of material surfaces. Marcel Dekker, Basel
22. Westall JC, Hohl H (1980) A comparison of electrostatic models for the oxide/solution interface. Adv Colloid Interface Sci 12:265–294

23. Machesky ML, Predota M, Wesolowski DJ, Vlcek L, Cummings PT, Rosenqvist J, Ridley MK, Kubicki JD, Bandura AV, Kumar N, Sofo JO (2008) Surface protonation at the rutile (110) interface: explicit incorporation of solvation structure within the refined MUSIC model framework. Langmuir 24:12331–12339

24. Vlcek L, Zhang Z, Machesky ML, Fenter P, Rosenqvist J, Wesolowski DJ, Anovitz L, Predota M, Cummings PT (2007) Electric double layer at metal oxide surfaces: static properties of the cassiterite-water interface. Langmuir 23:4925–4937

25. Rosenqvist J, Machesky ML, Vlcek L, Cummings PT, Wesolowski DJ (2009) Charging properties of cassiterite (α-SnO_2) surfaces in NaCl and RbCl ionic media. Langmuir 25:10852–10862

26. Cheng J, Sprik M (2010) Acidity of the aqueous rutile TiO2(110) surface from density functional theory based molecular dynamics. J Chem Theory Comput 6:880–889

27. Sulpizi M, Sprik M (2010) Acidity constants from DFT-based molecular dynamics simulations. J Phys Condens Matter 22:284116

28. Casey WH, Rustad JR (2007) Reaction dynamics, molecular clusters, and aqueous geochemistry. Annu Rev Earth Planet Sci 35:21–46

29. Casey WH, Rustad JR, Banerjee D, Furrer G (2005) Large molecules as models for small particles in aqueous geochemistry research. J Nanopart Res 7:377–387

30. Casey WH, Rustad JR, Spiccia L (2009) Minerals as molecules – use of aqueous oxide and hydroxide clusters to understand geochemical reactions. Chem Eur J 15:4496–4515

31. Casey WH, Swaddle TW (2003) Why small? The use of small inorganic clusters to understand mineral surface and dissolution reactions in geochemistry. Rev Geophys. doi:10.1029/2002RG000118

32. Rustad JR (2005) Molecular dynamics simulation of the titration of polyoxocations in aqueous solution. Geochim Cosmochim Acta 69:4397–4410

33. Sahai N, Sverjensky DA (1997) Sovation and electrostatic model for specific electrolyte adsorption. Geochim Cosmochim Acta 61:2827–2848

34. Sahai N, Sverjensky DA (1997) Evaluation of internally consistent parameters for the triple-layer model by the systematic analysis of oxide surface titration data. Geochim Cosmochim Acta 61:2801–2826

35. Sverjensky DA (1994) Zero-point-of-charge prediction from crystal chemistry and solvation theory. Geochim Cosmochim Acta 58:3123–3129

36. Sverjensky DA (2005) Prediction of surface charge on oxides in salt solutions: revisions for 1:1 (M+L-) electrolytes. Geochim Cosmochim Acta 69:225–257

37. Sverjensky DA, Sahai N (1996) Theoretical prediction of single-site surface-protonation equilibrium constants for oxides and silicates in water. Geochim Cosmochim Acta 60:3773–3797

38. Bickmore BR, Wander MCF, Edwards J, Maurer J, Shepherd K, Meyer E, Johansen WJ, Frank RA, Andros C, Davis M (2012) Electronic structure effects in the vectorial bond-valence model. Am Miner (in press)