The Bond Valence Model as a Tool for Teaching Inorganic Chemistry: The Ionic Model Revisited

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The concepts of atoms and bonds were introduced into chemistry in the early 19th century to provide a way of understanding and organizing the many compounds that were being discovered, particularly those containing carbon. According to the bond model, a compound was seen as a collection of atoms connected by bonds to form a molecular network. At this time the nature of neither the atoms nor the bonds was known, but the model was so successful that chemists soon accepted their reality. The development of atomic physics and X-ray diffraction in the early 20th century confirmed the existence of atoms as well as their geometric arrangements in organic molecules, but the nature of the chemical bond has remained elusive and continues to be the subject of much discussion.

In contrast to organic compounds, inorganic compounds form extended crystalline arrays of atoms that do not follow the established rules of organic chemistry. In 1918, to account for this different behavior, Born and Landé proposed the ionic model, in which the crystals were assumed to be held together by the Coulomb attraction between atoms carrying opposite charges (1). They postulated that the total energy of the crystal could be calculated as the sum taken over all pairs of atoms of interatomic potentials of the form

\[ U_{\text{electrostatic}} + U_{\text{shortrange}} \]

where the first term is the electrostatic potential that holds the crystal together and the second term is a short-range potential that describes the repulsion that keeps the atoms apart. The electrostatic term was calculated by Madelung for NaCl using classical electrostatics (2). In the absence of a proper theoretical model, the repulsive term was approximated by an inverse power law with empirically fitted parameters. While this model had some success in predicting the properties of simple solids like NaCl, the calculations were too difficult to perform for more complex structures.

In 1929 Pauling developed a more descriptive approach to the ionic model in his empirical “Principles Determining the Structure of Complex Ionic Solids” (3). Pauling's rules state that positively charged ions (cations) surround themselves with negatively charged ions (anions) in such a way as to preserve local charge neutrality. This latter condition he expressed in terms of the electrostatic valence principle in which the charge, \( V \), of a cation is divided between the \( N \) bonds that it forms to give each bond an electrostatic bond strength of \( V/N \). He showed that the sum of the bond strengths received by each anion was approximately equal to the negative charge on the anion. Bragg pointed out that this principle can be represented by a picture of lines of electrostatic field linking the cations to the anions (4). Because the energy is a minimum when the lines of field are as short as possible, each cation will surround itself with anions and vice versa. Bragg's picture was never developed further, but many newly determined structures, particularly those of minerals, were interpreted in terms of Pauling’s rules, which, in the last few decades, have been developed into the bond valence model that is the subject of this paper.

More recently the introduction of computers has put life back into the original ionic model. Madelung summations can now be rapidly performed and good empirical short-range potentials can be found by quantum mechanical calculation or by fitting the parameters to observed physical properties. By minimizing the energy, the ionic model can, in experienced hands, predict the positions of atoms in complex crystals to within a few picometers and can predict many of a crystal's physical properties (5). However, powerful as this form of the ionic model is, details of the calculation are lost inside the computer and the model does not provide the kind of intuitive insights that are required of a good teaching model.

These insights can, however, be recovered if the model is developed in terms of the electrostatic field rather than the energy. Such a derivation, presented in the following section, yields a simple model of chemical bonding that is identical to the empirically developed bond valence model (6–8). The remaining sections of the paper show how this model can be used to understand many chemical and physical properties of inorganic compounds, particularly the interesting and unusual properties of the new high-tech ceramics used in fuel cells and other electrical devices. Further, the model is simple and intuitive and permits predictions to be made without recourse to a computer. The printed version of this paper only outlines the basic ideas of the model. Further details and most of the applications can be found in the online version.

The Electrostatic Bond Model

The particular virtue of the ionic model is that the long-range forces are described by a classical electrostatic potential while all the properties that depend directly on quantum mechanics are contained a short-range potential, \( U_{\text{shortrange}} \), that is fitted empirically. Therefore for compounds that satisfy the assumptions of the model, quantum mechanical calculations are not needed. These assumptions limit the scope of the model but not as much as is generally supposed. They are:

1. Atoms can be treated as carrying a net charge, either positive (cation) or negative (anion). The charge on the anions is the charge necessary to complete the electron octet in the valence shell. The charge on the cations is then determined by the requirement of electroneutrality. In many cases this will leave the cation also with a filled shell configuration.

2. There is no bonding between two cations or between two anions. That is, all the bonds have a cation at one end and
an anion at the other. This means that all the bonds are between an electron donor and an electron acceptor, and the assumption effectively restricts the model to inorganic compounds. The assumption is, however, satisfied by some organic compounds (e.g., organic salts) and, on the other hand, there are some inorganic compounds (e.g., carbonyl complexes) to which the model does not apply.

3. The electron density of the atoms is spherically symmetric, so the electric field in the region outside the atom is the same as if the atom were replaced by a point charge equal to the net charge on the atom. However, the model can be adapted to situations where the electron density is not spherically symmetric by adding point multipoles to the point charges.

These assumptions are obeyed by most inorganic salts, minerals, and ceramics, but they are not obeyed by most organic and metallic compounds. Note that there is nothing in the assumptions that excludes covalent bonds per se, since most covalent bonding does not destroy the (approximate) spherical symmetry of the electron density. Covalent effects, together with any differences between formal and actual ionic charge, are included in the fitted short-range potential, \( U_{\text{short-range}} \).

Figure 1 shows the electrostatic field in a section through a crystal of rutile (TiO\(_2\)). Each Ti\(^{4+}\) ion is represented by a charge of +4 electrons and each O\(^{2-}\) ion by a charge of -2 electrons. Since lines of field cannot cross, they must connect nearest neighbor ions as pointed out by Bragg (4). As Figure 1 shows, this field, which includes all the long-range electrostatic effects, naturally partitions itself into localized cation–anion bonds.

A property that uniquely characterizes each bond, \( i \), is the electric flux (the number of lines of field), \( \Phi_i \), linking the ions. According to Gauss’s theorem, the total flux emanating from a charge, \( V \), is equal to the charge

\[
\sum \Phi_i = V
\]

The ionic charge and flux are measured in valence units, v.u., which formally correspond to units of electronic charge, though the actual charges may be smaller. Equation 1 necessarily holds for sums around both the ions and the cations.

The bonds can be treated as capacitors, since a charged capacitor consists of two equal and opposite charges, \( q_i \), connected by an electrostatic flux, \( \Phi_i \), which is equal to \( q_i \). By replacing each bond in a structure by an equivalent capacitor, \( C_i \), the chemical bond network can be converted to an equivalent electric circuit as shown in Figure 2 for the network illustrated in Figure 1.

By the law of conservation of energy, the sum of the electric potential differences around any loop in such a network is zero and, since the potential across a capacitor is given by \( q_i/C_i \), and \( q_i \) is equal to \( \Phi_i \), it follows that

\[
\sum \Phi_i / C_i = 0
\]

each term in the summation being taken as positive or negative depending on the direction in which the bond is traversed.

Equations 1 and 2 constitute the Kirchhoff equations for the equivalent circuit shown in Figure 2 and they allow the values of \( \Phi_i \) to be calculated provided one knows the values of the capacitances, \( C_i \), and the bond connectivity. Unfortunately, values of \( C_i \) depend on the positions of the atoms and can only be determined a priori from a quantum mechanical calculation. The problem of determining the capacitances is taken up again in a later section, but the next two sections describe some of the chemistry that can be derived using eq 1 alone.

**Bonding Strength and Bonding Strength Matching**

By recognizing that the flux tends to be distributed uniformly among the various bonds, one can use eq 1 to estimate how much flux each bond will have. If one knows the coordination number, \( N \), of one of the ions forming the bond, this estimate is provided by eq 3:

\[
\Phi_i = V/N
\]

Since cations have characteristic coordination numbers, this estimate can often be made even if the actual coordination number is not known. For example, S\(^{6+}\) is always 4-coordinated by O\(^{2-}\), so that S\(^{6+}\)–O\(^{2-}\) bonds always have an average flux of 1.5 v.u. When coordinated to O\(^{2-}\), Na\(^{+}\) is found with coordination numbers ranging from 3 to 12, but most frequently with a coordination number close to the average of 6.4 (10). One would expect then to find that the flux of Na–O bonds lies between 0.33 and 0.08 v.u., the most likely value of 0.16 v.u. being obtained by substituting the average coordination number into eq 3. Average coordination numbers found around a number of cations are listed in Table 1 online.
Ca\textsuperscript{2+} to form minerals such as apatite, which is a major constituent in bone and teeth, but PO\textsubscript{4}\textsuperscript{3-} is poorly matched with K\textsuperscript{+}. Even though K\textsubscript{3}PO\textsubscript{4} is a stoichiometrically allowed compound, it is unstable because of the poor match between the cation and anion bonding strengths (0.12 and 0.25 v.u., respectively). K\textsubscript{3}PO\textsubscript{4} is, in fact, deliquescent and readily absorbs water from the air to form H\textsubscript{3}PO\textsubscript{4}, ions as described in more detail online.\textsuperscript{w} Bonding strengths of a number of anions are shown on the right hand side of Figure 3 and are listed in Table 2 online.\textsuperscript{w} Anion bonding strengths are a measure of the Lewis base strength of the anion.

Since the anion and cation bonding strengths are both estimates of the flux that links the cation to the anion, it follows that the most favorable conditions for bonding will occur when the cation and anion have similar bonding strengths. This is expressed by the bonding strength matching rule, which states that the most stable bonds will be formed between cations and anions with similar bonding strengths.

A glance at Figure 3 immediately shows which cations and anions will readily form bonds. Mg\textsuperscript{2+} and SiO\textsubscript{4}\textsuperscript{4-} both form bonds with fluxes of 0.33 v.u., making Mg\textsubscript{3}SiO\textsubscript{4} the stable mineral, forsterite, which is believed to form a large portion of the earth's upper mantle.

O\textsubscript{2}\textsuperscript{2-} readily bonds to Ca\textsuperscript{2+} to form minerals such as apatite, which is a major constituent in bone and teeth, but PO\textsubscript{4}\textsuperscript{3-} is poorly matched with K\textsuperscript{+}. Even though K\textsubscript{3}PO\textsubscript{4} is a stoichiometrically allowed compound, it is unstable because of the poor match between the cation and anion bonding strengths (0.12 and 0.25 v.u., respectively). K\textsubscript{3}PO\textsubscript{4} is, in fact, deliquescent and readily absorbs water from the air to form H\textsubscript{3}PO\textsubscript{4}, ions as shown in the next section. Other examples of the matching principle can be found online.\textsuperscript{w} Cation bonding strengths depend on cation coordination numbers which are primarily determined by two factors more fully discussed online.\textsuperscript{w} The relative sizes of the cation and anion limit the number of anions that can be placed around the cation, but lower coordination numbers are found if the anion has a bonding strength much larger than the cation. For example, although it is physically possible to place 14 O\textsubscript{2}\textsuperscript{2-} ions around Cs\textsuperscript{+}, the bonds would have a flux of only 0.07 v.u., smaller than the bonding strength of any anion shown in Figure 3. Only 9 bonds are needed for Cs\textsuperscript{+} to bond to NO\textsubscript{3}\textsuperscript{-} (bonding strength 0.11 v.u.), and even fewer for stronger anions. For this reason the average coordination number found for Cs\textsuperscript{+} is 9.2 rather than 14, and the bonding strength of Cs\textsuperscript{+} is determined not by its size, but by the availability of suitable counterions. Ba\textsuperscript{2+}, though smaller, has a larger average coordination number (10.2) because of its larger charge. Ions that are polarizable (i.e., the ions classified by Pearson as soft (12–14)) are better able to adapt their bonding strength to form a good match and consequently show a wider range of coordination numbers than the hard ions found near the top of the periodic table.

**Solubility**

The process by which a solid is dissolved in water is a chemical reaction with an equation of the following form:

\[
AX + nH_2O \rightarrow A(H_2O)_n^+ + X^-
\]

The bonding strength matching rule can be used to decide whether the left- or right-hand side of this equation is the more stable, but first it is necessary to know the cation and anion bonding strengths of water. To calculate these requires, in turn, an understanding of the unique properties of hydrogen, which bonds asymmetrically between two O\textsubscript{2}\textsuperscript{2-} ions, an arrangement called a hydrogen bond. The asymmetry is a consequence of the repulsion between the two terminal O\textsubscript{2}\textsuperscript{2-} ions, which causes the H–O bonds to be stretched.\textsuperscript{w} This strain can be removed if the H\textsuperscript{+} ion is displaced toward one anion, but lower coordination numbers are found if the anion has a bonding strength much larger than the cation. For example, although it is physically possible to place 14 O\textsubscript{2}\textsuperscript{2-} ions around Cs\textsuperscript{+}, the bonds would have a flux of only 0.07 v.u., smaller than the bonding strength of any anion shown in Figure 3. Only 9 bonds are needed for Cs\textsuperscript{+} to bond to NO\textsubscript{3}\textsuperscript{-} (bonding strength 0.11 v.u.), and even fewer for stronger anions. For this reason the average coordination number found for Cs\textsuperscript{+} is 9.2 rather than 14, and the bonding strength of Cs\textsuperscript{+} is determined not by its size, but by the availability of suitable counterions. Ba\textsuperscript{2+}, though smaller, has a larger average coordination number (10.2) because of its larger charge. Ions that are polarizable (i.e., the ions classified by Pearson as soft (12–14)) are better able to adapt their bonding strength to form a good match and consequently show a wider range of coordination numbers than the hard ions found near the top of the periodic table.

An isolated water molecule contains O–H bonds of valence 1.00 v.u. (2), but in the liquid, each molecule has four neigh-
bonds with which it forms hydrogen bonds (3). In liquid water, therefore, the water molecule behaves as both a cation and an anion. The H⁺ ion acts as a cation with a bonding strength of 0.18 v.u. and the O⁻² ion acts as an anion with a bonding strength (based on 4-coordinated O) also of 0.18 v.u. (4).

From the matching rule it is clear that water molecules will readily bond to each other because they have equal cation and anion bonding strengths, but they can also bond to anions with a bonding strength between 0.10 and 0.25 v.u. and to cations with a bonding strength between 0.10 and 0.36 v.u. (5). Compounds whose ions have bonding strengths lying in these ranges can dissolve in water since the water molecule will be able to bond to them and eq 4 can proceed to the right. For example, Mg²⁺ will surround itself with six water molecules but, since the Mg-O bond must have a flux of 0.33 v.u., each O⁻² ion will bond to only one Mg²⁺ ion and the hydrogen atoms will form bonds of 0.17 v.u. with other water molecules or anions (6). Because the flux of the Mg-O bond (0.33 v.u.) is almost twice that of the bonds between water molecules, the Mg-O bond is stronger than those in the surrounding water and Mg(H₂O)₆²⁺ is a stable complex ion even in aqueous solutions.

We can identify four situations that might occur when an inorganic compound is placed in water. If the cation and anion are well matched and both have large bonding strengths, for example, Mg²⁺ and SiO₄²⁻ (see Fig. 3), then the solid will be insoluble because the match between the two ions is better than the match between either of them and water.

If the two ions are well matched but have bonding strengths that are small so that each is also well matched to water, for example, Na⁺ and Cl⁻, then the compound will be soluble but will also readily recrystallize when the water is removed.

More interesting are compounds in which a weak anion such as SO₄²⁻ is found with a strong cation such as Mg²⁺. As discussed above, water can readily bond to Mg²⁺ to give the hydrated cation Mg(H₂O)₆²⁺ with a bonding strength of 0.17 v.u., just right for forming bonds with both water and SO₄²⁻. Anhydrous MgSO₄ readily dissolves in water, even to the extent of picking up water from the atmosphere, but the solid that recrystallizes from aqueous solution is the well-matched heptahydrate epsomite, whose formula can be written Mg(H₂O)₆SO₄·H₂O, the seventh water molecule occupying an otherwise empty cavity between the ions. Compounds of strongly bonding cations with weakly bonding anions are normally found as hydrates and their anhydrous forms are hygroscopic.

The situation of a weakly bonding cation, for example Na⁺, and a strongly bonding anion, for example CO₃²⁻ (bonding strength 0.22 v.u.), is somewhat different, but again water is able to mediate the bonding. In this case the CO₃²⁻ ion binds a hydrogen atom from the water, lowering its anion bonding strength to 0.17 v.u. to match that of the surrounding water. Again one expects that, because of the poor match, Na₂CO₃ will dissolve in water and the carbonate anion will convert to bicarbonate (hydrogen carbonate), the excess OH⁻ ions leaving the solution alkaline. At neutral pH the salt that crystallizes is NaHCO₃ (baking soda). The original Na₂CO₃ (washing soda) will only crystallize if the solution is made sufficiently alkaline.

**Bond Flux and Bond Length**

Bond lengths are determined by the size of the bond flux and the mutual repulsion between the atoms: the larger the flux, the more closely the atoms can be brought together. The repulsion depends on the way the electron density is distributed in the atoms and can only be properly determined using quantum mechanics. However, the ionic model avoids the explicit use of quantum mechanics by treating this repulsion empirically, the effect being hidden in the unknown bond capacitances even of eq 2. It is no simple matter to calculate these capacitances even when the positions of the atoms are known, so an alternative approach is needed.

In the years following Pauling’s paper (3), it was noticed that there was an inverse relation between bond length and bond flux. This correlation, shown for Ca–O bonds in Figure 5 and represented by eq 5, is now well established for virtually all the bonds encountered in inorganic compounds.

\[
s = \exp((-r_0 - r)/B)
\]

Here \(r\) is the bond length and \(s\) is the bond flux, also known as the bond valence. The parameters \(r_0\) and \(B\) are chosen to ensure that the valences of bonds formed by an atom sum to its formal ionic charge according to eq 6, known as the valence sum rule,

\[
\sum_i q_i = V
\]

Because the calculation of the flux is not trivial, eq 5 is the preferred method of determining the bond valence or flux in cases where the bond distance is known.

New structure determinations are often checked by calculating bond valences using eq 5, since violations of eq 6 usually indicate a problem with the structural model. More interestingly, eq 6 can be used to distinguish between the different oxidation states of a cation even in metallorganic complexes and enzymes (16).
For a large group of compounds, those defined as having unstrained structures, the valences of the bonds determined from eq 5 are also found to obey eq 7:

$$\sum s = 0 \quad (7)$$

The summation in eq 7 is over any set of bonds that form a closed loop in the bond network, the sign of s depending on whether the bond is traversed from cation to anion or from anion to cation. Equation 7 is known as the equal valence rule because it leads to the most uniform distribution of valence between the bonds (17). Equations 6 and 7 taken together are known as the network equations and give a unique solution for s for every bond in the network. Together the network equations correspond to the statement that each atom shares its valence as equally as possible between the bonds that it forms. Methods of solving these equations are given online.\(^W\)

The equivalence of the bond flux and bond valence means that the Kirchhoff equations (1 and 2) and the network equations (6 and 7) are equivalent. Because of this, the bond capacitances in eq 2 must cancel. In unstrained equilibrium structures, therefore, the bond capacitances are all equal, further simplifying the model.

Two classes of compound do not obey eq 7 because the bonds are strained: namely, compounds containing atoms with electronically driven distortions, typically transition metals and atoms with stereoelectron lone electron pairs, and compounds in which sterically constrained require some bonds to be compressed and others stretched, typically perovskites and compounds with hydrogen bonds.\(^W\) Steric strain is responsible for many of the unusual and technologically important properties.\(^W\)

**Epilogue**

This alternative view of the ionic model is based on the properties of the electric field rather than on the properties of the energy. Although this approach has limitations (for example, it does not directly give the energy of the system), it provides many insights that the traditional ionic model does not. In either form, the ionic model is restricted to acid–base compounds—that is, to salts, ceramics, and minerals—but within these systems it describes all types of bond, ionic or covalent, equally well. Unlike other chemical models, the ionic model as developed here leads directly to the concept of a chemical bond whose flux obeys the valence sum rule (eq 1 or 6). The need for quantum mechanical solutions is avoided by treating the short-range forces empirically via the correlation between bond flux and bond length (eq 5).

This model differs in many important ways from the more traditional approaches to describing chemical bonding in inorganic compounds. Lewis structures are frequently used in teaching, but the difficulty is to know how much weight to give to each of the many possible Lewis structures that can be drawn. This is well illustrated by a recent discussion of how one should draw Lewis structures for the sulfate ion, $\text{SO}_4^{2-}$ (18). What are the criteria for preferring one Lewis structure over another? The large number of Lewis diagrams that can be drawn and the lack of clear criteria for choosing between them can be confusing for the neophyte chemist. Although one can argue that Lewis structures that obey the octet rule give a better physical description, Lewis structures in which all the atoms have zero formal charge necessarily obey the valence sum rule (eq 5) if one assigns a valence of 1.00 to each electron pair bond. Averaging all such structures gives a quantity known as the resonant bond number, which measures the number of electron pairs in the bond and should therefore be a measure of covalency. But averaging all equivalent structures leads to the most symmetric distribution of resonant bond number, thereby ensuring that the resonant bond number also satisfies the equal valence rule (eq 7). Since the resonant bond numbers thus satisfy the network equations, they must be identical to the fluxes or valences of the bond valence model. It is not trivial to calculate resonant bond numbers for crystals because in theory, one needs an infinite number of Lewis structures spanning every atom in the crystal, but the result has been verified for complex crystalline silicate minerals with the aid of some simplifying assumptions and a lot of computer time (19).

If the resonant bond number is a measure of the number of electron pairs (the covalency) in a bond and if it is identical to the bond valence, it follows that the bond valence itself is a measure of covalency—the larger the bond valence, the more covalent the bond (20). When describing structure and structure-related properties, it is therefore unnecessary and often unhelpful to worry about whether a bond is ionic or covalent. The simple theorems of network theory give the same qualitative description of both ionic and covalent chemical bonding because they describe how the bonding power (whether covalent or ionic) of an atom is distributed to give the most symmetric bonding arrangement. Such descriptions do not, of course, make any statement about how the electrons are distributed between the bonded atoms (21). But as this paper has shown, they can be used to understand a great deal of chemistry without any need to take electron distributions into account.

Atomic orbitals have not been mentioned in this paper. While a basis set of atomic orbitals is needed to calculate the energy and electron distribution in a molecule or crystal, the usefulness of an orbital description for inorganic compounds is limited. Atoms usually adopt the most symmetric arrangement of neighbors, and the frequency with which 4- and 6-coordination are found has less to do with the availability of s, p, or d orbitals than with the fact that the tetrahedron and octahedron are among the few geometries that allow all the bonds to be equivalent. Only for the electronically distorted atoms discussed online is it useful to invoke orbitals (22).\(^W\)
The simple model presented here has many applications in both solution and solid-state inorganic chemistry. The examples discussed here indicate how the model can account for many of the chemical and physical properties of inorganic compounds, and further examples are given online, some of which show how it is that inorganic solids can sometimes violate the traditional rules of chemistry.

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Supplemental Material

The full version of this article is available in this issue of JCE Online.

Note

1. The bond valence model was developed before it was realized that the bond flux was the same as the bond valence. Bond valence was originally defined in terms of the bond length using eq 7, so the term bond valence is retained here for the quantity derived experimentally from bond lengths or theoretically from the bond connectivity using eqs 8 and 9, to distinguish them from the bond flux calculated from the Coulomb field.

Literature Cited