Stoichiometric Valence and Structural Valence-Two Different Sides of the Same Coin: "Bonding Power"
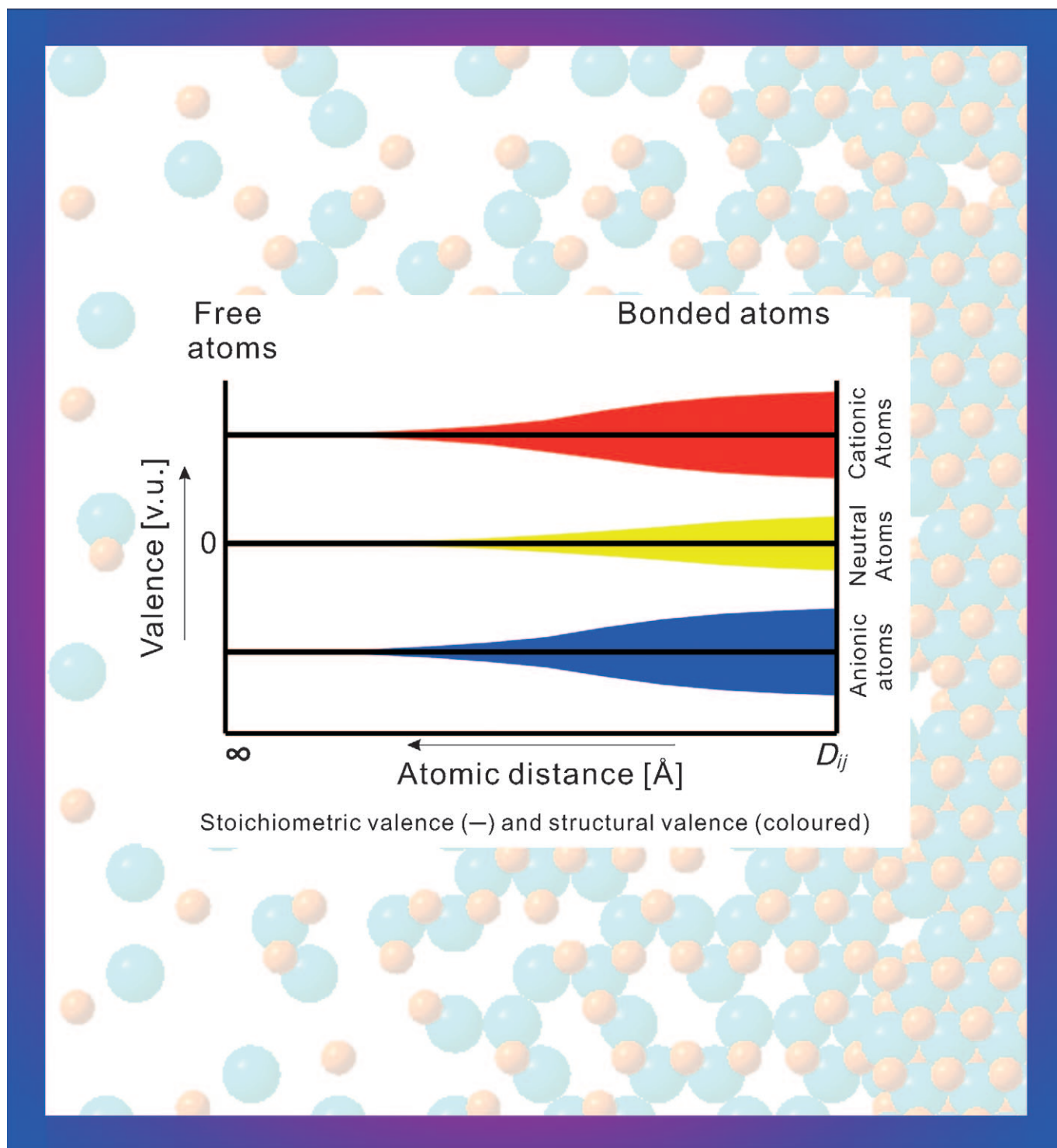
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Stoichiometric Valence and Structural Valence—Two Different Sides of the Same Coin: "Bonding Power"

Friedrich Liebau,*[a] Xiqu Wang,[b] and Waltrude Liebau[a]

Stoichiometric valence (—) and structural valence (coloured)

Abstract: Recent studies use the term valence to describe two distinct aspects of the phenomenon bonding power of an atom. Measured in valence units, one valence term, the classical chemical valence, has integer values and is derived solely from the composition of a compound. The second one, used mainly by solid-state physicists and crystallographers, has non-integer values. It is determined from structure data, which are derived from diffraction experiments, spectroscopy, or quantum-chemical calculations. To distinguish clearly between these two types of valencies, the descriptive terms *stoichiometric valence* and *structural valence* and the respective symbols $^{stoich}V$ and $^{struct}V$ should be used. For the majority of crystalline structures, values of $^{stoich}V$ and $^{struct}V$, both measured in valence units, differ by less than 5%. However, for p-block atoms with one lone electron pair, differences between $^{stoich}V$ and $^{struct}V$ of up to 30% have been reported.

Keywords: bond theory · oxidation · stoichiometric valence · structural valence · valence

Introduction

The valence concept is one of the cornerstones of chemistry. Valence,[1] that is, the bonding power of atoms,[2] not only determines whether atoms interact with each other and in which amounts, but it also strongly affects the structure and stability of compounds. Therefore, knowledge of atomic bonding power is not only essential for understanding the structures and properties of compounds, but it also can help to design new ones.

Every chemist uses the term "valence" as a matter of course. It is, therefore, surprising that in subject indexes of most modern chemistry textbooks one finds terms such as "valence electrons", "valence band" and "valence vibration", but not the term "valence" itself. In fact, no definition of valence is given in those books.

In the midst of the last century the valence of a chemical element was defined as the number of hydrogen atoms that one atom of this element is able to bind in a compound or

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to replace in other compounds.[3] This definition of valence, which is still used in the IUPAC Gold Book,[4] goes back to Edward Frankland,[5] who is considered to be the founder of the valence concept.[6] He realised that chemical compounds contain elements in certain weight or atom ratios. For example, in NH_3, PH_3, AsH_3 and SbH_3, one pnictide atom is *equivalent* to three hydrogen atoms and one mole of a pnictide is equivalent to three moles of hydrogen. The property of an atom to compensate the bonding power of an equivalent number of monovalent atoms such as hydrogen or chlorine was later termed *valence*. Strictly speaking, this classical valence of an atom in a compound is the ratio between the amount—atom or mole—of this atom and the amount of monovalent atoms such as hydrogen or chlorine. Due to the laws of constant and multiple proportions, this valence of an atom, measured in valence units (v.u.) has integer values. These values are derived from the composition of the compound.

In contrast, in the modern solid-state physics literature, the term "valence" is often used to describe an atomic property which has, in general, a non-integer value. These valence values are typically derived either from spectroscopic measurements[7] or from quantum-chemical calculations.[8]

Apparently, chemists and solid-state physicists often use the term "valence" to describe two different atomic properties. This has led to considerable confusion and is, for example, reflected in recent discussions of terms such as valence, covalence, hypervalence, oxidation number, and formal charges by Smith,[9] Parkin[10] and others.

In the present paper it is shown that the classical valence term as introduced by Frankland[5] and the term valence as used by solid-state physicists, are different in nature. Definitions for both are proposed and their properties described.

The Bond-Valence Model

In 1929 Pauling[11] postulated that the valence, V_i, of an atom in a compound is distributed between the bonds to surrounding atoms [Eq. (1)].

$$V_i = \sum_{j=1}^{n} s_{ij} \tag{1}$$

This postulate is valid independent of how the atom is bonded and the structure of the compound. For a molecular compound, for example, the postulate is valid for an atom in the free molecule, as well as for atoms of the molecule in the liquid and solid, crystalline or amorphous, state. The values of V_i and of the partial valences (s_{ij}) depend, of course, on the structural state of the molecule.

Pauling also showed[12] that for homoatomic bonds a logarithmic relationship can be formulated between the bond length and the partial valence ascribed to a bond. This is now called *bond valence*. After it had been established that

corresponding logarithmic correlations hold also for heteroatomic bonds,[13,14] Brown and Altermatt[15] used Pauling's empirical logarithmic relationship in the form of the exponential equation [Eq. (2)].

$$V_i = \sum_{j=1}^{n} s_{ij} = \sum_{j=1}^{n} \exp[(r_0 - D_{ij})/b] = (BVS)_i \qquad (2)$$

Here $(BVS)_i$ is the *bond-valence sum* for a central atom $\mathbf{A}_i$ of an $[\mathbf{A}_i(\mathbf{X}_j)_n]$ coordination polyhedron, and s_{ij} are the bond valences for the bonds between atom $\mathbf{A}_i$ and its ligands $\mathbf{X}_j$;[16] D_{ij} are experimentally determined bond lengths, r_0 and b are bond-valence fit parameters (see Supporting Information, Section 1), and V_i the valence of the atom under consideration. Although other functions have been proposed, (Supporting Information, Section 2[17–20]) Equation (2) is now generally used to describe bond-valence distributions.

Equation (2) was derived from bond-length values (D_{ij}), which were determined by crystal-structure analyses by X-ray diffraction methods. These data were chosen because their D_{ij} values are the most accurate ones known and this data set is by far larger than corresponding D_{ij} sets derived with other methods. It is expected that crystal structure data derived from other methods would result in slight variations in the bond-valence parameters r_0 and b. For non-crystalline compounds, in particular for energy-rich ones, even an equation other than Equation (2) may give a better fit to the structure data. Therefore, strictly speaking, Equation (2) is proven only for structures determined by X-ray analysis.

So far, it has tacitly been assumed that V_i [Eq. (1)] is the classical valence of an atom and, therefore, has integer values. Since this classical valence is derived from the chemical composition of a compound, it is sometimes called *stoichiometric valence*. We adopted this term and proposed the symbol $^{stoich}V$ for it.[21] The values of $^{stoich}V_i$, $(BVS)_i$ and s_{ij} are measured in valence units (v.u.).

It has become widespread practice by most authors to use $b = 0.37$ Å and tabulated r_0 values from references [15] and [22] to calculate the bond-valence sums of the atoms with Equation (1). This is usually done in order to confirm the correctness of a determined crystal structure or to decide between different $^{stoich}V$ values of an atom. For the large majority of inorganic structures, the calculated BVS values of an atom are equal to their corresponding $^{stoich}V$ values within 0.2 v.u. This would indicate that the bond-valence concept is, in principle, correct and that the value $b = 0.37$ Å and the tabulated r_0 values describe the valences well.

However, for some compounds, calculated BVS values deviate from their corresponding $^{stoich}V$ values by up to about 1 v.u. Such deviations can hardly be ascribed to errors in experimental bond-length values alone. Typical examples are structures that contain lanthanide atoms (Ln)[23] or cationic atoms with a lone electron pair.[24]

Estimated Accuracy of Calculated Bond-Valence-Sum Values

To put the discussion on deviations of BVS values from corresponding $^{stoich}V$ values on a solid basis, an error-propagation analysis was made[23,24b] (see Supporting Information, Section 3). Thus, estimated errors of the bond valences and the bond-valence sums that result from experimental bond-length errors were calculated.

Whenever, for a given atom, the absolute value of the difference between a calculated bond-valence sum and the integer value of the stoichiometric valence is higher than the corresponding estimated error [Eq. (3)], the difference is significant and should not be attributed solely to inaccuracies of the structure refinement.

$$\Delta V_i = |^{calcd}(BVS)_i - ^{stoich}V_i| \leq {}^{estim}|\delta(BVS)_i| \qquad (3)$$

If for a given atom $\Delta V_i > {}^{estim}|\delta(BVS)_i|$, this can have several explanations.

1) In a classical mixed-valence compound, one or several structural sites (Wyckoff positions) are occupied by atoms of the same or different elements, which have different $^{stoich}V$ values. Since diffraction methods average over all atoms at a Wyckoff position, in such cases non-integer values of $^{stoich}V$ are derived for the position. For example, in KOs_2O_6 stoichiometrically penta- and hexavalent osmium atoms in the ratio 1:1 occupy the same Wyckoff position,[25] thus leading to an averaged value of $^{stoich}V = 5.5$ v.u. Another example, magnetite Fe_3O_4, has been extensively studied. Below the Verwey transition at $T = 122$ K, magnetite has an inverse spinel-type structure with the structural formula $(Fe^{III})^{[4t]}(Fe^{II}Fe^{III})^{[6o]}O_4$. Its tetrahedrally coordinated Wyckoff position is occupied by ferric atoms Fe^{III}, its octahedral position by ferric and ferrous atoms, Fe^{III} and Fe^{II}, in the ratio 1:1 (see, for example, reference [26]). Diffraction methods lead to an averaged $^{stoich}V$ value of 2.5 v.u. for the latter Wyckoff position.

2) The coordination polyhedra are strongly distorted. This is particularly the case for polyhedra that are centred by cationic atoms of p-block elements that have a stereochemically active lone electron pair.[24b]

3) Strong steric effects are active in the structure. For example, in the chelate series $[Ln_3(C_{36}H_{32}N_7O_{10})(H_2O)]$ the Ln atoms are "squeezed" in small voids formed by the organic ligands.[27] The calculated BVS values for the Ln atoms are 12 to 22% higher than their stoichiometric valence values,[23] which is far more than the 2.7% estimated error according to Equation (3), listed in Table S1 of the Supporting Information.

4) The precision of tabulated values of r_0 and b that were used to calculate V_i is low. This may lead to ΔV_i values of up to about 0.3 v.u. for some $\mathbf{A}-\mathbf{X}$ pairs. In fact, several papers are published per year that try to derive improved r_0 and b values.[28] However, some of these ap-

CONCEPT

proaches just shift the problem from one type of atom to other types for the respective structures.[29]

Since compositional and structural reasons are responsible for large ΔV_i values, one has to be cautious when using ΔV_i to judge the reliability of crystal-structure models. In our opinion, statements such as "one of the best guides for accessing the accuracy of a structure determination has been the BVS"[30] are questionable. It is similarly questionable whether the so-called *global instability index* GII[31] is suitable to estimate the accuracy of a crystal-structure refinement, because the GII is directly related to ΔV_i given in Equation (3).

Instead, the correctness of a structure should be deduced from the values of the standard deviations of the atomic distances, $\sigma(D_{ij})$, calculated during structure refinement; be tested by the usual test programs used by the Inorganic Crystal Structure Database (ICSD) and the Cambridge Structural Database (CSD); and should be checked against crystal chemical and physical experience, including BVS and GII. Experimentally derived coordination polyhedra should not be excluded from statistical studies solely because their ΔV_i values are higher than 0.3 v.u., or because their GII values are higher than 0.25 v.u., as is sometimes suggested.[32] This might result in the omission of just those experimental data from the analysis that may be relevant to inadequate interpretations of the present bond-valence model.

Hence, deviations of calculated BVS values from corresponding $^{stoich}V$ values, which are larger than about 5%, are significant and require an explanation based on chemical or physical grounds, provided that experimentally determined atomic distances are accurate within 0.01 Å.

Coordination polyhedra that are centred by lanthanide atoms and those that are centred by p-block atoms with one lone electron pair, which demonstrate clearly the influence of the electronic structure of such atoms on the BVS values, are discussed below.

Bond-Valence Sums for Various Classes of Atoms

Bond-valence sums of lanthanide atoms: To obtain BVS values that are comparable, they should be derived from isostructural compounds with the same type of coordination polyhedron and that are, if possible, obtained in one and the same experimental study. These conditions are fulfilled for, for example, a series of compounds $Ln_3^{III}Te_2^{VI}Li_3^IO_{12}$, studied by O'Callaghan and co-workers.[33] All these compounds crystallise with the garnet-type structure. The LiO_4 tetrahedra share corners with TeO_6 octahedra to form dense and rigid three-dimensional frameworks. In each framework, the Ln atoms occupy triangular dodecahedral cavities forming LnO_8 polyhedra. A BVS analysis of all atoms within this structure series[23] revealed that the BVS values of the Li atoms and some of the Te and Ln atoms deviate significantly from their corresponding $^{stoich}V$ value. On the other hand, deviations of the BVS values of the O atoms are smaller than the estimated errors of BVS and, therefore, insignificant (see Supporting Information, Section 4).

In Figure 1a the calculated BVS values of the Ln atoms in the garnet-type series are plotted versus the atomic number Z_{Ln}. If the BVS values represent integer values of $^{stoich}V$, as has generally been assumed so far, then they should scatter randomly about the horizontal dotted line of Figure 1a. This
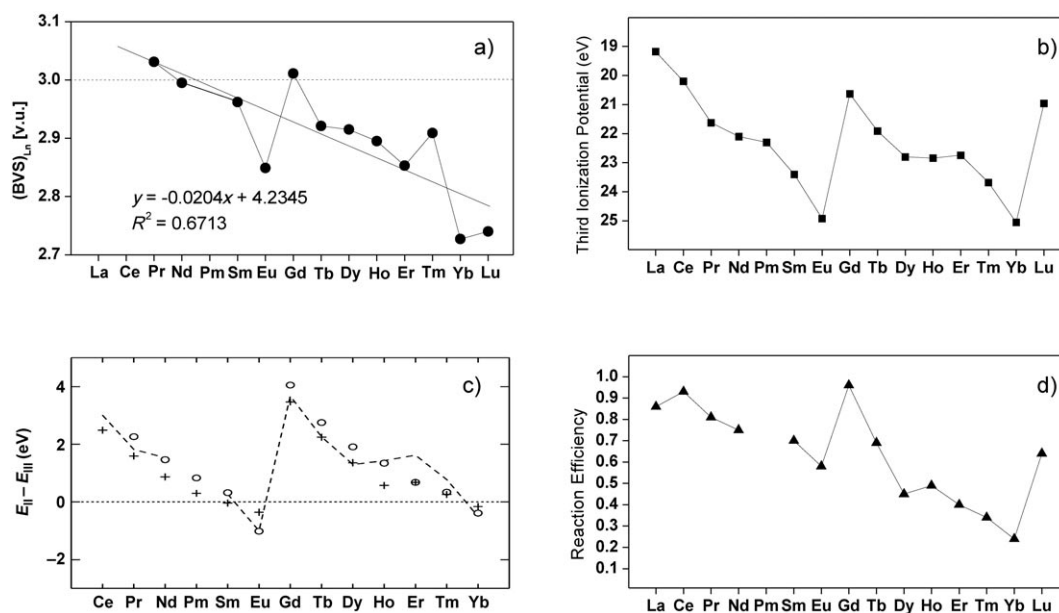

Figure 1. Plots of a) $(BVS)_{Ln}$ versus Z_{Ln}, b) the third ionisation potential[34] of Ln versus Z_{Ln}, c) valence values of Ln atoms in metallic Ln (open circles) and Ln sulfides (crosses), calculated with quantum chemical methods,[8] versus Z_{Ln}, and d) the efficiency of the reactions between Ln^I and SF_6[35] versus Z_{Ln}, respectively.

is, however, not the case. Instead, the $(BVS)_{Ln}$ follow a trend that is indicated by a solid line from the upper left to the lower right of the plot. In addition, the individual $(BVS)_{Ln}$ values deviate from this line in an irregular way.

At first sight these deviations from the trend appear difficult to explain. However, the plot shown in Figure 1a is very similar to a plot of the third ionisation potential[34] of Ln versus Z_{Ln} (Figure 1b). Since the ionisation potentials are strongly dependent on the electronic structure of the atoms, the similarity of the two plots suggests that for $Ln_3Te_2Li_3O_{12}$ phases, the $(BVS)_{Ln}$ values reflect the electronic structure of the lanthanide atoms. This suggestion is supported by two other observations.

1) Strange et al.[8] calculated with quantum-chemical methods the valences of Ln atoms in lanthanide metals and sulfides, and plotted them versus Z_{Ln} (Figure 1c). The similarity between Figures 1a and 1c suggests that these valence values and the calculated bond-valence sums $(BVS)_{Ln}$[23] represent the same valence property.
2) This conclusion is strengthened by a study of Cheng and Bohme,[35] who determined the reaction efficiency of the gas-phase reaction between singly ionised Ln^I and neutral SF_6 molecules. They proposed that this reaction efficiency, which is plotted in Figure 1d versus Z_{Ln}, is related to the energy to promote one electron of Ln from a 4f orbital to a $5d^1 6s^1$ configuration.

Comparison of the plots in Figure 1 shows that the bond-valence sum of Equation (2) does not represent the integer stoichiometric-valence values of the lanthanide atoms, but a non-integer valency that is dependent on the electronic structure of the atoms.

In the garnet-type $Ln_3Te_2Li_3O_{12}$ structures, the lanthanide atoms are too small to properly fill the dodecahedral cavities of the framework of corner-sharing tetrahedra and octahedra. On the other hand, the framework is too rigid to adjust to the small size of the Ln atoms. As a consequence, the Ln atoms have large vibration amplitudes and are said to "rattle" in their cavities. In such structures, the influence of the electronic structure of the Ln atoms on $(BVS)_{Ln}$ becomes apparent. However, this is not always the case. For example, in the series of lanthanide chelates $[Ln_3(C_{36}H_{32}N_7O_{10})(H_2O)]$ mentioned earlier[27] each Ln atom is "squeezed" between six short chelate Ln−O bonds. This coordination of Ln is supplemented by a longer bond to one H_2O molecule and three weak Ln−N bonds. The steric effects exerted on the Ln atoms by the surrounding oxygen atoms overcompensate the electronic effects of the Ln atoms.[23]

Bond-valence sums of transition-metal atoms: Within a crystal structure, different components have different spatial requirements. For instance, smaller coordination polyhedra have to adjust to neighbouring larger ones and vice versa. This is usually achieved through a shortening of some bonds and stretching of others. This causes lattice strain,[32] which

is the stronger, the more different the size of neighbouring polyhedra. In structures in which the bonds between central and peripheral atoms of polyhedra are considerably covalent, additional angular distortions of the polyhedra arise in order to achieve optimal overlap of the orbitals. This effect is observed in compounds with transition-metal atoms and is particularly strong if caused by electronic effects such as the Jahn–Teller effect. For example, in the series of compounds $Ln_2Cu_2O_5$ (Ln = Y, Ho, Er, Tm, Yb) calculated BVS values for the Cu1 and Cu2 atoms are in the ranges 1.86–1.93 v.u. and 1.78–1.85 v.u., respectively. This is significantly lower than the stoichiometric valence 2 v.u.[36]

Bond-valence sums of p-block atoms: Recently,[24b] a statistical analysis with more than 2500 $[LO_n]$ and $[LS_n]$ coordination polyhedra was carried out, in which **L** are p-block atoms from Groups 13–17 of the Periodic Table that have one lone electron pair.

The data for these polyhedra were retrieved from the Inorganic Crystal Structure Data (ICSD) files with stringent selection criteria so that the bond lengths are expected to fulfil the condition of Equation (3). It turned out that the bond-valence parameters, r_{0i}, for individual coordination polyhedra of the same $[LX_n]$ type are not constant as usually assumed, but can be fitted to the linear function [Eq. (4)] in which Φ_i is the *eccentricity parameter*. Φ is a measure of the eccentricity of the coordination polyhedra, that is, of a specific kind of polyhedron distortion.[37]

$$r_{0i} = E|\Phi| + F \qquad (4)$$

In Section 5 of the Supporting Information it is shown that r_{0i} is more precisely fitted to an exponential function of the form given in Equation (5).

$$r_{0i} = \exp[p(|\Phi_i| + q)] + t \qquad (5)$$

Not only the individual r_{0i} values, but also the BVS values of the lone-pair atoms **L** are a function of the eccentricity of the $[LX_n]$ polyhedra [Eq. (6)].

$$(BVS)_{Ln} = E'|\Phi_i| + F' \qquad (6)$$

They are neither constant, nor have necessarily integer values. Consequently, the bond-valence sums of the p-block atoms with one lone electron pair represent a bonding power that is different from $^{stoich}V$.

An increase of $(BVS)_i$ with increasing eccentricity parameter (Φ_i) is interpreted to be the result of the influence of the lone electron pair on the $[LX_n]$ polyhedra. As $|\Phi_i|$ increases, the distance of the lone electron pair from the nucleus of **L** increases, and these electrons are promoted to higher energy levels. How far can a lone electron pair depart from the nucleus of, for example, a stoichiometrically trivalent antimony atom Sb^{III}? Ultimately, it can fully dissociate from the antimony atom, which then turns from a Sb^{III} into a stoichiometrically pentavalent Sb^V atom. This hypo-

thetical process is a normal oxidation by 2 v.u. It seems, therefore, reasonable to divide this hypothetical dissociation process into two parts:

1) An *initial oxidation* in which $(BVS)_i$ increases continuously, whereas $^{stoich}V_i$ does not change.

2) A *final oxidation* in which, after a certain threshold value of $(BVS)_i$ has been reached during the initial oxidation, one or both electrons of the lone electron pair dissociate spontaneously from the Sb^{III} atom. As result of this second process, either a $\cdot Sb^{IV}$ radical or an Sb^V atom, respectively, is formed.

In the case of cetineite-type structures of general composition $A_6[Sb_{12}O_{18}][SbX_3]_2[D_xY_{6-y}]$, with $A = Na^I$, K^I, Rb^I, Sr^{II}, Ba^{II}; $X = S^{-II}$, Se^{-II}; $D = Na^I$, Sb^{III}, C^{IV}, and $Y = H_2O$, OH^{-I}, O^{-II}, $(BVS)_L$ values of Sb^{III} have been found to vary between 3.00 and 3.99 v.u.[24a] The hypothetical oxidation process $Sb^{III} \rightarrow Sb^V + 2e^-$ is shown in Scheme 1.
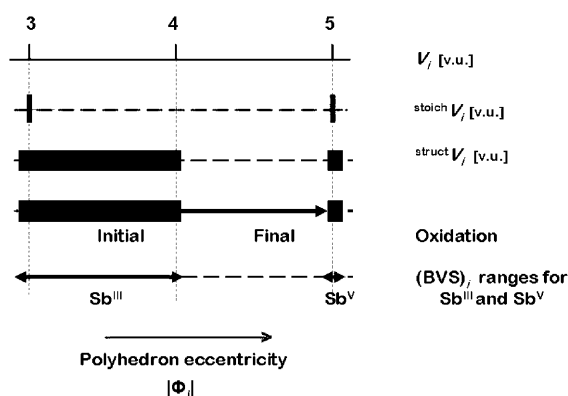
Scheme 1. Schematic representation of valence states of antimony and oxidation of Sb^{III} to Sb^V, as function of the eccentricity parameter Φ_i. Note that $^{stoich}V_{Sb}$ can have only the values +3 and +5 v.u., while $^{calcd}(BVS)_{Sb}$ can have any value within the large black region of the initial oxidation of Sb^{III} and the small black region around Sb^V. The intermediate range is available for neither $^{stoich}V_{Sb}$ nor for $(BVS)_{Sb}$.

Usually, in the final oxidation both electrons of the lone electron pair of a p-block atom **L** will dissociate from **L**, giving rise to an increase of $^{stoich}V_L$ by 2 v.u. This is particularly true if the **L** atoms are coordinated by strongly electronegative atoms such as O^{-II}, S^{-II}, halide atoms Hal^{-I} and so forth. An example is the reaction $[P^{III}O_3]^{3-} + \frac{1}{2}O_2 \rightarrow [P^VO_4]^{3-}$.

If, instead, the **L** atom is bonded to more electropositive ligands such as C, Si, P and so forth, which have a lower tendency to attract electrons, the **L** atom can transfer only one of the two electrons of the lone electron pair to its ligands. As a result, during the final oxidation $^{stoich}V_L$ increases by only 1 v.u. and the oxidation product has an unpaired electron and, therefore, a radical character. An example for such a reaction is shown in the following reaction formula.[38]
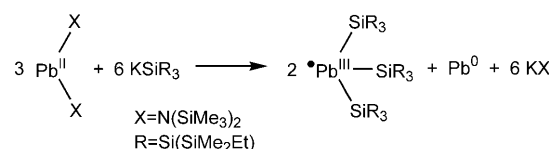
Further p-element atoms, which can be considered as products of an one-electron final oxidation, have been reported: Si^{III}, Ge^{III}, Sn^{III}, Pb^{III}.[39]

We have interpreted quasi-continuous and discontinuous increases of BVS as initial and final oxidation, respectively. In the same way, corresponding quasi-continuous and discontinuous decreases of BVS can be considered as initial and final reduction processes, respectively. Usually, final oxidation or reduction processes cause changes in composition or change of oxidation states of other atoms in the compound. In comparison, a change of BVS of one atom, during initial oxidation or reduction, is compensated by corresponding BVS changes of other atoms of a compound.

No extensive analysis of the influence of polyhedron distortion on BVS of p-block atoms with their highest oxidation number, that is, without lone electron pairs, is available. However, Smith et al.[40] have shown for a set of 30 SiO_4 tetrahedra from 20 well-refined silicate structures that the isotropic chemical shifts in ^{29}Si NMR spectra correlate ($R^2 = 0.93$) with the total $(BVS)_O$ values of these tetrahedra and also with their asymmetry parameters.

Bond-valence sums of atoms in the elemental state: According to the definition formulated in the Introduction, the stoichiometric valence of an atom is the number of univalent atoms, such as H or Cl, that compensates the bonding power of the atom. Thus, $^{stoich}V$ is 0 v.u. for atoms in the elemental state. However, in the solid-state science literature, fractional valence values for elemental atoms are reported that are derived from crystal structure data, spectroscopic measurements or quantum-chemical calculations.

For example, Trömel and co-workers, using the bond-valence Equation (2), derived fractional valence values for elemental atoms from measurements of atomic volumes $V_A =$ (unit-cell volume)/(number of atoms per unit cell), that is, from structure data. Tacitly assuming that the bond-valence parameters r_0 and b change only insignificantly with increasing pressure, they concluded, for example, that the valence of lithium increases steadily from 1.0 v.u. at ambient pressure to 3.0 v.u. at 47 GPa, that of sodium to 4.1 v.u. at 103 GPa and that of cesium to about 7 v.u. at 184 GPa.[41] This indicates that, within the pressure ranges applied, all the Li electrons are transferred to the conduction band, while in Na and Cs only some of them are transferred. Similarly, the valence of iodine increases from 1.0 v.u. in the vapour phase to 1.78 v.u. in crystalline I_2 at ambient pressure and further to 3.1 v.u. at 250 GPa.[41c]

Hence, BVS values calculated from structural data with Equation (2) do not represent the stoichiometric valence, but a valence property that depends on the electronic struc-

ture of the atoms. In contrast to $^{stoich}V$, which has integer values, BVS has, in general, non-integer values.

Non-Integer Valence Values of Atoms Derived from Physical Measurements

As already said, in the solid-state physics literature non-integer valence values are reported that have been derived from physical measurements without using structural data. For example, Dallera et al.[7b] determined with spectroscopic methods that the valence of metallic ytterbium increases steadily from 2.0 v.u. at ambient pressure to 2.55 v.u. at 20 GPa. From first-principles calculations they concluded that a further increase to approximately 2.73 v.u. at 60 GPa takes place.

Kondo insulators and heavy-fermion compounds have recently gained increasing interest because of their unusual electric and magnetic properties at low temperatures. Most of them contain lanthanide atoms such as SmX with $X = S$, Se, Te,[42] SmB_6,[43] $YbFe_4Sb_{12}$ and $SmOs_4Sb_{12}$ with filled skutterudite-type structures,[44] the fulleride $Sm_{2.75}C_{60}$,[45] and intermetallic compounds such as $YbInCu_4$[7] and $Yb_8Ge_3Sb_5$.[46]

In all these compounds the lanthanide atoms are described to have an *intermediate-valence state,* which is often less correctly called mixed-valence state.[47] In this state a non-integer number of lanthanide 4f electrons hybridise with either the conduction band or with d, p or/and s orbitals of their ligands, leading to fractional valence values. Using spectroscopic methods and band-structure calculations, it can be shown which of the orbitals are involved in the hybridisation. For several of these compounds, for example, SmS[42b] and YbInCu4,[7a] it has been shown that these valence values change with pressure and/or temperature, either gradually or abruptly. Such valence changes are linked with changes of their crystal structure, while the composition of the compound and, therefore, $^{stoich}V$ remains unchanged.

In heavy-fermion compounds containing actinide elements, such as UFe_4P_{12} (filled skutterudite-type), $U_3Sb_4Pt_3$ and $U_3Sb_4Pd_3$, intermediate valences have been attributed to hybridisation between 5f electrons of the actinide atoms and electrons in other orbitals.[48] This compares with 4f electron hybridisation of lanthanide atoms in corresponding Ln containing compounds.

Hence, non-integer valence values of lanthanide and actinide atoms, which are derived from spectroscopic measurements and band-structure calculations, represent the same valence property as the bond-valence sums. Both are different from $^{stoich}V$.

Structural Valence

Since valence values derived from BVS calculations and from spectroscopic measurements, band-structure calculations or quantum-chemical calculations are dependent on

the structure of the material considered, for this valence property the term *structural valence* and the symbol $^{struct}V$ have been proposed.[21]

Within the stability field of a compound, the structure changes continuously with physicochemical parameters, such as temperature, pressure, electric and magnetic fields and so forth, and so does $^{struct}V$. Consequently, $^{struct}V$ of an atom is not restricted to integer values but has, in general, fractional values. During first-order phase transitions $^{struct}V$ changes discontinuously, but not in large steps of 1 or 2 v.u. as $^{stoich}V$ does during full chemical oxidation and reduction. Since atoms are held together by electrons, it seems reasonable to define $^{struct}V$ on the basis of the electrons involved in bonding.

Definition: *For bonds that result from a transfer of electrons between atoms, the structural valence, $^{struct}V$, is, in general, the non-integer number of electrons that a bonded atom contributes to form bonds with neighbouring atoms of higher electronegativity or receives from more electropositive neighbours for bonding.*

According to this definition of $^{struct}V$, no distinction has to be made between ionic, covalent, metallic and hydrogen bonds.

1) If an atom forms only fully ionic bonds to its neighbours, its $^{struct}V$ values would numerically be equal to the formal charge of the atom, that is, numerically equal to its $^{stoich}V$ value.
2) If an atom forms only fully covalent bonds to neighbouring atoms, its $^{struct}V$ values would be equal to its number of bonding electron pairs.
3) In ideal metals, $^{struct}V$ of an atom is equal to the number of electrons that it has transferred to the conduction band (electron gas).
4) The hydrogen bond is partly covalent and partly ionic and, therefore, it is covered by the above definition of $^{struct}V$.
5) Van der Waals bonds are formed through attraction between permanent or fluctuating dipoles, without electron transfer between the participating atoms. Consequently, van der Waals bonds are not included in the definition given above.

In conclusion, $^{struct}V$ and not $^{stoich}V$ describes the bonding power of an atom that, according to Pauling,[11] is distributed between the bonds to neighbouring atoms. The equation for the bond-valence model [Eq. (2)] should, consequently, be given in the form of Equation (7).

$$(\text{BVS})_i = \sum_{j=1}^{n} s_{ij} = \sum_{j=1}^{n} \exp[(r_0 - D_{ij})/b] = {}^{struct}V_i \tag{7}$$

Stoichiometric Valence

In analogy to the definition of $^{struct}V$ given above, $^{stoich}V$ can be defined as follows.

Definition: *The stoichiometric valence, $^{stoich}V$, is the integer number of electrons that a bonded atom has formally lost ($^{stoich}V > 0$) or gained ($^{stoich}V < 0$), if the compound under consideration is assumed to consist of ions having integer-number charges.*

Whereas $^{struct}V$ is dependent on the structure of a compound, $^{stoich}V$ is not. Instead, $^{stoich}V$ is a function of the chemical composition of a compound. The terms "*stoichiometric valence*" and "*oxidation number*" are used synonymously, as are their symbols $^{stoich}V$ and ^{ox}N.

Valence Properties as Functions of Atomic Distances

To further illustrate the difference between $^{stoich}V$ and $^{struct}V$, the change of the bonding power of two atoms A and B, as a function of their distance r_{A-B}, is shown schematically in Figure 2. For a pair of free atoms or ions A and B ($r_{A-B} = $
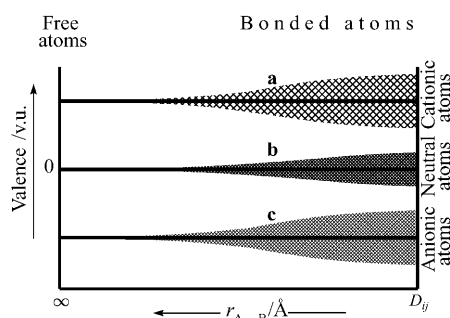

Figure 2. Schematic diagram illustrating changes of the valence properties as function of the atomic distance, r_{A-B}. D_{ij}: Experimental bond length. —— Stoichiometric-valence value, $^{stoich}V$, synonymous to oxidation number, ^{ox}N. Ranges of structural-valence values of a) cationic atoms, $^{struct}V_{cation}$, b) atoms in the elemental state, $^{struct}V_{atom}$, and c) anionic atoms, $^{struct}V_{anion}$ are differently shaded.

∞) only $^{stoich}V$ is defined, while $^{struct}V$ is undefined, because there is no bond between A and B. On decreasing the distance r_{A-B}, a bond between A and B may form that becomes increasingly stronger. Eventually, the equilibrium structure of the compound is formed, for which $r_{A-B} = D_{ij}$. During this process, the bonding power of the bonded atoms changes to the same degree as the overlap of their atomic orbitals increases. This bonding power, which depends on the structure of the compound, is the structural valence, $^{struct}V$. Values of $^{struct}V$ can deviate considerably from those of $^{stoich}V$ and vary within the ranges indicated in Figure 2 by the differently shaded regions for cationic, anionic and neutral atoms. In contrast to $^{struct}V$, which can vary greatly, $^{stoich}V$ of a bonded atom usually does not change over a large range of atomic distances.

Each bonded atom, irrespective of its distance r_{A-B}, has values for both valencies, $^{stoich}V$ ($\equiv\ ^{ox}N$) and $^{struct}V$. In addition, each atom has a value of effective electrostatic charge (Q). This charge is the difference between the atomic

number and the number of electrons within the volume occupied by an atom. This volume can be derived with the Bader method,[49] and Q is approximately equal to the X-ray scattering power of an atom.

To distinguish in chemical formulas between these three atomic properties, it is proposed to use, for example, for lithium polysilicate Li_2SiO_3[50] the notations $Li_2^ISi^{IV}O_3^{-II}$ for $^{stoich}V$ ($\equiv\ ^{ox}N$), $Li_2^{+1.00}Si^{+3.92}O^{-2.02}O_2^{-1.95}$ for $^{struct}V$, and $Li_2^{0.25+}Si^{0.57+}O^{0.18-}O_2^{0.45-}$ [51] for Q values.

Methods to Determine $^{stoich}V$ and $^{struct}V$

Determination of $^{stoich}V$ ($\equiv\ ^{ox}N$): Provided that all atoms of an element in a compound or alloy have the same value of stoichiometric valence, this value can readily be determined from the ratio between the number of atoms of this element to the numbers of atoms of the other elements in the compound or alloy. This means, $^{stoich}V$ can be determined from its chemical composition alone, without regard of the atomic structure. For example, for sulfuric acid, hydrogen, sulfur and oxygen have the respective $^{stoich}V$ values 1, 6 and -2 v.u. and the formula $H_2^IS^{VI}O_4^{-II}$.

If a system contains atoms of an element in two or more oxidation states, as in magnetite $Fe^{II}Fe_2^{III}O_4$ or sodium thiosulfate $Na_2^IS^{VI}O_3^{-II}S^{-II}$, additional chemical analyses are necessary to determine $^{stoich}V$ values of all the atoms. However, no information on the structure, such as experimental bond lengths and angles, is required. In cases such as $TlSbO_3$ and $FeTiO_3$, which may be formulated as either $Tl^ISb^VO_3^{-II}$ or $Tl^{III}Sb^{III}O_3^{-II}$ and $Fe^{II}Ti^{IV}O_3^{-II}$ or $Fe^{III}Ti^{III}O_3^{-II}$, respectively, further studies are necessary to decide which of these $^{stoich}V$ values are actually present.

Crystal-chemical experience shows that in most structures that have been determined with sufficient accuracy, $^{struct}V$ values deviate from their corresponding $^{stoich}V$ values by less than 5% (see Table S1 of Supporting Information, Section 3). Significantly larger deviations have been found for stereoactive p-block atoms,[24b] transition-element atoms in strongly Jahn–Teller distorted coordination polyhedra[36] and for atoms that are too small to fill the cavities they are in or too large so that they are "squeezed" in them. Examples for the latter are the lanthanide atoms in the two isostructural series described earlier.

As long as $\Delta V_i = |\ ^{calcd}(BVS)_i - ^{stoich}V_i| < \approx 0.30$ v.u., the value of $^{stoich}V_i$ will be equal to the nearest integer-number value of $^{calcd}(BVS)_i$. Thus, $^{stoich}V_i$ can be estimated from BVS although, strictly speaking, the latter represents $^{struct}V_i$.

Determination of $^{struct}V$: Because the values of $^{struct}V$ depend on atomic structure, any method yielding structure-dependent quantities may be used to deduce values of $^{struct}V$. This is particularly true for diffraction methods, independent of the kind of radiation used (X-rays, electrons, neutrons, etc.). It is also true for spectroscopic methods, independent of the specific wavelength of the radiation applied. In fact, in the modern solid-state science literature an increasing number

of studies are reported, in which fractional valence values are derived from spectroscopic measurements, such as X-ray absorption spectroscopy (XAS),[44a] hard X-ray photo-emission spectroscopy (HX PES),[44b] and with scattering experiments such as high-pressure nuclear forward scattering (HP NFS)[42b] and resonant inelastic X-ray scattering (RIXS).[7b]

To determine $^{struct}V$ of an atom it is not necessary to make a full (crystal) structure refinement. It is enough to measure the geometry of all atoms within a coordination sphere. Reasonably accurate values of $^{struct}V$ have been determined, for example, from crystallographic unit-cell data and atomic volumes of highly symmetrical structures.[52,53]

Quantum-chemical calculations can not only be used to derive the value of $^{struct}V$, but, in addition, can give information on the distribution of the electrons defining $^{struct}V$[8] among the orbitals.

Concluding Remarks

The bonding power of an atom, usually termed "valence", has two different aspects: 1) the stoichiometric valence, which is linked with the chemical composition of a compound, and 2) the structural valence, which is directly connected to the atomic structure of the compound. Recognition of the existence of these two valencies necessitates one, in many cases, to consider which of the two valencies is responsible for a given observation. An example will suffice to demonstrate the potential importance of distinguishing between $^{stoich}V$ and $^{struct}V$.

In high-temperature superconduction studies, usually only the role of $^{stoich}V$ of the constituting elements is discussed. It is widely assumed that in the cuprate high-temperature superconductors, coexistence of Cu^{I} and Cu^{II} or Cu^{II} and Cu^{III} may be a precondition for high-temperature superconductivity.[54] On the other hand, after the discovery in 1986 of high-temperature superconductors by Bednorz and Müller,[55] the critical temperature, T_c, below which a material becomes superconducting, increased within about two years from 35 K for $La_{2-x}Ba_xCuO_{4+\delta}$ to 120 K for $Tl_2Ca_{1.5}BaCu_3O_{8.5+x}$,[56] mainly by substitution of La^{III} atoms by the lone-pair atoms Tl^{I}, Pb^{II} and Bi^{III}. In a previous section, we have discussed that such stereoactive p-block atoms with a lone electron pair show particularly strong deviations of $^{struct}V$ values from their corresponding $^{stoich}V$ values. Preliminary results of applying the concept of dual valency to superconductors indicate that $^{struct}V$ plays an essential, probably larger role in high-temperature superconductivity than $^{stoich}V$.

Acknowledgements

[1] Where a term is introduced or defined in the text it is given in italics.

[2] Throughout this paper the term "atom" is used regardless of cationic or anionic character. When necessary, the terms "cationic atoms" and "anionic atoms" are used instead of "cations" and "anions".

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