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Internally Consistent Ion Volumes and Their Application in Volume-Based Thermodynamics

Leslie Glasser* and H. Donald Brooke Jenkins*

Nanochemistry Research Institute, Department of Applied Chemistry, Curtin University of Technology, G.P.O. Box U1987, Perth WA 6845, Australia, and Department of Chemistry, University of Warwick, Coventry CV4 7AL, West Midlands, United Kingdom

"Volume-based thermodynamics" (VBT) relates the thermodynamics of condensed-phase materials to their formula unit (or molecular) volumes, V_m. In order to secure the most accurate representation of these data, the volumes used are to be derived (in order of preference) from crystal structure data or from density or, in the absence of experimental data, estimated by ion-volume summation.

Introduction

Our early ion-volume assessments were based on published values of ionic radii by assuming hard, spherical cations, with the anion volumes obtained by difference (and thus including all void volume). In order to establish more consistent and accurate values for V_m as estimated by ion-volume summation and, consequently, for the individual single-ion volumes, we here provide an optimized, internally consistent set of ion volumes for 27 common cations and 16 common anions, plus water of crystallization, based on 237 ionic solids, both anhydrous and hydrated; these ion volumes provide considerably improved volume estimates. The resulting volumes assigned to the individual ions imply a new paradigm, in that the ions are not to be regarded as having predetermined regular shapes. The data are tested on ammonium and alkali-metal halide salts and on an array of complex ionic materials. Volumes of ions not listed may be estimated by difference from published crystal data for appropriate materials, based on the data set reported here. In this way, a substantial database of internally consistent volumes can rapidly be built up.

These updated ion sums should enable improved estimations of a number of thermodynamic quantities for unsynthesized, unmeasured, or even hypothetical, condensed-phase ionic materials.

* To whom correspondence should be addressed. E-mail: l.glasser@curtin.edu.au (L.G.), h.d.b.jenkins@warwick.ac.uk or harryjenkins693@btinternet.com (H.D.B.J.). Telephone: +61 8 9266-3126 (L.G.), +44 2476-523-265 or +44 2476-466-747 (H.D.B.J.). Fax: +61 8 9266-4699 (L.G.), +44 2476-524-112 (H.D.B.J.).

Volume-Based Approach to Thermodynamics

The thermodynamics of condensed-phase materials[1] has recently developed in an entirely new direction.[2] Formerly, thermodynamic properties of materials were seemingly only distantly related to such properties as densities or structures. However, as a result of considerable recent work,[2a] the principle of "volume-based thermodynamics" (VBT) has been rather firmly established by a convincing confirmation of simple empirical relations[3] between structural properties (in terms of the formula unit volume, V_m) and a variety of thermodynamic properties.

As an example, we may note that the standard entropy, $S°_{298}$, is closely linearly dependent on the molar volume, V_m.[3c,d]

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$$S°_{298}/\text{J K}^{-1} \text{ mol}^{-1} \approx k(V_m/\text{nm}^3 \text{ formula unit}^{-1}) + c \quad (1)$$

where k and c are constants.[3e] The relation can similarly be expressed in terms of the density,[4] ρ:

$$S°_{298}/\text{J K}^{-1} \text{ mol}^{-1} \approx k'[(M/\text{g})/(\rho/\text{g cm}^{-3})] + c \quad (2)$$

where k' is a related constant[3f] and M is the formula mass of the ionic material.

The lattice potential energy, U_{POT}, of ionic materials,[3a] including complex minerals,[3b] depends on the inverse cubic root of the formula unit volume ($V_m^{-1/3}$), together with an ionic strength factor, I, which is dependent on the number of integral ion charges.[3g,5] For materials with lattice energies that are less than 5000 kJ mol^{-1}:

$$U_{POT}/\text{kJ mol}^{-1} \approx 2I[\alpha/(V_m/\text{nm}^3)^{1/3} + \beta] \quad (3)$$

where α and β are stoichiometrically dependent[3g] fitted constants, although α varies only marginally in value. U_{POT} can also be related to the density, such that the analogous equation is

$$U_{POT}/\text{kJ mol}^{-1} \approx \gamma[(\rho_m/\text{g cm}^{-3})/(M_m/\text{g})]^{1/3} + \delta \quad (4)$$

with related stoichiometrically dependent fitted constants,[3h] γ and δ (in this form, also incorporating the ionic strength factor, I, simply for convenience).

For ionic materials with lattice energies greater than 5000 kJ mol^{-1}, the equation[4a] takes a generalized form, *with no fitted constants*:

$$U_{POT}/\text{kJ mol}^{-1} \approx AI[2I/(V_m/\text{nm}^3)]^{1/3} \quad (5)$$

where A ($=121.4$ kJ mol^{-1}) is a standard electrostatic constant or, in terms of density:

$$U_{POT}/\text{kJ mol}^{-1} \approx B[(I^4 \rho_m/\text{g cm}^{-3})/(M_m/\text{g})]^{1/3} \quad (6)$$

where $B = 1291.7$ kJ mol^{-1}. VBT can even encompass the lattice energy of partially covalent materials.[6]

These VBT concepts, as well as other aspects of volume usage, have been much applied in the very recent literature both by ourselves[7] and by others.[8]

Traditionally and historically, the measure of the ion size was vested in the ionic radius, which was early established as an additive quantity on the assumption of the existence of hard, spherical ions.[9] Thus, in the early part of the 20th century, it was noted that the larger anions are probably in mutual contact within ionic crystal structures, with the smaller cations located within the interstices. This enabled ion radii to be directly derived from geometric considerations of crystal lattice dimensions. Such ion radii are widely available[10] and have been used in many situations, generating such important results as the radius ratio rules for crystal packing,[11] the Hume−Rothery rules for metal−solid solutions,[12] and Pauling's rules relating to crystal structures.[13] We note that it may be possible that such rules could be improved (although perhaps only slightly) by considering volume in place of radius.

In thermodynamics, the Kapustinskii equation[14] for the lattice energy of *binary* ionic solids, M_pX_q (assuming complex ions, such as sulfate, to be single entities, X^-), is based on the inverse sum of ionic radii, r:

$$U_{POT} = \frac{A\nu|z_+z_-|}{\langle r \rangle}\left(1 - \frac{\rho}{\langle r \rangle}\right) \quad (7)$$

where $A = 121.4$ kJ mol^{-1} nm and $\rho = 0.0345$ nm. This equation has been in use in this form, and has appeared in undergraduate texts, for over half a century. It was early recognized that the implicit assumption (by the use of radii) of sphericity for ions like the planar carbonate or nitrate anions was untenable. Furthermore, some of the reported ion radii did not result in reliable lattice energies when inserted into the Kapustinskii equation. Accordingly, the Kapustinskii equation has also been used in reverse, to generate so-called *thermochemical* radii,[15] using known lattice energies derived from Born−Haber−Fajans cycles. These thermochemical radii have then been used in the reliable estimation of lattice energies for other salts containing examples of the ion in question, thus further demonstrating that the ion size is rather consistent among different ionic materials. The Kapustinskii equation was generalized, beyond binary systems, to ionic solids of essentially any complexity, by our introduction[5] of the ionic strength factor, I.

Independently, Mallouk et al.[16a] noted a linear relationship for simple binary solids between the lattice enthalpy, $\Delta_L H$ (which is itself closely related[16b] to the lattice energy, U_{POT}), and the inverse cubic root of the formula unit volume, that is, to $V_m^{-1/3}$ (which has the same dimension, of inverse distance, as the inverse ion radius sum in the Kapustinskii equation). We have successfully extended this observation to complex ionic solids,[4a] and more generally to condensed phases, in the form of ionic liquids.[4d]

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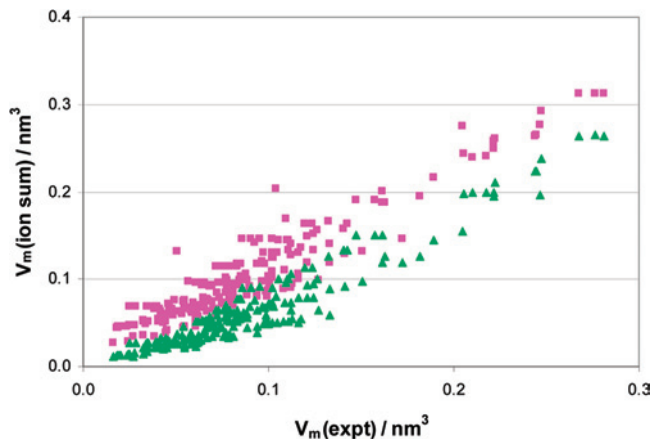
Figure 1. Ion-sum formula unit volumes, V_m, for 204 ionic solids, with 174 being anhydrous and 30 hydrated, using sums of ion volumes from Glasser and Jenkins[3b] (squares) and Marcus et al.[17] (triangles) plotted against crystal structure-based experimental formula unit volumes.

Figure 1 shows that the current ion volumes,[3b,17a] while providing useful (and usable) starting points for volume estimations to be applied in subsequent VBT estimations, are not entirely satisfactory and are deserving of improvement. Thus, we have judged it timely to switch from the *radius-based* ionic size paradigm to one that is *volume-based*; moreover, so doing increases the portfolio of compounds for which we can now obtain thermodynamic relationships.[3a,b,18]

There is no intention that volume-based ion sizes will supersede ionic radii because these two measures are complementary, the first relating to the volume occupied by the ion (with no reference to shape) and the second relating to ion distances but assuming hard spheres.

New Paradigm for Single-Ion Volumes

The general procedure used by which to determine single-ion volumes, V_+ and V_-, in our original VBT paper[3b] was to convert the ionic radii, r_+, of the simple cations to volume, V_+, using the mathematical relation for a sphere

$$V_+ = 4\pi r_+^{\,3}/3 \tag{8}$$

and then derive the anion volumes, V_-, by difference from the measured crystallographic unit cell volume of the formula unit, V_{cell}/Z (where Z = number of formula units in the crystallographic unit cell of a compound containing the cation(s) and anion(s) in question). By this procedure (as was recognized at the time), the volume of voids in the structure is necessarily allocated to the anion. It is, however,

important to note that any overestimate in the volume of an anion, X^-, by assigning voidage inappropriately, leads to a compensating underestimate for the volume of any other cation that has been derived by difference. Thus, the ion-volume sum for the reconstituted ionic material will still be correct.

As cation radii, either the Goldschmidt values[10a] or those of Shannon and Prewitt[10b] have been used. A rough correlation has also been obtained between these ionic volumes and those derived from molar refraction and volume diamagnetic susceptibility.[17a]

Other workers[19a] have produced additive volume parameters but generally for a limited number of atomic species and in covalent coordination. Following Mighell et al.,[19b] Hofmann[19c] performed an extensive analysis of the CSD crystal structure database and derived additive *elemental* volumes therefrom; he notes that these volumes may not be strictly applicable to mainly inorganic materials but, to some extent, this has been addressed by Stalick,[19d] who has provided additional sets of volumes for inorganic materials (and also for metals and intermetallics). Nevertheless, these elemental volumes can be, and have been, usefully adopted in some applications in the absence of other information. The various volumes thus determined have been widely used to estimate the volumes of materials either where data are not available (whether they are not yet reported or measured or where the material may not yet have been synthesized, is unstable, or might even be hypothetical) or where the data are possiby unreliable. Although these are generally of the correct order of magnitude, some of the previously published ion-volume data may occasionally generate rather poor ion sums when compared with reliable, X-ray-determined, experimental formula unit volumes.[20] In addition, a rather different set of covalent radii that have not yet been tested with respect to their volume relations has very recently been published.[19e]

Generation of Internally Consistent Single-Ion Volumes

The aim of this paper is to generate an improved, internally consistent, set of satisfactorily additive ion volumes. We have performed this analysis by generating the ion sums for 237 binary ionic solids, both anhydrous and hydrated, containing a set of 43 common cations and anions, as well as water of crystallization. A nonlinear minimization of the error in the least-squares sum of the calculated ion-volume sums against the experimental volumes was undertaken (using the Microsoft Excel routine Solver), by allowing the contributing ion volumes to vary while constrained to be non-negative. In order to avoid the undetermined constant that such a procedure yields (see for example ref,[21a] in which standard entropies of diatomic gases are partitioned into single-atom contributions, ref,[21b] in which combined experimental hydra-

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Table 1. Optimized Ion Volumes (in nm³) for 27 Cations and 16 Anions[a]

cation	volume/nm³	StdDev[b]	anion	volume/nm³	StdDev[b]
NH_4^+	0.0356	2.117×10^{-4}	F^-	0.0140	4.836×10^{-5}
Li^+	0.0067	1.132×10^{-4}	Cl^-	0.0298	4.825×10^{-5}
Na^+	0.0158	2.064×10^{-4}	Br^-	0.0363	4.829×10^{-5}
K^+	0.0277	2.063×10^{-4}	I^-	0.0488	4.989×10^{-5}
Rb^+	0.0341	2.064×10^{-4}	N_3^-	0.0416	5.286×10^{-5}
Cs^+	0.0420	2.066×10^{-4}	O^{2-}	0.0134	3.020×10^{-5}
Mg^{2+}	0.0049	4.147×10^{-4}	OH^-	0.0184	4.830×10^{-5}
Ca^{2+}	0.0201	4.080×10^{-4}	S^{2-}	0.0320	9.906×10^{-5}
Sr^{2+}	0.0213	4.119×10^{-4}	CO_3^{2-}	0.0426	1.087×10^{-4}
Ba^{2+}	0.0270	4.060×10^{-4}	NO_3^-	0.0492	5.021×10^{-5}
Fe^{2+}	0.0067	4.161×10^{-4}	PO_4^{3-}	0.0570	1.593×10^{-4}
Zn^{2+}	0.0125	4.082×10^{-4}	SO_4^{2-}	0.0611	9.728×10^{-5}
Cu^{2+}	0.0053	4.123×10^{-4}	ClO_4^-	0.0619	5.500×10^{-5}
Ni^{2+}	0.0004	4.118×10^{-4}	MnO_4^-	0.0665	5.591×10^{-5}
Co^{2+}	0.0019	4.117×10^{-4}	AsO_4^{3-}	0.0658	1.432×10^{-4}
Fe^{3+}	0.0061	6.352×10^{-4}	VO_4^{3-}	0.0663	1.432×10^{-4}
Sc^{3+}	0.0035	9.039×10^{-4}	H_2O	0.0245	
Lu^{3+}	0.0102	8.034×10^{-4}			
Yb^{3+}	0.0111	8.034×10^{-4}			
Tm^{3+}	0.0110	8.034×10^{-4}			
Er^{3+}	0.0126	8.034×10^{-4}			
Y^{3+}	0.0131	8.034×10^{-4}			
Dy^{3+}	0.0137	8.034×10^{-4}			
Tb^{3+}	0.0148	8.034×10^{-4}			
Gd^{3+}	0.0133	8.034×10^{-4}			
Eu^{3+}	0.0146	8.041×10^{-4}			
Sm^{3+}	0.0164	1.812×10^{-3}			

[a] The volume of the well-characterized water molecule has been fixed. [b] The standard deviations reported are derived using the Microsoft Excel routine Solver followed by an automated "jack-knife" procedure.

tion parameters are appropriated into single-ion contributions, or ref,[21c] in which radii are assigned), we have arbitrarily fixed the volume of the water molecule (a parameter independent of the pairing of the cation and anion volumes) at 0.0245 nm³, as generated by extensive prior analyses.[22]

There is a significant problem in the assumption of strict volume additivity in that the cation and anion volumes are closely linearly correlated; that is, a change in an ion volume implies an opposite change in the volume of the counter-ion(s). Consequently, a simple nonlinear minimization of the least-squares error in the computed volumes leads to a breakdown in the estimation of the errors in the individual ion volumes (using de Levie's excellent SolverAid[23]). Futhermore, the parameter space of the error is very flat, so that no global minimum set has been identified by us.

In order to develop a satisfactory result, the following procedure has been adopted. First, the optimization was initialized with the set of Marcus ion volumes[17] and Solver was invoked to optimize the volumes: the cation volumes were first optimized while keeping the anion volumes fixed, and then the cation volumes were optimized using the resultant anion volumes. Finally, the full set of ion volumes was optimized simultaneously. Other sequences of operation led to essentially the same values. In order to obtain an estimation of the errors in the derived volumes, resort was had to a "jack-knife" procedure[24] in Excel, using Solver together with a simple Excel macro to automate the process. Jack-knife methods are widely used for variance estimation in sample surveys and have the effect of reducing the bias. The basic idea behind the jack-knife estimator lies in the systematic recomputation of the statistical estimate by omitting one observation at a time from the sample set. From this set of "observations" for the statistic, an estimate for the bias and also an estimate for the variance of the statistic can be calculated. The first application of a jack-knife usually reduces the bias without affecting the variance. Second and higher (iterative) applications (which we have not done) can, in general, increase the variance of the estimator.

The resultant ion-volume sums were optimal but, of course, a degree of freedom still remains in that an arbitrary volume per unit charge may be added to (or subtracted from) each ion volume and a corresponding amount per unit charge subtracted from (or added to) each counterion volume, to yield unchanged ion-volume sums. Furthermore, the resultant ion volumes then have to be reoptimized because the statistical weighting of the ions within our reference data set is not uniform. Following appropriate adjustments in order to ensure that cation and anion volumes conform to an expectation of having a larger sized chloride anion than the potassium cation, our volume set was finally optimized to an unaltered sum of squares of errors. The volumes so optimized are listed in Table 1. Our internally consistent set

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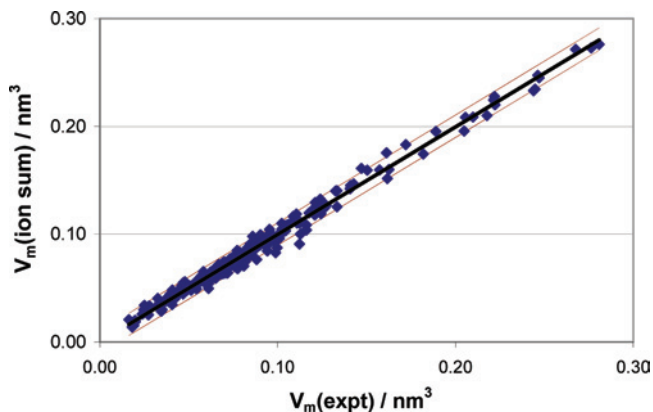
Figure 2. Ion-volume summations for 237 binary ionic solids, both anhydrous and hydrated, using the optimized ion-volume set of Table 1, plotted against X-ray diffraction-based experimental volumes. "Imprecision contours" at 2 standard deviations (where SD = 0.0051 nm^3) estimated for the individual observations are drawn about the central fitted line and data (following de Levie[23b]). The central line, constrained to pass through the origin, has a slope of 0.997 ± 0.003. The largest outlier is for CsI.
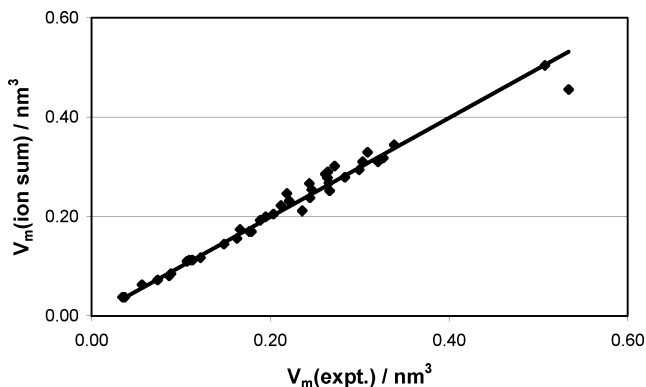

Figure 3. Ion-volume sums versus experimental volumes for 42 complex ionic solids, both anhydrous and hydrated, none of which were included in the fitting of the individual ion volumes (see Table S2 in the Supporting Information for the complete list). The fitted line with slope = 1.00 was constrained to pass through the origin. (If the final datum, for the aberrant $K_3Fe_5(PO_4)_6$, is omitted, the slope becomes 1.02.)

of volumes is, however, by no means unique because it is not possible to ensure a global minimum in the fitting process. Accordingly, this set of volumes is representative of many others, with minor variations.

As was pointed out by one of our reviewers, the reader may be surprised to note certain seemingly counterintuitive relations among the volumes in Table 1: for example, the optimized volume of the phosphate ion is less than that of the sulfate ion in spite of the former's larger negative charge. The question of phosphate versus sulfate volume is addressed in ref 25c. The volumes here derived depart from conventionally recognized regular shapes, and rationalization of their values is not simple.

Figures S1 and S2 (in the Supporting Information) show the distribution of errors between the experimental formula unit volumes and the corresponding ion sums for all 237 solids included in the fitting procedure. Generalizing, we note that the largest percentage discrepancies between the experimental and fitted volumes lie among the materials composed of the smallest ions (cf. Figure S1 in the Supporting Information), and there are large percentage errors among the simple oxides and sulfides. This arises because the standard error in the estimation of the ion-volume sum (at about 0.0035 nm^3) is roughly constant over the full data set (cf. Figure S2 in the Supporting Information), so that the errors in the small volumes are most noticeable. The percentage errors tend consistently toward zero as the formula unit volume increases, with most volumes being in error by less than 10% throughout the range of volumes examined.

In Figure 2, we observe that the optimized ion-volume sums are better than 99% of the experimental volumes and that the correlation coefficient between the ion-volume sum and experiment, R^2, is 0.989.

Table 2 gives examples of the application of the ion-volume-sum data to the ammonium and alkali-metal halides, MX, the archetypal examples of truly ionic materials and long regarded as the benchmark by which to test the accuracy of lattice energy calculations and to test the potentials used in term-by-term procedures for obtaining U_{POT}. Here the

newly generated ion volumes, added to give V_m(ion sum), are compared with the density-based volume, $V_m(M/\rho)$, and the experimental volume, V_m(expt). (Note that the experimental volumes refer to ambient-stable structures, some fcc and others bcc, but these differences cannot be accounted for by our simple, structure-independent, single-ion volumes.) Standard entropies, $S(V)$, derived from the additively combined volumes from Table 1 are used in eq 1 and compared with the known experimental values, S(expt). Lattice potential energies, $U_{POT}(V)$, derived using eq 3 with the volumes from Table 1 are also displayed in Table 2 and are compared with the density-based, $U_{POT}(\rho/M)$, value (using eq 5) and also with the results obtained from large-scale term-by-term calculations, U_{POT}(t-by-t).[9a,17] The thermodynamic predictions obtained using the data reported in Table 1 are very satisfactory and suggest that the volume-based procedures are reliable.

In essence, the void volumes in these internally consistent single-ion volumes are now distributed optimally among both cations and anions, resulting in the cations being (very roughly) more voluminous than those in earlier hard-sphere estimates, while the anions are correspondingly smaller. The oxide anion, for example, turns out to be much smaller by this analysis.

The previously published lists of ion volumes[3b,17a,18] are much more extensive than the list we present here. An optimization procedure is really only effective when the number of examples included is reasonably large, so we have

(25) (a) Flora, N. J.; Yoder, C. H.; Jenkins, H. D. B. *Inorg. Chem.* **2004**, *43*, 2340–2345. (b) Landolt-Börnstein. Crystal and Solid State Physics, Crystal Structure Data of Inorganic Compounds. *Numerical Data and Functional Relationships in Science and Technology*; Hellwege, K.-H. Ed.; Group III; Springer-Verlag: Berlin, 1979. (c) In their study of alkaline-earth apatites, Flora, Yoder, and Jenkins[25a] determined phosphate ion volumes in the range $0.058 \leq V(PO_4^{3-}) \leq 0.068$, averaging to $V(PO_4^{3-}) \approx 0.063 \pm 0.003$ nm^3 (based on our earlier volume data set in ref 3a. This is a good deal smaller than the former sulfate volume estimate and bears out our present contention that it is the smaller ion.

(26) (a) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Nutall, R. L. *Selected Values of Chemical Thermodynamic Properties*; U.S. Department of Commerce, National Bureau of Standards: Washington, DC, 1982. (b) NIST database: http://www.webbook.nist-.gov/chemistry/.

Table 2. Volumes,[a] Densities,[b] Entropies,[c] and Lattice Energies[d] for Ammonium[17] and Alkali-Metal Halides

	alkali halide salts	NH_4^+	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	V(ion sum)/nm^3	0.0496	0.0207	0.0298	0.0417	0.0481	0.0560
	ρ/g cm^{-3}	1.015	2.64	2.809	2.5053	3.557	4.115
	M/g	37.037	25.9394	41.9882	58.1004	104.4462	151.9038
	$V(M/602.3\rho)$	0.0606	0.0163	0.0248	0.0385	0.0488	0.0613
	V(expt)/nm^3	0.0611	0.0163	0.0247	0.0382	0.0451	0.0545
	$S(V$(ion sum))/J K^{-1}mol^{-1}	82.4	43.1	55.6	71.7	80.4	91.1
	S(expt)/J K^{-1} mol^{-1}	72.0	35.65	51.46	88.7		92.8
	$U_{POT}(V$(ion sum))/kJ mol^{-1}	742	959	860	780	749	717
	$U_{POT}(V$(expt))/kJ mol^{-1}	682	1029	909	800	763	723
	$U_{POT}(\rho/M)$/kJ mol^{-1}	1027	1028	908	799	746	699
	U_{POT}(t-by-t)/kJ mol^{-1}	801	1030	910	808	774	744
Cl^-	V(ion sum)/nm^3	0.0653	0.0364	0.0456	0.0575	0.0638	0.0717
	ρ/g cm^{-3}	1.519	2.068	2.1678	1.9891	2.803	3.988
	M/g	53.492	42.394	58.4428	74.55	120.9208	168.3584
	$V(M/602.3\rho)$	0.0585	0.0340	0.0448	0.0622	0.0716	0.0701
	V(expt)/nm^3	0.0582	0.0339	0.0448	0.0623	0.0715	0.0699
	$S(V$(ion sum))/J K^{-1} mol^{-1}	103.8	64.5	77.0	93.1	101.8	112.5
	S(expt)/J K^{-1} mol^{-1}	94.6	59.33	72.13	82.59	95.9	101.17
	$U_{POT}(V$(ion sum))/kJ mol^{-1}	686	811	760	712	691	668
	$U_{POT}(V$(expt))/kJ mol^{-1}	709	829	764	696	669	673
	$U_{POT}(\rho/M)$/kJ mol^{-1}	827	828	765	696	669	673
	U_{POT}(t-by-t)/kJ mol^{-1}	676	834	769	701	680	657
Br^-	V(ion sum)/nm^3	0.0719	0.0430	0.0522	0.0640	0.0704	0.0783
	ρ/g cm^{-3}	2.429	3.464	3.203	2.75	3.349	4.455
	M/g	97.943	86.85	102.8988	119.11	165.3768	212.8144
	$V(M/602.3\rho)$	0.0669	0.0416	0.0533	0.0719	0.0820	0.0793
	V(expt)/nm^3	0.0669	0.0416	0.0533	0.0718	0.0817	0.0792
	$S(V$(ion sum))/J K^{-1} mol^{-1}	112.8	73.5	86.0	102.1	110.8	121.5
	S(expt)/J K^{-1} mol^{-1}	113	74.27	86.82	95.9	109.96	113.05
	$U_{POT}(V$(ion sum))/kJ mol^{-1}	668	773	732	690	672	652
	$U_{POT}(V$(expt))/kJ mol^{-1}	682	781	727	668	644	650
	$U_{POT}(\rho/M)$/kJ mol^{-1}	780	781	727	668	644	650
	U_{POT}(t-by-t)/kJ mol^{-1}	644	788	732	671	651	632
I^-	V(ion sum)/nm^3	0.0844	0.0555	0.0646	0.0765	0.0829	0.0908
	ρ/g cm^{-3}	2.514	4.061	3.655	3.129	3.564	4.51
	M/g	144.943	133.8454	149.8942	166.0064	212.3722	259.8098
	$V(M/602.3\rho)$	0.0957	0.0547	0.0681	0.0881	0.0989	0.0956
	V(expt)/nm^3	0.0956	0.0543	0.0678	0.0882	0.0989	0.0952
	$S(V$(ion sum))/J K^{-1} mol^{-1}	129.7	90.4	102.9	119.0	127.7	138.4
	S(expt)/J K^{-1} mol^{-1}	117	86.78	98.53	106.32	118.41	123.05
	$U_{POT}(V$(ion sum))/kJ mol^{-1}	639	719	688	656	642	626
	$U_{POT}(V$(expt))/kJ mol^{-1}	617	723	679	631	611	618
	U_{POT}(t-by-t)/kJ mol^{-1}	609	730	682	632	617	600

[a] Comparison of ion-sum additive volumes, V_m(ion sum)/nm^3, and experimental[25b] volumes, V_m(expt)/nm^3. [b] Experimental[25b] densities, ρ/g cm^{-3}, and their corresponding formula volume, $V_m(M/602.3\rho)$/nm^3. [c] Standard entropy, $S(V$(ion sum))/J K^{-1} mol^{-1} [=1360V(ion sum)/nm^3 + 15], compared with the experimental standard entropy,[26] S(expt)/J K^{-1} mol^{-1}. [d] Lattice energies, $U_{POT}(V$(ion sum))/kJ mol^{-1} [=234.6/$V^{1/3}$(ion sum)/nm^3 + 103.8], $U_{POT}(V$(expt))/kJ mol^{-1}, calculated using V_m(expt)/nm^3, and $U_{POT}(\rho/M)$/kJ mol^{-1} calculated using ρ/M, compared with results obtained from an extended term-by-term calculation,[17b] U_{POT}(t-by-t)/kJ mol^{-1}.

not attempted to include ions for which only a few examples currently exist (except for the rather similar lanthanide cations). The volumes of missing (target) ions can most readily and consistently be found by the difference from known crystal data volumes for compounds in which the target ion is paired with an ion or ions listed in Table 1. For example, re-evaluation of the ferrocyanide ion volume, using the newly optimized ion volumes, yields 0.199 nm^3 in place of the previously published[7,27] radius-based volume of 0.252 nm^3 for the ferrocyanide anion, [Fe(CN)$_6$]$^{4-}$. Similarly, the ion-sum volume for the AlCl$_4^-$ anion is 0.146 nm^3, while its radius-based value[17] is 0.161 nm^3.

In addition to the ammonium and alkali-metal halides, we have tested the ion-sum results on a number of complex materials (largely minerals) absent from the initial optimization and found that these ion sums yield volumes comparable with the experimental formula unit volumes and considerably better than the earlier collections of ion volumes (see Figures 1 and 3 and Table S2 in the Supporting Information).

It should not, however, be automatically assumed that volume sums will work well for all possible combinations of species. We have examined the volumes of alloys and found that additivity is generally poor (but see also Stalick[19d]). Similarly, there may be rather unusual situations where different, reconstructed, polymorphs may have very different volumes. A salient example is silicon dioxide, SiO$_2$, whose ambient-stable α-quartz polymorph has a formula unit volume of 0.037 67 nm^3, whereas the high-pressure form, stishovite, has the much reduced formula unit volume of 0.023 26 nm^3 while that of the high-temperature form, tridymite, is 0.044 05 nm^3.

(27) In Table 2 in ref 7f (in Supporting Information), the third K$_4$[Fe(CN)$_6$]·3H$_2$O volume has been transposed inappropriately from the first row of Table 1; the correct volume is 0.369 74 nm^3 rather than 0.284 97 nm^3. However, the remainder of the data in this row are correct .

Table 3. Reported and Ion-Summed Formula Volumes of a Number of Phosphates[a]

formula	V_m(expt)/ nm³	ref	$S°_{298}$/J K⁻¹ mol⁻¹= 1360V_m(expt) + 15	V_m(sum)/ nm³	V_m% diff	$S°_{298}$/J K⁻¹ mol⁻¹= 1360V_m(sum) + 15	$S°_{298}$(expt) ($S°_{298}$[Latimer])ᶜ/J K⁻¹mol⁻¹	ref
Li₃PO₄	0.0778	25b	121	0.0771	0	120	− (94)	b
Na₃PO₄	0.1023	25b	154	0.1046	−2	157	173.8, 173.799 (144)	26a, 40, b
K₃PO₄	0.1334	25b	196	0.1401	−5	206	211.7 (166)	40, b
Rb₃PO₄	0.1504	25b	220	0.1593	−6	232	− (200)	b
Cs₃PO₄	0.1721	25b	249	0.1830	−6	264	− (221)	b
α-FePO₄	0.0679	29	107	0.0631	−7	101	93.7 (95 ± 8)	35, 37
	0.0823	30	127					
	0.0825	31	127					
	0.0821	31	127					
	0.0940	31	143					
FePO₄·2H₂O (strengite)	0.1122	20b	168	0.1121	−0	168	171.25	26, 36
	0.1126ᵇ	32	168					
	0.1123	20b	168					
	0.1084	31	162					
	0.1071	36	161					
LiFePO₄(triphylite)	0.0728	29	114	0.0704	−3	111	(110 ± 9)	37
NaZnFe₂(PO₄)₃	0.2358	33	336	0.2116	−10	303	(296 ± 11)	37
Fe₃(PO₄)₂·4H₂O	0.2212	20b	316	0.2313	5	330		
Fe₃(PO₄)₂(OH)₃·5H₂O	0.3204	20b	451	0.3099	−3	437		
K₃Fe₅(PO₄)₆	0.5339	34	741	0.4557	−15	635	(676 ± 18)	37
K₃Fe₃(PO₄)₄	0.3643	39	510	0.3295	−3	463	(526 ± 14)	37
α-Ca₃(PO₄)₂(high-T form)	0.1795	36	235	0.1745	3	252	240.9	26
							235.98	36
							(238 ± 5)	37
β-Ca₃(PO₄)₂(low-T form)	>0.1689	36	235	0.1745	−3	252	236.0	26
							235.98	36
							(238 ± 5)	37
Mg₃(PO₄)₂	0.1429	38	209	0.1286	−10	190	189.2	26
							188	35
							(191 ± 7)	37
Ca₅(PO₄)₃F (fluorapatite)	0.2616	36	371	0.2858	9	404	387.86	36
							(398 ± 6)	37
Ca₅(PO₄)₃OH (hydroxyapatite)	0.2644	36	375	0.2902	10	410	390.37	36
							(395 ± 6)	37

[a] Calculated standard entropies, $S°_{298}$ (using eq 1), are compared with experimental values, $S°_{298}$(expt). ᵇ Table 1 in ref 32 has a large number of transcription errors; however, the measured value seems to be correct as reported. ᶜ Latimer estimates[37] (in this case using ref 37b) are provided in addition to experimental data.

Applications

The thermodynamic correlations under consideration, like those between the entropy and the experimental volume, between the lattice energy and the inverse cubic root of experimental volume, between the conductivity of ionic liquids and the experimental volume,[28] etc., can be expected to generate even more reliable thermodynamic values using these internally consistent ion-sum volume data because the sums of the volumes now more closely fit the experimental volumes of ionic solids than did the earlier volume sums.

Case of Phosphates and Phosphate Hydrates

We examine the sample cases of a series of phosphates, based on alkali-metal phosphates, FePO₄ and its hydrates, and calcium and magnesium phosphates, to illustrate both the kinds of problems that may arise in examining the literature and the resolutions possible when a reliably consistent set of ion volumes is available. Table 3 records the reported and ion-summed formula volumes of a number of phosphates.

Examination of the table shows considerable discrepancies among the reported formula volumes for α-FePO₄. We can, however, analyze the situation and thereby suggest (on two counts) that only the volume of 0.0679 nm³ (row 6 of the table) is acceptable: (i) the experimental volume of 0.1122 nm³ for the dihydrate yields a volume of 0.0632 nm³ when the volume of the two water molecules is subtracted and (ii) the computed ion-sum volume in the fifth column concurs. Of course, small differences will correctly arise among different polymorphs, but the reported range is well beyond

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(37) (a) Standard entropy is estimated using Latimer's approach, taking data from Tables 4 and 5 of Spencer's paper,³⁷ᵈ which quote Mills' values.³⁷ᵉ(b) Latimer, W. M. *Oxidation Potentials*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1956. (c) Latimer, W. M. *J. Am. Chem. Soc.* **1951**, *73*, 1480–1482. (d) Spencer, P. J. *Thermochim. Acta* **1998**, *314*, 1–21. (e) Mills, K. C. *DCS Note 20*; National Physical Laboratory: Washington, DC, 1974.
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expectation. We regard the smaller reported volumes of the dihydrate (in rows 13 and 14) to be unreliable. These phosphate compounds show the reasonable success of both the addition of ion volumes in reproducing the volumes of sometimes exceedingly complex ionic materials and in the estimation of the standard entropies. The additive volume relationships are treated, for example, as follows:

$$V(Fe_3(PO_4)_2(OH)_3 \cdot 5H_2O) \approx 3V(Fe^{3+}) +$$
$$2V(PO_4{}^{3-}) + 3V(OH^-) + 5V(H_2O) \quad (9)$$

and similarly for the other phosphates. For most phosphates, the errors in the predicted volumes are usually considerably less than the 15% error found for the 14-ion $K_3Fe_5(PO_4)_6$.

Consider the following example for the estimation of the volume of a related phosphate ion species, $V(HPO_4{}^{2-})$: the experimental volume $V(CaHPO_4) = 0.074$ nm^3 while $V(Ca^{2+}) = 0.0201$ nm^3 (Table 1); hence, $V(HPO_4{}^{2-}) = 0.054$ nm^3. If

we assume[7] that $V(H^+) \approx 0$, then we find that $V(HPO_4{}^{2-})$ is slightly larger than $V(PO_4{}^{3-})$ ($=0.570$ nm^3).

Supporting Information Available: Figures S1 and S2 show the distribution of errors among the 237 ionic materials used in a fitting of the ion volumes, Table S1 lists the experimental volumes and the ion-volume sums for each of the 237 ionic materials, Table S2 lists the experimental and computed volume sums for 42 complex ionic materials, independent of the fitted set, and an extensive list of recent publications utilizing VBT is appended as refs 7 and 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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