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Volumes of Solid State Ions and Their Estimation

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Formula unit volume, V_m, has recently been identified as the key link to a number of thermodynamic functions and has given rise to an alternative approach to thermodynamics for modern inorganic materials (volume-based thermodynamics, VBT). In an earlier publication, we reported over 400 ion volumes for commonly encountered cations and anions derived from crystal structure data which can, in turn, be used to generate formula unit volumes for those ionic salts, for which crystal structure data, which is the preferred source of such volume data, is not available. The purpose of the present paper is to report a further 147 supplementary ion volumes. These are compared to ion volumes obtained from the summation of Hofmann's elemental volumes, a convenient and alternative approach for the estimation of V_m. It is shown that many elusive ion volumes can be estimated using these databases in tandem by adopting the newly proposed isomegethic rule and other volume additivity rules. Generation of volume data for new, hypothetical, and counterintuitive ions, as well as for traditional ions, is now a reality, as is demonstrated.

Introduction

Jenkins and co-workers, in a series of publications,[1a−z] have been able to demonstrate the crucial role played by formula unit volume, V_m, in providing a direct link to important thermodynamic data [1a−g,i−u,w−z] (e.g., lattice potential energy,[1a−d] U_{POT} , and standard entropy,[1k,m] $S^0{}_{298}$) via the simple relationships

$$U_{POT} \approx 2I[\alpha/(V_m)^{1/3} + \beta] \qquad (1a)$$

$$U_{POT} \approx AI[(2I/(V_m)]^{1/3} \qquad (1b)$$

where I is the ionic strength[2a] of the lattice ($I = {}^1/_2\sum n_i z_i{}^2$, where n_i is the number of ions in the formula unit having a charge of z_i and where the summation is performed over all the ions of the lattice), α and β are stoichiometrically dependent coefficients,[2b] and $A = 121.39$ kJ mol^{-1} nm. Equation 1a applies to lattices for which $U_{POT} < 5000$ kJ mol^{-1} (i.e., to normal inorganic materials), and eq 1b applies for lattices for which $U_{POT} > 5000$ kJ mol^{-1} (i.e., to more complex lattices and minerals). There further exists an, even more direct, rectilinear relationship[2c] between standard entropy, $S°_{298}$ and the volume V_m

$$S°_{298} \approx k(V_m) + c \qquad (2)$$

This equation applies to inorganic materials and their hydrates, including minerals[1k] as well as to organic liquids and solids.[1m] Terms k and c are constants.

The identification of the above equations has raised the prominence of volume, V_m, in respect to thermodynamics and has given rise to a unified approach to estimation of thermodynamics for inorganic and other materials (volume-based thermodynamics, VBT). As a consequence of this development, the ability to estimate volume data has become an issue of some importance which has been moved up the chemical agenda.

Quite separately from this context, volume is enormously useful and of general interest to a wide range of materials scientists, as well as to chemists generally. While, for the purposes of the estimation of thermodynamic properties, it

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appears that volume is much more satisfactory as a measure of ion size. Although ionic radius (originally used to estimate lattice energies via thermochemical radii), of course, still retains its importance in the sphere of crystallography (e.g., for use in discussion of structural types and structure distortion, etc.), it is a concept that describes predominantly spherical ion shapes and is now frequently unsuitable for describing the shape of ions of topical interest, which are often patently nonspherical.

The most direct (and preferred) route for obtaining V_m is directly from (experimentally based) X-ray structural determinations using

$$V_m = V_{cell}/Z \qquad (3)$$

where V_{cell} is the unit cell volume and Z is the number of molecules in the unit cell.

In the absence of such experimental data, the formula unit volume, V_m (in nm^3), of a given molecule, M_pX_q, can be estimated from the (suitably weighted) additive sum of the individual component *ion* volumes, $V(M^{q+})$ and $V(X^{p-})$, with the following equation:

$$V_m(M_pX_q) \approx p(V(M^{q+})) + q(V(X^{p-})) \qquad (4)$$

One source of this ion volume data is our database[1c] which lists the data for 400 commonly encountered cations and anions and another is Table 1 of this paper. These ion volumes[1b] were derived (as was explained in the final paragraph of the Ion Parameters section on page 3613 of ref 1b) so that cation volumes (V_+) were equated to $4/3\pi r_G{}^3$ (r_G = Goldschmidt radius) and corresponding anion volumes (V_-) were assigned by subtraction of V_+ from the formula unit volume V_m. This had the (recognized) effect that cation volumes tended to be too small (i.e., $V_+ = V_{+,true} - \delta$) and anion volumes to be too large; all of the "free space" in the crystal was (arbitrarily) assigned to the anion (i.e., say $V_- = V_{-,true} + \delta$). Thus our assigned ion volumes are not *absolute* ion volumes in the strictest sense. Recombination of these ion volumes using ion additivity, to generate formula unit volume data V_m, is not affected because parameter δ

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(1) (a) Brownridge, S.; Krossing, I.; Passmore, J.; Jenkins, H. D. B.; Roobottom, H. K. *Coord. Chem. Rev.* **1999**, *197*, 397. (b) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609. (c) Jenkins, H. D. B. In *Mass & Charge Transport of Inorganic Materials*, Proceedings of the International Conference, Lido di Jesolo, Venezia, Italy, May 28−June 3, 2000; Vincenzini, P., Ed; Technica. S.r.l.: Faenza (RA) Italy, 2000; Part B, p 613. (d) Jenkins, H. D. B.; Glasser, L. *J. Am. Chem. Soc.* **2000**, *122*, 632. (e) Cameron, T. S.; Deeth, R. J.; Dionne, I.; Du, H.; Jenkins, H. D. B.; Krossing, I.; Passmore, J.; Roobottom, H. K. *Inorg. Chem.* **2000**, *39*, 5614. (f) Cameron, T. S.; Dionne, I.; Jenkins, H. D. B.; Parsons, S.; Passmore, J.; Roobottom, H. K. *Inorg. Chem.* **2000**, *39*, 2042. (g) Jenkins, H. D. B.; Tudela, D.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 2364. (h) Marcus, Y.; Jenkins, H. D. B.; Glasser, L. *J. Chem. Soc., Dalton Trans.* **2002**, 3795. (i) Jenkins, H. D. B.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 4378. (j) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J. *Inorg. Chem.* **2003**, *42*, 2886. (k) Jenkins, H. D. B.; Glasser, L. *Inorg. Chem.* **2003**, *42*, 8702. (l) Jenkins, H. D. B.; Tudela, D. *J. Chem. Educ.* **2003,** *80*, 1482. (m) Glasser, L.; Jenkins, H. D. B. *Thermochim. Acta* **2004**, *414*, 125. (n) Christe, K. O.; Jenkins, H. D. B. *J. Am. Chem Soc.* **2003**, *125*, 14210. (o) Christe, K. O.; Vij, A.; Wilson, W. W.; Vij, V.; Dixon, D. A.; Feller, D.; Jenkins, H. D. B. *Chem. Br.* **2003**, *39*, 17. (p) Christe, K. O.; Jenkins, H. D. B. *J. Am. Chem Soc.* **2003**, *125*, 9457. (q) Flora, N. J.; Yoder, C. H.; Jenkins, H. D. B. *Inorg. Chem.* **2004**, *43*, 2340. (r) Rosseinsky, D. R.; Glasser, L.; Jenkins, H. D. B. *J. Am. Chem. Soc.* **2004**, *126*, 10472. (s) Nikiforov, G. B.; Passmore, J.; Decken, A.; Jenkins, H. D. B. *Dalton Trans.* **2004**, 2496. (t) Jenkins, H. D. B.; Glasser, L. *J. Am. Chem. Soc.* **2004**, *126*, 15809. (u) Jenkins, H. D. B.; Glasser, L.; Klapötke, T. M, Crawford, M.-J.; Bhasin, K. K.; Lee, J.; Schrobilgen, G. J.; Sunderlin, L. S.; Liebman, J. F. *Inorg. Chem.* **2004**, *43*, 6238. (v) megeqos (megethos) = modern Greek for bigness, dimension, extent, magnitude, and size). (w) Dixon, D. A.; Feller, D.; Christe, K. O.; Wilson, W. W.; Vij, A.; Vij, V, Jenkins, H. D. B.; Olson, R. M.; Gordon, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 834. (x) Jenkins, H. D. B. *J. Chem. Educ.* **2005**, *82*, 950 (y) Decken, A.; Nikiforov, G. B.; Passmore, J.; Jenkins, H. D. B. In preparation. (z) Glasser, L.; Jenkins, H. D. B. *Chem. Soc. Rev.* **2005**, sumbitted for publication.

(2) (a) Glasser, L. *Inorg. Chem.* **1995**, *34*, 4935. (b) α and β take the following values, governed by the stoichiometry of the ionic salt being considered

stoichiometry	α (kJ mol^{-1} nm^3)	β (kJ mol^{-1})
MX (1:1)	117.3	51.9
MX_2 (2:1)	133.5	60.9
M_2X (1:2)	165.3	−29.8
M_pX_q (*q*:*p*) (general case)	138.7	27.6

(c) Hofmann, D. W. M. *Acta Crystallogr.* **2002**, *B57*, 489. (d) If $V_{Hofmann}$(ion) is plotted versus $V_{Jenkins}$(ion) for the same ion from Table 1, we find that, for monovalent cations, $V_{Hofmann}(\text{ion})/\text{nm}^3 = 1.434V_{Jenkins}(\text{ion})/\text{nm}^3 + 0.021$ ($R^2 = 0.982$, $n = 5$), for monovalent anions, $V_{Hofmann}(\text{ion})/\text{nm}^3 = 1.111V_{Jenkins}(\text{ion})/\text{nm}^3 - 0.022$ ($R^2 = 0.882$, $n = 44$), for divalent anions, $V_{Hofmann}(\text{ion})/\text{nm}^3 = 1.019V_{Jenkins}(\text{ion})/\text{nm}^3 - 0.018$ ($R^2 = 0.903$, $n = 50$), and for trivalent anions, $V_{Hofmann}(\text{ion})/\text{nm}^3 = 1.015V_{Jenkins}(\text{ion})/\text{nm}^3 - 0.064$ ($R^2 = 0.888$, $n = 35$). (e) For example, consider the $Rb_3Ti_2Cl_9$ salt: Hofmann elemental volumes (Table 2, ref 2c) lead to $V_m(Rb_3Ti_2Cl_9)/\text{nm}^3 \approx [3\{42 \pm 5\} + 2\{27.3 \pm 1.8\} + 9\{25.8 \pm 0.3\}]/1000 \approx 0.412 \pm 0.009$; Jenkins' ion volumes (Tables 4 and 5 from ref 1b and Table 1 from this work) lead to $V_m(Rb_3Ti_2Cl_9)/\text{nm}^3 \approx 3V_m(Rb^+) + V_m(Ti_2Cl_9{}^{3-}) \approx 3\,(0.014) + 0.355 \approx 0.397$. Note that the volumes of the anions are $V_J(Rb^+)/\text{nm}^3 = 0.014$ and $V_H(Rb^+)/\text{nm}^3 = 42/1000 = 0.042$ respectively (implying that Rb^+ is roughly too small, on our scale, by about 0.028 nm^3; compare the intercept of the regression line in 2d above). The cation volumes are $V_J(Ti_2Cl_9{}^{3-}) = 0.355$ nm^3; $V_H(Ti_2Cl_9{}^{3-}) = 0.287 \pm 0.003$ nm^3 (implying that $Ti_2Cl_9{}^{3-}$ is roughly too large, on our scale, by about 0.068 nm^3; compare the intercept of the regression line in 2d above). Because 0.068 nm^3 is appoximately 3 × 0.028 nm^3, then on additivity, both the elemental and ion volumes *for the formula unit* would be anticipated to yield similar volumes in the majority of cases. (f) One can think[1y] of salts (e.g., $[M^{2+}][Ti_4F_{18}{}^{2-}]$ and $[M^{2+}][Ti_2F_9{}^-]_2$) with identical chemical empirical formulas (and hence chemical mass) for which their volumes will be similar and yet their ionic strengths are different (i.e., $I = 3$ and 4, respectively).

(3) (a) *Crystal Data and Inorganic Compounds*; Hellwege, K.-H., Ed; Landolt-Börnstein Series, Group III, Vol 7; Springer-Verlag: Berlin, 1973. (b) Morss, L. R.; Robinson, W. R. *Acta Crystallogr.* **1972**, *B28*, 653. (c) Müller, U.; Bärnighausen, H. *Acta Crystallogr.* **1970**, *B26*, 1671. (d) Witt, J. R.; Britton, D. *Acta Crystallogr.* **1971**, *B27*, 1835. (e) Hodgson, D. J.; Ibers, J. A. *Acta Crystallogr.* **1969**, *B25*, 469. (f) Macintyre, W. M.; Werkema, M. S. *J. Chem. Phys.* **1964**, *40*, 3563. (g) Baenzinger, N.; Hegenbarth, J. J. *J. Am. Chem. Soc.* **1964**, *86*, 3250. (h) Hunter, F. D.; Jeffrey, G. A. *J. Chem. Phys.* **1967**, *47*, 3297. (i) Adams, J. M.; Small, R. W. H. *Acta Crystallogr.* **1973**, *B29*, 2317. (j) Lofgren, P. *Acta Crystallogr.* **1973**, *B29*, 2141. (k) McGinnety, J. A. *Acta Crystallogr.* **1972**, *B28*, 2845. (l) Philippot, E.; Lindqvist, O. *Acta Crystallogr.* **1970**, *B26*, 877. (m) Bertrand, J. A.; Kelley, J. A. *Inorg. Chem.* **1969**, *8*, 1982. (n) Lauher, J. W.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 348. (o) Gatehouse, B. M.; Miskin, B. K. *Acta Crystallogr.* **1975**, *B31*, 1293. (p) Cox, G. W.; Sabine, T. M.; Padmanabhan, N. T.; Ban, M. K.; Surjadi, A. J. *Acta Crystallogr.* **1967**, *23*, 578. (q) Faggiani, R.; Gillespie, R. J.; Lock, C. J. L.; Tyre, J. D. *Inorg. Chem.* **1978**, *17*, 2975. (r) Jones, P. E.; Katz, L. *Acta Crystallogr.* **1969**, *B25*, 745. (s) Ryan, R. R.; Cromer, D. T. *Inorg. Chem.* **1972**, *11*, 2322. (t) Ryan, R. R.; Martin, S. H.; Larsen, A. C. *Inorg. Chem.* **1971**, *10*, 2793. (u) Mark, W.; Lindqvist, O.; Junas, J. C.; Philippot, E. *Acta Crystallogr.* **1974**, *B30*, 2620. (v) Zak, Z.; Kosicka, M. *Acta Crystallogr.* **1978**, *B34*, 38. (w) Johansson, G. B. *Acta Crystallogr.* **1978**, *B34*, 2830. (x) Brusset, H.; Dao, N. Q.; Chowov, S. *Acta Crystallogr.* **1974**, *B30*, 768. (y) Zachariasen, W. H. *Acta Crystallogr.* **1954**, *7*, 783. (z) Bukovec, P.; Golic, L. *Acta Crystallogr.* **1980**, *B36*, 1925. (aa) *Crystal Structure Determinative Tables*, 3rd ed., Vol 2; Donnay, J. D. H., Ondik, H. M., Eds; U.S. Department of Commerce, National Bureau of Standards: Washington, DC, 1973.

cancels once additivity is imposed on the individual ion volumes. Since $V_m = V_+ + V_- = [(V_{+,\mathrm{true}} - \delta) + (V_{-,\mathrm{true}} + \delta)] = V_{+,\mathrm{true}} + V_{-,\mathrm{true}}$ as used in eqs 1a, 1b, or 2.

A further convenient source of $V_m(M_pX_q)$ comes from the use Hofmann's scale of *elemental* volumes,[2c] $\nu(E)$, where E is an element and an additivity rule in the form

$$V_m(M_pX_q) \approx [p(\nu(M)) + q(\nu(X))]/1000 \qquad (5)$$

where $\nu(M)$ and $\nu(X)$ are the appropriately listed (in Å^3) elemental volumes (Table 2, ref 2c). A suitable scaling factor (division by 10^3, as shown in eq 5) has to be imposed on Hofmann's values to obtain volumes in cubic nanometers, as required for our equations. Hofmann[2c] employed a statistical approach to examine 182 239 structures from the Cambridge crystallographic database in order to derive *average elemental* volumes (along with estimated errors, $\Delta\nu$) for each of 100 elements within solid state materials. For materials containing the elements C, H, N, O, and F, he notes that an improvement in the estimated volumes (and hence densities) can be obtained if the local environment is additionally considered and functional group terms are introduced. However , a caveat should be introduced at this point since estimation of the volumes of the three ions, $V(MX_n^{z+})$ and $V(MX_n^{(z\pm1)+})$, by Hofmann's approach would yield *identical* volumes because the only consideration is the elemental presence and no charge considerations are made. Hofmann's volumes will usually tend to yield slightly larger volumes for cations when compared to ours and slightly smaller values for anions,[2d] although this is not always the case. Comparison of the two ion volumes can in some senses give an idea of the approximate magnitude of the free space volume factor (δ). Hofmann values for the ions are listed in parentheses below the ion volume entries in Table 1. Formula unit volumes, V_m, derived from additivity of the elemental Hofmann volumes would be expected to be *very similar in magnitude* to the values generated from our ion additivity procedures,[2e] and this is demonstrated at various points in this paper (see for example 2e) Hofmann's approach thus provides a valuable additional source of V_m data.

In most instances, it is fortuitously the case that the equations (1a, 1b, and 2) linking volume to standard thermodynamic variables are such that the effect of any small error in the estimated or experimental volume, V_m, is mitigated either because the mathematical form of the equation itself dictates this (see ref 1b) or else as a result of the usual manner in which the equations are employed during thermodynamic usage. Thus, a change of units (e.g., from J K^{-1} mol^{-1} for standard entropy to kJ mol^{-1} for the $T\Delta S$ contribution to free energy requires (at 298 K) multiplication of any error in the estimated $S°_{298}$ values involved by the factor 0.298 K kJ J^{-1}.

Ion Volumes

Ion Volume Generation from Crystal Structure Data. The volumes of the individual cations, $V(M^{q+})$, and anions, $V(X^{p-})$, (listed in Table 1 in nm^3) are derived from crystal structure data on condensed (ionic) materials by partitioning the formula unit volume, $V(M_pX_q)$, obtained from eq 4 into single ion volumes. Thus, a target anion volume, for example $V(X^{p-})$, is obtained by subtraction of the appropriately weighted (and assumed known) cation volume, $V(M^{q+})$, from $V(M_pX_q)$ as shown in eq 6.

$$V(X^{p-}) \approx [V(M_pX_q) - pV(M^{q+})]/q \qquad (6)$$

Analogously an anion volume can be used to generate a cation volume.

Table 1 presents data for 147 new ions derived from crystal structure data.

The formula unit volume, $V(M_pX_q)$, of an ionic material is related inversely[1d] to its density, ρ (in g cm^{-3}), and thus, the estimation of $V(M_pX_q)$ by the combination of individual ion volumes[1c] (eq 4) or elements[2c] (eq 5) can form the basis of a prediction of the density of an ionic material. Knowledge of the density of a material (and its chemical mass) can also be used to obtain an estimate for V_m (using eq 7).

Ion Volume Generation Using the Isomegethic Rule. The isomegethic rule,[1u−v] simply stated, is that isomeric ionic salts with identical chemical empirical formulas (having same chemical mass, M_m) and (usually)[2f] having identical lattice ionic strengths[2a] will have approximately equal molecular (formula unit) volumes, V_m. It is this assumption that permits us to use Hofmann's elemental volumes[2c] (eq 5) in the manner we have described in this paper. If the volumes and chemical masses are approximately equal, the properties of density,[1e] ρ, will also be approximately equal because

$$\rho = 1.66 \times 10^{-3}\,(M_m/\mathrm{g})/(V_m) \qquad (7)$$

with the lattice potential energy,[1a,c] U_{POT} (eqs 1a and 1b with equal I values), and standard entropy,[1l,m] $S°_{298}$ (eq 2).

Use of Ion Volume Generation Rules.[54−6] If ion volumes are unlisted, this is usually because there are no representative crystal structures available in the sources cited. In this case, there are a number of possible routes available which are suitable for estimating values. The remainder of this section focuses in on some of these methods. In all cases, Hofmann's elemental volumes can be utilized to make an estimate for an *ion* volume (see, however, the earlier discussion and footnotes 2d and 2e of this paper).

I. Isomegethic Rule for Ionic Salts. The volumes (in nm^3) of AuF_4^- (0.088 ± 0.013) and $AuCl_4^-$ (0.157 ± 0.010) are listed in ref 1c, while that for $AuBr_4^-$ (0.177 ± 0.003) is given in Table 1 of this paper. No value is cited for $V(AuI_4^-)$. This problem can typically arise. However, the problem becomes solvable because suitable volumes of halogen

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[4] *Handbook of Chemistry and Physics*, 80th ed; Lide, D. R., Ed.; C. R. C. Press, Inc.: Baco Raton, FL, 2002−3; pp 4−77.

[5] When no errors for the quoted volumes are listed in our databases (Table 1 and ref 1c), a value of ± 0.02 nm^3 can reasonably be assumed. To some extent, the error is also possibly related to the size of the ion.

[6] (a) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nutall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Supplement 2. (b) Karapet'yants, M. Kh.; Karapet'yants, M. L. *Thermodynamic Constants of Inorganic and Organic Compounds*; translated by Schmorak, J.; Humphrey Science Publications: Ann Arbor, MI, 1970.

Table 1. Intrinsic Ion Volumes (in nm^3) Derived from X-ray Crystallographic Sources[a]

ion	molecule	vol (V) (nm^3) this work (Hofmann[2c])	error(nm^3)	no. of salts[b]	ref [d,f]
$Ag(CN)_2^-$	Cs and Rb monohydrates	0.110 (0.086 ± 0.004)	0.005	2	3a c4386, c4387
AgF_4^- [b]	Na and K salts	0.082 (0.080 ± 0.002)	0.005	2	3a a427, a428
$AlCl_4^-$ [c]	Na and K salts	0.161 (0.143 ± 0.001)	0.004	2	3a a2625, a2627
$Au(CN)_4^-$	K monohydrate	0.171 (0.146 ± 0.002)		1	3a c4388
$AuBr_4^-$	Na and K dihydrates	0.177 (0.174 ± 0.002)	0.003	2	3a a3423, a3424
BeF_3^-	Na, K, Rb and Cs salts	0.068 (0.070 ± 0.004)	0.009	4	3a a445, a460, a475, a484
BeF_4^{2-}	LiCs and Ca salt	0.078 (0.081 ± 0.004)	0.011	2	3a a490, a499
$Bi(CNS)_4^-$	Rb salt	0.266 (0.263 ± 0.004)		1	3a c4662
$Bi_2Cl_7^-$	Rb monhydrate	0.278 (0.301 ± 0.006)		1	3a a2983
$Bi_2I_9^{3-}$	Cs salt	0.593 (0.536 ± 0.006)		1	3a a3748
$BiBr_4^-$	K monohydrate	0.177 (0.191 ± 0.004)		1	3a a3438
$BiBr_5^{2-}$	K and NH_4^+ dihydrates	0.240 (0.224 ± 0.004)	0.012	2	3a a3439, a3440
$BiCl_4^-$	K monohydrate	0.150 (0.163 ± 0.004)		1	3a a2981
$BiCl_5^{2-}$	K dihydrate	0.210 (0.189 ± 0.004)		1	3a a2982
$BiCl_6^{3-}$	Cs salt	0.277 (0.215 ± 0.004)		1	3b
$BkCl_6^{2-}$	Cs salt	0.253 (0.224 ± 0.001)[g]		1	3a a2707
$BkCl_6^{3-}$	Cs salt	0.274 (0.224 ± 0.001)[g]		1	3a a2708
$C(N_3)_3^+$	$SbCl_6^-$ salt	0.154 (0.120 ± 0.001)		1	3c
$(CN)_3C^-$	K salt	0.134 (0.091)		1	3d
$COONH_2^-$	NH_4^+ salt	0.075 (0.058)		1	3i
$C_2O_4^{2-}$	K monohydrate	0.098 (0.073)		1	3e
$C_4O_4^{2-}$	K monohydrate	0.125 (0.101)		1	3f
$C_5O_5^{2-}$	NH_4^+ salt	0.134 (0.126)		1	3g
CS_3^{2-}	K monohydrate	0.174 (0.089 ± 0.001)		1	3l
$Cd(CN)_4^{2-}$	Na trihydrate	0.179 (0.153 ± 0.003)		1	3a c4390
$Cd_2Cl_6^{2-}$	Ba salt	0.321 (0.257 ± 0.004)		1	3a a2616
$CdBr_3^-$	Cs salt	0.133 (0.149 ± 0.003)		1	3a a3322
$CeCl_6^{3-}$	Cs_2Na salt	0.286 (0.263 ± 0.007)		1	3a a2672
$CeCl_6^{2-}$	Cs salt	0.255 (0.209 ± 0.005)		1	3a a2671
$CoBr_5^{3-}$	Cs salt	0.294 (0.193 ± 0.002)		1	3a a3402
$CoCl_3^-$	NH_4^+ salt	0.110 (0.107 ± 0.001)	0.005	3	3a 2895
$Cr_2Cl_9^{3-}$	K salt	0.330 (0.288 ± 0.002)		1	3a a2812
$Cr_2I_9^{3-}$	Cs salt	0.473 (0.472 ± 0.002)		1	3a a3755
$Cr_4O_{13}^{2-}$	Rb salt	0.284 (0.260 ± 0.003)		1	3j
$CrBr_3^-$	Cs salt	0.138 (0.126 ± 0.002)		1	3a a3382
$CrCl_3^-$	Rb and Cs salts	0.120 (0.106 ± 0.002)	0.004	2	3a a2815, a2819

Table 1. Continued

ion	molecule	vol (*V*) (nm^3) this work (Hofmann[2c])	error(nm^3)	no. of salts[b]	ref [d,f]
$CrCl_4^{2-}$	Rb and NH_4^+ salts	0.178 (0.131 ± 0.002)	0.002	2	3a a2814, a2816
CrO_4^{2-} [c]	K salt	0.098 (0.074 ± 0.002)		1	3k
$Cu_2(CN)_3^-$	K monohydrate	0.150 (0.131 ± 0.002)		1	3a c4385
$Cu_2Cl_7^{3-}$	Cs dihydrate	0.370 (0.234 ± 0.002)		1	3a a2942
$Cu_4Cl_{10}O^{4-}$	$(CH_3)_4N^+$ salt	0.447 (0.377 ± 0.002)		1	3m
$CuBr_4^-$	NH_4^+ dihydrate	0.176 (0.158 ± 0.002)		1	3a a3422
$CuCl_3^-$	Li dihydrate	0.103 (0.104 ± 0.001)		1	3a a2937
$EuCl_6^{3-}$	Cs_2Na and Cs_2K salts	0.288 (0.208 ± 0.004)	0.014	2	3a a2680, a2681
FCl^{2-}	Ca and Sr salts	0.049 (0.056 ± 0.001)	0.002	2	3a a3066, a3067
$Fe(CN)_6^{4-}$	data gathered from 23 compounds listed in ref 1r	0.246 (0.184 ± 0.001)	0.017	23	1r
$Fe_2Cl_9^{3-}$	Cs salt	0.352 (0.293 ± 0.001)		1	3a a2886
$FeCl_3^-$	K and Cs salts	0.116 (0.108 ± 0.001)	0.003	2	3a a2878, a2883
$FeCl_4^{2-}$	$(CH_3)_4N^+$ salt	0.207 (0.134 ± 0.001)		1	3n
$FeCl_5^{2-}$	K and NH_4^+ monohydrates	0.169 (0.159 ± 0.001)	0.024	2	3a a3008, a3009
$FeCl_5^{3-}$	Rb salt	0.265 (0.159 ± 0.001)		1	3a a2882
$Ge_2O_7^{6-}$	Rb salt	0.224 (0.163 ± 0.002)		1	3a d2398
$Ge_6O_{13}^{2-}$	Rb salt	0.289 (0.398 ± 0.003)		1	3a d2400
GeO_4^{4-}	Mg salt	0.082 (0.087 ± 0.001)	0.010	4	3a d2414
$HgBr_3^-$	Cs salt	0.174 (0.136 ± 0.002)		1	3a a3324
$HgBr_4^{2-}$	Ca salt	0.216 (0.169 ± 0.002)		1	3a a3325
$HgCl_3^-$	Na, Rb, Cs, and NH_4^+ salts	0.145 (0.115 ± 0.001)	0.032	4	3a a2617, a2618, a2619, a2620
HgI_3^-	K monohydrate	0.197 (0.177 ± 0.002)		1	3a a3767
$InCl_4^-$	NH_4^+ salt	0.173 (0.158 ± 0.003)	0.005	2	3a a2646
$InCl_6^{3-}$	Rb salt	0.263 (0.210 ± 0.003)	0.012	2	3a a2650
$Ir(CN)_6^{3-}$	K salt	0.271 (0.188 ± 0.001)		1	3a c4383
$IrBr_6^{2-}$	K and Rb salts	0.248 (0.231 ± 0.002)	0.006	2	3a a3413, a3414
$LaCl_6^{3-}$	Cs_2Na and Cs_2K salts	0.306 (0.213 ± 0.005)	0.016	2	3a a2669, a2670
$Mn(CN)_6^{4-}$	Na decahydrate	0.233 (0.186 ± 0.001)		1	3a c4406
$Mn_2Cl_7^{3-}$	K salt	0.290 (0.244 ± 0.002)		1	3a a2851
$MnCl_3^-$	K and Rb dihydrates	0.117 (0.141 ± 0.001)	0.001	2	3a a2994, a3000
$MnCl_4^{2-}$	Na and Rb salts	0.165 (0.167 ± 0.001)	0.014	2	3a a2847, a2855
$Mo(CN)_8^{3-}$	Na tetrahydrate and Cs dihydrate	0.338 (0.243 ± 0.002)	0.018	2	3a c4401, c4402
$Mo(CN)_8^{4-}$	K dihydrate	0.333 (0.243 ± 0.002)		1	3a c4400
$Mo_5O_{16}^{2-}$	Cs salt	0.322 (0.372 ± 0.005)		1	3o
$Mo_7O_{22}^{2-}$	Cs salt	0.437 (0.517 ± 0.005)		1	3o
$MoCl_6^{3-}$	K salt	0.247 (0.193 ± 0.002)		1	3a a2825

Table 1. Continued

ion	molecule	vol (V) (nm^3) this work (Hofmann[2c])	error(nm^3)	no. of salts[b]	ref[d,f]
NS_2^+	$SbCl_6^-$ salt	0.059 (0.062 ± 0.001)		1	3q
$Nb_2Br_9^{3-}$	Rb and Cs salts	0.411 (0.368 ± 0.003)	0.003	2	3a a3367, a3369
$Nb_2Cl_9^{3-}$	Cs salt	0.321 (0.306 ± 0.003)		1	3a a2788
$Nb_2I_9^{3-}$	Cs salt	0.519 (0.490 ± 0.003)		1	3a a3749
$Nb_4Br_{11}^-$	Cs salt	0.418 (0.507 ± 0.004)		1	3a a3370
$Nb_4Cl_{11}^-$	Cs salt	0.354 (0.432 ± 0.004)		1	3a a2789
$NbCl_6^-$	K and Rb salts	0.443 (0.192 ± 0.002)	0.030	2	3a a2779, a2783
$NH_2SO_3^-$	K salt	0.092 (0.081 ± 0.006)		1	3p
$Ni(CN)_4^{2-}$	Li, Na, and Rb trihydrates and K monohydrate	0.171 (0.129 ± 0.004)	0.018	4	3a c4470, c4471, c4473, c4476
$NiBr_3^-$	Cs salt	0.123 (0.124 ± 0.002)		1	3a a3404
$NiCl_3^-$	NH_4^+ and Rb salts	0.106 (0.103 ± 0.002)	0.004	2	3a a2903, a2904
$Pb_2Br_2^-$	Rb salt	0.243 (0.169 ± 0.006)		1	3a a3341
$Pb_2Br_5^-$	NH_4^+ salt	0.237 (0.268 ± 0.006)		1	3a a3340
$Pb_2Cl_5^-$	K and NH_4^+ salts	0.208 (0.233 ± 0.006)	0.004	2	3a a2724, a2726
$Pb_2I_6^{2-}$	Sr heptahydrate	0.416 (0.381 ± 0.006)		1	3a a3770
$Pb_2O_3^{2-}$	K salt	0.129 (0.138 ± 0.006)		1	3a d3296
$PbBr_6^{4-}$	Cs salt	0.396 (0.248 ± 0.004)		1	3a a3345
$PbCl_6^{4-}$	Cs salt	0.342 (0.207 ± 0.004)		1	3a a2732
PbI_3^-	Cs salt and K dihydrate	0.217 (0.191 ± 0.004)	0.001	2	3a a3743, a3769
PbI_6^{4-}	Cs salt	0.483 (0.329 ± 0.004)		1	3a a3745
$PoCl_6^{2-}$	NH_4^+ salt	0.235 (0.205 ± 0.001)		1	3a a2811
$PrCl_6^{3-}$	Cs and Cs_2K salts	0.299 (0.212 ± 0.007)	0.016	2	3a a2673, a2674
$Pt(S_5)_3^{2-}$	NH_4^+ dihydrate	0.411 (0.416 ± 0.002)		1	3r
$PtCl_4^{2-}$	K salt	0.184 (0.141 ± 0.002)		1	3a a2924
PtI_6^{2-}	K and NH_4^+ salt	0.309 (0.315 ± 0.002)	0.004	2	3a a3762, a3763
$PuCl_6^{2-}$	Cs salt	0.252 (0.225 ± 0.001)		1	3a a2702
$PuCl_6^{3-}$	Cs_2Na salt	0.281 (0.225 ± 0.001)		1	3a a2705
$Re(CN)_6^{4-}$	K trihydrate	0.244 (0.197 ± 0.002)		1	3a c4415
$Re_2Br_8^{2-}$	Cs salt	0.377 (0.347 ± 0.003)		1	3a a3398
$Re_2Cl_8^{2-}$	K and Cs salts	0.305 (0.292 ± 0.003)	0.025	2	3a a3006, a3007
$Re_3Br_{11}^{2-}$	Cs salt	0.490 (0.488 ± 0.004)		1	3a a3400
$Re_3Br_{12}^{3-}$	Cs salt	0.548 (0.521 ± 0.004)		1	3a a3401
$ReCl_4^-$	Cs salt	0.157 (0.146 ± 0.002)		1	3a a2872
$RuCl_5^{2-}$	K and Cs salts	0.196 (0.166 ± 0.001)	0.016	2	3a a3011, a3012
$SbBr_6^{2-}$	NH_4^+ and Rb salts	0.274 (0.244 ± 0.002)	0.010	2	3a a3357, a3358
$SbCl_5^{2-}$	NH_4^+ salt	0.205 (0.177 ± 0.002)		1	3a a2755

Table 1. Continued

ion	molecule	vol (V) (nm^3) this work (Hofmann^{2c})	error(nm^3)	no. of salts^b	ref ^{d,f}
SbF_5^{2-}	NH_4^+ salt	0.114 (0.104 ± 0.002)		1	3s
$Sb_2F_7^-$	Cs salt	0.167 (0.167 ± 0.002)		1	3t
ScF_6^{3-}	Na and NH_4^+ salts	0.128 (0.109 ± 0.006)	0.008	2	3a a799, a804
$ScCl_6^{3-}$	Cs_2Na salt	0.247 (0.197 ± 0.001)		1	3a a2666
$SmCl_6^{3-}$	Cs_2Na and Cs_2K salts	0.291 (0.205 ± 0.004)	0.015	2	3a a2678, a2679
$Sn_3O_7^{2-\ e}$	K salt	0.148 (0.238 ± 0.002)		1	3a d3150
$SnBr_3^-$	Cs salt	0.175 (0.151 ± 0.002)		1	3a a3334
$SnCl_4^{2-}$	K monohydrate	0.182 (0.156 ± 0.001)		1	3a a2972
$SnO_3^{2-\ e}$	Li, Na, and K salts	0.071 (0.087 ± 0.001)	0.015	3	3a d3142, d3145, d3149
SnO_4^{4-}	Na and Mg salts	0.099 (0.098 ± 0.001)	0.022	2	3a d3144, d3152
SnS_3^{2-}	Na salt	0.138 (0.128 ± 0.001)		1	3u
$SO_3F^{-\ c}$	Li salt	0.079 (0.071)		1	3v
$TaCl_6^{2-}$	K and Rb salts	0.232 (0.198 ± 0.002)	0.002	2	3a a2795, a2796
$TcCl_8^{3-}$	NH_4^+ salt	0.349 (0.244 ± 0.005)		1	3a a3005
$Te_2O_5^{2-}$	NH_4^+ dihydrate	0.141 (0.150 ± 0.003)		1	3w
$TeCl_6^{2-}$	K, NH_4^+, and Rb salts	0.234 (0.202 ± 0.002)	0.012	3	3a a2806, a2807, a2808
$Ti_2Br_9^{3-}$	Rb salt	0.406 (0.349 ± 0.003)		1	3a a3351
$Ti_2Cl_9^{3-}$	K salt	0.355 (0.287 ± 0.003)		1	3a a2735
$TiBr_3^-$	Rb and Cs salts	0.135 (0.125 ± 0.002)	0.002	2	3a a3348, a3352
$TiBr_6^{2-}$	K and NH_4^+ salts	0.250 (0.224 ± 0.002)	0.008	2	3a a3346, a3347
$Tl_2Cl_9^{3-}$	Cs salt	0.377 (0.340 ± 0.006)		1	3a a2663
$Tl_2F_8^{2-}$	Ba salt	0.138 (0.197 ± 0.006)		1	3a a795
$Tl_3F_6^-$	Na salt	0.167 (0.229 ± 0.007)		1	3a a779
TlF_4^-	Rb and Cs salts	0.094 (0.099 ± 0.004)	0.004	2	3a a785, a788
TlF_5^{2-}	Ba salt	0.094 (0.110 ± 0.004)		1	3a a794
TlF_6^{3-}	K_3, K_2Na, and $(NH_4^+)_2Na$ salts	0.139 (0.121 ± 0.004)	0.012	3	3a a781, a783, a784
TlI_4^-	Cs salt	0.327 (0.239 ± 0.004)		1	3a a3738
$U_2O_4F_9^{5-}$	K salt	0.297 (0.262 ± 0.004)		1	3v
$UO_2F_5^{3-}$	K salt	0.161 (0.137 ± 0.004)		1	3y
$V_2Cl_9^{3-}$	Cs salt	0.351 (0.280 ± 0.003)		1	3a a2777
VCl_3^-	K and Cs salts	0.116 (0.101 ± 0.002)	0.003	2	3a a2774, a2776
VOF_4^{2-}	NH_4^+ salt	0.090 (0.080 ± 0.002)		1	3z
$W_2Br_9^{2-}$	K salt	0.418 (0.372 ± 0.003)		1	3a a3389
$W(CN)_8^{3-}$	Na tetrahydrate and Cs dihydrate	0.332 (0.244 ± 0.002)	0.015	2	3a c4404, c4405
$W_2Cl_9^{3-}$	K and Rb salts	0.338 (0.310 ± 0.002)	0.006	2	3a a2826, a2839
YCl_6^{3-}	Cs_2Na and Cs_2K salts	0.282 (0.199 ± 0.003)	0.015	2	3a a2667, a2668

Table 1. Continued

ion	molecule	vol (V) (nm^3) this work (Hofmann^{2c})	error(nm^3)	no. of salts[b]	ref [d,f]
$Zn(CN)_4^{2-}$	Na trihydrate	0.178 (0.142 ± 0.003)		1	3a c4389
$ZnCl_3^-$	Li and K dihydrate	0.134 (0.116 ± 0.003)	0.001	2	3a a2950, a2953
ZnI_3^-	K dihydrate	0.182 (0.178 ± 0.003)		1	3a a3766

[a] Ions arranged alphabetically by symbol. Hofmann volumes are given in parentheses and are based on the sum of the values given in ref 2c for the atoms involved in the ion. [b] Number of salts considered to estimate the volume of individual ion. [c] Ions that appeared in the original database[1b] which are relisted appear here for one of the following reasons: (i) the error quoted has been reduced or (ii) the value is based on consideration of an *increased number* of example salts. In cases where no error is displayed for the ion volume, a value of ±0.02 nm^3 should be assumed (see text). [d] All data was extracted from entries in ref 3a or else taken from the individual references indicated. [e] Although these materials would not normally be regarded as consisting of $2M^+$ and an SnO_3^{2-} ion or $2M^+$and an $Sn_3O_7^{2-}$ ion, regarding them as such leads to an estimate of the volume of the (hypothetical) SnO_3^{2-} ion, $V(SnO_3^{2-})$, and the $Sn_2O_7^{2-}$ ion, $V(Sn_2O_7^{2-})$), and these values, in turn, agree with the additivity rules, $V(SnO_3^{2-}) + V(O^{2-}) \approx V(SnO_4^{4-})$ and $V(Sn_3O_7^{2-}) + 2V(O^{2-}) \approx 3V(SnO_3^{2-})$, and lie within the standard deviations recorded for the latter (established) ions. [f] Ref 3a contains crystal structure data and the serial numbers (e.g., a2667 or c4389), which refer to the volumes (e.g., the letters a and c refer to volume 7a or 7c, respectively) in which these data are found. The number (e.g., 2667 refers to the entry number of the salt within the appropriate volume (in this case 7a). [g] Using Mighell[2e] volumes ($V(Bk) = 70$ Å^3 = 0.070 nm^3).

Table 2. Application of Isomegethic Rule to Estimate $V(AuI_4^-)$ (nm^3) Using the $V(AuI_4^-) \approx V(AuX_4^-) + {}^2/_3[V(EI_6^{2-}) - V(EX_6^{2-})]$ Relationship[a]

E	X	$V(AuX_4^-)$ (nm^3)	error (nm^3)	$V(EI_6^{2-})$ (nm^3)	error (nm^3)	$V(EX_6^{2-})$ (nm^3)	error (nm^3)	$V(AuI_4^-)$ (nm^3)	error (nm^3)
Re	Br	0.177	0.003	0.344	0.014	0.263	0.003	0.231	0.015
Re	F	0.088	0.013	0.344	0.014	0.124	0.007	0.235	0.020
Re	Cl	0.157	0.014	0.344	0.014	0.244	0.007	0.224	0.021
Sn	Br	0.177	0.003	0.362	0.004	0.274	0.004	0.236	0.006
Sn	Cl	0.157	0.01	0.362	0.004	0.234	0.006	0.242	0.012
Sn	F	0.088	0.013	0.362	0.004	0.11	0.014	0.256	0.020
Tc	Br	0.177	0.003	0.333	0.001	0.259	0.001	0.226	0.003
Tc	Cl	0.157	0.01	0.333	0.001	0.219	0.002	0.233	0.010
Tc	F	0.088	0.013	0.333	0.001	0.119	0.003	0.231	0.013
Te	Br	0.177	0.003	0.357	0.009	0.286	0.002	0.224	0.010
Te	Cl	0.157	0.01	0.357	0.009	0.244	0.005	0.232	0.014
							average	0.234	0.013

[a] Note that Hofmann[2c] elemental volumes yield a comparative volume of $V(AuI_4^-) \approx 0.228 \pm 0.002$ nm^3.

containing complex anions can be chosen in conjunction with the additivity rules. Four, seemingly reliable, sets of volumes for hexahalometalates are provided by the transition metals Re, Sn, Tc, and Te. From the isomegethic rule we deduce that

$$V_m([M^+][AuX_4^-]) + {}^2/_3\,V_m([M'^+]_2[EX'_6]^{2-}) \approx V_m([M'^+][AuX'_4{}^-]) + {}^2/_3 V_m([M^+]_2[EX_6]^{2-}) \quad (8)$$

from which, using additivity relationships we find that

$$V_m(AuX_4^-) + {}^2/_3 V_m([EX'_6]^{2-}) \approx V_m(AuX'_4{}^-) + {}^2/_3 V_m([EX_6]^{2-}) \quad (9)$$

or that

$$V_m(AuI_4^-) \approx V_m(AuX_4^-) + {}^2/_3 V_m([EI_6]^{2-}) - {}^2/_3 V_m([EX_6]^{2-}) \quad (10)$$

Table 2 lists estimated values for $V(AuI_4^-)$ (in nm^3) leading to the assignment

$$V(AuI_4^-) \approx 0.234 \pm 0.013 \text{ nm}^3 \quad (11)$$

This can be compared with a value

$$V(AuI_4^-) \approx [43 \pm 2 + 4(46.2 \pm 0.4)]/1000 \approx 0.228 \pm 0.002 \text{ nm}^3 \quad (12)$$

obtained using Hofmann's elemental volumes. The latter equations take no specific account of the charge on the ion in question however and are governed solely by the empirical formula.

II. Volume Additivity Rules Applied to Anions and Cations. From the additivity rules for ion volumes, we can write the following equation for a complex ion:

$$V(MX_n^{z-}) + mV(X^-) \approx V(MX_{(n+m)}^{(z+m)-}) \quad (13)$$

where m and z take integer values, usually 1, 2, or 3, and n can be (typically) 4, 5, and 6 (see below), and these rules can be used to examine and quantify (or verify) the volumes for selected target ions. We anticipate (see Tables 1, 3b, 3e, and 3f) that the following relationships should apply:

$$V(Re_3Br_{12}^{3-}) \approx V(Re_3Br_{11}^{2-}) + V(Br^-) \quad (14)$$

$$V(TlF_6^{3-}) \approx V(TlF_5^{2-}) + V(F^-) \approx V(TlF_4^-) + 2V(F^-) \quad (15)$$

$$V(BiBr_5^{2-}) \approx V(BiBr_4^-) + V(Br^-) \quad (16)$$

$$V(BiCl_6^{3-}) \approx V(BiCl_5^{2-}) + V(Cl^-) \approx V(BiCl_4^-) + 2V(Cl^-) \quad (17)$$

Thus in Table 1, to take one example, the entries for the ions $BiCl_n^{z-}$ ($n = 4, 5, 6$ and $z = 1, 2, 3$) are each based on crystal structure data from a single salt and an examination of the data leads to the following comments. From the relationship in eq 17, one can determine that

$$V(BiCl_6^{3-}) \approx 0.277 \pm 0.010 \text{ nm}^3 \quad (18)$$

from Table 1, while

$$V(BiCl_6^{3-}) \approx V(BiCl_5^{2-}) + V(Cl^-) \approx$$
$$0.210 \pm 0.010 + 0.047 \pm 0.013 \approx 0.257 \pm 0.013 \text{ nm}^3 \quad (19)$$

and the error ranges make these two estimates for $V(BiCl_6^{3-})$ mutually compatible. We also anticipate that

$$V(BiCl_6^{3-}) \approx V(BiCl_4^-) + 2V(Cl^-) \approx$$
$$0.150 \pm 0.010 + 0.094 \pm 0.018 \approx 0.244 \pm 0.018 \text{ nm}^3 \quad (20)$$

While the relationship does not quite show exact compatibility with the entry for $V(BiCl_6^{3-})$ in Table 1, this value suggests that the assumption concerning the magnitude of the error of $V(BiCl_6^{3-})^5$ should be of the order of ± 0.020 nm^3. Using Hofmann's elemental volumes,[2c] for which

$$V(BiCl_6^{3-}) \approx [60 \pm 4 + 6(25.8 \pm 0.3)]/1000 \approx$$
$$0.215 \pm 0.004 \text{ nm}^3 \quad (21)$$

also confirms this conclusion. In the case of the associated formula unit volumes, both the Hofmann and Jenkins approaches lead to similar results. For example, considering Na_3BiCl_6 where

$$V_m(Na_3BiCl_6) \approx 3V(Na^+) + V(BiCl_6^{3-}) \approx$$
$$3(0.004) + 0.277 \pm 0.010 = 0.289 \pm 0.010 \text{ nm}^3 \quad (22)$$

using ion volumes (eq 22), while Hofmann's approach leads to a similar result based on average elemental volumes (eq 23)

$$V_m(Na_3BiCl_6) \approx 3\nu(Na) + \nu(Bi) + 6\nu(Cl) \approx [3(26 \pm 3) +$$
$$60 \pm 4 + 6(25.8 \pm 0.3)]/1000 = 0.293 \pm 0.007 \text{ nm}^3 \quad (23)$$

Relationships 13− 17 above are broadly satisfied by the data in Table 1.

Neutral molecules (e.g., TiF_4, H_2O) can sometimes be employed [1z] to estimate data for ion volumes. For example, for the complex ions $Ti_2F_9^-$ and $Ti_4F_{18}^{2-}$, we can conceive that

$$V(Ti_2F_9^-) \approx 2V(TiF_4) + V(F^-) \quad (24)$$

and

$$V(Ti_4F_{18}^{2-}) \approx 4V(TiF_4) + 2V(F^-) \quad (25)$$

and we anticipate that $V(Ti_4F_{18}^{2-})$ is to equal $2V(Ti_2F_9^-)$.

Discussion

Tables 3a−h summarize volume data (converted into units of Å^3) taken from our original database[1b] and from Table 1 of this paper. Volumes are listed in Tables 3a−h in such a way that the *integer values listed should be divided by a factor of 1000 in order to convert them directly back to nm^3*, the units used throughout this paper. Thus, in Table 3a, $V(BeF_3^-)$ is listed as 68 ± 9 Å^3 and can be converted to 0.068 ± 0.009 nm^3 by the division described above. The tables show (see footnotes) how further ion volume data can be generated using the techniques discussed in the sections above. We can now estimate volumes for most ionic species and for most formula units (real or hypothetical), and furthermore, we can usually devise *more than one* route for establishing such data.

We considered the following series of ions: MX_n^- ($n = 3-7$), MX_n^{2-} ($n = 4-6, 8$), MX_n^{3-}($n = 5-8$), and MX_n^{4-} ($n = 6$). As noted earlier, if errors are not listed, they may be assumed to be on the order of 0.020 nm^3 (i.e., 20 Å^3, as expressed in Tables 3a−h). The entries listed in **bold** type are those derived from crystal structure sources, while those bracketed and in ordinary type are those derived from these ion volumes by one of the routes indicated in the relevant footnote. Footnotes are placed at the end of the final table (i.e., Table 3h). In principle, volumes could be generated for *all* of the species listed in the accompanying tables, but we have stopped short of doing this. This gives rise to the occasional empty row in some of the tables, we have retained the format to enable ease of comparison across tables and so, hopefully, to inspire the volume measurement of an appropriate new salt.

Although the relationships 26−30 can also be conceived, none of the ion volumes in Tables 3a−h were generated using them.

$$[V(MX_7^{3-}) - V(MX_6^{2-})] \approx V(X^-) \quad (26)$$

$$[V(MX_6^{2-}) - V(MX_5^-)] \approx V(X^-) \quad (27)$$

$$[V(MX_7^{3-}) - V(MX_5^-)] \approx 2V(X^-) \quad (28)$$

$$[V(MX_8^{3-}) - V(MX_6^-)] \approx 2V(X^-) \quad (29)$$

$$[V(MX_8^{2-}) - V(MX_7^-)] \approx V(X^-) \quad (30)$$

This is because of the esoteric nature of at least one of the species involved in the relationship. Such volumes can be estimated as and when required, and as also discussed, Hofmann's approach[2c] can be adopted (with the caveats already noted with respect to ion volume data generated from elemental data). However, these (and similar) equations demonstrate that for *almost any complex ion* (real, hypothetical, counterintuitive, etc.) an approximate estimate of its volume can usually be made and (more importantly) very often using not just one but a variety of sources.

Equations 1a, 1b, and 2 are important because of the direct link they forge between crystal structure derived data and thermodynamics; they are the essence of VBT.[1z] We cite examples below of how volume data can be utilized, practically, to estimate missing thermodynamic data. The volume and elemental additivity rules are powerful and indeed, if they were they absolutely true, then the isomegethic

Table 3. Ion Volumes (listed here in Å^3) for Ions MX_n^- ($n = 3-7$), MX_n^{2-} ($n = 4-6, 8$), MX_n^{3-}($n = 5-8$), and MX_n^{4-} ($n = 6$)

(a) M = Be, Sc, Ti, Zr, Hf, V, Nb, and Ta^{k}

	Be	Sc	Ti	Zr	Hf	V	Nb	Ta
MX_3^-	**F 68 ± 9**					**Cl 116** (Br 134)^{a} (I 153)^{c}		
MX_4^-	**F 78 ± 11** (Cl 147)^{a} (Br 167)^{a}	(F 78 ± 16)^{e}	(Br 123 ± 21)^{e}					
MX_5^-								
MX_6^-						**F 112** ± 9	**F 125** ± 8 **Cl 232** ± 30	**F 128** ± 8 **Cl 206**
MX_7^-								
MX_4^{2-}	(F 93 ± 13)^{h}					(Cl 163 ± 13)^{g} (Br 190 ± 14)^{g} (I 225 ± 16)^{g}		
MX_5^{2-}	(F 103 ± 15)^{e} (Cl 194 ± 13)^{e} (Br 223 ± 14)^{e}	(F 103 ± 13)^{c}	(Br 179 ± 15)^{c}					
MX_6^{2-}		**F 124**	**F 122 ± 8** **Cl 221 ± 9** **Br 256 ± 3**	**F 121 ± 20** **Cl 242 ± 4** **I 218**	**F 126 ± 15**		**Cl 231 ± 6** **(Br 271± 8)^{b}**	**Cl 232** **(Br 272± 5)^{b}**
MX_5^{3-}					F 130			
MX_6^{3-}		**F 128 ± 8**	**Br 235 ± 11**					
MX_6^{4-}								
MX_7^{3-}								
MX_8^{2-}								
MX_8^{3-}								**F 137**

(b) M = Ta, Cr, Mo, W, Mn, Tc, Re, and Fe^{k}

	Ta	Cr	Mo	W	Mn	Tc	Re	Fe
MX_3^-		**Cl 120 ± 4** **Br 138** (I 143 ± 2)^{c}			(F 72 ± 10)^{h} **Cl 117 ± 1**^{i} (Br 135)^{a} (I 140 ± 3)^{c}			**Cl 116 ± 3**^{i} (Br 134)^{a} (I 139 ± 4)^{c}
MX_4^-		(F 77 ± 14)^{e}					(F 88)^{a} **Cl 157** (Br 177)^{a}	(F 86)^{a} **Cl 155** ^{g} (Br 175)^{a}
MX_5^-								
MX_6^-	**F 128 ± 8** **Cl 206**		**F 113 ± 17**	**F 125 ± 32** **Cl 208** ± 4			**F 117 ± 8**	
MX_7^-								
MX_4^{2-}		**Cl 178** ± 2 (Br 194 ±14)^{h} (I 215 ± 16)^{h}			**F 97 ± 1** **Cl 135 ± 4**^{i} (Br 191 ± 14)^{h} (I 212 ± 16)^{h}			**Cl 207**^{i} (Br 190 ± 14)^{h} (I 211 ± 16)^{h}
MX_5^{2-}		(F 102 ± 10)^{c}					(F 113 ± 10)^{e} (Cl 204 ± 13)^{e} (Br 233 ±14)^{e}	(F 130 ± 30)^{c} **Cl 169 ± 24**^{g} (Br 231 ± 14)^{e}
MX_6^{2-}	**Cl 232** (Br 272± 5)^{b}	**F 148 ± 29**	**F 123** **Cl 228 ± 7** **Br 266 ± 3**	**Cl 222 ± 1** **Br 263 ± 6**	**F 115 ± 29** **Cl 195 ± 19** (Br 235 ± 25)^{b}	**F 119 ± 3** **Cl 219 ± 2** **Br 259 ± 1** **I 333 ± 1**	**F 124 ± 7** **Cl 224 ± 7** **Br 263 ± 3** **I 344 ± 14**	
MX_5^{3-}		(Cl 225 ± 13)^{g}			(F 122 ± 10)^{g} (Cl 182 ± 14)^{g}			**Cl 256**
MX_6^{3-}		**F 127**						**F 155 ± 28** (Cl 216 ± 27)^{c}
MX_6^{4-}					**Cl 264**			
MX_7^{3-}								
MX_8^{2-}							**F 149 ± 4**	
MX_8^{3-}	**F 137**							

(c) M = Ru, Os. Co, Rh, Cu, Ir, Ni, and Pd^{k}

	Ru	Os	Co	Rh	Cu	Ir	Ni	Pd
MX_3^-			(F 64 ± 10)^{h} **Cl 110**^{i} (Br 130)^{a,i}		(F 62 ± 13)^{h} **Cl 103**^{i} (Br 120)^{a} (I 126 ± 2)^{c}		(F65 ± 14)^{h} **Cl 106** Br 123 (I 129 ± 2)^{c}	**(Cl 158 ± 13)**^{h}
MX_4^-	(F 102 ± 11)^{e} (Cl 149 ± 13)^{e} (Br 195 ± 15)^{e}		(F 89 ± 10)^{e}		**F 87** ± 8 (Cl 156)^{a} **Br 176**		(F 71 ± 14)^{e}	
MX_5^-	**F 118 ± 16**							
MX_6^-	**F 116 ± 7**							
MX_7^-								

Table 3. Continued

(c) M = Ru, Os. Co, Rh, Cu, Ir, Ni, and Pd^{k}

	Ru	Os	Co	Rh	Cu	Ir	Ni	Pd
MX_4^{2-}			**F 89** **Cl 196** ^{i} (Br 238 ± 14)^{g,i}		**F 87 ± 8** **Cl 192** ^{i} (Br 176 ± 14)^{h} (I 198 ± 16)^{h}		**F 80 ± 10** (Cl 153 ± 13)^{h} (Br 179 ± 14)^{h} (I 201 ± 16)^{h}	**Cl 183**
MX_5^{2-}	**F 127 ± 5** **Cl 196** (Br 251 ± 5)^{b}		(F 114)^{c}		(F 112 ± 13)^{e} (Cl 203 ± 13)^{e} (Br 232 ± 14)^{e}		(F 96 ± 10)^{c}	
MX_6^{2-}	**Cl 211**	**F 124** **Cl 223 ± 8** **Br 261 ± 4**		**F 116 ± 3**		**Cl 299** (Br 269 ± 5)^{c}	**F 126 ± 14**	**F 143 ± 31** **Cl 218 ± 8** **Br 247 ± 14**
MX_5^{3-}			(F 114 ±10)^{g} **Cl 253** **Br 294**		(F 112 ± 13)^{g} (Cl 239 ±13)^{g}		(F 105 ± 14)^{g}	(Cl 230 ±13)^{g}
MX_6^{3-}	(F 150 ± 11)^{c} (Cl 244 ± 13)^{c} (Br 307 ± 15)^{c}		**F 139**				**F 121**	
MX_6^{4-}								
MX_7^{3-}	**Cl 258**							
MX_8^{2-}								
MX_8^{3-}								

(d) M = Pt, Au. Ag, Zn, Cd, Hg, B, and Al^{k}

	Pt	Au	Ag	Zn	Cd	Hg	B	Al
MX_3^{-}	(Cl 159 ±13)^{h} (Br 142 ± 14)^{h}			(F 59 ± 15)^{h} **Cl 134** (Br 151)^{a} **I 182**^{i}	(Cl 149 ± 13)^{h}	**Cl 145** **Br 174** **I 197**^{i}		
MX_4^{-}		**F 88 ± 13** **Cl 157** **Br 177**	**F 89 ± 14** **I 242 ± 10**				**F 73 ± 9**	**F 68 ± 3** **Cl 156** **Br 198 ± 5** **I 243 ± 10**
MX_5^{-}								
MX_6^{-}	**F 109 ± 20**	**F 115 ± 14**						
MX_7^{-}								
MX_4^{2-}	**Cl 184** **Br 198**			**F 84 ± 11** **Cl 185 ± 11** **Br 216 ± 12** **I 218**^{i}	**Cl 196**	(Cl 170 ± 13)^{h} **Br 216** **I 245**^{i}		
MX_5^{2-}		(F 113 ± 16)^{e} (Cl 204 ± 13)^{e} (Br 233 ±14)^{e}	(F 114 ± 17)^{e} (I 314 ± 19)^{e}				(F 98 ± 13)^{e}	(F 94 ±10)^{e} (Cl 203 ± 13)^{e} (Br 254 ± 15)^{e} (I 315 ± 19)^{e}
MX_6^{2-}	**F 119 ± 12** **Cl 219 ± 9** **Br 258 ± 6** **I 309**							
MX_5^{3-}	(Cl 231 ±13)^{g} (Br 254 ± 14)^{g}			(F 109 ± 15)^{g} (Cl 232 ± 17)^{g} (Br 272 ± 18)^{g} (I 290 ± 16)^{g}	(Cl 243 ± 13)^{g}	(Br 272 ± 14)^{g} (I 317 ± 16)^{g}		
MX_6^{3-}								
MX_4^{4-}				**Cl 288**^{j} **Br 326**^{j}				
MX_6^{4-}								
MX_7^{3-}								
MX_8^{2-}								
MX_8^{3-}								

(e) M = Ga, In, Tl, Si, Ge, Sn, and Pb^{k}

	Ga	In	Tl	Si	Ge	Sn	Pb
MX_3^{-}						(Cl 145)^{a} **Br 175** (I 197)	(Cl 122 ± 13)^{h}
MX_4^{-}	**Cl 145**	(F 102 ± 16)^{e} **Cl 173**	**F 94** (Cl 164)^{a} (Br 238)^{a} **I 327**				
MX_5^{-}							
MX_6^{-}							
MX_7^{-}						**F 167**	
MX_4^{2-}						**Cl 182** (Br 231 ± 14)^{h} (I 269 ± 16)^{h}	**Cl 147**

Table 3. Continued

(e) M = Ga, In, Tl, Si, Ge, Sn, and Pb[k]

	Ga	In	Tl	Si	Ge	Sn	Pb
MX_5^{2-}	(Cl 192 ± 13)[e]	(F 127 ± 13)[c] (Cl 216 ± 13)[c]	**F 94**[d,f] (Cl 211 ± 13)[e] (Br 294 ± 14)[e] (I 399 ± 16)[e]				
MX_6^{2-}				**F 112 ± 28**	**F 113 ± 25** **Cl 230**	**Cl 234 ± 6** **Br 274 ± 4** **I 362 ± 4**	**F 112 ± 15** **Cl 243 ± 4** (Br 283 ± 6)
MX_5^{3-}						(Cl 229 ± 13)[g]	(Cl 194 ± 13)[g]
MX_6^{3-}		**F 152 ± 8** **Cl 263**	**F 148 ± 9**[d]				
MX_6^{4-}							**Cl 342** **Br 396**
MX_7^{3-}							
MX_8^{2-}							
MX_8^{3-}							

(f) M = As, Sb, Bi, Se, Te, Po, and Ce[k]

	As	Sb	Bi	Se	Te	Po	Ce
MX_3^{-}							
MX_4^{-}		(F 89 ± 10)[e] (Cl 158 ± 13)[e] (Br 184 ± 14)[e]	(F 87)[a] **Cl 150** **Br 177** (I 222)[a]				(F 117 ± 14)[e]
MX_5^{-}							
MX_6^{-}	**F 110 ± 7**	**F 121 ± 12** **Cl 203 ± 17**	**F 121 ± 14**				
MX_7^{-}							
MX_4^{2-}							
MX_5^{2-}		**F 114** **Cl 205** **Br 240**	(F 112 ± 10)[e] **Cl 210** (Br 223 ± 14)[e] (I 294 ± 16)[e]				(F 142 ± 10)[c]
MX_6^{2-}			**Cl 156**	**Cl 229 ± 7** **Br 267 ± 4**	**Cl 234 ± 2** **Br 286 ± 2** **I 357 ± 9**	**Cl 235** **Br 296** **I 372**	**F 127** **Cl 255** (Br 295 ± 5)[b]
MX_5^{3-}							
MX_6^{3-}		(F 139 ± 10)[c] (Cl 252 ± 13)[c] (Br 296 ± 14)[c]	**Cl 277**				**F 167**
MX_6^{4-}							
MX_7^{3-}							
MX_8^{2-}							
MX_8^{3-}							

(g) M = Pr, Sm, Eu, Tb, Th, and Pu[k]

	Pr	Sm	Eu	Tb	Th	Pu
MX_3^{-}		(F 48 ± 10)[h]				
MX_4^{-}	(F 121 ± 14)[e] (Cl 141 ± 18)[e]	(Cl 197 ± 18)[e]	(Cl 193 ± 23)[e]			(Cl 187 ± 18)[e]
MX_5^{-}						**F 96 ± 8**
MX_6^{-}						
MX_7^{-}						
MX_4^{2-}		**F 73**				
MX_5^{2-}	(F146 ± 10)[c] (Cl 188 ± 13)[c]	(Cl 244 ± 13)[c]	(Cl 241 ± 19)[c]			(Cl 234 ± 13)[c]
MX_6^{2-}					**F 126 ± 25** **Cl 267** (Br 307 ± 5)[b]	**(F 124)**[a] **Cl 252**
MX_5^{3-}		(F 98 ± 10)[g]				
MX_6^{3-}	**F 171** **Cl 235**	**Cl 291**	**Cl 288 ± 14**			**Cl 281**
MX_6^{4-}						
MX_7^{3-}				**F 163 ± 16**	**F 166 ± 41**	
MX_8^{2-}						
MX_8^{3-}						

(h) M = U, Am, Pa, and Bk[k]

	U	Am	Pa	Bk
MX_3^{-}				
MX_4^{-}				(Cl 202 ± 18)[e]

Table 3. Continued

(h) M = U, Am, Pa, and Bk[k]

	U	Am	Pa	Bk
MX_5^-				
MX_6^-			**F 124 ± 11**	
MX_7^-	**F 167 ± 41**			
MX_4^{2-}				
MX_5^{2-}				(Cl 227 ± 13)[c]
MX_6^{2-}	**F 114 ± 10** **Cl 258**	**F 132**		(F 125)[a] **Cl 253** (Br 293 ± 5)[b]
MX_5^{3-}				
MX_6^{3-}				**Cl 274**
MX_6^{4-}				
MX_7^{3-}	**F 152 ± 28**			
MX_8^{2-}				
MX_8^{3-}			**F 158 ± 20**	

[a] Estimation was made by inspection (i.e., by comparison with similar trends found for neighboring metal ions, for example for the MX_3^- ion bold type entries for F, Cl, Br, or I are very similar regardless of M so in cases where entries are missing these can be estimated by comparison with neighboring MX_3^- ions). [b] Calculated using Table 8 of the isomegethic paper[1u] with the following equation: $V(MBr_6^{2-}) - V(MCl_6^{2-}) \approx 0.040 \pm 0.005$ nm^3. The following estimates are based on the volumes for the halogen ions: $V(F^-) = 0.025 \pm 0.010$ nm^3, $V(Cl^-) = 0.047 \pm 0.013$ nm^3, $V(Br^-) = 0.056 \pm 0.014$ nm^3, and $V(I^-) = 0.072 \pm 0.016$ nm^3. While it is recognized that some of these ions may not exist in reality, the estimates for the volumes will still be valid and may be useful in the context of probing their instability. [c] Estimated using the following equation: $[V(MX_6^{3-}) - V(MX_5^{2-})] \approx V(X^-)$. [d] This pair of results is not compatible with the relationship in c. [e] Estimated using the following equation: $[V(MX_5^{2-}) - V(MX_4^-)] \approx V(X^-)$. [f] This value is likely to be in error. A value for $V(TlF_5^{2-})$ of ~0.074 ± 0.010 nm^3 is commensurate with both the relationships, $[V(TlF_6^{3-}) - V(TlF_5^{2-})] \approx V(F^-)$ and $[V(TlF_5^{2-}) - V(TlF_4^-)] \approx V(F^-)$. Hofmann's elemental volume data[2c] leads to a $V(TlF_5^{2-})$ value of ≈ 0.083 ± 0.002 nm^3. [g] Estimated using the following equation: $[V(MX_5^{3-}) - V(MX_4^{2-})] \approx V(X^-)$. [h] Estimated using the following equation: $[V(MX_4^{2-}) - V(MX_3^-)] \approx V(X^-)$. [i] This pair of results is not compatible with the relationship in h. It should be noted also that, in Table 1, the $V(CoBr_5^{3-})$ volumes from Jenkins and Hofmann volume data do not agree. [j] Note additional row (not present in other tables) has been inserted for ions MX_4^{4-}. [k] To obtain the volume in nm^3 for any listed ion, divide the integer entries in the table below by 1000.

rule would be a corollary to these rules and vice versa. Throughout the work to date,[1a−y] the agreement found between the experimental and predicted values has given us much confidence in the ion volume data so far generated.

Applications

Density Estimation. First, yellow trihydrate $K_4Fe(CN)_6 \cdot 3H_2O$ (M = 422.390) whose experimental density,[4] ρ, is reported to be 1.85 g cm^{-3}, the pink − red K_2PtCl_4 (M = 415.09) with a reported density, ρ, of 3.38 g cm^{-3}, and the red $K_3Fe(CN)_6$ (M = 329.246) for which the density, ρ, is reported to be 1.89 g cm^{-3} were considered. Using the data in the Table 1, $V(Fe(CN)_6^{4-}) = 0.246 \pm 0.017$ nm^3 and $V(PtCl_4^{2-}) = 0.184$ nm^3, while $V(K^+) = 0.0099$ nm^3 and $V(Fe(CN)_6^{3-}) = 0.265 \pm 0.011$ nm^3 (Table 4 in ref 1c). Therefore, $V_m(K_3Fe(CN)_6) = 0.295 \pm 0.011$ nm^3, $V_m(K_2PtCl_4) = 0.204 \pm 0.011$ nm^3, and since $V(H_2O) = 0.025$ nm^3,[1k] then $V_m(K_4Fe(CN)_6 \cdot 3H_2O) = 0.347 \pm 0.011$ nm^3. Using the relationship between volume and density (eq 7), we *predict* that $\rho(K_3Fe(CN)_6) = 1.86 \pm 0.07$ g cm^{-3} and $\rho(K_2PtCl_4) = 3.38$ g cm^{-3}, while $\rho(K_4Fe(CN)_6 \cdot 3H_2O) = 2.01$ g cm^{-3}.

Hofmann's approach[2c] (specifically developed for the "fast estimation" of density) leads to $V_m(K_3Fe(CN)_6) = 0.292 \pm 0.028$ nm^3, $V_m(K_2PtCl_4) = 0.213 \pm 0.005$ nm^3, and $V_m(K_4Fe(CN)_6 \cdot 3H_2O) = 0.359 \pm 0.006$ nm^3 and, hence, to the densities $\rho(K_3Fe(CN)_6) = 1.87 \pm 0.16$ g cm^{-3}, $\rho(K_2PtCl_4) = 3.23 \pm 0.07$ g cm^{-3}, and $\rho(K_4Fe(CN)_6 \cdot 3H_2O) = 1.95 \pm 0.03$ g cm^{-3} which offer similar agreement with experimental data.

Lattice Energy Estimation. Second, we can consider the estimation of the lattice energy, $U_{POT.}$ For the two salts K_2TiBr_6, and K_2PtCl_4, the Born−Fajans−Haber cycle values of the lattice energies are found[4] to be 1379 and 1550 kJ mol^{-1}, respectively. The ionic strength of both salts is $I = 3$, and for this stoichiometry (M_2X), the coefficients in eq 1 take the following values:[2b] $\alpha = 165.3$ kJ mol^{-1} nm and $\beta = -29.8$ kJ mol^{-1}. Since $V(TiBr_6^{2-}) = 0.259 \pm 0.008$ nm^3 (see table), then $V_m(K_2TiBr_6) = 0.270 \pm 0.008$ nm^3, and the predicted lattice energy, U_{POT}, is approximately 1356 ± 15 kJ mol^{-1} (K_2TiBr_6). In the case of K_2PtCl_4, using the volume above, $U_{POT}(K_2PtCl_4) \approx 1506$ kJ mol^{-1}. Hofmann's elemental volumes give $V_m(K_2TiBr_6) = 0.296 + 0.005$ nm^3 leading to $U_{POT}(K_2TiBr_6) = 1309 \pm 8$ kJ mol^{-1} and to $U_{POT}(K_2PtCl_4) = 1482 \pm 13$ kJ mol^{-1}.

Standard Entropy Estimation. Using eq 2 (k = 1360 J K^{-1} mol^{-1} nm^{-3}, c = 15 J K^{-1} mol^{-1}),[11] we can test the data further by predicting the standard entropies, $S°_{298}$ (in J K^{-1} mol^{-1}) of the two salts above. $S°_{298}(K_2PtCl_4)$ is predicted to be 265 J K^{-1} mol^{-1}, using our value of V_m above, while using the experimental density ($\rho(K_2PtCl_4) = 3.38$ g cm^{-3}), leads to a larger volume and an estimated standard entropy value of 292 J K^{-1} mol^{-1}, closer to the experimental value of 283 J K^{-1} mol^{-1}.[6a] Hofmann's[2c] volumes lead to an $S°_{298}(K_2PtCl_4)$ value of 305 ± 6 J K^{-1} mol^{-1}. Our result for $S°_{298}$ (K_2TiBr_6) is 382 ± 11 J K^{-1} mol^{-1} (Hofmann's value is 418 + 6 J K^{-1} mol^{-1} for the latter salt). No experimental value has yet been reported for this compound. However, we were able to establish experimental values[6a] for for $S°_{298}(K_2TiF_6)$ and for $S°_{298}(K_2TiCl_6)$ which are 308 and 376 J K^{-1} mol^{-1}, respectively. Hofmann's volumes, and eq 2, lead to values of 241 ± 6 and 360 ± 7 J K^{-1} mol^{-1}, respectively. Because we use eq 2 to estimate that the anticipated entropy increase in going from a chloride to a bromide (using the fact[1u] that $[V(\mathrm{Br}^-) - V(\mathrm{Cl}^-)] \approx 0.009\ \mathrm{nm}^3$) is approximately 12 J K^{-1} mol^{-1}, this leads us to predict that the experimental value for S°_{298} (K_2TiBr_6) should be approximately 388 J K^{-1} mol^{-1}, which is within the range of our predicted value and close to the value estimated using Hofmann's data.

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