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The Ionic Isomegethic Rule and Additivity Relationships: Estimation of Ion Volumes. A Route to the Energetics and Entropics of New, Traditional, Hypothetical, and Counterintuitive Ionic Materials

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By virtue of our recently established relationships, knowledge of the formula unit volume, V_m, of a solid ionic material permits estimation of thermodynamic properties such as standard entropy, lattice potential energy, and, hence, enthalpy and Gibbs energy changes for reactions. Accordingly, development of an approach to obtain currently unavailable ion volumes can expose compounds containing these ions to thermodynamic scrutiny, such as predictions regarding stability and synthesis. The isomegethic rule, introduced in this paper, states that the formula unit volumes, V_m, of isomeric ionic salts are approximately the same; this rule then forms the basis for a powerful and successful means of predicting unknown ion volumes (as well as providing a means of validating existing volume and density data) and, thereby, providing solid state thermodynamic data. The rule is exploited to generate unknown ion and (by additivity) corresponding formula unit volumes.

Introduction

The capability of making theoretical thermodynamic predictions for complex inorganic materials in the gas phase, using ab initio molecular orbital procedures, has developed rapidly in recent years,[1a−j] notably for enthalpies of formation, adiabatic electron affinities, or ionization potentials for crucial gas phase species without reliance on embedded empirical parameters. Such developments are continuing.[1k]

In parallel, new tools have recently been developed (and used to explore a number of topical problems[2]) to make thermodynamic predictions for complex inorganic materials in the condensed phase.[3a−m] These methods are empirically based and are substantially simpler to use than their gas phase

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counterparts. They extend the long tradition of the Born,[3n,o] Born–Landé,[3p,q] Born–Mayer,[3r] Huggins–Meyer,[3s–u] Kapustinskii,[3v–y] Kapustinskii–Yatsirmirskii,[3z] and Ladd–Lee[3aa,ab] equations which have played a vital role in the development of inorganic energetics (for an account of these, see refs 3ac–ae).

The key step in recent work has been the identification of formula unit volume as the structurally based link to thermodynamics. Originally confined to 1:1 ionic salts,[4] further relationships have been developed by Jenkins, Passmore, Glasser, Tudela, and co-workers.[3a–j,l,m] Two significant features emerge: lattice potential energy, U_{POT}, is inversely related to the cube root of the formula unit volume, V_m (eq 1a,b), and standard molar entropy, S_m (100 kPa, 298 K),[3b,c] is directly related to volume, V_m (eq 2). These equations apply over a whole range of stoichiometries, requiring no other parameter than the chemical formula and integer ion charges as input.[3k]

$$U_{POT} = 2I(\alpha/V_m^{1/3} + \beta) \tag{1a}$$

$$U_{POT} = AI(2I/V_m)^{1/3} \tag{1b}$$

$$S_m = kV_m + c \tag{2}$$

I is the lattice ionic strength factor ($= {}^1/_2\sum n_i z_i^2$), summation being made over all the ions in the formula unit where n_i is the number of ions of integer charge z_i; α and β are constants which depend on the stoichiometry of the material.[3a] V_m, the formula unit volume, is obtainable from available crystal structure data (equal to the unit cell volume divided by the number of formula units in the unit cell) while A is a constant ($=121.4$ kJ mol^{-1} nm). While eq 1a applies to simple ionic salts[3a] having $U_{POT} < 5$ MJ mol^{-1}, eq 1b applies to more complicated ionic salts[3g] (including minerals) having $U_{POT} > 5$ MJ mol^{-1}. In eq 2, $k = 1360$ J K^{-1} mol^{-1} nm^{-3} and $c = 15$ J K^{-1} mol^{-1} for inorganic materials. For an overview of the use of these equations, see refs 3e and 3f. Volume offers a convenient (ion-additive) descriptor for both spherical and nonspherical ion shapes alike, in contrast to the historically adopted ionic radius.[5a]

The isomegethic rule explored in this paper provides a means of establishing volumes for unknown ions, using existing ion volumes predominantly, in an ingenious way at the sacrifice of a certain degree of rigor, however. The advantage is that thermodynamics of hypothetical, counterintuitive, as well as traditional ionic materials can be estimated from the derived volumes.[6] New materials are inevitably becoming increasingly exotic,[7] and the corresponding trend toward simplicity in calculation which this approach offers is likely to broaden interest in its use by specialists and nonspecialists alike.

DiSalvo[8a] has documented the challenges and opportunities facing the solid state chemist in exploring such new materials and gives an interesting perspective on just how many new candidates there are for potential study. It is from such materials that exciting new and advanced properties are most likely to emerge. To offer a means by which to immediately

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(5) (a) It can be noted that the radius ratio rules[4b] are very much influenced by the slightest departure from a true ionic lattice (caused by the presence of covalent influences) and as a result often predict too high a coordination number in many lattices (e.g., 8 instead of 6). If these rules had been formulated with volume instead of radius, a better account of these structural relationships might well have been developed. (b) Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (c) Ion additivity is not always an appropriate assumption, and we need to proceed with caution. For example, in cases where there is an anion–anion contact, e.g., as in LiBr, subtracting an overall anion or cation volume from a unit cell volume does not give a true cation or anion volume. (d) Volumes obtained from the state of the art, top of the range diffractometers, studying several orientations of the crystal, should be to a precision of 1 in 10^5 (e.g., V_m/nm^3 = 0.96942 ± 0.00012) with the estimated standard deviation routinely provided in the output. Unit cell volumes obtained using modern diffractometers, which automatically study several orientations of the crystal and use charge-coupled device (CCD) detectors, are capable of precisions of 1 in 10^4. Such a precision is probably possible even with older photographic techniques, but here data are not automatically processed and achievement of that precision (and reasonable accuracy) would depend on careful measurements and efficient manual data processing by the operator. Modern instrumentation also ensures more careful control of the operating temperature, and for that reason, the accuracy of the volume determination should be better than that for older methodology.

(6) It should also be recognized that the main source of error in the volumes we utilize emerges from the limitation of the extent to which volumes are ion additive. This is best seen in the original ion volume database[3a] (Tables 5 and 6) where standard deviations arising from estimation of ion volumes from a series of salts containing the ion in question are given.

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acquire their basic thermodynamic properties at a formative stage in their discovery must represent an encouraging development. The important link between volume and thermodynamic parameters has been noted (in a different context) in biomolecular chemistry.[8b]

Although the aim of this paper is to report the isomegethic rule (and some corollaries), and to use it for estimating ion volume data, primarily for use in provision of thermodynamic data, the rule also has a role in gauging size-related chemical and physical properties. While the rule has been tested primarily using solid state volumes, some gas phase ion volumes,[9] calculated by ab initio routes, are also shown (not unexpectedly) to satisfy the isomegethic rule. A cautionary note to the reader: ions considered in some of the examples which follow may be regarded as being unusual (often bizarre, perhaps). In the sections that follow, we introduce the isomegethic rule formally, use our existing database[3a] of ion volumes to validate the rule, and consider its advantages, uses, and consequences.

The Isomegethic Rule

The isomegethic [$\mu\epsilon\gamma\epsilon\theta o\varsigma$ (megethos) = size] rule, a name introduced in this paper,[10] is simply stated as follows: Ionic salts of the same empirical chemical formula having identical charge states (i.e., lattice ionic strength factors,[3l] I) will have approximately equal formula unit volumes, V_m. Immediately, since their volumes are approximately equal, so also will be their densities, ρ (eq A12, Supporting Information), lattice potential energies, U_{POT} (eq 1a,b), and standard absolute entropies, $S_m°$ (eq 2).

In this paper, we restrict our applications mainly to ionization isomerism in noncoordination compounds, although the rule should apply equally to other kinds of isomerism in ionic solids.

Selecting as our first examples the species NO_x and ClO_y, which can occur either as cations or anions, enables us to display both the principle behind, and the versatility of, the isomegethic rule. The isomegethic formula units employed can involve both well-documented ions as well as ions not usually encountered, always provided that charge and atom balance are maintained in the pairings selected. Thus we can write[11]

$$V_m\{NO_x{}^+ClO_y{}^-\} \approx V_m\{NO_y{}^+ClO_x{}^-\} \approx V_m\{ClO_y{}^+NO_x{}^-\} \approx V_m\{ClO_x{}^+NO_y{}^-\} \quad (3)$$

and further develop more sophisticated (extreme) forms

$$V_m\{NO_x{}^+ClO_y{}^-\} \approx V_m\{NO^+ClO_{(x+y-1)}{}^-\} \approx V_m\{N^+ClO_{(x+y)}{}^-\} \quad (4)$$

or even

$$V_m\{NO_x{}^+ClO_y{}^-\} \approx V_m\{NCl^+O_{(x+y)}{}^-\} \approx V_m\{O_y{}^+NClO_x{}^-\} \approx V_m\{O_{(x+y)}{}^+NCl^-\} \quad (5)$$

involving experimentally ever less-precedented ions. Some approximations will inevitably work more satisfactorily than others possibly because of secondary issues concerning the degree of covalent bonding which might exist between one isomegethic ion when compared to another. Experience in the use of these rules, and identification of how best to quantify a given target ion volume, will inevitably improve the quality of the results.

Specifically considering $V_m\{NO_x{}^+ClO_y{}^-\}$ where $x + y = 5$, we can write

$$V_m\{NO^+ClO_4{}^-\} \approx V_m\{NO_2{}^+ClO_3{}^-\} \approx V_m\{ClO_2{}^+NO_3{}^-\} \quad (6)$$

and hence, by ion volume additivity, we have

$$V\{NO^+\} + V\{ClO_4{}^-\} \approx V\{NO_2{}^+\} + V\{ClO_3{}^-\} \approx V\{ClO_2{}^+\} + V\{NO_3{}^-\} \quad (7)$$

[Note: We omit the "molar" subscript, m, when denoting single ion volumes.] We possess, in our database,[3a] inter alia, the following single ion volume data (/nm^3): $V\{ClO_4{}^-\} = 0.082\ (\pm 0.013)$; $V\{ClO_3{}^-\} = 0.073\ (\pm 0.006)$; $V\{ClO_2{}^+\} = 0.031\ (\pm 0.009)$; $V\{NO^+\} = 0.010\ (\pm 0.010)$; $V\{NO_2{}^+\} = 0.022\ (\pm 0.009)$; $V\{NO_3{}^-\} = 0.064\ (\pm 0.011)$; $V\{ClO_2{}^-\} = 0.056$; and $V\{NO_2{}^-\} = 0.055\ (\pm 0.007)$.

The three pairs of volume sums in eq 7 are virtually identical, as is required for the rule to apply. Thus

$$V_m\{NO^+ClO_4{}^-\} = (0.092 \pm 0.016)\ \text{nm}^3 \quad (8a)$$

$$V_m\{NO_2{}^+ClO_3{}^-\} = (0.095 \pm 0.011)\ \text{nm}^3 \quad (8b)$$

$$V_m\{ClO_2{}^+NO_3{}^-\} = (0.095 \pm 0.014)\ \text{nm}^3 \quad (8c)$$

These same formula unit volumes can be equated (eq 9) to two further volumes, $V_m\{NO_3{}^+ClO_2{}^-\}$ and $V_m\{ClO_3{}^+NO_2{}^-\}$:

$$V_m\{NO^+ClO_4{}^-\} \approx V_m\{NO_2{}^+ClO_3{}^-\} \approx V_m\{ClO_2{}^+NO_3{}^-\} \approx V_m\{NO_3{}^+ClO_2{}^-\} \approx V_m\{ClO_3{}^+NO_2{}^-\} \quad (9)$$

Assuming additivity of ion volumes, we can provide estimates for the currently unknown single ion volumes:

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(9) The volume of an ion is not uniquely defined. However, quantum mechanical calculations on gaseous ions permit us to define a boundary. It is therefore an interesting point of comparison as to whether the isomegethic rule holds for gaseous species as calculated by an ab initio route. Volumes for gaseous ions are included in the various tables of this paper. While computationally generated gas phase values of volumes of ions in themselves are not particularly useful (and therefore of minor interest in this paper), the possession of a rule for the generation of computationally elusive volumes (e.g., for multicharged ions) may be of some possible interest.

(10) We needed a name to imply both constant composition and ionic strength, and so, "isomegethic" was finally chosen [isomegethic ($\mu\epsilon\delta\epsilon\theta o\varsigma$ (megethos) = Greek for bigness, dimension, extent, magnitude, size].

(11) By virtue of ion additivity, we can also write that $V\{NO_x{}^+\} + V\{ClO_y{}^-\} \approx V\{NO_y{}^+\} + V\{ClO_x{}^-\} \approx V\{ClO_y{}^+\} + V\{NO_x{}^-\} \approx V\{ClO_x{}^+\} + V\{NO_y{}^-\}$, etc., so enabling, by appropriate rearrangement, individual unknown ion volumes to be quantified and then reutilized in other desired combinations.

Table 1. Estimation of Ion Volumes $V\{NO_3^+\}$ and $V\{ClO_3^+\}$ Using the Isomegethic Rule[a]

isomegethic rule, $V\{ClO_3^+\}$	database[b] $V\{ClO_3^+\}$/nm^3	ab initio[c] $V\{ClO_3^+\}$/nm^3
$= V\{ClO_4^+\} + V\{HCO_2^-\} - V\{HCO_3^-\}$	0.039 ± 0.004	0.042
$= V\{ClO_2^+\} + V\{NCO^-\} - V\{CN^-\}$	0.035 ± 0.004	0.033
$= V\{NO^+\} + V\{ClO_4^-\} - V\{NO_2^-\}$	0.036 ± 0.008	0.029
$= V\{NO_2^+\} + V\{ClO_3^-\} - V\{NO_2^-\}$	0.039 ± 0.001[c]	0.035
average (of mean values)	0.037	0.035
ab initio computation		0.037

isomegethic rule: $V\{NO_3^+\}$	database $V\{NO_3^+\}$/nm^3	ab initio $V\{NO_3^+\}$/nm^3
$= V\{ClO_4^-\} + V\{NO^+\} - V\{ClO_2^-\}$	0.038 ± 0.005[d]	0.026
$= V\{NO_2^+\} + V\{ClO_3^-\} - V\{ClO_2^-\}$	0.039 ± 0.005[d]	0.032
$= V\{ClO_2^+\} + V\{NO_3^-\} - V\{ClO_2^-\}$	0.039 ± 0.005[d]	0.029
$= V\{NO_2^+\} + V\{HCO_3^-\} - V\{HCO_2^-\}$	0.038 ± 0.005[d]	0.027
$= V\{NO_2^+\} + V\{NCO^-\} - V\{CN^-\}$	0.026 ± 0.005	0.027
$= V\{NO_2^+\} + V\{OH^-\} - V\{H^-\}$	0.021 ± 0.005[d]	0.026
average (of mean values)	0.034	0.028
ab initio computation		0.028

[a] Column 2 values computed from the rule (column 1) using database ion volumes.[3a] Column 3 values computed by B3LYP/LANL2DZpd method for individual ions listed in column 1. The averaged values in column 3 are similar to the values calculated for the two ions themselves using the B3LYP/LANL2DZpd method (listed below the averages). [b] Reference 3a. Where no standard deviation is given in the database,[3a] a value of ±0.005 nm^3 is assumed. [c] Values calculated using the B3LYP/LANL2DZpd method as described in the text. [d] Because of the statistical problems involved in estimating an overall standard deviation when (i) both individual central values and individual (estimated) standard deviations vary and (ii) individual standard deviations have different (and probably uncertain) weights, no standard deviation has been attached to overall averages. This applies also to subsequent tables.

$V\{NO_3^+\}$ and $V\{ClO_3^+\}$. This type of application is likely to be the commonest use of the isomegethic rule (see Table 1).

There are two significant points to be made here. Neither nitrate nor chlorate (NO_3^+, ClO_3^+) occurs as a solid state ion. However, since the isomegethic rule generally gives consistency in its predictions and, in this sense, appears to work for hypothetical materials as well as for experimentally realized species whose volumes are known, their volumes may nevertheless be used as intermediate data in the acquisition of yet further volumes (for established ions or otherwise). Further, combining $V\{NO_3^+\}$ with appropriate known anion volumes, $V\{X^-\}$ or $V\{Y^-\}$, leads to the formula unit volume data for the salts NO_3X and NO_3Y and, hence (by virtue of eq 1a or 2), immediately to their corresponding lattice energies and standard entropies.

Effect of Propagation of Errors in Volumes when Deriving Thermodynamic Data

Given that thermodynamic data are to be estimated using the rule, we need to ascertain that any likely error in any volume estimate derived from the rule will not compromise the thermodynamic information it provides. Suppose that we have a 1:1 salt ($I = 1$) having an estimated formula unit volume, V_m, with an arbitrary (say 18%) uncertainty. Then, the corresponding uncertainty in U_{POT}, as predicted by eq 1a, is reduced to only 5% (or 7% in the extreme).[12a]

In the prediction of standard molar entropy (S), any uncertainty in V_m is directly propagated through to the entropy estimate. However, the effect of this uncertainty on the overall thermodynamics of a process under consideration, as measured by the molar Gibbs energy change, ΔG, is, once again, mitigated. The most usual application of molar entropies involves their products with temperature to generate "$T\Delta S$" terms contributing directly to the Gibbs energy change, ΔG. At common ambient temperatures, the uncertainty in the energy term $T\Delta S$/kJ mol^{-1} is about one-third of the uncertainty in S/J K^{-1} mol^{-1},[12b] reducing even further at lower temperatures. Thus, the presence of some uncertainty in V_m does not prevent useful quantitative thermodynamic prediction using the volume-based eqs 1a,b and 2.

The accuracy of volume prediction by use of the rule would not suffice for all applications, however. There are several considerations here. For example, the ion volumes emerging from our database[3a] are recognized to have a tendency to be slightly too small in the case of the cations and to be slightly too large (by a similar amount) in the case of the anions. This arises from the method used to apportion voidage in the unit cells (see discussion below eq 5 in ref 3a). Those ion volumes generated using the isomegethic rule will likely have this feature also. However, when recombined, the increments and decrements will tend to cancel, yielding reliable formula unit volumes. A good example of a less useful application of the rule would be in high-pressure chemistry (such as the graphite-diamond conversion), where enthalpy is a strong function of pressure: this would exacerbate the uncertainties in the present model.

The isomegethic rule can have a validating role for checking on established ion volumes. Solid state ion volumes have been found to correlate well[3m] with ion volumes from solution studies, and so they forge a link between thermodynamic properties in both solid and aqueous media. Thus, the ability of the rule to expand the known ion volume data has implications for other areas of chemistry beyond the immediate applications suggested in this paper.

In circumstances where crystal structure data are unavailable or no other representative compound(s) have been isolated which contain the target ion whose volume is sought, the isomegethic rule is a tool to provide the thermodynamics

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(12) (a) Considering the relationship in eq 1a, and assuming no errors in α and β, then, using σ for the standard deviation:

$$\sigma(U) = \left|\frac{dU}{dV}\right|\sigma(V) = {}^{1}/_{3}2I\alpha V^{-4/3}\sigma(V) = \frac{2I\alpha}{3\sqrt[3]{V^4}}\sigma(V)$$

Using $I = 1$, $V = 0.110$ nm^3 with standard deviation $\sigma(V) = 0.020$ nm^3 (about 18%), $\alpha = 117.3$ kJ mol^{-1} nm and $\beta = 51.9$ kJ mol^{-1}, $U_{POT} = 593$ kJ mol^{-1} with standard deviation $\sigma(U_{POT}) = 30$ kJ mol^{-1} (about 5%). If we include standard deviations for α and β of 5.3 kJ mol^{-1} nm and 10.1 kJ mol^{-1} with a covariance, cov(α, β) = −7.2 kJ^2 mol^{-2} nm (these values being characteristic of Figure 1 in ref 2a), then:

$$\sigma^2(U) = \left(\frac{\partial U}{\partial V}\right)^2\sigma^2(V) + \left(\frac{\partial U}{\partial \alpha}\right)^2\sigma^2(\alpha) + \left(\frac{\partial U}{\partial \beta}\right)^2\sigma^2(\beta) + \left(\frac{\partial U}{\partial \alpha}\right)\left(\frac{\partial U}{\partial \beta}\right)\mathrm{cov}(\alpha,\beta)$$

$$= \frac{4I^2\alpha^2}{9\sqrt[3]{V^8}}\sigma^2(V) + \frac{4I^2}{\sqrt[3]{V^2}}\sigma^2(\alpha) + 4I^2\sigma^2(\beta) + \frac{4I^2}{\sqrt[3]{V}}\mathrm{cov}(\alpha,\beta)$$

Now, $\sigma(U_{POT}) = 41$ kJ mol^{-1} (about 7%). Thus, even if we allow for standard deviation in the fitted parameters, α and β, the error found in U_{POT} is only increased by a further 2%. (b) The error in the entropy term can be treated as follows. Since T is precisely measurable, then $\sigma(TS) = T\sigma(S)$, so that $\sigma(TS/\text{kJ mol}^{-1}) = T\sigma(S)/\text{kJ mol}^{-1} = T\sigma(S)/(\text{J K}^{-1}\text{ mol}^{-1} \times \text{kK}) = (T/\text{kK})\,\sigma(S/\text{J K}^{-1}\text{ mol}^{-1}) \approx (1/3)\sigma(S/\text{J K}^{-1}\text{ mol}^{-1})$.

of this new class of materials. Hypothesised and counterintuitive ionic materials, as well as stable and well-characterized materials, are equally amenable to study. The only assumption necessary is that of approximate ion volume additivity, an already proven concept, which has been well-tested by the establishment of our existing database.[3a] This latter concept is illustrated in Appendix 1 (see Supporting Information) using the example of the estimation of $V\{As_2F_{11}^-\}$.

As a side issue, it is interesting also to examine whether the rule of additivity of volumes, on which the isomegethic rule is based, will work outside the arena of solid state chemistry. Therefore, relevant ion volumes were calculated employing the Gaussian 98 program package,[13] using the B3LYP model[14] and the LANL2DZpd basis set.[15] The volumes are calculated using a Monte Carlo technique with a precision of roughly 5%, are displayed in a number of the tables (see Tables 1, 2b, 3, 4, 5c), and correspond to the region in space where the electron density is greater than 0.001 electrons per cubic Bohr (1 Bohr = 0.529 Å). These results arise directly from the calculations with no scaling or other corrections being applied. The volumes are typically lower than experimental solid state values by 10−40%, possibly because of voidage or the choice of density cutoff. Thus, the calculated volumes should not be directly compared to the solid state volumes derived from crystal structure data. Also, calculations for ions with more than one charge center were not carried out because charge−charge repulsion within these ions will be significantly different in the gas phase than in condensed phases, making comparisons questionable. That is, multiply charged ions, when unsolvated and/or uncomplexed in the absence of solvent or counterion, are generally unstable with regard to homolytic bond cleavage and/or (when anionic) autodetachment. However, the main conclusion of this latter work is that there is agreement between the rules and the ab initio calculations, while noting that the rules are much simpler to use for ions of any size.

A selection of evidence for the validity of the rule, for established solid state materials, is assembled in Appendix 2 (see Supporting Information), and a brief discussion of the likely magnitude of errors accumulated by its use is made in the section discussing errors below. It is clear that, although approximate, and it is important to acknowledge this fact, the rule can provide an adequate basis of volume estimation for a number of topical applications. The general applicability of the isomegethic rule to ionic materials which do not currently feature as conventional salts (counterintuitive materials) is confirmed here by testing alternative isomegethic combinations of ion volume data freely chosen from our database.[3a]

Verification of the Validity of the Isomegethic Rule using Existing Data

Ad hoc selection of pairs of isomegethic ionic salts and comparison of the sum of the ion volumes for the pairs shows the volumes to be closely similar (usually well within the error limits specified). Table 2 cites just a few of the many possible combinations. The average discrepancy found in the examples is about 0.008 nm^3, rising to 0.014 nm^3 for the larger ions. Recommended practice would be that, whenever possible, multiple estimates should be calculated from several alternative combinations of ion volumes (consistent with the rule), as is illustrated in Tables 1 and 2, for example. The rule is seen to hold and have broad applicability.

Replacement of Boolean Relationships by the Isomegethic Rule

Earlier use of eq 1a to obtain the lattice energy for salts containing an ion whose volume was unavailable (usually because no representative salts existed which contained the specific ion in question)[3i] resorted to rather crude estimation. Ions of known volume which were, in turn, larger and smaller than the target ion (while being as close as possible in size to it) were selected from the database. A Boolean relationship was then used to “bracket” the target ion volume. To cite an example, when estimating $V\{S_2^+\}$ (ref 3i, footnote 121), we assumed that

$$V\{Br_2^+\} > V\{S_2^+\} > V\{SN^+\} \qquad (10)$$

Since the volumes $V\{Br_2^+\}$ and $V\{SN^+\}$ were known[3a] to be (0.057 ± 0.014) and (0.032 ± 0.007) nm^3, respectively, the average of the two (extreme) volumes was equated to $V\{S_2^+\}$, leading to prediction that $V\{S_2^+\} \approx 0.045 \pm 0.016$ nm^3.

The weakness of this approach is, of course, that the magnitude of the target volume estimated is dictated solely by the particular pair of “end-member” ions arbitrarily chosen. The isomegethic rule, in the form of equations represented by eq 11, provides a much improved methodology (see Table 3) and does not have the above disadvantage.

$$V_m\{S_2^+NO_x^-\} \approx V_m\{S_2N^+O_x^-\} \quad x = 2,3 \qquad (11)$$

The volume estimated for $V\{S_2^+\}$ by eq 11 (0.055 ± 0.010 nm^3) using our existing database of ion volumes[3a] lies within the bounds specified by relationship 10, is close to the crude estimate made earlier, and is preferable to it. It should be noted that the salts $S_2^+NO_2^-$, $S_2N^+O_2^-$, $S_2^+NO_3^-$, and $S_2N^+O_3^-$ used in eq 11 are hypothetical materials. However, this is of no relevance to the calculation of $V\{S_2^+\}$ in our

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(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998. Note: “Volume = tight” option used to increase the size of the sample set to improve precision on the volume determinations.

(14) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(15) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310. (d) Check, C. E.; Faust, T. O.; Bailey, J. E.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. *J. Phys. Chem. A* **2001**, *105*, 8111−8116.

Table 2. Isomegethic Pairs of Ionic Salts from the Database[3a]

(a) Solid State Ion Volumes

isomeric salts	ion volume sum of first salt/nm^3	ion volume sum of second salt/nm^3	difference[a] in ion volume sums/nm^3
1:1 Salts, One Way Transfer[b]			
$NO_2^+Br_3^-:Br_3^+NO_2^-$[c]	0.146 (±0.014)	0.151 (±0.010)	0.005
$Br_3^+O_2^-:O_2^+Br_3^-$[c]	0.142 (±0.010)	0.139 (±0.016)	0.003
$I_3^+O_2^-:O_2^+I_3^-$[c]	0.177 (±0.010)	0.185 (±0.011)	0.009
$I_3^+ICl_2^-:ICl_2^+I_3^-$[c]	0.253 (±0.007)	0.254 (±0.013)	0.001
$I_3^+IBr_2^-:IBr_2^+I_3^-$[c]	0.273 (±0.007)	0.266 (±0.017)	0.007
$NO_2^+HCO_2^-:NO^+HCO_3^-$	0.078 (±0.009)	0.074 (±0.010)	0.004
$NO_2^+CN^-:NO^+NCO^-$	0.072 (±0.011)	0.064 (±0.010)	0.008
$NO_2^+ClO_2^-:NO^+ClO_3^-$	0.078 (±0.009)	0.083 (±0.012)	0.005
$SCl_3^+CN^-:Cl_3^+SCN^-$	0.146 (±0.013)	0.133 (±0.008)	0.013
$SBr_3^+H^-:Br_3^+SH^-$	0.156 (±0.018)	0.153 (±0.011)	0.003
$SeI_3^+H^-:I_3^+SeH^-$	0.192 (±0.018)	0.201 (±0.011)	0.009
$Br_3^+Br_3^-:Br_5^+Br^-$	0.220 (±0.013)	0.203 (±0.017)	0.017
$I_3^+I_3^-:I_5^+I^-$	0.302 (±0.007)	0.282 (±0.021)	0.020
$N(SCl)_2^+I^-:S_2N^+Cl_2I^-$	0.187 (±0.023)	0.182 (±0.009)	0.006
		average	0.008
2:1 Salts, One Way Transfer			
$(NO_2^+)_2S_2O_4^{2-}:(NO^+)_2S_2O_6^{2-}$	0.157 (±0.013)	0.173 (±0.020)	0.016
$(S_2N^+)_2S_4O_6^{2-}:(SN^+)_2S_6O_6^{2-}$	0.329 (±0.013)	0.334 (±0.010)	0.005
$(SCl_3^+)_2S_4O_6^{2-}:(Cl_3^+)_2S_6O_6^{2-}$	0.393 (±0.017)	0.394 (±0.010)	0.001
$(SI_3^+)_2S_4O_6^{2-}:(I_3^+)_2S_6O_6^{2-}$	0.527 (±0.010)	0.532 (±0.010)	0.005
		Average	0.007
Two Way Transfer			
$(Cl_3^+)_2SnI_6^{2-}:(I_3^+)_2SnCl_6^{2-}$	0.486 (±0.013)	0.496 (±0.010)	0.010
$(Br_3^+)_2ReI_6^{2-}:(I_3^+)_2ReBr_6^{2-}$	0.536 (±0.024)	0.525 (±0.010)	0.011
$(Br_3^+)_2TcI_6^{2-}:(I_3^+)_2TcBr_6^{2-}$	0.525 (±0.010)	0.521 (±0.010)	0.004
		average	0.008
1:2 Salts, Two Way Transfer			
$(Te_2(esu)_4Br_2)^{2+}(Cl^-)_2:(Te_2(esu)_4Cl_2)^{2+}(Br^-)_2$[d]	0.690 (±0.026)	0.700 (±0.025)	0.010
$(Te_2(esu)_4Br_2)^{2+}(I^-)_2:(Te_2(esu)_4I_2)^{2+}(Br^-)_2$[d]	0.740 (±0.029)	0.724 (±0.027)	0.016
$I_4^{2+}(SCN^-)_2:S_2I_4^{2+}(CN^-)_2$	0.274 (±0.014)	0.304 (±0.012)	0.030
$I_4^{2+}(SeCN^-)_2:Se_2I_4^{2+}(CN^-)_2$	0.316 (±0.013)	0.304 (±0.019)	0.012
$S_6N_4^{2+}(CN^-)_2:S_4N_4^{2+}(SCN^-)_2$	0.265 (±0.010)	0.265 (±0.021)	0.000
$Se_{19}^{2+}(CN^-)_2:Se_{17}^{2+}(SeCN^-)_2$	0.570 (±0.010)	0.640 (±0.021)	0.070
		average	0.014

(b) Volumes Calculated Using the B3LYP/LANL2DZpd Method as Described in the Text

isomeric salts	ion volume sum of first salt/nm^3	ion volume sum of second salt/nm^3	difference[e] in ion volume sums/nm^3
1:1 Salts, One Way Transfer			
$NO_2^+Br_3^-:Br_3^+NO_2^-$	0.110	0.098	0.012
$Br_3^+O_2^-:O_2^+Br_3^-$	0.088	0.100	0.012
$I_3^+O_2^-:O_2^+I_3^-$	0.117	0.110	0.007
$I_3^+ICl_2^-:ICl_2^+I_3^-$	0.171	0.145	0.026
$I_3^+IBr_2^-:IBr_2^+I_3^-$	0.174	0.160	0.014
$NO_2^+HCO_2^-:NO^+HCO_3^-$	0.065	0.058	0.007
$NO_2^+CN^-:NO^+NCO^-$	0.059	0.052	0.007
$NO_2^+ClO_2^-:NO^+ClO_3^-$	0.067	0.064	0.003
$SCl_3^+CN^-:Cl_3^+SCN^-$	0.095	0.103	0.008
$SBr_3^+H^-:Br_3^+SH^-$	0.112	0.098	0.014
$SeI_3^+H^-:I_3^+SeH^-$	0.133	0.131	0.002
$Br_3^+Br_3^-:Br_5^+Br^-$	0.143	0.145	0.002
$I_3^+I_3^-:I_5^+I^-$	0.183	0.185	0.002
$N(SCl)_2^+I^-:S_2N^+Cl_2I^-$	0.125	0.124	0.001
		average	0.008

[a] The small value in this column represents residual differences arising from the use of the isomegethic rule. [b] One-way transfer involves movement of an atom(s) from one ion to the other; two-way transfer refers to exchange of atoms between anion and cation. [c] The first five examples can be regarded simply as charge transfer. [d] esu = ethyleneselenourea. [e] The small value in this column represents a measure of the deviation from the use of the isomegethic rule.

Table 3. Estimates of $V\{S_2^+\}$

isomegethic rule, $V\{S_2^+\}$	database[a] $V\{S_2^+\}$/nm^3	ab initio[b] $V\{S_2^+\}$/nm^3
$= V\{S_2N^+\} + V\{O_2^-\} - V\{NO_2^-\}$	0.051 ± 0.013	0.032
$= V\{S_2N^+\} + V\{O_3^-\} - V\{NO_3^-\}$	0.059 ± 0.016	0.036
average	0.055	0.038[c]

[a] Reference 3a. [b] Values calculated using the B3LYP/LANL2DZpd method as described in the text. [c] Direct computation for the ion.

application of the composite of the additivity rule, the isomegethic rule, and a knowledge of volumes of the other ions in the salts of eq 11.

Application and Extensions of the Isomegethic Rule

In the concluding section of the paper, we provide a straightforward example of how it is envisaged the rule might be used to examine the thermodynamics or stability of a new material (viz., CsF_3). Using the example of salts IBr^+Cl^- and ICl^+Br^-, we show how the underlying thermodynamics (relative stability) can be estimated from volume data. Finally, we discuss the implications of the isomegethic rule in a number of specific cases. These are the volume of hermaphroditic anion and cation pairs, relationships between the volumes of homopolyatomic ions, and, finally, constancy of differences between $[V\{MX_6^{2-}\} - V\{MX'^{2-}_6\}]$, where X and X′ are halogen, independent of M.

Stability of CsF_3 Solid

Suppose we wish to consider the thermodynamics relating to CsF_3 solid. The F_3^- anion may be understood as the lightest trihalide ion, analogous to its valence isoelectronic counterparts with heavier halogens,[16] such as the well-established I_3^- ion. No such F_3^- salt is known as a solid state species, although there is evidence for existence of a $Cs^+F_3^-$ ion pair within a matrix.[17] Clearly, no crystal structure (or thermodynamic) data are available for this salt. As a gas phase species, F_3^- has comparable bond energy to its iodine counterpart.[16a] Experimental studies[16a] have been made on the following reactions

$$F_3^-(g) \rightarrow F_2^-(g) + F(g) \quad \Delta H_1 = 125 \pm 13 \text{ kJ mol}^{-1} \tag{12}$$

$$F_3^-(g) \rightarrow F^-(g) + F_2(g) \quad \Delta H_2 = 98 \pm 11 \text{ kJ mol}^{-1} \tag{13}$$

from which we can deduce ($\Delta_f H°\{F^-, g\} = -249$ kJ mol^{-1} [16b]) that

$$\Delta_f H°(F_3^-, g) = -347 \pm 11 \text{ kJ mol}^{-1} \tag{14}$$

$$\Delta_f H°(F_2^-, g) = -301 \pm 13 \text{ kJ mol}^{-1} \tag{15}$$

Consideration of our database suggests six alternative isomegethic relationships (Table 4) enabling $V\{F_3^-\}$ to be esti-

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(16) (a) Artau, A.; Nizzi, K. E.; Hill, B. T.; Sunderlin, L. S.; Wenthold, P. G. *J. Am. Chem. Soc.* **2000**, *122*, 10667−10770. (b) Nizzi, K. E.; Pommerening, C. A.; Sunderlin, L. S. *J. Phys. Chem.* **1998**, *102*, 7674−7679.

(17) (a) Ault, B. S.; Andrews, L. *J. Am. Chem. Soc.* **1976**, *98*, 1591−1593. (b) Ault, B. S.; Andrews, L. *Inorg. Chem.* **1977**, *16*, 2024−2028.

Table 4. Estimates (One-Way) of $V\{F_3^-\}$

isomegethic rule, $V\{F_3^-\}$	database[a] $V\{F_3^-\}$/nm^3	ab initio[b] $V\{F_3^-\}$/nm^3
$= V\{ClF_6^+\} + V\{F^-\} - V\{ClF_4^+\}$	0.058 ± 0.013	0.030
$= V\{BrF_6^+\} + V\{F^-\} - V\{BrF_4^+\}$	0.085 ± 0.017	0.025
$= V\{IF_6^+\} + V\{F^-\} - V\{IF_4^+\}$	0.072 ± 0.024	0.027
$= V\{SF_3^+\} + V\{Br_3^-\} - V\{SBr_3^+\}$	0.063 ± 0.020	0.017
$= V\{SeF_3^+\} + V\{Br_3^-\} - V\{SeBr_3^+\}$	0.063 ± 0.020	0.034
$= V\{SeF_3^+\} + V\{I_3^-\} - V\{SeI_3^+\}$	0.065 ± 0.013	0.019
average	0.068	0.025
		0.033[c]

[a] Reference 3a. [b] Values calculated using the B3LYP/LANL2DZpd method as described in the text. [c] Direct computation for the F_3^- ion.

mated. The average result obtained is that

$$V\{F_3^-\} \approx (0.068 \pm 0.017)\ \text{nm}^3 \tag{16}$$

and accordingly

$$V_m\{CsF_3\} = [V\{Cs^+\} + V\{F_3^-\}] \approx 0.087\ \text{nm}^3 \tag{17}$$

Using eq 1a, a lattice energy,[3a] $U_{POT}\{CsF_3\} \approx (633 \pm 30)$ kJ mol^{-1}, and from eq 2, $S_m°_{298}(CsF_3, s) \approx (133 \pm 23)$ J K^{-1} mol^{-1} can be established. It is worth noting again that, despite the considerable uncertainty (20%) in $V_m\{CsF_3\}$ and hence in the standard entropy estimate (later reduced when incorporated as the $-T\Delta S$ term), the uncertainty in the lattice energy is only 5%. We can consider the stability of CsF_3 vis-à-vis CsF (whose lattice energy,[18a] $U_{POT}\{CsF\}$, is 759 kJ mol^{-1}, and standard entropy[18b] $S_m°_{298}\{CsF, s\} = 51.1$ J K^{-1} mol^{-1}). For the decomposition process in which CsF_3 loses F_2

$$CsF_3(s) \rightarrow CsF(s) + F_2(g) \tag{18}$$

in the absence of a value for $\Delta_f H°\{CsF_3, s\}$ to calculate ΔH_{18} directly we can construct a thermochemical cycle centered on this reaction in which $U_{POT}\{CsF_3\}$, $U_{POT}\{CsF\}$, and the enthalpy change, ΔH_{13}, with the addition of an RT term (to correct the lattice energy of CsF to lattice enthalpy[1af]) leading to

$$\Delta H_{18} \approx (-30 \pm 32)\ \text{kJ mol}^{-1} \tag{19}$$

The corresponding entropy change, ΔS_{18},[18c] is evaluated from the data above (taking $S_m°_{298}\{F_2, g\} = 202.4$ J K^{-1} mol^{-1} [18b]) to be $\Delta S_{18} \approx +121 \pm 21$ J K^{-1} mol^{-1} leading to the overall result

$$\Delta G_{18} \approx -66 \pm 34\ \text{kJ mol}^{-1} \tag{20}$$

indicating that CsF_3 will decompose to CsF and F_2, although this instability could be fairly marginal, which may explain the observation of the formation of the Cs^+ and F_3^- ion pairs within a matrix host. Also, since the Gibbs energy for reaction (18) is moderately small, it may be possible to produce CsF_3 by the application of a sufficiently high pressure of F_2 to CsF. However, the required pressure may be very difficult to achieve in the laboratory.

Use of Isomegethic Rule for the Consideration of Thermochemistry of Hypothetical Salts

The isomegethic rule is able to assist with the development of new areas of thermochemistry. Gas phase values of the standard enthalpy of formation of IBr^+, $\Delta_f H°\{IBr^+, g\} = 991.65$ kJ mol^{-1} at 298 K (standard pressure = 100 kPa), and ICl^+, $\Delta_f H°\{ICl^+, g\} = 997.5$ kJ mol^{-1}, have been listed.[18b] Using data for $\Delta_f H°\{Cl^-, g\}$ and $\Delta_f H°\{Br^-, g\}$, we can therefore establish that $\Delta H° \approx -20$ kJ mol^{-1} for the gas phase reaction $ICl^+(g) + Br^-(g) \rightarrow IBr^+(g) + Cl^-(g)$. We can now link the left and right sides of this equation in a thermochemical cycle with the (hypothetical) ionic solids $ICl^+Br^-(s)$ and $IBr^+Cl^-(s)$ for which we assume (by the isomegethic rule) that $U_{POT}\{ICl^+Br^-\} \approx U_{POT}\{IBr^+Cl^-\}$, since the two salts are isomeric and so have similar volumes. The closing loop of this cycle is then the reaction $ICl^+Br^-(s) \rightarrow IBr^+Cl^-(s)$, for which, therefore, $\Delta H°$ must also approximately equal -20 kJ mol^{-1}, suggesting that IBr^+Cl^- is slightly more stable than ICl^+Br^-. The assumption of equality of the lattice energies can be checked by estimating $V\{ICl^+\}$ and $V\{IBr^+\}$,[19a] leading to $U_{POT}\{ICl^+Br^-\} \approx 568$ kJ mol^{-1} and $U_{POT}\{IBr^+Cl^-\} = 563$ kJ mol^{-1}. ΔS for the reaction $ICl^+Br^-(s) \rightarrow IBr^+Cl^-(s)$ is estimated[18b] (eq 2) to be $+6$ J K^{-1} mol^{-1}, and on this basis, the Gibbs energy stability of IBr^+Cl^- over ICl^+Br^- amounts to approximately 17 kJ mol^{-1}. In the absence of any thermodynamic information concerning the above compounds, and without the volume-based equations and the isomegethic rule, no quantitative conclusions at all would have been possible.

Derived Routes for Volume Estimation at Individual Ion Level

Intuitively, the volume of the fulminate and cyanate ions (i.e., CNO^- and OCN^-) should be approximately the same.

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(18) (a) *Handbook of Chemistry and Physics*, 79th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1998; Chapter 9, p 1222. (b) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. *N. B. S. Tables of Chemical Thermodynamic Properties*; N. B. S.: Washington, DC, 1982. Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. *J. Phys. Chem. Ref. Data* **1982**, *11*, supplement 1. (c) Alternatively, ΔS_{18} can be written as $\Delta S_{18} = S_m°_{298}\{CsF, s\} - S_m°_{298}\{CsF_3, s\} + S_m°_{298}\{F_2, g\}$ and, in view of eq 2, has the particularly simple form $\Delta S_{18} = k[V_m\{CsF, s\} - V_m\{CsF_3, s\}] + S°_{298}\{F_2, g\} \approx k[V\{F^-\} - V\{F_3^-\}] + S_m°_{298}\{F_2, g\}$ corresponding to a term involving the difference in volume of the two anions plus the $S_m°_{298}\{F_2, g\}$ term. Use is made of the additivity rule of ion volumes to eliminate $V\{Cs^+\}$. $k = 1360$ J K^{-1} mol^{-1} nm^{-3}.

(19) (a) $V\{IBr^+\}$ can be estimated from the isomegethic rule $V_m\{IBr_2^+O_3^-\} \approx V_m\{IBr^+BrO_3^-\}$ leading to a value $V\{IBr^+\} = 0.086$ nm^3 and hence to $V_m\{IBr^+Cl^-\} = 0.133$ nm^3 leading to values (eq 1a) of $U_{POT}\{IBr^+Cl^-\} = 563$ kJ mol^{-1} and (eq 2) of $S_m\{IBr^+Cl^-\} = 196$ J K^{-1} mol^{-1}. Similarly, $V\{ICl^+\}$ can be estimated from the isomegethic rules $V_m\{ICl_2^+O_3^-\} \approx V_m\{ICl^+ClO_3^-\}$ and $V_m\{ICl_2^+O_2^-\} \approx V_m\{ICl^+ClO_2^-\}$ both leading to a value $V\{ICl^+\} = 0.073$ nm^3 and hence to $V_m\{ICl^+Br^-\} = 0.129$ nm^3 leading in turn to values (eq 1a) of $U_{POT}\{ICl^+Br^-\} = 568$ kJ mol^{-1} and (eq 2) of $S_m\{ICl^+Br^-\} = 190$ J K^{-1} mol^{-1}. (b) This value for ΔS of $+6$ J K^{-1} mol^{-1} differs slightly from the anticipated zero difference in entropy values for these isomeric salts but indicates that the degree of uncertainty arising from the use of the isomegethic rule is reasonably small.

(20) (a) Latimer, W. M. *Oxidation Potentials*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1956. (b) Latimer, W. M. *J. Am. Chem. Soc.* **1921**, *43*, 818−826.

In general, provided individual ions have the same charge and identical elemental composition (albeit in different crystallographic environments), this approximation should be valid. This idea can further be extended to multiply charged species, for which it also appears to be satisfactory. For example, we can conjecture that

$$V\{PF_6^-\} + V\{AsO_4^{3-}\} \approx V\{AsF_6^-\} + V\{PO_4^{3-}\} \quad (21)$$

Equation 21 is derived from the subtraction of a pair of isomegethic equations:

$$V\{MO_4^+\} + V\{PF_6^-\} \approx V\{MF_6^{3+}\} + V\{PO_4^{3-}\} \quad (22)$$

$$V\{MO_4^+\} + V\{AsF_6^-\} \approx V\{MF_6^{3+}\} + V\{AsO_4^{3-}\} \quad (23)$$

Using our database,[3a] the sum of the known ion volumes on the left side of eq 21 equals 0.197 nm^3 while that for the right side pair gives a volume sum close to this (=0.200 nm^3) (that is, we need not make any assumptions about the MO_4^+ and MF_6^{3+} ions), again testifying to the validity of the isomegethic rule. We can also derive other subsidiary relationships (amounting to ion combination and partition relationships). Thus, for the series of anions of type $M_mF_{5m+1}^-$ (M = As, Sb, Bi, Ru) we can write, variously

$$V\{M_2F_{11}^-\} \approx 2V\{MF_6^-\} - V\{F^-\} \quad (24)$$

$$V\{M_3F_{16}^-\} \approx 3V\{MF_6^-\} - 2V\{F^-\} \quad (25)$$

$$V\{M_3F_{16}^-\} \approx V\{M_2F_{11}^-\} + V\{MF_6^-\} - V\{F^-\} \quad (26)$$

which can be regarded as derived from isomegethic-type origins; to exemplify with eq 24 (eqs 25 and 26 are quite similar), if we introduce an arbitrary cationic species E^+, the isomegethic rule would give the pair of equations

$$V\{E^+\} + V\{M_2F_{11}^-\} \approx V\{EMF_5^+\} + V\{MF_6^-\} \quad (27)$$

$$V\{E^+\} + V\{MF_6^-\} \approx V\{EMF_5^+\} + V\{F^-\} \quad (28)$$

which when subtracted give eq 24.

Table 5 shows that the use of eq 24 can equally well provide a satisfactory estimate of the volume of the $As_2F_{11}^-$ ion, as can the sources discussed in Appendix 1 (see Supporting Information). The results are predicted without reference to the conformation of the ion, whether the two AsF_4 planes are staggered or eclipsed, nor for the *cis* or *trans* conformation of the $M_3F_{16}^-$ ions.

Table 5. Estimation of $V\{M_mF_{5m-1}^-\}$ for $m = 2$ and 3 from Individual Ion Volume[3a] Combination Relationships for Solid State Ions (a and b), and for Gas Phase Ions (c)

(a) Solid State Ion Volumes

M	$V\{M_2F_{11}^-\}$/nm^3	$V\{M_3F_{16}^-\}$/nm^3	$V\{F^-\} = 0.025$ nm^3 (using eqs 25, 26)
As	0.195 ± 0.014	0.280 ± 0.019	$V\{AsF_6^-\} = 0.110$ nm^3
Sb	0.217 ± 0.026	0.313 ± 0.025	$V\{SbF_6^-\} = 0.110$ nm^3
Bi	0.223 ± 0.022	0.322 ± 0.028	$V\{BiF_6^-\} = 0.110$ nm^3
Ru	0.229 ± 0.012	0.331 ± 0.017	$V\{RuF_6^-\} = 0.110$ nm^3

(b) Solid State Ion Volumes as Derived in Appendix 1 (See Supporting Information)

$V\{As_2F_{11}^-\}$/nm^3		
$(MeS)_2CSH^+$ salts	$(m\text{-}CF_3C_6H_5)(C_6H_5)CF^+$ salts	X_3PH^+ salts
0.212 ± 0.017[a]	0.221 ± 0.007[b]	0.205 ± 0.008[c] 0.193 ± 0.005[d]

(c) Volumes Calculated Using the B3LYP/LANL2DZpd Method as Described in the Text

	ab initio						
M	$V\{F^-\}$/nm^3	$V\{MF_6^-\}$/nm^3	$V\{M_2F_{11}^-\}$/nm^3	$V\{M_3F_{16}^-\}$/nm^3	eq 24 $V\{M_2F_{11}^-\}$/nm^3	eq 25 $V\{M_3F_{16}^-\}$/nm^3	eq 26 $V\{M_3F_{16}^-\}$/nm^3
As	0.018	0.065	0.112	0.155	0.112	0.159	0.158
Sb	0.018	0.071	0.118	0.188	0.124	0.177	0.171
Bi	0.018	0.073	0.125	0.188	0.128	0.183	0.180

[a] Equation A2. [b] Equation A6. [c] Equation A9. [d] Equation A11.

Table 6. Evaluation of the Term $[V\{X^+) - V\{X^-)]$ for Hermaphroditic[6] Anion/Cation Pairs

X	$V\{X^+\}$/nm^3	$V\{X^-\}$/nm^3	$[V\{X^-\} - V\{X^+\}]$/nm^3
$AlCl_4$	0.117 ± 0.013	0.156	0.039 ± 0.013
ICl_2	0.083 ± 0.013	0.122	0.039 ± 0.013
IBr_2	0.095 ± 0.017	0.142	0.047 ± 0.017
BrF_4	0.044 ± 0.012	0.096	0.052 ± 0.012
NO_2	0.022 ± 0.009	0.055 ± 0.007	0.033 ± 0.011
O_2	0.015 ± 0.011	0.046 ± 0.007	0.036 ± 0.013
Br_3	0.096 ± 0.007	0.124 ± 0.011	0.028 ± 0.013
I_3	0.131 ± 0.007	0.171	0.040 ± 0.007
ClO_2	0.031 ± 0.009	0.056	0.025 ± 0.009
		average	0.037

Consequences of the Isomegethic Rule

Assumption that the isomegethic rule is perfectly obeyed leads to a number of interesting ion volume relationships which should apparently hold. They are discussed because they provide an indication of the level of the errors associated with the isomegethic rule in specific circumstances.

Relationship between the Volumes of Hermaphroditic Anion or Cation Pairs (Species for which the Same Ionic Formula and Structure Exists in Both Isolable Cation and Anion Forms). Since we anticipate that

$$V_m\{M^+X^-\} \approx V_m\{X^+M^-\} \quad (29)$$

then we infer also that

$$V\{M^-\} - V\{M^+\} \approx V\{X^-\} - V\{X^+\} \approx c_1 \quad (30)$$

In other words, an approximately constant difference (=c_1) ought to exist between hermaphroditic anion and cation volumes, X^- and X^+ (or M^- and M^+). Table 6 shows this difference using suitable examples from our database;[3a] the relationship is only roughly obeyed. Overall, the difference c_1 is seen to vary over the range

$$0.021 \le c_1/\text{nm}^3 \le 0.052 \quad (31)$$

for the ions listed, averaging to

$$c_1 = 0.037 \text{ nm}^3 \quad (32)$$

This result (eq 32) is consistent with our database[3a] in another respect. The proton (H^+) can be regarded as a mathematical point (i.e., $V\{\mathrm{H}^+\} = 0$) while $V\{\mathrm{H}^-\} = 0.033$ nm^3, hence (for X = H)

$$V\{\mathrm{H}^-\} - V\{\mathrm{H}^+\} = 0.033\ \mathrm{nm}^3 \qquad (33)$$

Errors Inherent in Using the Isomegethic Rule. Suppose atom X, when added to an existing complex cation, AB_y^+, contributes an additional volume increment, $a\{\mathrm{X}\}$, i.e.

$$V\{\mathrm{XAB}_y^{\ +}\} - V\{\mathrm{AB}_y^{\ +}\} = a\{\mathrm{X}\} \qquad (34)$$

while, when X is placed into an existing anion, CD_z^-, it increases the volume by $b\{\mathrm{X}\}$, i.e.

$$V\{\mathrm{XCD}_z^{\ -}\} - V\{\mathrm{CD}_z^{\ -}\} = b\{\mathrm{X}\} \qquad (35)$$

According to our isomegethic rule, we would expect that

$$V\{\mathrm{XAB}_y^{\ +}\mathrm{CD}_z^{\ -}\} \approx V\{\mathrm{AB}_y^{\ +}\mathrm{XCD}_z^{\ -}\} \qquad (36)$$

Subtraction of eq 35 from 34 yields

$$\begin{aligned}[V\{\mathrm{XAB}_y^{\ +}\} + V\{\mathrm{CD}_z^{\ -}\}] - [V\{\mathrm{AB}_y^{\ +}\} + V\{\mathrm{XCD}_z^{\ -}\}] \\ \approx \mathrm{V}\{\mathrm{XAB}_y^{\ +}\mathrm{CD}_z^{\ -}\} - \mathrm{V}\{\mathrm{AB}_y^{\ +}\mathrm{XCD}_z^{\ -}\} \\ \approx a\{\mathrm{X}\} - b\{\mathrm{X}\} \qquad (37)\end{aligned}$$

from which we see that deviations from the rule can be expected to arise as inconstancy of $a\{\mathrm{X}\}$ and $b\{\mathrm{X}\}$, typical values for which are assembled in Table 7.

Table 7c presents mean values of $a\{\mathrm{X}\}$ and of $b\{\mathrm{X}\}$, designated $\langle a\{\mathrm{X}\}\rangle$ and $\langle b\{\mathrm{X}\}\rangle$, for individual X. In a few cases (as indicated in the table), averaging is over a substantial range of values but, by and large, ranges are sufficiently small to give reasonable validity to such averaging. Comparing the means, we note that (i) there are the same number of situations when $\langle a\{\mathrm{X}\}\rangle$ exceeds $\langle b\{\mathrm{X}\}\rangle$ as when the reverse occurs, and more importantly perhaps, (ii) the difference between the corresponding $\langle a\{\mathrm{X}\}\rangle$ and $\langle b\{\mathrm{X}\}\rangle$ is generally small. These points give some support to the isomegethic rule, which would necessitate approximate equality of $\langle a\{\mathrm{X}\}\rangle$ and $\langle b\{\mathrm{X}\}\rangle$.

Types of Isomegethic Rule. We can divide volume equalities originating from the isomegethic rule into two broad categories. The relationship in eq 36 can be regarded as involving a "one-way" transfer of an atom from cation to anion, i.e., XAB_y^+ to XCD_z^-, for which the deviations from ideality of the rule will be $[a\{\mathrm{X}\} - b\{\mathrm{X}\}]$. Relationship 38 involves a simultaneous "two-way" transfer of X from cation XAB_y^+ to anion XCD_z^-, and Y from anion YCD_z^- to cation YAB_y^+:

$$V_\mathrm{m}\{\mathrm{XAB}_y^{\ +}\mathrm{YCD}_z^{\ -}\} \approx V_\mathrm{m}\{\mathrm{YAB}_y^{\ +}\mathrm{XCD}_z^{\ -}\} \qquad (38)$$

and thus

$$\begin{aligned}[V\{\mathrm{XAB}_y^{\ +}\} + V\{\mathrm{YCD}_z^{\ -}\}] - [V\{\mathrm{YAB}_y^{\ +}\} + \\ V\{\mathrm{XCD}_z^{\ -}\}] \approx [a\{\mathrm{X}\} - b\{\mathrm{X}\}] - [a\{\mathrm{Y}\} - b\{\mathrm{Y}\}] \qquad (39)\end{aligned}$$

Table 7. Typical Incremental Volume Increases Found for (a) Cations and (b) Anions[a]

(a) Cations

cation	cation after addition of atom(s)	volume increase/nm^3	added atom(s)	volume increase per atom = $a\{\mathrm{X}\}$/nm^3
$\mathrm{Br_2^+}$	$\mathrm{Br_3^+}$	0.039	Br	0.039
$\mathrm{Br_2^+}$	$\mathrm{Br_5^+}$	0.090	3Br	0.030
$\mathrm{Br_3^+}$	$\mathrm{Br_5^+}$	0.051	2Br	0.026
$\mathrm{BrF_4^+}$	$\mathrm{BrF_6^+}$	0.100	2F	0.050
$\mathrm{IF_4^+}$	$\mathrm{IF_6^+}$	0.047	2F	0.023
$\mathrm{ClF_2^+}$	$\mathrm{ClF_6^+}$	0.066	4F	0.017
$\mathrm{XeF^+}$	$\mathrm{XeF_5^+}$	0.032	4F	0.008
$\mathrm{Xe_2F_3^+}$	$\mathrm{Xe_2F_{11}^+}$	0.061	8F	0.008
$\mathrm{O_2^+}$	$\mathrm{ClO_2^+}$	0.016	Cl	0.016
$\mathrm{Se_3N_2^+}$	$\mathrm{Se_3N_2Cl^+}$	0.043	Cl	0.043
$\mathrm{O_2^+}$	$\mathrm{NO_2^+}$	0.007	N	0.007
$\mathrm{I_2^+}$	$\mathrm{I_3^+}$	0.059	I	0.059
$\mathrm{I_2^+}$	$\mathrm{I_5^+}$	0.138	3I	0.046
$\mathrm{I_3^+}$	$\mathrm{I_5^+}$	0.079	2I	0.040
$\mathrm{NO^+}$	$\mathrm{NO_2^+}$	0.012	O	0.012
$\mathrm{Br_3^+}$	$\mathrm{S_3Br_3^+}$	0.073	3S	0.024
$\mathrm{Br_5^+}$	$\mathrm{S_2Br_5^+}$	0.070	2S	0.035
$\mathrm{SN^+}$	$\mathrm{S_2N^+}$	0.028	S	0.028
$\mathrm{Br_3^+}$	$\mathrm{SeBr_3^+}$	0.018	Se	0.018
$\mathrm{Br_3^+}$	$\mathrm{Se_3Br_3^+}$	0.089	3Se	0.029
$\mathrm{I_3^+}$	$\mathrm{SeI_3^+}$	0.028	Se	0.028

(b) Anions

anion	anion after addition of atom(s)	volume increase/nm^3	added atom(s)	volume increase per atom = $b\{\mathrm{X}\}$/nm^3
$\mathrm{H^-}$	$\mathrm{SH^-}$	0.024	S	0.024
$\mathrm{CN^-}$	$\mathrm{SCN^-}$	0.021	S	0.021
$\mathrm{H^-}$	$\mathrm{SeH^-}$	0.037	Se	0.037
$\mathrm{CN^-}$	$\mathrm{SeCN^-}$	0.042	Se	0.042
$\mathrm{H^-}$	$\mathrm{SeH^-}$	0.047	Se	0.047
$\mathrm{O_2^-}$	$\mathrm{NO_2^-}$	0.009	N	0.009
$\mathrm{I^-}$	$\mathrm{IBr_2^-}$	0.070	2Br	0.035
$\mathrm{I^-}$	$\mathrm{ICl_2^-}$	0.050	2Cl	0.025
$\mathrm{ICl_2^-}$	$\mathrm{ICl_4^-}$	0.062	2Cl	0.032
$\mathrm{I^-}$	$\mathrm{ICl_4^-}$	0.112	4Cl	0.028
$\mathrm{I^-}$	$\mathrm{I_3^-}$	0.099	2I	0.050
$\mathrm{HCO_2^-}$	$\mathrm{HCO_3^-}$	0.008	O	0.008
$\mathrm{IO_3^-}$	$\mathrm{IO_4^-}$	0.013	O	0.013
$\mathrm{ClO_2^-}$	$\mathrm{ClO_3^-}$	0.017	O	0.017
$\mathrm{ClO_3^-}$	$\mathrm{ClO_4^-}$	0.009	O	0.009
$\mathrm{NCO^-}$	$\mathrm{CN^-}$	0.004	O	0.004
$\mathrm{NO_2^-}$	$\mathrm{NO_3^-}$	0.009	O	0.009
$\mathrm{O_2^-}$	$\mathrm{O_3^-}$	0.017	O	0.017
$\mathrm{Cl^-}$	$\mathrm{ClO_2^-}$	0.009	2O	0.005
$\mathrm{Cl^-}$	$\mathrm{ClO_3^-}$	0.026	3O	0.009
$\mathrm{Cl^-}$	$\mathrm{ClO_4^-}$	0.035	4O	0.009
$\mathrm{Br^-}$	$\mathrm{BrO_3^-}$	0.016	3O	0.005
$\mathrm{Br^-}$	$\mathrm{BrF_4^-}$	0.040	4F	0.010
$\mathrm{Br^-}$	$\mathrm{BrF_4^-}$	0.040	4F	0.010
$\mathrm{H^-}$	$\mathrm{HF_2^-}$	0.014	2F	0.007

(c) Elemental Increments in Volume Found in Parts a and b Compared with Estimates Based on Latimer[20]

X	$\langle a\{\mathrm{X}\}\rangle$/nm^3	$\langle b\{\mathrm{X}\}\rangle$/nm^3
F	0.021[b] (0.021)[c]	0.009 (0.017)[d]
Cl	0.029[b] (0.027)[c]	0.028 (0.031)[d]
Br	0.032 (0.036)[c]	0.035 (0.040)[d]
I	0.048 (0.041)[c]	0.050 (0.045)[d]
N	0.007 (0.018)[c]	0.009
O	0.012	0.009 (0.007)[d]
S	0.029 (0.026)[c]	0.023 (0.025)[d]
Se	0.025 (0.036)[c]	0.042 (0.049)[d]

[a] Values in the final column represent typical magnitudes of $a\{\mathrm{X}\}$ (part a) and $b\{\mathrm{X}\}$ (part b). Differences among these (already small) numbers quantify the size of likely errors in applying the isomegethic rule which arise largely as a result of the deviation from additivity found within individual salts containing a common ion. [b] Wide variation in individual $a\{\mathrm{X}\}$ values. [c] $\langle a\{\mathrm{X}\}\rangle$ values in parentheses calculated from $S\{\mathrm{E}\}$ values for the elements X (in kcal mol^{-1} from Table 87, Appendix III, ref 20a). [d] $\langle b\{\mathrm{X}\}\rangle$ values in parentheses calculated from $S\{\mathrm{E}\}$ values for the elements X (in kcal mol^{-1}) and for the case where the charge on the positive ion =+1, from Table 90, Appendix III, ref 20a.

where $a\{Y\} = V\{YAB_y^+\} - V\{AB_y^+\}$ and $b\{Y\} = V\{YCD_z^-\} - V\{CD_z^-\}$, from which it is seen that error involved in using a rule derived from consideration of two-way transfer will be small and, in most cases (although not in all, see below and Table 2), should be less than that involved in using a relationship derived from a "one-way" atom transfer, provided always that the errors in the volumes used in the two relationships are comparable. The ability to devise two-way relationships is, however, severely limited until the existing ion volume database[3a] is further expanded.

As an example, we consider the isomegethic rule estimation of the volume, $V\{SeCl_3^+\}$, known from a consideration of six crystal structures[3a] to be (0.092 ± 0.012) nm^3. Employing, first, a "one-way" isomegethic rule

$$V_m\{SeCl_3^+CN^-\} \approx V_m\{Cl_3^+SeCN^-\} \tag{40}$$

or

$$V\{SeCl_3^+\} \approx V\{Cl_3^+\} + V\{SeCN^-\} - V\{CN^-\} \tag{41}$$

which leads to $V\{SeCl_3^+\} \approx (0.104 \pm 0.009)$ nm^3.

Two "two-way" isomegethic rules can be written. The first is

$$V_m\{SeCl_3^+SH^-\} \approx V_m\{SCl_3^+SeH^-\} \tag{42}$$

or

$$V\{SeCl_3^+\} \approx V\{SCl_3^+\} + V\{SeH^-\} - V\{SH^-\} \tag{43}$$

which leads to the estimate of $V\{SeCl_3^+\} \approx\times 93\ (0.109 \pm 0.018)$ nm^3 (a less certain value than the "one-way" estimate because the accumulated magnitude of the errors associated with the individual ion volumes used is greater in this case). Another "two-way" relationship involves the use of the ion volume, $V\{SeCN^-\}$, which has uncertain errors and, probably because of this, gives rise to an even poorer estimate

$$V_m\{SeCl_3^+SCN^-\} \approx V_m\{SCl_3^+SeCN^-\} \tag{44}$$

or

$$V\{SeCl_3^+\} \approx V\{SCl_3^+\} + V\{SeCN^-\} - V\{SCN^-\} \tag{45}$$

which leads to the estimate of $V\{SeCl_3^+\} \approx 0.117$ nm^3.

As further experience is gained, a clearer picture will emerge, but for the examples selected here, it appears that uncertainties in the single ion volumes used tend to be the predominant factor over the choice of one- or two-way relationship selection.

The Cascade Relationship: Volumes of Homonuclear Polyatomic Ions: $V\{E_n-\}$ and $V\{E_n^+\}$

For cations E_n^+ and anions E_n^-, a generalized isomegethic rule can be written:

$$V\{E_n^+X^-\} \approx V\{E_{n-1}^+XE^-\} \tag{46}$$

$$V\{X^+E_n^-\} \approx V\{XE^+E_{n-1}^-\} \tag{47}$$

This leads to the expectation that

$$V\{E_n^+\} \approx V\{E_{n-1}^+\} + [V\{XE^-\} - V\{X^-\}] \approx V\{E_{n-1}^+\} + c_2\{E^+\} \tag{48}$$

$$V\{E_n^-\} \approx V\{E_{n-1}^-\} + [V\{XE^+\} - V\{X^+\}] \approx V\{E_{n-1}^-\} + c_3\{E^-\} \tag{49}$$

Since the cation or anion differences in square brackets ($=c_2$ and c_3) are independent of n, although dependent on the nature of the elements E and X, this implies that volumes of polyatomic cation and anions should have a roughly constant volume increment as n is changed, thus

$$c_2\{E^+\} = V\{E_n^+\} - V\{E_{n-1}^+\} = [V\{E_m^+\} - V\{E_n^+\}]/(m-n) \tag{50}$$

We have limited data in order to test this relationship. Consider the volumes $V\{Br_n^+\}$ and $V\{I_n^+\}$ available for Br_n^+, $n = 2, 3, 5$, and for I_n^+, $n = 2, 3, 5$. Examples in Table A4(a) (see Supporting Information) show volume increments per atom ($=[V\{Br_m^+\} - V\{Br_n^+\}]/(m-n) = c_2\{Br^+\}$) for Br_n^+ ions and ($=[V\{I_m^+\} - V\{I_n^+\}]/(m-n) = c_2\{I^+\}$) for I_n^+ ions, leading to the conclusion that

$$0.026 \le c_2\{\ Br^+\} = \{[V\{Br_m^+\} - V\{Br_n^+\}]/(m-n)\}/\text{nm}^3 \le 0.039 \tag{51}$$

and

$$0.040 \le c_2\{I^+\} = \{[V\{I_m^+\} - V\{I_n^+\}]/(m-n)\}/\text{nm}^3 \le 0.059 \tag{52}$$

averaging to

$$c_2\{\ Br^+\} = \{[V\{Br_m^+\} - V\{Br_n^+\}]/(m-n)\}/\text{nm}^3 = 0.032 \pm 0.007 \tag{53}$$

and

$$c_2\{I^+\} = \{[V\{I_m^+\} - V\{I_n^+\}]/(m-n)\}/\text{nm}^3 = 0.048 \pm 0.011 \tag{54}$$

again showing plausible, but only approximate, constancy (with quite high standard deviations) arising from the small differences between larger quantities.

Equality of Volume Increments for $[V\{MX_6^{2}-\} - V\{MX'_6{}^{2}-\}]$

For the higher stoichiometric 2:1 isomeric salts $(Cl_3)_2MBr_6$ and $(Br_3)_2MCl_6$, the isomegethic rule can be written

$$2V\{Cl_3^+\} + V\{MBr_6^{2-}\} \approx 2V\{Br_3^+\} + V\{MCl_6^{2-}\} \tag{55}$$

and, hence

$$[V\{MBr_6^{2-}\} - V\{MCl_6^{2-}\}] \approx 2[V\{Br_3^+\} - V\{Cl_3^+\}] \approx c_4 \tag{56}$$

Table 8. Approximate Constancy of Magnitude of $c_4 = [V\{\mathrm{MBr_6}^{2-}) - V\{\mathrm{MCl_6}^{2-})]$ from Ion Volume Database[3a]

M	$V\{\mathrm{MCl_6}^{2-}\}$/nm^3	$V\{\mathrm{MBr_6}^{2-}\}$/nm^3	$c_4 = V\{\mathrm{MBr_6}^{2-}\} - V\{\mathrm{MCl_6}^{2-}\}$/nm^3
Mo	0.225	0.266	0.041
Os	0.223	0.261	0.038
Re	0.224	0.263	0.039
Se	0.229	0.267	0.038
Sn	0.234	0.274	0.040
Tc	0.219	0.259	0.040
Te	0.244	0.286	0.042
Ti	0.221	0.256	0.035
W	0.222	0.263	0.041
		Average	0.040

Since the right side of the second equality in eq 56 is independent of M, this implies that if the isomegethic rule is valid, we should see an approximately constant difference ($=c_4$) between the ion volumes $V\{\mathrm{MBr_6}^{2-}\}$ and $V\{\mathrm{MCl_6}^{2-}\}$, independent of the nature of M (which only influences their absolute magnitudes). This should extend to differences $[V\{\mathrm{MX_6}^{2-}\} - V\{\mathrm{MX'_6}^{2-}\}]$, etc., for other pairs of halogens (X and X′).

Table 8 uses volume[3a] data for $\mathrm{MBr_6}^{2-}$ and $\mathrm{MCl_6}^{2-}$ salts to apply this test. It is clearly seen that the isomegethic rule returns an approximately constant value for c_4. The right side of eq 56 should also equate to this incremental difference. From the existing database,[3a] a value for

$$2[V\{\mathrm{Br_3}^{+}\} - V\{\mathrm{Cl_3}^{+}\}] \approx (0.034 \pm 0.010)\ \mathrm{nm}^3 \quad (57)$$

emerges being 0.006 nm^3 smaller than the average found in Table 8 (equal to $[V\{\mathrm{MX_6}^{2-}\} - V\{\mathrm{MX'_6}^{2-}\}]$). Alternatively, using the isomegethic rule we can write other routes to establish $V\{\mathrm{Br_3}^{+}\}$ and $V\{\mathrm{Cl_3}^{+}\}$, thus

$$V\{\mathrm{Br_3}^{+}\} \approx V\{\mathrm{Br_5}^{+}\} + V\{\mathrm{Br}^{-}\} - V\{\mathrm{Br_3}^{-}\} \approx 0.079\ \mathrm{nm}^3 \quad (58)$$

$$V\{\mathrm{Br_3}^{+}\} \approx V\{\mathrm{IBr_2}^{+}\} + V\{\mathrm{Br}^{-}\} - V\{\mathrm{I}^{-}\} \approx 0.079\ \mathrm{nm}^3 \quad (59)$$

yielding identical values for $V\{\mathrm{Br_3}^{+}\}$ (although different from the database value of 0.096 nm^3) while

$$V\{\mathrm{Cl_3}^{+}\} \approx V\{\mathrm{ICl_2}^{+}\} + V\{\mathrm{Cl}^{-}\} - V\{\mathrm{I}^{-}\} \approx 0.058\ \mathrm{nm}^3 \quad (60)$$

$$V\{\mathrm{Cl_3}^{+}\} \approx V\{\mathrm{Cl_2F}^{+}\} + V\{\mathrm{Cl}^{-}\} - V\{\mathrm{F}^{-}\} \approx 0.056\ \mathrm{nm}^3 \quad (61)$$

averaging to $V\{\mathrm{Cl_3}^{+}\} \approx 0.057$ nm^3 and leading to

$$\mathrm{c}_4 \approx 2[V\{\mathrm{Br_3}^{+}\} - V\{\mathrm{Cl_3}^{+}\}] \approx 0.044\ \mathrm{nm}^3 \quad (62)$$

some 0.004 nm^3 larger than c_4 found for the nine pairs of ions considered in Table 8.

Conclusion

A procedure has been established enabling several alternative estimates of a target ion volume, limited only by the ingenuity and inventiveness of the isomegethic relationships employed. The use of this rule in conjunction with the volume-based equations connecting volume to thermodynamic functions enables the study of the thermodynamics of counterintuitive as well as traditional inorganic materials. Aside from its (considerable) value for explaining the energetics of future ionic materials, this rule also has pedagogical value.

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Supporting Information Available: Appendix 1 containing a study of crystal structure data for compounds $\mathrm{M^{+}As_2F_{11}^{-}}$ and confirmation of the validity of the ion volume additivity relationship. Appendix 2 containing observations of the validity of the isomegethic rule among known materials, including listings of densities (Table A1), enthalpies of formation (Table A2), standard absolute entropies (Table A3), and incremental volume increases for cations and anions (Table A4). This material is available free of charge via the Internet at http://pubs.acs.org.

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