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Relationships among Ionic Lattice Energies, Molecular (Formula Unit) Volumes, and Thermochemical Radii

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The linear generalized equation described in this paper provides a further dimension to the prediction of lattice potential energies/enthalpies of ionic solids. First, it offers an alternative (and often more direct) approach to the well-established Kapustinskii equation (whose capabilities have also recently been extended by our recent provision of an extended set of thermochemical radii). Second, it makes possible the acquisition of lattice energy estimates for salts which, up until now, except for simple 1:1 salts, could not be considered because of lack of crystal structure data. We have generalized Bartlett's correlation for MX (1:1) salts, between the lattice enthalpy and the inverse cube root of the molecular (formula unit) volume, such as to render it applicable across an extended range of ionic salts for the estimation of lattice potential energies. When new salts are synthesized, acquisition of full crystal structure data is not always possible and powder data provides only minimal structural information—unit cell parameters and the number of molecules per cell. In such cases, lack of information about cation—anion distances prevents use of the Kapustinskii equation to predict the lattice energy of the salt. However, our new equation *can* be employed even when the latter information is not available. As is demonstrated, the approach can be utilized to predict and rationalize the thermochemistry in topical areas of synthetic inorganic chemistry as well as in emerging areas. This is illustrated by accounting for the failure to prepare diiodinetetrachloroaluminum(III), $[I_2^+][AlCl_4^-]$ and the instability of triiodinetetrafluoroarsenic(III), $[I_3^+][AsF_6^-]$. A series of effective close-packing volumes for a range of ions, which will be of interest to chemists, as measures of relative ionic size and which are of use in making our estimates of lattice energies, is generated from our approach.

Introduction

Lattice potential energies are important in considering the stability of new inorganic materials.[1−6] When deciding whether a new compound can be synthesized, or when judging the merits of various bench synthetic routes toward the preparation of ionic salts containing new and novel cations (or anions), it is essential to be able to assess the likely thermochemistry involved. The ability, also, to judge the plausibility of any particular decomposition or disproportionation mode may influence the choice of a counteranion (or cation) employed to stabilize the salt. The present work offers much progress toward the above goals.

When, for example, a new compound is reported as being the first example of a salt possessing a specific new cation (anion) a crystal structure is usually/often reported in evidence. In cases where single crystals cannot be obtained, powder crystallographic properties are often reported. From such minimal crystal structure data, and employing the generalized correlation reported here between the inverse cube root molecular volume and the lattice potential energy, we can now estimate the latter. We can then begin to explore the thermochemistry/energetics of new (and related salts), which was previously only possible for 1:1 salts via Bartlett's relationship[7] (vide infra, eq 1 below). It is also required that ancillary thermochemical data (for example, enthalpies of formation of potential decomposition products, etc.) be available.

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Table 1. Some Thermochemical Radii of Complex Ions

ion	thermochemical radius/nm	ref 10
$AlCl_4^-$	0.317 ± 0.019	0.295
AsF_6^-	0.243 ± 0.019	
BF_4^-	0.205 ± 0.019	0.232
MoF_6^-	0.241 ± 0.019	
ReO_4^-	0.227 ± 0.019	
WCl_6^-	0.337 ± 0.019	
CoF_6^{2-}	0.256 ± 0.019	0.244
HgI_4^{2-}	0.377 ± 0.019	
$MoBr_6^{2-}$	0.364 ± 0.019	
$MoCl_6^{2-}$	0.338 ± 0.019	0.340
$Sn(OH)_6^{2-}$	0.279 ± 0.020	
ZrF_6^{2-}	0.258 ± 0.019	
$CdCl_6^{4-}$	0.352 ± 0.038	
CeF_6^{3-}	0.278 ± 0.038	
PaF_8^{3-}	0.299 ± 0.042	
$N(CH_3)_4^+$	0.234 ± 0.019	0.201
$NH(C_2H_5)_3^+$	0.274 ± 0.019	
Br_2^+	0.155 ± 0.027	
IF_6^+	0.209 ± 0.027	
S_8^{2+}	0.182 ± 0.035	

Thus we report in this paper an empirical equation which permits the *direct* estimation of lattice energies (to within a few percent of the true value) of a range of ionic salts using information about the molecular (formula unit) volume of the salt. Furthermore, we have provided elsewhere[8] an extended set of self-consistent thermochemical radii (examples of which are given in Table 1) for use with the traditional Kapustinskii equation[9,10] thus (i) extending the scope of the use of this latter equation to a larger range of compounds than was previously possible, (ii) providing a set of self-consistent radii which can be used as parameters of ionic size in other contexts,[11] and (iii) improving the accuracy with which lattice energies can be estimated. In addition, individual (and additive) effective "single ion" volumes are reported which can be employed in our new equation (much in a manner similar to the way in which thermochemical radii are employed within the Kapustinskii equation). By way of illustration we use these approaches to probe and rationalize the thermochemistry of a specific area of homopolyatomic cation chemistry in which there are examples of stable and unstable materials.

Theory

Full-Scale Calculations. Historically the calculation/estimation of lattice potential or cohesive energy has been made at varying levels of sophistication[12−15] and has been characterized by various milestones. Full scale calculations, needing high level crystal structure data and involving extensive lattice summations, have been made on alkali halides and alkaline earth halide salts,[16−18] using a plethora of potentials, some of which are capable of achieving excellent agreement with Born−Fajans−Haber cycle values.[19] Extended calculations have been made on salts containing complex ions[20,21] of various kinds using purpose-written software (e.g. LATEN[15,22]) designed to model the distributed charges found on the complex ions and for the purposes of acquiring accurate thermochemical data (enthalpies of formation and solvation) for such ions. Large-scale computations on micas,[23−26] phyllosilicates,[27−29] and many other ionic solids have similarly been made. With known structures and partial charge assignments it is certainly possible to make an accurate evaluation of the electrostatic component (Madelung term) of the lattice potential energy. There are, however, other terms more difficult to evaluate (e.g. dipole−dipole, dipole−quadrupole dispersion energies), yet which make an appreciable contribution. The simple form of our generalized equation therefore renders it an attractive alternative to that of making a full-scale calculation.

Kapustinskii Calculations. At the opposite end of the spectrum, and for the purposes of rapid estimation of thermochemical data, the Kapustinskii equation has, for more than 40 years, been enormously powerful and useful in providing approximate, yet reliable, values of the lattice energy for inorganic salts of varying complexity. The scope of the equation has been extended in recent years, for example, to handle macrocycles.[30,31] An extension of the Kapustinskii equation in order to treat more complex (ternary and other) salts has been suggested by Glasser.[32,33] The limited set of thermochemical radii originally assigned by Kapustinskii[9] was subsequently extended,[10] and we have recently calculated and published the largest set of self-consistent thermochemical radii now available, for over 400 individual ions.[8]

Where new materials are involved, the $(r_a + r_c)$ term of the Kapustinskii equation can be equated to the shortest anion−cation distance found by X-ray examination of the crystal structure and from this approximation lattice energy can be estimated. It may not be possible, however, to partition this anion−cation distance into thermochemical radii for the individual ions (unless the radius of one of them is already known). Indeed, to acquire knowledge of the anion−cation distance itself usually means that a single-crystal X-ray structure has been obtained. If this is not the situation then only a minimal set of values (cell parameters and number of molecules (formula units) per unit cell) can usually be extracted from powder data. However, in such cases our new equation *can* provide an estimate of the lattice energy for all binary ionic salts (previously only available for salts having 1:1 stoichiometry), since it requires less structural information than does the Kapustinskii equation.

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Estimation of lattice energies of new materials containing a novel cation (anion) employing the traditional equations proceeds as follows: the thermochemical radius of the counteranion (cation) already being known we can employ the Kapustinskii[8,9] (or Glasser[32,33]) equation to obtain an estimate of the thermochemical radius of the newly incorporated cation (anion). Armed with this radius value, we are then able to predict the lattice potential energy of any family of salts containing the new cation (anion) in combination with any other counteranion (cation) whose thermochemical radius is available.

Volume-Based Calculations. Mallouk et al.[7] have previously demonstrated a linear correlation between lattice enthalpy/kJ mol^{-1} and the inverse cube root of the molecular (formula unit) volume/nm (eq 1) for simple MX (1:1) salts, which has been widely cited in the literature,[4,34−39] where it is often referred to as Bartlett's relationship:

$$\Delta H_L = \frac{232.8}{\sqrt[3]{V}} + 110 \text{ kJ mol}^{-1} \qquad (1)$$

where ΔH_L is the lattice enthalpy (kJ mol^{-1}), the enthalpy change involved in the process of the crystalline solid converting to its constituent gaseous ions, and V is the molecular volume/nm^3. Accordingly Bartlett's equation often provided a more convenient estimate of the lattice enthalpies than did Kapustinskii's equation. The $V^{1/3}$ dependence, in eq 1, at least for MX (1:1) salts, is both dimensionally and conceptually equivalent to the sum of ionic radii, $f(r_a + r_c)$, function found in the Kapustinskii equation, of course. It is also striking to note that the empirical factor, 232.8 kJ mol^{-1} nm, is within 4% of the Born−Mayer electrostatic conversion factor for NaCl type lattices, viz., 242.8 kJ mol^{-1} nm. The equation's advantage is that it permits estimation of lattice enthalpy (and hence lattice energy) using less detailed, more fundamental structural parameters since these volumes are often available directly from X-ray structures, or can be derived or estimated.

The total lattice potential energy, U_{POT}, of a salt, M_pX_q, is related[19] to the lattice enthalpy, ΔH_L, by means of a simple relationship (2):

$$U_{POT}(M_pX_q) = \Delta H_L - [p(n_M/2-2) + q(n_X/2-2)]RT \qquad (2)$$

where n_M and n_X are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for polyatomic nonlinear ions. Equation 2 assumes that the vibrational degrees of freedom are equally excited in both the crystal and the gaseous ions while applying corrections for rotational degrees of freedom possessed by the product gaseous ions.

By means of equations of the type (1) we can thus obtain an estimated lattice enthalpy—if we have information concerning the molecular (formula unit) volume − and from this, the lattice potential energy via eq 2.

Generalization of Bartlett's Method. Our aim is to develop our latest correlation so that it can be employed in a similar manner. Accordingly we have developed effective "single ion" volumes ("thermochemical" volumes). Possession of structural data for a salt in the form of the lattice unit cell parameters (a, b, c, α, β, γ) and the number of molecules (formula units), Z, contained within the unit cell, enables the computation of the unit cell volume and hence the molecular (formula unit) volume, V. We have here extended Bartlett's approach by examining correlations between the lattice potential energy and the inverse cube root volume for MX (1:1) i.e., uni-univalent salts, MX_2 (1:2), i.e., uni-divalent salts, and M_2X (2:1) di-univalent salts and have provided a generalized equation. This generalized equation also subsumes the above lattice enthalpy correlation for 1:1 salts. With a single unambiguous integral value for each z_+, z_- (the cationic and anionic charges) and ν (the number of ions contained in the formula unit) it can be applied to salts of type MX_2, M_2X. We use a wide variety of salts to arrive at the simple rectilinear equations we have derived. This procedure has the effect of averaging the nonelectrostatic energy contributions, and therefore reduces the associated uncertainties with regard to dispersion energies etc. mentioned earlier. This makes the approach of considerable value. Furthermore, we are developing procedures for dealing with more complex ionic systems; these will be reported in due course.

From this new equation, we are now able to estimate lattice potential energies for a whole range of inorganic materials possessing unusual or novel cations (anions) provided minimal crystal structure data has been reported such that Z and V (and therefore $V^{-1/3}$) are known, for at least *one* salt containing each target cation (anion). In the course of our attempts to understand the behavior of the homopolyatomic cations[4] of groups 16 and 17 and as a guide to synthetic endeavors (J.P.) we have been interested to obtain the lattice energies of MX_2 (1:2), M_2X (2:1) and other salts of these cations. We show later, how the ability to make estimates *even when no structural information is available*, for example, for S_4^{2+} salts with 1:2 stoichiometry and no molecules of solvation, enables us to probe the chemistry of the S_4^{2+} cation.

"Single Ion" Volumes. A further, and alternative, approach to using the inverse of the cube root of the total (formula unit) volume, $V^{-1/3}$, emerges from our new correlation. It differs from the Kapustinskii approach, although similar in strategy, in that it avoids the use of radii. In place of these it introduces the concept of "single ion" volume estimations. This latter approach stems from recognition of the fact that the rectilinear form of our equation (relating the lattice potential energy and the inverse cube root of the molecular (formula unit) volume) demonstrates that the effective close-packing volume of an ion may possibly be a *more directly* useful parameter than the thermochemical radius.

The effective close-packing molecular (formula unit) volume, V, may be simply regarded as being the additive sum of the individual anion and cation effective ion volumes, V_+ and V_-. Provided that these can adequately be defined, they can be used in an analogous fashion to thermochemical radii.

As a general feature of our new equation, employing volume data has two immediate advantages over the conventional Kapustinskii approach. First, it avoids the fundamental difficulties associated with assigning thermochemical radii to patently nonspherical ions such as I_2^+, S_4^{2+}, $S_3N_2^{2+}$, etc. and, second, the relationship existing between the volume and the lattice energy is directly linked to basic structural information.

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However, practicalities dictate that the procedure used for ion volume estimation, in the new approach we are reporting, will incorporate voids within the salt structure from which the estimation was derived and thus may over-estimate the “true” ion volume. The interpretation of the resultant single ion volumes must, therefore, be tinged with caution. This potential source of error, however, can be quantified and minimized by including as many examples as possible of salts which contain the *same* specific ion in the dataset used to estimate a particular effective ion volume. In usage, any error which exists in those volumes which are employed in order to predict lattice potential energies (involving relationships which require the extraction of the cube root of the sum of these effective close packing single ion volumes) will, of course, be much diminished in the process of taking the negative exponent.

Such procedures for estimating lattice potential energies enable us to examine the likely energetics implicated in the formation of, and potential synthetic routes to preparation of, new salts formed between the cation (anion) and other anions (cations). In addition, potential decomposition modes of the target material can also be analyzed in terms of the thermodynamics likely to be involved, as we will illustrate.

In other words the approach developed in this paper allows us, inter alia,

(i) to explore previously uncharted thermochemistry by use, via the Kapustinskii equation, of the extended set of thermochemical radii developed[8] with our new equation;

(ii) to estimate lattice potential energies of a greater range of salts by a method which also requires less detailed structural information than was previously the case;

(iii) to estimate the lattice potential energy from the derived ion volumes for unsynthesized salts;

(iv) to estimate thermochemical radius and close packed single ion volume data for ions for which no salts have yet been prepared, by virtue of the extended database of ion parameters which we provide in this study.

In addition the effective single ion volumes as well as the more traditional thermochemical radii[8] can be used to provide parameters of molecular size to correlate with other ion properties. These are *not* simply related by a $V = 4/3\pi r^3$ relationship. Apart from the fact that thermochemical radii are generated as a result of a quadratic dependency, $f\{1/(r_a + r_c), 1/(r_a + r_c)^2\}$ while our single ion volume has a rectilinear dependency $f\{V^{-1/3}\}$, the ions in the lattice will not usually be spheres. Partitioning of the formula unit volume into V_+ and V_- components divides the space while not necessarily assuming a spherical form for the ions.

The capability of prediction of the molecular (formula unit) volume of a new and as yet unprepared material—by combination of tabulated single ion volumes—can also provide an estimate of the density of that material. Apart from being a useful additional property in its own right, density is employed in crystallography to determine the number of molecules, *Z*, contained within the unit cell when new materials are investigated.

Table 2. Lattice Potential Energies and Cube Roots of Molecular Volumes for MX_2 Salts

	U_{POT} (kJ mol^{-1}) from refs 10 and 40		
MX_2 salt	extended calculation	estimated Kapustinskii	$V^{1/3}$/nm
BaF_2	2341	2361	0.3903
$BaCl_2$	2033	2059	0.4442
$BaBr_2$	1950	1971	0.4751
BaI_2	1831	1861	0.5020
CaF_2	2609	2673	0.3442
$CaCl_2$	2223	2255	0.4384
$CaBr_2$	2132	2186	0.4614
CaI_2	1905	2053	0.4946
MgF_2	2913		0.3206
$MgCl_2$	2326	2512	0.4031
$MgBr_2$	2097	2383	0.4288
MgI_2	1944	2226	0.4674
$Ca(NO_3)_2$	2209	2246	0.4788

Generalized Formula. To estimate the lattice potential energy for salts of type MX (1:1), MX_2 (1:2), and M_2X (2:1) we examined a generalization of the correlation of the form of eq 1 of Mallouk et al.[7] The generalized correlation—now between the lattice potential energy and the inverse cube root molecular (formula unit) volume—applies across a wide range of inorganic salts. These correlations were established using data from alkali and alkaline earth metal salts for the estimation of lattice potential energies of MX (1:1), MX_2 (1:2), and M_2X (2:1). The equation developed takes the generalized form of eq 3 for any salt M_pX_q:

$$U_{POT} = |z_+||z_-|\nu\left(\frac{\alpha}{\sqrt[3]{V}} + \beta\right) = \sum n_k z_k^{\,2}\left(\frac{\alpha}{\sqrt[3]{V}} + \beta\right)\ \text{kJ mol}^{-1} \tag{3}$$

where α (kJ mol^{-1} nm) and β (kJ mol^{-1}) are coefficients of best fit, z_+ and z_- are the respective charges on the cations and anions, ν is the number of ions per molecule and is equal to $(p + q)$, and V (nm^3) is the molecular (formula unit) volume of the salt. In the alternative form of eq 3, n_k is the number of ions of charge z_k in the formula unit. These two forms are equivalent for the compounds dealt with in this paper. It is the simplicity of the form of eq 3 and the awareness that any user will have that the values generated will only be approximations to the true energies that give it practical value.

As noted above, the Kapustinskii equation[9] for the calculation of lattice potential energy is a quadratic function of the inverse ion radii sum $(r_a + r_c)^{-1}$. It might be anticipated from this equation therefore that the relationship between the lattice potential energy and the inverse cube root of the molecular (formula unit) volume would also be of a quadratic form. However, such a quadratic fit to the experimental data, when examined, did not significantly improve the correlation. A rectilinear form (eq 3) of the correlation between the lattice potential energy and the inverse cube root of the molecular (formula unit) volume was therefore adopted for simplicity, and so constitutes our new equation.

Results and Discussion

The following parameters were found for the generalized correlation in the form of eq 3: $\alpha = 138.7$ kJ mol^{-1} nm, $\beta = 27.6$ kJ mol^{-1} with a correlation coefficient $R = 0.91$. The data for the lattice potential energies of the salts were taken from ref 40, and the corresponding crystal structure data, in the main, from Donnay.[41] The data utilized to make the correlations for the MX_2 (1:2) and M_2X (2:1) salts are displayed in Tables 2 and 3, respectively. More reliable estimates of lattice potential energies result if data for MX, MX_2, and M_2X salts are treated

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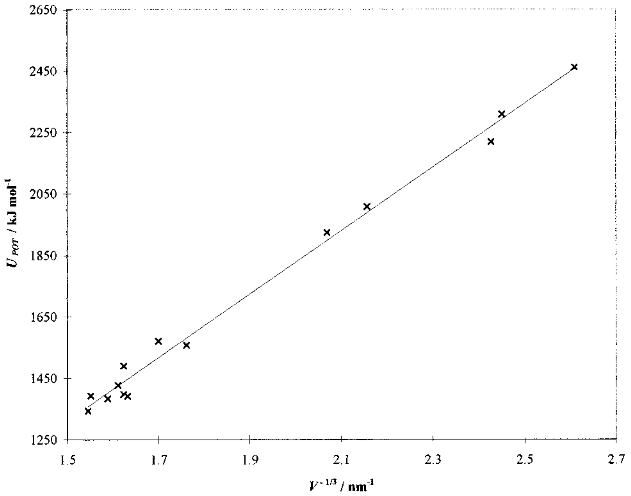

Figure 1. Plot of the correlation between the lattice potential energy, U_{POT}/kJ mol^{-1}, and the inverse cubic root molecular volume, $V^{-1/3}$/nm: for the M_2X salts, [M = alkali metal], with X = S^{2-}, CO_3^{2-}, SO_4^{2-}, $MoCl_6^{2-}$, etc.

Table 3. Lattice Potential Energies and Cube Roots of Molecular Volumes for M_2X Salts

	U_{POT} (kJ mol^{-1}) from refs 10 and 40		
M_2X salt	extended calculation	estimated Kapustinskii	$V^{1/3}$/nm
Cs_2CoCl_4	1391	1398	0.6157
Cs_2CuCl_4	1393	1392	0.6126
Cs_2GeCl_6	1375		0.6444
Cs_2GeF_6	1573	1559	0.5675
Cs_2MoCl_6	1347	1344	0.6470
Cs_2SO_4	1596		0.5193
Cs_2ZnBr_4	1454	1453	0.6445
Cs_2ZnCl_4	1429	1491	0.6157
K_2S	1979	2008	0.4637
K_2MoCl_6	1418	1428	0.6205
K_2PtCl_4	1574	1571	0.5881
K_2SO_4	1700		0.4770
Li_2CO_3	2523	2462	0.3832
Li_2S	2464		0.3603
Li_2SO_4	2229		0.4530
Na_2CO_3	2301	2309	0.4079
Na_2S	2192	2220	0.4119
Na_2SO_4	1827		0.4279
Rb_2MoCl_6	1399	1384	0.6293
Rb_2S	1929	1925	0.4832
Rb_2SO_4	1636		0.4954

independently: then, for MX (1:1) salts (i.e. uni-univalent), $\alpha = 117.3$ kJ mol^{-1} nm and $\beta = 51.9$ kJ mol^{-1} with a correlation coefficient of $R = 0.94$ (cf. 116.4 kJ mol^{-1} nm and 55 kJ mol^{-1} from the Bartlett equation (1) for the system of MX salts); for MX_2 (1:2) salts (i.e. bivalent cation–univalent anion), $\alpha = 133.5$ kJ mol^{-1} nm and $\beta = 60.9$ kJ mol^{-1} with a correlation coefficient $R = 0.83$ (based on data for the salts in Table 2); and for M_2X (2:1) salts (i.e. univalent cation–bivalent anion; Figure 1), $\alpha = 165.3$ kJ mol^{-1} nm and $\beta = -29.8$ kJ mol^{-1} with a correlation coefficient of $R = 0.95$ (based on data for the salts in Table 3).

It will be noted that the values for α are reasonably consistent (varying by about 20% about the system value) while the values for β vary widely, as might be expected for linear correlations of this kind, the gradients being better defined than the intercepts.

Ion Parameters. In view of the satisfactory correlation coefficients obtained, these relationships can be utilized in a number of ways. First, given the molecular (formula unit) volume, *V*—usually obtained from unit cell parameters, using eq 4:

Table 4. Volumes V_+ Generated using Goldschmidt Radii for Alkali Metal and Alkaline Earth Cations

cation	V_+/nm^3	cation	V_+/nm^3
Li^+	0.00199	Mg^{2+}	0.00199
Na^+	0.00394	Ca^{2+}	0.00499
K^+	0.00986	Sr^{2+}	0.00858
Rb^+	0.01386	Ba^{2+}	0.01225
Cs^+	0.01882		

$$V = [abc\sqrt{(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)}]/Z \quad (4)$$

where *a*, *b*, and *c* are the unit cell edges (in nm), α, β, and γ are the unit cell angles (in degs)—and *Z* (the number of molecules per unit cell), the lattice potential energy, U_{POT}, can be established for the salt by using the $V^{-1/3}$ dependence via our new equation, eq **3**. An example of the estimation of the lattice potential energy from unit cell parameters is given for $[I_3^+][AlCl_4^-]$ later in this section. Second, we can use the relationships to estimate the combined radii ($r_a + r_c$) of salts, via the Kapustinskii equation with lattice enthalpy, as estimated from our eq 3, as the input, which can then, in turn, be used to predict individual ion radii. A few typical values of ion radii are given in Table 1 (along with their assigned errors and citing previously assigned[10] radii where possible). Further extensive tabulations (for over 400 ions) are given elsewhere for thermochemical radii of ions of varying complexity.[8] Third, considering the fact that our effective close-packing ion volumes are additive, since for a salt, M_pX_q

$$V = pV_+ + qV_- \quad (5)$$

then, providing we can define the effective volume of the anion, V_- (cation, V_+), the corresponding effective volume of the cation, V_+ (anion, V_-) can be obtained. For the purposes of initial calibration of the effective single ion volumes we face a classical problem of physical chemistry: that of separating an additive property into its single ion components.[42] We have adopted a simple procedure, paralleling that followed by Kapustinskii in his original assignment of thermochemical radii. Namely, we used the Goldschmidt radii,[43] of alkali metal cations, r_+ (which can be found tabulated in ref 2) to define the corresponding effective cation volumes, V_+, taking them to be equal to $^4/_3\pi r_+^3$. The results of such an exercise for alkali metal and alkaline earth ions are listed in Table 4. The volume of the anion is then estimated by subtracting the appropriate number of cation volumes from the molecular volume, *V*, of the salt containing an alkali metal cation, the corresponding remaining effective single ion volumes defined accordingly. This approach, as was alluded to earlier, assigns any "free space" in the crystal structure[44] to the anion volumes, V_-.

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(42) See for example discussion in Jenkins, H. D. B.; Pritchett, M. S. F. *J. Chem. Soc., Faraday Trans 1* **1984**, *80*, 721.

(43) Goldschmidt, V. M. *Skrifter Norske Videnskaps-Akad. Oslo, I, Mat.-Naturn. Kl*, **1926**.

(44) We investigated several alternative approaches to partitioning the effective close packing molecular (formula unit) volume, *V*, into its ion additive components, V_+ and V_-. Specifically we tried to identify a salt for which $V_+ \approx V_-$ but such attempts led to results which did not appear to be valid. For example, negative volumes emerged for ions such as Li^+.

Table 5. Anion Volumes Obtained from Alkali and Alkaline Earth Metal Salts[a]

anion	volume/ nm^3	error/ nm^3	no. of salts considered	anion	volume/ nm^3	error/ nm^3	no. of salts considered	anion	volume/ nm^3	error/ nm^3	no. of salts considered
AgF_4^-	0.096	± 0.014	4	H^-	0.033	± 0.014	4	OH^-	0.032	± 0.008	3
$AlBr_4^-$	0.198	± 0.005	3	HCO_2^-	0.056	± 0.002	2	OsF_6^-	0.124	± 0.008	3
$AlCl_4^-$	0.156		1	HCO_3^-	0.064	± 0.003	2	PaF_6^-	0.124	± 0.011	4
AlF_4^-	0.068	± 0.003	4	HF_2^-	0.047	± 0.009	5	PF_6^-	0.109	± 0.008	4
AlH_4^-	0.067		1	HSO_4^-	0.089	± 0.002	2	PO_3^-	0.067	± 0.006	5
AlI_4^-	0.244		1	I^-	0.072	± 0.016	4	PuF_5^-	0.096	± 0.008	4
AsF_6^-	0.110	± 0.007	4	I_2Br^-	0.155		1	ReF_6^-	0.117	± 0.008	4
$Au(CN)_2^-$	0.092	± 0.008	2	I_3^-	0.171		1	ReO_4^-	0.086	± 0.013	5
$AuCl_4^-$	0.157		1	IBr_2^-	0.142		1	RuF_6^-	0.116	± 0.007	3
AuF_4^-	0.088	± 0.013	2	ICl_2^-	0.122		1	S_6^-	0.226		1
$B(OH)_4^-$	0.058		1	ICl_4^-	0.184		1	$SbCl_6^-$	0.203	± 0.017	2
BF_4^-	0.073	± 0.009	5	$IO_2F_2^-$	0.095		1	SbF_6^-	0.121	± 0.112	6
BH_4^-	0.066	± 0.015	4	IO_3^-	0.075	± 0.006	6	SbO_3^-	0.060	± 0.007	3
BiF_6^-	0.124	± 0.014	4	IO_4^-	0.088	± 0.009	4	SCN^-	0.071	± 0.003	5
Br^-	0.056	± 0.014	4	IrF_6^-	0.117	± 0.007	2	$SeCN^-$	0.092		1
BrF_4^-	0.096		1	MnO_4^-	0.088	± 0.008	4	SeH^-	0.070	± 0.008	5
BrO_3^-	0.072	± 0.008	6	MoF_6^-	0.113	± 0.017	4	SH^-	0.057	± 0.009	5
Cl^-	0.047	± 0.013	3	$MoOF_5^-$	0.123	± 0.005	2	SO_3F^-	0.088	± 0.004	3
ClO_2^-	0.056		1	N_3^-	0.058	± 0.014	3	$TaCl_6^-$	0.206		1
ClO_3^-	0.073	± 0.006	5	NbF_6^-	0.125	± 0.008	5	TaF_6^-	0.128	± 0.008	4
ClO_4^-	0.082	± 0.013	6	NbO_3^-	0.053	± 0.002	2	TaO_3^-	0.054	± 0.001	2
CN^-	0.050	± 0.006	4	NCO^-	0.054	± 0.002	3	UF_6^-	0.167	± 0.041	4
$Cr_3O_8^-$	0.151	± 0.013	3	NH_2^-	0.043	± 0.008	4	VF_6^-	0.112	± 0.009	3
$CuBr_4^-$	0.244		1	NO_2^-	0.055	± 0.007	3	VO_3^-	0.070	± 0.006	4
F^-	0.025	± 0.010	4	NO_3^-	0.064	± 0.011	5	WCl_6^-	0.208	± 0.004	2
$FeCl_4^-$	0.155		1	O_2^-	0.046	± 0.007	4	WF_6^-	0.125	± 0.032	4
$GaCl_4^-$	0.145		1	O_3^-	0.063	± 0.007	3	WOF_5^-	0.129		1
AmF_6^{2-}	0.132		1	$PdCl_4^{2-}$	0.183		1	SiF_6^{2-}	0.112	± 0.028	4
$CdCl_4^{2-}$	0.196		1	$PdCl_6^{2-}$	0.218	± 0.008	3	SiO_3^{2-}	0.062	± 0.007	2
$CeCl_6^{2-}$	0.255		1	PdF_6^{2-}	0.143	± 0.031	4	SmF_4^{2-}	0.073		1
CeF_6^{2-}	0.127		1	$PoBr_6^{2-}$	0.296		1	$Sn(OH)_6^{2-}$	0.137	± 0.000	2
CO_3^{2-}	0.061	± 0.005	3	PoI_6^{2-}	0.372		1	$SnBr_6^{2-}$	0.274	± 0.004	3
$CoCl_4^{2-}$	0.196		1	$Pt(NO_2)_3Cl_3^{2-}$	0.247		1	$SnCl_6^{2-}$	0.234	± 0.006	3
CoF_4^{2-}	0.089	± 0.000	2	$Pt(NO_2)_4Cl_2^{2-}$	0.272		1	SnF_6^{2-}	0.110	± 0.014	2
CoF_6^{2-}	0.139		1	$Pt(OH)_2^{2-}$	0.385		1	SnI_6^{2-}	0.362	± 0.004	2
$Cr_2O_7^{2-}$	0.167	± 0.004	2	$PtBr_4^{2-}$	0.198		1	SO_3^{2-}	0.071		1
CrF_6^{2-}	0.148	± 0.029	3	$PtBr_6^{2-}$	0.258	± 0.006	3	SO_4^{2-}	0.091	± 0.013	6
CrO_4^{2-}	0.097	± 0.009	5	$PtCl_6^{2-}$	0.219	± 0.009	3	$TcBr_6^{2-}$	0.259	± 0.001	2
$CuCl_4^{2-}$	0.192		1	PtF_6^{2-}	0.119	± 0.012	3	$TcCl_6^{2-}$	0.219	± 0.002	2
CuF_4^{2-}	0.087	± 0.008	3	$PuCl_6^{2-}$	0.251		1	TcF_6^{2-}	0.119	± 0.003	2
$GeCl_6^{2-}$	0.230		1	$ReBr_6^{2-}$	0.263	± 0.003	3	TcH_9^{2-}	0.129		1
GeF_6^{2-}	0.113	± 0.025	4	$ReCl_6^{2-}$	0.224	± 0.007	3	TcI_6^{2-}	0.333	± 0.001	2
HfF_6^{2-}	0.126	± 0.015	3	ReF_6^{2-}	0.124	± 0.007	4	Te^{2-}	0.091	± 0.020	3
HgI_4^{2-}	0.245		1	ReF_8^{2-}	0.149	± 0.004	2	$TeBr_6^{2-}$	0.286	± 0.002	3
$IrCl_6^{2-}$	0.229		1	ReH_9^{2-}	0.127		1	$TeCl_6^{2-}$	0.244	± 0.005	3
$MnCl_6^{2-}$	0.195	± 0.019	3	ReI_6^{2-}	0.344	± 0.014	3	TeI_6^{2-}	0.357	± 0.009	2
MnF_4^{2-}	0.097	± 0.001	2	RhF_6^{2-}	0.116	± 0.003	2	TeO_4^{2-}	0.110		1
MnF_6^{2-}	0.115	± 0.029	3	$RuCl_6^{2-}$	0.211		1	$ThCl_6^{2-}$	0.267		1
$MoBr_6^{2-}$	0.266	± 0.003	2	RuF_6^{2-}	0.127	± 0.005	3	ThF_6^{2-}	0.126	± 0.025	3
$MoCl_6^{2-}$	0.225	± 0.007	3	S^{2-}	0.067	± 0.019	4	$TiBr_6^{2-}$	0.256	± 0.003	2
MoF_6^{2-}	0.123		1	$S_2O_3^{2-}$	0.104		1	$TiCl_6^{2-}$	0.221	± 0.009	3
MoO_4^{2-}	0.088	± 0.001	3	$S_2O_4^{2-}$	0.113		1	TiF_6^{2-}	0.122	± 0.008	4
$NbCl_6^{2-}$	0.231	± 0.006	3	$S_2O_5^{2-}$	0.139		1	UCl_6^{2-}	0.258		1
NH^{2-}	0.028		1	$S_2O_6^{2-}$	0.153	± 0.014	4	UF_6^{2-}	0.114	± 0.010	2
$Ni(CN)_4^{2-}$	0.195		1	$S_2O_7^{2-}$	0.144		1	VO_3^{2-}	0.071		1
NiF_4^{2-}	0.080	± 0.010	3	$S_2O_8^{2-}$	0.169	± 0.012	2	WBr_6^{2-}	0.263	± 0.006	3
NiF_6^{2-}	0.126	± 0.014	3	$S_3O_6^{2-}$	0.172		1	WCl_6^{2-}	0.222	± 0.001	3
O^{2-}	0.043	± 0.015	5	$S_4O_6^{2-}$	0.209		1	WO_4^{2-}	0.088	± 0.003	2
O_2^{2-}	0.052	± 0.016	5	$S_6O_6^{2-}$	0.270		1	$WOCl_5^{2-}$	0.231		1
$OsBr_6^{2-}$	0.261	± 0.004	2	ScF_6^{2-}	0.124		1	$ZnBr_4^{2-}$	0.216	± 0.012	4
$OsCl_6^{2-}$	0.223	± 0.008	2	Se^{2-}	0.072	± 0.023	3	$ZnCl_4^{2-}$	0.185	± 0.011	4
OsF_6^{2-}	0.124		1	$SeBr_6^{2-}$	0.267	± 0.004	2	ZnF_4^{2-}	0.084	± 0.001	2
$PbCl_4^{2-}$	0.147		1	$SeCl_6^{2-}$	0.229	± 0.007	2	$ZrCl_6^{2-}$	0.242	± 0.004	2
$PbCl_6^{2-}$	0.243	± 0.004	2	SeO_4^{2-}	0.103	± 0.010	4	ZrF_6^{2-}	0.121	± 0.020	4
PbF_6^{2-}	0.112	± 0.015	2					ZnI_4^{2-}	0.218		1
$PdBr_6^{2-}$	0.247	± 0.014	3								

Table 5. (Continued)

anion	volume/ nm^3	error/ nm^3	no. of salts considered	anion	volume/ nm^3	error/ nm^3	no. of salts considered	anion	volume/ nm^3	error/ nm^3	no. of salts considered
AlH_6^{3-}	0.108		1	FeF_6^{3-}	0.155	± 0.028	4	PaF_8^{3-}	0.158	± 0.020	3
AsO_4^{3-}	0.088	± 0.010	2	HfF_7^{3-}	0.130		1	PO_4^{3-}	0.090		1
$CdBr_6^{4-}$	0.326	± 0.003	2	InF_6^{3-}	0.152	± 0.008	3	PrF_6^{3-}	0.171		1
$CdCl_6^{4-}$	0.280	± 0.003	2	$Ir(CN)_6^{3-}$	0.271		1	$Rh(NO_2)_6^{3-}$	0.285	± 0.011	3
CeF_6^{3-}	0.167		1	$Ir(NO_2)_6^{3-}$	0.294		1	$Rh(SCN)_6^{3-}$	0.462		1
CeF_7^{3-}	0.174		1	$Mn(CN)_6^{3-}$	0.276		1	SbO_4^{3-}	0.071		1
$Co(CN)_6^{3-}$	0.263	± 0.003	2	$Mn(CN)_6^{5-}$	0.380		1	TaF_8^{3-}	0.137		1
$Co(NO_2)_6^{3-}$	0.269		1	$MnCl_6^{4-}$	0.264		1	TbF_7^{3-}	0.163	± 0.016	4
$CoCl_5^{3-}$	0.253		1	N^{3-}	0.062	± 0.022	3	$Tc(CN)_6^{5-}$	0.394		1
CoF_6^{3-}	0.139		1	$Ni(NO_2)_6^{3-}$	0.261		1	ThF_7^{3-}	0.166	± 0.041	3
$Cr(CN)_6^{3-}$	0.279		1	$Ni(NO_2)_6^{4-}$	0.337		1	$TiBr_6^{3-}$	0.235	± 0.011	2
CrF_6^{3-}	0.127		1	NiF_6^{3-}	0.121		1	TlF_6^{3-}	0.157	± 0.009	3
$Cu(CN)_4^{3-}$	0.209		1	O^{3-}	0.194		1	UF_7^{3-}	0.152	± 0.028	4
$Fe(CN)_6^{3-}$	0.265	± 0.011	3	P^{3-}	0.083	± 0.029	3				

[a] Using cation volumes from Table 4, the anion volumes listed are obtained.

As an example we consider the anion $[AgF_4^-]$. In Table 5 the four salts considered having the anion $[AgF_4^-]$ were $[Na^+][AgF_4^-]$, $[K^+][AgF_4^-]$, $[Rb^+][AgF_4^-]$, and $[Cs^+][AgF_4^-]$. The tetragonal unit cell volumes[41] are respectively: 0.328, 0.412, 0.456, and 0.131 nm^3 with $Z = 4$ for the Na^+, K^+, and Rb^+ salts and $Z = 1$ for the Cs^+ salts for the lattices, leading to molecular volumes for the formula units of 0.082, 0.103, 0.114, and 0.131 nm^3. For the cations involved the Goldschmidt radii[43,2] are 0.098, 0.133, 0.149, and 0.165 nm which correspond to volumes (Table 4), V_+, of 0.00394, 0.00986, 0.01386, and 0.01882 nm^3, respectively. From rearranged eq 5 ($p = q = 1$) for these salts, V_- for individual $[AgF_4^-]$ salts are found to be 0.078, 0.095, 0.100, and 0.112 nm^3 which average to 0.096 nm^3 with a standard deviation of 0.014 nm^3 as listed in Table 5. These estimated ion volumes can be used to generate further ion volume data (predominantly for cations and listed in Table 6). These values are adopted and used in the remainder of this paper.

A fundamental question is, of course, how well do the estimated lattice potential energies generated (a) using thermochemical radii (as derived from our correlations) and used in the Kapustinskii equation and (b) using our new eq 3 with the effective single ion volumes, agree with the lattice potential energies which result from full scale computational methods[19] and with values derived from thermochemical cycles? Table 7 shows the comparison for typical simple salts and more complex oxides. We select the example of the calculation of the lattice potential energy of $[Cs^+]_2[ReCl_6^{2-}]$, cited in Table 7, which was not a salt used to generate any of the primary data. Taking the value $V(Cs^+)$ (Table 4) with $V(ReCl_6^{2-}) = 0.224$ nm^3 (Table 5) the molecular (formula unit) volume, $V = 2V(Cs^+) + V(ReCl_6^{2-}) = 0.262$ nm^3 (using eq 5), and hence $V^{1/3} = 0.640$ nm. This value substituted into our generalized eq 3, using $\alpha = 165.3$ kJ mol^{-1} nm and $\beta = -29.8$ kJ mol^{-1} (for M_2X salt) with $|z_+||z_-|\nu = 6$, leads to the prediction that $U_{POT}(Cs_2ReCl_6) = 1371$ kJ mol^{-1}. Agreement for most salts is usually to within less than 4%, thus providing a very acceptable basis on which to probe unknown thermochemical areas. It also questions whether, in actual fact, we need more extended calculations for most practical purposes. Also listed in Table 7 are some results for the complex series of oxides of titanium. Especially for the higher oxides there exist uncertainties as to what the true values (columns 2 and 3 of Table 7) of the lattice potential energies actually should be and so, accordingly, our estimates of the errors involved in the cases of these oxides are also uncertain. What emerges from these studies is that, while the Kapustinskii estimates remain reasonably good throughout, estimates of the lattice energy based volumes that are obtained directly from the published crystal structure data become increasingly poorer as the oxide becomes more complex. This is probably because the equation we are using is founded predominantly on a study of results for MX_2 (2:1) and M_2X (1:2) salts while the study of the complex oxides involves M_2X_3 and even more complex (M_3X_5 and M_4X_7 type) oxides (see footnote to Table 7), where the interactions among the ions require further analysis. Table 7 is intended to show that, at least for simpler stoichiometries, our new approach can offer a satisfactory alternative to the traditional Kapustinskii approach. In general, then, as might be anticipated Kapustinskii estimates based on our new thermochemical radii[8] are exceptionally good. Estimates based on the "thermochemical effective ion volumes" generated in this paper may be marginally less satisfactory but, in turn, do require less detailed structural information for their generation. This will, in any case, be the subject to further development and these additional studies on the generation of these volumes may lead to enhanced agreement. A mere 1 or 2% improvement would make their predictive power equivalent to that of the radii.

Estimation of Ion Volumes Not Listed in the Tables. To extend the applicability of this work further, so as to apply to a greater range of salts, one can sometimes estimate volumes for ions which are not actually listed in the tables. We have, within the tables so far presented, generated ion volume data for a range of ions of varying sizes, and it is, of course possible to interpolate the data. Using either size criteria or relevant correlations one can sometimes make educated approximations as to the volume of an ion not listed. To give two examples of such a procedure, one can cite the cases of the estimation of the ion volumes of the disulfur monocation S_2^+ and of the tetrasulfur dication S_4^{2+}, neither of which has volumes listed in our tables.

In the case of S_2^+ there are no known salts containing this cation, so no crystal structure data exists and hence no volume data can be extracted from any of its salts. Despite this fact we can conjecture that it is likely that $V(SN^+) < V(S_2^+) < V(S_2N^+)$. The volumes of the bracketing ions *are* listed in Table 6: $V(SN^+) = 0.032 \pm 0.007$ nm^3 and $V(S_2N^+) = 0.060 \pm 0.009$ nm^3. An estimate, taken midway between these two latter ion volumes, can be assigned as the estimated volume of the S_2^+ ion. This gives a value for $V(S_2^+)$ of $\sim 0.045 \pm 0.011$ nm^3. Combining this volume with that for AsF_6^- (found in Table 5), $V(AsF_6^-) = 0.110 \pm 0.007$ nm^3, and we can estimate that for the salt, $[S_2^+][AsF_6^-]$, $V([S_2^+][AsF_6^-]) \approx 0.115 \pm 0.013$ nm^3

Table 6. Ion Volumes Obtained from Known Counterion Volumes

ion	volume/ nm^3	error/ nm^3	no. of salts considered	ion	volume/ nm^3	error/ nm^3	no. of salts considered	ion	volume/ nm^3	error/ nm^3	no. of salts considered
NH_4^+	0.021	± 0.015	3	$NH_3C_3H_7^+$	0.100	± 0.014	3	$N(C_2H_5)_4^+$	0.199	± 0.016	1
$N(CH_3)_4^+$	0.113	± 0.013	3	$NH(C_2H_5)_3^+$	0.177	± 0.016	2	$N_2H_6^{2+}$	0.075	± 0.013	1
$NH_3CH_3^+$	0.051	± 0.016	2	$N_2H_5^+$	0.028	± 0.013	1	$Na[222]^+$	0.527	± 0.016	1
$NH_3C_2H_5^+$	0.064	± 0.014	1	NH_3OH^+	0.021	± 0.014	2	$K[222]^+$	0.531	± 0.016	1
AgF_4^-	0.082	± 0.013	1	$O_2(SCCF_3Cl)_2^+$	0.237	± 0.017	1	$SCl_2CF_3^+$	0.105	± 0.017	1
AlI_4^-	0.242	± 0.010	1	$ONCH_3CF_3^+$	0.089	± 0.017	1	$SCl_2CH_3^+$	0.095	± 0.017	1
$As_3S_4^+$	0.172	± 0.014	2	$OsOF_5^-$	0.121	± 0.011	1	SCl_3^+	0.096	± 0.014	5
$As_3Se_4^+$	0.195	± 0.012	1	$P(CH_3)_3Cl^+$	0.142	± 0.017	1	$Se_3Br_3^+$	0.185	± 0.007	1
$AsCl_4^+$	0.124	± 0.007	1	$P(CH_3)_3D^+$	0.138	± 0.017	1	$Se_3Cl_3^+$	0.169	± 0.012	1
AuF_6^-	0.115	± 0.014	1	PtF_6^-	0.109	± 0.020	3	$Se_3N_2Cl^+$	0.139	± 0.007	1
Br_2^+	0.057	± 0.014	1	$ReOF_5^-$	0.121	± 0.018	1	$Se_3NCl_2^+$	0.140	± 0.007	1
Br_3^+	0.096	± 0.007	1	RuF_5^-	0.118	± 0.016	1	Se_6I^+	0.207	± 0.012	2
Br_3^-	0.124	± 0.011	1	$S(CH_3)_2Cl^+$	0.103	± 0.017	1	$SeBr_3^+$	0.114	± 0.012	1
Br_5^+	0.147	± 0.009	2	$S(NP(C_2H_5)_3)_3^+$	0.621	± 0.017	1	$SeCl_3^+$	0.092	± 0.012	6
$BrClCNH_2^+$	0.092	± 0.007	1	$S_2(CH_3)_2Cl^+$	0.222	± 0.017	1	SeF_3^+	0.053	± 0.007	4
BrF_2^+	0.040	± 0.007	1	$S_2(CH_3)_2CN^+$	0.128	± 0.017	1	SeI_3^+	0.159	± 0.007	2
BrF_4^+	0.044	± 0.012	1	$S_2(CH_3)_3^+$	0.147	± 0.017	1	$SeNCl_2^+$	0.129	± 0.012	1
BrF_6^+	0.104	± 0.007	1	$S_2Br_5^+$	0.217	± 0.007	1	$(SeNMe_3)_3^+$	0.493	± 0.017	1
$C_{10}F_8^+$	0.213	± 0.007	1	S_2N^+	0.060	± 0.009	3	$SF(C_6F_5)_2^+$	0.300	± 0.017	1
$C_6F_6^+$	0.136	± 0.007	1	$S_2N_2C_2H_3^+$	0.106	± 0.017	1	$SF_2CF_3^+$	0.088	± 0.009	2
$CH_2(SCl)N(SCl)CH_2^+$	0.404	± 0.007	1	$S_2NC_2(PhCH_3)_2^+$	0.333	± 0.017	1	$SF_2N(CH_3)_2^+$	0.105	± 0.017	1
$Cl_2C{=}NH_2^+$	0.087	± 0.017	1	$S_2NC_3H_4^+$	0.119	± 0.017	1	SF_3^+	0.053	± 0.011	4
Cl_2F^+	0.034	± 0.007	1	$S_2NC_4H_8^+$	0.131	± 0.017	1	$SFS(C(CF_3)_2)_2^+$	0.248	± 0.017	1
Cl_3^+	0.062	± 0.007	1	$S_3(CH_3)_3^+$	0.157	± 0.017	1	$SH_2C_3H_7^+$	0.109	± 0.017	1
ClF_2^+	0.032	± 0.016	4	$S_3Br_3^+$	0.169	± 0.007	1	SN^+	0.032	± 0.007	1
ClF_6^+	0.098	± 0.020	1	$S_3C_3H_7^+$	0.145	± 0.017	1	$(SNPMe_3)_3^+$	0.227	± 0.017	1
ClO_2^+	0.031	± 0.009	1	$S_3C_4F_6^+$	0.204	± 0.017	1	$SNSC(CH_3)N^+$	0.096	± 0.017	1
I_2^+	0.072	± 0.017	1	$S_3CF_3CN^+$	0.152	± 0.017	1	$SNSC(CN)CH^+$	0.103	± 0.017	1
I_3^+	0.131	± 0.007	1	$S_3Cl_3^+$	0.146	± 0.007	1	$SNSC(Ph)N^+$	0.182	± 0.017	1
I_5^+	0.210	± 0.014	2	$S_3N_2^+$	0.097	± 0.011	2	$SNSC(Ph)NS_3N_2^+$	0.267	± 0.017	1
IBr_2^+	0.095	± 0.017	1	$S_4N_3^+$	0.118	± 0.011	2	$SNSC(PhCH_3)N^+$	0.210	± 0.017	1
ICl_2^+	0.083	± 0.013	4	$S_4N_3(Ph)_2^+$	0.351	± 0.017	1	$(Te(N(SiMe_3)_2)_2^+$	0.547	± 0.017	1
IF_4^+	0.057	± 0.017	1	$S_4N_4H^+$	0.139	± 0.007	1	$Te(N_3)_3^+$	0.139	± 0.017	1
IF_6^+	0.104	± 0.014	2	$S_5N_5^+$	0.215	± 0.059	2	$Te_4Nb_3OTe_2I_6^+$	0.602	± 0.017	1
$N(S_3N_2)_2^+$	0.197	± 0.012	1	S_7I^+	0.213	± 0.011	3	$TeBr_3^+$	0.117	± 0.012	2
$N(SCl)_2^+$	0.115	± 0.017	1	$Sb(NPPh_3)_4^+$	1.54	± 0.017	1	$TeCl_3^+$	0.100	± 0.013	8
$N(SeCl)_2^+$	0.277	± 0.017	1	$Sb_2F_{11}^-$	0.227	± 0.020	4	$TeCl_3(15\text{-crown-}5)^+$	0.407	± 0.017	1
$N(SF_2)_2^+$	0.112	± 0.017	1	SBr_3^+	0.123	± 0.014	2	TeI_3^+	0.168	± 0.010	2
N_2F^+	0.029	± 0.007	1	$SCH_3O_2^+$	0.064	± 0.017	1	$Xe_2F_{11}^+$	0.184	± 0.007	1
NF_4^+	0.060	± 0.011	2	$SCH_3P(CH_3)_3^+$	0.153	± 0.017	1	$Xe_2F_3^+$	0.123	± 0.007	1
NO^+	0.010	± 0.010	7	$SCH_3PCH_3Cl_2^+$	0.162	± 0.017	1	XeF^+	0.045	± 0.012	1
NO_2^+	0.022	± 0.009	2	$SCl(C_2H_5)_2^+$	0.167	± 0.017	1	XeF_5^+	0.077	± 0.013	1
O_2^+	0.015	± 0.011	1								
$Al_2Cl_7^-$	0.275	± 0.012	1	SCN^-	0.044	± 0.008	1	$Te_2(esu)_4Br_2^{2+}$	0.596	± 0.018	3
$Co_2S_2(CO)_6^{2+}$	0.320	± 0.009	1	Se_{10}^{2+}	0.256	± 0.011	2	$Te_2(esu)_4Cl_2^{2+}$	0.588	± 0.015	1
$FeW(Se)_2(CO)^{2+}$	0.321	± 0.015	1	Se_{17}^{2+}	0.456	± 0.006	1	$Te_2(esu)_4I_2^{2+}$	0.612	± 0.018	1
I_4^{2+}	0.132	± 0.013	3	Se_{19}^{2+}	0.470	± 0.014	1	$Te_2Se_2^{2+}$	0.098	± 0.024	1
$Mo(Te_3)(CO)_4^{2+}$	0.221	± 0.015	1	$Se_2I_4^{2+}$	0.204	± 0.017	1	$Te_2Se_4^{2+}$	0.177	± 0.012	4
S_{19}^{2+}	0.466	± 0.009	1	$Se_3N_2^{2+}$	0.075	± 0.011	4	$Te_2Se_8^{2+}$	0.285	± 0.012	2
$S_2(S(CH_3)_2)_2^{2+}$	0.206	± 0.015	1	Se_4^{2+}	0.094		1	$Te_3S_3^{2+}$	0.162	± 0.009	3
$S_2I_4^{2+}$	0.204	± 0.009	1	$Se_4S_2N_4^{2+}$	0.195	± 0.015	2	Te_3Se^{2+}	0.099	± 0.024	1
$S_3N_2^{2+}$	0.061	± 0.009	2	Se_8^{2+}	0.214		1	Te_4^{2+}	0.115	± 0.011	4
$S_3NCCNS_3^{2+}$	0.167	± 0.009	1	SeI_4^{2+}	0.204	± 0.024	1	Te_7^{2+}	0.221	± 0.009	1
S_3Se^{2+}	0.623	± 0.009	1	$SeN_2S_2^{2+}$	0.067	± 0.009	1	Te_8^{2+}	0.200	± 0.006	1
$S_4N_4^{2+}$	0.123	± 0.021	4	$(SNP(C_2H_5)_3)_2^{2+}$	0.382	± 0.015	1	$VOCl_4^-$	0.148	± 0.006	1
$S_6N_4^{2+}$	0.165	± 0.006	1	$Te(trtu)_4^{2+}$	0.595	± 0.015	1	$W(CO)_4(\eta 3\text{-}Te)^{2+}$	0.220	± 0.017	1
S_8^{2+}	0.174	± 0.009	1	$Te(tu)_4^{2+}$	0.353	± 0.015	3	$W_2(CO)_{10}Se_4^{2+}$	0.447	± 0.017	1
$Sb_3F_{14}^-$	0.317	± 0.021	2								
$Bi_2Br_8^{2-}$	0.479	± 0.015	1	$Nb_2OCl_{10}^{2-}$	0.353	± 0.015	1	$SeS_2N_2^+$	0.089	± 0.007	1
$Bi_6Cl_{20}^{2-}$	0.875	± 0.015	1	$Se_3N_2^+$	0.096	± 0.007	1	$Te_2(su)_6^{4+}$	0.568	± 0.003	1
I_{15}^{3+}	0.636	± 0.015	1								

[a] Using the anion volumes generated in Table 5, the cation volumes listed are obtained. In some cases these cation volumes can be used to generate further anion volumes, as listed, e.g. $Al_2Cl_7^-$. [b] NB: su = selenourea, trtu = trimethylthiourea, esu = ethyleneselenourea, tu = thiourea, Ph = phenyl, [222] = cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane).

and hence using the parameters $\alpha = 117.3$ kJ mol^{-1} nm and $\beta = 51.9$ kJ mol^{-1} (applicable to an MX (1:1) salt) in eq 3, we predict that $U_{POT}([S_2^+][AsF_6^-]) \approx 541 \pm 36$ kJ mol^{-1}.

Turning to the tetrasulfur dication S_4^{2+}, there are no simple salts, so far reported, as being formed by the S_4^{2+} cation, other than ones having solvent molecules present in the lattice. So, for example, we find: $[S_4^{2+}][AsF_6^-]_2{\cdot}0.60\ SO_2$[47,48] and $[S_4^{2+}][AsF_6^-]_2{\cdot}0.9\ AsF_3$[49] have been prepared and characterized. In the absence of crystal structure data for the parent salt, $[S_4^{2+}][AsF_6^-]_2$, no volume can be estimated for the ion from

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Table 7. Lattice Potential Energies Compared; Full-Scale Computations vs Correlation Estimates[a]

salt	full scale computation of U_{POT} (kJ mol^{-1})	Born−Fajans−Haber thermochemical cycle calculation of U_{POT} (kJ mol^{-1})	thermochemical radii (Kapustinskii equation) correlation estimate of U_{POT} (kJ mol^{-1}) [cation, anion thermochemical radius/nm, $Z_+Z_-\nu$]	% error	ion volumes or formula unit volume (nm^3) [cation volume (source), anion volume (source), or crystal unit cell volume (nm^3), Z, $Z_+Z_-\nu$]	eq 3 parameters, α (kJ mol^{-1} nm) and β (kJ mol^{-1})	ion volume (V_+, V_-) or crystal structure volume (V) correlation estimate of U_{POT} (kJ mol^{-1})	% error
KBr	671[40]	682[40]	671 [0.133, 0.190, 2]	0	K^+= 0.00986 (Table 4); Br^- = 0.056 (Table 5)	α = 117.3 $\beta = 51.9$	685	2.1
BaO	3029[40]	3054[40]	3004 [0.143, 0.141, 8]	0.8	Ba^{2+}=0.0122 (Table 4); O^{2-} = 0.043 (Table 5)	α = 138.7 $\beta = 27.6$	3134	3.5
$KAsF_6$	566[45]		586 [0.133, 0.243, 2]	3.5	K^+ = 0.00986 (Table 4); $AsF_6{}^-$ = 0.110 (Table 5)	α = 117.3 $\beta = 51.9$	579	2.5
Cs_2ReCl_6	1398[13,14]		1351 [0.165, 0.237, 6]	3.4	Cs^+ = 0.01882 (Table 4); $ReCl_6{}^{2-}$ = 0.224 (Table 5)	α = 165.3 $\beta = -29.8$	1372	1.8
$I_4(AsF_6)_2$	1520 [45]		1495 [0.207, 0.243, 6]	1.6	$I_4{}^{2+}$ = 0.132 (Table 6); $AsF_6{}^-$ = 0.110 (Table 5)	α = 133.5 $\beta = 60.9$	1500	1.3
$Na[222]^+I^-$	358[30]		382 [0.388, 0.211, 2]	6.7	$Na[222]^+$ = 0.527 (Table 6); I^- = 0.072 (Table 5)	α = 117.3 $\beta = 51.9$	382	6.7
$K[222]^+I^-$	351[30]		381 [0.390, 0.211, 2]	8.5	$K[222]^+$ = 0.531 (Table 6); I^- = 0.072 (Table 5)	α = 117.3 $\beta = 51.9$	381	8.5
TiO_2 rutile	12150[32], 11830[32]	11914	11126 [0.080, 0.141, 24]	7.2	crystal cell volume[41] = 0.0624 $Z = 2$ $Z_+Z_-\nu = 24$	α = 138.7 $\beta = 27.58$	11233	6.3
TiO_2 anatase	(10163−12351)[32] 11860[32]		11126 [0.080, 0.141, 24]	3.7	crystal cell volume[32] = 0.1363 $Z = 4$ $Z_+Z_-\nu = 24$	α = 138.7 $\beta = 27.58$	10930	5.4
TiO_2 brookite	11820[32]		11126 [0.080, 0.141, 24]	5.9	crystal cell volume[32] = 0.26061 $Z = 8$ $Z_+Z_-\nu = 24$	α = 138.7 $\beta = 27.58$	11085	6.2
TiO_2−II	11810[32]		11126 [0.080, 0.141, 24]	5.8	crystal cell volume[32] = 0.122581 $Z = 4$ $Z_+Z_-\nu = 24$	α = 138.7 $\beta = 27.58$	11299	4.3
Ti_2O_3	14702[32] 14820[32]		14329 [0.072, 0.141, 30]	2.9	crystal cell volume[41] = 0.3106; $Z = 6$ $Z_+Z_-\nu = 30$	α = 138.7 $\beta = 27.58$	11991	18.8
Ti_3O_5	26580[32] (24594)[46]		25750 [0.069, 0.141, 53.3]	0.6	crystal cell volume[41] = 0.3467; $Z = 4$ $Z_+Z_-\nu = 53.3$	α = 138.7 $\beta = 27.58$	18174	28.9
Ti_4O_7	38409[32] (35445)[46]		37343 [0.068, 0.141, 77]	1.1	crystal cell volume[32] = 0.7160; $Z = 4$ $Z_+Z_-\nu = 77$	α = 138.7 $\beta = 27.58$	21074	42.9

[a] NB: $TiO_2 = Ti^{4+}(O^{2-})_2$; $Ti_2O_3 = (Ti^{3+})_2(O^{2-})_3$; $Ti_3O_5 = (Ti^{4+})_2Ti^{2+}(O^{2-})_5$; $Ti_4O_7 = (Ti^{4+})_3Ti^{2+}(O^{2-})_7$.

this source. However, we can estimate the volume of the tetrasulfur dication, $V(S_4^{2+})$ by extrapolation of the known ion volumes of Se_4^{2+} and Te_4^{2+} (Table 6) against their respective atomic covalent radii. Such an approach leads to the estimate that $V(S_4^{2+}) \approx 0.084$ nm^3 and hence to a lattice energy for $[S_4^{2+}][AsF_6^-]_2$. Prior to the development of the generalized eq 3 reported in this work, the possibility of being able to estimate the volume per formula unit for $[S_4^{2+}][AsF_6^-]_2$ would not have resulted in an estimate of the lattice energy for the salt since, apart from that for MX (1:1) salts, no equation existed which connected volumes and lattice enthalpy or energy for salts possessing MX_2 (2:1) stoichiometry. However, this present work now provides a means to estimate the lattice potential energy of such a salt, as well as for salts having other stoichiometries as well. Using the values for $\alpha = 133.5$ kJ mol^{-1} nm and for $\beta = 60.9$ kJ mol^{-1} in eq 3 with $|z_+||z_-|\nu = 6$ we now predict that $U_{POT}([S_4^{2+}][AsF_6^-]_2) = 1557$ kJ mol^{-1} and so can investigate further the energetics of stabilization of the solvated lattices and the lattice stabilization of the S_4^{2+} cation.[49] Using these two sets of data we can examine the energetics of the dimerization reaction $2[S_2^+][AsF_6^-]$ (c) → $[S_4^{2+}][AsF_6^-]_2$ (c) in the solid state and the lattice stabilization of the S_4^{2+} cation.

We have recently carried out an extended term by term calculation[49] of the lattice energy of a solvated form, finding a value for U_{POT} ($[S_4^{2+}][AsF_6^-]_2$. 0.9 AsF_3) = 1734 kJ mol^{-1}. If, for example, we wished to study the stabilization energy[49] provided by the incorporation of 0.9 molecule of AsF_3 solvent into the lattice, we would need also to know the lattice potential energy for the parent salt $[S_4^{2+}][AsF_6^-]_2$.

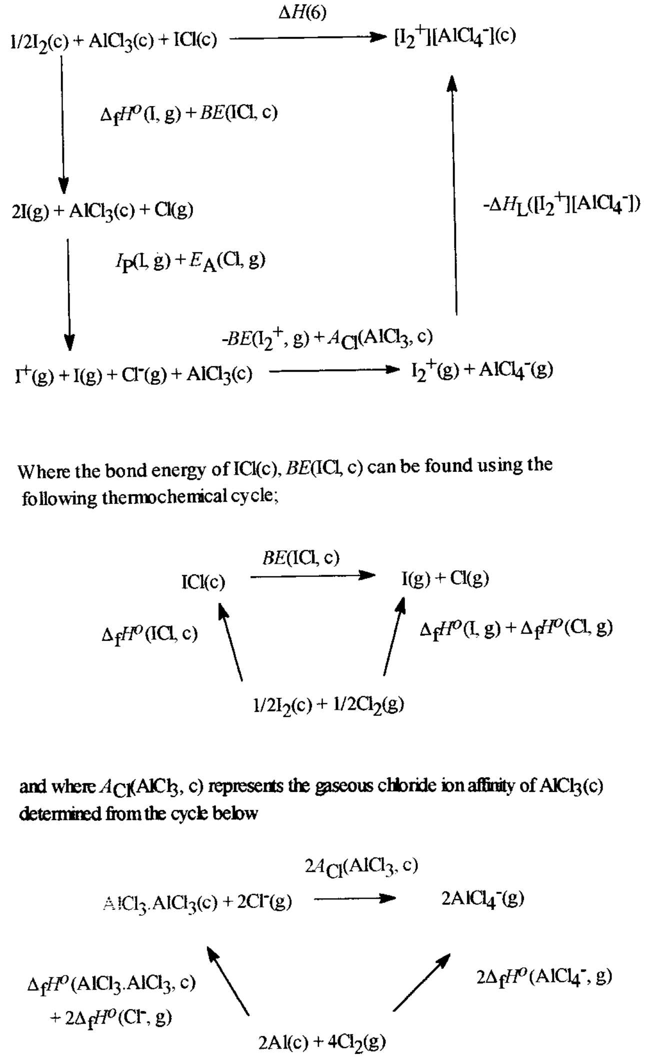
Additional Thermochemical Applications. Finally, to indicate the projected use of our new approach, we select a specific area of homopolyatomic cation chemistry on which to base a thermochemical study. We compare our two approaches: the Kapustinskii traditional treatment using our new set of thermochemical radii and the single ion volumes also generated in this paper.

In the literature the following experimental findings are reported. First $[I_2^+][AlCl_4^-]$ remains unsynthesized despite attempts to obtain the salt;[50] second, the $[I_3^+][AsF_6^-]$ salt is reported to be "moderately stable",[51] and it decomposes, either by hydrolysis, or slowly on prolonged storage in a sealed glass tube at −5 °C.[51] Brownridge and Passmore, in unpublished work, have observed using FT-Raman spectroscopy that solutions of $[I_3^+][AsF_6^-]$ in liquid sulfur dioxide disproportionate to give I_4^{2+} ($2I_2^+$) and I_5^+. We use our methodology to investigate the thermochemistry lying behind these three observations, considering each salt in turn. The examples were selected to encompass stable as well as unstable salts.

$[I_2^+][AlCl_4^-]$. Attempts by Corbett et al.[50] to synthesize $[I_2^+][AlCl_4^-]$ according to eq 6 were unsuccessful;

$$^1/_2 I_2\ (c) + AlCl_3\ (c) + ICl\ (c) \xrightarrow{\Delta H(6)} [I_2^+][AlCl_4^-]\ (c) \qquad (6)$$

The entropy change for this process will be negative (products more ordered than reactants) and therefore any stabilization will be *enthalpy* dependent. We can estimate the latter employing the cycle given in Figure 2. To estimate $\Delta H(6)$ the cycle requires us to estimate the lattice potential energy of $[I_2^+][AlCl_4^-]$, $U_{POT}[I_2^+][AlCl_4^-]$, where there is obviously no crystal structure data reported. Using the derived thermochemical radii[8] for the $[I_2^+]$ and $[AlCl_4^-]$ moieties we estimate, using the Kapustinskii equation,[9] $U_{POT}[I_2^+][AlCl_4^-]$ to be 450 ± 32 kJ mol^{-1} and via combination of single ion volumes, we find $U_{POT}[I_2^+][AlCl_4^-]$ to be 488 ± 25 kJ mol^{-1}. The estimates differ by 38 kJ mol^{-1} and average to 469 ± 41 kJ mol^{-1} and, by means of eq 2, the lattice enthalpy is calculated to be 473 ± 41 kJ mol^{-1}. The ancillary thermochemical data needed comprises the following data. For the estimation of the bond energy of the I−Cl bond in the crystalline salt, *BE* (ICl,c) [second cycle, Figure 2] we employ the standard enthalpy of formation of gaseous monoiodine,[52] $\Delta_f H°(I, g) = 107$ kJ mol^{-1}; the standard enthalpy of gaseous monochlorine,[52] $\Delta_f H°(Cl, g) = 122$ kJ mol^{-1} and the standard enthalpy of formation of crystalline ICl,[53] $\Delta_f H°(ICl, c) = -35$ kJ mol^{-1} leading to the prediction that $BE(ICl,c) =$ 264 kJ mol^{-1}. To estimate the chloride ion affinity of $AlCl_3$, $A_{Cl}(AlCl_3,c)$ [lower cycle, Figure 2] we require: the standard enthalpy of formation of $AlCl_3$ (c),[52] $\Delta_f H°(AlCl_3,c) = -706$ kJ mol $^{-1}$, the standard enthalpy of formation of gaseous



Where the bond energy of ICl(c), *BE*(ICl, c) can be found using the following thermochemical cycle;

and where $A_{Cl}(AlCl_3$, c) represents the gaseous chloride ion affinity of $AlCl_3$(c) determined from the cycle below

Figure 2. Thermochemical cycles for the preparation of $[I_2^+][AlCl_4^-]$ via preparative route (6).

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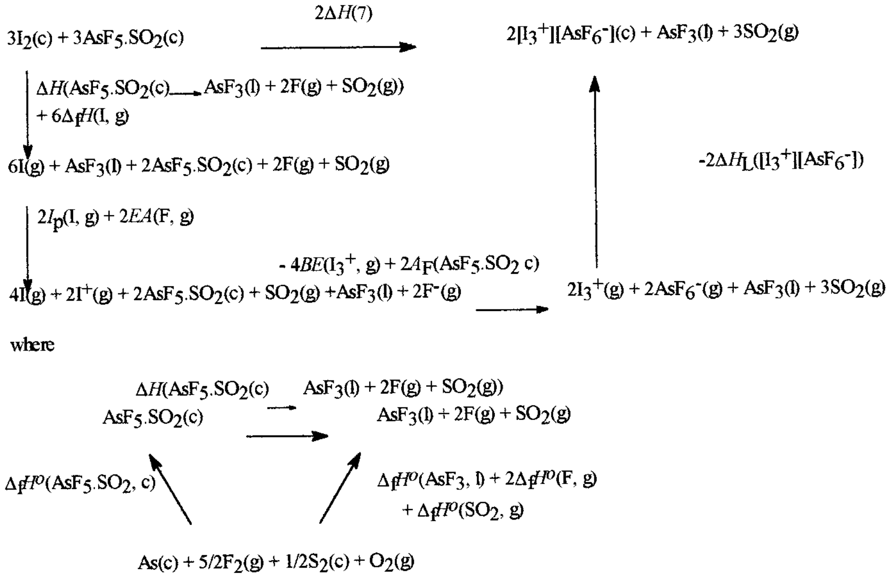

Figure 3. Thermochemical cycles for the preparation of $[I_3^+][AsF_6^-]$ via preparative route (**7**).

chloride ion,[54] $\Delta_f H°(Cl^-,g) = -227$ kJ mol^{-1} and the standard enthalpy of formation of the gaseous $AlCl_4^-$ ion,[55] $\Delta_f H°(AlCl_4^-,g) = -1196$ kJ mol^{-1}. The chloride ion affinity, $A_{Cl}(AlCl_3,c)$ is thus calculated to be -263 kJ mol^{-1}. Finally, to obtain an estimate of $\Delta H(6)$ [upper cycle, Figure 2] we require the bond enthalpy of gaseous $[I_2^+]$, $BE(I_2^+, g) = 253$ kJ mol^{-1} [56]; [i.e. for the process: $I_2^+(g) \rightarrow I^+(g) + I(g)$] estimated using the standard enthalpy I(g),[52] $\Delta_f H°(I,g) = 107$ kJ mol^{-1} and the enthalpy of formation of gaseous monoiodine cation,[54] $\Delta_f H°(I^+,g) = 1115$ kJ mol^{-1}, the electron affinity of gaseous Cl ($= -349$ kJ mol^{-1}), the ionization potential of gaseous I ($= 1008$ kJ mol^{-1}) and the enthalpy of formation of gaseous diiodide cation,[54] $\Delta_f H°(I_2^+,g) = 969$ kJ mol^{-1}. Employing the lattice potential energy value estimation: $\Delta H(6) = +45$ kJ mol^{-1}. Therefore, the route in eq 6 is endothermic (and $\Delta G(6)$ also positive) so accounting for the failure of Corbett et al. to prepare this salt via this synthetic route.

$[I_3^+][AsF_6^-]$. There a number of possible synthetic routes[61] which could be adopted in order to prepare homopolyiodine salts as hexafluoroasenic(V) salts, the most convenient being that of reaction 7.[51]

$$3\,I_2\,(c) + 3\,AsF_5{\cdot}SO_2\,(c) \xrightarrow{\Delta H(7)} 2\,[I_3^+][AsF_6^-]\,(c) + AsF_3\,(l) + 3\,SO_2\,(g) \quad (7)$$

For this reaction the entropy change, $\Delta S(7)$, is positive, and roughly equal to $3\,S°(SO_2,g) = 744.1$ J K^{-1} mol^{-1}, so making a favorable contribution to $\Delta G(7)$ with regard to the stability of the target salt. It is not possible to calculate the precise entropy contribution for reaction 7 as there is limited energetic data for the $AsF_5{\cdot}SO_2(c)$ adduct.

An estimation of the *enthalpy* change for reaction 7, $\Delta H(7)$, can be acquired via a thermochemical cycle such as that in Figure 3. The cycle in Figure 3 requires an estimate of the lattice potential energy of $[I_3^+][AsF_6^-]$, $U_{POT}([I_3^+][AsF_6^-])$, which is estimated via our new eq 3 employing the crystal structure data for the triclinic salt $[I_3^+][AsF_6^-]$[51] (with parameters: $a = 0.805$ nm, $b = 0.594$ nm, $c = 1.050$ nm, $\alpha = 103.1°$, $\beta = 89.0°$, $\gamma = 100.4°$, $Z = 2$). These parameters substituted into eq 4 lead to a value of $V = 0.241$ nm^3 ($V^{1/3} = 0.622$ nm) which, via eq 3 gives a value for $U_{POT}[I_3^+][AsF_6^-] = 481 \pm 25$ kJ mol^{-1}. Correcting for RT terms by means of eq 2, $\Delta H_L = 486 \pm 25$ kJ

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(56) *$BE(I_3^+,g) = 230$ kJ mol^{-1}*: [2 $BE(I_3^+,g)$ corresponds to the enthalpy change for the process: $I_3^+(g) \rightarrow 2I(g) + I^+(g)$]. We have considered several possible routes which lead to an estimate of the bond enthalpy term, $BE(I_3^+, g)$. (i) Consideration of the bond enthalpy terms required for the dissociation of the gaseous I_3^+ species. The dissociation of the gaseous molecule would require the cleavage of an $[I-I^+]$ bond (253 kJ mol^{-1} (derived from $BE(I_2^+,g) = \Delta_f H°(I,g) + \Delta_f H°(I^+,g) - \Delta_f H°(I_2^+,g)$) and subsequent cleavage of an [I–I] bond (150 kJ mol^{-1}). This approach has limitations since a more complex charge distribution exists within the I_3^+ cation than is inherent in the simplified view inferred above. This results in the estimate $BE(I_3^+,g) \approx 202$ kJ mol^{-1}; (ii) a lower limit can be set upon the bond energy term, $BE(I_3^+,g)$, by consideration of the work by Corbett et al.[50] and by considering that the compound $[I_3^+][AlCl_4^-]$ is of borderline stability and that ΔH for the reaction:

$$ICl(c) + I_2(c) + AlCl_3(c) \rightarrow [I_3^+][AlCl_4^-](c)$$

is approximately zero results in $BE(I_3^+,g) > 213 \pm 34$ kJ mol^{-1}. (iii) Finally, ab initio calculations at the B3PWPI/3121G* level[57] gave $BE(I_3^+,g) = 230$ kJ mol^{-1} (adopted value).
$4BE(I_4^{2+},g) \approx 79$ kJ mol^{-1}: [4BE(I_4^{2+},g) involves two strong and two weak bonds and corresponds to the enthalpy change which takes place during the process: $I_4^{2+}(g) \rightarrow 2I(g) + 2I^+(g)$]. Thermochemical cycles[58] can be employed to estimate the enthalpy of dimerization of gaseous I_2^+, $\Delta H_D(I_2^+,g)$ which is related, via $2BE(I_2^+,g)$ [$=2\Delta_f H°(I^+,g) + 2\Delta_f H°(I,g) - 2\Delta_f H°(I_2^+,g)$], to the term $4BE(I_4^{2+},g)$. This dimerization term, $\Delta H_D(I_2^+,g)$, is estimated[54] to be 429 kJ mol^{-1}. Using the fact that crystalline $[I_2^+][Sb_2F_{11}^-]$[59] and crystalline $[I_4^{2+}][AsF_6^-]_2$[58] have been synthesized.

$$[I_4^{2+}][Sb_2F_{11}^-]_2\,(c) \rightarrow 2[I_2^+][Sb_2F_{11}^-]\,(c)$$

$$2\,[I_2^+][AsF_6^-]\,(c) \rightarrow [I_4^{2+}][AsF_6^-]\,(c)$$

we are able[58] to estimate that $BE(I_4^{2+}) \approx 79$ kJ mol^{-1}.
$BE(I_5^+,g) > 177 \pm 7$ kJ mol^{-1}: [4$BE(I_5^+,g)$ corresponds to the enthalpy change for the process $I_5^+(g) \rightarrow 4I(g) + I^+(g)$]. We considered[58] two reactions for the formation of $[I_3^+][AsF_6^-]$ (that given in eq 7 above) and for $[I_5^+][AsF_6^-]$ the equation

$$5I_2(c) + 3AsF_5{\cdot}SO_2(c) \rightarrow 2\,[I_5^+][AsF_6^-]\,(c) + AsF_3(l) + 3\,SO_2(g)$$

Along with the value $BE(I_3^+,g)$ above, the enthalpy change of reaction 7 is estimated to be -44 ± 35 kJ mol^{-1}. From knowledge that the above reaction *does* proceed, it is possible to estimate the unknown bond enthalpy of the gaseous I_5^+ cation species whose lower limit we establish to be $BE(I_5^+) > 177 \pm 35$ kJ mol^{-1}.[58]

mol^{-1}. Ancillary thermochemical data needed are $\Delta_f H°(\mathrm{I, g})^{52} = 107$ kJ mol^{-1}, $\Delta_f H°(\mathrm{F, g})^{52} = 79$ kJ mol^{-1}, $\Delta_f H°(\mathrm{AsF_5, g})^{62} = -1237$ kJ mol^{-1}, $\Delta_f H°(\mathrm{SO_2, g})^{52} = -296.8$ kJ mol^{-1}, $\Delta H[\mathrm{SO_2(g) + AsF_5(g) \rightarrow AsF_5 \cdot SO_2(c)}]^{63} = -31$ kJ mol^{-1}, $\Delta_f H°(\mathrm{AsF_3,l})^{52} = -821$ kJ mol^{-1}, the ionization potential, $I_P(\mathrm{I,g})^{54} = 1008$ kJ mol^{-1}, the electron affinity, $\mathrm{EA(F, g)}^{54} = -328$ kJ mol^{-1}, the bond enthalpy, $BE(\mathrm{I_3^+, g})^{56} = 230$ kJ mol^{-1} and the fluoride ion affinity of the crystalline complex, $\mathrm{AsF_5 \cdot SO_2}$: $A_F(\mathrm{AsF_5 \cdot SO_2, c})^{58} = -402$ kJ mol^{-1}. The corresponding enthalpy change is estimated to be $\Delta H(7) = -44 \pm 35$ kJ mol^{-1} and hence using the estimation of $\Delta S(7)$ above leads us to predict $\Delta G(7) = -276$ kJ mol^{-1}, consistent with the observation that the $\mathrm{AsF_6^-}$ salt can be prepared as per eq 7. Thus we see that our predicted thermodynamics are such that they are consistent with the experimental observation that the $\mathrm{AsF_6^-}$ salt is stable with respect to the starting materials.

A possible decomposition mode for the salt $[\mathrm{I_3^+}][\mathrm{AsF_6^-}]$ can be considered, by analogy with the behavior in SO$_2$ solution, to be

$$3\,[\mathrm{I_3^+}][\mathrm{AsF_6^-}]\ (\mathrm{c}) \xrightarrow{\Delta H(8)} [\mathrm{I_5^+}][\mathrm{AsF_6^-}]\ (\mathrm{c}) + [\mathrm{I_4^{2+}}][\mathrm{AsF_6^-}]_2\ (\mathrm{c}) \quad (8)$$

This example is included because it illustrates the potential to develop and expand missing thermochemical data in the future on the basis of making sensible estimates initially (using approaches such as ours) and refining them later on the basis of experimental or other observations. In this way we can develop "bracketing" techniques for data which are gradually narrowed as further information is acquired. Thus, for example, using similar approaches to those described above we obtain an estimate for the enthalpy of reaction 8, $\Delta H(8) < +105 \pm 97$ kJ mol^{-1}. This upper limit estimation obtained for this decomposition reaction is derived from the lower limit placed upon the average bond enthalpy of the gaseous $\mathrm{I_5^+}$ species (the bond enthalpies of $\mathrm{I_3^+}$, $\mathrm{I_4^{2+}}$, and $\mathrm{I_5^+}$ have to be approximated because of the lack of certain gas-phase data required). Four bond enthalpy terms for the gaseous $\mathrm{I_5^+}$ species actually contribute to $\Delta H(8)$ and for these terms we cannot assign an absolute value but can only determine a lower limit: $BE(\mathrm{I_5^+,g})^{58} > 177$ kJ mol^{-1} . This presents a problem in interpreting the value we assign for $\Delta H(8)$. Since it would not be unreasonable to suppose that, in practice, the average bond enthalpy of the $\mathrm{I_5^+}$ is some 25 kJ mol^{-1} greater than our estimated lower limit we are left with the possibility that the actual value of $\Delta H(8)$ would be approximately zero or less, thus making the decomposition by the above route in eq 8 a possibility. Further experimentation in this area of chemistry will allow more precise thermochemical values to be assigned to the specific parameters involved and, in this way, we can use experimentation to improve our existing database for thermochemical magnitudes whose absolute values are not determined. At present, our method of estimation proves capable of providing useful indications of stabilities and likely decomposition modes for both existent and nonexistent materials.

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