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Single-Ion Values for Ionic Solids of Both Formation Enthalpies, $\Delta_f H(298)_{ion}$, and Gibbs Formation Energies, $\Delta_f G(298)_{ion}$

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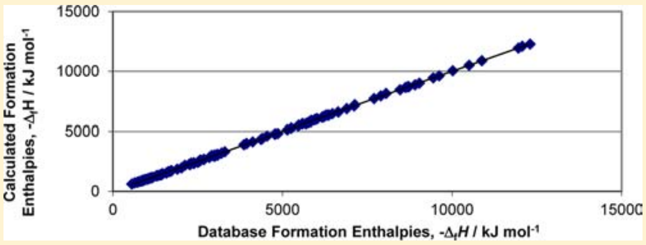
S Supporting Information



ABSTRACT: Formation enthalpies, $\Delta_f H(298)$, are essential thermodynamic descriptors of the stability of materials, with many available from the numerous thermodynamic databases. However, there is a need for predictive methods to supplement these databases with missing values for known and even hypothetical materials, and also as an independent check on the not-always reliable published values. In this paper, we present 34 additive single-ion values, $\Delta_f H(298)_{ion}$, from the formation enthalpies of 124 ionic solids, including an extensive group of silicates. In addition, we have also developed an additive set of 29 single-ion formation Gibbs energies, $\Delta_f G(298)_{ion}$, for a smaller group of 42 materials from within the full set, constrained by the limited availability of the corresponding experimental data. Such single-ion values may be extended among related materials using simple differences from known thermodynamic values, but always with critical consideration of the results. Using the excellent available data for silicates, we propose that the solid-state silicate ion formation enthalpies can be estimated as $-\Delta_f H(298)_{silicate}/\text{kJ mol}^{-1} = -252[n(\text{Si}) + n(\text{O})] - 27$, where $n(\text{X})$ represents the number of species X in the silicate. More speculatively, we estimate the contribution per silicon and oxygen species as -490 and -184 kJ mol^{-1}, respectively. Similarly, $-\Delta_f G(298)_{silicate}/\text{kJ mol}^{-1} = -266[n(\text{Si}) + n(\text{O})] - 7$, with the contribution per silicon and oxygen species being -140 and -300 kJ mol^{-1}, respectively. We compare and contrast these results with the extensive collection of "modified lattice energy" (MLE) ion parameters from the M.S. thesis of C. D. Ratkey. Our single-ion formation enthalpies and the MLE parameters may be used in complementary predictions. While lattice energies, U_{POT}, entropies, S°_{298}, and heat capacities, $C_{p,298}$, of ionic solids are reliably estimated as proportional to their formula volumes (using our Volume-Based Thermodynamic, VBT, procedures), this is not the case in general for thermodynamic formation properties, other than within select groups of related materials.

■ INTRODUCTION

A principal application of thermodynamics for chemists and engineers is the assessment of the stability of materials, whether natural, manufactured, or even hypothesized. In such assessments, enthalpy plays a central role through its association with the strength of interaction of constituent atoms or ions. A secondary role is played by entropy as a measure of the chaotic effects of rising temperature in inducing weakening and destruction of the interactions. These properties are conveniently combined in the Gibbs energy which encapsulates their relative influence under conditions of fixed pressure (typically, ambient) over changes of temperature:

$$\Delta G = \Delta H - T\Delta S$$

There exist extensive tables of these three thermodynamic properties.[1] However, the measurement of these properties for a material requires expertise and is time-consuming, so that it is not embarked upon lightly. As a consequence, and also of the need for values of new and hypothesized materials, there will always be gaps in the tables which need to be filled by predictive methods.[2] Predictive methods also provide independent checks on published results.

Over the past decade and more, colleagues and I have developed a number of empirical predictive methods for ionic solids and liquids. The most significant of these has been Volume-Based Thermodynamics (VBT)[3] which demonstrates that many thermodynamic properties (both thermal and mechanical) are linearly correlated with molar (strictly, formula unit) volume. In addition, we have more recently shown that the thermodynamic and thermomechanical properties (such as volume,[4] entropy,[5] heat capacity,[6] compressibility[7]) of the constituent ions of ionic materials are broadly additive. These two observations are of great utility since the resultant methods are complementary, require only that most readily experimentally available thermodynamic property, density (and, thereby, molar volume), or lists of additive ion properties, to easily generate profound results otherwise unavailable.

The most widely useful and accessible thermodynamic property is formation enthalpy, $\Delta_f H$, but even this is—of necessity—incomplete. The present contribution adds both single-ion formation enthalpies and a more limited set of single-ion formation Gibbs energies, $\Delta_f G$, to the growing list of

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additive ion properties by collecting data for a wide range of ionic materials, including many silicate minerals. The silicate mineral data is based on the extensive, internally consistent thermodynamic data set of Holland and Powell (H&P)[8] which we have often used, also in its earlier incarnations, in the development of our predictive methods.

Generation of Internally-Consistent Single Ion Formation Enthalpies, $\Delta_f H_{ion}$. Supporting Information, Table S1 lists formation enthalpies of 124 ionic solids collated from the NIST-NBS database[1e] and from the H&P database.[8b] This is essentially the same set of materials as contained in our recent analysis of their room temperature heat capacities.[6]

In determining our optimized set of single-ion formation enthalpies, the formation enthalpy of water of crystallization was fixed at −285.8 kJ mol^{-1}, as determined in our earlier work,[9] thus serving as a reference value for the set of single-ion values. Ion enthalpies for the 34 single ions contained in the list were set at initial arbitrary values (such as 0, 50, and 100 kJ mol^{-1} in different runs) and the resultant ion sums for the solids generated. The differences squared between these sums and the database formation enthalpies were summed to yield a sum-of-squares of differences. This sum was minimized using the Excel SOLVER routine,[10] with no constraints applied. A reliable minimum in the set of single ion values was readily obtained (differing slightly using different starting values), and a set of these values is listed in Table 1. This data set was subjected to a jackknife process, whereby the SOLVER routine was repeatedly run, omitting each ionic material in succession, to generate averages and standard deviations for each of the single ion values. These are also listed in Table 1. Figure 1 plots the summed formation enthalpies against the database values, with a slope and correlation coefficient indistinguishable from 1.

Notable omissions from our optimized set of single-ion enthalpies are those of the fluoride and oxide anions, F^- and O^{2-}. These have been deliberately omitted since the values generated are rather unreliable. Their variable behavior in different materials is ascribed to the high charge density of these species, strongly affecting their interactions with neighbors in ionic solids. Nevertheless, a usable value for the F^- ion is included, based upon optimization within the five alkali halides only.

A data set of about 800 values of critically selected formation enthalpies is collected in the M.S. thesis of C. D. Ratkey,[12] containing not only recognized ionic salts but also large numbers of more problematic materials such as sulfides, azides, nitrides, and so forth. This set was here subjected to the same single-ion analysis as described above for the current data set with very poor results, especially for the simpler salts (such as a −20% error for NaCl) — this latter is a natural consequence of minimizing the sum-of-squares of differences, which effectively gives lesser weighting to the differences for the smaller values. The resulting poor general fit to this wide set of materials confirms that the single-ion additivities that we have here established apply to strictly ionic materials, and care should be observed for application to materials where there are increased levels of covalency, such as those with anions similar to those mentioned above, or cations such as silver, thallium, and even copper. Such effects may be observed in Supporting Information, Table S3, which lists formation enthalpies of 111 solids from Ratkey[12a] together with ion-summed formation enthalpies using our single-ion data in Table 1, sorted by % difference. It is notable that the errors for materials for which we might expect covalency are large (both negative and positive), while the results for the more strictly ionic materials are generally more satisfactory.

Table 1. Thirty-Four Single-Ion Solid-State Formation Enthalpies, $-\Delta_f H(298)_{\text{ion}}$, As Optimized against a Set of 124 Ionic Solids (see Supporting Information, Table S1), Where *N* Is the Total Number of Each Type of Ion in the Data Set

	optimized	mean[a]	StdDev[a]	N[b]
Li^+	310.4	*308.7*	1.0	4.0
Na^+	278.3	*278.3*	1.3	19.0
K^+	316.0	*316.0*	1.3	9.0
Rb^+	311.7	*311.7*	1.0	2.0
Cs^+	315.4	*315.4*	1.0	2.0
Mg^{2+}	491.4	*491.4*	2.1	80.0
Ca^{2+}	579.8	*579.8*	2.1	50.0
Sr^{2+}	627.2	*627.2*	3.4	10.0
Ba^{2+}	655.0	*655.0*	2.8	5.0
Mn^{2+}	262.9	*262.9*	2.1	19.0
Fe^{2+}	138.5	*138.5*	2.1	53.0
Cu^{2+}	0.0	*0.0*	0.0	4.0
Ni^{2+}	126.6	*126.7*	5.3	3.0
Co^{2+}	161.8	*161.8*	2.0	2.0
Al^{3+}	630.1	*630.1*	3.2	95.0
La^{3+}	785.9	*785.9*	5.9	4.0
Cr^{3+}	282.1	*282.1*	3.1	5.0
Fe^{3+}	208.2	*208.2*	3.2	8.0
F^-	(−257)[d]			5
Cl^-	110.8	*110.8*	1.5	20.0
Br^-	66.3	*66.3*	2.3	6.0
I^-	−8.2	*-8.2*	2.1	8.0
OH^-	228.6	*228.6*	1.1	132.0
ClO_3^-	68.5	*68.5*	1.4	2.0
BrO_3^-	39.7	*39.7*	1.4	2.0
CO_3^{2-}	594.3	*594.3*	2.8	5.0
SO_4^{2-}	812.2	*812.2*	2.0	34.0
SiO_3^{2-}	1056.9	*1056.9*	2.1	26.0
SiO_4^{4-}	1198.5	*1198.5*	4.2	41.0
SiO_5^{6-}	1344.4	*1344.4*	6.4	10.0
$Si_2O_5^{2-}$	1962.7	*1962.7*	2.3	14.0
$Si_2O_7^{6-}$	2246.4	*2246.4*	7.1	4.0
$Si_3O_{10}^{8-}$	3315.1	*3315.1*	8.4	13.0
$Si_5O_{18}^{16-}$	5660.3	*5660.3*	17.1	3.0
$Si_4O_{11}^{6-}$	4098.6	*4098.6*	6.3	16.0
H_2O	285.8[c]			105.5

[a]The means and standard deviations were determined using a "jackknife" procedure, as described in the text. [b]N = number of ions included in the fitting set of ionic materials. [c]The value of −285.8 kJ mol^{-1} for water of crystallization[9] was kept fixed during the optimizations. This ensures that the features of our TDR (Thermodynamic Difference Rule)[11] for prediction of the values for hydrates is preserved, in the form

$$[\Delta_f H(298)(M_pX_q\cdot nH_2O,\ s) - \Delta_f H(298)(M_pX_q,\ s)]/\mathrm{J\,K^{-1}\,mol^{-1}}$$
$$\approx n\,\Theta_H(H_2O,\ \text{s-s}) = -285.8n$$

[d]$\Delta_f H(298)\{F^-,s\}$ is the optimized value using the five alkali halides only.

Generation of Internally-Consistent Single Ion Formation Gibbs Energies, $\Delta_f G_{ion}$. We have been able to collect a set of Gibbs formation energies, $\Delta_f G$, using the facilities of the HSC Chemistry program and database.[1h] This is an incomplete

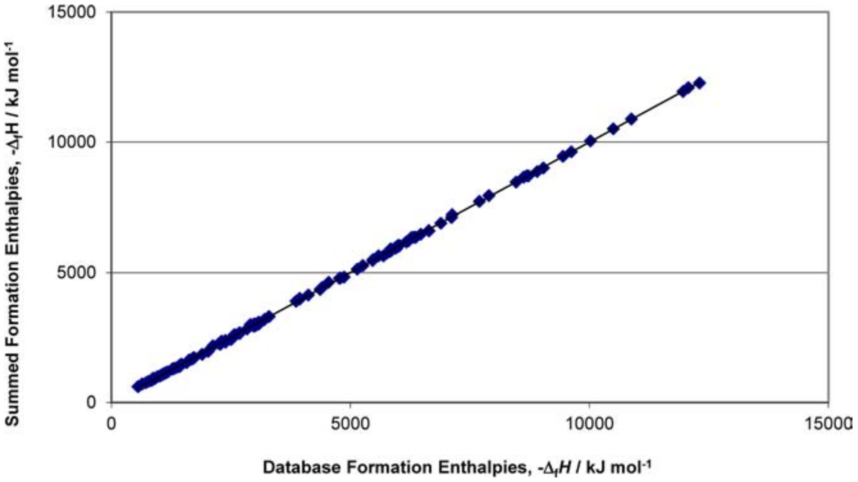

Figure 1. Plot of the summed single-ion formation enthalpies of 124 ionic materials against their database formation enthalpies, as listed in Supporting Information, Table S1. The plotted line has the formula $-\Delta_fH(\text{sum})/\text{kJ mol}^{-1} = -0.9988\ (\pm 0.0010)\ \Delta_fH(\text{database}) - 5.2\ (\pm 5.1)$ or, since the intercept is statistically indistinguishable from zero, $-\Delta_fH(\text{sum}) = -0.9996\ (\pm 0.0006)\ \Delta_fH(\text{database})$.

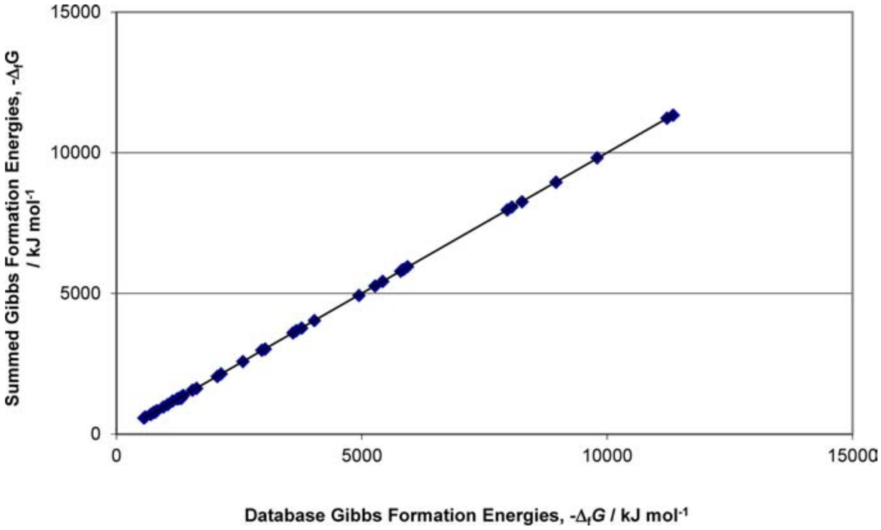

Figure 2. Plot of the summed single-ion formation Gibbs energies of 42 ionic materials against their database formation Gibbs energies, as listed in Supporting Information, Table S2. The plotted line has the formula $-\Delta_fG(\text{sum})/\text{kJ mol}^{-1} = -0.9998\ (\pm 0.006)\ \Delta_fG(\text{database}) - 1.3\ (\pm 3.0)$ ($R^2 = 1$) or, since the intercept is statistically indistinguishable from zero, $-\Delta_fG(\text{sum}) = -1.000\ (\pm 0.0004)\ \Delta_fG(\text{database})$.

set of our current enthalpy database since many of the experimental values are missing. Nevertheless, we can present these results in the plot of Figure 2. The corresponding set of single-ion Gibbs energies is presented in Table 2. Since no hydrates are included in this list, no anchoring value was available for the SOLVER optimization; however, the single-ion enthalpies were used as starting values and generated satisfactory results.

■ RESULTS AND DISCUSSION

Since our fitted data set includes a large number of silicate species, it is worthwhile to consider their formation enthalpies in detail. Figure 3 plots their values of $-\Delta_fH$ versus the number of atoms (Si + O) in each anion, with values ranging from 4 to 23, and Figure 4 is a corresponding plot of values of Δ_fG.

Using the data from the fitted lines in Figure 3, we may estimate (from the difference in intercept) the contribution of each Si to the formation enthalpy of silicates as -490 kJ mol^{-1} and then, by difference, the contribution per O is roughly -184 kJ mol^{-1}. We now use these results to estimate the single-ion formation enthalpy of $Si_3O_{10}^{8-}$, for which we have already established (see Table 1) the value -3315 kJ mol^{-1}. From the fitted linear relation, we find a value of -3249 kJ mol^{-1} while, from the independent atom sum, -3310 kJ mol^{-1}. These results are most satisfactory.

Similarly, using the data from the fitted lines in Figure 4, we may estimate (from the difference in intercept) the contribution of each Si to the Gibbs energy of silicates as -140 kJ mol^{-1} and then, by difference, the contribution per O is roughly -300 kJ mol^{-1}.

We have tested the relation between formation enthalpies and formula volume for these ionic materials, and find that the correlation is very poor indeed, in contrast to the excellent VBT volume-correlation for lattice energies and entropies.[13] We ascribe this significant difference to the fact that the formation properties are calculated as differences relative to the properties of the independent constituent elements, whereas lattice energies and entropies are internal properties of the materials concerned. However, such volume correlations do tend to work well within a group of related materials.[14]

Table 2. Twenty-Nine Solid-State Single-Ion Formation Gibbs Energies, $-\Delta_f G(298)_{\text{ion}}$, As Optimized against a Set of 42 Ionic Solids, Where N Is the Total Number of Each Type of Ion in the Data Set

	optimized	mean	StdDev	N
Li^+	259.7	*259.8*	7.6	2.0
Na^+	232.0	*232.2*	7.6	7.0
K^+	258.6	*258.7*	7.6	2.0
Rb^+	257.3	*257.4*	7.6	2.0
Cs^+	260.3	*260.4*	7.6	2.0
Mg^{2+}	374.1	*374.0*	14.1	37.0
Ca^{2+}	466.7	*468.2*	14.5	17.0
Sr^{2+}	558.7	*558.7*	5.2	3.0
Ba^{2+}	570.0	*570.1*	13.0	2.0
Mn^{2+}	161.3	*161.3*	14.5	4.0
Fe^{2+}	33.6	*32.3*	14.1	19.0
Al^{3+}	462.2	*462.5*	21.5	23.0
La^{3+}	595.1	*595.3*	22.7	2.0
Cr^{3+}	85.5	*85.6*	22.7	2.0
Fe^{3+}	62.8	*60.0*	21.3	2.0
F^-	(−265)[a]			5
Cl^-	113.7	*113.7*	5.2	6.0
Br^-	70.6	*70.6*	2.6	2.0
I^-	0.0	*0.0*	0.0	2.0
OH^-	247.7	*247.9*	7.0	38.0
CO_3^{2-}	583.1	*582.7*	15.4	1.0
SO_4^{2-}	802.4	*802.3*	15.1	16.0
SiO_3^{2-}	1090.8	*1090.1*	14.3	4.0
SiO_4^{4-}	1300.4	*1300.8*	28.4	12.0
SiO_5^{6-}	1522.0	*1520.9*	43.6	3.0
$Si_2O_5^{2-}$	1920.6	*1920.0*	14.7	5.0
$Si_2O_7^{6-}$	2364.8	*2361.2*	43.3	2.0
$Si_3O_{10}^{8-}$	3479.0	*3476.7*	57.5	3.0
$Si_5O_{18}^{16-}$	6048.4	*6050.0*	114.3	1.0
$Si_4O_{11}^{6-}$	4109.1	*4108.7*	42.9	8.0
$H_2O(s)$[b]	237.1			

[a] $\Delta_f H(298)\{F^-,s\}$ is the optimized value using the five alkali halides only. [b] The value of −237.1 kJ mol^{-1} for water of crystallization[9] is noted for convenient additive use in estimation of hydrate Gibbs formation energies, if required.

Finally, we compare our results to those of Ratkey and Harrison[12b] who established a much larger set (75 cations and 42 anions) of ion properties which provide generally reasonable formation enthalpy values (within about 5%), but with a number of large outliers. This is at the expense of requiring three parameters for each ion, namely, a measure of the lattice energy (through the Kapustinskii equation[15]), a cation electronegativity or anion electron affinity, and a measure of the van der Waals forces present for the ion, together with a slightly complex combination scheme. Each of these parameters was adjusted for best fit to the set of formation enthalpies, in what is termed the MLE ("modified lattice energy") method. Obviously, adjustment of the three parameters provides greater flexibility to the fit than does our simple ion additive property. Additional ion parameters cannot, however, be independently developed from the published set because of the need for a statistical fitting process, nor can the values be used for materials with multiple ions, such as $CaMgSiO_4$. The resultant fit of the calculated to experimental formation enthalpies is shown in Figure 5.

Tests of Data. Our data set does not include the alkali halides, so they can provide a useful test of our single-ion values since their thermodynamic values are well-established. Table 3 compares the enthalpy and Gibbs energy ion-sums with literature values for the alkali halides.

It is notable that the errors are sometimes quite large, reflecting the fact noted above that the values have been optimized for the more complex ionic solids. Nevertheless, even within this limitation, the single-ion values can be reliably utilized to generate enthalpies and even estimate Gibbs energies for the *mixed* alkali halides, as seen in Table 4. There are no literature values for these Gibbs energies, so the single-ion sums provide valuable starting points.

In developing single-ion thermodynamic values, it is often easy to find literature errors. We have noted that the thermodynamic values reported[1h,19] for $Cr_2(SO_4)_3 \cdot 18H_2O$ are seriously in error. For example, the formation enthalpy is reported as −609 kJ mol^{-1}, while a single-ion summation yields −8145 kJ mol^{-1}. This value is supported by summing the formation enthalpy of the parent $Cr_2(SO_4)_3$ with 18 water

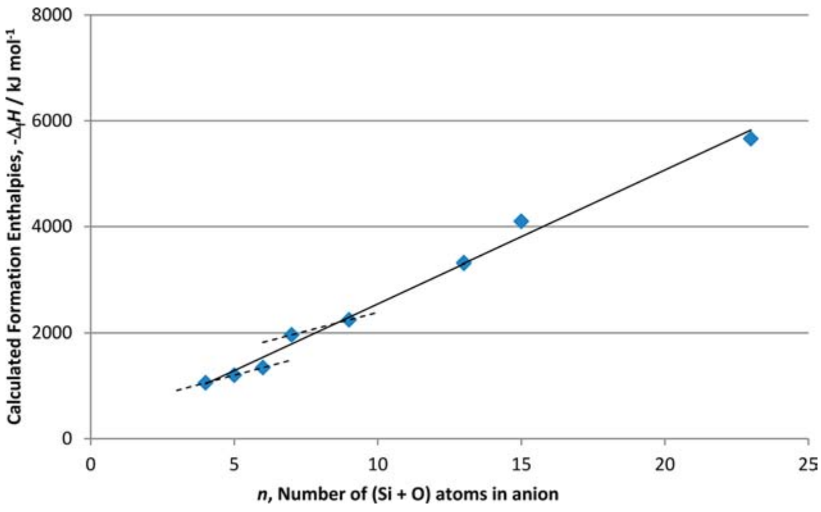

Figure 3. Plot of formation enthalpies, $-\Delta_f H$/kJ mol^{-1}, of 73 silicate species against the number of atoms (Si + O), n, in each type of anion. There is a general relation: $-\Delta_f H/\text{kJ mol}^{-1} = -252.0n - 27$ ($R^2 = 0.990$), and there is sufficient data to establish that for species containing only one Si (lower broken line), $-\Delta_f H/\text{kJ mol}^{-1} = -144n - 481$ ($R^2 = 1$) and for two Si (upper broken line), $-\Delta_f H/\text{kJ mol}^{-1} = -142n - 970$ ($R^2 = 1$).

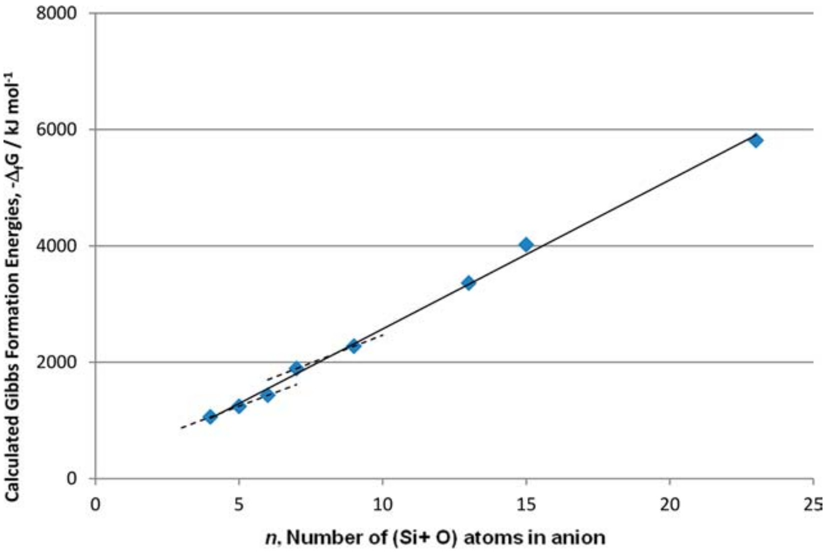

Figure 4. Plot of formation Gibbs energies, $-\Delta_f G$/kJ mol^{-1}, of 24 silicate species against the number of atoms (Si + O), *n*, in the anion. There is a general relation: $-\Delta_f G$/kJ mol^{-1} = $-265.6n - 7.0$ ($R^2 = 0.999$), and there is sufficient data to establish that for species containing only one Si (lower broken line), $-\Delta_f G$/kJ mol^{-1} = $-215.6n - 226$ ($R^2 = 1$) and for two Si (upper broken line), $-\Delta_f G$/kJ mol^{-1} = $-222n - 366$ ($R^2 = 1$).

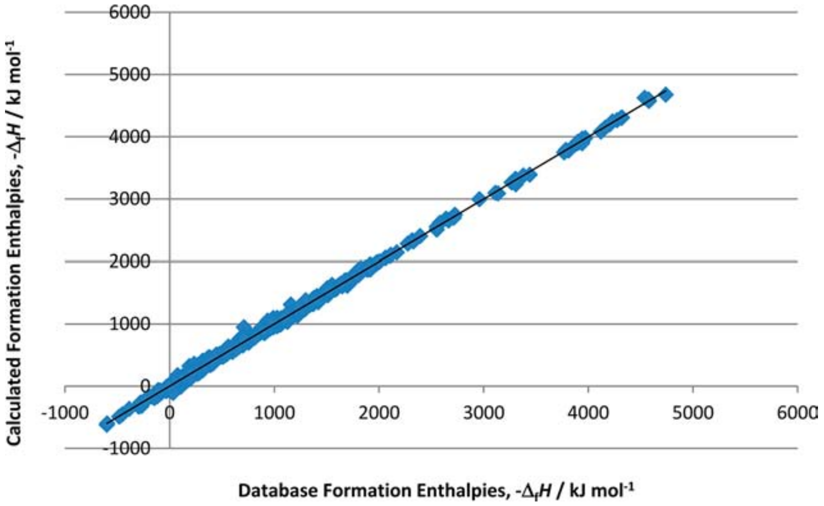

Figure 5. Plot of formation enthalpies, $-\Delta_f H$/kJ mol^{-1}, calculated by the MLE method of Ratkey and Harrison[12b] against experimental formation enthalpies.[16] The fitted line has the formula: $-\Delta_f H_{calc}$/kJ mol^{-1} = -0.9989 (± 0.0014) $\Delta_f H_{expt} - 1.50$ (± 1.77), $R^2 = 0.9984$.

molecules, yielding $-[2910.8 + 18 \times 285.8] = -8055$ kJ mol^{-1}. Another value may be estimated by adding the formation enthalpies of four water molecules to that of $Cr_2(SO_4)_3 \cdot 14H_2O$, yielding $-[7439.4 + 4 \times 285.8] = -8583$ kJ mol^{-1}; this last value is probably the most reliable since the reference tetradecahydrate is closest in composition to the calculated octadecahydrate.

We have tested these results by extensive cross-comparison of our enthalpy ion-summations with the MLE summations of Ratkey and Harrison,[12b] as may be seen in Figure 6, using the 136 data in Supporting Information, Table S3.

The graph shows clustering of the results, but with large outliers. These are most obvious for the Ratkey list (open red circles), which includes many materials with significant covalency. The ion sum method has been applied to a more selected set of ionic solids (filled blue circles) with a consequent reduction in the outliers. It is also noticeable that the vertical spread of the ion-sum differences around zero is less than the horizontal spread for the MLE differences, even among the selected ionic solids; the corresponding standard deviations are listed in the legend to Figure 6. In spite of the many large errors in prediction, an inspection of Supporting Information, Table S3 will demonstrate that the less covalent materials receive adequate prediction of their formation enthalpies.

As earlier mentioned, the high charge-density anions, F^- and O^{2-}, may generate unreliable results from simple differences if unwisely applied. For example, if Cs_2O is used as an enthalpy reference (with $\Delta_f H(298) = -345.8$ kJ mol^{-1}), then $\Delta_f H(298)\{O^{2-}\} = +285.0$ kJ mol^{-1}, so that $\Delta_f H(298)\{Rb_2O\} = -338.4$ kJ mol^{-1}, which compares very well with an experimental value of -339.0 kJ mol^{-1}, while $\Delta_f H(298)\{Li_2O\} = -335.7$ kJ mol^{-1} calculated for the considerably smaller and so charge-dense Li^+ ion, differs considerably from the experimental value of -597.9 kJ mol^{-1}.

Table 3. Comparison of Literature-Published and Ion-Summed Enthalpies for the Alkali Halides As Well As Corresponding Values of Their Gibbs Energies, Together with the Percentage Differences

	kJ mol^{-1}			kJ mol^{-1}		
	Δ_fH(lit)[a]	Δ_fH(sum)	% diff.	Δ_fG(lit)	Δ_fG(sum)	% diff.
LiF	−616.9	−567.4	8.0	−588.7	−540.1	8.3
LiCl	−408.6	−421.2	−3.1	−384.0	−377.8	1.6
LiBr	−350.9	−376.8	−7.4	−341.6	−340.4	0.4
LiI	−270.1	−302.3	−11.9	−269.7	−275.5	−2.1
NaF	−575.4	−535.3	7.0	−545.1	−512.0	6.1
NaCl	−411.2	−389.1	5.4	−384.0	−349.7	8.9
NaBr	−361.1	−344.7	4.6	−349.3	−312.3	10.6
NaI	−287.8	−270.1	6.1	−284.5	−247.4	13.0
KF	−568.6	−573.0	−0.8	−538.9	−539.0	0.0
KCl	−436.7	−426.8	2.3	−408.8	−376.7	7.9
KBr	−393.8	−382.4	2.9	−380.4	−339.3	10.8
KI	−327.9	−307.8	6.1	−323.0	−274.4	15.1
RbF	−557.7	−568.7	−2.0	−528.5	−537.7	−1.7
RbCl	−435.3	−422.5	3.0	−407.8	−375.4	7.9
RbBr	−394.6	−378.0	4.2	−381.8	−338.0	11.5
RbI	−333.9	−303.5	9.1	−329.0	−273.1	17.0
CsF	−554.7	−572.4	−3.2	−525.4	−540.7	−2.9
CsCl	−443.0	−426.2	3.8	−414.4	−378.4	8.7
CsBr	−405.4	−381.7	5.8	−391.0	−341.0	12.8
CsI	−346.6	−307.2	11.4	−340.6	−276.1	18.9

[a] Reference 1b.

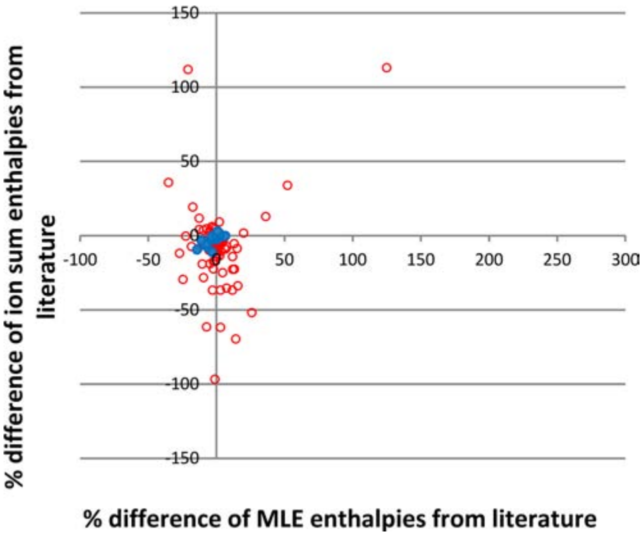

Figure 6. Plot of the % differences between selected literature values of formation enthalpies[12a,16,20] using both the current single-ion sum method and the MLE method of Ratkey and Harrison. The filled blue circles represent ionic solids from the current list (standard deviation of % difference by ion-sum method: 3.3; by MLE method: 4.8) while the open red circles represent the much wider set of materials in the Ratkey list, including many with some covalent characteristics (standard deviation by ion-sum method: 24.0; by fitted MLE method: 16.0).

CONCLUSIONS

We have established adequately reliable sets of additive single-ion formation enthalpies and formation Gibbs energies for ionic solids, including many silicate minerals, which can be used to predict the corresponding thermodynamic data, and can be extended by appropriate difference to related materials. An extensive set of parameters for enthalpy of formation for a wide range of materials with less certain ionicity has been prepared by Ratkey and Harrison, but this set cannot readily be extended, nor can it be applied to materials with multiple differing cations, such as $CaMgSiO_4$ since there is no provision for such extension. While the latter set also cannot be applied to hydrates, their formation enthalpies may be estimated from an anhydrated value by using our additive contribution of −285.8 kJ per mole of water in the chemical formula.

As a general recommendation, we suggest that all available methods be used with critical consideration of the results when

Table 4. Comparison of Literature-Published and Ion-Summed Enthalpies for Examples of Some Mixed Alkali Halides Together with the Percentage Differences, As Well As Corresponding Estimates of Their Gibbs Energies

	Δ_fH(lit)[a]	Δ_fH(sum)	% diff.	SSA[b]	Δ_fH mean of cols. (2) and (4)	% lit. diff	Δ_fG(sum)	DFT SSA[c]	Δ_fG mean of cols. (7) and (8)
column number	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
LiNaClI	−694.1	−691.4	0.4	−688.9	−690.1	0.6	−691.4	−661.1	−676.2
LiKClI	−736.4	−729.0	1.0	−721.9	−725.4	1.5	−729.0	−692.8	−710.9
NaKClI	−736.7	−696.9	5.4	−727.5	−712.2	3.3	−696.9	−700.2	−698.5
KCsClI	−780.3	−734.0	5.9	−777.2	−755.6	3.2	−734.0	−743.4	−738.7
$KRbCl_2$	−873.9	−849.2	2.8	−872.1	−860.7	1.5	−849.2	−816.6	−832.9
$NaKI_2$	−610.4	−578.0	5.3	−615.9	−596.9	2.2	−578.0	−607.5	−592.7
$NaKBr_2$	−748.9	−727.0	2.9	−754.8	−740.9	1.1	−727.0	−729.7	−728.4
$NaKCl_2$	−839.0	−815.9	2.8	−847.9	−831.9	0.8	−815.9	−792.8	−804.3
				DFT SSA[c]		% diff. cols. (2)−(5)			
Cs_3LiF_4		−2284.6		−2283.6	−2284.1	0.0	−2162.1	−2164.9	−2163.5
Cs_3LiCl_4		−1699.7		−1734.5	−1717.1	−1.0	−1512.9	−1627.2	−1570.1
Cs_3LiBr_4		−1522.0		−1567.1	−1544.5	−1.5	−1363.2	−1514.6	−1438.9
Cs_3LiI_4		−1223.9		−1310.5	−1267.2	−3.5	−1103.7	−1291.5	−1197.6

[a] Reference 1b. [b] Value generated by the Simple Salt Approximation (SSA),[17] by adding the formation enthalpies (or Gibbs formation energies) of the contributing alkali halides. [c] Value generated by adding the formation enthalpies (or Gibbs formation energies) of the contributing alkali halides and subtracting the very small DFT-calculated stabilization energies.[18] An arbitrary selection has here been made from the 28 compositions in the series CsX−LiX (X = F, Cl, Br, I) which have been considered. The full sets may be found in Supporting Information, Tables S5 and S6.

attempting the prediction of an unknown thermodynamic quantity, as well as comparison with values for related materials.

■ ASSOCIATED CONTENT

S Supporting Information

Table S1 lists the literature and ion-summed formation enthalpies of 124 ionic solids, using the single-ion data in Table 1. Table S2 lists the literature and ion-summed formation Gibbs energies of 42 ionic solids using the single-ion data in Table 2. Table S3 lists formation enthalpies of 111 solids from Ratkey and Harrison[12a,b] together with ion-summed formation enthalpies using the single-ion data in Table 1, sorted by % difference, MLE formation enthalpies, and their % differences. In addition, Table S3 lists those 25 ionic solids from the current list whose formation enthalpies may be calculated using the MLE data of Ratkey and Harrison. Table S4 lists reference values for $\Delta_f H$ and $\Delta_f G$ for the alkali halides, used in evaluating the corresponding values for the mixed alkali halides in Tables S5 and S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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