Thermodynamic Estimation: Ionic Materials

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Abstract

Thermodynamics establishes equilibrium relations among thermodynamic parameters ("properties") and delineates the effects of variation of the thermodynamic functions (typically temperature and pressure) on those parameters. However, classical thermodynamics does not provide values for the necessary thermodynamic properties, which must be established by extra-thermodynamic means such as experiment, theoretical calculation, or empirical estimation.

While many values may be found in the numerous collected tables in the literature, these are necessarily incomplete because either the experimental measurements have not been made or the materials may be hypothetical. The current paper presents a number of simple and relible estimation methods for thermodynamic properties, principally for ionic materials. The results may also be used as a check for obvious errors in published values.

The estimation methods described are typically based on addition of properties of individual ions, or sums of properties of neutral ion groups (such as "double" salts, in the Simple Salt Approximation), or based upon correlations such as with formula unit volumes (Volume-Based Thermodynamics).

Keywords: thermodynamics; ionic materials; additivity of properties; properties correlated with volume.

1 Introduction

Thermodynamics has a forbidding aspect because of its generality and because of its wide applicability (to physics, to chemistry, to biology, indeed to all of nature, at pressures and temperatures both low and high), with numerous seemingly-esoteric relations to be mastered. However, chemical thermodynamics is – in its commonest applications – relatively simple, involving only a few parameters (principally: heat capacity, entropy, enthalpy, and Gibbs energy) and moderate ranges of pressure and temperature. As an example of a simple application, one may need to estimate the enthalpy of an exothermic reaction in order to establish the cooling required in order to maintain the reaction within a moderate temperature range.

The rôle of thermodynamics is to establish equilibrium connections among thermodynamic parameters (such as entropy, enthalpy, thermal expansivity, etc.) and to delineate the effects of variation of the thermodynamic functions (typically temperature and pressure) on those parameters.[1] Classical thermodynamics does not provide values for the parameters, which must be found by experiment, by calculation, or by estimation. This paper provides a brief general introduction to methods for estimation of simple thermodynamic parameters followed by a discussion of current methods, principally for solid ionic materials. These methods for ionic materials are worthy of particular consideration since materials science is a subject of current significance, and since they apply to a wide range of materials, from simple common salts to complex minerals and even to ionic liquids.

Values of the needed thermodynamic parameters (which are also known as "properties") in the gas, liquid and solid phases have been collected for many materials into numerous published tables,[2-8] providing important resources for understanding the behaviour of those materials under various conditions and in chemical reactions among them. Extensive as these tables may be, they can never be complete since new materials are continually being discovered, prepared, or even hypothesised. Furthermore, thermodynamic experimentation is difficult and demanding so that it is an unpopular activity, leaving many gaps and possibly unreliable values within the current tables.[9]

Computational methods, including statistical thermodynamics, can fill some of the gaps but these methods, too, can be complex and demanding for materials in liquid or solid states. Therefore, simple methods for estimation of thermodynamic parameters have an important and, indeed, permanent place in the repertoire of chemistry.

2 General Estimation Methods

A previously developed hierarchy of general predictive methods for thermodynamic parameters, based upon the number of parameters required in order to provide the prediction, provides a systematic description of estimation methods.[10]

*Zero order* methods require information only on the class of material or property. Examples are the long-established Dulong-Petit Rule that the heat capacity of solids is approximately $3R \cong 25$ J K^{-1} (mol of atoms)$^{-1}$; similarly, Trouton's Rule predicts that the entropy of vaporisation of organic molecules at their boiling point is ~90 J K^{-1} mol^{-1}.

First order estimations depend on a single property of the material considered; for example molar entropies of liquids and solids are proportional to their molar volumes – crucially, entropies do not depend upon the structure of the material resulting, for example, in the close equality of the entropies of polymorphs. *Second order* methods rely on additivity of atomic (or ionic) properties: molar mass is the sum of atomic mass; molar volume is the sum of atom or ion volumes; molar heat capacity is the sum of the atomic heat capacities of the constituent elements (this is termed the Neumann-Kopp Rule) – each species involved in the addition has its own unique associated value. In *third order* methods, the additivity of local linkages is involved: thus, the bond energy of a molecule is the sum of the individual bond contributions. Finally, *fourth order* methods use the additivity of molecular groups (such as methyl, hydroxyl, etc.), possibly supplemented by extra steric parameters describing the proximity of groups to one another and electronic interaction factors.

3 Ionic Estimation Methods

In general, ionic estimation methods rely on three principles: (i) additivity of properties; (ii) the overwhelming contribution of coulombic forces to attractive interactions; together with (iii) the effective incompressibility of ions and molecules. The last two deserve some explanation. The strength of the coulombic forces and their long range ($\sim 1/r^2$) ensures that ions are pulled close together, with opposite charges in closest proximity, while the incompressibility ensures that the system of charges does not simply collapse together in a heap.

Fig. 1 illustrates the interactions between species in an ionic system. Curve 3, which corresponds to the Lennard-Jones 12-6 potential, is the sum of the repulsions between species (curve 1) and their van der Waals attractions (curve 2). Curve 4 is the coulombic energy, scaled so that it corresponds to approximately 85% of the total attractive energy,[11] and curve 5 is the sum of all the energy contributions (curves 1, 2, and 4). As may be observed from the Figure, the coulombic term so dominates the attractive energetics of ionic systems that, for many purposes, only the coulombic and repulsive terms need to be taken into account in considering the energetics of the system, much simplifying calculations. It is worth noting that, since the species in the chemical formula (for example, sulfate ions) are incompressible, the very short-range repulsive interactions occur only near the surfaces of these species and are very similar across all species.
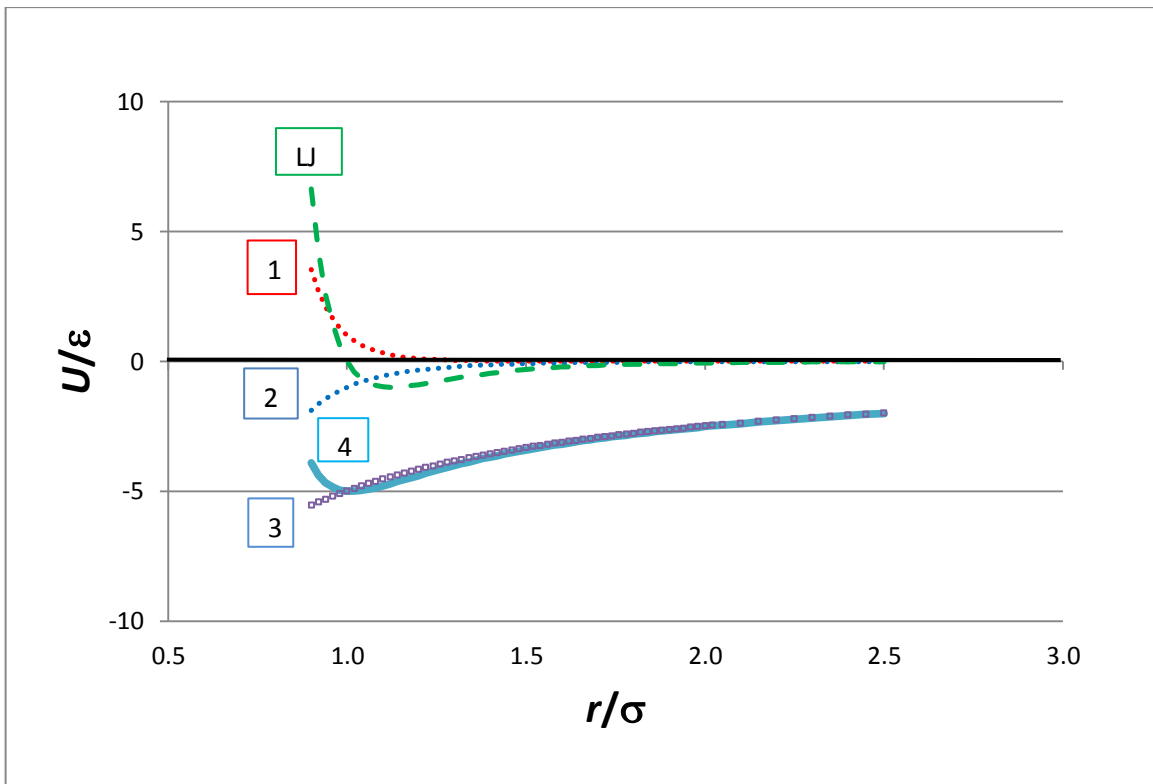
Figure 1: Normalised potential energies, *U/ε*, in an ionic system, plotted against normalised distance, *r/σ*, between the species. The distance σ is is the finite distance at which the inter-particle potential in the Lennard-Jones potential (curve LJ) is zero, and *ε* is the depth of that potential well. Dotted curve 1: repulsive energy $\propto 1/r^{12}$; Dotted curve 2: van der Waals attractive energy $\propto 1/r^6$; Broken curve LJ: sum of 1 and 2: this is the Lennard-Jones (or 12-6) potential energy; Curve 3 (with open square markers): scaled coulombic energy $\propto 1/r^2$ (see text); Solid curve 4: sum of 1, 2 and 3: total energy of an ionic system.

An important consideration in estimation of thermodynamic properties for ionic materials is the assignment of charge to the ions; in the estimation methods discussed here, integer charges are always assigned. However, it is only for independent gaseous ions that this can truly be the case, and some form of charge transfer (covalency) will necessarily occur in real materials, the extent of which will be difficult to assess.[12, 13] This is less of a problem in these estimation methods than may be anticipated since the methods rely on correlations among similar materials where the fitted constants of the correlations allow, in effect, for common deviations from strict integer ionicity. Of course, such considerations must be kept in mind when attempting estimations, and can result in significant error when extrapolating outside the range of a correlation.

3.1 Ionic Additive Estimation Methods

As a zero order method, the Dulong-Petit heat capacity sum[14] of a fixed value of 25 J K^{-1} mol^{-1} for all elements applies reasonably well to the heavier elements, and to binary

and ternary ionic solids, but needs to be supplanted for more complex materials by the second order Neumann-Kopp Rule,[15] which sums the individual elemental heat capacity values.

More generally reliably, the simplest estimation methods are summation of values for the single ions comprising the formula unit. Tables of such single ion values have been developed for a range of ions and for a number of properties, including volume,[16] heat capacity,[14] entropy,[17] enthalpy and Gibbs energy.[18] Table 1 is an incomplete selection of such values for a large number of the most common ions.

These simple relations are enhanced by the recent observation that ambient entropy values for the more complex ionic solids, such as minerals, are closely similar to their ambient heat capacities. The Debye phonon distribution provides a theoretical basis for this previously unremarked relation.[19]

As an example of the application of ion summation, the molar ambient formation enthalpy of $MgCl_2$ may be estimated as $-(20.5 + 2\times36.1) = -92.7$ J K^{-1} mol^{-1}, whereas the literature value is -89.6 J K^{-1} mol^{-1} (-3% error, relative to the literature value). Similarly, the formation enthalpy of $Ba(OH)_2\cdot3H_2O$ may be estimated as -1970 kJ mol^{-1}, whereas the literature value is -1840.5 kJ mol^{-1} (-7% error).

Table 1: A selection of additive single ion thermodynamic parameters for ionic solids under ambient conditions.

Cations	Volume[16] V_m / nm^3	Heat Capacity[14] C_p / J K^{-1} mol^{-1}	Entropy[17] S^o / J K^{-1} mol^{-1}	Formation Enthalpy[18] $-\Delta_f H$ / kJ mol^{-1}	Formation Gibbs Energy[18] $-\Delta_f G$ / kJ mol^{-1}
NH$_4^+$	0.0356		67.0		
Li$^+$	0.0067	21.07	19.4	310.4	259.7
Na$^+$	0.0158	29.74	37.2	278.3	232
K$^+$	0.0277	31.38	50.5	316	258.6
Rb$^+$	0.0341	31.26	63.1	311.7	257.3
Cs$^+$	0.0420	31.68	69.2	315.4	260.3
Mg^{2+}	0.0049	26.09	20.5	491.4	374.1
Ca^{2+}	0.0201	28.86	32.5	579.8	466.7
Sr^{2+}	0.0213	30.32	37.9	627.2	558.7
Ba^{2+}	0.0270	30.21	55.1	655	570
Fe^{2+}	0.0067	31.78	38.6	138.5	33.6
Zn^{2+}	0.0125		37.3		
Cu^{2+}	0.0053	*25.10*[a]	33.5	0	
Ni^{2+}	0.0004	*27.61*[a]	29.6	126.6	

Co^{2+}	0.0019	31.95	39.5	161.8	
Fe^{3+}	0.0061	30.69	28.2	208.2	62.8
Sc^{3+}	0.0035				
Al^{3+}		20.91	17.3	630.1	462.2
Anions					
F^-	0.0140		20.6	(257)[b]	(265)[b]
Cl^-	0.0298	23.5	36.1	110.8	113.7
Br^-	0.0363	26.61	48.6	66.3	70.6
I^-	0.0488	28.33	56.8	−8.2	0
N^{3-}	0.0416		54.8		
O^{2-}	0.0134		7.4		
OH^-	0.0184	21.15	20.7	228.6	247.7
S^{2-}	0.0320		22.1		
CO_3^{2-}	0.0426	57.53	52.6	594.3	583.1
NO_3^-	0.0492		78.5		
PO_4^{3-}	0.0570		71.8		

SO_4^{2-}	0.0611	71.54	74.3	812.2	802.4
ClO_4^-	0.0619		105.8		
Water					
H_2O	0.0245	41.30	40.90	285.8	

[a] The heat capacities of Cu^{2+} and Ni^{2+} may be variable.

[b] The fluoride values in parentheses are derived from the alkali halides only.

A notable omission from the energy terms in the above table is for the oxide anion, O^{2-}. This is because there is considerable variation in the value which must be assigned to this multiply-charged single atom ion (as also for other examples of such species, e. g., Si^{4+}), because of the strong interactions between such ions and their neighbours, which require detailed consideration.[20, 21] However, if similar materials (such as Cs_2O and Rb_2O) are considered, then a common value may be assigned; in this case -285 kJ mol^{-1}, as an estimated formation enthalpy for the oxide anion. This value may be usefully used in estimations for related materials, but results in significant error when extended to Li_2O, for example, with its very different ionicity.

More generally, many thermodynamic properties for ionic solids may be approximated by Yoder and Flora's Simple Salt Approximation (*SSA*).[22] The composition of a complex mineral is often expressed in analytical terms as a sum of its constituent simpler minerals. In similar fashion, its thermodynamic properties may be regarded as the sum of

the thermodynamic properties of its analytical constituents. Consider the case of

malachite,[22] $Cu_2(OH)_2CO_3$, with experimental formation enthalpy -1054.7 kJ mol^{-1},

which may be considered to be represented by the "double" salt, $CuCO_3 \cdot Cu(OH)_2$, with

an estimated formation enthalpy of (-596) + (-450.4) = -1046 kJ mol^{-1} (+1% error).

Similarly, addition of the single-ion values, $\Delta_f H[2Cu^{2+} + CO_3^{2-} + 2(OH^-)_2] = 2\times0 +$

(-594.3) + 2×(-228.6), leads to a value of -1052 kJ mol^{-1} (+1% error). These results are

remarkable since copper, as a transition metal, has strong covalent characteristics which

lead to errors when thermodynamic estimations are based upon solely coulombic

interactions. (Thus, simple application to each of $CuCO_3$ and $Cu(OH)_2$ of a coulomb-

based lattice energy equation from Table 4 leads to values with serious errors.) It seems

that the covalent characteristic is already accounted for in the experimental formation

enthalpies of the partially-covalent simple salts and ions which are summed. The

program HSC[3] has a proprietory thermodynamic estimation procedure which yields a

formation enthalpy of -1100.6 kJ mol^{-1} (a still acceptable -4% error).

The *SSA* applies equally well to the additivity of the entropies and lattice energies[22]

(see below for discussion of the latter) of many "double" and "multiple" salts.

3.2 Ionic Liquids

Ionic liquids (ILs) are an important class of materials, recently applied as non-aqueous

solvents and catalysts for their exceptional properties of thermal stability and low vapour

pressure leading to low environmental impact in use. Furthermore, because they may be

synthesised in almost limitless variety by variation in the functional groups attached to

the organic cation and inorganic/organic anion, their properties may even be adjusted to fit the needs of the application.[23]

An important group of ILs where the effects of addition of methylene groups have been much studied is the organic cation series $[C_n mim]^+$ (1-methyl-3-alkyl- imidazolium). Not unexpectedly, thermodynamic properties associated with each added methylene group are rather constant but, furthermore, the values are closely similar with values associated with addition of alkyl groups in other situations. Table 2 lists some additive values by which thermodynamic properties of related ionic liquids may be estimated.

Table 2: Additive methylene thermodynamic parameters for $[C_n mim]^+$ ionic liquids under ambient conditions.

Contribution per –CH$_2$- group in C$_n$mim alkyl chains	Ionic Liquids	Organic Materials
Volume[24] / nm3	0.275	0.242
Entropy[24] / J K^{-1} mol^{-1}	34.5	32.2
Total phase change entropy^a $\Delta_{tpc}S$[24] / J K^{-1} mol^{-1}	6	8, 17.3[25]
$\Delta_f H(l)$[26] / kJ mol^{-1} ($n \geq 2$)	-26	-25.5
$\Delta_l^g H$[26] / kJ mol^{-1} ($n \geq 2$)	4.0	4.95
$\Delta_f H(g)$[26] / kJ mol^{-1} ($n \geq 2$)	-21	-20.9

^{a} Total entropy change per methylene group from crystalline solid to clear liquid.

4 Thermodynamic Difference Rules (*TDR*)[27, 28]

If there is an additive relation then, by implication, there must also be a corresponding difference relation (for example, if $2 + 3 = 5$, then $5 - 3 = 2$). In the thermodynamic case, difference relations permit use of the properties of related materials to estimate the properties of their chemical neighbours, and are most readily applied graphically. The most developed application is to hydrates (and, indeed, to solvates in general). We here demonstrate a rather unusual application, in an investigation of the formation enthalpies of the francium halides, FrX.

Table 3: Formation Enthalpies, $\Delta_f H$, of Alkali Metal Halides.[3] (The value for FrF[29, 30] is suspect, as may be seen in Fig. 2, and is thus italicised in the Table.)

| $\Delta_f H$ / kJ mol^{-1}	Li	Na	K	Rb	Cs	Fr
F	-617.9	-577.8	-568.6	-561.0	-558.4	*-524.2*
Cl	-409.4	-412.4	-438.0	-436.5	-443.6	-436.4
Br	-352.4	-362.4	-394.8	-396.1	-406.9	-398.7
I	-271.7	-289.1	-328.9	-334.9	-349.4	-348.5

The differences of the formation enthalpies of the alkali halides relative to that of NaX are plotted in Fig. 2 versus the formation enthalpy of NaX.   We see that the differences alter in a smooth monotonic sequence as the alkali metals change down the Periodic Table, except for FrF whose difference lies well apart from the corresponding values of the other alkali metal fluorides. While this may possibly be a real effect, due to some special structural features of FrF, it is more likely to be a faulty experimental value for this exceptionally difficult material. By extrapolation of the data in Table 3, we estimate a value for $\Delta_f H$(FrF) of -555 kJ mol^{-1}.
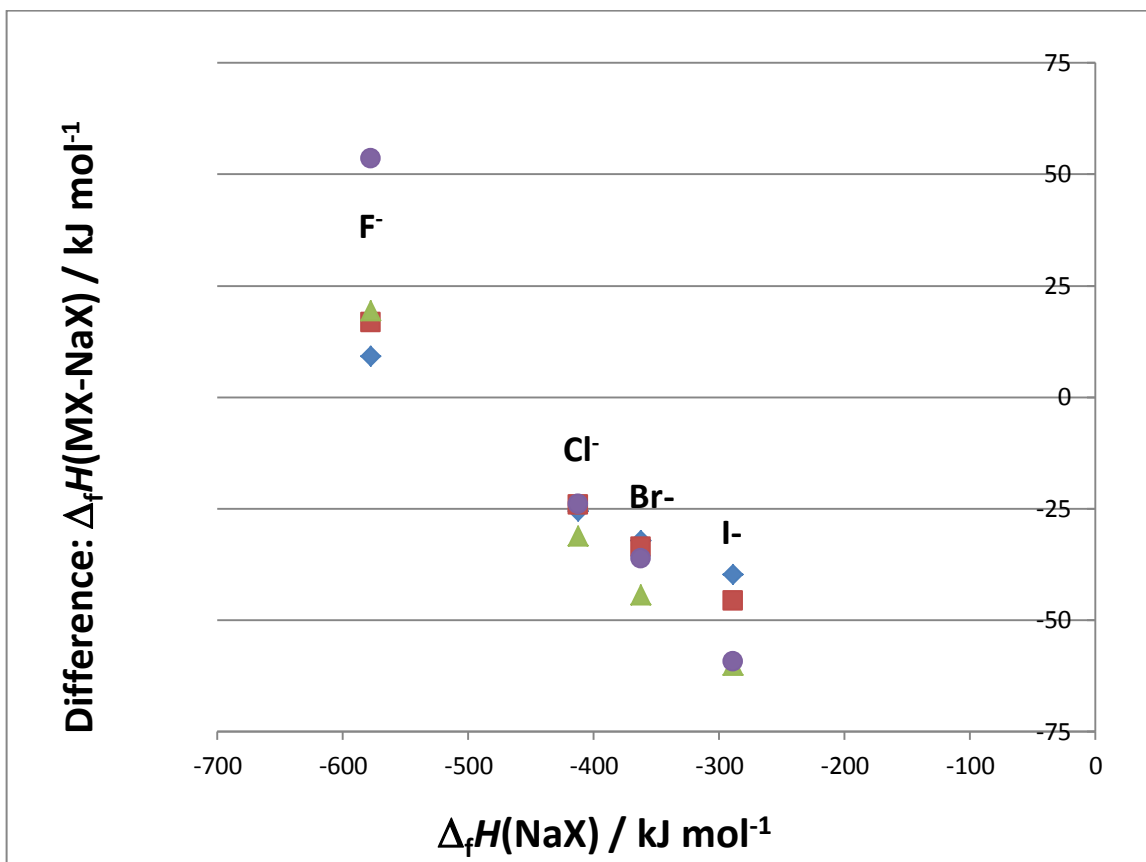
Figure 2: Plot of formation enthalpy differences, Δ_fH(MX-NaX), of alkali metal (M = $Na^+ \rightarrow Fr+$) halides versus the formation enthalpies of NaI $\rightarrow$ NaF. Blue diamonds: (KX-NaX); red squares: (RbX-NaX); green triangles: (CsX-NaX); purple circles: (FrX-NaX). The LiX halides are omitted because their behaviour is rather anomalous.
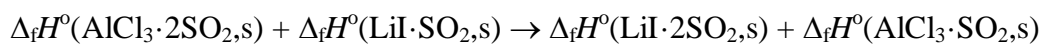
Fig. 3 is a surface plot of the formation enthalpies of all the alkali halides, using our adjusted value for FrF. Furthermore, we may estimate a single-ion formation enthalpy of Fr^+ from the FrX data in Table 3, by subtracting the halide ion contributions in Table 1. This leads to a mean value for $\Delta_fH(Fr^+)$ of about -340 kJ mol^{-1} (omitting the value for FrF).
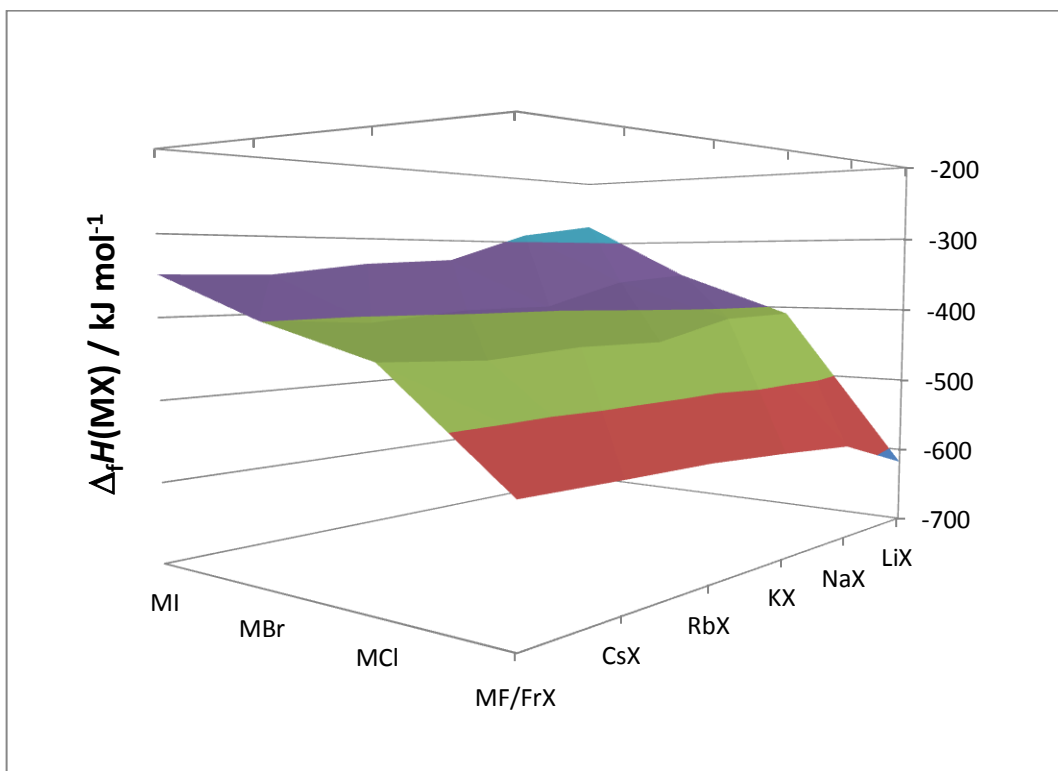
Figure 3: Perspective surface plot of the formation enthalpies of the alkali halides, with the value for FrF (front corner) adjusted to our estimated value of -555 kJ mol^{-1}.

An impressive application of TDR is represented in an estimation[27] of the formation enthalpy of $AlCl_3 \cdot SO_2$. Consider the formal chemical equilibrium:

$$\Delta_f H^o(AlCl_3 \cdot 2SO_2,s) + \Delta_f H^o(LiI \cdot SO_2,s) \rightarrow \Delta_f H^o(LiI \cdot 2SO_2,s) + \Delta_f H^o(AlCl_3 \cdot SO_2,s)$$

Using[4] $\Delta_f H^o(LiI \cdot SO_2,s)$/kJ mol^{-1} = -607.9, $\Delta_f H^o(LiI \cdot 2SO_2,s)$ /kJ mol^{-1} = -944.3, and $\Delta_f H^o(AlCl_3 \cdot SO_2,s)$/kJ mol^{-1} = -1061.1, we estimate by difference $\Delta_f H^o(AlCl_3 \cdot 2SO_2,s) \cong$ [-1061.1 − 944.3 + 607.9] = -1398. This agrees exactly with the literature value reported.[31]

5 Volume-Based Thermodynamics (*VBT*)[10, 32]

If two properties correlate with each other, then it is straightforward to use a value of one to estimate a value of the other. In Fig. 4, we plot formation Gibbs energies against formation enthalpies for 59 ionic solids (selected from the data used to generate single ion enthalpies and Gibbs energies for formation).[18] It is clear from the excellent correlation that a reliable value of the one may be estimated from the other; indeed this correlation is much more general than an earlier demonstration[33] of the same relation which was simply for a group of similar materials.
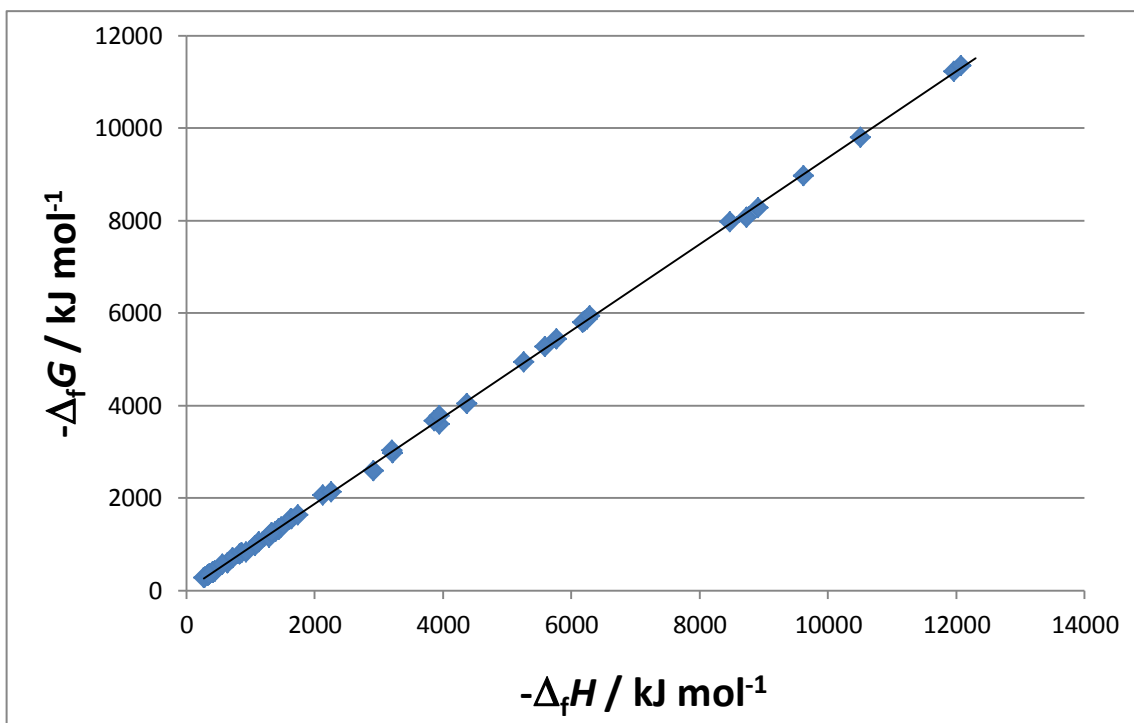
Figure 4: Gibbs formation energies plotted against formation enthalpies for 59 ionic solids. The linear correlation (constrained through the origin) has a slope of 0.935 with a correlation coefficient, $R^2 = 0.999(8)$.

It has been found that many properties correlate rather closely with *formula unit volume*. This is particularly useful since formula volume is the most-easily and -commonly

determined thermodynamic property, whether directly from chemical formula and density, or from unit cell dimensions by X-ray crystallography, or even by ion volume summation.

In Table 4, we list linear correlations that we have observed between formula volume and each of heat capacity, entropy, lattice energy and compressibility. The heat capacity, entropy and compressibilty correlations are linear in formula volume, apparently because larger volumes imply greater freedom of motion of the species involved. Conversely, the strength of ion interactions account for lattice energies and so the smaller the distance between charges the larger the lattice energy; hence lattice energy is proportional to $V_m^{-1/3}$ (where the 1/3 exponent is required to convert volume to distance).

It should be noted that formula volume, V_m, and density, ρ, may be appropriately subsituted for one another since they have the inverse mathematical relation:

$$V_m\,/\,\mathrm{nm}^3 = \frac{M\,/\,\mathrm{g\,mol^{-1}}}{602.2\times \rho\,/\,\mathrm{g\,cm^{-3}}}$$

where the factor 602.2 derives from the Avogadro constant, 6.022×10^{23} mol^{-1}, and M is the formula mass.

It is particularly striking that the linear correlation coefficient between heat capacity and formula volume is smaller, at about 80%, for the important class of ionic liquids than for ionic solids. This difference suggests that the covalent degrees of freedom in the complex bonding within the ionic liquids may not be excited at ambient temperatures.

Table 4: Constants for a Selection of Volume-Based Thermodynamic Relations

Lattice Energy from Volume data,[34] U_{POT} / kJ mol^{-1} = 2I(α/$V_m^{1/3}$ + β)			
Material	**Ionic Strength Factor, I**	**α / kJ mol^{-1} (nm^3 formula unit^{-1})$^{1/3}$**	**β / kJ mol^{-1}**
MX (1:1)	1	117	52
MX$_2$ (2:1)	3	134	61
M$_2$X (1:2)	3	165	-30
MX (2:2)	4	119	60
M$_p$X$_q$	½($pq^2 + qp^2$)	139	28
Lattice Energy from Density data,[34] U_{POT} / kJ mol^{-1} = γ(ρ/M)$^{1/3}$ + δ			
Material	**Ionic Strength Factor, I**	**γ / kJ mol^{-1} cm^{-1}**	**δ / kJ mol^{-1}**
MX (1:1)	1	1981.2	103.8
MX$_2$ (2:1)	3	8375.6	-178.8
M$_2$X (1:2)	3	6764.3	365.4
MX (2:2)	4	6864.0	732.0
M$_p$X$_q$	½($pq^2 + qp^2$)	2347.6I	55.2 I
Entropy,[35, 36] S / J K^{-1} mol^{-1} = kV_m + c			
		k / J K^{-1} mol^{-1} (nm^{-3} formula unit)	**c / J K^{-1} mol^{-1}**
anhydrous ionic salts		1360 ± 56	15 ± 6
hydrated ionic salts		1579 ± 30	6 ± 6
organic liquids		1133 ± 7	44 ± 2
organic solids		774 ± 21	57 ± 6
Heat Capacity,[37] C$_p$ / J K^{-1} mol^{-1} = k'V_m + c'			
		k' / J K^{-1} mol^{-1} (nm^{-3} formula unit)	**c' / J K^{-1} mol^{-1}**
non-framework		1465	11

silicates			
general ionic solids		1322	-0.8
ionic liquids		1037	45
Isothermal Compressibility,[38] β / GPa^{-1} = k''V_m			
		k'' / GPa^{-1} (nm^{-3} formula unit)	
general ionic solids		0.159	
perovskites		0.118	

In the case of lattice energy estimation (that is, the energy to evaporate an ionic solid into its constituent ions), account also needs to be taken of the ionic charges involved since coulombic forces are predominant in the interactions required to form the solid.

The lattice energy for smaller ionic solids[39] is:

$$U_{POT} = 2I\left(\frac{\alpha}{V_m^{1/3}} + \beta\right)$$

where I is the ionic strength factor, $\frac{1}{2}\sum_i n_i z_i^2$, with n_i being the number of species of charge z_i in the formula unit, and α and β are empirical constants appropriate to the ion charges (charge ratio 1:1, 1:2, 2:1, 2:2, and even the general $q:p$, for materials having composition M_pX_q), as listed in Table 4.

For larger ionic solids[39] (when $U_{POT} > 5\ 000$ kJ mol^{-1}):

$$U_{POT} = AI\left(\frac{2I}{V_m}\right)^{1/3}$$

where the general electrostatic constant A has the value 121.4 kJ mol^{-1} nm. This limiting equation is notable since it contains *no empirical factor at all*, and applies to $U_{POT} > 70$

000 kJ mol^{-1}, and probably beyond. The resultant estimation errors are generally within 7%, and often significantly less.

6 Conclusion

We have here shown that simple procedures are available by which to reliably estimate thermodynamic properties of ionic materials. These include: (i) simple summation of assigned values for the individual ions of which the material is comprised (Table 1 lists many such values); (ii) correlation of one property with another (volume is most usefully used as the base property, with relevant parameters in Table 4); (iii) summation of properties of constituent salts ("Simple Salt Approximation"): and (iv) a variety of difference relations (Section 4). In general, experience suggests that estimated values lie within 7% of experimental values, but often much better when reference is made to closely-related materials. These procedures provide extensive resources by which missing values may be estimated, and published values may be checked for obvious errors.

7 Acknowledgement

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