

Single-Ion Heat Capacities, $C_p(298)_{\text{ion}}$, of Solids: with a Novel Route to Heat-Capacity Estimation of Complex Anions

Leslie Glasser*

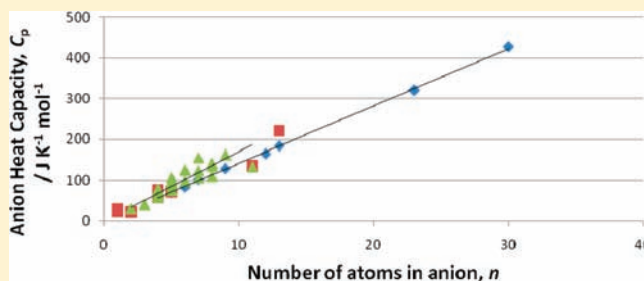
Nanochemistry Research Institute, Department of Chemistry, Curtin University, G.P.O. Box U1987, Perth, Western Australia 6845, Australia

H. Donald Brooke Jenkins*

Department of Chemistry, University of Warwick, Coventry CV4 7AL, West Midlands, United Kingdom

Supporting Information

ABSTRACT: Single-ion heat capacities, $C_p(298)_{\text{ion}}$, are additive values for the estimation of room-temperature (298 K) heat capacities of ionic solids. They may be used for inferring the heat capacities of ionic solids for which values are unavailable and for checking reported values, thus complementing our independent method of estimation from formula unit volumes (termed volume-based thermodynamics, VBT). Analysis of the reported heat-capacity data presented here provides a new self-consistent set of heat capacities for both cations and anions that is compatible (and thus may be combined) with an extensive set developed by Spencer. The addition of a large range of silicate species permits the estimation of the heat capacities of many silicate minerals. The single-ion heat capacities of individual silicate anions are observed to be *strictly* proportional to the total number of atoms (Si plus O), n , contained within the silicate anion complex itself (e.g., for the anion $\text{Si}_2\text{O}_7^{2-}$, $n = 9$, for SiO_4^{2-} , $n = 5$), $C_p(\text{silicate anion})/\text{J K}^{-1} \text{mol}^{-1} = 13.8n$, in a new rule that is an extension of the Neumann–Kopp relationship. The same linear relationship applies to other *homologous anion series* (for example, oxygenated heavy-metal anion complexes such as niobates, bismuthates, and tantalates), although with a different proportionality constant. A similar proportionality, $C_p(\text{complex anion})/\text{J K}^{-1} \text{mol}^{-1} \approx 17.5n$, which may be regarded as a convenient “rule of thumb”, also applies, although less strictly, to complex anions in general. The proportionality constants reflect the rigidity of the complex anion, being always less than the Dulong–Petit value of $25 \text{ J K}^{-1} \text{mol}^{-1}$. An emergent feature of our VBT and single-ion approaches to an estimation of the thermodynamic properties is the identification of anomalies in measured values, as is illustrated in this paper.



INTRODUCTION

Values for the standard chemical thermodynamic quantities (heat capacity, enthalpy, entropy, Gibbs energy, compressibility, etc.) are required in order to be able to understand the equilibrium properties of materials and so predict their stability, reactivity, and possibility of synthesis. Many thermodynamic databases that contain such information are available (a current list appears in ref 1), but these cannot include values not yet measured or values for materials not yet synthesized, and errors may even occur, either by experiment or by transcription. Furthermore, new values are slow in coming because thermodynamic measurements are demanding, require skill, and are currently undertaken by few.

Thus, in order to fill the gaps, it is necessary that predictive methods be developed. Quantum and empirical computational methods can provide some of the missing data, but these may be difficult to apply and, in any case, require validation by experimental data. In order to supplement the available data, we and colleagues have developed volume-based thermodynamics (VBT) methods, largely for condensed ionic materials, which

correlate experimental thermodynamic values against formula volume (whether determined by X-ray analysis, from density, or by simple estimation).² Their results have been demonstrated to be both reliable and useful.

The present paper provides an extended and optimized set of additive values for the heat capacities of many ions constituting condensed ionic materials. It thus complements current VBT procedures for estimating the room-temperature (298 K) heat capacities of ionic solids.³ These single-ion values, including for a number of silicate anions, are compatible, and may be combined, with a set earlier established by Spencer⁴ (whose full set is included in Table S1 in the Supporting Information (SI) and partially in Table 1). Furthermore, the single-ion heat capacities of a homologous anion series, such as silicates, are observed to be *strictly* proportional to the total number of atoms,

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Table 1. Single-Ion Heat Capacities, $C_p(298)_{\text{ion}}$, As Optimized against a Set of 121 Ionic Solids, Where N Is the Total Number of Each Type of Ion in the Data Set^a

ion	$C_p(298)_{\text{ion}}$ optimized/ $\text{J K}^{-1} \text{mol}^{-1}$	std dev ^b / $\text{J K}^{-1} \text{mol}^{-1}$	N^c	$C_p(298)_{\text{ion}}$ Spencer ^d / $\text{J K}^{-1} \text{mol}^{-1}$
Li ⁺	21.07	0.26	4	19.66
Na ⁺	29.74	0.20	24	25.94
K ⁺	31.38	0.17	17	25.94
Rb ⁺	31.26	0.10	2	26.36
Cs ⁺	31.68	0.10	2	26.36
Ag ⁺	29.92	0.10	2	25.73
Mg ²⁺	26.09	0.07	85	19.66
Ca ²⁺	28.86	0.08	50	24.68
Sr ²⁺	30.32	0.19	10	25.52
Ba ²⁺	30.21	0.18	5	26.36
Mn ²⁺	30.42	0.10	19	23.43
Fe ²⁺	31.78	0.06	51	25.94
Cu ²⁺				25.10
Ni ²⁺				27.61 ^e
Co ²⁺	31.95	0.33	2	28.03
Al ³⁺	20.91	0.10	86	19.66
La ³⁺	28.77	0.57	4	25.52 ^e
Cr ³⁺	31.04	0.34	5 ² / ₃	23.01
Fe ³⁺	30.69	0.19	8	25.94
Cl ⁻	23.50	0.08	20	24.69
Br ⁻	26.61	0.35	6	25.94
I ⁻	28.33	0.36	8	26.36
OH ⁻	21.15	0.08	118	30.96
ClO ₃ ⁻	70.09	0.10	2	
BrO ₃ ⁻	76.14	0.09	2	
CO ₃ ²⁻	57.53	0.44	6	58.58
SO ₄ ²⁻	71.54	0.20	29	76.57
B ₄ O ₇ ²⁻	134.90	1.02	2	134.26
Fe(CN) ₆ ⁴⁻	219.83	1.74	2	
SiO ₃ ²⁻	57.58	0.11	24	62.93
SiO ₄ ⁴⁻	68.93	0.11	41	78.34
SiO ₅ ⁶⁻	82.18	0.23	4	
Si ₂ O ₅ ²⁻	101.86	0.15	14	106.79
Si ₂ O ₇ ⁶⁻	127.40	0.37	4	
Si ₂ O ₁₀ ¹²⁻	162.20	0.43	3	
Si ₃ O ₁₀ ⁸⁻	182.77	0.27	11	
Si ₃ O ₁₈ ¹⁶⁻	317.21	0.41	3	
Si ₄ O ₁₁ ⁶⁻	213.09	0.21	18	
H ₂ O	41.30 ^f		112.5	

^aThe corresponding values from the Spencer set⁴ are listed for comparison. ^bThe standard deviations were determined using a “jack-knife” procedure, as described in the text. ^c N = number of ions included in the fitting set of ionic materials. For the case of $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, the reference values were divided by 3, thus corresponding to $\text{Cr}_{2/3}\text{SO}_4 \cdot 6\text{H}_2\text{O}$, in order to not overweigh the contribution of the material in the optimization. ^dNo ion charges are listed for the Spencer set and so, presumably,¹⁰ values are to be used whatever the ion charge: for example, Fe^{2+} and Fe^{3+} ; Cu^+ and Cu^{2+} . ^eThe italicized values are listed by Spencer as approximate. ^fThe value of $41.3 \text{ J K}^{-1} \text{mol}^{-1}$ for the water of crystallization³ was kept fixed during the optimizations. This ensures that the features of our thermodynamic difference rule¹⁶ for prediction of the values for hydrates are preserved, in the form $[C_p(298)(M_p X_q \cdot n\text{H}_2\text{O}, s) - C_p(298)(M_p X_q, s)] / \text{J K}^{-1} \text{mol}^{-1} \approx n \Theta_{c_p}(\text{H}_2\text{O}, s-s) = 41.3$.

n , contained within the silicate anion:

$$C_p(\text{silicate anion}) / \text{J K}^{-1} \text{mol}^{-1} = 13.8n \quad (1)$$

in a new rule that is an extension of the Neumann–Kopp relationship.⁵ Thus, for example, $n = 9$ in the anion $\text{Si}_2\text{O}_7^{2-}$ and $n = 15$ in $\text{Si}_3\text{O}_{12}^{12-}$. Waters of crystallization in hydrated compounds are treated separately, with additive C_p contributions from each water molecule; see examples in Table 3. The same relationship applies to other homologous anion series, as shown below, but with a different proportionality constant.

A similar proportionality, which should be regarded as a convenient “rule of thumb”,

$$C_p(\text{complex anion}) / \text{J K}^{-1} \text{mol}^{-1} \approx 17.5n \quad (2)$$

also applies, but less strictly, to complex anions in general. Again, n is the number of atoms contained within the anion considered.

ESTIMATION OF THE HEAT CAPACITIES

The VBT method for heat-capacity estimation relies on a rather close linear correlation between the heat capacity and molar volume of condensed materials. Thus, heat capacities, $C_p(298)$, are related to molar volumes, V_m , by

$$C_p(298) / \text{J K}^{-1} \text{mol}^{-1} \approx k(V_m / \text{nm}^3 \text{ formula unit}^{-1}) + c \quad (3)$$

where, for *general ionic solids*, $k = 1322 \text{ J K}^{-1} \text{mol}^{-1} \text{nm}^{-3}$ and $c = -0.8 \text{ J K}^{-1} \text{mol}^{-1}$, with this and values for other groupings of materials reported elsewhere.³ The relationship can equivalently be expressed in terms of density, ρ :

$$C_p(298) / \text{J K}^{-1} \text{mol}^{-1} \approx k'[(M / \text{g mol}^{-1}) / (\rho / \text{g cm}^{-3})] + c \quad (4)$$

where k' is a related constant and M is the formula mass of the ionic material.

The values of the constants mentioned above are comparable over a range of materials but do differ considerably for those ionic liquids for which data are available (where $k = 1037 \text{ J K}^{-1} \text{mol}^{-1} \text{nm}^{-3}$ and $c = 45 \text{ J K}^{-1} \text{mol}^{-1}$)⁶ with the implication that the complex cations of the ionic liquids are somewhat rigid, with reduced heat capacities relative to their volumes.³

While the VBT linear correlation may be considered generally satisfactory, it is desirable to have an independent confirmatory procedure. As will be noted, the single-ion method introduced here does just that while also providing its own insight.

The Dulong–Petit rule (1819) states (in modern terms) that the heat capacities per mole for *atoms* in metals approximate to $3R \approx 25 \text{ J K}^{-1} \text{mol}^{-1}$, where R is the gas constant. Complementing this, the Neumann–Kopp law claims that the heat capacities of condensed materials may be estimated by summing the contributions of the constituent *elements*. This principle has been adopted for *ions* by a number of workers,^{7–9} in order to develop an additive single-ion procedure for the heat capacities of ionic materials. The early work culminated in an extensive set, as further developed by Spencer,⁴ containing 49 cations together with 41 anions, which are both simple and oxygen-based, such as Cl^- and SO_4^{2-} . As anticipated, the published cation values are consistent with the Neumann–Kopp law, being very roughly constant around $25 \text{ J K}^{-1} \text{mol}^{-1}$, with the largest outliers being P^{5+} ($14.23 \text{ J K}^{-1} \text{mol}^{-1}$) and Ti^- ($27.61 \text{ J K}^{-1} \text{mol}^{-1}$).

The Spencer set, which has been used by Leitner et al.,¹⁰ together with an extensive early set by Moiseev and Šesták,¹¹ provides data for estimation of the heat capacities of many ionic materials. However, there are only three silicate anions in the

set (SiO_3^{2-} , SiO_4^{4-} , and $\text{Si}_2\text{O}_5^{2-}$) so that application to mineral species is severely limited. In order to obviate this problem, we have used the experimental heat-capacity data from our previous paper³ (where heat capacities were estimated in relation to formula volumes, in a VBT application) to develop single-ion heat capacities for three further anion complexes (ClO_3^- , BrO_3^- , and $\text{Fe}(\text{CN})_6^{4-}$) and six new silicate anions (SiO_5^{6-} , $\text{Si}_2\text{O}_7^{6-}$, $\text{Si}_2\text{O}_{10}^{12-}$, $\text{Si}_3\text{O}_{10}^{8-}$, $\text{Si}_4\text{O}_{11}^{6-}$, and $\text{Si}_5\text{O}_{18}^{16-}$ and where also the multiple silicon anions $\text{Si}_2\text{O}_6^{4-}$, $\text{Si}_2\text{O}_8^{8-}$, $\text{Si}_2\text{O}_{10}^{12-}$, $\text{Si}_3\text{O}_{12}^{12-}$, and $\text{Si}_8\text{O}_{22}^{12-}$ are represented by 2SiO_3^{2-} , 2SiO_4^{4-} , 2SiO_5^{6-} , 3SiO_4^{4-} , and $2\text{Si}_4\text{O}_{11}^{6-}$, respectively, yielding 14 silicate anions in total).

■ GENERATION OF INTERNALLY CONSISTENT SINGLE-ION HEAT CAPACITIES

As a database, we have used the published heat capacity data from our earlier paper³ for 133 ionic materials, ranging from simple chlorides and sulfates to hydrates and complex silicate minerals. (Note: the chlorite formulas in the previous paper, copied from the well-known database of Holland and Powell (H&P),¹² all have *four* OH^- groups. These should rather each have *eight* OH^- groups, and the formulas have been so corrected in the current H&P data set.^{13,14} This has no consequence for our previous paper, where the formulas were used merely for identification. The correct formulas, which are now charge-balanced as required for ion additivity, have been used in the current calculations.) The ions selected are those present in common ionic solids and in a range of silicate minerals, but materials with considerable covalency, such as hydrides, borides, carbides, and nitrides, are omitted. The value of $C_p(298)$ for H_2O was fixed during optimization at the value $\Theta_{C_p,298}(\text{H}_2\text{O},s-s) = 41.3 \text{ J K}^{-1} \text{ mol}^{-1}$ as generated in our earlier paper.³ The ion heat-capacity sums for each of these 133 solids were generated using initial values for the individual ion heat capacities from Spencer's tables,⁴ together with rough estimates for the various silicate anions. A nonlinear minimization of the error in the least-squares sum of the calculated ion heat-capacity sums against the reported heat capacities was undertaken (using the Microsoft EXCEL routine, SOLVER) by allowing the contributing ion heat capacities to vary, using the following sequence of optimizations. In a first run, only the cation values were optimized, while the other values remained fixed; this was followed by a second run in which the cation and water values were fixed and the anion values were optimized; third, the full set of values, except that for water, were permitted to vary during optimization. A stable set of values was obtained, but the generated values for Cu^{2+} and Ni^{2+} were very small (about $10 \text{ J K}^{-1} \text{ mol}^{-1}$, perhaps reflecting some enhanced covalency) and the sum values for the minerals sudoite [$\text{Mg}_2\text{Al}_4\text{Si}_3\text{O}_{10}(\text{OH})_8$] and ferrosudoite [$\text{Fe}_2\text{Al}_4\text{Si}_3\text{O}_{10}(\text{OH})_8$] were about 17% lower than their experimental values. Because the number of copper and nickel species was small (only sulfates and hydrates, four materials in all for copper and three for nickel), these and the pair of sudoites were omitted from the reference set of materials [together with duplicate NiAlSiO_6 , $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$, and $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$], leaving 121 materials in our reference data set.

The above set of optimization runs was repeated, yielding a stable set of single-ion heat capacities, with a low mean absolute deviation (MAD) of $4.1 \text{ J K}^{-1} \text{ mol}^{-1}$ from a mean heat capacity of $282 \text{ J K}^{-1} \text{ mol}^{-1}$, with a standard deviation of 2.6%. Finally, in order to establish the statistical variability of the optimized values, a "jack-knife"¹⁵ was run against the full set of data.

The "jack-knife" operates by running the SOLVER optimization repeatedly while omitting each of the contributing species in turn. The heat capacities and standard deviations of each of the resultant single-ion values is listed in the accompanying Table 1, together with the corresponding values from Spencer.⁴

The nonlinear sum of least-squares optimization performed here provides, in effect, weighting to the contributing values. In order to confirm that these weightings are not crucial to the set of values obtained, two further optimizations were performed that alter the relative weightings of the terms: (i) minimizing the sum of the absolute deviations between experimental and optimized heat capacity sums and (ii) minimizing the sum of the percent differences. The resultant optima are essentially identical ($R^2 = 0.9926$ and 0.9936 , respectively, compared with 0.9945 for the least-squares optimization).

■ RESULTS AND DISCUSSION

Figure 1 plots the summed single-ion heat capacities, using the current optimized set of values for the 121 ionic materials

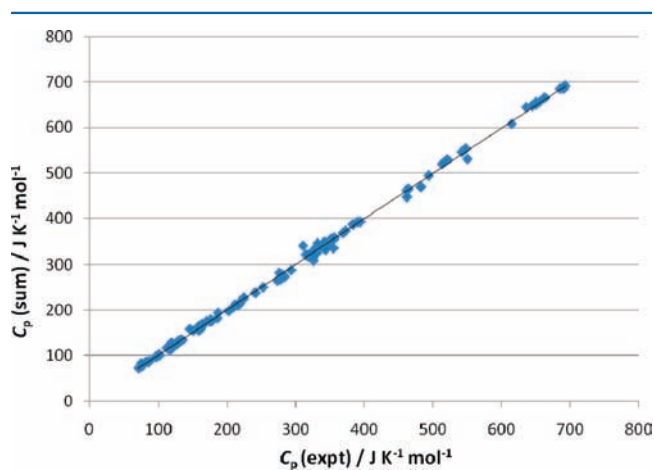


Figure 1. Plot of summed single-ion heat capacities, using the current optimized set of values for the 121 ionic materials included in the optimization, against the experimental heat capacities. The linear least-squares fit has the equation $C_p(\text{sum}) = 0.9940C_p(\text{expt}) + 1.70$, with correlation coefficient $R^2 = 0.995$. The largest (9.3%) deviation visible is for $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}/3$. The data have a MAD of $4.1 \text{ J K}^{-1} \text{ mol}^{-1}$ and a standard deviation of 2.6%.

included in the optimization, against the experimental heat capacities. It is clear that a very adequate result has been obtained.

Table 2 contains an eclectic mix of ionic materials, most not included in the training set of materials. Here, the summed single-ion heat capacities using both the current and Spencer sets are compared with the reference heat capacities, together with the linear VBT estimate for silicates of our earlier paper.³

$$C_p / \text{J K}^{-1} \text{ mol}^{-1} = 1502.8V_m / \text{nm}^3 \quad (5)$$

Table 2 demonstrates satisfactory agreement between the experimental and summed single-ion heat capacities for both sets, except for alunite, $\text{K}_2\text{Al}_6(\text{OH})_{12}(\text{SO}_4)_4$, where the considerable difference, arising from the large number of $C_p(298)_{\text{ion}}(\text{OH}^-)$ values, renders the Spencer value unreliable.

Similarly, the VBT estimate is generally satisfactory, with the stand-out exception of the group of framework-structured aluminosilicates: eucryptite (LiAlSiO_4), nepheline (NaAlSiO_4), and kaliophilite (KAlSiO_4). These are members of the

Table 2. Summed Single-Ion Heat Capacities (in $\text{J K}^{-1} \text{mol}^{-1}$) for a Range of Ionic Materials, Most Not Included in the Optimization, Using Both the Current and Spencer Single-Ion Value Sets^a

mineral name	ionic material	expt/ $\text{J K}^{-1} \text{mol}^{-1}$	optimized/ $\text{J K}^{-1} \text{mol}^{-1}$	Spencer ^d / $\text{J K}^{-1} \text{mol}^{-1}$	% diff optimized	% diff Spencer	volume-based ^b / $\text{J K}^{-1} \text{mol}^{-1}$	% diff VBT
<i>c</i>	MgCl ₂	71.03	73.1	69.0	2.9	-2.8		
	CaCl ₂	72.45	75.9	74.1	4.7	2.2		
<i>c</i>	BaCl ₂	75.14	77.2	75.7	2.8	0.8		
	FeCl ₂	76.18	78.8	75.3	3.4	-1.1		
	NiCl ₂	71.67	74.6 ^d	77.0	4.1	7.4		
	MnCl ₂	72.71	77.4	72.8	6.5	0.1		
	CrCl ₃	91.8	101.5	97.1	10.6	5.8		
	BaCO ₃	85.35	87.7	84.9	2.8	-0.5		
	MgSiO ₃	82.09	83.7	82.6	1.9	0.6		
<i>c</i>	CaSiO ₃	86.48	86.4	87.6	0.0	1.3		
	SrSiO ₃	87.08	87.9	88.5	0.9	1.6		
	CuSO ₄	100	97.1 ^d	101.7	-2.9	1.7		
<i>c</i>	SrBr ₂ ·6H ₂ O	345.5	331.3	325.2	-4.1	-5.9		
eucryptite	LiAlSiO ₄	113.3	110.9	165.2	-2.1	45.8	118.5 ^e	4.6
nepheline	NaAlSiO ₄	115.81	119.6	123.9	3.3	7.0	135.3 ^e	16.8
kaliophilite	KAlSiO ₄	119.79	121.2	123.9	1.2	3.5	151.0 ^e	26.1
larnite ^c	Ca ₂ SiO ₄	128.6	126.7	127.7	-1.5	-0.7	128.8	0.1
α-spodumene ^c	LiAlSi ₂ O ₆	158.9	157.1	165.2	-1.1	4.0	149.8	-5.7
protoenstatite ^c	Mg ₂ Si ₂ O ₆	164.1	167.3	170.2	2.0	3.7	161.6	-1.5
diopside ^c	CaMgSi ₂ O ₆	166.52	170.1	170.2	2.2	2.2	165.2	-0.8
ferriprehnite	Ca ₂ FeAlSi ₃ O ₁₀ (OH) ₂	341.8	334.4	339.7 ^d	-2.2	-0.6	369.3	8.1
piemontite	Ca ₂ MnAl ₂ Si ₃ O ₁₂ (OH)	354	357.9	378.1	1.1	6.8	344.9	-2.6
minnesotaite	Fe ₃ Si ₄ O ₁₀ (OH) ₂	340	341.4	353.3	0.4	3.9	370.4	8.9
alunite ^e	K ₂ Al ₆ (OH) ₁₂ (SO ₄) ₄	745.17	728.2	847.6	-2.3	13.8	733.1	-1.6
sudoite ^e	Mg ₂ Al ₄ Si ₃ O ₁₀ (OH) ₈	593.3	487.8	548.4 ^d	-17.8	-7.6	506.6	-14.6
ferrisudoite ^e	Fe ₂ Al ₄ Si ₃ O ₁₀ (OH) ₈	605.4	499.2	561.0 ^d	-17.5	-7.3	509.1	-15.9

^aWhere the relevant set does not contain a given single-ion value, the summations use values mixed from the two sets. ^bThe volume-based heat capacities are calculated as $C_p/J \text{K}^{-1} \text{mol}^{-1} = 1502.8 V_m/\text{nm}^3$. This calculation applies only to silicates. ^cThese materials were included in the optimization. ^dThese sums mix single-ion values from both the current and Spencer sets. ^eSee the text for an explanation for the discrepant values for these materials.

feldspathoid group of minerals, containing large isolated holes and so of low density, which will lead to the observed deviations from the VBT estimate of heat capacities.^{17,18} It is noteworthy that the ion summation, on the other hand, leads to a satisfactory estimate of the heat capacity because this is independent of the crystal structure.

Another feature to note is the very poor estimation for both sudoite and ferrisudoite, in spite of the fact that the heat capacities of 11 other $\text{Si}_3\text{O}_{10}^{8-}$ species are adequately represented in the fitted set. This suggests either that the structures of both sudoite and ferrisudoite differ significantly from their congeners or (more likely, we believe) that their reported heat capacities are in error.

Figure 2 compares the single-ion heat capacities from the set published by Spencer with the corresponding values for the same ions from the current analysis. There are two significant observations. First, these monatomic cations all have roughly the same Dulong–Petit value, about $25 \text{ J K}^{-1} \text{mol}^{-1}$. Second, the monatomic and polyatomic anions which are in common yield comparable values, as shown by the good linear relationship between them. From these observations, it seems perfectly reasonable to combine these sets to yield an extended data set and use their values interchangeably in estimating the heat capacities of ionic solids.

It is instructive to consider the contribution to the heat capacity of atoms contained within a complex, such as the 5 in SO_4^{2-} or the 15 in $\text{Si}_4\text{O}_{11}^{6-}$. In Figure 3 are plotted the single-ion heat capacities from the current optimization for the

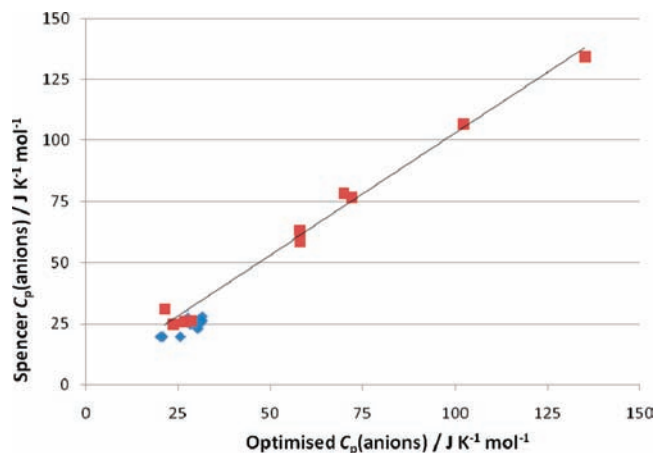


Figure 2. Plot of the single-ion heat capacities of Spencer against those of the currently developed set. The monatomic cations (blue diamonds) have similar heat capacities, near the Dulong–Petit value of $25 \text{ J K}^{-1} \text{mol}^{-1}$. The linear relationship for the monatomic and polyatomic anions (red squares) has the formula $C_p(298)_{\text{ion}}/J \text{K}^{-1} \text{mol}^{-1}(\text{Spencer}) = 0.9978 C_p(298)_{\text{ion}}/J \text{K}^{-1} \text{mol}^{-1}(\text{current}) + 3.48$, with $R^2 = 0.988$.

silicates, for the remaining anions, and for the complex ions in Spencer's compilation. We note from the figure that the contribution per atom in the set of silicate anions is remarkably constant at $13.8 \text{ J K}^{-1} \text{mol}^{-1}$, while the same contribution for

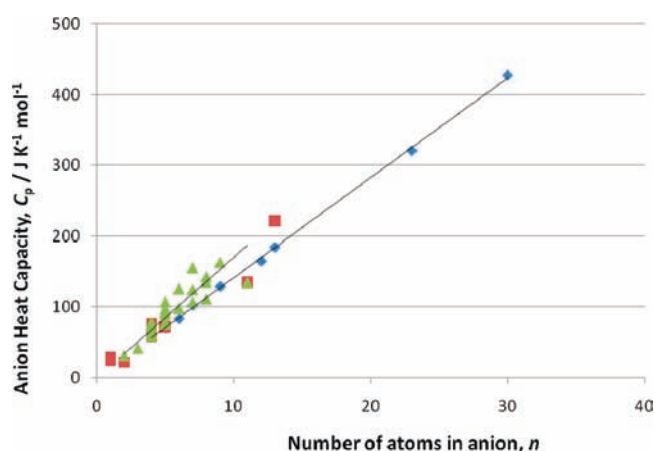


Figure 3. Plot of the single-ion heat capacities of anions versus the number of atoms, n , within the complex. The linear least-squares line for the set of silicate ions (blue diamonds) has a slope of $13.8 \text{ J K}^{-1} \text{ mol}^{-1}$ with an intercept of $2.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ($R^2 = 0.999$), while that for the wide variety of complex anions in Spencer's compilation (green triangles) is approximately $17.1 \text{ J K}^{-1} \text{ mol}^{-1}$ ($R^2 = 0.75$). The comparable set of complex anions from the current optimization yield the values depicted with red squares. The principal (low-value) outlier seen in the latter two sets is for $\text{B}_4\text{O}_7^{2-}$.

the broad range of complex anions, although more variable, is about $17\text{--}18 \text{ J K}^{-1} \text{ mol}^{-1}$. The constancy of these values implies that the heat capacity of complex anions may be estimated simply by multiplying the values noted above by the number of atoms, n , contained within the anion. For example, we estimate the heat capacity of the nitrate anion, NO_3^- , as $17.5 \times 4 \approx 70 \text{ J K}^{-1} \text{ mol}^{-1}$ (compared with our optimized value of $64.4 \text{ J K}^{-1} \text{ mol}^{-1}$), so that the heat capacity of NaNO_3 is

estimated to be $30 + 70 \approx 100 \text{ J K}^{-1} \text{ mol}^{-1}$ (the reported experimental value is $92.9 \text{ J K}^{-1} \text{ mol}^{-1}$, yielding a difference of 7%). Direct ion summation (using Spencer's value for NO_3^-) yields $94 \text{ J K}^{-1} \text{ mol}^{-1}$, a difference of only 3%, while the VBT estimation³ for a density of 2.261 g cm^{-3} and a mass of 85 g mol^{-1} is $93.8 \text{ J K}^{-1} \text{ mol}^{-1}$ (a difference of about 1%). While these results are instructive, it should be realized that the anions cover a wide range of types, and the results may, in general, be less satisfactory. Table 3 presents some further examples, using the various ion sums available.

Because the homologous series of silicate anions produces the exceedingly useful proportionality of the anion heat capacity to the number of atoms contained within the anion, it was deemed useful to see if a similar behavior is exhibited by other homologous oxygenated anion groups. Table 4 collects together data for niobates, bismuthates, and tantalates, and these data are plotted in Figure 4, where a common linear relationship is to be noted for these oxygenated heavy-metal anions.

These observations are in accordance with Hazen's polyhedral approach to crystal structures,^{19,20} namely, that cation coordination polyhedra within ionic materials are relatively rigid. Consequently, the polyhedra will tend to vibrate as a unit within the structure, contributing $17.5 \text{ J K}^{-1} \text{ mol}^{-1}$ (in general) to the heat capacity of the material, which is less than the Dulong–Petit value of $25 \text{ J K}^{-1} \text{ mol}^{-1}$. The very low contribution of $13.8 \text{ J K}^{-1} \text{ mol}^{-1}$ for the silicate anions, compared also with $18.6 \text{ J K}^{-1} \text{ mol}^{-1}$ for the heavy-metal homologous series of anions (Figure 4), implies greater rigidity in the silicates than for the more general group of polyhedra. This is not dissimilar in concept to the low contribution to the specific heat by the cations in ionic liquids.³

Table 3. Comparison of Various Combinations of the Tabulated Single-Ion Heat Capacities To Generate the Heat Capacities of Compounds

compound	$C_p / \text{J K}^{-1} \text{ mol}^{-1}$				
	experimental value	using tabulated values from Tables 1 and S1 in the SI	% difference	using cation tabulated values + $17.5n(\text{anion}) + m(\text{H}_2\text{O})^a$	% difference
CaMoO_4	114.3	121.6	-6.0	116.4	1.8
	114.3	117.5	-2.7	112.2	-1.8
Na_3AlF_6	215.9	no data for AlF_6^{3-}		211.7	-1.9
	215.9			200.3	-7.2
NaOH	59.5	50.9	16.9	64.7	8.8
	59.5	47.1	26.4	60.9	2.4
	59.5	60.7	-2.0		
	59.5	56.9	4.6		
$\text{K}_2\text{B}_6\text{O}_{10}$	321.3	no data for $\text{B}_6\text{O}_{10}^{2-}$		342.8	6.7
	321.3			331.9	3.3
$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	N/A	469.3		476.9	0.0
	N/A	447.5		455.2	0.0
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	143.1	143.3	-0.1	159.2	11.3
	143.1	136.3	5.0	152.2	6.4
	143.1	148.3	-3.5		
	143.1	141.3	1.3		
$\text{Sr}(\text{NO}_3)_2$	149.9	159.2	-5.8	170.3	13.6
	149.9	154.4	-2.9	165.5	10.4
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	574.5	544.0	5.6	560.0	-2.5
	574.5	536.4	7.1	552.4	-3.9
	574.5	549.1	4.6		
	574.5	541.5	6.1		

^a $m(\text{H}_2\text{O})$ is the number of waters of crystallization in the compound. $n(\text{anion})$ is the number of atoms in the anion.

Table 4. Experimental Heat Capacities, $C_p(298)$, of Niobates, Tantalates, and Bismuthates, and Their Anion Heat Capacities Calculated by Subtracting Their Spencer Contributions^a

formula	$C_p(298)/$ $J K^{-1} mol^{-1}$	$C_p(\text{anion}, 298)/$ $J K^{-1} mol^{-1}$	$n(\text{anion})$
Niobates			
BiNbO ₄	121.3	94.5	5
SrNb ₂ O ₆	170.2	139.8	8
CaNb ₂ O ₆	171.8	143.0	8
MnNb ₂ O ₆	181.2	150.8	8
Sr ₂ Nb ₂ O ₇	216.6	155.9	9
Ca ₂ Nb ₂ O ₇	218.1	160.4	9
SrBi ₂ Nb ₂ O ₉	286.4	202.5	11
Sr ₃ Nb ₄ O ₁₅	478.5	326.9	19
BiNb ₅ O ₁₄	386.8	360.0	19
Sr ₂ Nb ₁₀ O ₂₇	746.1	685.4	37
Tantalates			
BiTaO ₄	119.3	92.5	5
Bi ₃ TaO ₇	235.2	154.8	8
SrBi ₇ Ta ₂ O ₉	286.6	202.7	11
Bi ₄ Ta ₂ O ₁₁	363.2	256.1	13
Bi ₇ Ta ₃ O ₁₈	602.7	415.3	21
Bismuthates			
SrBi ₂ O ₄	155.8	125.5	6
Sr ₂ Bi ₂ O ₅	201.9	141.2	7

^aThe final column gives the number of atoms in the anion. A list of the sources of these values appears as Table S3 in the Supporting Information.

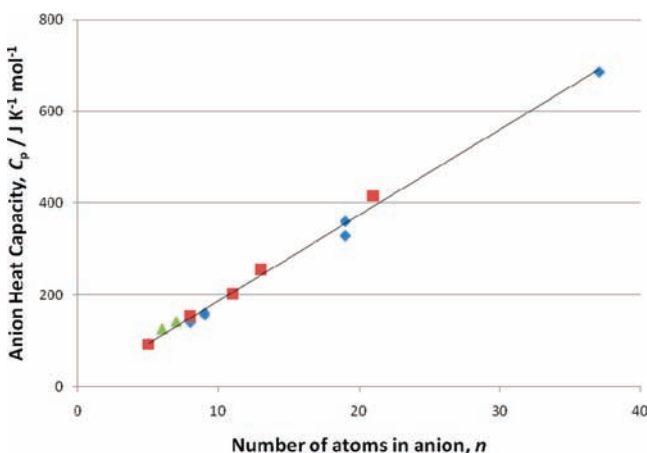


Figure 4. Anion heat capacities for niobates (blue diamonds), tantalates (green triangles), and bismuthates (red squares) plotted against the number of atoms, n , in the anion. The linear least-squares-fitted line has the formula $C_p(\text{anion}, 298)/J K^{-1} mol^{-1} = 18.6 n$ ($R^2 = 0.994$).

The proportionalities reported in Figures 3 and 4 are especially valuable in that the heat capacities for a homologous anion series may be reliably estimated.

CONCLUSIONS

A set of single-ion heat capacities has been developed by optimization of their sums against the known heat capacities of 121 ionic materials, including a large group of silicates. These single-ion heat capacities are shown to be compatible with an earlier set developed by Spencer and so the two sets may be combined to yield a much-enhanced set, suitable for estimation

of the heat capacities of a wide range of both simple ionic solids and complex minerals. It is also possible to estimate, by difference, the single-ion heat capacities of other ions missing from the sets, either from the linear relationships established in Figure 3 or by use of the current single-ion values and known ionic material heat capacities. As an example of the former, the heat capacity of NaNO₃ is estimated to within about 7%, although, in general (Table 3), errors in estimates can be somewhat larger.

It has also been demonstrated that the heat capacities of anions in a homologous series, such as silicates, are proportional to the number of atoms contained within the anion and that the size of the proportionality constant reflects inversely the rigidity of the anion.

An emergent feature of our VBT and single-ion approaches to the estimation of the properties is identification of the anomalies in measured values, as illustrated in the discussion in this paper.

ASSOCIATED CONTENT

Supporting Information

Single-ion heat capacities, $C_p(298)_{\text{ion}}/J K^{-1} mol^{-1}$, from Spencer, together with our current optimized values (Table S1), the 121 ionic materials used in the single-ion optimization, together with their reported room-temperature heat capacities and the corresponding ion heat-capacity sums, as well as the differences from the reported heat capacities (Table S2), and sources of the heat capacity data in Table 4 (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: l.glasser@curtin.edu.au (L.G.), h.d.b.jenkins@warwick.ac.uk (H.D.B.J.). Tel: + 61 8 9266-3126 (L.G.), +44 2476-523-265 (H.D.B.J.). Fax: + 61 8 9266-4699 (L.G.), + 44 2476-524-112 or +44 2476-466-747 (H.D.B.J.).

Notes

The authors declare no competing financial interest.

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