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Ambient Isobaric Heat Capacities, $C_{p,m}$, for Ionic Solids and Liquids: An Application of Volume-Based Thermodynamics (VBT)

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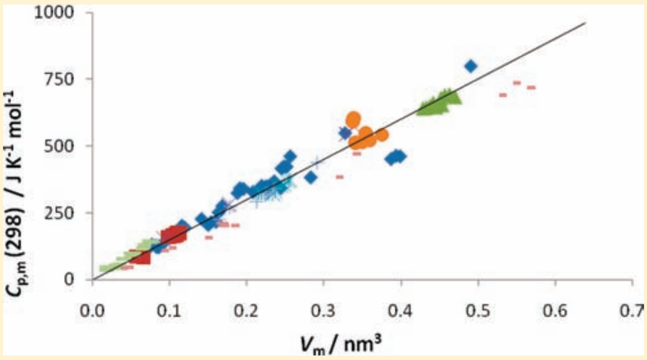
Supporting Information

ABSTRACT: Thermodynamic properties, such as standard entropy, among others, have been shown to correlate well with formula volume, V_m, thus permitting prediction of these properties on the basis of chemical formula and density alone, with no structural detail required. We have termed these procedures "volume-based thermodynamics" (VBT). We here extend these studies to ambient isobaric heat capacities, $C_{p,m}$, of a wide range of materials. We show that heat capacity is strongly linearly correlated with formula volume for large sets of minerals, for ionic solids in general, and for ionic liquids and that the results demonstrate that the Neumann–Kopp rule (additivity of heat capacity contributions per atom) is widely valid for ionic materials, but the smaller heat capacity contribution per unit volume for ionic liquids is noted and discussed. Using these correlations, it is possible to predict values of ambient (298 K) heat capacities quite simply. We also show that the heat capacity contribution of water molecules of crystallization is remarkably constant, at 41.3 ± 4.7 J K^{-1} (mol of water)$^{-1}$, so that the heat capacities of various hydrates may be reliably estimated from the values of their chemical formula neighbors. This result complements similar observations that we have reported for other thermodynamic differences of hydrates.



Over recent years, we and our colleagues have developed volume-based thermodynamics (VBT),[1−3] a technique whereby certain thermodynamic quantities (entropy, lattice potential energy, and compressibility) of condensed (usually ionic) phases may readily be estimated using reliable correlation relations against formula unit volume, V_m, while requiring little or even no structural information. The reason for the success of these correlations seems to be that volume provides a measure of the strength of the interactions between ionic species, with smaller volumes (for a given number of constituent atoms) corresponding to stronger interactions; thus lattice energies (U_{POT}) increase in proportion to $V_m^{-1/3}$. On the other hand, entropies ($S°_{298}$) and compressibilities (β) increase with V_m, corresponding to the greater freedom for motion in the larger volumes. Whereas lattice energy and entropy values have proven to be largely independent of structure, it has been necessary for the evaluation of compressibilities to group materials within suitable classes in order to achieve satisfactory correlations.[1b]

The current contribution investigates the relation between ambient (room temperature and pressure) isobaric heat capacity ($C_{p,m}$) and formula unit volume. This is, in principle, likely to be more problematic than the investigations mentioned above because heat capacity is temperature-dependent, in contrast with the comparatively negligible temperature dependence of lattice energy, entropy, and compressibility values. In broad terms, heat capacity follows the Debye (or Einstein) thermal relation, increasing from low temperatures toward limiting Dulong–Petit values at high temperatures (perhaps interrupted by phase changes). For many materials, ambient conditions represent low temperatures (i.e., their Debye temperatures are much greater than ambient), leading to strong temperature dependence, but, for ionic solids, this effect is ameliorated by the strength of the long-range Coulombic forces, which militate against large structural changes and thus reduce the influence of temperature.

The ability to estimate $C_{p,m}$ from V_m, in order to acquire particularly elusive thermochemical $C_{p,m}$ data, can provide (via Kirchoff's Law[4]) a means of determining enthalpy changes at temperatures other than 298 K. The ability to provide even rather approximate $C_{p,m}$ data (approximate because of the nature of the relation) can nevertheless offer an increased dimension to VBT.

■ CORRELATION OF ISOBARIC HEAT CAPACITY, $C_{p,m}$(298), WITH FORMULA UNIT VOLUME, V_m

In Figure 1 we display $C_{p,m}$(298) data plotted versus V_m for a large group of silicate minerals of petrologic interest (see the Supporting

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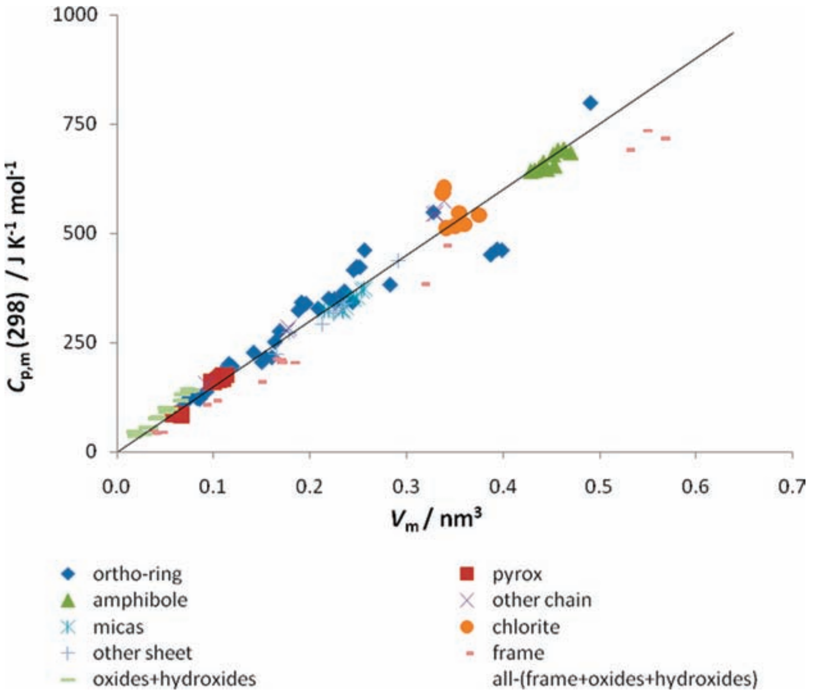

Figure 1. $C_{p,m}(298)$ versus V_m for a consistent set of 113 silicate minerals of petrologic interest together with their 19 constituent oxides and hydroxides,[5] listed in Table S1 of the Supporting Information. The fitted line omits the framework silicates, oxides, and hydroxides. It has the formula $C_{p,m}(298) = 1502.8V_m$ (correlation coefficient, $R^2 = 0.962$) with the intercept constrained to zero. Without this constraint: $C_{p,m}(298) = 1464.8V_m + 11.42$ (correlation coefficient, $R^2 = 0.963$). The heat capacity data for this Figure are also plotted, in Supporting Figure S1, against formula mass and are shown to exhibit a somewhat less satisfactory correlation coefficient of 0.931.

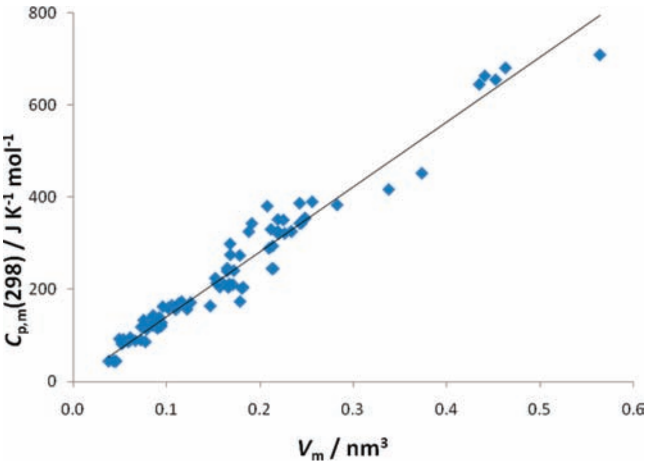

Figure 2. $C_{p,m}(298)$ versus V_m for 93 silicate minerals from the database program FREED, collated from publications of the (now defunct) U.S. Bureau of Mines and its successor, the U.S. Geological Survey.[6] The fitted line has the formula $C_{p,m}(298) = 1408.2V_m$ (correlation coefficient, $R^2 = 0.958$) with the intercept constrained to zero. The line without constraint hardly differs: $C_{p,m}(298) = 1388.1V_m + 4.58$ (correlation coefficient, $R^2 = 0.958$).

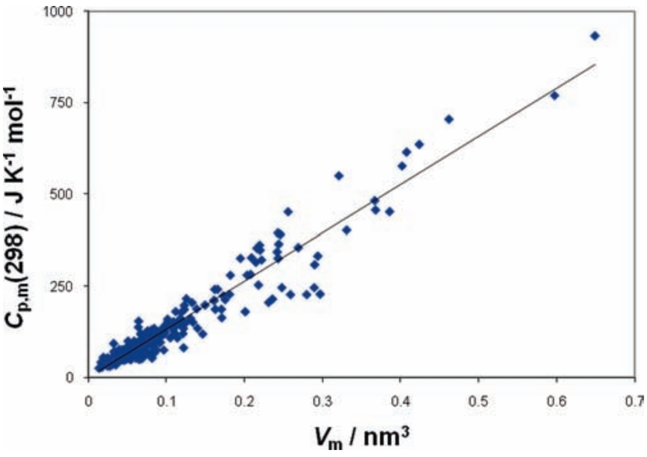

Figure 3. $C_{p,m}(298)$ versus V_m for 257 ionic materials of diverse kind (anhydrous, hydrates, complex anions, etc.) from the critically evaluated NBS database of Wagman, et al.[4] The fitted line has the formula: $C_{p,m}(298) = 1316.9V_m$ (correlation coefficient, $R^2 = 0.926$). The line without constraint hardly differs: $C_{p,m}(298) = 1321.6V_m - 0.845$ (correlation coefficient, $R^2 = 0.926$).

Information, calculated from the database of Holland and Powell[5]), together with their constituent oxides and hydroxides, the data of which have been optimized as a consistent group but without overt reliance on any volume or formula mass dependence.

The same heat capacity data are also plotted in Supporting Figure S1, but against formula mass, yielding a somewhat less satisfactory correlation coefficient of 0.931.

Figure 2 plots $C_{p,m}(298)$ versus V_m for 93 silicate minerals from the database program FREED, using data collated from publications of the (now defunct) U.S. Bureau of Mines (USBM) and its successor, the U.S. Geological Survey (USGS).[6] A plot of $C_{p,m}(298)$ versus formula-unit mass (not shown) has an equivalent quality of fit.

Figure 3 plots $C_{p,m}(298)$ versus V_m for 257 ionic materials of diverse kind (anhydrous, hydrates, complex anions, etc.) from the critically evaluated NBS database of Wagman et al.[4]

If a value of $C_{p,m}$ is unavailable for one member of a family of compounds, an improved correlation can generally be achieved by making a plot of $C_{p,m}$ versus V_m restricted to inclusion of only the known members of the family possessing, say, the common anion.[7] Figure 4 illustrates this situation in the case of sulfates. The plot contains data for 30 sulfates (see Supporting Information, Table S2) from as simple as Li_2SO_4 to complex hydrates such as $NH_4Cr(SO_4)_2 \cdot 12H_2O$.

An important development in current thermodynamics[8] is the emergence of recently acquired thermochemical databases for ionic liquids,[9−26] an area recently reviewed by one of us.[27] From within this area of frenzied activity have emerged data for the molar $C_{p,m}$ for a series of ionic liquids. Strechan et al.[14] have listed data for density, ρ, and molar mass, M, of some typical ionic liquids (based on liquids containing 1-*n*-alkyl-3-methylimidazolium cations and including one that has a methyl group in the 2 position) along with their $C_{p,m}$. The liquid V_m is readily calculated from the formula mass and density. These data are reproduced in Table 1, with formula volume quoted in nm^3, from density and molar mass, and taking the form $V_m(\text{nm}^3) = M(\text{g mol}^{-1})/[602.2(\text{cm}^3\ \text{nm}^{-3}\ \text{mol}^{-1}) \times \rho(\text{g cm}^{-3})]$, while the data are plotted in Figure 5. We find that the $C_{p,m}/V_m$ correlations here have even higher correlation coefficients (0.990, 0980) than those found for the 113 solid silicate minerals (0.963, 0.962), for the 93 silicate minerals from the FREED database (0.958, 0.958), for the 257 ionic materials (0.926, 0.926), and for the 30 ionic sulfates (0.985, 0.985) in Figure 4. A tested correlation between $C_{p,m}$ and M is once again found to be considerably less satisfactory (R^2 = 0.936) than the corresponding C_p/V_m correlation for these ionic liquids.

It is noticeable that the slope of the $C_{p,m}/V_m$ plot for the ionic liquids is about 80% of that for the ionic solids. By contrast, and for example, the heat capacity of solid KCl at 298 K is listed[28] as 51 J K^{-1} mol^{-1} while that of liquid KCl at the same temperature is 74 J K^{-1} mol^{-1}. It is a common observation that the isobaric heat capacities of liquids are greater than those of their corresponding solids at common temperatures.[29] This discrepancy suggests that the extra degrees of freedom in the complex

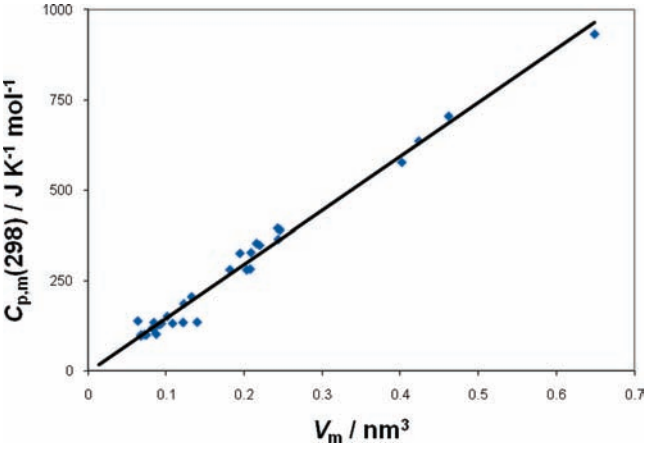

Figure 4. $C_{p,m}(298)$ versus V_m for 30 ionic sulfates (including hydrates) using data from the critically evaluated NBS database of Wagman et al.[4] The fitted line has the formula: $C_{p,m}(298) = 1479.7V_m$ (correlation coefficient, R^2 = 0.985, whether with intercept constrained to zero or unconstrained).

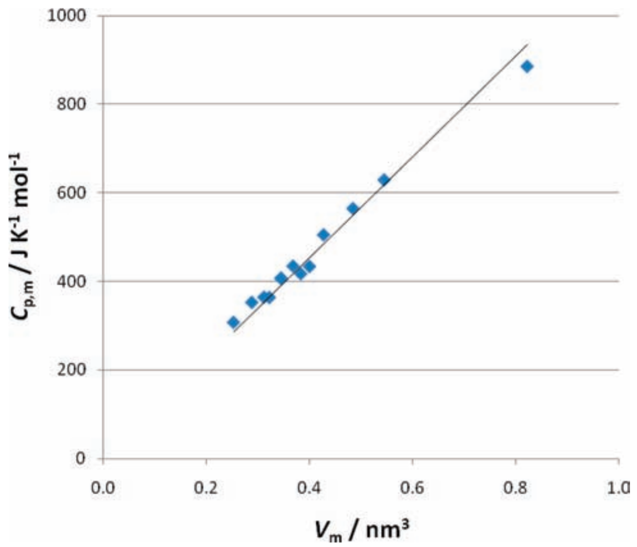

Figure 5. Plot of $C_{p,m}$ versus V_m/nm^3 for a series of ionic liquids. The plot of $C_{p,m}$ versus V_m exhibits a fit constrained to the origin with correlation coefficient R^2 = 0.980 and $C_{p,m} = 1136.3V_m$. The unconstrained fit, for which R^2 = 0.990, has $C_{p,m} = 1037.0V_m + 45.3$.

Table 1. Heat Capacity, $C_{p,m}$, and Molar Volume, V_m, Derived from Density Measurements for Ionic Liquids

ionic liquid	M/g mol^{-1}	ρ/g cm^{-3}	V_m/nm^3 = M/(602.2ρ)[a]	$C_{p,m}$/J K^{-1} mol^{-1}
$[C_2mim][NTf_2] = [C_2mim][N(SO_2CF_3)_2]$	391.3	1.520	0.4275	505.7
$[C_2mim][BF_4]$	198.0	1.300	0.2529	308.1
$[C_4mim][CF_3CO_2]$	252.2	1.215	0.3447	407.9
$[C_4mim][NO_3]$	201.2	1.159	0.2883	353.3
$[C_4mim][PF_6]$	284.2	1.366	0.3455	407.6
$[C_4mim][NTf_2] = [C_4mim][N(SO_2CF_3)_2]$	419.4	1.438	0.4843	565.1
$[C_4mim][CF_3SO_3]$	288.2	1.300	0.3681	435.2
$[C_4mim][N(CN)_2]$	205.3	1.058	0.3222	364.5
$[C_4mim][BF_4]$	226.1	1.204	0.3118	365.1
$[C_6mim][NTf_2] = [C_6mim][N(SO_2CF_3)_2]$	447.4	1.364	0.5447	629.6
$[C_6mim][BF_4]$	254.1	1.101	0.3832	417.8
$[C_{14}mim][NTf_2] = [C_{14}mim][N(SO_2CF_3)_2]$	559.6	1.131	0.8216	885.9
$[C_4Mmim][PF_6]$	298.2	1.238	0.4000	434.3

[a] The factor 602.2 converts formula volume from cm^3 mol^{-1} to nm^3: $N_A/(\text{nm}/\text{cm})^3 = 6.022 \times 10^{23}/(10^7)^3$ where N_A is Avogadro's constant.

covalent bonding within the ionic liquids may not be fully excited at ambient temperatures.

An alternative procedure for the evaluation of thermophysical properties of ionic liquids (with their large organic ions) is the use of group contribution methods,[30] which may provide reliable estimates complementary to those of the VBT methods here discussed.

DISCUSSION

The Dulong–Petit heat capacity limit is 3R per mole of atoms ($3 \times 8.314 = 24.9$ J K^{-1} mol^{-1}). According to the Neumann–Kopp law,[31,32] the heat capacity may be estimated as the sum of the heat capacities of the atoms of the constituent elements, with the mean heat capacity of the elements in the Handbook of Chemistry and Physics[33] having the rather similar value of 24.5 J K^{-1} mol^{-1}. If one accepts an overall average volume of 0.018 nm^3 per atom in compounds,[34] then the heat capacity per atom from the mineral data of Figure 1 is 1502.8 J K^{-1} mol^{-1} nm^{-3} $\times$ 0.018 nm^3 atom^{-1} = 27.1 J K^{-1} mol^{-1}, while, from Figure 2, the value corresponds to 1408.2 J K^{-1} mol^{-1} nm^{-3} $\times$ 0.018 nm^3 atom^{-1} = 25.4 J K^{-1} mol^{-1}. The slope from Figure 3 yields 23.5 J K^{-1} mol^{-1}. Similarly, the slope from Figure 4 yields $C_{p,m}$(sulfate) = 26.6 J K^{-1} mol^{-1}. These values per mole of atoms are remarkable vindications of the Neumann–Kopp law over a vast range of ionic solids, but the current correlated values will be more suitable for predictions than simple Neumann–Kopp values.

We note that correlations of isobaric heat capacity against formula mass are somewhat less reliable than correlations against formula volume. This contrasts markedly from our earlier observation that entropies of ionic solids fail to correlate with formula mass.[35] For both these reasons, we suggest that the correlation against formula volume is more suitable.

We can also make use of our thermodynamic difference rule (TDR),[7,36] using this data set,[4] by taking the difference per water molecule between materials of the same composition with differing amounts of water of crystallization to find the contribution per water molecule to the isobaric heat capacity. For example,

$$\begin{aligned}\Delta C_{p,m}(\mathrm{H_2O}) &= [C_{p,m}(\mathrm{FeSO_4 \cdot 7H_2O}) - C_{p,m}(\mathrm{FeSO_4})]/7 \\ &= [394.5 - 100.6]/7 = 42.0\ \mathrm{J\ K^{-1}\ mol^{-1}}\end{aligned}$$

The 30 examples found in the data set yield a mean value of 41.3 ± 4.7 J K^{-1} mol^{-1}. This may be compared with the corresponding value for ice near its melting point at 0 °C, which is reported as 36.9 J K^{-1} mol^{-1},[37] implying (through the Einstein/Debye relations) a larger and thus more consistent value at 25 °C (= 298 K).

Values of $C_{p,m}$ for the hydrates $FeSO_4 \cdot H_2O$ and $FeSO_4 \cdot 4H_2O$ are not listed in the databases we have used but can be estimated from Figure 4 using either volume (VBT) or neighbor (TDR) data. $V_m(FeSO_4 \cdot H_2O)/nm^3 = 0.0978$ and $V_m(FeSO_4 \cdot 4H_2O)/nm^3 = 0.1818$. These lead to estimates of $C_{p,m}(FeSO_4 \cdot H_2O)$/J K^{-1} mol^{-1} = 144.7 and $C_{p,m}(FeSO_4 \cdot 4H_2O)$/J K^{-1} mol^{-1} = 269.0. Alternatively,[38] we may add or subtract the heat capacity contribution, $\Delta C_{p,m}(H_2O)$, from chemical formula neighbors, such as $FeSO_4$ and $FeSO_4 \cdot 7H_2O$, to yield the corresponding values for $FeSO_4 \cdot H_2O$ and $FeSO_4 \cdot 4H_2O$ of 141.9 and 270.6 J K^{-1} mol^{-1}, respectively.

CONCLUSION

We conclude that it is possible to predict the ambient isobaric heat capacities of minerals and ionic liquids quite reliably using the fitted data from Figures 2, 3 and 5, with the fractional reliability of the correlations seeming to improve for the larger volumes. There is a much weaker correlation of heat capacity, $C_{p,m}$, with formula-unit mass, M ("molecular weight").

By selection it may be possible to provide more reliable correlations within a group of materials with a common anion, as has been demonstrated here for sulfates.

The heat capacities of hydrates and (by extension) of solvates in general[38] may be estimated from the properties of neighboring materials.

We find that the $C_{p,m}/V_m$ correlation for ionic liquids (Figure 5) is very satisfactory in that it displays higher correlation coefficients (0.990, 0980) compared to those found for the solid ionic materials. This suggests that VBT may be very suitable for the latter materials,[9] while complementary group methods are also available.[30] It is noticeable that the slope of the $C_{p,m}/V_m$ plot for the ionic liquids is only about 80% of that for the ionic solids. This difference suggests that the extra degrees of freedom in the complex bonding within the ionic liquids may not be excited at ambient temperatures.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Table S1 lists formula mass, formula volume, and molar isobaric heat capacities of minerals from the Holland and Powell database,[5] while Figure S1 plots the same heat capacity against formula mass. Table S2 lists formula volumes, heat capacities, and hydrate differences for both sulfates and hydrates from the NBS database.[4] This material is available free of charge via the Internet at http://pubs.acs.org.

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