

Additive Single Atom Values for Thermodynamics

I: Volumes, Entropies, and Heat Capacities of Ionic Solids

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Abstract

In an earlier simple “group contribution” method, molar volumes of organic and inorganic materials are predicted by summing optimised single atom values weighted according to the molecular formula. We here first revisit this procedure for volumes and then apply the method to entropies and heat capacities, providing an updated predictive method. This atom sum method has the unique advantage of working with an essentially complete parameter set because of the finite number of chemical elements but at the expense of omitting the nuance of special interactions as in other more sophisticated and complex group contribution methods. Thus, it does not distinguish among materials with the same chemical formula (that is, among phases or isomers).

We here analyse data for nearly 3 500 inorganic materials, both anhydrous and hydrated. On analysing this wealth of data, we note that the optimised atom sum volume data follow the atomic sequence pattern of element volume data quite closely, but with relatively reduced values for the alkali metals and alkaline earths. The entropy atom sum values are similarly dispersed across the atomic sequence. Heat capacity atom sum values have a much reduced range, corresponding to the relatively small range of the ambient heat capacities of inorganic solids as implied by the Dulong-Petit upper limit of $3R$ per atom. We provide estimates of linear temperature effects for each of the three properties: volume, entropy and heat capacity.

The properties of water in hydrates versus pure liquid water are compared for each thermodynamic property yielding information on the effects of incorporation of water into the solid.

In summary, summations encompassing inorganic anhydrate and hydrate volumes, entropies and heat capacities over temperature ranges are available from this work, enabling simple first-order thermodynamic predictions and checks.

Introduction

The number of possible chemical compounds is essentially unlimited while availability of thermodynamic data, even for known materials, is severely restricted by the dual requirements of access to the relevant material with the ability to undertake the onerous measurements. While much of the published thermodynamic data has been collected into numerous databases which are readily available through the Internet, there will always be a need for predictive methods.¹ These may provide missing data or may act as a check for possible errors in the published results.

Many predictive thermodynamic procedures have been proposed. The most sophisticated of these methods are theoretical, relying upon quantum-based computer programs which are tested against known material data.² For larger models, it may be necessary to resort to the less compute-intensive molecular mechanics methods³ which again are parametrised against known materials. A number of methods, termed group contributions, rely on summing the interactions of transferable groups into which the material is divided,⁴ an online version of which is available in the NIST Chemistry Webbook⁵ while "HSC Chemistry"⁶ has a proprietary procedure for estimating enthalpy, entropy and heat capacity over a range of temperatures. There will necessarily be a large number of groups required to cover a range of materials, with a smaller number to cover a selected set of similar materials. In the case of solid ionic materials, it has been possible to use *cations and anions* as the summable groups in an additive thermodynamic scheme.⁷⁻⁸

In the current contribution, we propose the simple alternative of additive *single atoms* as the contributing entities. Our method consists in establishing an optimised contribution per to the relevant thermodynamic property atom, and then compared to the same property of the element. In addition, for gaseous and liquid elements, an otherwise absent additive volume can be established: for example, in the case of hydrogen an atom sum volume of 6.08 \AA^3 is determined for 4460 hydrogen atoms in inorganic solids (cf. Table 1); similarly, the molar volume of sodium is 39.36

Å³ at 25°C while an optimised value for 216 sodium atoms in inorganic sodium compounds is 24.97 Å³.

The unique advantage of the single atom sum contribution method is that it can be largely complete for inorganic systems because of the finite number of the elements, compared with the larger number of charge groups required to represent a wide range of ions, such as nitride, nitrite, nitrate and ammonium for nitrogen-containing ions. On the other hand, atom sums only allow implicitly for averaged chemical interaction. Of course, any resultant sum properties are not without error: even atomic masses are dependent on isotope proportions which may vary slightly with the source of the material under consideration.⁹⁻¹⁰ Similarly, densities of the elements themselves are not fixed quantities since they may well vary with allotropy.¹¹ Organic materials are not well-suited for inclusion in the current analysis of thermodynamic properties because of the large presence of indistinguishable isomer formulae (except in the case of volumes where detailed structure is less important, as noted below).

The most basic thermodynamic atomic sum property of a material is its molar volume, derived from molar mass and density – the latter of which may be found by direct experiment, from X-ray structural determination, or even by a predictive method. Fabry, et al.,¹² report in some detail on organic volume estimation methods by linear correlation; this is possible for such materials because volume is little affected by isomerism. The predictive density method currently most favoured is that of Hofmann,¹³ based on single atoms and yielding atom volume sums for organic solids. An equivalent set of volume sum terms by Mighell, et al.,¹⁴ based upon organics and organometallics,¹⁵ is also reported by Hofmann, who notes that their results are not suitable for inorganic solids. Stalick¹⁵⁻¹⁶ has published a set of atom volumes for inorganic materials but this is poorly available and consequently little-known. For other more general thermodynamic properties the Neumann-Kopp Rule¹⁷ for heat capacity prediction consists, in its unmodified form, of summing the heat

capacities of the elements forming the material under consideration while Latimer has suggested¹⁸⁻¹⁹ summing elemental entropy values.

Data Mining and Computation

There are many databases available (summarized in the referenced Electronic Supplementary Information file¹) from which collected thermodynamic data may be gleaned – for the present exercise, we need to collect data for inorganic solids. Among the most accessible has been the “HSC Chemistry” program⁶ which contains an Excel add-in providing immediate access to its extensive database (some 25 000 items) as well as convenient calculation and graphic facilities. Another ready resource is the “Handbook of Chemistry and Physics”²⁰ with a large inorganic database. It must be appreciated that their data generally derives from other secondary sources rather than the primary literature so that these databases cannot be regarded as having been as thoroughly curated than FactSage,²¹⁻²² for example, although care may have been devoted to confirming the data reliability.²³

Our data processing for atomic sums commenced with selection of inorganic solids data (formula, atomic mass, density, standard entropy and heat capacity) from the “HSC Chemistry” program.⁶ This selection yielded data for about 1 500 inorganic solids. A further set of 1 800 items was obtained from the “Handbook of Chemistry and Physics”²⁰ which includes some carbon-containing species such as carbonates. The combined data for a particular property evaluation was installed into an Excel spreadsheet and sets of unique data for that property (for example, entropy) were selected using the Excel “AdvancedFilter” VBA function.

Each chemical formula was then parsed to generate its contents of chemical elements and their number; for example the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is parsed to H10, O9, S1, and Cu1. This is done with the aid of the program *ChemicalParsing.xls* by A. Yundt, made available in VBA Express.²⁴ (Note that the formulae of ligands such as H_2O need to be edited from their standard format, such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, to $\text{CuSO}_4(\text{H}_2\text{O})_5$ in order to accommodate the programming of the parser.) The parsed data was used to create a table of the count of individual elements in each formula which were then

summed to generate numbers corresponding to the total number of atoms of each element contained in the unique formula data set.

For each formula, the product of the number of atoms of each constituent element multiplied by an estimate of the value of the atom property (volume, entropy, or heat capacity) is summed to give an estimate of the formula property. The differences between the estimate and the known property for each formula is squared and summed over the complete data set. Finally, the Excel "Solver" routine is invoked to minimise the sum of squares by adjusting the initial atom property estimates. This proved to be an effective procedure generally reporting a probable global minimum. Starting atom volume estimates were taken from the dataset developed by Stalick¹⁵⁻¹⁶ for inorganic solids.

It should be appreciated that erroneous data is likely to deviate from the main run of data which means that such data will make large contributions to the sum of squares thus distorting the intended fit. Attention is seldom drawn to this unfortunate feature of a sum-of-squares optimization. It is thus desirable to omit clearly erroneous data. We have listed each of the sum-of-squares terms, examining the largest to check if omission is appropriate; this is effectively a "jack-knife" or "leave-one-out-cross-validation" (LOOCV) test.²³ Clearly, excessive omission of data must be guarded against as it will distort the dataset.

Results and Discussion

Volumes: In our preparation for the development of sets of thermodynamic atom sums, we here report a new set of atom volume sums for inorganic solids, including hydrates (Table 1).

Table 1: Atom volumes, $V / \text{\AA}^3$ of those elements which are solid under ambient conditions and corresponding elemental Atom Sum terms for ambient conditions.

	Symbol	At. No.	Solid Elements ²⁵⁻²⁶	Atom Sum Volume (Stalick ¹⁵)	Atom Sum Volume (optimised)	No. of Atoms
Hydrogen	H	1		6.7	6.08	4460
Deuterium	D	(2)		0.01	7.18	11
Lithium	Li	3	21.58	6.5	10.26	79
Beryllium	Be	4	8.09	11	9.15	54
Boron	B	5	7.67	10.5	10.08	292
Carbon	C	6	8.83	22	15.28	801
Nitrogen	N	7		12	18.15	528
Oxygen	O	8		10	10.07	6227
Fluorine	F	9		11.5	13.15	717
Neon	Ne	10		22	22.03	
Sodium	Na	11	39.36	16.5	24.97	216
Magnesium	Mg	12	23.20	5	6.85	140
Aluminium	Al	13	16.59	13	7.42	130
Silicon	Si	14	20.02	20.5	24.23	327
Phosphorus (white)	P	15	28.21	19.5	21.16	220
Sulfur	S	16	25.72	24.5	24.13	598
Chlorine	Cl	17		28.5	29.11	741
Argon	Ar	18		30	30.08	
Potassium	K	19	75.50	27	27.90	157
Calcium	Ca	20	42.94	18	19.44	109
Scandium	Sc	21	24.98	12	14.99	19
Titanium	Ti	22	17.64	11	10.40	77
Vanadium	V	23	14.19	17.5	9.94	62
Chromium	Cr	24	12.01	17	13.37	128
Manganese	Mn	25	12.28	11	13.56	103
Iron	Fe	26	11.80	11.5	10.92	153
Cobalt	Co	27	11.05	8	9.90	100
Nickel	Ni	28	10.95	5.5	4.91	72
Copper	Cu	29	11.78	9	11.09	85
Zinc	Zn	30	15.21	11.5	14.55	91
Gallium	Ga	31	19.59	11.5	17.86	36
Germanium	Ge	32	22.66	16	23.59	44
Arsenic	As	33	21.64	21.5	23.23	105
Selenium	Se	34	27.26	31	31.59	228
Bromine	Br	35	45.32	34	35.77	346
Krypton	Kr	36		40	36.24	1
Rubidium	Rb	37	92.64	36	38.88	41
Strontium	Sr	38	55.11	23.5	23.36	49

Yttrium	Y	39		14.5	18.36	26
Zirconium	Zr	40	23.34	19	18.87	32
Niobium	Nb	41	18.48	23.5	12.79	54
Molybdenum	Mo	42	15.62	25	20.78	77
Technetium	Tc	43	14.15	34	30.66	3
Ruthenium	Ru	44		13	17.46	19
Rhodium	Rh	45	13.78	16.5	28.02	19
Palladium	Pd	46	14.70	13.5	10.07	18
Silver	Ag	47	17.06	20	17.64	65
Cadmium	Cd	48	21.48	15.5	22.72	56
Indium	In	49	26.08	24.5	24.45	37
Tin	Sn	50	27.13	21.5	30.54	43
Antimony	Sb	51	30.25	24.5	29.85	76
Tellurium	Te	52	33.90	25.5	36.19	138
Iodine	I	53	42.83	51	44.97	339
Xenon	Xe	54		53.5	38.71	13
Cesium	Cs	55	114.35	47	49.35	35
Barium	Ba	56	63.00	29.5	35.32	92
Lanthanum	La	57	37.54	23	24.72	28
Cerium	Ce	58	34.37	17.5	21.41	36
Praseodymium	Pr	59	34.55	19	20.48	24
Neodymium	Nd	60	34.17	19.5	22.39	21
Promethium	Pm	61		25	27.56	3
Samarium	Sm	62	33.20	18.5	20.68	28
Europium	Eu	63	48.13	20.5	16.18	24
Gadolinium	Gd	64	33.10	18.5	15.74	28
Terbium	Tb	65	32.07	17	13.93	15
Dysprosium	Dy	66	31.56	16	19.90	17
Holmium	Ho	67	31.14	16.5	20.00	13
Erbium	Er	68	30.62	15	23.58	20
Thulium	Tm	69	30.10	15.5	19.39	9
Ytterbium	Yb	70	41.65	15.5	18.05	19
Lutetium	Lu	71	29.53	14	21.02	18
Hafnium	Hf	72	22.63	18.5	13.99	15
Tantalum	Ta	73	18.32	18.5	13.52	35
Tungsten	W	74	15.82	25.5	15.10	69
Rhenium	Re	75		10	22.99	29
Osmium	Os	76			24.60	16
Iridium	Ir	77	14.19		6.61	12
Platinum	Pt	78	15.10		16.97	20
Gold	Au	79	16.95		30.89	18
Mercury	Hg	80	24.61	2.31	27.88	55
Thallium	Tl	81	28.64	14.14	30.57	45
Lead	Pb	82	30.33	7.24	29.09	89

Bismuth	Bi	83	35.41		28.10	47
Polonium	Po	84	36.92		25.52	3
Radium	Ra	88	75.06		46.17	6
Actinium	Ac	89	37.43		28.87	7
Thorium	Th	90	32.93	6.21	27.20	46
Protactinium	Pa	91	24.96		27.79	3
Uranium	U	92	20.69	5.73	21.09	76
Neptunium	Np	93		8.18	18.36	10
Plutonium	Pu	94		5.28	21.00	21
Americium	Am	95			19.80	13
Curium	Cm	96		5.28	23.49	5
Berkelium	Bk	97		7.24	29.36	2
Californium	Cf	98			0.51	1

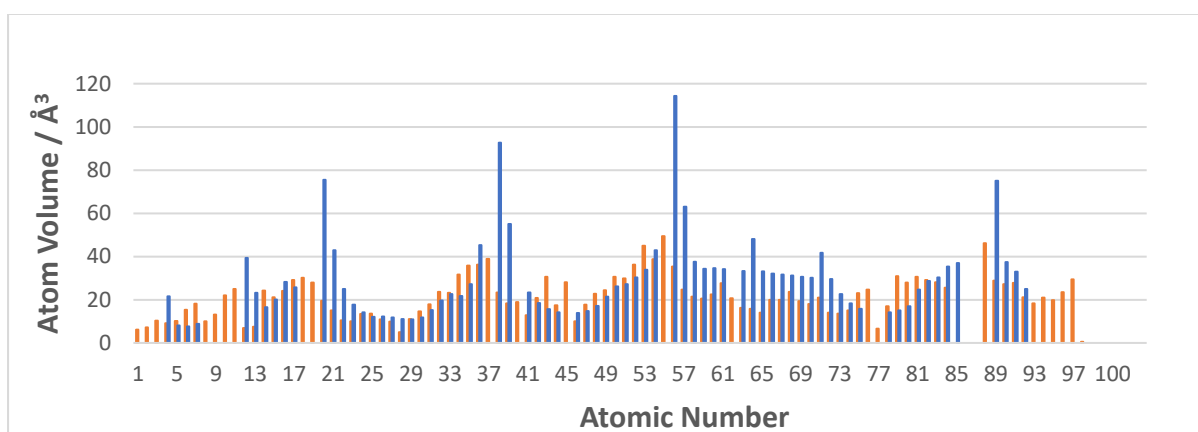


Figure 1: Volumes of the chemical elements / \AA^3 against atomic number under ambient conditions in a bar chart where, for each element, the initial orange bar represents the current inorganic solid optimised value, followed by the blue bar for the literature volume of the solid element.²⁵⁻²⁶ The data appear in Table 1.

The atom volumes in Fig. 1 show that the derived atom values rather closely follow the periodic values of the elements even though the derived values refer to atoms combined in formula units. The major discrepancies between the atom sum and elemental volumes occur for the alkali metals and alkaline earths which form closed-shell cations in their compounds with their volumes in combination thus reduced relative to those of their open shell elements.

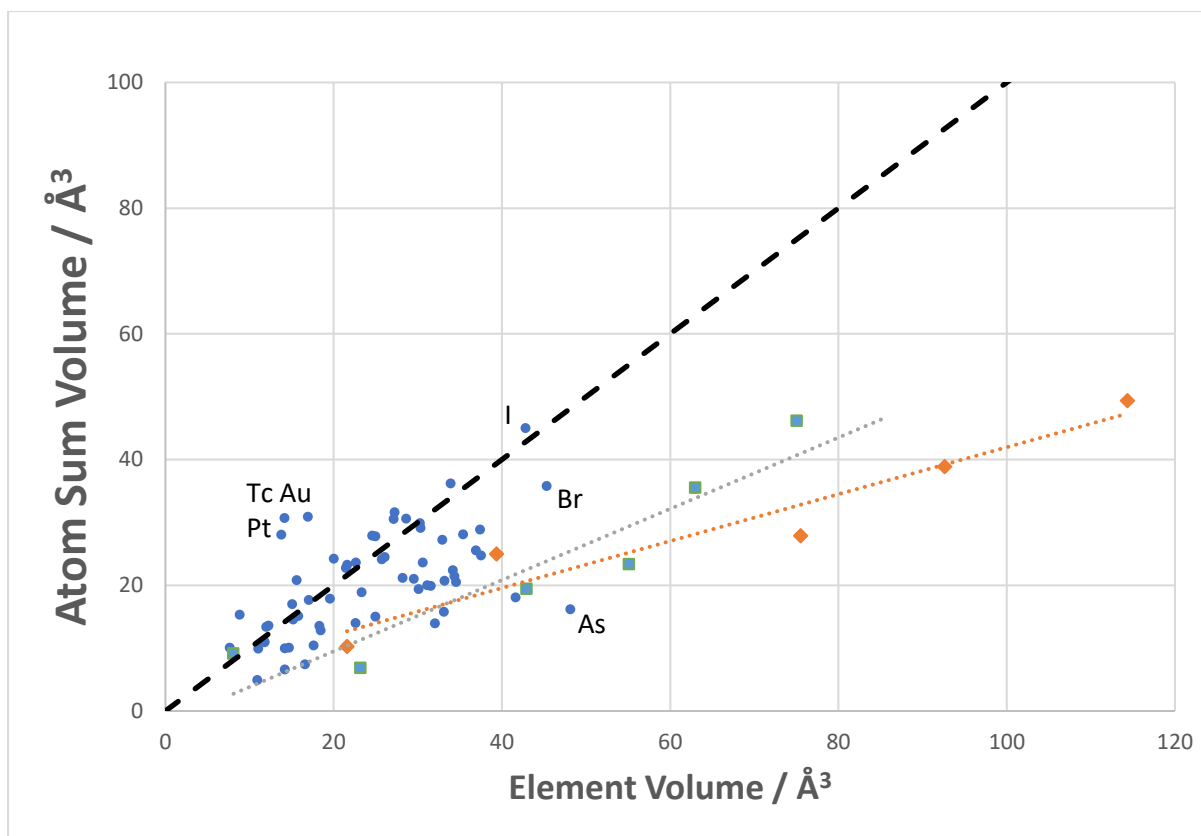


Figure 2: Optimised atom volume terms / \AA^3 for ionic solids plotted versus experimental elemental atomic volumes²⁵⁻²⁶ (blue circles) under ambient conditions using data in Table 1. Overlaid orange diamonds represent alkali metals, while overlaid green squares represent alkaline earths. Trendlines are included simply to delineate the elemental groups. The broken black diagonal line represents equality of the optimised atomic sum term and the literature volume. A few prominent outliers have been labelled.

Figure 2 compares the optimised inorganic atom sum volume with the corresponding elemental volume, as listed in Table 1. For the thermal expansion coefficient, which is assumed to be linear, Hofmann has established a value,¹³ α , of $0.95 \times 10^{-3} \text{ K}^{-1}$, which may reasonably be applied quite generally to these materials.

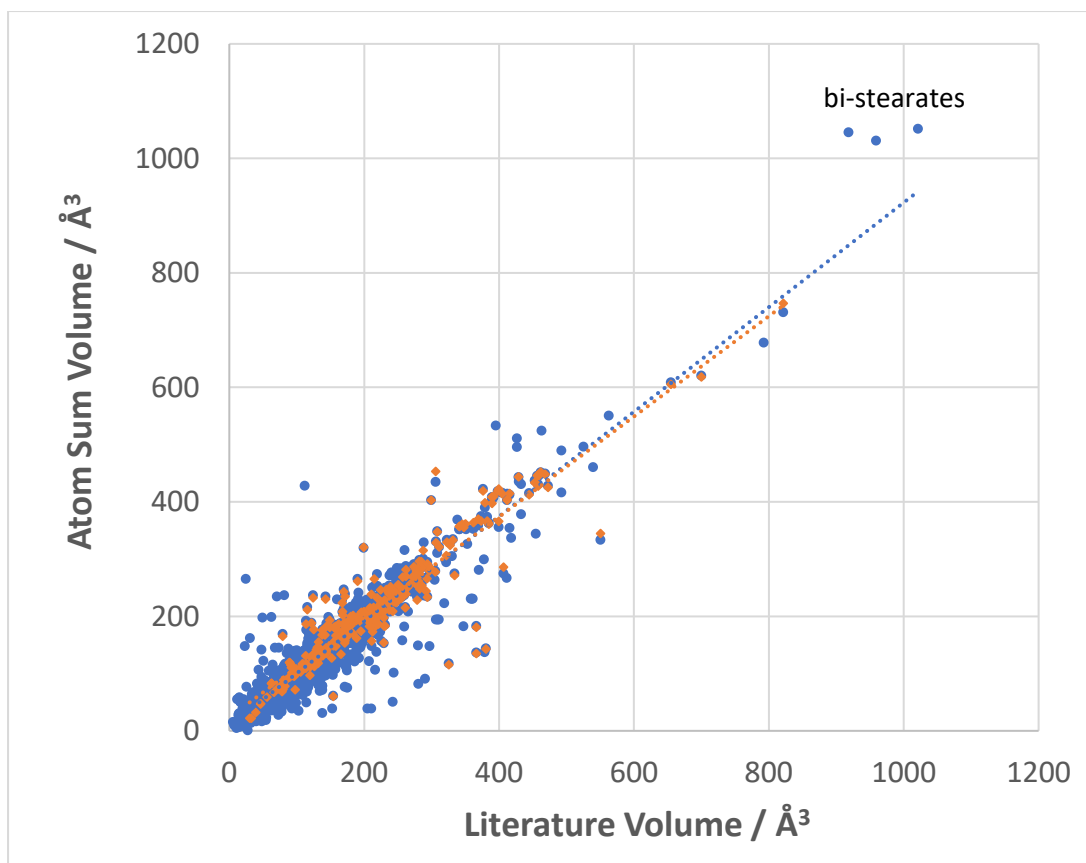


Figure 3: Optimised atom sum volumes / \AA^3 versus literature element volumes for 2 621 unique inorganic solids (blue circles) under ambient conditions, which include data for 325 hydrates (overlaid as orange diamonds). The fitted line for the full set 2 621 inorganic solids is $V/\text{\AA}^3 = 0.914 (\pm 0.006) V_{\text{sum}} + 9.2 (\pm 0.8)$ with correlation coefficient $R^2 = 0.90$, while for the 325 hydrated solids it is $V/\text{\AA}^3 = 0.876 (\pm 0.018) V_{\text{sum}} + 23 (\pm 4)$ with $R^2 = 0.88$. The three extreme blue circles represent Pb, Zn and Ba bi-stearates.

Fig. 3 demonstrates that the atomic sums are adequate predictive values for the volumes of inorganic solids. For example, the atom sum volume of H_2O is $2 \times 6.08 + 10.07 = 22.23 \text{\AA}^3$ which accords exactly with a generic value of the volume of waters of crystallization earlier established for ionic systems.²⁷ This volume is only 70% of the volume of liquid water reflecting the tighter binding in the hydrate. A histogram in Fig. 4 demonstrates that the errors are symmetrically distributed. The standard error of the overall estimate (or regression) is $\pm 26.7 \text{\AA}^3$ and for the hydrates it is ± 36.2

\AA^3 . The 95% confidence interval for the overall mean volume is $\pm 3.16 \text{\AA}^3$ based upon 3 347 chemical formulae, a mean volume of 104.0\AA^3 , and a standard deviation of 93.30\AA^3 .

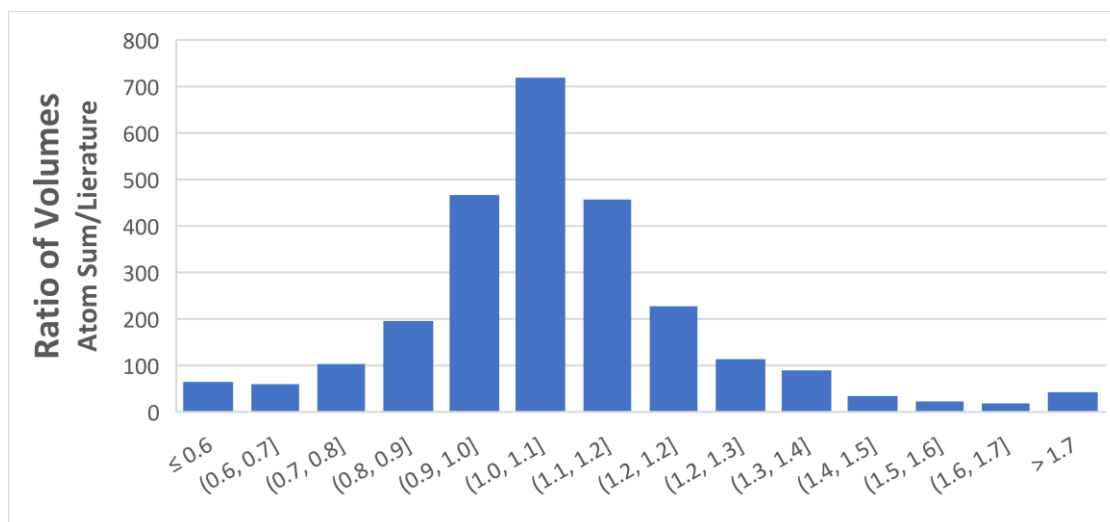


Figure 4: Ratio of atom sum to literature volumes under ambient conditions for 2 621 inorganic solids, including 325 hydrates. The data is roughly symmetrically distributed. Outliers have been omitted.

Predicted volumes are readily converted to densities, with the formula²⁷

$$V/\text{\AA}^3 = M/\text{g mol}^{-1}/[0.6022/\text{cm}^3 \text{\AA}^{-3} \text{mol}^{-1} \times \rho/\text{g cm}^{-3}]$$

where the terms are: molar mass is $M/\text{g mol}^{-1}$; density is $\rho/\text{g cm}^{-3}$; the length conversion constant is $10^{-8}/\text{cm \AA}^{-1}$; Avogadro's Constant, $N_A = 6.022 \times 10^{23}/\text{mol}$, and $N_A \times (10^{-8}/\text{cm \AA}^{-1})^3 = 0.6022/\text{cm}^3 \text{\AA}^{-3} \text{mol}^{-1}$.

Example: Estimate the molar volume of alumina, Al_2O_3 .

$$\text{Given } M = 101.96 \text{ g mol}^{-1}; \rho = 3.96 \text{ g cm}^{-3}; V = 42.84 \text{ \AA}^3 \text{ mol}^{-1}.$$

$$V_{\text{sum}}(\text{Al}_2\text{O}_3) = 2 \times V_{\text{sum}}(\text{Al}) + 3 \times V_{\text{sum}}(\text{O}) = 2 \times 7.4 + 3 \times 10.1 = 45.1 \text{ \AA}^3 (+5\% \text{ error}^6).$$

Thermodynamic Properties: In earlier studies, we established that entropy is strongly correlated with formula volume and, similarly, so must be heat capacity.²⁸⁻³² However, a volume correlation is not

universally true for all thermodynamic functions: for example, the formation enthalpy of each element is independently defined as zero under standard conditions so cannot support a common correlation. We report here on the correlation under ambient conditions of each of standard absolute entropy and of heat capacity with corresponding atom sum terms, and their linear temperature coefficients.

Entropies: Table 2 lists the optimised atom sum entropies, including the number of atoms contributing to each quantity. Fig. 5 shows the periodic behaviour of entropies. Fig. 6 plots the optimised single atom entropies against their elemental values while Fig. 7 plots the atom sum entropies against their literature values. Fig. 8 is a histogram depicting the distribution of the atom sum to literature entropies.

Table 2: Atom entropies, $S^\circ / \text{J K}^{-1} \text{mol}^{-1}$, of those elements which are solid under ambient conditions and related Atom Sum terms under ambient conditions.

	Symbol	At. No.	Solid Element ⁶ $S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	Atom Sum Term $S / \text{J K}^{-1} \text{mol}^{-1}$	No. of Atoms
Hydrogen	H	1		10.64	1225
Deuterium	D	(2)		7.72	11
Lithium	Li	3	29.12	18.26	50
Beryllium	Be	4	9.50	8.23	36
Boron	B	5	5.90	6.73	136
Carbon	C	6	5.74	17.73	136
Nitrogen	N	7		23.37	176
Oxygen	O	8		14.06	2679
Fluorine	F	9		25.25	360
Neon	Ne	10			
Sodium	Na	11	51.30	33.48	115
Magnesium	Mg	12	32.53	15.87	102
Aluminium	Al	13	28.28	9.87	91
Silicon	Si	14	18.82	13.55	212
Phosphorus (white)	P	15	41.10	23.64	107
Sulfur	S	16	32.07	23.25	365
Chlorine	Cl	17		38.69	432
Argon	Ar	18			
Potassium	K	19	64.68	54.21	81
Calcium	Ca	20	41.59	26.75	71

Scandium	Sc	21	34.64	28.49	15
Titanium	Ti	22	30.72	26.03	58
Vanadium	V	23	28.91	23.79	49
Chromium	Cr	24	23.54	15.93	66
Manganese	Mn	25	32.22	38.73	70
Iron	Fe	26	27.28	33.13	98
Cobalt	Co	27	30.04	31.77	45
Nickel	Ni	28	29.80	31.35	59
Copper	Cu	29	33.15	39.63	52
Zinc	Zn	30	41.63	36.20	40
Gallium	Ga	31	40.73	29.36	23
Germanium	Ge	32	31.09	30.22	27
Arsenic	As	33	35.69	32.30	59
Selenium	Se	34	42.44	38.15	135
Bromine	Br	35	76.11	48.87	232
Krypton	K	36			
Rubidium	Rb	37	76.78	59.07	30
Strontium	Sr	38	52.30	45.63	26
Yttrium	Y	39	44.79	29.04	14
Zirconium	Zr	40	39.18	34.85	20
Niobium	Nb	41	36.27	35.38	27
Molybdenum	Mo	42	28.56	28.20	41
Technetium	Tc	43	32.99	0.02	2
Ruthenium	Ru	44	28.61	18.41	13
Rhodium	Rh	45	31.56	27.86	10
Palladium	Pd	46	37.82	30.40	13
Silver	Ag	47	42.68	58.06	40
Cadmium	Cd	48	51.80	39.49	30
Indium	In	49	57.65	39.74	25
Tin	Sn	50	51.18	48.05	23
Antimony	Sb	51	45.52	43.71	47
Tellurium	Te	52	49.41	48.47	112
Iodine	I	53	58.07	57.26	219
Xenon	Xe	54		62.90	3
Cesium	Cs	55	85.23	75.59	24
Barium	Ba	56	62.50	50.76	46
Lanthanum	La	57	56.90	40.86	22
Cerium	Ce	58	72.01	50.46	30
Praseodymium	Pr	59	73.93	54.76	19
Neodymium	Nd	60	71.09	55.56	17
Promethium	Pm	61	72.00	56.89	2
Samarium	Sm	62	69.50	57.91	20
Europium	Eu	63	77.82	56.51	15
Gadolinium	Gd	64	68.09	57.20	19

Terbium	Tb	65	73.30	69.48	11
Dysprosium	Dy	66	74.96	66.25	12
Holmium	Ho	67	75.02	57.07	8
Erbium	Er	68	74.40	57.64	12
Thulium	Tm	69	73.01	34.03	8
Ytterbium	Yb	70	59.83	48.66	12
Lutetium	Lu	71	50.96	35.50	10
Hafnium	Hf	72	43.56	28.67	8
Tantalum	Ta	73	41.51	42.71	22
Tungsten	W	74	32.62	36.94	46
Rhenium	Re	75	36.48	34.69	20
Osmium	Os	76	32.64	32.47	9
Iridium	Ir	77	35.51	24.34	9
Platinum	Pt	78	41.63	31.89	16
Gold	Au	79	47.49	48.42	14
Mercury	Hg	80	76.03	73.40	29
Thallium	Tl	81	64.30	65.43	23
Lead	Pb	82	64.80	58.44	44
Bismuth	Bi	83	56.74	52.84	20
Polonium	Po	84	62.00	48.10	2
Radium	Ra	88	69.00	54.52	3
Actinium	Ac	89	62.00	29.35	4
Thorium	Th	90	51.80	44.61	40
Protactinium	Pa	91	51.88	46.47	2
Uranium	U	92	50.20	55.50	64
Neptunium	Np	93	50.46	49.22	8
Plutonium	Pu	94	51.50	53.28	17
Americium	Am	95	55.40	41.11	9
Curium	Cm	96	71.96	57.90	4

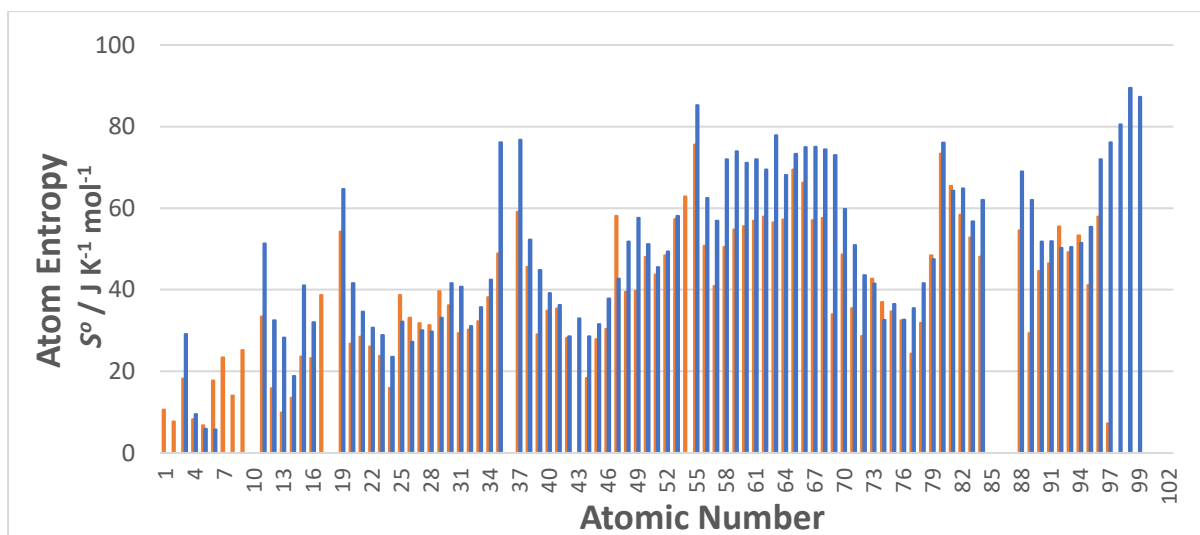


Figure 5: Standard absolute entropies of the chemical elements, $S^\circ / \text{J K}^{-1} \text{mol}^{-1}$ against atomic number under ambient conditions in a bar chart where, for each element, the initial orange bar represents the optimised atom sum value for inorganic solids, paired with the blue literature entropy bar of the solid element.²⁵⁻²⁶ The data appear in Table 2.

Fig. 5 demonstrates that the atom sum entropies follow the general periodic sequence of the elements.

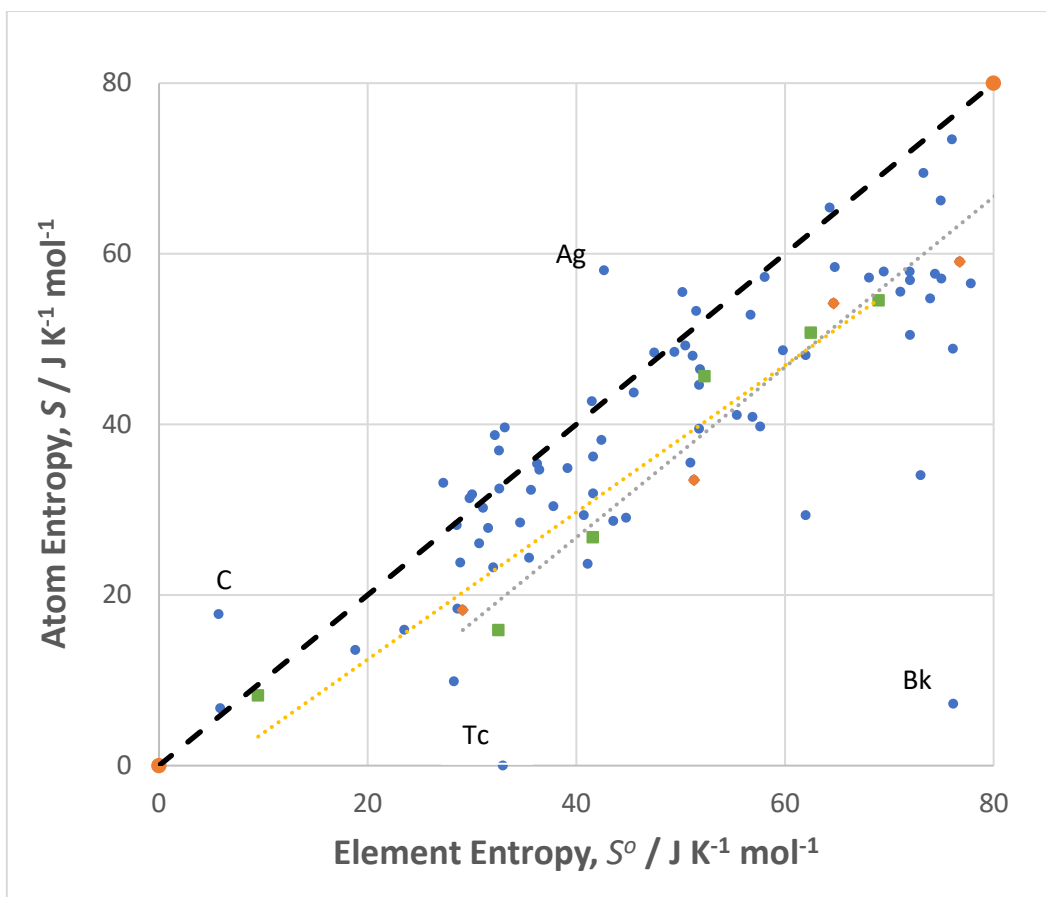


Figure 6: Single atom entropy terms optimised for ionic solids plotted versus experimental elemental atomic entropies under ambient conditions, using data in Table 2. Overlaid orange diamonds represent alkali metals, while overlaid green squares represent alkaline earths. Trendlines are included simply to delineate the elemental groups. The broken black diagonal line represent equality of the atomic term and the literature elemental entropy.

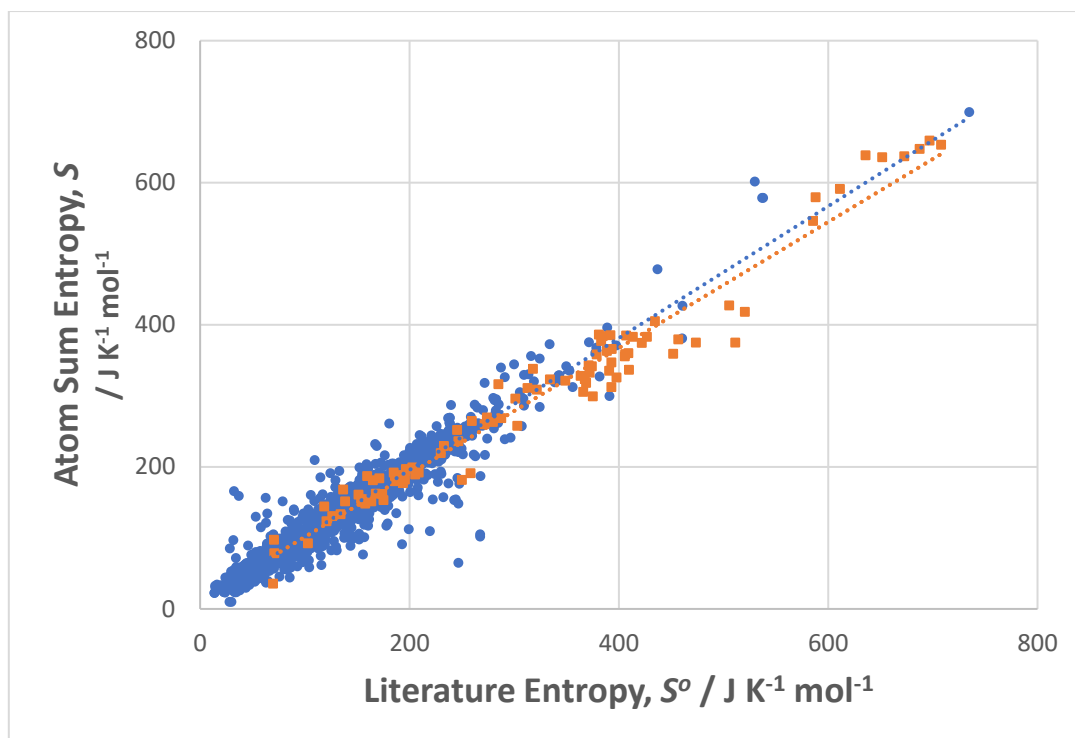


Figure 7: Optimised atom sum entropies, $S/\text{J K}^{-1} \text{mol}^{-1}$ versus literature element entropies under ambient conditions for 1 441 unique inorganic solids (blue circles), together with data for 95 hydrates (overlaid orange squares). The fitted line for the 1 441 inorganic solids is $S/\text{J K}^{-1} \text{mol}^{-1} = 0.928 (\pm 0.008) S_{\text{sum}} + 9.9 (\pm 1.1)$ with correlation coefficient $R^2 = 0.91$, while for the 95 hydrates it is $S/\text{J K}^{-1} \text{mol}^{-1} = 0.887 (\pm 0.018) S_{\text{sum}} + 12.6 (\pm 6.3)$ with $R^2 = 0.96$.

The standard error of the overall estimate (or regression) is $\pm 21.6 \text{ J K}^{-1} \text{mol}^{-1}$. The 95% confidence interval for the overall mean entropy is $\pm 41.62 \text{ J K}^{-1} \text{mol}^{-1}$ based upon 1 536 chemical formulae, a mean entropy of $140.6 \text{ J K}^{-1} \text{mol}^{-1}$, and a standard deviation of $93.32 \text{ J K}^{-1} \text{mol}^{-1}$.

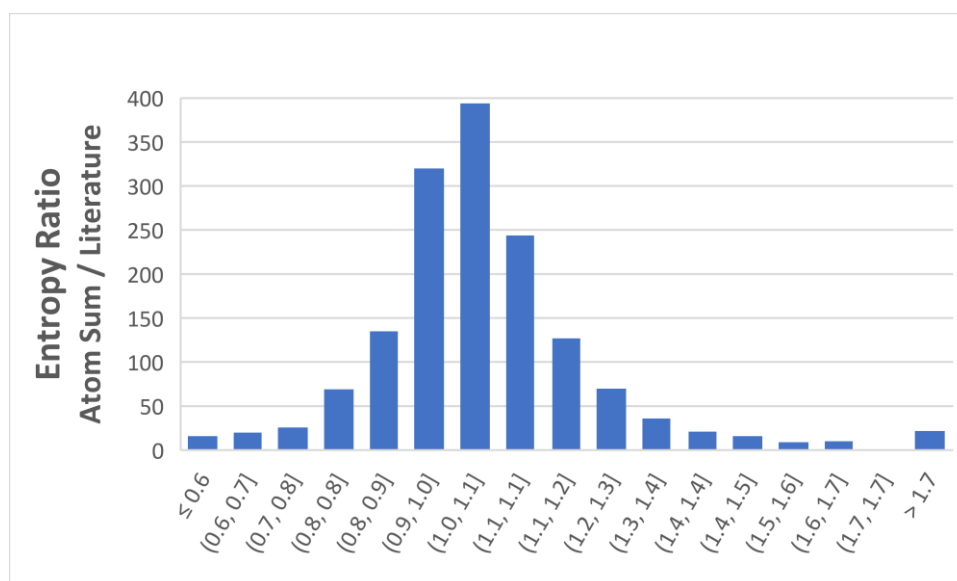


Figure 8: Ratio of single atom entropy sum to literature entropies for 1 536 inorganic solids under ambient conditions, including hydrates. The data is roughly symmetrically distributed.

Fig. 6 shows that the atom sum entropies broadly follow the elemental entropies. Fig. 7 and 8 show a rather wide distribution of entropies for the inorganic solids, increasing somewhat in width with increasing entropy. It is suggested that this probably reflects the difficulty in reliable measurement of entropy.

Table 3: Standard entropy difference, $\Delta S_{298}^{\circ} / \text{J K}^{-1} \text{mol}^{-1}$, between 87 inorganic hydrates and their anhydrides under ambient conditions. Entropy difference; number of water molecules per hydrate, $n(\text{H}_2\text{O})$; and entropy difference per hydration water molecule.

Hydrate	ΔS_{298}°	$n(\text{H}_2\text{O})$	$\frac{\Delta S_{298}^{\circ}}{n(\text{H}_2\text{O})}$
$\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$	9.80	1	9.80
$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	19.72	1	19.72
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	27.81	1	27.81
$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$	27.99	1	27.99
$\text{LiOH} \cdot \text{H}_2\text{O}$	28.19	1	28.19
$\text{CdSO}_4 \cdot \text{H}_2\text{O}$	31.02	1	31.02
$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	31.43	1	31.43
$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	33.08	1	33.08
$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	34.76	1	34.76
$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	36.78	1	36.78
$\text{UO}_3 \cdot \text{H}_2\text{O}$	38.20	1	38.20

Sr(BrO ₃) ₂ ·H ₂ O	41.51	1	41.51
BeSO ₄ ·H ₂ O	42.99	1	42.99
LiCl·H ₂ O	43.70	1	43.70
Ba(BrO ₃) ₂ ·H ₂ O	44.86	1	44.86
FeCl ₂ ·2H ₂ O	47.04	2	23.52
CaC ₂ O ₄ ·2H ₂ O	48.68	2	24.34
Li ₂ SO ₄ ·H ₂ O	49.69	1	49.69
Ca(H ₂ PO ₄) ₂ ·H ₂ O	70.29	1	70.29
CuF ₂ ·2H ₂ O	73.66	2	36.83
NaI·2H ₂ O	75.44	2	37.72
FePO ₄ ·2H ₂ O	77.53	2	38.76
CaHPO ₄ ·2H ₂ O	78.16	2	39.08
BaCl ₂ ·2H ₂ O	79.23	2	39.62
BaBr ₂ ·2H ₂ O	80.00	2	40.00
BaI ₂ ·2H ₂ O	81.71	2	40.86
Al ₂ O ₃ ·3H ₂ O	85.95	3	28.65
CuCl ₂ ·2H ₂ O	87.23	2	43.62
CaSO ₄ ·2H ₂ O	87.41	2	43.70
NaBr·2H ₂ O	88.38	2	44.19
NiCl ₂ ·2H ₂ O	88.55	2	44.27
KF·2H ₂ O	89.45	2	44.73
UO ₂ SO ₄ ·3H ₂ O	119.28	3	39.76
CaSeO ₄ ·2H ₂ O	121.82	2	60.91
FeCl ₂ ·4H ₂ O	127.54	4	31.89
MgCO ₃ ·3H ₂ O	130.55	3	43.52
AlF ₃ ·3H ₂ O	142.49	3	47.50
MnSO ₄ ·4H ₂ O	144.96	4	36.24
BeSO ₄ ·4H ₂ O	155.08	4	38.77
CuSeO ₃ ·2H ₂ O	155.23	2	77.61
Ba(ClO ₄) ₂ ·3H ₂ O	156.90	3	52.30
LiI·3H ₂ O	163.49	3	54.50
Sr(NO ₃) ₂ ·4H ₂ O	174.44	4	43.61
CaCl ₂ ·6H ₂ O	176.63	6	29.44
Ca(NO ₃) ₂ ·4H ₂ O	182.08	4	45.52
MnCl ₂ ·4H ₂ O	184.76	4	46.19
Cd(NO ₃) ₂ ·4H ₂ O	185.01	4	46.25
CuSO ₄ ·5H ₂ O	191.99	5	38.40
AlCl ₃ ·6H ₂ O	207.33	6	34.55
Na ₂ S ₂ O ₃ ·5H ₂ O	217.57	5	43.51
MgSeO ₃ ·6H ₂ O	221.28	6	36.88
Cu(NO ₃) ₂ ·6H ₂ O	221.68	6	36.95
YbCl ₃ ·6H ₂ O	223.77	6	37.30
SmCl ₃ ·6H ₂ O	230.96	6	38.49
NdCl ₃ ·6H ₂ O	231.50	6	38.58
CoBr ₂ ·6H ₂ O	239.48	6	39.91
CoCl ₂ ·6H ₂ O	239.80	6	39.97
GdCl ₃ ·6H ₂ O	240.54	6	40.09
NiSO ₄ ·6H ₂ O	242.42	6	40.40
CuSeO ₄ ·5H ₂ O	243.35	5	48.67
CoSO ₄ ·6H ₂ O	250.26	6	41.71

ZnSO ₄ ·6H ₂ O	253.09	6	42.18
SrBr ₂ ·6H ₂ O	262.49	6	43.75
Zn(NO ₃) ₂ ·6H ₂ O	262.89	6	43.82
EuCl ₃ ·6H ₂ O	263.17	6	43.86
UO ₂ (NO ₃) ₂ ·6H ₂ O	264.60	6	44.10
MnSO ₄ ·7H ₂ O	266.30	7	38.04
SrCl ₂ ·6H ₂ O	275.99	6	46.00
MgCl ₂ ·6H ₂ O	276.48	6	46.08
ZnSO ₄ ·7H ₂ O	278.19	7	39.74
MgSO ₄ ·7H ₂ O	279.70	7	39.96
Na ₂ HPO ₄ ·7H ₂ O	279.91	7	39.99
CaBr ₂ ·6H ₂ O	280.00	6	46.67
MgBr ₂ ·6H ₂ O	281.00	6	46.83
NiSO ₄ ·7H ₂ O	286.89	7	40.98
Na ₂ CO ₃ ·7H ₂ O	287.18	7	41.03
Mg(NO ₃) ₂ ·6H ₂ O	288.00	6	48.00
FeSO ₄ ·7H ₂ O	288.24	7	41.18
CoSO ₄ ·7H ₂ O	288.69	7	41.24
Co(NO ₃) ₂ ·6H ₂ O	296.88	6	49.48
Mg(ClO ₄) ₂ ·6H ₂ O	309.70	6	51.62
La ₂ (SO ₄) ₃ ·9H ₂ O	316.97	9	35.22
Ni(NO ₃) ₂ ·6H ₂ O	319.24	6	53.21
Ba(OH) ₂ ·8H ₂ O	319.72	8	39.96
Na ₂ B ₄ O ₇ ·10H ₂ O	396.27	10	39.63
KCr(SO ₄) ₂ ·12H ₂ O	467.93	12	38.99
NH ₄ ·Al(SO ₄) ₂ ·12H ₂ O	480.74	12	40.06
KAl(SO ₄) ₂ ·12H ₂ O	482.80	12	40.23

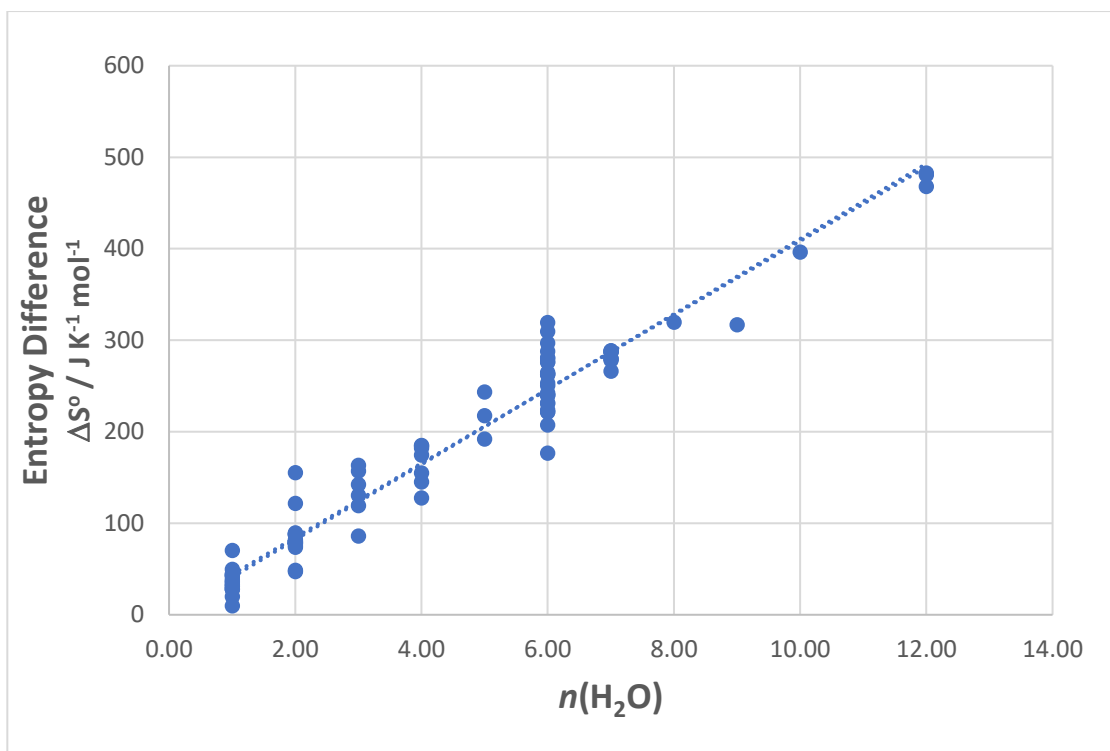


Figure 9: Plot of the entropy difference between hydrate and its corresponding anhydrate for 88 inorganic pairs at 25°C. Data in Table 3. The trendline (with intercept constrained to zero) is $S/J\ K^{-1}\ mol^{-1} = 41.07(\pm 0.52)n(H_2O)$, $R^2 = 0.99$.

From the slope of the trendline in Fig. 9, each water molecule contributes an entropy of $41\ J\ K^{-1}\ mol^{-1}$ into the formation of a corresponding hydrate which is only 70% of the standard entropy of pure water, $70\ J\ K^{-1}\ mol^{-1}$. This reduction in entropy contribution indicates that water molecules are rather constrained when confined within an hydrate.³³

In order to establish an entropy temperature coefficient, the entropy values at 80°C (in addition to those at 25°C) were calculated using the Excel add-in for “HSC Chemistry”. This was not available for each material, yielding 1 421 pairs of 80°C /25°C entropy values, plotted in Fig. 10.

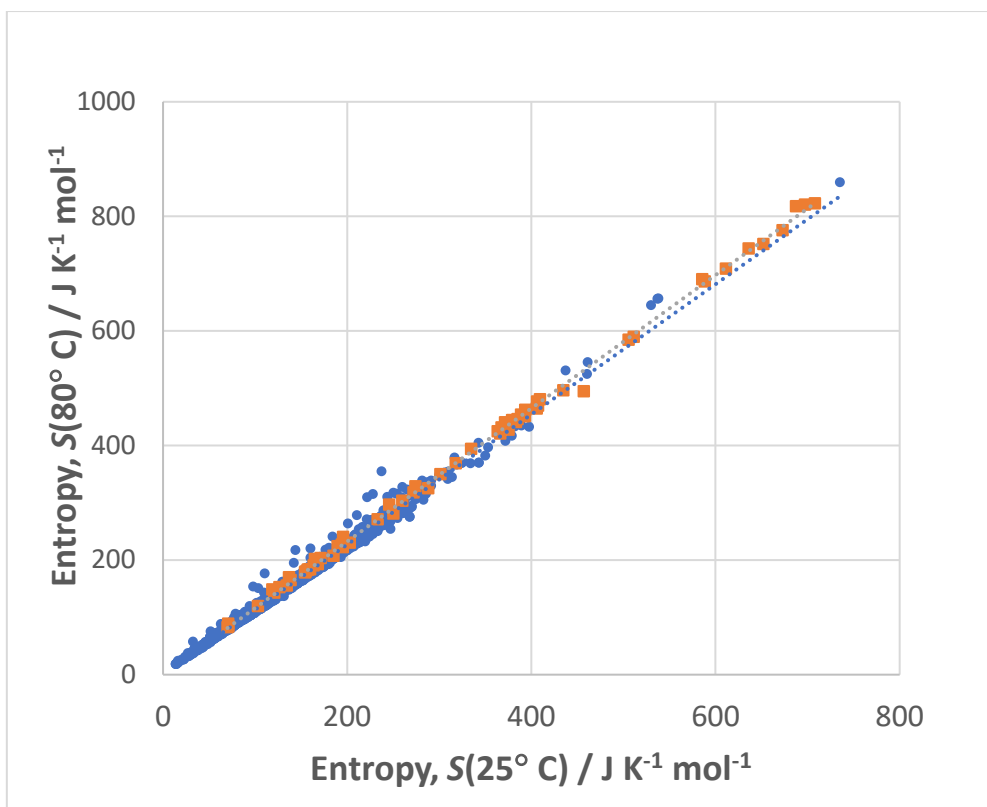


Figure 10: Entropy at 80°C plotted versus entropy at 25°C. The regression lines show the offset for the temperature increase from 25 to 80°C. Data for anhydrites (with blue circles, constrained to pass through the origin) follows the equation $S(80^{\circ}\text{C}) = 1.136(\pm 0.001) \cdot S(25^{\circ}\text{C})$, $R^2 = 0.99$. The orange squares represent hydrates with $S(80^{\circ}\text{C}) = 1.163(\pm 0.001) \cdot S(25^{\circ}\text{C})$, $R^2 = 0.99$. A linear temperature coefficient is calculated from the slope of each line (see text), with $\alpha_s = 2.5 \times 10^{-2} \text{ K}^{-1}$ for anhydrites, $\alpha_s = 9.4 \times 10^{-3} \text{ K}^{-1}$ for hydrates.

The regression lines in Fig. 10 show the offset in entropy for the temperature increase from 25 to 80°C. We assume a linear temperature coefficient for entropy: $S(T) = S(0) \cdot (1 + \alpha_s T)$ as was earlier assumed for volume.¹³ The ratio of the entropy for two temperatures is given by the slope of the regression line, thus:

$$(1 + \alpha_s T_2) / (1 + \alpha_s T_1) = \text{slope}$$

This equation for the temperature coefficient, α_s , together with a given slope is readily solved numerically using the Excel “Solver”.

Heat Capacities: Table 4 lists the optimised atom sum heat capacities, including the number of atoms contributing to each quantity. Fig. 11 plots the optimised single atom heat capacities against their elemental values while Fig. 12 plots the atom sum heat capacities against their literature values. Fig. 13 is a histogram depicting the distribution of the ratio of the atom sum to literature elemental heat capacities. Fig. 14 compares the heat capacities at 80°C against those at 25°C.

Table 4: Atom heat capacities, C_p , of those elements which are solid under ambient conditions and related Atom Sum terms under ambient conditions.

	Symbol	At. No.	Solid Element ⁶ $C_p / \text{J K}^{-1} \text{mol}^{-1}$	Atom Sum Term $C_p / \text{J K}^{-1} \text{mol}^{-1}$	No. of Atoms
Hydrogen	H	1		11.72	347
Deuterium	D	(2)		12.07	9
Lithium	Li	3	24.79	21.53	45
Beryllium	Be	4	16.41	15.03	33
Boron	B	5	11.07	12.13	131
Carbon	C	6	8.53	12.44	122
Nitrogen	N	7		15.78	125
Oxygen	O	8		15.95	1852
Fluorine	F	9		20.88	343
Neon	Ne	10			
Sodium	Na	11	28.70	26.37	93
Magnesium	Mg	12	24.80	20.62	88
Aluminium	Al	13	24.20	18.31	83
Silicon	Si	14	19.79	12.27	207
Phosphorus (white)	P	15	23.81	18.08	97
Sulfur	S	16	22.69	22.10	277
Chlorine	Cl	17		24.10	375
Argon	Ar	18			
Potassium	K	19	29.58	42.55	70
Calcium	Ca	20	25.94	23.60	63
Scandium	Sc	21	25.51	23.10	7
Titanium	Ti	22	25.06	32.68	49
Vanadium	V	23	24.90	26.14	47
Chromium	Cr	24	23.43	27.08	62
Manganese	Mn	25	26.30	29.38	61
Iron	Fe	26	24.82	27.96	94
Cobalt	Co	27	25.27	25.53	34
Nickel	Ni	28	25.98	26.25	53
Copper	Cu	29	24.44	24.89	41

Zinc	Zn	30	25.39	22.67	37
Gallium	Ga	31	26.12	27.96	22
Germanium	Ge	32	23.23	25.48	24
Arsenic	As	33	24.67	23.03	51
Selenium	Se	34	25.02	23.68	72
Bromine	Br	35	35.77	25.51	202
Krypton	Kr	36			
Rubidium	Rb	37	31.05	28.82	24
Strontium	Sr	38	26.82	26.85	21
Yttrium	Y	39	26.52	19.51	10
Zirconium	Zr	40	25.99	25.65	19
Niobium	Nb	41	24.42	27.27	25
Molybdenum	Mo	42	23.97	27.36	41
Technetium	Tc	43	24.66	25.53	2
Ruthenium	Ru	44	24.30	20.68	11
Rhodium	Rh	45	24.99	26.81	8
Palladium	Pd	46	25.94	19.39	9
Silver	Ag	47	25.36	27.06	34
Cadmium	Cd	48	26.02	30.00	27
Indium	In	49	26.90	25.45	24
Tin	Sn	50	27.10	25.89	23
Antimony	Sb	51	25.33	24.18	48
Tellurium	Te	52	25.71	25.33	64
Iodine	I	53	27.22	25.71	196
Xenon	Xe	54		38.27	3
Cesium	Cs	55	32.21	31.23	22
Barium	Ba	56	28.11	27.17	36
Lanthanum	La	57	27.10	24.02	17
Cerium	Ce	58	26.89	29.44	25
Praseodymium	Pr	59	27.55	31.56	12
Neodymium	Nd	60	27.43	30.29	15
Promethium	Pm	61	28.00	33.35	2
Samarium	Sm	62	29.55	30.66	11
Europium	Eu	63	27.11	35.89	10
Gadolinium	Gd	64	36.87	24.70	9
Terbium	Tb	65	28.87	25.74	8
Dysprosium	Dy	66	27.77	28.52	7
Holmium	Ho	67	27.12	29.10	6
Erbium	Er	68	26.63	29.34	5
Thulium	Tm	69	27.36	31.64	5
Ytterbium	Yb	70	26.69	29.54	6
Lutetium	Lu	71	26.62	26.71	4
Hafnium	Hf	72	25.69	26.73	8
Tantalum	Ta	73	25.36	27.76	22

Tungsten	W	74	24.30	30.00	39
Rhenium	Re	75	25.00	24.37	19
Osmium	Os	76	24.65	34.30	7
Iridium	Ir	77	25.00	24.20	7
Platinum	Pt	78	25.55	21.97	13
Gold	Au	79	25.29	28.14	13
Mercury	Hg	80	27.97	24.98	22
Thallium	Tl	81	26.30	28.88	22
Lead	Pb	82	26.65	28.25	43
Bismuth	Bi	83	26.05	26.82	17
Polonium	Po	84	26.00	25.59	2
Astatine	At	85			
Radon	Rn	86			
Francium	Fr	87			
Radium	Ra	88	29.00	30.23	
Actinium	Ac	89	27.00	31.70	4
Thorium	Th	90	26.20	25.92	37
Protactinium	Pa	91	28.21	28.32	2
Uranium	U	92	27.66	33.50	52
Neptunium	Np	93	29.62	31.28	8
Plutonium	Pu	94	31.49	30.74	16
Americium	Am	95	25.50	38.14	7

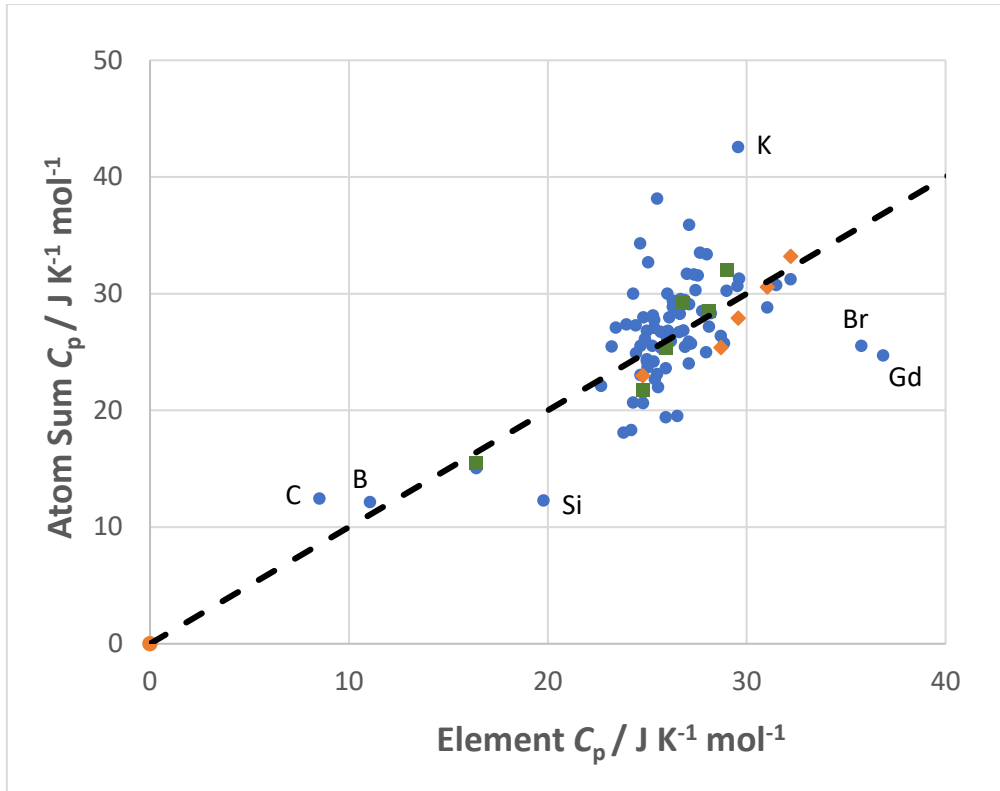


Figure 11: Atom sum heat capacity terms, $C_p / J K^{-1} mol^{-1}$, for ionic solids plotted versus literature elemental atomic heat capacity values under ambient conditions, using data in Table 3. Overlaid orange diamonds represent alkali metals, while overlaid green squares represent alkaline earths. The broken black diagonal line represent equality of the atomic term and the literature value of the elemental heat capacity. The upper limit of the elemental values corresponds approximately to the Dulong-Petit value of $3R \cong 25 J K^{-1} mol^{-1}$, while the atom sum values cover a rather wider range of about $20-40 J K^{-1} mol^{-1}$. The significant outlier elements are labelled.

Fig. 11 is strikingly different from the corresponding Figures for volume (Fig. 2) and entropy (Fig. 6) in exhibiting a limited spread in the data. This is a consequence of heat capacity having an upper temperature limit of about $3R$ per atom according to the Dulong-Petit Rule, arising from full excitation of lattice vibrations.

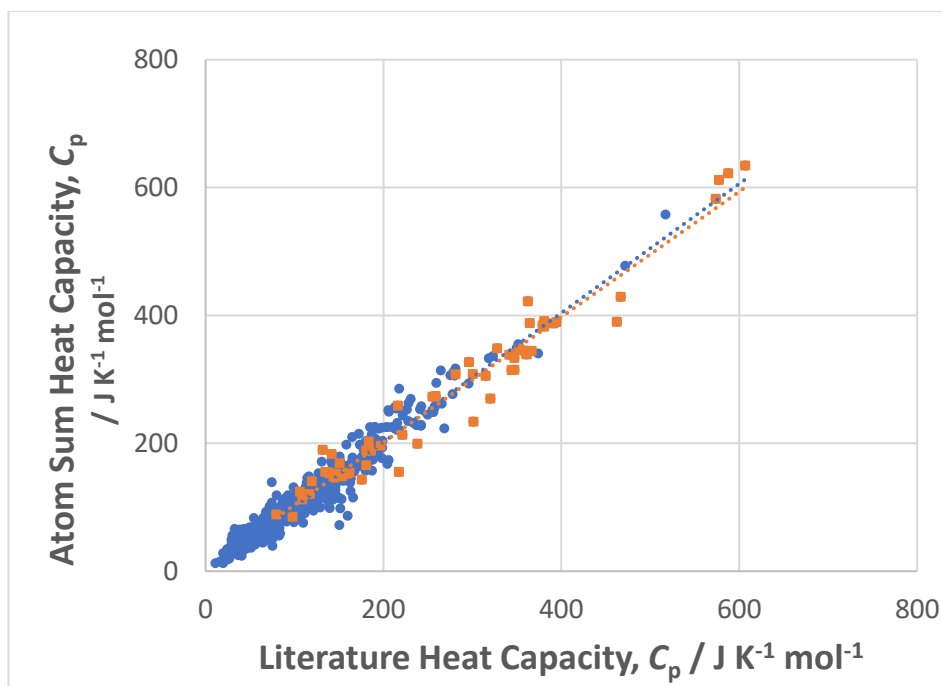


Figure 12: Optimised atom sum heat capacities, C_p , versus literature heat capacities for 1 315 inorganic solids under ambient conditions. Data for 94 hydrates is overlaid with orange squares. The equation for the fitted line is $C_p / \text{J K}^{-1} \text{ mol}^{-1} = 0.980 (\pm 0.004) C_{\text{sum}} + 1.4 (\pm 0.5)$ with correlation coefficient $R^2 = 0.97$. The standard error of the estimate/regression is $\pm 9.5 \text{ J K}^{-1} \text{ mol}^{-1}$. The 95% one-tailed confidence interval for the overall mean heat capacity is $2.96 \text{ J K}^{-1} \text{ mol}^{-1}$ based upon 1 429 chemical formulae, a mean heat capacity of $98.8 \text{ J K}^{-1} \text{ mol}^{-1}$, and a standard deviation of $68.06 \text{ J K}^{-1} \text{ mol}^{-1}$.

The heat capacity of liquid water is $75.23 \text{ J K}^{-1} \text{ mol}^{-1}$ which contrasts with the atom sum value of $39.4 \text{ J K}^{-1} \text{ mol}^{-1}$, again demonstrating the limited freedom of water molecules in hydrates.

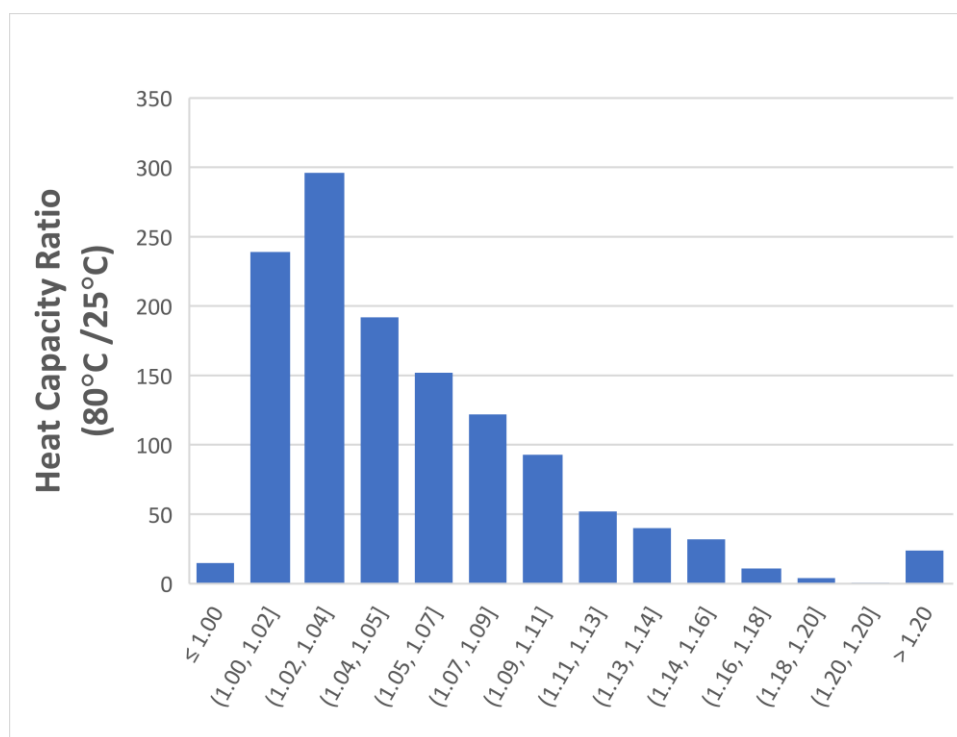


Figure 13: Ratio between 80°C and 25°C of heat capacity atom sum to literature heat capacities for 1 315 inorganic solids under ambient conditions. The data is asymmetrically distributed from a ratio of 1, but with a number of underflow entries having heat capacity ratios below 0.7 and overflow entries having heat capacity ratios above 1.5.

The standard error of the overall estimate (or regression) is $\pm 12.3 \text{ J K}^{-1} \text{ mol}^{-1}$. The one-tailed 95% confidence interval for the overall mean heat capacity is $2.96 \text{ J K}^{-1} \text{ mol}^{-1}$ based upon 1 429 chemical formulae, a mean heat capacity of $98.80 \text{ J K}^{-1} \text{ mol}^{-1}$, and a standard deviation of $68.06 \text{ J K}^{-1} \text{ mol}^{-1}$.

In Fig. 13 we again observe that there is an upper limit to heat capacities such that the largest heat capacities are similar while they drop away at lower temperatures. Thus, the higher temperature heat capacity should always exceed the lower temperature value, leading to an lower limit of one for the ratio – but experimental errors may occasionally defeat this conclusion as seen in the underflow block in Fig. 13!

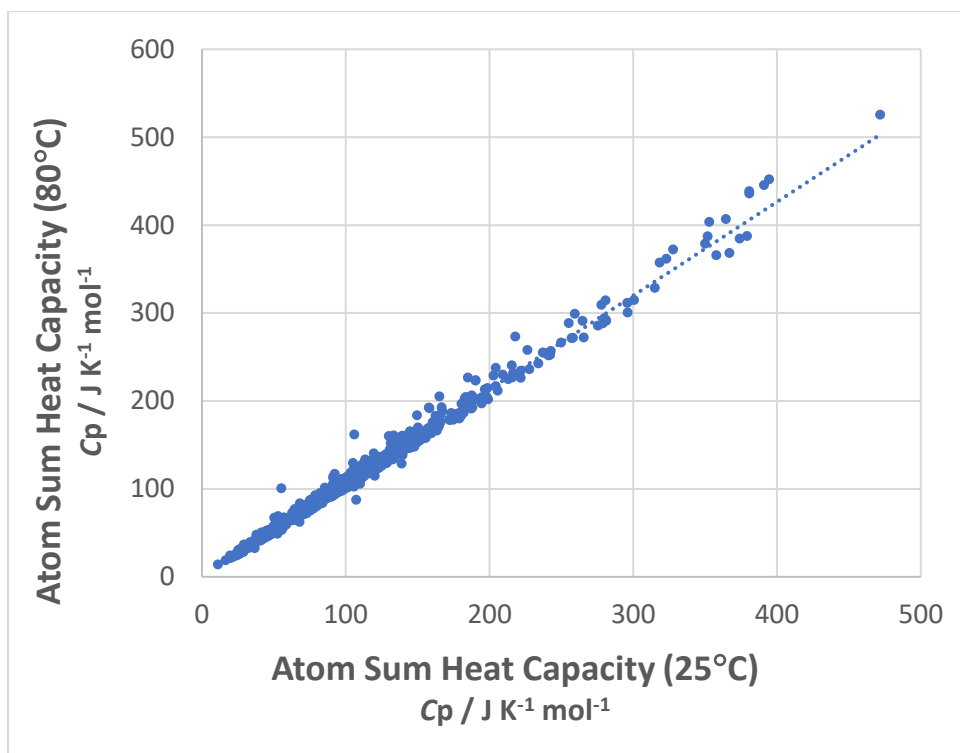


Figure 14: Heat capacity at 80°C plotted versus heat capacity at 25°C for 1 272 inorganic solids. The regression line with blue circles (constrained to pass through the origin), $C_p(80^\circ\text{C}) = 1.07 \cdot C_p(25^\circ\text{C})$, $R^2 = 0.99$, shows the offset for the temperature increase from 25 to 80°C. The linear temperature coefficient, $\alpha_{C_p} = 8.7 \times 10^{-3} \text{ K}^{-1}$, may be calculated from the slope of this line (see text).

Conclusions

A database of nearly 3 500 inorganic solids has been used to develop an updated set of atom sum terms for their volumes, and new values for entropies and heat capacities and their temperature coefficients. For the volumes and heat capacities, the atom sum terms follow slightly modified atomic sequence relations but for heat capacities the Dulong-Petit value of $3R$ per atom acts as a rough limit to the range of values. It must be appreciated that the reference data values are not definitive and carry their own experimental errors. However, additivity seems to be well-established such that extreme outliers invite detailed scrutiny. Careful investigators will seek out related data in order to confirm their conclusions.³⁴

These collections of atom sum terms (Tables 1, 2 and 4) provide predictive procedures by which missing thermodynamic values may be estimated and published values checked.

Acknowledgement

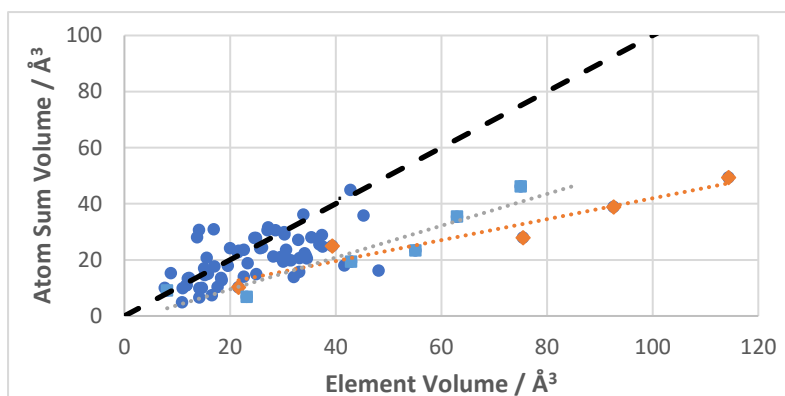
Use of the excellent *ChemicalParsing* program by Albert “Brad” Yundt (Florida, USA) for extraction from chemical formulae of constituent atoms and their numbers is gratefully acknowledged.

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Table of Contents Graphic



Optimised single atom values for inorganic solids are summed to generate predictive values for formula unit volumes, standard absolute entropies and heat capacities at 80°C and 25°C. This simple additive group contribution method requires no interaction terms, and applies to the full range of inorganic solids for which the individual sum atom values are listed. However, it does not distinguish among structures with the same composition.