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Additive single atom values for thermodynamics II: Enthalpies, entropies and Gibbs energies for formation of ionic solids

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ABSTRACT

In part I of this series we established optimised sum values, for each of the chemical elements, of formula volumes, of absolute entropies, and of constant pressure heat capacities, together with their temperature coefficients. These atom values, when summed for a chemical formula, provided zero-level estimates of the corresponding property of that chemical material. Atom sums have the particular advantage of being essentially complete because of the finite number of chemical elements and are of use in prediction and checking of values for chemical materials. However, this is at the expense of an inability to distinguish among isomers and phases with the same chemical formula nor do they allow for effects of atom interactions.

In the present publication, we present optimised atom sums for formation entropies, formation enthalpies and their relation to formation Gibbs energies.

In order to check the reliability of the results, comparison is made among methods of prediction using each of DFT calculations, a proprietary group contribution method, and the proposed single atom sum method. The single atom sum method is found to be most suitable as an initial estimate for large formation entropies and also for large values of formation enthalpies, which includes ionic hydrates.

The *energy contributions* of the elements group into the Groups of the Periodic Table so that strict atom independence and thus additivity is not predominant while *entropy terms* are relatively constant (for the non-gaseous elements) implying that the atoms behave independently and thus additively in contributing to the entropy terms resulting from their vibrations within the ionic solids. This is possibly a unique demonstration resulting from this single atom sum collection.

This now comprises a complete set for simple zero-order thermodynamic prediction and for checking, which should be complemented by whatever other resources are available to the researcher.

Introduction

Chemical thermodynamics provides the quantitative basis, through enthalpy, entropy and heat capacity, for synthesising, understanding and manipulating materials in respect of their stability, their reactions, and their energetics. The necessary experimental data may be available from the literature or collected into various thermodynamic databases [1–3]. However, because of the essentially limitless number of potential chemical compounds [4], it is possible (even likely) that the data required may never have been determined. For this reason, predictive methods are both desired and developed. These methods range from sophisticated quantum mechanical systems and the less compute-intensive molecular mechanics to various additive schemes where the thermochemical properties of simple groups are summed to yield the corresponding property of the desired material [1,5]. This additivity may range from direct simple addition to more complex group contribution methods where the simple addition is supplemented by interaction terms of various complexities [6,7].

The most generally successful predictive methods have been such group contributions together with their possibly numerous interaction terms [8]. It is no surprise that these methods perform best for gaseous organic molecular systems where the interactions are minimised and also within sets of similar materials, generally excluding charged species. By contrast, our interest in the present contribution is with condensed ionic systems for which there is a more limited range of options. Group contribution methods have been most successful for these systems when applied to a limited set of materials. For example, Hisham and Benson [9,10] developed methods for relating groups of chemically related materials together through (in a particular example) the general two-parameter equation for anions, A, $[A_n H^o(MX_n)\text{-} A_n H^o(MY_n)] = a[A_n H^o(MX_n)\text{-} A_n H^o(MZ_n)] + b$ which was found to correlate the standard enthalpies of formation of any three classes of compounds MX_n, MY_n, and MZ_n (all solids) of any main-group metal cation M from groups 1 (including NH_4^+) and 2. The coefficients a and b are the same for any particular group. Spencer [11] has reviewed many application for metallurgical systems, including alloys. More recently, Mostafa et al. [3] devised group contributions for inorganic salts for their enthalpies, Gibbs energies and heat capacities [12].

Glasser and Jenkins [13] established a self-consistent set of *single ion entropies* for ionic solids. This single ion procedure was extended [14] to optimization of the *enthalpies of single ions* which could then be combined to yield the formation enthalpies of 29 ionic solids, yielding some useful correlations among silicate ions. Leal [15] has developed a method combining lattice energies from Born-Haber thermochemical cycles with

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thermochemical radii for estimating the formation enthalpies of binary ionic solids.

Methods such as these rely on thermodynamic values from the literature [16]. The source databases [17] have not always performed a detailed error analysis and so predicted results must be regarded as relative to the reported database values [18]. However, Kriplovich and Paukov [19] in 1979 did attempt an analysis of predicted absolute entropy values while Sanchez-Segado, et al. [20], have compared the methods for formation enthalpy predictions for rare earth compounds devised by themselves with those of Mostafa, et al. [3], and of Jenkins and Glasser [21]. As an example of an attempt to ensure reliability of a set of values, Verevkin, et al. [22], have examined the vaporization enthalpies for 18 amino-alcohols based on group contribution methods.

The present author, principally with H. D. B. Jenkins and other colleagues, has taken a rather different approach in attempting to establish broad relationships among condensed ionic materials. The established Kapustinskii Equation for lattice energies of binary solids [23] was generalised to ionic systems of any charge complexity by introducing the ionic strength, $I = \frac{1}{2}\sum n_k z_k^2$, to replace the charge pair interactions[24,25] in that equation together with the cube-root of the formula unit volume, V_m, to represent the mean ion distance [1]. Based upon these generalisations, a system of Volume-Based Thermodynamics (VBT) [1,21,26,27] was developed which is now widely applied to prediction of thermodynamic values of condensed ionic materials, both as ionic solids and as ionic liquids.

There are various specialist thermodynamic resources available to the researcher. The widely-available “Handbook of Chemistry and Physics” [28] contains a large collection of chemical and thermodynamic data for both organic and inorganic systems. The commercial systems FactSage [29,30], ThermoCalc [31,32] and the program “HSC Chemistry” (with ~25 000 inorganic entries) [33] each provide databases of assessed quality as well as procedures to predict thermodynamic values. CASTEP [34] provides DFT programming for the individual user. The open “Materials Project” [35,36] provides online DFT programming and lists energy and related values for nearly 150 000 mostly smaller inorganic solids (but no hydrates are included). Even at this sophisticated level of calculation there is an ever-present need for cross-checking and correction [37–40].

Single atom values

Proceeding on the basis of attempting to develop very simple predictive procedures which provide at least initial zero-level approximations to thermodynamic values, we are now examining the use of summations of optimised single atom values as the basic predictive process [41]. Such a procedure is already in place for estimation of partition coefficients [42]. Since the range of elements is finite the atom sum system is essentially complete but does lack the nuance of differentiation of the element sum property according to its interactions with neighbours and depends upon strict additivity of terms. Thus, our additive atom sums cannot distinguish among isomers or among different phases of the same material.

In our first application of this atom sum scheme [41], we developed atom sum terms for volume (or density - V_m or ρ), absolute entropy (S), and heat capacity (C_p) over the limited temperature range from 25 to 80 °C. It turned out that the atom sum terms for these properties are generally quite similar to the corresponding atom terms of the elements themselves, indicating that the atoms are little changed by their interactions and justifying the basic assumption of additivity for these properties, especially volume.

In the present contribution, we supplement the above atom sum terms with terms for formation entropy ($\Delta_f S$) and for formation enthalpy ($\Delta_f H$), and compare the predictive quality of three independent schemes against the reference formation enthalpies and formation entropies.

While the atom sum scheme may on occasion provide the sole access to needed data, it should only be regarded as complementary to other predictive systems which may be more precise with their additional parameters accounting for interactions. However, the most significant uses of single atom values are the appearance of anomalies in the data and the observation of significantly different patterns of additivity between energy and entropy data, as noted below.

Data mining and computation

The data used in the current presentation is derived as in the prior publication [41], being approximately 1 700 inorganic materials from the set of ~25 000 entries in the curated “HSC Chemistry 8″ [17,33] software database. The data were entered into an Excel worksheet and the chemical formulae were parsed [43] into their constituent chemical elements and their number; for example, $(NH_4)_2SO_4.3NH_3$ (first converted to $(NH_4)_2SO_4(NH_3)_3$ to accommodate the programming of the parser) parses to H17, N5, S1, O4. The parsed data were 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 formula data set.

For each chemical formula, the product of the number of atoms of each constituent element multiplied by an initial estimate of the value of the atom property (formation enthalpy or formation entropy) is summed to give an initial estimate of the formula property. The differences between this 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 minimize the sum of squares by adjusting the initial atom property estimates.

Formation enthalpies

We here wish to establish atom sum terms for each of the elements whose weighted sum for a chemical formula will yield a predicted value for the formation enthalpy of the material with that formula. The standard formation enthalpies of the elements are each defined to be zero so that we have no reference values against which to compare our optimised values, as was our procedure for our earlier atom sum developments. Thus, we arbitrarily set an initial value of 10 kJ mol^{-1} for each element and used Solver to provide an optimised set of values relevant to the formation enthalpies of the included inorganic materials, including values for each of the gaseous elements as well as for liquid bromine. Optimization was readily achieved but the resultant values for technetium and for xenon were an order of magnitude larger than for their elements. Since this was an unacceptable difference as discussed below, those chemical formulae containing either of these two elements (namely TcF_6, XeF_2, XeF_4, and XeF_6) were deleted and the optimization repeated with the results listed in Table 1 and plotted in Figs. 1 and 2.

The values below atomic number 18 include the gaseous elements while the large and positive values for carbon and nitrogen (atomic numbers 6 and 7) relate to the presence of a number of CO and CN groupings in materials such as $Fe_3(CO)_{12}$ with their differing interactions from those in such as the ionic carbonates, CO_3^{2-}, and nitrates, NO_3^-. The anomalous results for Tc and Xe may arise either from some unique interaction of these elements or from errors in the experimental values of the reference compounds. There are no obvious reasons to expect the former, which suggests re-examination of their reported formation enthalpies. $\Delta_f H°$/kJ mol^{-1}: TcF_6 = −1284.49 [33]; XeF_2, XeF_4, XeF_6= −162.76, −267.11, −338.15 [33,44] In support of this contention, it should be noted that the mean contribution per fluorine atom (as determined by difference) for the xenon fluorides is −43.8 kJ mol^{-1} whereas the final sum optimised contribution for fluorine (Table 1) is −328.47 kJ mol^{-1}.

The slope of a plot of sum formation enthalpy at 80 °C versus 25 °C (not shown) is 1.0044. From this slope we determine [41] the mean temperature coefficient of formation enthalpy over this range as 8.2×10^{-5} K^{-1}.

Table 1
Atom sum formation enthalpies, $\Delta_f H_{sum}$ / kJ mol^{-1} for the chemical elements, excluding Tc and Xe, and the numbers of contributing atoms.

	Symbol	At. No.	Atom Sum Formation Enthalpy $\Delta_f H_{sum}$ / kJ mol^{-1}	No. of Atoms
Hydrogen	H	1	−22.61	1519
Deuterium	D	(2)	20.76	11
Lithium	Li	3	−201.88	59
Beryllium	Be	4	−27.89	39
Boron	B	5	−0.72	145
Carbon	C	6	77.34	256
Nitrogen	N	7	107.33	217
Oxygen	O	8	−240.88	3191
Fluorine	F	9	−328.27	379
Neon	Ne	10		0
Sodium	Na	11	−247.95	136
magnesium	mg	12	−319.30	97
aluminum	al	13	−478.27	96
Silicon	Si	14	−310.48	205
Phosphorus	P	15	−129.10	117
Sulfur	S	16	−40.66	382
Chlorine	Cl	17	−118.15	460
Argon	Ar	18		0
Potassium	K	19	−251.70	100
Calcium	Ca	20	−379.94	79
Scandium	Sc	21	−143.15	15
Titanium	Ti	22	−210.78	60
Vanadium	V	23	−70.90	51
Chromium	Cr	24	−55.95	80
Manganese	Mn	25	−10.74	77
Iron	Fe	26	−62.69	111
Cobalt	Co	27	−25.34	56
Nickel	Ni	28	34.68	63
Copper	Cu	29	60.51	51
Zinc	Zn	30	−70.12	45
Gallium	Ga	31	−137.98	23
Germanium	Ge	32	−4.82	27
Arsenic	As	33	−1.47	68
Selenium	Se	34	−17.60	144
Bromine	Br	35	−96.80	247
Krypton	Kr	36		0
Rubidium	Rb	37	−70.48	32
Strontium	Sr	38	−396.72	31
Yttrium	Y	39	−494.90	14
Zirconium	Zr	40	−142.22	23
Niobium	Nb	41	−0.05	30
Molybdenum	Mo	42	5.16	47
Technetium	Tc	43		0
Ruthenium	Ru	44	169.45	13
Rhodium	Rh	45	143.72	11
Palladium	Pd	46	53.62	14
Silver	Ag	47	131.73	47
Cadmium	Cd	48	0.79	32
Indium	In	49	−82.11	25
Tin	Sn	50	−0.06	26
Antimony	Sb	51	68.12	49
Tellurium	Te	52	−1.18	117
Iodine	I	53	−5.78	235
Xenon	Xe	54		0
Cesium	Cs	55	−54.31	25
Barium	Ba	56	−351.17	53
Lanthanum	La	57	−471.41	22
Cerium	Ce	58	−493.48	32
Praseodymium	Pr	59	−481.89	20
Neodymium	Nd	60	−467.78	17
Promethium	Pm	61	−543.79	2
Samarium	Sm	62	−495.27	20
Europium	Eu	63	−462.33	16
Gadolinium	Gd	64	−460.57	20
Terbium	Tb	65	−459.48	12
Dysprosium	Dy	66	−439.92	12
Holmium	Ho	67	−547.99	10
Erbium	Er	68	−523.07	13
Thulium	Tm	69	−572.40	8
Ytterbium	Yb	70	−504.52	12
Lutetium	Lu	71	−538.45	10
Hafnium	Hf	72	−463.83	8
Tantalum	Ta	73	−0.76	23
Tungsten	W	74	−29.22	59
Rhenium	*Re*	75	30.84	22
Osmium	Os	76	135.92	12
Iridium	Ir	77	133.66	9
Platinum	Pt	78	46.74	16
Gold	Au	79	164.52	13
Mercury	Hg	80	143.57	27
Thallium	Tl	81	70.00	25
Lead	Pb	82	62.61	48
Bismuth	Bi	83	40.35	23
Polonium	Po	84	128.84	2
Radium	Ra	88	−4.34	3
Actinium	Ac	89	−630.08	4
Thorium	Th	90	−176.76	40
Protactinium	Pa	91	−589.71	2
Uranium	U	92	−298.26	69
Neptunium	Np	93	−457.36	8
Plutonium	Pu	94	−383.07	17
Americium	Am	95	−479.26	9
Curium	Cm	96	−494.02	4

(*continued on next column*)

Formation entropies

The values of the optimised atom sum formation entropies are listed in Table 2 and plotted in Fig. 3. The large positive value for silver (Ag, atomic no. 47) is probably unreliable as are the negative values for Thulium and Actinium (Th and Ac, atomic no. 69 and 89). Atom formation entropy values for most of the elements (Fig. 3) are roughly constant at −8 J K^{-1} mol^{-1}.

Fig. 4 plots the summed atom formation entropies for 1 668 inorganic solids against values obtained from the literature.

Formation Gibbs energies

Gibbs energies are a formal combination of enthalpy and entropy through the equation $\Delta G = \Delta H - T\Delta S$. We accept that this same periodic relation holds for atom sum contributions of ionic solids at 25 °C as depicted in Fig. 1. In Fig. 5 we show that formation Gibbs energies at 25 °C are closely linearly correlated with formation enthalpies, with the formation entropies contributing about 9% (Fig. 6) to the Gibbs energies and so to the stabilities of ionic solids.

Comparison of predictions

Formation enthalpies

In order to assess the reliability of formation enthalpy predictions against literature values, we compare in Table 3 such predictions from three databases: the “Materials Project” [36] collection of DFT-calculated energies at 0 K, the proprietary “HSC Chemistry” [33] group contribution procedure available within a purchased copy of “HSC Chemistry”, and our single atom sum procedure.

A comparison for 16 materials selected by random number from our collected set is first listed. These are followed by lists for perchlorates and chlorates where the silver homologues (highlighted *in italics*) are seen to be very poorly modelled against the literature enthalpies by each of the three predictive procedures, suggesting that it is the literature formation enthalpies of these two materials which may be seriously underestimated.

Table 3 also demonstrates that each of the three programs are rather poor predicters in general for formation enthalpies with the least sophisticated atom sum procedure being the worst. However, if we examine Fig. 2, we note that the agreement between predicted and literature en-

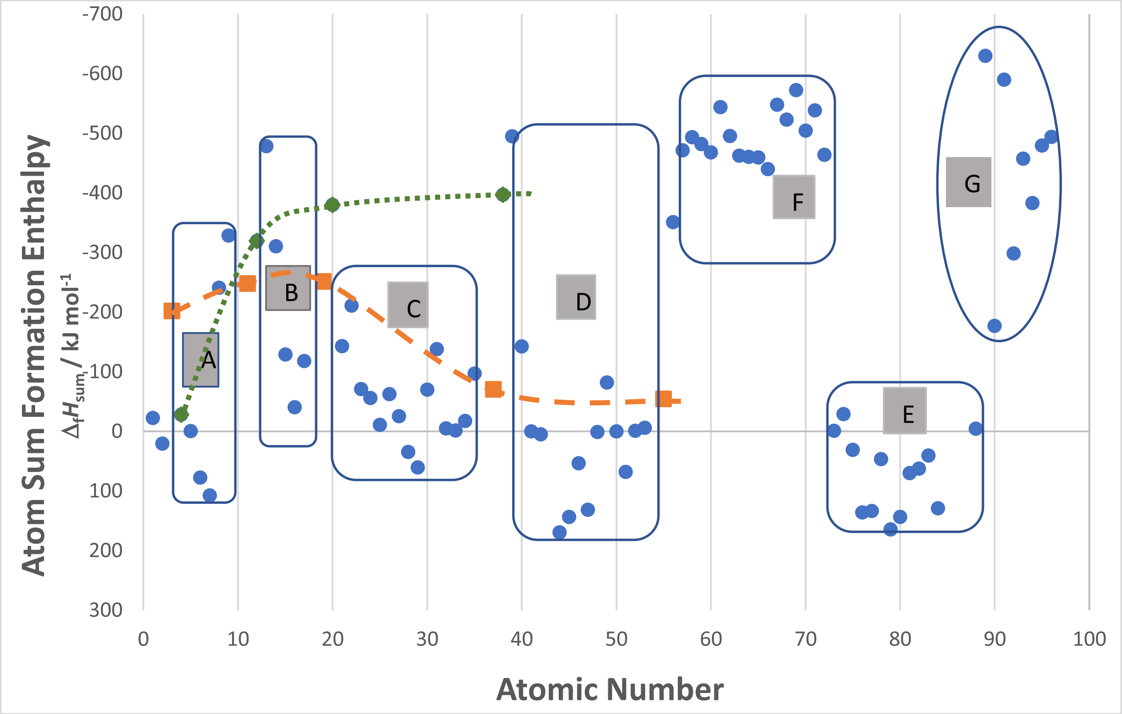

Fig. 1. Atom sum formation enthalpies, $\Delta_f H_{sum}$ / kJ mol^{-1} for the chemical elements, excluding Tc and Xe. The boxed areas enclose the named periods of the Periodic Table: A: 1st period; B: 2nd period; C: 1st transition metals; D: 2nd transition metals; E: lanthanides; F: 3rd transition metals; G: actinides. The lower dashed curve and squares (orange) follow the atom sum formation enthalpies of the alkali metals while the upper dotted curve and diamonds (green) follow the atom sum formation enthalpies of the alkaline earths. The constancy of the contributions from the lanthanides, Box F (being inner transition elements) is striking. Note: The enthalpy axis is plotted in reverse order (positive to negative) in order to match our earlier volume, entropy and heat capacity charts [41].

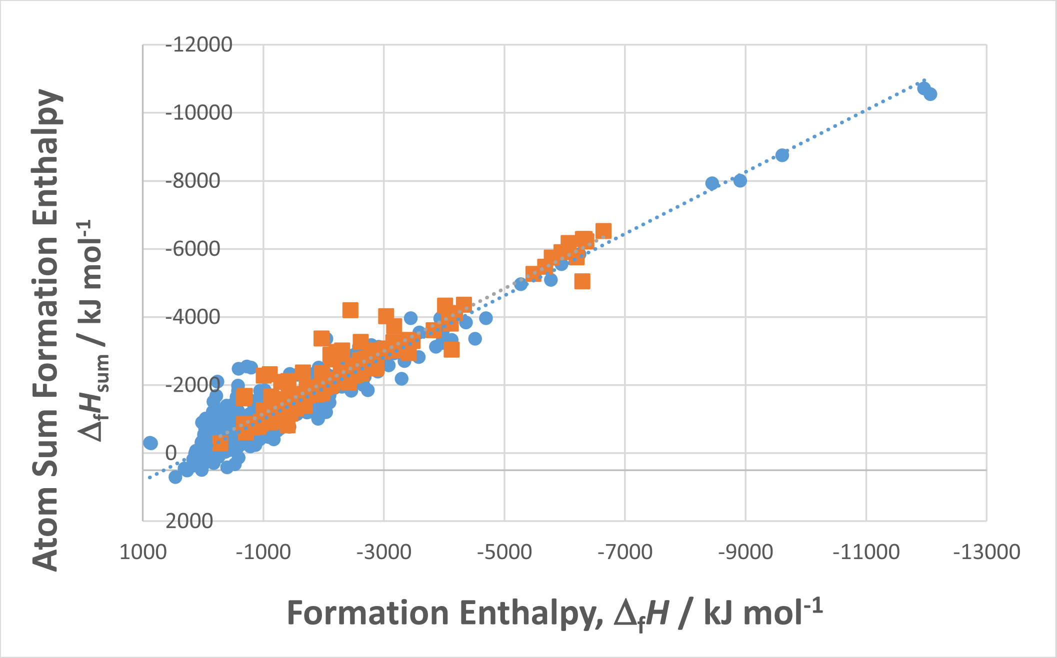

Fig. 2. Atom sum formation enthalpy, $\Delta_f H_{sum}$ /kJ mol^{-1}, vs literature formation enthalpy, $\Delta_f H$ /kJ mol^{-1}, at 25 °C for 1 668 inorganic solids (overlaid with orange squares) for 131 hydrates. The enthalpy axis is plotted in reverse order (positive to negative). The slope of the fitted trendline for the full data set is 0.909 ± 0.007 with intercept −87.8 ± 9 kJ mol^{-1} and R^2 = 0.913. The standard error of the regression is 305 kJ mol^{-1}. The 95% confidence range of the slope is between 0.895 and 0.922.

Table 2

Elemental atom sum formation entropies, $\Delta_f S_{sum}$ / J K^{-1} mol^{-1} for the chemical elements, excluding Tc and Xe, and the number of contributing atoms.

	Symbol	At. No.	Atom Sum Formation Entropy $\Delta_f S_{sum}$ / J K^{-1} mol^{-1}	No. of Atoms
Hydrogen	1	H	−53.12	1519
Deuterium	(2)	D	−63.47	11
Lithium	3	Li	−13.42	59
Beryllium	4	Be	−1.44	39
Boron	5	B	−0.40	145
Carbon	6	C	22.91	256
Nitrogen	7	N	−76.32	217
Oxygen	8	O	−87.51	3191
Fluorine	9	F	−76.39	379
Neon	10	Ne		
Sodium	11	Na	−19.48	136
magnesium	12	mg	−18.07	97
aluminum	13	al	−21.54	96
Silicon	14	Si	−5.76	205
Phosphorus	15	P	−20.22	117
Sulfur	16	S	−7.78	382
Chlorine	17	Cl	−72.68	460
Argon	18	Ar		
Potassium	19	K	−18.53	100
Calcium	20	Ca	−17.32	79
Scandium	21	Sc	−6.24	15
Titanium	22	Ti	−4.02	60
Vanadium	23	V	−1.11	51
Chromium	24	Cr	0.65	80
Manganese	25	Mn	4.70	77
Iron	26	Fe	3.15	110
Cobalt	27	Co	1.13	56
Nickel	28	Ni	0.44	63
Copper	29	Cu	2.16	51
Zinc	30	Zn	−4.39	45
Gallium	31	Ga	−12.88	23
Germanium	32	Ge	−1.61	27
Arsenic	33	As	−2.48	68
Selenium	34	Se	−2.47	144
Bromine	35	Br	−27.50	244
Krypton	36	Kr		
Rubidium	37	Rb	−19.03	32
Strontium	38	Sr	−10.81	31
Yttrium	39	Y	−22.58	14
Zirconium	40	Zr	−6.41	23
Niobium	41	Nb	−0.05	30
Molybdenum	42	Mo	0.59	47
Technetium	43	Tc		
Ruthenium	44	Ru	−10.19	13
Rhodium	45	Rh	−4.74	11
Palladium	46	Pd	−6.63	14
Silver	47	Ag	15.12	47
Cadmium	48	Cd	0.01	32
Indium	49	In	−19.67	25
Tin	50	Sn	−0.06	26
Antimony	51	Sb	−4.39	49
Tellurium	52	Te	−0.85	117
Iodine	53	I	−1.58	235
Xenon	54	Xe		
Cesium	55	Cs	−12.54	25
Barium	56	Ba	−13.86	53
Lanthanum	57	La	−20.40	22
Cerium	58	Ce	−24.63	32
Praseodymium	59	Pr	−20.46	20
Neodymium	60	Nd	−17.54	17
Promethium	61	Pm	−14.38	2
Samarium	62	Sm	−16.82	20
Europium	63	Eu	−26.67	16
Gadolinium	64	Gd	−13.13	20
Terbium	65	Tb	−7.36	12
Dysprosium	66	Dy	−11.31	12
Holmium	67	Ho	−19.85	10
Erbium	68	Er	−17.81	13
Thulium	69	Tm	−39.09	8
Ytterbium	70	Yb	−15.06	12
Lutetium	71	Lu	−16.40	10
Hafnium	72	Hf	1.15	8
Tantalum	73	Ta	−0.74	23
Tungsten	74	W	4.41	59
Rhenium	75	Re	0.55	22
Osmium	76	Os	−1.34	12
Iridium	77	Ir	1.05	9
Platinum	78	Pt	−8.14	16
Gold	79	Au	3.33	13
Mercury	80	Hg	−3.98	27
Thallium	81	Tl	−0.24	25
Lead	82	Pb	−6.94	48
Bismuth	83	Bi	−5.55	23
Polonium	84	Po	−16.03	2
Radium	Ra	88	−5.22	3
Actinium	Ac	89	−33.99	4
Thorium	Th	90	−7.17	40
Protactinium	Pa	91	−10.19	2
Uranium	U	92	4.17	69
Neptunium	Np	93	−1.57	8
Plutonium	Pu	94	−2.19	17
Americium	Am	95	−14.97	9
Curium	Cm	96	−15.37	4

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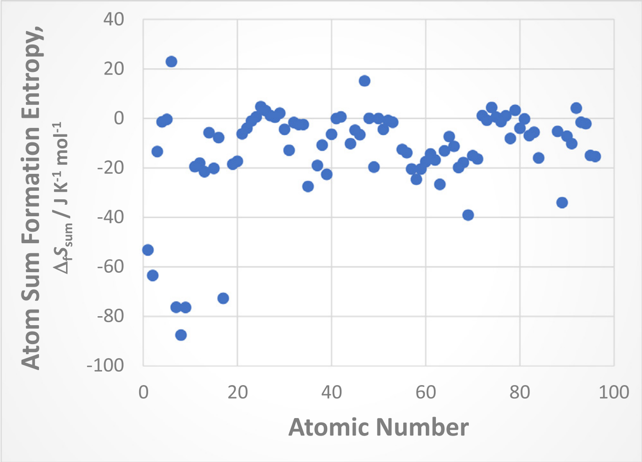

Fig. 3. Optimised atom sum formation entropies, $\Delta_f S_{sum}$ / J K^{-1} mol^{-1}, for the chemical elements, excluding Tc and Xe. The large negative values below atomic number 20 correspond to the gaseous elements: H, D, N, O, F and Cl. The large positive value for C (#6) arises from the inclusion of carbon-containing materials such as Fe(CO)5 in the data set. It is suggested that the outlier values for Ag (#47), Tm (#69) and Ac (#89) should be regarded as aberrant. The mean value of $\Delta_f S_{sum}$ for the elements above #18, excluding these aberrant values, is −8 J K^{-1} mol^{-1}.

thalpies improves as the enthalpy becomes more negative. As an additional indicator of the problems associated with the enthalpies of small formula units, we note the opposite signs of the optimised atom sum enthalpies in Table 1 for H and D.

Formation entropies

Table 4 compares literature entropy of formation values against atom sum values for 22 ionic solids. As Fig. 4 shows, the fit is quite close for larger entropy values but there is much scatter for the smaller values. In the first part of Table 4, the mean A%D has thus been calculated omitting the three small entropy values in italics which have exaggerated absolute difference values. The entropy values for the silver perchlorates and chlorates are not anomalous, unlike their enthalpy values (cf. Table 3).

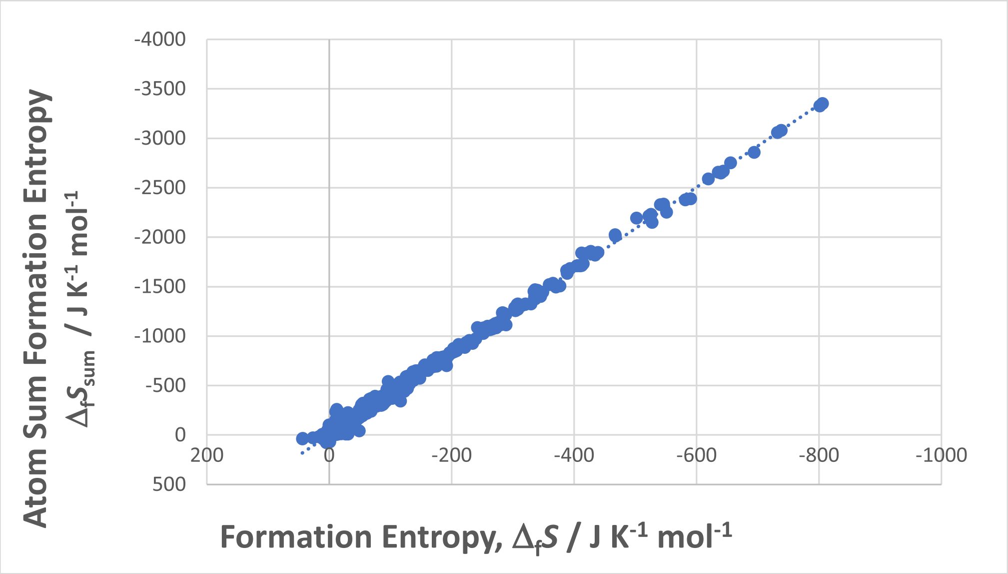

Fig. 4. Optimised atom sum formation entropies, $\Delta_f S_{sum}$ / J K^{-1} mol$^{-1,}$ for 1 668 inorganic solids, excluding Tc and Xe. The slope of the fitted line is 0.997 ± 0.001 with intercept −0.22 ± 0.74 J K^{-1} mol^{-1} and R^2 = 0.996. The standard error of the regression is 24.9 J K^{-1} mol^{-1}. The 95% confidence range of the slope is between 0.994 and 1.000. From the slope of a plot of the sum formation entropy [41] at 80 °C versus 25 °C of 1.0104 (not shown), the mean formation entropy thermal coefficient is 2.0 × 10^{-4} K^{-1}.

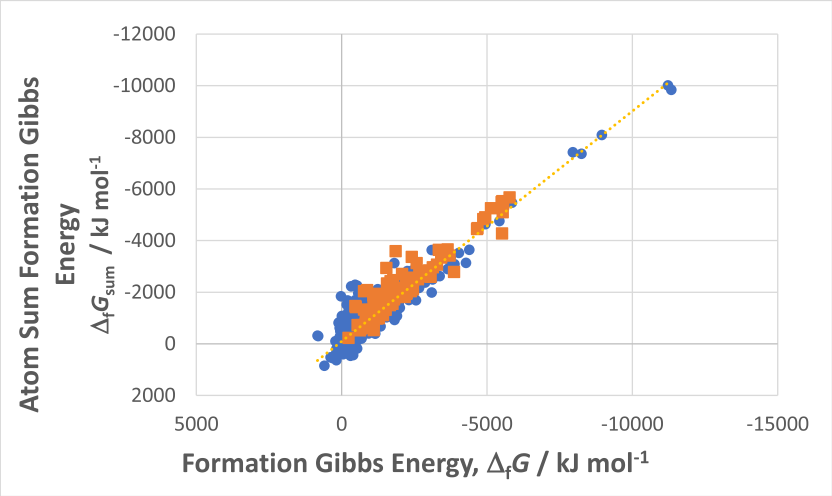

Fig. 5. Optimised atom sum formation Gibbs Energies, $\Delta_f G_{sum}$ / kJ mol^{-1}, for 1 668 inorganic solids, excluding Tc and Xe, with 131 inorganic hydrates (overlaid as orange squares) plotted against literature values of the formation Gibbs energies, $\Delta_f G$. The slope of the fitted line for the full system is 0.892 ± 0.007 with intercept −91.1 ± 9 kJ mol^{-1} with R^2 = 0.898. The 95% confidence interval of the slope is between 0.878 and 0.907. The standard error of the regression is 300 kJ mol^{-1}.

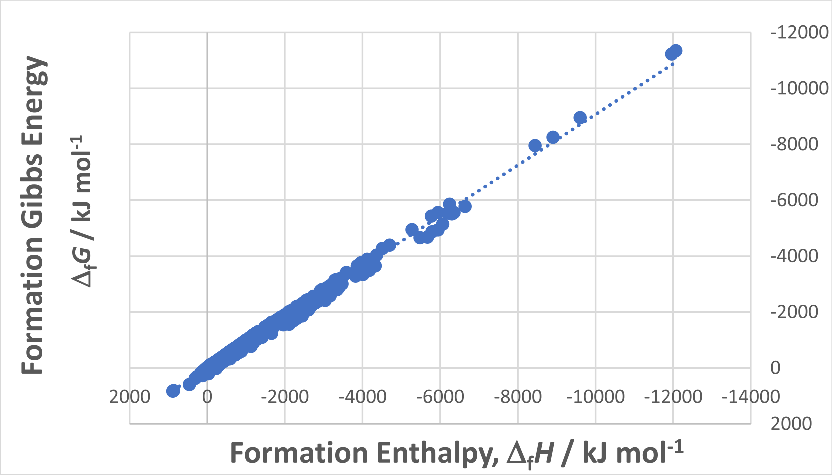

Fig. 6. Formation Gibbs energies, $\Delta_f G$ / kJ mol^{-1}, plotted against formation enthalpies, $\Delta_f H$ / kJ mol^{-1}, for 1 668 ionic solids including hydrates. The slope of the fitted line, constrained to pass through the origin, has a value of 0.906 ± 0.001 with correlation coefficient R^2 = 0.997. The value of the slope implies that formation entropy contributes about 9% to the Gibbs energy.

Table 3
Formation enthalpies, $\Delta_f H$ / kJ mol^{-1}, for 16 ionic solids selected by random number from the full data set. Predictions from the "Materials Project" [36], "HSC Chemistry" [33], and the current atom sum procedure are listed and compared with the literature values. A%D = absolute percentage difference from the literature value datum in the 2nd column. The mean A%D value in the final column has been calculated omitting the value (*in italics*) for the carbon-containing compound C_2Cl_4. In addition, enthalpies for the perchlorates and chlorates are shown, where the formation enthalpies of the *silver compounds* are in large error.

	HSC Chemistry		Materials Project			HSC Chemistry Estimate		Atom Sum Enthalpy	
	$\Delta_f H$ / kJ mol^{-1}	n(atoms)	U / eV atom^{-1}	U^a / kJ mol^{-1}	A%D	$\Delta_f H_{est}$ / kJ mol^{-1}	A%D	$\Delta_f H_{sum}$ / kJ mol^{-1}	A%D
				Mean	26	Mean	57	Mean	72
AgCN	146.00	3	0.336	77.70	47	27.51	84	316.40	117
Al_2O_3	−1675.69	5	−3.4	−1310.39	22	−1645.85	2	−1679.19	0
As_2O_3	−654.80	5	−1.63	−628.22	4	−588.04	10	−725.59	11
$BeSO_4$	−1200.81	6	−2.423	−1120.61	7	−1222.77	3	−1032.07	14
C_2Cl_4	−64.16	6	−0.37	−171.12	*167*	−396.92	469	−317.91	*395*
$Ce(SO_4)_2$	−2343.00	11	−2.56	−2170.62	7	−2334.71	1	−2501.85	7
Ce_2S_3	−1188.30	5	−2.425	−934.61	21	−1053.30	14	−1108.94	7
$Co(NO_3)_2$	−421.55	9	−1.046	−725.65	72	−569.12	23	−1255.98	198
Cu_2S	−83.30	3	−0.32	−74.00	11	−86.38	38	80.36	196
Fe_3P	−142.84	4	−0.206	−63.52	56	−53.81	69	−317.18	122
$FeBr_3$	−265.70	4	−0.363	−111.92	58	−324.05	19	−353.10	33
MnI2	−242.67	3	−0.454	−131.41	46	−3147.25	5	−22.31	91
NaHCO3	−950.81	5	−1.889	−911.28	4	−966.18	44	−915.86	4
$PbSeO_4$	−609.62	6	−1.414	−653.96	7	−601.25	2	−918.52	51
PuH_2	−139.33	3	−0.47	−108.69	22	−306.80	87	−428.29	207
Rb_2SO_4	−1435.90	7	−2.369	−1278.24	11	−1362.22	5	−1145.15	20
	$\Delta_f H$ / kJ mol^{-1}	n(atoms)	U / eV atom^{-1}	U^a / kJ mol^{-1}	A%D	$\Delta_f H$ / kJ mol^{-1}	A%D	$\Delta_f H_{sum}$ / kJ mol^{-1}	A%D
Perchlorates									
$AgClO_4$	−31.10	6	−0.409	−189.16	*508*	−261.60	*741*	*−949.94*	*2955*
$NaClO_4$	−382.75	6	−1.007	−465.73	22	−635.00	66	−1329.63	247
$KClO_4$	−432.75	6	−1.157	−535.10	24	−713.27	65	−1333.38	208
$RbClO_4$	−434.59	6	−1.178	−544.81	25	−694.89	60	−1152.16	165
$CsClO_4$	−437.23	6	−1.203	−556.37	27	−621.19	42	−1135.99	160
Chlorates									
$AgClO_3$	−30.29	5	−0.544	−209.66	*592*	−63.76	*110*	*−709.06*	*2241*
$NaClO_3$	−357.73	5	−1.179	−454.40	27	−437.16	22	−1088.74	204
$KClO_3$	−397.73	5	−1.281	−493.71	24	−515.43	30	−1092.49	175
$RbClO_3$	−392.46	5				−497.05	27	−911.28	132
$CsClO_3$	−386.18	5	−1.285	−495.25	28	−423.35	10	−895.11	132

[a] Values collected from "Materials Project" are energies, U, per atom at 0 K. The small conversion to enthalpies [45] at 25 °C has not been implemented.

Table 4
Formation entropies, $\Delta_f S$ / J K^{-1} mol^{-1}, for 22 ionic solids selected by random number from the full data set. (For the sake of comparison, these include those listed in Table 3 for formation enthalpies). Literature values from "HSC Chemistry" [33] and the current atom sum procedure are listed and compared. A%D = absolute percentage difference from the literature value datum in the 2nd column. The italicised entries have small $\Delta_f S$ values and, consequently, unreliable A%D values.

	HSC Chemistry	Atom Sum Entropy	
	$\Delta_f S$ / J K^{-1} mol^{-1}	$\Delta_f S_{sum}$ / J K^{-1} mol^{-1}	A%D
AgCN	−37.03	−29.43	20.54
Al_2O_3	−313.33	−291.85	6.85
As_2O_3	−262.10	−267.48	2.05
BaS	−16.12	−19.16	18.83
$BeSO_4$	−373.90	−362.86	2.95
C_2Cl_4	−226.94	−198.17	12.68
$Ce(SO_4)_2$	−755.07	−747.19	1.04
Ce_2S_3	−59.89	−71.81	19.90
$Co(NO_3)_2$	−660.11	−676.86	2.54
Cu_2S	*17.85*	*−15.14*	*184.82*
Fe_3P	−21.35	−12.48	41.56
$FeBr_3$	−69.80	−63.32	9.28
GeS	*3.32*	*−9.10*	*373.82*
InS	−20.68	−29.81	44.13
LaS_2	−31.09	−28.52	8.26
$MnSO_4 \cdot 7H_2O$	−1714.07	−1602.39	6.52
$NaClO_4 \cdot H_2O$	−429.34	−431.34	0.47
Ni_3C	11.15	−1.02	109.13
NiAl	*−3.97*	*−22.05*	*455.14*
$PbSeO_4$	−349.74	−370.10	5.82
PuH_2	−122.35	−88.94	27.31
Rb_2SO_4	−398.42	−402.04	0.91
		Mean *(italicised omitted)*	17.93
Perchlorates			
$AgClO_4$	−402.18	−399.85	0.58
$NaClO_4$	−429.34	−431.34	0.47
$KClO_4$	−435.48	−427.18	1.91
$RbClO_4$	−435.21	−435.38	0.04
$CsClO_4$	−431.80	−429.67	0.49
		Mean	0.70
Chlorates			
$AgClO_3$	−320.10	−311.49	2.69
$NaClO_3$	−344.21	−342.98	0.36
$KClO_3$	−340.85	−338.82	0.60
$RbClO_3$	−345.42	−347.02	0.47
$CsClO_3$	−343.83	−341.30	0.73
$TlClO_3$	−1714.07	−1602.39	6.52
		Mean	1.89

(*continued on next column*)

Table 4 (*continued*)

Conclusions

We now have a set of optimised atom terms which may be summed to yield values of the standard state functions of chemical thermodynamics over a temperature range from 25 to 80 °C. These simple sums are only suitable for predicting formation enthalpies more negative than about −1 000 kJ mol^{-1} or for formation entropies more negative than about −200 J K^{-1} mol^{-1}. In this range the formation enthalpies for ionic solids may be more reliable than DFT calculations.

Overall, DFT calculations, atom sum formation enthalpies and atom sum formation entropies are generally unsuitable for phase prediction studies [46]. Nevertheless, these methods provide a useful service in initial prediction of otherwise unavailable data and for checking published data.

The single atom enthalpies (Fig. 1) and Gibbs energies (not shown) form groups as in the Periodic Table, while the formation entropies (Fig. 3) are more nearly constant after the gaseous elements. This distinction implies that *energy interactions* between atoms are somewhat differentiated while the atoms are effectively independent and similar in their internal motions leading to the observed *entropy constancy*. This is possibly a unique demonstration resulting from this single atom sum collection.

Supplementary materials

The Supplementary Information file collects the full set of 1 668 ionic solids, their literature enthalpies and entropies from “HSC Chemistry” [33], and the corresponding optimised single atom sums. The data include values for different phases of some of the chemical species. Data for hydrates is highlighted in yellow.

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ctta.2022.100069.

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