

The Cohesive Entropy of Condensed Materials, Empirical Relations and Restrictions

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Supplementary Information File: Figures S1-S5, Table S1

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Abstract

Entropy factors of a material are connected through an equation which relates three independent

experimental values specific to each material: $\Delta_f S = S - \sum_i^n S_{atoms,i}$. (Note: our results refer to

independently summed $\sum_1^n S_{atoms,i}$ values rather than calculation by simple difference of the third

dependent value from the other two of these values.) We define the cohesive entropy coefficient,

$\alpha_{S_{coh}}$, through $\Delta_f S = \alpha \sum_i^n S_{atoms,i}$.

Having ready access to a large database of thermodynamic data for solid ionic materials from earlier studies, we have investigated the generalisations that may be made among these entropy quantities for this group of materials.

We find that the data points of this three-dimensional system are confined to a fan-shaped **tilted** plane which has rather strict lateral limits, with the upper limits controlled by the entropies of gaseous elements and the lower limits by the entropies of solid elements. This has the consequence of providing insight into the understanding of entropy values and their limits as a check on experimental determinations. In particular, formation and standard entropies for condensed phases are shown to be proportional to one another with a fixed proportionality constant, the cohesive entropy coefficient, $\alpha_{S_{coh}} = -0.831$.

Evidence is provided that the same restrictions apply to condensed organic materials, and we suggest that these entropy relations are applicable to condensed materials in general.

Introduction

Entropy, S , is a fundamental state function of thermodynamics, describing the condition of a system rather than its history. The principal application of entropy in chemical thermodynamics is in respect of the effects of temperature on the material under consideration where it is applied together with the state function enthalpy, H - which relates to energetic changes - to form the Gibbs energy function, $G = H - TS$. Entropies are generally reported¹ as standard absolute values, S° , at 298.15 K relative to their zero values at 0 K as determined by calorimetric measurements integrated over the relevant temperature range (so-called Third Law values). For gases, statistical mechanical calculations may also be reported. Recently, interaction entropies have been computed between proteins and their ligands.² Alternatively, formation entropies, $\Delta_f S$, may be reported,³ being the difference between the standard absolute entropy and the sum of the standard entropies of the constituent chemical elements, $\sum_1^n S_{atoms,i}$ (here named *the atom entropy sum*) at the relevant temperature, as in equation (1) below.

$$\Delta_f S = S_{products} - S_{reactants} = S - \sum_i^n S_{atoms,i} \equiv S - \sum S_i \quad (1)$$

where $\sum S_i$ will be used as a convenient abbreviation for the atom entropy sum $\sum_1^n S_{atoms,i}$.

As an example: $\Delta_f S(\text{NaCl}\{s\}) = S(\text{NaCl}\{s\}) - [S(\text{Na}\{s\}) + \frac{1}{2}S(\text{Cl}_2\{g\})]$

with, at 25°C, $S(\text{NaCl}\{s\}) = 72.13 \text{ kJ mol}^{-1}$, $S(\text{Na}\{s\}) = 51.30 \text{ kJ mol}^{-1}$ and $S(\text{Cl}_2\{g\}) = 223.08 \text{ kJ mol}^{-1}$

yielding the standard formation entropy: $\Delta_f S(\text{NaCl}\{s\}) = -90.71 \text{ kJ mol}^{-1}$.

Since the entropies of the elements summed in $\sum S_i$ (such as those enclosed in square brackets in the example) are well-known, equation (1) demonstrates that the absolute and formation entropies are equivalent measures, each useful in appropriate circumstances. However, since the elements

constituting a material will generally differ from material to material, each with their own entropy contribution, the absolute and formation entropy values of a range of materials are not expected to be simple functions of one another. The current paper demonstrates that they are, in fact, simply related to one another in their condensed phases and for both inorganic and organic materials.

Cohesive Entropy Coefficient, α_{Scoh}

A cohesive property in chemistry⁴ describes the interaction among a given collection of independent atoms which combine to form a material. The entropy of formation, $\Delta_f S$, is defined in equation (1) as the difference between the entropy, S , of the material and of the collection of independent atoms, $\sum S_i$, which combine to form the material. We here define the cohesive entropy coefficient, α_{Scoh} , which quantifies the extent of the interaction stabilising the product material:

$$\Delta_f S = S - \sum_1^n S_{\text{atoms},i} = \alpha_{\text{Scoh}} \sum_1^n S_{\text{atoms},i} \equiv \alpha_{\text{Scoh}} \sum S_i \quad (2)$$

To be useful in relating S and $\Delta_f S$ in equation (1), the coefficient α_{Scoh} should behave in a predictable manner but it is not obvious that α_{Scoh} would show consistent behaviour among materials since the atoms involved generally belong to dissimilar groupings. Below we consider this issue for both condensed inorganic and a small set of organic materials.

Condensed Materials

We have recently prepared a comprehensive set of the thermodynamics of condensed inorganic materials⁵ which we here use in Fig. 1 to test for the constancy of the cohesive entropy coefficient, α_{Scoh} , for condensed inorganic and a small set of organic materials.

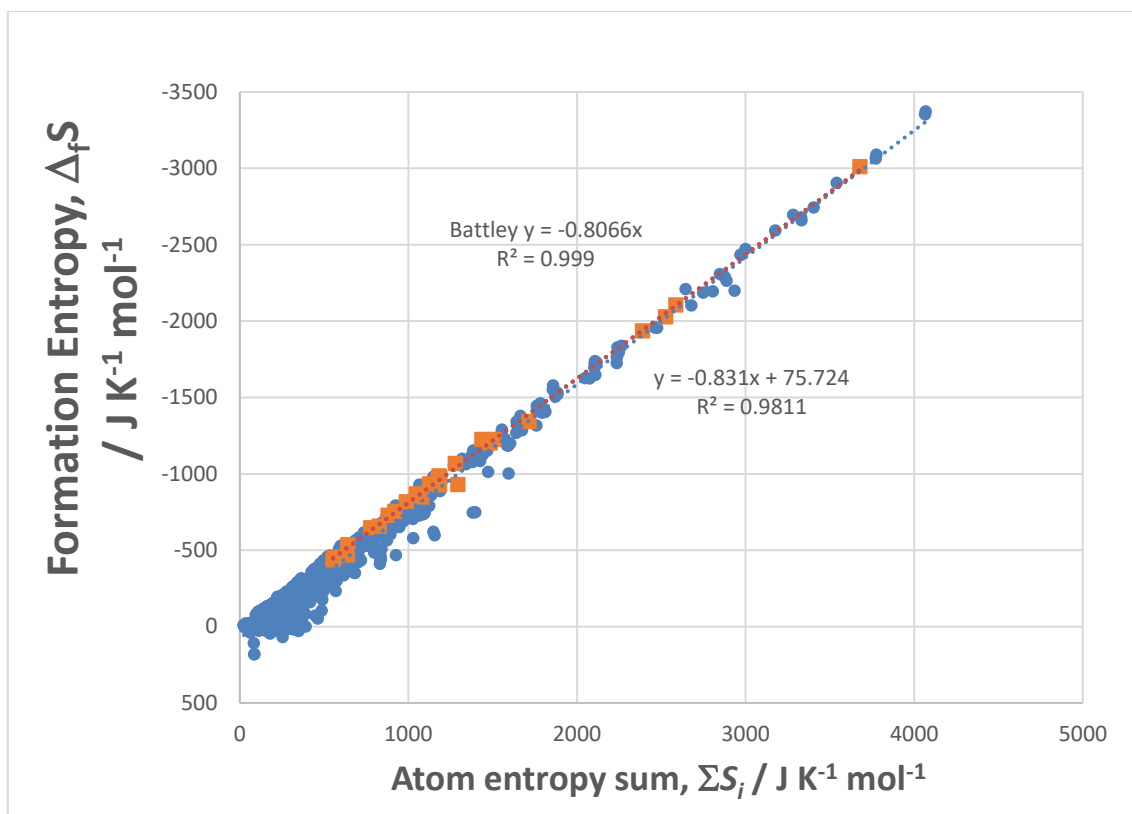


Figure 1: Formation entropy, $\Delta_f S$, plotted against atom entropy sum, $\sum S_i$, for 1 658 condensed inorganic materials (blue circles) together with the 30 lower-range organic data (orange squares) from Supplementary Table S1.⁶⁻⁷ The fitted line for the inorganic materials has the formula

$$\Delta_f S^\circ = -0.831 \times \sum_1^n S_{atoms,i} + 75.72 \quad \text{with correlation coefficient } R^2 = 0.98.$$

The slope of -0.831 corresponds to the cohesive entropy coefficient $\alpha_{S_{coh}}$ (ignoring the asymmetric data group near the origin contributing to the large intercept). 95% confidence limits for the slope of -0.831 are -0.837 and -0.825. For the fitted range of the organics, the line constrained to pass through the origin has a similar slope of -0.807 ($R^2 = 0.99$).

It is clear that $\alpha_{S_{coh}}$ may be regarded as constant for both these condensed inorganic and organic materials and thus provides a general procedure for generation of entropy values of condensed materials. The slope value obtained for the full organic set is identical to that reported by Battley and Battley and Stone.⁶⁻⁷

Using this result, we obtain in eq(3) a simple proportionality between entropy and the corresponding atom entropy sum.

$$\text{Given} \quad \Delta_f S = S - \sum S_i \quad (1)$$

Substituting $\alpha_{S_{coh}}$ into eq(1) for $\Delta_f S$ from the slope of Fig. 1, while ignoring the intercept:

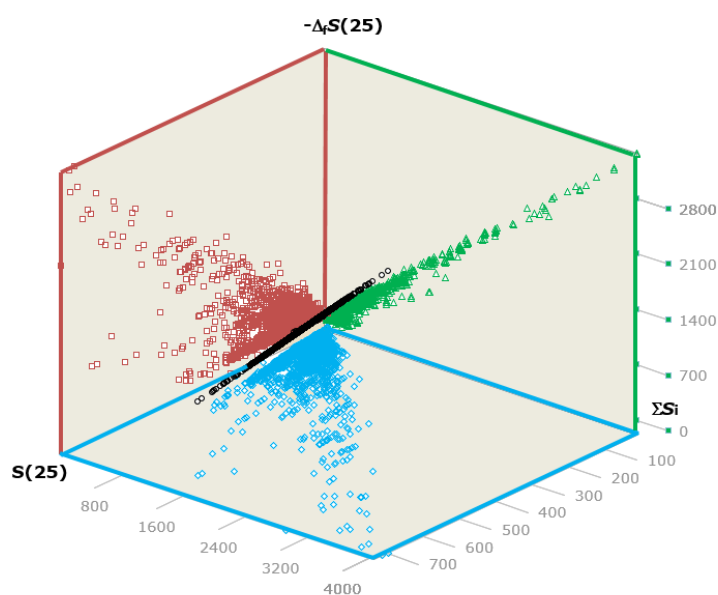
$$\begin{aligned} \Delta_f S &= \alpha_{coh} \sum S_i = -0.813 \sum S_i = S - \sum S_i \\ \text{or} \quad S &= \sum S_i - 0.813 \sum S_i = 0.187 \sum S_i \quad (3) \end{aligned}$$

The slope of -0.807 may similarly be used for organic materials.

Formation Entropy, $\Delta_f S^\circ$, and Limits

Since we already have access to this extensive set of inorganic data,⁵ we have also examined their entropy relations in greater detail. We wish to investigate if the three terms in equation (1) are related to one another in some way. Clearly, it is trivial if one of the terms is calculated as a difference of the other two. Instead, we wish to determine if the terms can be related as independent quantities.

In three dimensions the data line shown in Fig. 1 necessarily represents the projection of a plane, as shown in Fig. 2. This fan-shaped tilted plane is highlighted in the scatter plot⁸ in Fig. 2.



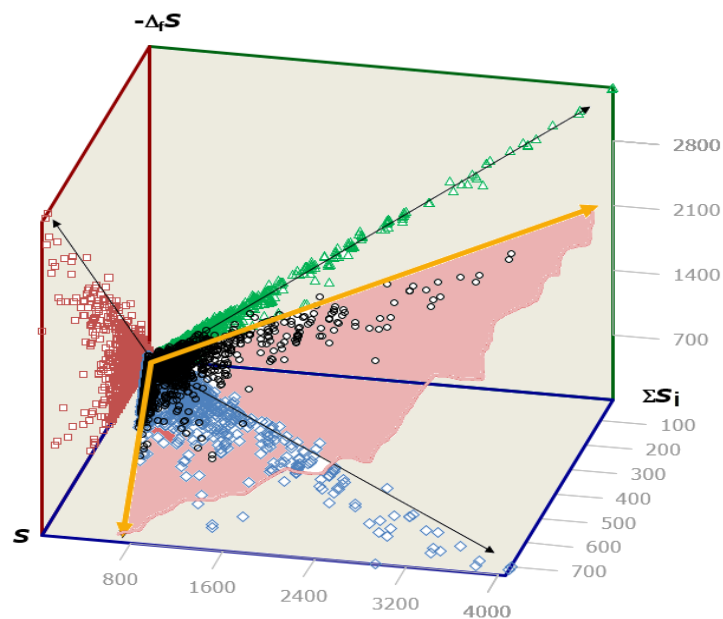


Figure 2: Three-dimensional scatter plot of entropy-related data ($\text{J K}^{-1} \text{mol}^{-1}$) for 1 658 inorganic

solid materials where $\sum_1^n S_{atoms,i}$ is labelled as ΣS_i for simplicity. The plot depicts the input literature data, including experimental errors. The data is plotted as black circles in the highlighted fan-shaped area, with projections onto the three orthogonal planes: green triangles on the $-\Delta_f S$ versus ΣS_i plane; red squares on the $-\Delta_f S$ versus S plane; and blue diamonds on the S versus ΣS_i base plane. (Note that the $\Delta_f S$ axis has been reversed for the graphics.) Detailed plots of the three projection planes may be found in the Supplementary file.

The data points in Fig. 2 lie on a highlighted fan-shaped **tilted** plane which has rather strict lateral limits while extending indefinitely towards the larger entropies of more complex materials. Fig. 3 shows the same data re-oriented in order to demonstrate the flat plane of the three-dimensional data.

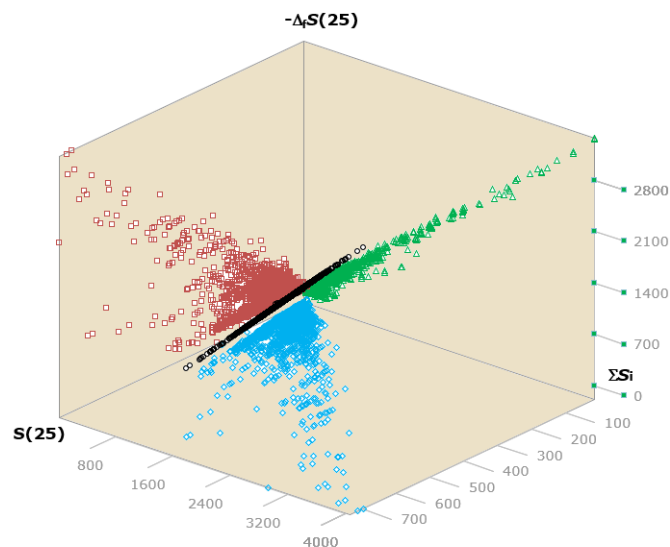


Figure 3: The three-dimensional data of Fig. 3 re-oriented to show the flat fan-shaped plane with black circles for the experimental data.

Since there are two independent variables, S and $\sum S_i$, contributing to the dependent variable $\Delta_f S$, it is helpful to determine how closely they are correlated with each other. This is accomplished by evaluating their VIF (Variance Inflation Factor)⁹ through a linear regression of one against the other which yields a correlation factor $R^2 = 0.682$, leading to $VIF = 1/(1 - R^2) = 3.144$. This value, being less than 5, is generally interpreted⁹ as “not severe enough to require attention”. Alternatively, one may simply use the regression of Fig. 1 with only one of the independent variables, such as:

$$\Delta_f S^o = -0.831 \times \sum_1^n S_{atoms,i} \cdot$$

The projection onto the base plane of the data in Fig. 2 and 3 is plotted as Fig. 4.

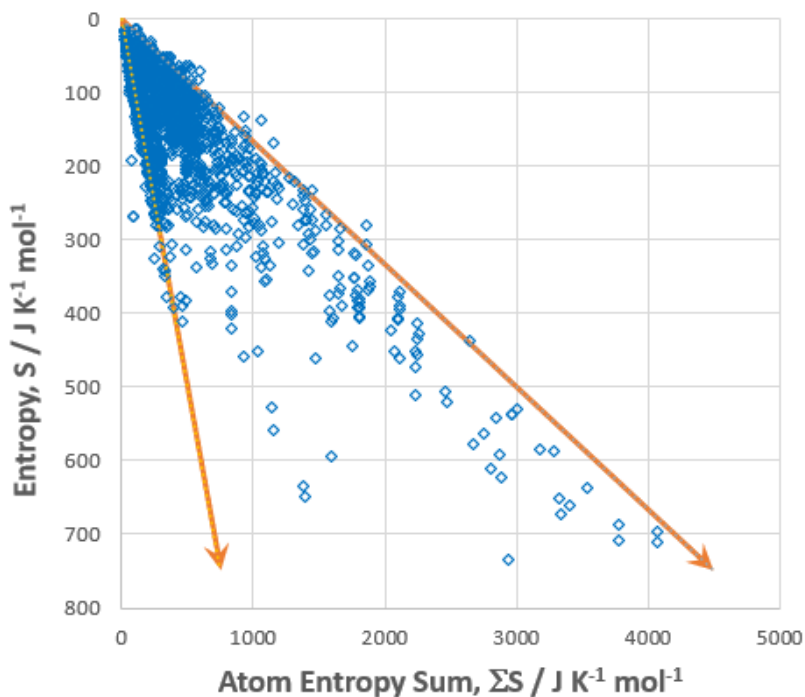


Figure 4: Standard entropy, S° , plotted against element sum entropy, $\sum S_i$, for 1 658 condensed inorganic materials. The orange lines are the arbitrarily chosen strict limits (apart from minor experimental errors) of the data set.

Fig.4 shows clear limits to the range of the inorganic solids entropy data, with upper and lower limits delineated by orange lines (selected by hand). The upper (right) limit roughly represents the largest possible atom sum entropies for the full range of materials, corresponding to formation from generally gaseous elements. On the other hand, the lower (left) limit roughly represents the smallest possible atom sum entropies for the full range of materials, corresponding to formation from the most stable solid elements. The largest gas phase atom entropy is for $O_2(g)$ at $-88.4 \text{ J K}^{-1} \text{ mol}^{-1}$ while among the smallest solid phase atom entropies is for Ag, at $15.6 \text{ J K}^{-1} \text{ mol}^{-1}$. The slopes of the two chosen limit lines are 6 and 1 so that the ratio of the largest to the smallest is 6. The ratio of these limiting gaseous to solid entropies is $(88.4 + 15.6)/15.6 = 6.7$. The similarity of these ratios supports the correctness of our description of the source of the limits.

Discussion and Conclusions

We have here demonstrated that entropy datapoints for condensed ionic materials at a given temperature lie on a fan-shaped tilted plane in three-dimensional space, with upper limits controlled by the reactions of gaseous elements and lower limits by the reactions of solid elements. In addition, formation and standard entropies for condensed phases are shown to be proportional to one another with a fixed proportionality constant, the cohesive entropy coefficient, α_{Scoh} , with a mean value -0.82.

It should be noted that the fan-shaped tilted plane which appears in the three-dimensional diagram is a direct consequence of the mathematical relationship of a difference or sum between the two independent, even random, variables (x and y) yielding a dependent variable (z). Selecting another thermodynamic relation for a number of materials as an example, $\Delta G = H - T\Delta S$ with fixed temperature, T , will yield a similar diagram with the tilt changing as the temperature alters the relation between the independent variables. However, the chosen data set controls any limits across the resulting tilted fan and across its three projections.

These results provide improved understanding of the entropy behaviour of materials and predictive opportunities.

Acknowledgements

We acknowledge the use of Gabor Doka's excellent and freely available program "Excel 3D Scatter Plot"⁸ without which this research could not have been successfully accomplished.

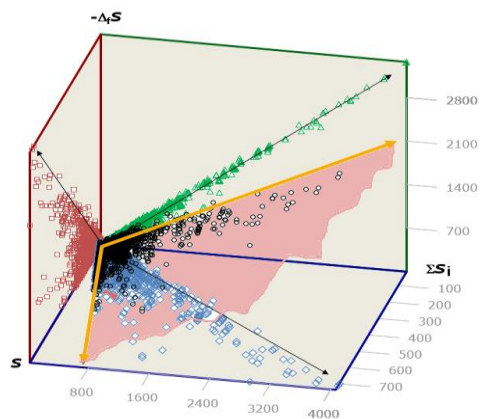
Supplementary Information

The Supplementary Information file contains (i) a group of four figures consisting of a three-dimensional scatter diagram of the entropy data for 1 658 solid inorganics together with plots of projections of the data onto the three orthogonal planes, and (ii) Table S1 listing entropy data for 46 condensed organic materials with an entropy plot (Fig. S5) corresponding to Fig. 1 of the main text but containing the full data set.

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Table of Contents Graphic



From the general entropy equation $\Delta_f S = S - \sum_i^n S_{atoms,i}$ applied to condensed phases, both organic and inorganic, we demonstrate that entropy data-points lie within a fan-shaped tilted plane which has rather strict lateral limits, with the upper limits controlled by the reactions of gaseous elements and the lower limits by the reactions of solid elements. These results provide improved understanding of the entropy behaviour of materials.