

Standard Absolute Entropy, S_{298}° , Values from Volume or Density. 1. Inorganic Materials

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Standard absolute entropies of many inorganic materials are unknown; this precludes a full understanding of their thermodynamic stabilities. It is shown here that formula unit volume, V_m , can be employed for the general estimation of standard entropy, S_{298}° , values for inorganic materials of varying stoichiometry (including minerals), through a simple linear correlation between entropy and molar volume. V_m can be obtained from a number of possible sources, or alternatively density, ρ , may be used as the source of data. The approach can also be extended to estimate entropies for hypothesized materials. The regression lines pass close to the origin, with the following formulas: For inorganic ionic salts, $S_{298}^{\circ}/\text{J K}^{-1} \text{ mol}^{-1} = 1360 (V_m/\text{nm}^3 \text{ formula unit}^{-1}) + 15$ or $= 2.258 [M/(\rho/\text{g cm}^{-3})] + 15$. For ionic hydrates, $S_{298}^{\circ}/\text{J K}^{-1} \text{ mol}^{-1} = 1579 (V_m/\text{nm}^3 \text{ formula unit}^{-1}) + 6$ or $= 2.621 [M/(\rho/\text{g cm}^{-3})] + 6$. For minerals, $S_{298}^{\circ}/\text{J K}^{-1} \text{ mol}^{-1} = 1262 (V_m/\text{nm}^3 \text{ formula unit}^{-1}) + 13$ or $= 2.095 [M/(\rho/\text{g cm}^{-3})] + 13$. Coupled with our published procedures, which relate volume to other thermodynamic properties via lattice energy, the correlation reported here complements our development of a predictive approach to thermodynamics and ultimately permits the estimation of Gibbs energy data. Our procedures are simple, robust, and reliable and can be used by specialists and nonspecialists alike.

Introduction

Absolute standard entropy, S_{298}° , represents thermodynamic data of special significance, forging the link between enthalpy and Gibbs energy, which is the true arbiter of chemical equilibrium and stability in processes whose outcome is determined by thermodynamic (as opposed to kinetic) considerations. While enthalpy data are widely published¹ or can be estimated² for many solid materials, entropy values are often unavailable, when simple estimation procedures become particularly useful.

Latimer^{3a} reported an additive method for the estimation of the standard entropies of solids, monatomic aqueous ions, and nonpolar molecules, based on summation of elemental contributions obtained from the equation

$$S_{298}^{\circ}/\text{J K}^{-1} \text{ mol}^{-1} = \frac{3}{2}R \ln M - 3.93 \quad (1)$$

where R is the gas constant ($= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and M is

the atomic mass of the element in question. Contributions from anions are dependent on the charge residing on the cation.

- (1) (a) *Handbook of Chemistry and Physics*, 82nd ed.; Lide D. R., Ed.; CRC Press: Boca Raton, FL, 2001–2002; pp 5-20 to 5-50. (b) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Nutall, R. L. *Selected Values of Chemical Thermodynamic Properties*; U. S. Department Commerce, National Bureau of Standards: Washington, DC, 1982. (c) Robie, R. A.; Hemingway, B. S.; Fisher, J. R. *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10⁵ Pascals) Pressure and at Higher Temperatures*; Geological Survey Bulletin 1452; U. S. Government Printing Office: Washington, DC, 1978. (d) Saxena, S. K.; Chatterjee, N.; Fei, Y.; Shen, G. *Thermodynamic Data on Oxides and Silicates*; Springer: Berlin, 1993. (e) *Thermal Constants of Substances*; Yungman, V. S., Glushko, V. P., Medvedev, V. A., Gurvich, L. V., Eds.; Wiley: New York, 1999; 8 vols. (f) NIST database, <http://www.webbook.nist.gov/chemistry/>.
- (2) (a) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609. (b) Glasser, L.; Jenkins, H. D. B. *J. Am. Chem. Soc.* **2000**, *122*, 632. (c) Jenkins, H. D. B.; Tudela, D.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 2364. (d) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 4358. (e) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J. *Inorg. Chem.* **2003**, *42*, 2886. (f) Jenkins, H. D. B.; Tudela, D. *J. Chem. Educ.* **2003**, *80*, 1482. (g) Christie, K. O.; Jenkins, H. D. B. *J. Am. Chem. Soc.* **2003**, *125*, 9457.

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Standard Absolute Entropies

A more complex summation procedure was used for minerals by Fyfe et al.,⁴ who employed the entropy and volume of component oxides to derive an estimate for multiple oxide phases, effectively applying a “volume correction” to the individual oxide entropy contributions. Their equation takes the form

$$(S_{298,j}^{\circ} - k''V_j) = \sum n_i(S_i - k''V_i) \quad (2)$$

$S_{298,j}^{\circ}$ represents the target entropy for the multiple oxide phase of interest, volume V_j , which is made up of n_i individual oxides, volume V_i , whose entropies are S_i , and k'' is a constant. Thus, for example, for the mineral akermanite, $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, whose volume is $V_{\text{ak}}/\text{cm}^3 \text{ mol}^{-1}$, its standard entropy at 298 K is estimated (on expanding eq 2) to be

$$S_{298,j}^{\circ}(\text{akermanite})/\text{J K}^{-1} \text{ mol}^{-1} = k''V_{\text{ak}} + 2(S - k''V)_{\text{CaO}} + (S - k''V)_{\text{MgO}} + 2(S - k''V)_{\text{SiO}_2} \quad (3)$$

Holland⁵ has further developed this approach by adopting different $(S - k''V)$ parameters for each different coordination site, so that

$$S_{298}^{\circ}(\text{akermanite})/\text{J K}^{-1} \text{ mol}^{-1} = k''V_{\text{ak}} + (S - k''V)_{\text{CaO}(8)} + (S - k''V)_{\text{CaO}(6)} + (S - k''V)_{\text{MgO}(4)} + 2(S - k''V)_{\text{SiO}_2(4)} \quad (4)$$

This also provides a method of correcting for magnetic disorder (in cases where this is required), while taking⁶ an average value of $k'' = 1$ (see Appendix). Using these techniques, the standard entropies of silicates and multiple oxide phases can be estimated to within $\pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ for most materials. Holland⁵ also investigated the effect of ignoring volume in eq 2, so following the approach of Robinson and Hass⁷ for minerals

$$S_{298,j}^{\circ} = \sum n_i S_i \quad (5)$$

This yields the standard deviation of the residuals and the mean absolute deviation of the residuals of 3.26 and 2.50 $\text{J K}^{-1} \text{ mol}^{-1}$, respectively. These deviations correspond to about twice those of the volume-corrected method.

In the work discussed here, we seek a much simpler and more straightforward approach, not requiring the identification of component volumes and other contributions, while allowing some compromise in the predicted accuracy. Thus,

(3) (a) Latimer, W. M. *Oxidation Potentials*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1961. Latimer, W. M. *J. Am. Chem. Soc.* **1951**, *73*, 1480. (b) See the example calculation for K_2PtCl_6 as shown on p 365 of Appendix III of ref 3a.

(4) Fyfe, W. S.; Turner, F. J.; Verhoogen, J. *Metamorphic Reactions and Metamorphic Facies*; Geological Society of America: Boulder, CO, 1958; Memoir 73.

(5) Holland, T. J. B. *Am. Mineral.* **1989**, *74*, 5.

(6) When adopted in eqs 2–4, this value of unity for k'' leads to a simplification in the form of the equation. Note that if k'' were to equal k of our correlation (eq 6), then eq 2 would collapse to zero since $S = kV$. The discussion in the Appendix makes clear the distinction between k and k'' , however.

(7) Robinson, G. R.; Haas, J. L. *Am. Mineral.* **1983**, *68*, 541.

we report a simple and direct relationship between standard absolute entropy, S_{298}° , and molecular (formula unit) volume, V_m .

Volume-Based Entropy Equation

Almost two decades ago, Mallouk and Bartlett⁸ reported an entropy/volume relationship for a small set of MX (1:1) ionic salts and a few covalent compounds⁹ and used this relationship without discussion or explanation. The work reported in this paper undertakes a thorough study of the direct relationship between standard absolute entropy, S_{298}° , and molecular (formula unit) volume, V_m , finding that it applies for a whole range of stoichiometries,¹⁰ for minerals, and even for organic liquids and solids.¹¹

Figure 1 displays a combined plot of standard molar entropy, $S_{298}^{\circ}/\text{J K}^{-1} \text{ mol}^{-1}$, values against the corresponding formula unit volumes, $V_m/\text{nm}^3 \text{ formula unit}^{-1}$, for 65

(8) (a) Mallouk, T. E. Doctoral Thesis. University of California, Berkeley, 1983, Chapter IV. (b) Bartlett, N.; Yeh, S.; Kourtakis, K.; Mallouk, T. E. *J. Fluorine Chem.* **1984**, *26*, 97.

(9) The correlation dataset of Mallouk and Bartlett⁸ was restricted to 1:1 salts in contrast to the present more comprehensive study which establishes that this relationship is much more general than was earlier intimated. They considered only the following salts and a few covalent materials: the alkali and ammonium halides, NaBH_4 , KBH_4 , KBF_4 , NaClO_4 , PbSO_4 , KReO_4 , NH_4ClO_4 , NH_4ReO_4 , KPF_6 , ClO_2GeF_5 , NH_4PF_6 , Na_3AlF_6 , SF_3PF_6 , SF_3BF_4 , $(\text{SF}_3)_2\text{GeF}_6$, MgSO_4 .

(10) (a) The dataset used for the anhydrous inorganic salts, M_pX_q , in the present study is made up of the following range of stoichiometries and is not confined to (1:1) salts exclusively.

M_pX_q	ratio	included
MX	1:1	18
MX	2:2	6
MX_2	2:1	17
M_2X	1:2	15
MX_3	3:1	1
M_3X	1:3	3
MX_4	4:1	1
M_4X	1:4	1
other complex salts	-	2

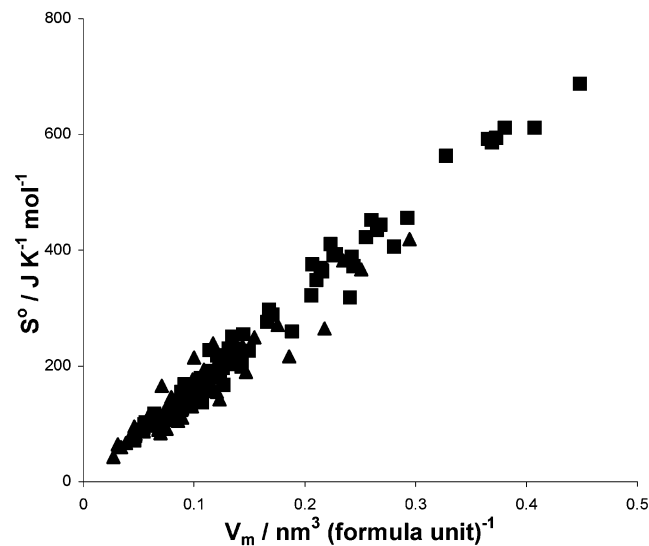
(b) The dataset used for the inorganic hydrates, $\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}$, is made up of the following different stoichiometries.

stoichiometry	charge ratio	no of salts included
$\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}$		
$\text{MX} \cdot n\text{H}_2\text{O}$	1:1	18
$\text{MX} \cdot n\text{H}_2\text{O}$	2:2	14
$\text{MX}_2 \cdot n\text{H}_2\text{O}$	2:1	20
$\text{M}_2\text{X} \cdot n\text{H}_2\text{O}$	1:2	10
$\text{MX}_3 \cdot n\text{H}_2\text{O}$	3:1	1
$\text{M}_2\text{X}_3 \cdot n\text{H}_2\text{O}$	3:2	2
$\text{M}_4\text{X} \cdot n\text{H}_2\text{O}$	1:4	2
$\text{M}_3\text{X} \cdot n\text{H}_2\text{O}$	1:5	1

(11) Glasser, L.; Jenkins, H. D. B. Submitted for publication.

Table 1. Unconstrained and Constrained ($c = 0$) Linear Relationships between Standard Entropy, $S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$, and Formula Unit Volume, V_m/nm^3

compd type	no. compds considered	fitted params for eqs 6 and 7				
		$k/\text{J K}^{-1} \text{mol}^{-1}$ (nm^{-3} formula unit)	$k'/\text{J K}^{-1} \text{cm}^{-3}$	$c/\text{J K}^{-1} \text{mol}^{-1}$	corr coeff for volume-based eq 6, R^2	av unsigned % error for S_{298}° , using eq 6
anhydrous ionic solids (Table A1)	65	1360 ± 56	2.258 ± 0.093	15 ± 6	0.90	11.5
		1481 ± 27	2.458 ± 0.045	0	0.88	12.6
hydrated ionic solids (Table A2)	67	1579 ± 30	2.621 ± 0.050	6 ± 6	0.98	7.4
		1606 ± 14	2.666 ± 0.023	0	0.96	7.4

**Figure 1.** Standard absolute molar entropy, $S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$, values versus formula unit volumes, V_m/nm^3 formula unit $^{-1}$, for the combined set of 132 anhydrous (▲) and hydrated (■) ionic solids

anhydrous ($M_p X_q$) 10a and 67 hydrated ($M_p X_q \cdot n\text{H}_2\text{O}$) 10b inorganic ionic solids (see Tables A1 and A2 in the Supporting Information for the actual data). The data used involve inorganic materials exhibiting varying stoichiometries 10 for which entropy values are listed in standard tables 1 and establish the relationship between S_{298}° and V_m as being a quite general one. That such an empirical correlation of this form might exist can (at least in part) be rationalized in terms of thermodynamics (see Appendix).

The fitted equation takes the form

$$S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1} = k(V_m/\text{nm}^3 \text{ formula unit}^{-1}) + c \quad (6)$$

where V_m is obtainable from crystal structure data, 1 or is estimated by a combination, using our database, of individual ion volume data, 12 or by using extrapolation, interpolation, or other similar procedures, 13 or by correlation with other size-dependent properties, or from density, as described below.

Density-Based Entropy Equation

A simple experimental measurement of density, $\rho/\text{g cm}^{-3}$, which requires a minimum amount of material, is nondestructive and easy to establish can similarly be used to

estimate standard entropy in conjunction with a knowledge of the formula unit molar mass, M , of the material. By virtue of the relationship which exists 14 between volume, V_m/nm^3 formula unit $^{-1}$, and density, $\rho/\text{g cm}^{-3}$, the corresponding density-based equation takes the form

$$S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1} = k' [M/(\rho/\text{g cm}^{-3})] + c \quad (7)$$

where

$$k' = (1.66 \times 10^{-3})k \quad (8)$$

with eqs 6 and 7 having the parameters listed in Table 1.

The following comments can be made: (i) the qualities of the correlations are much the same whether the intercept is constrained ($c \equiv 0$) or unconstrained; (ii) the correlation holds even for ionic hydrates with their mixed Coulombic, hydrogen bonding, and dispersion interactions.

Estimation of Standard Entropy

It is useful to be able to estimate standard entropy data for several reasons. First, there is a paucity of standard entropy data for inorganic materials 15 in standard thermochemical tables. 1 Second, experimental determination of absolute entropy, S_{298}° , by calorimetry is both a lengthy and nontrivial procedure; such measurements are no longer fashionable science and, for this reason, increasing reliance has to be placed on estimation techniques for thermochemical data. Third, in the context of our continuing work, 2 we wish to establish procedures which are robust and which offer a simple approach to the estimation of thermodynamic data. The present correlation forms a useful addition to these tools such that nonspecialists and specialists alike can use our approach. Entropy estimation involves only simple arithmetic, easily performed even on a pocket calculator. The procedure can be applied for new (or even hypothetical) salts, as well as for already synthesized, existing, inorganic materials. The approach's ultimate importance is in its use to estimate changes in Gibbs energy for reactions, etc.

In the estimation of Gibbs energy data via the $T\Delta S$ contribution to the ΔG term (in kJ mol^{-1}) at 298 K, the value of $\Delta S/\text{J K}^{-1} \text{mol}^{-1}$, derived as the absolute standard entropy differences of products and reactants, is multiplied by the factor $T/(\text{K J kJ}^{-1}) = 0.298$. Effectively, a consequence of this factor is that a larger error can be tolerated in the standard

(12) Roobottom, H. K.; Jenkins, H. D. B.; Passmore, J.; Glasser, L. *J. Chem. Educ.* **1999**, *76*, 1570. Marcus, Y.; Jenkins, H. D. B.; Glasser, L. *J. Chem. Soc., Dalton Trans.* **2002**, 3795.

(13) See footnotes 121 and 129 in the following reference: Cameron, T. S.; Deeth, R. J.; Dionne, I.; Du, H.; Jenkins, H. D. B.; Passmore, J.; Roobottom, H. K. *Inorg. Chem.* **2000**, *39*, 5614.

(14) The relationship between molar volume, V_m , and density, ρ , is $V_m/\text{cm}^3 \text{mol}^{-1} = (M/\text{g mol}^{-1})/(\rho/\text{g cm}^{-3}) = (M/\text{g mol}^{-1}) \times (10^7)^3/\text{nm}^3 \text{cm}^{-3}/(N_A/\text{molecules formula unit}^{-1} \times \rho/\text{g cm}^{-3}) = 10^{21}M/(6.023 \times 10^{23} \times \rho) = [1.66 \times 10^{-3}M/\rho]/(\text{nm}^3 \text{ formula unit}^{-1})$ where M is the chemical formula mass.

(15) Jenkins, H. D. B.; Elliot, H. St. A.; Schrobilgen, G. J.; Lehman, J. F. Manuscript in preparation.

Table 2. Unconstrained and Constrained ($c = 0$) Linear Relationships between Standard Entropy, $S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$, and Formula Unit Volume, V_m/nm^3 , for Minerals and Silicates

mineral type	no. compds considered	eq 6 params			
		$k/\text{J K}^{-1} \text{mol}^{-1}$ (nm^{-3} formula unit)	$c/\text{J K}^{-1} \text{mol}^{-1}$	corr coeff, R^2	av unsigned % error
minerals (Table A3)	99	1262 ± 28	13 ± 5	0.95	12.6
silicates combined, subset of data for minerals	53	1317 ± 18	0	0.94	11.6
		1303 ± 30	0 ± 5	0.97	9.1
ortho and ring structure silicates (O) subset of data for silicates	20	1305 ± 16	0	0.95	9.1
		1265 ± 99	10 ± 13	0.89	13.3
chain and band structure silicates (C) subset of data for silicates	11	1338 ± 39	0	0.84	12.1
		1176 ± 56	9 ± 9	0.98	9.9
sheet structure silicates (S) subset of data for silicates	8	1216 ± 36	0	0.88	10.9
		1490 ± 205	-51 ± 43	0.88	4.8
framework structure silicates (F) subset of data for silicates	14	1251 ± 32	0	0.73	5.5
		1384 ± 27	-10 ± 6	0.99	5.1
		1350 ± 16	0	0.92	4.5

entropies. This significant point renders the correlation reported here of enhanced value. Furthermore, the $T\Delta S$ term in ΔG is generally quite small relative to ΔH at or near room temperature, where much of chemistry is studied, so that rule-of-thumb procedures are likely to prove suitable even when the entropy may be somewhat in error.

Consider the following example (data from ref 1a), for $\text{BaCl}_2(\text{s})$, for which the error in the predicted entropy is quite large, at nearly 10%.

$\Delta_f H^{\circ} = -855.0 \text{ kJ mol}^{-1}$; $S^{\circ} = 123.7 \text{ J K}^{-1} \text{mol}^{-1}$. Then, $\Delta_f S^{\circ} = -161.9 \text{ J K}^{-1} \text{mol}^{-1}$, after subtracting the entropy data for the reactants, $\text{Ba}(\text{s})$ and $\text{Cl}_2(\text{g})$. From these data, $\Delta_f G^{\circ} = -806.8 \text{ kJ mol}^{-1}$ at 298 K. Using, instead, our predicted value of $S_{298}^{\circ} = 135.8 \text{ J K}^{-1} \text{mol}^{-1}$ yields $\Delta_f G^{\circ} = -810.3 \text{ kJ mol}^{-1}$ at 298 K, an error of +3.5 kJ mol^{-1} or only 0.4%. In general, of course, the error in the free energy will depend on the relative values of the enthalpy and entropy terms, but this result may be regarded as typical for ionic materials. Even for an error in the predicted entropy as large as 23%, as in the case of AlCl_3 , the error in $\Delta_f G^{\circ}$ is only 1.2% (error of -7.7 kJ mol^{-1}).

Use of Volume- and Density-Based Correlations to Estimate Entropy

If it is desired to estimate missing standard entropy values using eqs 6 or 7 for a particular group of materials for which some of the experimental standard entropies are known, then our recommended procedure is to determine the appropriate values of the parameters, k (or k') and c , using as many of the established values of entropy as possible. Such a strategy is likely to give more reliable estimates of the missing entropy values than the alternative of assuming global values of k , k' , and c from Table 1. This is illustrated below from some of the results cited in Table 2 for a dataset of minerals.

Minerals, Silicates, and Individual Structural Types

Table 2 shows the results of analysis of the effect of studying subsets of the entropy–volume data listed in Table A3 in the Supporting Information for a set of 99 minerals. Analysis of the data for the whole set of minerals gives a

slightly poorer correlation (0.95, 0.94) than does taking a subset of the 53 silicates included in the 99 minerals (0.97, 0.95), and the average unsigned error involved in this latter estimate is smaller also. This illustrates the contention concerning the efficacy of choosing a more select set of data when possible. In turn, Table 2 illustrates further that selection of 14 framework structure silicates from within the 53 silicates yields yet a smaller average unsigned error than from either the silicates or the minerals represented in the larger sets.

It is worthwhile commenting that use of the S_{298}° versus V_m correlation to predict entropy for minerals is (as might be anticipated) not as accurate as is the adoption of the more sophisticated procedures of Holland and others^{5–7} mentioned in our Introduction. However, Holland's results conform well to the present approach. For example, if we add the data from Holland's Table 1⁵ to that used to establish our correlation (eq 6), we find that the combined data leads to

$$S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1} = 1285.4 V_m/\text{nm}^3 \text{ formula unit}^{-1} \quad (\text{with } R^2 = 0.956) \quad (9)$$

while the further addition of the data from his Table 4 leads to

$$S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1} = 1224.8 V_m/\text{nm}^3 \text{ formula unit}^{-1} \quad (\text{with } R^2 = 0.977) \quad (10)$$

These observations support our relationship (eq 6), with the correlation coefficient improved by the addition of Holland's supplementary data.

Further, if we use the data from Holland's Table 4 alone we find a correlation.

$$S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1} = 1387.6 V_m/\text{nm}^3 \text{ formula unit}^{-1} \quad (\text{with } R^2 = 0.966) \quad (11)$$

To illustrate the difference between our correlation and the equation of Holland,⁵ we consider results for the four types of silicate structures: chain/band, framework, ortho/ring, and sheet. Table 3 compares the results.

Table 3. Comparison of Estimation of Standard Entropy, $S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$, for Silicates, Using Various Approaches

silicate (type)	diopside (chain/band)	anorthite (framework)	akermanite (ortho/ring)	chrysotile (sheet)
composition	CaO·MgO·2SiO ₂	CaO·Al ₂ O ₃ ·SiO ₂	2CaO·MgO·2SiO ₂	3MgO·2SiO ₂ ·2H ₂ O
V_m , formula unit volume/nm ³	0.1100	0.1674	0.1537	0.1785
$S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$				
minerals, constrained correlation (Table 2)	145	221	202	235
minerals, unconstrained correlation (Table 2)	152	224	207	238
structure-based ^a constrained correlation (Table 2)	134	226	206	223
structure-based ^a unconstrained correlation (Table 2)	138	222	204	215
Holland ⁵ calcd	144.2	198.9	208.0	221.0
exptl (Holland ⁵)	142.7	199.3	209.2	221.3
exptl (Saxena ^{1d})	143.0	203.0	208.2	219.8

^a Structure-based refers to the use of the appropriate correlation in Table 2 corresponding to the structure type of the mineral being considered, i.e., for diopside (C), anorthite (F), akermanite (O), and chrysotile (S).

Table 4. Comparison of Latimer's Estimation of Standard Entropy, $S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$, with the Approach Presented in This Paper

salt	V_m/nm^3	Latimer estimate $S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$	estimate using $S_{298}^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$ $= 1360 V_m + 15$
XeF ⁺ AsF ₆ ⁻	0.1490 ¹⁵	222	218
XeF ⁺ SbF ₆ ⁻	0.1591 ¹⁵	229	231
KrF ⁺ BiF ₆ ⁻	0.1544 ¹⁶	233	225
(Kr ₂ F ₃ ⁺) ₂ (SbF ₆ ⁻) ₂ KrF ₂	0.4675 ¹⁶	<i>a</i>	651

^a No description in ref 3a as to how to treat this salt.

These are broadly in line with the earlier discussion, although our anorthite results are rather large, by about 10%.

We illustrate Latimer's approach^{3a} as used to estimate the standard entropy of some noble gas fluorocation salts, NgF⁺X⁻ where Ng = Xe, Kr and X⁻ = SbF₆⁻, AsF₆⁻, etc., and compare the results with those obtained using the global inorganic correlation presented in this paper. What emerges is the following: (i) the similarity of the results (i.e., within the error limits expected); (ii) the simplicity and ease of our approach in comparison to that of Latimer; and (iii) the fact that for some more complex salts (e.g., (Kr₂F₃⁺)₂(SbF₆⁻)₂KrF₂) the format of Latimer's rules prevents evaluation of an estimate. Consider the salts listed in Table 4. The two XeF⁺ salts and the KrF⁺ salt are regarded, according to Latimer's approach,^{3a} as consisting of two "positive ions": NgF⁺ (Ng = Xe or Kr) and M⁵⁺ (M = As, Sb or Bi) returning an overall average charge of +⁶/₂ = +3 and fluoride anions, F⁻. The elemental entropy contributions for $S^{\circ}(\text{Ng})/\text{J K}^{-1} \text{mol}^{-1}$ = 56.9 (Xe), 51.3 (Kr), and values for the main group elements (M) are taken from Table 87 of ref 3b, while $S^{\circ}(\text{F})/\text{J K}^{-1} \text{mol}^{-1}$ corresponding to a cation charge of +3 is 16.7. The fluorine atom of the cation is treated as though it were an anion-based F atom.

Alternative Correlations

We have also investigated alternative correlations.¹⁷ These are absolute entropies against number of atoms (n), and absolute entropies against formula masses (M). Analysis of the former shows, however, very poor correlation for the ionic solids ($R^2 = 0.58$), for example, against n . This is not

entirely unexpected a priori since the factor n simply lumps together groups such as binary compounds, ternaries, etc., whatever their other properties (such as charge). For minerals (where n extends to much larger values), the atom number correlation is rather better, but it adds nothing to the quality of the correlation (see Figure 2) and only confuses the issue.¹⁵ Any correlation of S with M has proven to be essentially nonexistent.

Discussion

We have here demonstrated that there is a close linear relation (see Figure 1 and Table 1) between the standard entropies and volumes of a wide range of materials in differing classes of condensed phases: ionic solids, mineral solids, ionic hydrate solids, and also organic solids and liquids.¹¹ The slopes of the rectilinear relations differ little among the ionic solids but are rather smaller for the organics,¹¹ and the mean unsigned errors of the predicted entropies relative to the literature values are generally about 10% (but as low as 6% for organic liquids). This somewhat large error range is unfortunate and arises from two sets of causes. First, there are intrinsic differences within the group of materials which are not accounted for by correlation with volume alone, and second, there are widely acknowledged

(17) As an illustration, in the database^{1b} of 306 inorganic salts, only 83 (i.e., 27%) have recorded entropy values, while for their associated 356 hydrates, only 97 (i.e., again 27%) standard entropy values are listed. By contrast, reporting of the standard entropies of minerals^{1c,d} is impressively close to almost 100% for the (admittedly limited) sets selected. We have examined thoroughly the set of minerals for which $n > 3$ and find that (a) if entropy (S) is fitted with both n (number of atoms) and V_m (formula unit volume) in a multiple linear regression, then the correlation coefficient, R^2 , is 0.94, the mean unsigned error is 13.7%, and $S/\text{J K}^{-1} \text{mol}^{-1} = 1005.3(\pm 297.2)V_m/\text{nm}^3 \text{ formula unit}^{-1} + 2.297(\pm 3.304)n + 20.9(\pm 10.0)$ where the large error shows that the coefficient of n is excessively poorly determined. Furthermore, a large covariance is found between the two parameters, V_m and n , leading to elimination of one of these. (b) If entropy is fitted with V_m alone, then R^2 is 0.94, the mean unsigned error is 13.4%, and $S/\text{J K}^{-1} \text{mol}^{-1} = 1209.3(\pm 46.9)V_m/\text{nm}^3 \text{ formula unit}^{-1} + 21.7(\pm 9.8)$. (c) If entropy is fitted with n alone, then R^2 is 0.92, the mean unsigned error is 17.1%, and $S/\text{J K}^{-1} \text{mol}^{-1} = 13.33(\pm 0.58)n + 21.0(\pm 11.1)$. These values demonstrate that use of n alone (even when $n < 4$ are omitted) in the correlation is poorer than use of V_m alone. The use of both V_m and (even the limited set of) n simply confuses the issue, without adding further to the quality of the correlation. We believe that our selection of a correlation between S and V_m remains the correct choice.

(16) Lehman, J. F.; Dixon, D. A.; Schrobilgen, G. J. *Inorg. Chem.* **2001**, *40*, 3002.

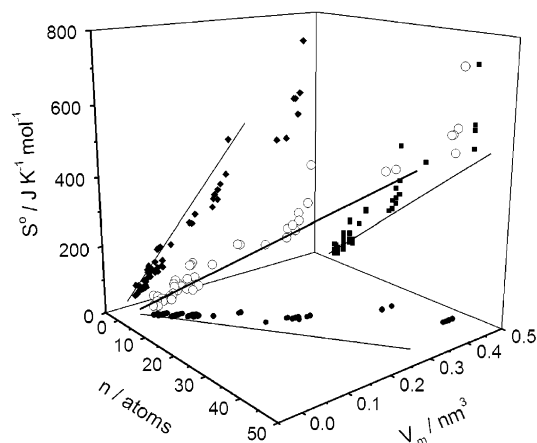


Figure 2. A multiple linear regression plot for a group of minerals of the absolute standard entropy, S_{298}° , versus both number of atoms (n) in the chemical formula and formula unit volume (V_m) (\circ), together with projections onto the planes of S_{298}° versus V_m (\blacklozenge), S_{298}° versus n (\blacksquare), and V_m versus n (\bullet).

errors in the fundamental data (including each of entropy, X-ray volumes, and densities, and, among minerals, at least, compositional effects such as nonstoichiometry). On the other hand, the paucity of entropy data (against the much wider availability of enthalpies and of volume-related data) renders valuable even an approximate relation. The slopes, which represent the entropy gain per unit volume increase, increase in the sequence organics < minerals \approx ionic solids < ionic hydrates, corresponding to increasing strength of the intermolecular forces, or increasing “hardness” of the materials (see Appendix).

The net effect of our present results on entropy estimation, together with our earlier work on the estimation of enthalpies of ionic solids,² is that estimations of the Gibbs energies of a wide range of ionic solids and their hydrates, as well as of organic liquids and solids, are now readily accessible via simple procedures, even to the occasional user. However, users are cautioned against overinterpretation of the estimated results and are reminded of the existence of more sophisticated approaches if accuracy is paramount.

We note that our general methodology² of thermochemical correlation against the single molecular parameter of volume (and charge,^{2b,18} where appropriate) has little precedent (but see ref 8) in contrast with the standard procedures of group additivity.^{3–5}

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Appendix: Rationalization of the S_{298}° versus V_m Rectilinear Relationship

A linear relationship between entropy and volume has been clearly demonstrated in Figure 1. In the absence of thermodynamic proof¹⁹ (because our relationship is essentially and

necessarily an empirical one), we list below a number of factors supporting the observation that S_{298}° and V_m are linearly correlated.

1. In terms of one of the set of Maxwell relationships, we can write

$$\left(\frac{\partial S}{\partial V_m}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa} \quad (\text{A1})$$

where α = coefficient of cubic thermal expansion

$$\left(\frac{\partial V_m}{\partial T}\right)_p = V_m \alpha \quad (\text{A2})$$

and κ = coefficient of isothermal compressibility

$$\left(\frac{\partial V_m}{\partial p}\right)_T = -V_m \kappa \quad (\text{A3})$$

The derivative $(\partial p/\partial T)_V$ represents the increase in pressure, p (at fixed volume, V), arising from a rise in absolute temperature, T . This increase in pressure results from attempts at reduction in the free volume (rather than of the excluded volumes of the molecular groups themselves, which are largely incompressible) against the intermolecular forces.

2. Fyfe et al.⁴ have discussed the relationship between entropy and volume and have reported that, for most inorganic silicates and oxides

$$1.3 < [\alpha/\kappa = (\partial S/\partial V)_T / \text{J K}^{-1} \text{ cm}^{-3}] < 5.5 \quad (\text{A4})$$

which implies an approximate constancy for the ratio of α/κ , corresponding to

$$800 < [\alpha/\kappa / \text{J K}^{-1} \text{ mol}^{-1} \text{ formula unit nm}^{-3}] < 3500 \quad (\text{A5})$$

Figure 1 has a gradient, $(\partial S/\partial V_m)_T$, whose value of about $1300 \text{ J K}^{-1} \text{ mol}^{-1} \text{ formula unit nm}^{-3}$ is well within this range.

3. The Einstein model for solids, as applied by Holland,⁵ to estimate $(\partial S/\partial V)_T$ for silicate and oxide minerals at 298 K, leads to the expression

$$(\partial S/\partial V)_T = nRu^2/[V(e^u - 1)(1 - e^{-u})] \quad (\text{A6})$$

where $u = hv/kT$, h and k being Planck's and Boltzmann's constants, respectively. This theory confirms the approximate constancy of $(\partial S/\partial V)_T$ since n , the number of moles present, is correlated with, and so will cancel with, the V term. Holland has estimated⁵ from eq A6 that

$$(\partial S/\partial V_m)_T = k'' \approx 1.07 \pm 0.11 \text{ J K}^{-1} \text{ cm}^{-3} \quad (\text{A7})$$

Holland also determined, from the Debye theory of specific heats, that

$$(\partial S/\partial V_m)_T = k'' \approx 0.9 \pm 0.10 \text{ J K}^{-1} \text{ cm}^{-3} \quad (\text{A8})$$

The average⁶ of k'' is $1 \pm 0.10 \text{ J K}^{-1} \text{ cm}^{-3}$, equivalent to $602 \pm 60 \text{ J K}^{-1} \text{ mol}^{-1} (\text{nm}^{-3} \text{ formula unit})$, a value which is considerably lower than the value of about $1300 \text{ J K}^{-1} \text{ mol}^{-1} (\text{nm}^{-3} \text{ formula unit})$ derived from Figure 1.

(18) Glasser, L. *Inorg. Chem.* **1995**, *34*, 4935.

(19) It is pertinent that Boltzmann's relationship: $S = k \ln W$ has never enjoyed formal proof although the evidence for its validity is overwhelming.

4. We ascribe this difference to the fact that the estimations in points 2 and 3 above relate (as mentioned in point 1) to effects arising from changes in the intermolecular (free) volume. In contrast, the data in Figure 1, involving addition/removal of material, involve a different process from that of addition/removal of free space; since the added/removed material is essentially incompressible, the resulting gradient is larger.

5. Latimer³ based his method of estimating standard entropy on defining elemental and ionic contributions to the entropy which, when added, gave the estimated value. Since

ion volumes are similarly additive in their contribution to V_m , the relation between S_{298}° and V_m discussed in this paper also involves a relationship between two ion-additive properties.

Supporting Information Available: Three tables, each containing values of molar volume and standard absolute entropy (both experimental and predicted, following Tables 1 and 2 in the main text) for 65 anhydrous ionic solids (Table A1), 67 hydrated ionic solids (Table A2), and 99 minerals (Table A3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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