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Volume-Based Thermodynamics: Estimations for 2:2 Salts

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The lattice energy of an ionic crystal, U_{POT}, can be expressed as a linear function of the inverse cube root of its formula unit volume (i.e., $V_m^{-1/3}$); thus, $U_{POT} \approx 2I(\alpha/V_m^{1/3} + \beta)$, where α and β are fitted constants and I is the readily calculated ionic strength factor of the lattice. The standard entropy, S, is a linear function of V_m itself: $S \approx kV_m + c$, with fitted constants k and c. The constants α and β have previously been evaluated for salts with charge ratios of 1:1, 1:2, and 2:1 and for the general case q:p, while values of k and c applicable to ionic solids generally have earlier been reported. In this paper, we obtain α and β, k and c, specifically for 2:2 salts (by studying the ionic oxides, sulfates, and carbonates), finding that $U_{POT}\{\text{MX 2:2}\}/(\text{kJ mol}^{-1}) \approx 8(119/V_m^{1/3} + 60)$ and $S°\{\text{MX 2:2}\}/(\text{J K}^{-1}\text{ mol}^{-1}) \approx 1382V_m + 16$.

Introduction

Volume-based thermodynamics[1] (VBT) provides a means of estimating thermodynamic data using the formula unit volume of materials, V_m, which is easily and readily determined directly from crystal structure data ($V_m = V_{cell}/Z$, where Z is the number of formula units in the unit cell, of volume V_{cell}) or from density or by ion volume additivity ($V_m = V_+ + V_-$), using the individual ion volumes found in our databases.[2a−c] The VBT approach (as well as the use of *volume* as a criterion of the ion size) is gaining wide acceptance,[2d] finding application in tackling diverse topical problems. The link to earlier work on 1:1 charged salts by Mallouk et al.[2e] has been referred to elsewhere.[2a]

The constants, α and β (whose values vary slightly with the stoichiometry of the lattice and with the set of materials used in the statistical fitting), of the lattice potential energy equation (1) have previously been evaluated[3] for salts with charge ratios of 1:1, 1:2, and 2:1 and for the general case M_pX_q, with a charge ratio q:p, but not specifically for the important case of ionic lattices for the 2:2 case, of salts possessing both a divalent cation and anion:

$$U_{POT} \approx 2I(\alpha/V_m^{1/3} + \beta) \qquad (1)$$

The ionic strength factor,[4] I, in this equation is defined by the equation

$$I = \frac{1}{2}\sum_{\text{ions}}^{\text{formula unit}} n_i z_i^2 \qquad (2)$$

where n_i is the number of each type of ion, of integer charge z_i, in the formula unit (with complex ions such as sulfate being counted as a single, doubly charged ion[5,6]), yielding

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(5) Note that complex ions can equally well be regarded as decomposing into separated single ions, such as SO_4^{2-} yielding S_6^+ plus O^{2-}; this will result in a different, and much larger, value of the lattice energy, which includes the self-energy of the complex ion. For a more detailed outline, see, for example: Jenkins, H. D. B.; Waddington, T. C. *J. Chem. Phys.* **1972**, *56*, 5323. For lattice energies greater than 5000 kJ mol^{-1}, the linear equation (1) does not apply and, instead, a generalized equation[6] should be used. Conventionally, however, recognized complex ions, such as sulfate, are often treated as single entities although this may not apply when dealing with more complex materials such as in silicate minerals.

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the value $I = 4$ for 2:2 salts. Similarly, the values of standard entropies, $S°$, of ionic solids are observed to be rather closely linearly related to the formula unit volume,[7] as in eq 3. These

$$S° \approx kV_m + c \tag{3}$$

empirical constants are here determined for 2:2 salts by plotting the lattice potential energies, U_{POT} (as determined from Born−Fajans−Haber thermochemical cycles[8]), against $V_m^{-1/3}$ of known ionic salts (by studying the ionic oxides, sulfates, and carbonates). In general, it is recommended that, whenever possible, such plots be made by employing compounds as closely generic as possible to the target compound under study. The resulting predictions will then, inevitably, be more reliable.

Equations 1 and 3 form the backbone of VBT, which has considerably extended the range of materials for which thermodynamics can be estimated. The key factor giving this approach its range of application and simplicity when compared to other methods is the ease by which formula unit volumes may be assigned to hypothetical as well as known salts. It can therefore be adopted and used with ease by nonspecialists, requiring only a calculator. The VBT approach challenges presently used approaches based on complex theoretical calculations, while it can often be used effectively in tandem with them[1,2d] but does assume that the materials are fully ionic; procedures are currently in development to deal with materials that have a substantial component of covalency.

Calculations for U_{POT} and $S°$

Materials have been selected for the current exercise as those being generally regarded as having a high degree of ionicity, that is, oxides, sulfates, and carbonates of the divalent metallic elements; formula unit volumes have been obtained from crystallographic sources[9] as being most reliable. Standard entropies have been collected from the *Handbook of Chemistry and Physics*,[10] and lattice energies have been calculated, in a Born−Haber−Fajans thermochemical cycle, by summing the standard enthalpies of formation, $\Delta_f H°$, of the relevant ions[11] (also see the table in the Supporting Information) and subtracting the standard enthalpy of formation of the corresponding ionic solid.[10] While $\Delta_f H°$ for the cations is well-established (being the sum of the sublimation enthalpy of the solid metal plus the first and second ionization potentials of the gaseous species),[11] the corresponding formation enthalpies of the doubly charged anions are unknown because they do not have bound gaseous states. Instead, for the anions, values are determined by backcalculation of the thermochemical cycles for 1:2 compounds of known formation enthalpy (say, Na_2SO_4); the resulting average values are assumed to apply equally to the 2:2 compounds.

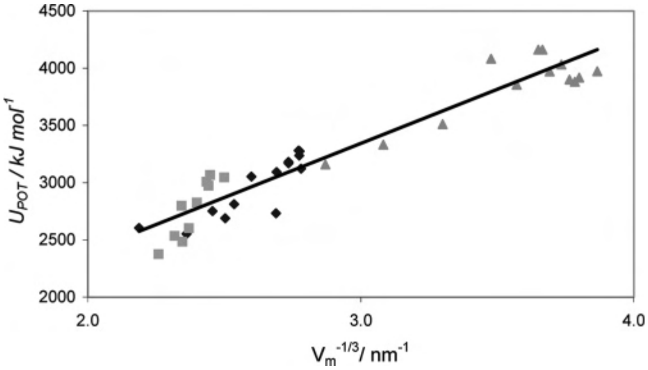

Figure 1. Plot of U_{POT} versus $V_m^{-1/3}$ for the 2:2 salts in Table 1: diamonds for carbonates, squares for sulfates, and triangles for oxides. Linear least-squares-fitted equation: $U_{POT}\{MX\ 2{:}2\}/(kJ\ mol^{-1}) \approx 8(119/V_m^{1/3} + 60)$ [correlation coefficient $R^2 = 0.91$ and degrees of freedom = (no. of points − 2) = 33, leading to the statistically based conclusion that there is greater than 99.9% probability that the assumption of linearity between U_{POT} and $V_m^{-1/3}$ is correct].

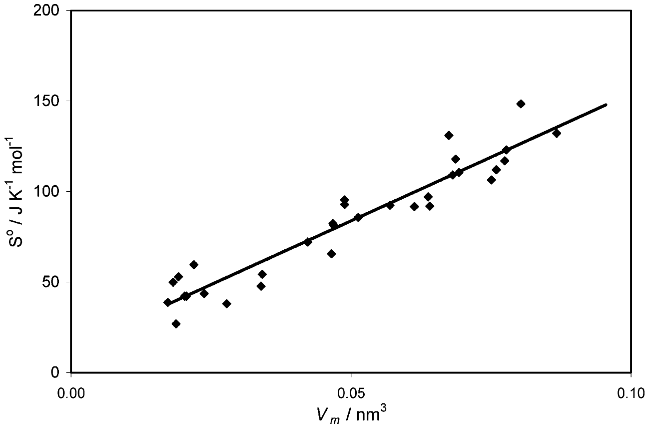

Figure 2. Plot of $S°$ versus V_m for the 2:2 salts in Table 1. Linear least-squares-fitted equation: $S°\{MX\ 2{:}2\}/(J\ K^{-1}\ mol^{-1}) \approx 1412V_m + 14$ [correlation coefficient $R^2 = 0.90$ and degrees of freedom = (no. of points − 2) = 28, leading to the statistically based conclusion that there is greater than 99.9% probability that the assumption of linearity between $S°$ and V_m is correct]. See also the Note Added in Proof.

The least-squares linear fit of the plot of U_{POT} versus the crystallographic-based $V_m^{-1/3}$ (Figure 1) takes the form

$$U_{POT}\{MX\ 2{:}2\}/(kJ\ mol^{-1}) \approx 8(119/V_m^{1/3} + 60) \tag{4}$$

The mean absolute error of the fit is only 4.4%, with the largest error being 11.2% for $CuCO_3$, which may be expected to have significant covalency. The values of α and β in eq 4 (119 and 60, respectively) may be compared with the original estimations (102 and 95, respectively).

A corresponding plot for standard entropies ($S°$ versus V_m) appears in Figure 2. The least-squares linear fit of the plot of $S°$ versus the crystallographic-based V_m for the ionic solids[7] in Table 1 (taking into account asterisked data, see Note Added in Proof) (Figure 2) takes the form

$$S°\{MX\ 2{:}2\})/(J\ K^{-1}\ mol^{-1}) \approx 1382V_m + 16 \tag{5}$$

The mean absolute error of the fit is 7.7 J K^{-1} mol^{-1}, while

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Table 1. $\Delta_f H°$, V_m, U_{POT}, and $S°$ Values for 2:2 Ionic Salts

mineral	formula	$\Delta_f H°$/(kJ mol^{-1})	V_m/nm^3	U_{POT}/(kJ mol^{-1})	$S°$/(J K^{-1} mol^{-1})
rhodochrosite	$MnCO_3$	−894.1	0.0513	3093	85.8
siderite	$FeCO_3$	−740.6	0.0489	3170	92.9
sphaerocobaltite	$CoCO_3$	−713	0.0468	3236	88.7*
	$ZnCO_3$	−812.8	0.0468	3275	82.4
otavite	$CdCO_3$	−750.6	0.0570	3053	92.5
cerussite	$PbCO_3$	−699.1	0.0675	2751	131
smithsonite	$ZnCO_3$	−818.9	0.0469	3281	81.2
siderite	$FeCO_3$	−752	0.0489	3181	95.47
rutherfordine	UO_2CO_3	−1716.4	0.0955	2605	
	$CuCO_3$	−596.2	0.0514	2733	87.9*
	$MgCO_3$	−1095.8	0.04651	3123	65.7
	$CaCO_3$	−1207.6	0.06131	2813	91.7
	$SrCO_3$	−1220.1	0.06378	2690	97.1
	$BaCO_3$	−1213	0.07595	2552	112.1
	$BaSO_4$	−1473.2	0.0867	2376	132.2
	$CaSO_4$	−1434.5	0.0751	2602	106.5
	$SrSO_4$	−1453.1	0.0775	2486	117
	$PbSO_4$	−920	0.0803	2535	148.5
	$MnSO_4$	−1065.3	0.0724	2827	122.2*
	$CoSO_4$	−888.3	0.0687	2975	118
	$ZnSO_4$	−982.8	0.0693	3008	110.5
	$NiSO_4$	−872.9	0.0641	3046	92
	$CuSO_4$	−771.4	0.0682	3067	109.2
	$CdSO_4$	−933.3	0.0778	2799	123
	MgO	−601.6	0.01875	3900	27
	CaO	−634.9	0.02783	3511	38.1
	SrO	−592	0.03415	3333	54.4
	BaO	−548	0.04228	3158	72.1
	TiO	−519.7	0.01822	3918	50
	VO	−431.8	0.0173	3973	38.9
tenorite	CuO	−157.3	0.0203	4161	42.3
manganosite	MnO	−385.2	0.0220	3855	59.7
wustite	FeO	−272	0.0199	3972	50.8*
	CoO	−237.9	0.0192	4032	53
zincite	ZnO	−350.5	0.0238	4083	43.7

the maximum error of 21.8 J K^{-1} mol^{-1} is for $PbCO_3$. The values of k and c in eq 5 (1382 and 16, respectively) may be compared with the estimations for all ionic solids[7] (1360 and 15, respectively).

Table 2. Updated Coefficients α and β for Various Stoichiometries in Equation 1

salt (charge ratio)[a]	ionic strength factor, I	α/(kJ mol^{-1} nm)[b]	β/(kJ mol^{-1})	correlation coefficient, R^2	notes
MX (1:1)	1	117	52	0.94	
MX_2 (2:1)[a]	3	134	61	0.83	$n = 13$
M_2X (1:2)[a]	3	165	−30	0.95	$n = 21$, plot shown in Figure 1[2a]
MX (2:2)	4	102	92		as originally quoted[3]
		119	60	0.91	values in this study (n =35)
M_pX_q (q:p)[a] general salts	$\frac{1}{2}(pq^2 + qp^2)$	139	28	0.91	

[a] The ratios have been revised to represent *charge* ratios and are different from the *ion* ratios used in the original paper.[2a] [b] As always, the magnitude of α/(kJ mol^{-1} nm) is similar to that of the electrostatic factor, A/(kJ mol^{-1}) = 121.4 but is fitted to the data available.

Discussion

By establishing the constants for the lattice potential energy and standard entropy equations for handling 2:2 salts, we have now completed the suite of equations[3] that is commonly needed for the application of the VBT approach (collected in Table 2).

Note Added in Proof: The asterisked $S°$/(J K^{-1} mol^{-1}) values in Table 1 were not included in the original data set, but, if added, they lead to a modified fit, $S°\{MX\ 2{:}2\}$/(J K^{-1} mol^{-1}) $\approx 1381.7V_m + 16.0$, having $R^2 = 0.90$ and $n = 34$; this modified fit value is actually closer to our previously quoted[7] value for general ionic solids.

Supporting Information Available: Table of enthalpies of formation of gaseous ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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