

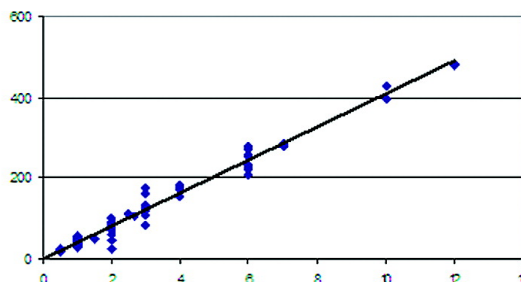
## Difference Rule A New Thermodynamic Principle: Prediction of Standard Thermodynamic Data for Inorganic Solvates

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$$\begin{aligned}
 &P\{n\text{-solvate}\} \\
 &- P\{\text{parent}\} \\
 &= n\theta\{\text{solvate}\}
 \end{aligned}$$



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## Difference Rule—A New Thermodynamic Principle: Prediction of Standard Thermodynamic Data for Inorganic Solvates

H. Donald Brooke Jenkins\*<sup>†</sup> and Leslie Glasser<sup>‡</sup>

Contribution from the Department of Chemistry, University of Warwick, Coventry CV4 7AL, West Midlands, United Kingdom and Nanochemistry Research Institute, Department of Applied Chemistry, Curtin University of Technology, GPO Box U1987, Perth WA, 6845, Australia

Received May 15, 2004; E-mail: Don.Jenkins@warwick.ac.uk

**Abstract:** We present a quite general thermodynamic “difference” rule, derived from thermochemical first principles, quantifying the difference between the standard thermodynamic properties,  $P$ , of a solid  $n$ -solvate (or  $n$ -hydrate),  $n$ -S, containing  $n$  molecules of solvate, S (water or other) and the corresponding solid parent (unsolvated) salt:  $[P\{n\text{-solvate}\} - P\{\text{parent}\}]/n = \text{constant} = \theta_P\{S, s-s\}$ , or  $n$ -S and other solvate,  $n'$ -S:  $[P\{n\text{-solvate}\} - P\{n'\text{-solvate}\}]/(n - n') = [P\{n\text{-S}\} - P\{n'\text{-S}\}]/(n - n') = \text{constant} = \theta_P\{S, s-s\}$  where  $P$  may be any one of:  $U_{\text{POT}}$  (the lattice potential energy),  $V_m$  (the molecular or formula unit volume),  $\Delta_f H^\circ$ ,  $\Delta_f S^\circ$ ,  $\Delta_f G^\circ$  or  $S_{298}^\circ$  (the standard thermodynamic functions of formation and the absolute entropy), and  $n$  can be noninteger. The constants,  $\theta_P\{S, s-s\}$ , for each property,  $P$ , of solvate of type S, are established by correlation of the available set of experimental data. We also show that, when solid-state data for a particular solvate is sparse,  $\theta_P\{S, s-s\}$  can be reliably predicted from liquid-state values,  $P\{S, l\}$ , or even gas-state values,  $P\{S, g\}$ . This rule offers a powerful means for predicting unknown thermodynamic data, extending the compass of currently known thermodynamic information. Systems considered involve the following solvates: H<sub>2</sub>O (hydrates), D<sub>2</sub>O, NH<sub>3</sub>, ND<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>O, NaOH, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, (CH<sub>2</sub>OH)<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, HF, KOH, and (CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>O. Detailed examples of usage are given for hydrates and for SO<sub>2</sub>.

### Introduction

Significant developments<sup>1,2</sup> beyond traditional thermodynamic approaches have recently been made by adopting molecular (formula unit) volume,  $V_m$ , as a convenient structure-based parameter. This has led to a series of simple and easy to use equations, initially for the estimation of lattice potential energy,  $U_{\text{POT}}$ , and latterly for the wider provision of otherwise unavailable thermodynamic data<sup>2</sup> such as standard entropy for inorganic

and organic materials. The aim has been to create a series of simple and straightforward, yet accurate, equations that can be used by specialists and nonspecialists alike. These can be applied to both traditional materials (where volume is taken from density or crystal structure data) and for speculative materials (where volume is estimated from individual ion volumes or by use of the ‘isomegetic rule’, which relates isomeric materials of identical charge-states,<sup>1b</sup> that is, of identical ionic strength factor,  $I$ ). Typical has been the development of a molar volume-based equation<sup>1a-c</sup> for the estimation of lattice energy (based on earlier work on [1:1] binary ionic solids by Bartlett<sup>3</sup> and colleagues, with extension to ionic solids of essentially any complexity by Glasser<sup>4</sup>). This was followed by the formulation of a corresponding equation for lattice energy based on density.<sup>1d</sup> Both equations exhibit an inverse cube-root dependence on the property used to estimate  $U_{\text{POT}}$ , so considerably reducing propagation of any experimental errors in the input parameters. The equations have two other distinct advantages. First, they allow departure from the traditional dependence of  $U_{\text{POT}}$  on thermochemical radii<sup>1f,5</sup> as is imposed, for example, by the Kapustinskii equation. In this way, the (unnecessary) imposition of sphericity onto ions (often patently nonspherical) is avoided.

<sup>†</sup> Department of Chemistry, University of Warwick.

<sup>‡</sup> Nanochemistry Research Institute, Department of Applied Chemistry, Curtin University of Technology.

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Second, they forge a provocative link between structural and thermodynamic data. On this latter theme, we have further developed<sup>2</sup> a correlation between standard entropy and volume as earlier proposed by Bartlett and Mallouk for simple [1:1] salts<sup>6</sup> and adapted to density. The correlation

$$S = k V_m + c \quad (1)$$

possesses a generality which renders it of considerable and wide-ranging applicability (to minerals, inorganic ionic salts, and their hydrates, and also to organic liquids and solids,<sup>2b</sup> each group requiring their own fitted values of the constants  $k$  and  $c$ ). Finally, and as part of the suite of equations, we have derived, from thermochemical first principles<sup>1e</sup> (see also below), equations which enable estimation of the lattice energy,  $U_{\text{POT}}$ , enthalpy of formation,  $\Delta_f H^\circ$ , and molecular (formula unit) volume,  $V_m$ , of *hydrated* salts. These equations are able to probe areas of chemistry for which no thermodynamic data was previously available<sup>1h,1i,1m,1o</sup> as well as enabling important and generalizing conclusions to be made<sup>1j</sup> arising from the simplicity of the approach.

In the present paper, we focus on the estimation of thermodynamic data by, first, reporting a thermodynamic *difference rule* for hydrates, and evaluating the associated difference constants,  $\theta_P\{\text{H}_2\text{O}, s-s\}$ , for several standard thermodynamic functions,  $P$ , of hydrates. Second, we use the rules to derive thermodynamic data—for both hydrated and anhydrous salts—which are currently absent from the databases<sup>7a</sup> chosen as our source of working data (an extract from which is given in Table S1, see Supporting Information). Finally, we generalize the *difference rule* from hydrated to solvated salts,  $M_p X_q \cdot nS$ , where  $S$  is  $\text{D}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{ND}_3$ ,  $(\text{CH}_3)_2\text{O}$ ,  $\text{NaOH}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $(\text{CH}_2\text{-OH})_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{HF}$ ,  $\text{KOH}$ , and  $(\text{CH}(\text{CH}_3)_2)_2\text{O}$ . Using the specific case of  $\text{SO}_2$  solvates, we show how data can be estimated, using the rule, even when *minimal* thermodynamic information is available.

**Thermodynamic Difference Rule.** In the course of the derivation<sup>1e</sup> from thermochemical principles of the aforementioned equation for the estimation of lattice energies of hydrates, three equations of similar format emerged for the hydrates (but see below for an analysis of all relevant thermochemical relations for solvates in general). These equations involved difference relationships between fundamental thermodynamic formation (and other) functions,  $P$ , of hydrated salts,  $M_p X_q \cdot n\text{H}_2\text{O}$ , and their corresponding parent (anhydrous) salt,  $M_p X_q$ . The difference function,  $[P\{M_p X_q \cdot n\text{H}_2\text{O}, s\} - P\{M_p X_q, s\}]$ , was observed to be linearly dependent on the number of molecules of water of crystallization,  $n$  (which need not be an integer), contained in the hydrate. The equations take the general form

$$P\{M_p X_q \cdot n\text{H}_2\text{O}, s\} - P\{M_p X_q, s\} = n \cdot \theta_P\{\text{H}_2\text{O}, s-s\} \quad (2)$$

where  $P$  is, variously, the enthalpy of formation,  $\Delta_f H^\circ$ , the molar

volume,  $V_m$ , and the lattice potential energy,  $U_{\text{POT}}$ , whereas  $\theta_P\{\text{H}_2\text{O}, s-s\}$  is the associated constant term [ $= \theta_{\text{HF}}\{\text{H}_2\text{O}, s-s\}$ ,  $\theta_V\{\text{H}_2\text{O}, s-s\}$ , and  $\theta_U\{\text{H}_2\text{O}, s-s\}$ , respectively], with ‘ $s-s$ ’ denoting that the quantity is derived from the difference between solid-state parent and solid state solvate. The equation is obeyed by salts of varying stoichiometries and charge ratios ( $p$  and  $q$ ).

The constants for hydration were found to have the values

$$\theta_{\text{HF}}\{\text{H}_2\text{O}, s-s\}/\text{kJ mol}^{-1} (\text{H}_2\text{O molecule})^{-1} = -298.6 \quad (3)$$

$$\theta_V\{\text{H}_2\text{O}, s-s\}/\text{nm}^3 (\text{H}_2\text{O molecule})^{-1} = 0.0245 \quad (4)$$

with the corresponding plots having correlation coefficients,  $r^2 = 0.999$  and  $0.988$ , respectively, and a value:

$$\theta_U\{\text{H}_2\text{O}, s-s\}/\text{kJ mol}^{-1} (\text{H}_2\text{O molecule})^{-1} = 54.3 \quad (5)$$

was obtained when  $P = U_{\text{POT}}$ , the lattice energy. By inference, the rule (2) leads also to the difference function:

$$P\{M_p X_q \cdot n\text{H}_2\text{O}, s\} - P\{M_p X_q \cdot n'\text{H}_2\text{O}, s\} = (n - n') \cdot \theta_P\{\text{H}_2\text{O}, s-s\} \quad (6)$$

The  $\theta_P\{\text{H}_2\text{O}, s-s\}$  constants describe, in effect, the change in property,  $P$ , when a new water molecule is inserted into or removed from the crystal lattice. Latimer<sup>8a</sup> and Fyfe et al.,<sup>9</sup> have earlier reported values for  $\theta_S^\circ\{\text{H}_2\text{O}, s-s\}$  of 39 and 40  $\text{J K}^{-1} \text{mol}^{-1} (\text{H}_2\text{O molecule})^{-1}$ , respectively. The relationship when  $P = \Delta_f H^\circ$  was earlier noted by Le Van My,<sup>10</sup> almost without comment, while the other two (when  $P = V_m$  or  $U_{\text{POT}}$ ) are new observations.

The existence of this group of relationships led to anticipation of the generality of the rules (2) and (3) for other, similar, thermodynamic *solvate difference* relationships, such as  $P = \Delta_f S^\circ$  and  $\Delta_f G^\circ$  for other solvents,  $S$ , related to the well-known thermodynamic additivity relations.<sup>9</sup> Such difference relationships, which are here verified, become very powerful for the estimation of unknown thermodynamic data for hydrates and solvates in general, for their parent salts, or for both. The main premise of this paper is that, given sufficient data to enable the difference parameter,  $\theta_P$  ( $P = V_m$ ,  $U_{\text{POT}}$ ,  $\Delta_f H^\circ$ ,  $S_{298}^\circ$ ,  $\Delta_f G^\circ$ ,  $\Delta_f S^\circ$ , etc.) to be established for a given solvate, then the following statement is true:

We can estimate the corresponding thermodynamic property,  $P$ , of any parent or solvate (hydrate), real or hypothetical, irrespective of whether there is a previously known example of a solvate (hydrate) formed in this series. Furthermore, we can estimate  $\theta_{\text{HF}}\{S, s-s\}$  for solvates not yet studied in the solid state (based upon liquid- or even gas-state values of  $\Delta_f H$ ) and (in principle, we believe)  $\theta_P\{S, s-s\}$  in general.

### Difference Rules from First Principles

*Note:*  $A_x B$  is used in this theoretical section to represent the solvent (in place of  $S$ ) in order to remove possible confusion

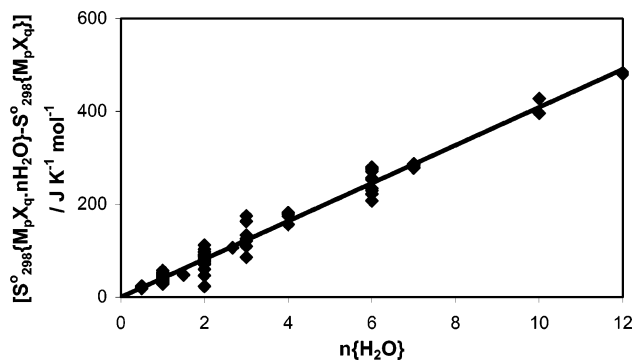
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**Figure 1.**  $[S_{298}^{\circ}\{M_p X_q \cdot n H_2 O, s\} - S_{298}^{\circ}\{M_p X_q, s\}] / J K^{-1} mol^{-1}$  plotted versus the number of water molecules of crystallization,  $n$ , in the hydrate  $M_p X_q \cdot n H_2 O$ . 83 salt pairs are included in this plot whose gradient is  $40.9 J K^{-1} mol^{-1} (H_2 O \text{ molecule})^{-1}$  with correlation coefficient,  $r^2 = 0.978$ .

with entropy,  $S$ . The accompanying descriptor, ‘ $s-s$ ’, is omitted since the thermodynamic relations described are (in principle, at least) independent of the states of parent and solvate.

**Absolute Entropy.** Latimer<sup>8a,b</sup> has shown that entropy is an additive quantity of the elemental composition at the Dulong and Petit heat-capacity high-temperature limit, when all vibrational motions have been fully excited. This limit is approached by many materials at room temperature, except for particularly hard and rigid materials (such as diamond):

$$S_{298}^{\circ} / J K^{-1} mol^{-1} = 3/2 R \ln(A_r) - 3.9 = S^{\circ}\{E\} \quad (7)$$

where  $A_r$  is the atomic mass of the element,  $E$ , and 3.9 is a fitted constant.

Hence

$$S_{298}^{\circ}\{M_p X_q \cdot n A_x B\} - S_{298}^{\circ}\{M_p X_q\} = n[x(S_{298}^{\circ}\{A\} - 3.9) + (S_{298}^{\circ}\{B\} - 3.9)] = n \theta_S\{A_x B\} \quad (8)$$

where the terms for  $M$  and  $X$  have canceled by subtraction.

$\theta_S\{A_x B\}$  is thus a constant for the solvent  $A_x B$  at this limit. Latimer<sup>8a</sup> has noted that the heat capacities of oxides (for example) are well below the relevant Dulong-Petit limit; nevertheless, examination of Figure 1 of our text demonstrates that the constancy of  $\theta_S\{H_2 O, s-s\}$  is maintained for a wide range of ionic solids.

#### Entropy of Formation.

$$\begin{aligned} \Delta_f S^{\circ}\{M_p X_q \cdot n A_x B\} - \Delta_f S^{\circ}\{M_p X_q\} &= [S_{298}^{\circ}\{M_p X_q \cdot n A_x B\} - S_{298}^{\circ}\{M_p X_q\}] + n[x S_{298}^{\circ}\{A, ss\} + S_{298}^{\circ}\{B, ss\}] = \\ n \theta_S^0\{A_x B\} + n \phi\{A_x B\} &= n [\theta_S^0\{A_x B\} + \phi\{A_x B\}] = \\ n \theta_{Sf}\{A_x B\} &\quad (9) \end{aligned}$$

where ‘ $ss$ ’ represents ‘standard reference state’ and the terms in [...] are each constants, being state functions, so that their sums are also constants.

#### Enthalpy/Gibbs Energy of Formation.

$$\Delta_f S^{\circ} = [\Delta_f H^{\circ} - \Delta_f G^{\circ}] / T \quad (10)$$

Therefore, for the differences:  $P\{M_p X_q \cdot n A_x B\} - P\{M_p X_q\}$  (where  $P = \Delta_f H^{\circ}, \Delta_f G^{\circ}$ ), since  $\Delta_f S^{\circ}$  is linearly dependent on  $n$  by eq 9, so must be each of  $\Delta_f H^{\circ}$  and  $\Delta_f G^{\circ}$ , except, perhaps, for any accidental cancellation of their dependencies on  $n$  at some

temperature.<sup>11</sup> That is

$$[\Delta_f H^{\circ}\{M_p X_q \cdot n A_x B\} - \Delta_f H^{\circ}\{M_p X_q\}] = n \theta_{Hf}\{A_x B\} \quad (11)$$

and

$$[\Delta_f G^{\circ}\{M_p X_q \cdot n A_x B\} - \Delta_f G^{\circ}\{M_p X_q\}] = n \theta_{Gf}\{A_x B\} \quad (12)$$

#### Lattice Potential Energy, $U_{POT}$ .

$$\begin{aligned} U_{POT}(M_p X_q \cdot n A_x B) - U_{POT}(M_p X_q) &= \\ [\Delta_f H^{\circ}\{M_p X_q \cdot n A_x B, s\} - \Delta_f H^{\circ}\{M_p X_q, s\}] + \\ n \Delta_f H^{\circ}\{A_x B, ss\} &= n \theta_{Hf}\{S\} + n \Delta_f H^{\circ}\{A_x B, ss\} = \\ n \theta_U\{A_x B\} &\quad (13) \end{aligned}$$

**Approximate Volume Additivity.** According to Jenkins and Glasser,<sup>1c,2a</sup> for ionic solids and their hydrates

$$S_{298}^{\circ}\{M_p X_q \cdot n H_2 O, s\} = k V_m\{M_p X_q \cdot n H_2 O, s\} + c \quad (14)$$

where  $n$  may be zero or positive. The constants  $k$  and  $c$  were chosen by least-squares best fit, independently for anhydrous and hydrated solids; they proved to be close enough in value ( $k = 1360$  and  $1579 J K^{-1} mol^{-1} nm^{-3}$ ; and  $c = 15$  and  $6 J K^{-1} mol^{-1}$ , respectively) to be taken as equal for present purposes. Similar results were observed for organic liquids.<sup>2b</sup> So, for the solvent  $A_x B$

$$\begin{aligned} S_{298}^{\circ}\{M_p X_q \cdot n A_x B\} - S_{298}^{\circ}\{M_p X_q\} &= \\ n \theta_S\{A_x B\} &\quad (\text{by eq. (10)}) \\ = [k V_m(M_p X_q \cdot n A_x B) + c] - [k V_m(M_p X_q) + c] &= \\ k [V_m\{M_p X_q \cdot n A_x B\} - V_m\{M_p X_q\}] &\quad (15) \end{aligned}$$

or

$$[V_m\{M_p X_q \cdot n A_x B\} - V_m\{M_p X_q\}] = n \theta_V\{A_x B\} \quad (15)$$

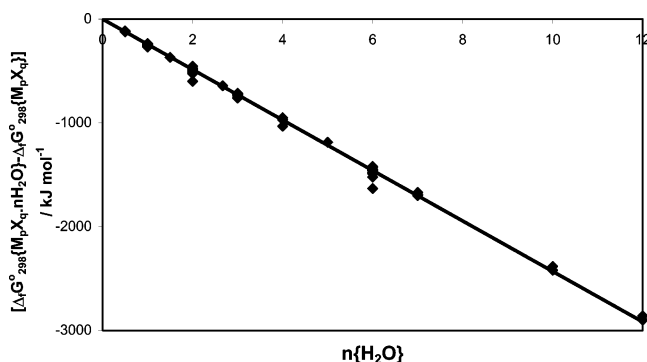
demonstrating that solvate volumes are additive to those of their parent ionic compound at this level of approximation.

#### Applications of the Difference Rule

**Validity of the Difference Rule.** A significant feature of the relationship (2) when  $P = \Delta_f H^{\circ}$  is the fact that data for over 340 hydrate salts and their corresponding parents, taken from experimental calorimetric measurements, fit this relationship almost exactly (correlation coefficient  $r^2 = 0.999$ ).<sup>1c</sup> Such precision promotes the relationship to the status of a previously unrecognized thermodynamic rule (but of greater generality than,

(11) In eq 9, we have already shown that  $\Delta_f S^{\circ}$  is linearly dependent on  $n$ :  $\Delta_f S^{\circ} = S_{298}^{\circ}\{M_p X_q, s\} + n \theta_{Sf}\{A_x B, s-s\}$  (9). So, the right-hand side of the equality (10) must also be linearly dependent on  $n$ :  $\Delta_f S^{\circ} = [\Delta_f H^{\circ} - \Delta_f G^{\circ}] / T$  (10). Suppose that only one of  $\Delta_f H^{\circ}$  or  $\Delta_f G^{\circ}$  is linearly dependent on  $n$  (say,  $\Delta_f H^{\circ}$ ), while the other is independent of  $n$ , then:  $\Delta_f H^{\circ} = \Delta_f H^{\circ}\{M_p X_q, s\} + n \theta_{Hf}\{A_x B, s-s\}$  and  $\Delta_f G^{\circ} = [\Delta_f H^{\circ}\{M_p X_q, s\} + n \theta_{Hf}\{A_x B, s-s\}] - T [S_{298}^{\circ}\{M_p X_q, s\} + n \theta_{Sf}\{A_x B, s-s\}] = [\Delta_f H^{\circ}\{M_p X_q, s\} - T S_{298}^{\circ}\{M_p X_q, s\}] + n[\theta_{Hf}\{A_x B, s-s\} - T \theta_{Sf}\{A_x B, s-s\}]$ . Thus, since the right-hand side is shown to be linearly dependent on  $n$ , so also is  $\Delta_f G^{\circ}$  unless there is an exact cancellation of the dependence on  $n$ , through the equality:  $\theta_{Hf}\{A_x B, s-s\} = T \theta_{Sf}\{A_x B, s-s\}$ . Such a cancellation can only be true at some special temperature,  $T$ , since enthalpy and entropy themselves are only slightly temperature dependent. Using data from Table 1, the formal corresponding temperature for  $H_2 O$  is 1550 K, while those for  $NH_3$  and  $(CH_3)_2 O$  are 460 and 770 K, respectively. Furthermore, Figures 1 and 2 (for  $H_2 O$  at 298 K) show both  $\Delta_f S^{\circ}$  and  $\Delta_f G^{\circ}$  to be linearly dependent on  $n$ ; Table 1 gives values for  $\theta_{Sf}\{H_2 O, s-s\}$  of  $-192.4 J K^{-1} mol^{-1}$  and for  $\theta_{Hf}\{H_2 O, s-s\}$  of  $-242.4 kJ mol^{-1}$ , so that  $\theta_{Hf}\{H_2 O, s-s\} = -242.4 - 192.4 \times 0.298 = -299.7 kJ mol^{-1}$  while Table 1 lists an independently determined value for  $\theta_{Hf}\{H_2 O, s-s\}$  of  $-298.6 kJ mol^{-1}$ , which is closely similar. All three thermodynamic quantities are clearly linearly dependent on  $n$  in almost any circumstance.





**Figure 2.**  $[\Delta_f G^\circ\{M_p X_q \cdot n H_2 O, s\} - \Delta_f G^\circ\{M_p X_q, s\}]/\text{kJ mol}^{-1}$  plotted versus the number of molecules of water of crystallization,  $n$ , in the hydrate  $M_p X_q \cdot n H_2 O$ . 93 salt pairs are included in this plot whose gradient per water molecule is  $-242.4 \text{ kJ mol}^{-1} (\text{H}_2\text{O molecule})^{-1}$  with correlation coefficient,  $r^2 = 0.998$ .

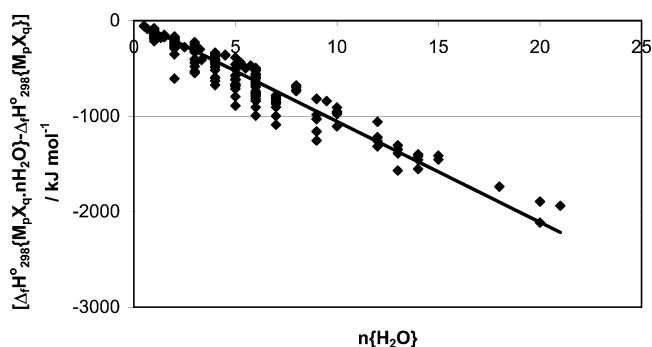
**Table 1.** Tabulated Results for Thermodynamic Difference Plots,  $[P\{\text{solvate}\} - P\{\text{parent}\}] = n\theta_P\{S, s-s\}$  for Various Solvated Salts,  $M_p X_q \cdot n S^a$

solvate S	type of difference plot, P	gradient $\theta_P$ {S}	correlation coefficient $r^2$	no. of salts included	range of values for $n$
H <sub>2</sub> O	$V_m$	0.0245	0.988	34	$1/2 \leq n \leq 10$
H <sub>2</sub> O	$U_{\text{POT}}$	54.3	0.999	342	$1/4 \leq n \leq 19$
H <sub>2</sub> O	$\Delta_f H^\circ$	-298.6	0.999	342	$1/4 \leq n \leq 19$
H <sub>2</sub> O	$\Delta_f G^\circ$	-242.4	0.998	93	$1/4 \leq n \leq 19$
H <sub>2</sub> O	$S_{298}^\circ$	40.9	0.978	83	$1/4 \leq n \leq 19$
H <sub>2</sub> O	$\Delta_f S^\circ$	-192.4 <sup>b</sup>			
	$\Delta_f S^\circ$	(-188.6) <sup>c</sup>			
D <sub>2</sub> O	$\Delta_f H^\circ$	-307.8	1.000	3	$1 \leq n \leq 6$
NH <sub>3</sub>	$\Delta_f H^\circ$	-105.5	0.932	270	$0.5 \leq n \leq 21$
NH <sub>3</sub>	$\Delta_f G^\circ$	-21.0	0.922	4	$1 \leq n \leq 3$
NH <sub>3</sub>	$S_{298}^\circ$	64.1	0.989	9	$1 \leq n \leq 5$
NH <sub>3</sub>	$\Delta_f S^\circ$	-227.8 <sup>b</sup>			
	$\Delta_f S^\circ$	(-283.6) <sup>c</sup>			
ND <sub>3</sub>	$\Delta_f H^\circ$	-103.6	0.966	8	$1 \leq n \leq 4.5$
ND <sub>3</sub>	$\Delta_f G^\circ$	-31.4	0.992	3	$1 \leq n \leq 4$
ND <sub>3</sub>	$S_{298}^\circ$	68.8	0.997	3	$1 \leq n \leq 4$
ND <sub>3</sub>	$\Delta_f S^\circ$	-242.3 <sup>b</sup>			
(CH <sub>3</sub> ) <sub>2</sub> O	$\Delta_f H^\circ$	-282.1	0.999	3	$1/2 \leq n \leq 2$
(CH <sub>3</sub> ) <sub>2</sub> O	$\Delta_f G^\circ$	-173.5	0.999	3	$1/2 \leq n \leq 2$
(CH <sub>3</sub> ) <sub>2</sub> O	$S_{298}^\circ$	141.3	0.999	3	$1/2 \leq n \leq 2$
(CH <sub>3</sub> ) <sub>2</sub> O	$\Delta_f S^\circ$	-364.8 <sup>b</sup>			
	$\Delta_f S^\circ$	(-364.4) <sup>c</sup>			
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	$\Delta_f H^\circ$	-311.0	0.999	4	$1/2 \leq n \leq 2$
NaOH	$\Delta_f H^\circ$	-430.0	0.999	3	$1 \leq n \leq 2$
CH <sub>3</sub> OH	$\Delta_f H^\circ$	-272.3	0.969	5	$1 \leq n \leq 6$
C <sub>2</sub> H <sub>5</sub> OH	$\Delta_f H^\circ$	-301.1	0.993	11	$1 \leq n \leq 6$
(CH <sub>2</sub> OH) <sub>2</sub>	$\Delta_f H^\circ$	-483.4	0.999	4	$1 \leq n \leq 3$
H <sub>2</sub> S	$\Delta_f H^\circ$	-53.6	0.933	4	$1 \leq n \leq 2$
SO <sub>2</sub>	$\Delta_f H^\circ$	-339.7	0.998	9	$1/2 \leq n \leq 4$

<sup>a</sup> Values are listed of  $\theta_P\{S, s-s\}$  and of correlation coefficients,  $r^2$ , for the  $n\{S\}$  solvates. <sup>b</sup> Calculated using  $S_{298}^\circ$  (cf. final section). <sup>c</sup> Calculated using  $\theta_{\text{SR}}\{S, s-s\} = [\theta_{\text{HR}}\{S, s-s\} - \theta_{\text{GR}}\{S, s-s\}]/0.298$ . Reliability reduced due to calculation by difference.

for example, that of Trouton) governing the difference properties of hydrates (and, by extension, solvates) and their associated parent salts.

**Extension of the Difference Rules.** Table S1 (see Supporting Information) lists data<sup>7</sup> for further differences involving, in this case, absolute standard entropies,  $[S_{298}^\circ\{M_p X_q \cdot n H_2 O, s\} - S_{298}^\circ\{M_p X_q, s\}]$ , and standard Gibbs energies of formation,  $[\Delta_f G^\circ\{M_p X_q \cdot n H_2 O, s\} - \Delta_f G^\circ\{M_p X_q, s\}]$ , for salts possessing differing stoichiometries and charge ratios, and a range of values



**Figure 3.**  $[\Delta_f H^\circ\{M_p X_q \cdot n \text{NH}_3, s\} - \Delta_f H^\circ\{M_p X_q, s\}]/\text{kJ mol}^{-1}$  plotted versus number of molecules of  $\text{NH}_3$ ,  $n$ , in the solvate,  $M_p X_q \cdot n \text{NH}_3$ . 265 ammoniates ( $0.5 \leq n \leq 21$ ) are plotted. Gradient  $\theta_{\text{HR}}\{\text{NH}_3, s-s\} = -105.5 \text{ kJ mol}^{-1} (\text{NH}_3 \text{ solvate molecule})^{-1}$ . Correlation coefficient,  $r^2 = 0.932$ .

**Table 2.** Thermodynamic Data Available for  $\text{SO}_2$  Solvate Salts (from Wagman et al.<sup>7</sup>)

solvate $M_p X_q \cdot n \text{SO}_2(s)$	$\Delta_f H^\circ\{M_p X_q \cdot n \text{SO}_2, s\}/\text{kJ mol}^{-1}$	$S_{298}^\circ\{M_p X_q \cdot n \text{SO}_2, s\}/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta_f G^\circ\{M_p X_q \cdot n \text{SO}_2, s\}/\text{kJ mol}^{-1}$
$\text{NH}_4\text{CNS} \cdot \text{SO}_2$	-413.0		
$\text{AlCl}_3 \cdot \text{SO}_2$	-1061.1		
$\text{AlCl}_3 \cdot 1/2 \text{SO}_2$	-890.8		
$\text{Li} \cdot \text{SO}_2$	-607.9		
$\text{Li} \cdot 2 \text{SO}_2$	-944.3		
$\text{NaCNS} \cdot 2 \text{SO}_2$	-851.0		
$\text{KI} \cdot 4 \text{SO}_2$	-1676.1		
$\text{KCNS} \cdot 1/2 \text{SO}_2$	-372.4	174	-330.1
$\text{KCNS} \cdot 2 \text{SO}_2$	-876.5	339	-777.7

of  $n\{\text{H}_2\text{O}\}$ . A correlation of the form of (1) is again established (Figure 1):

$$\theta_S^\circ\{\text{H}_2\text{O}, s-s\}/\text{J K}^{-1} \text{mol}^{-1} (\text{H}_2\text{O molecule})^{-1} = 40.9 \quad (16)$$

and this value is adopted for the purposes of estimation in this paper; as mentioned above, corresponding values from Latimer<sup>8a</sup> and Fyfe et al.,<sup>9</sup> are 39 and 40  $\text{J K}^{-1} \text{mol}^{-1} (\text{H}_2\text{O molecule})^{-1}$ , respectively.

For the corresponding standard Gibbs energy data,<sup>7</sup> we find (Figure 2)

$$\theta_{\text{GR}}\{\text{H}_2\text{O}, s-s\}/\text{kJ mol}^{-1} (\text{H}_2\text{O molecule})^{-1} = -242.4 \quad (17)$$

Our newest linear correlation result (eq 1),<sup>2</sup> by which absolute standard entropies may be determined from molar volumes, depends on only two parameters. It is thus much more accessible than Latimer's Rules,<sup>8</sup> which require his tables of cation and anion values. We find that absolute entropies calculated using Latimer's Rules correlate rather less well with tabulated values of absolute entropies (slope of graph of Latimer values versus tabulated values = 0.928,  $r^2 = 0.84$ ). Although this implies (through our earlier correlations<sup>1e</sup>) that the Latimer values are also correlated with the molar volumes of the salts and hydrates concerned, separation into cation and anion contributions on the basis of the Latimer Rules is not possible because of Latimer's arbitrary division between cation and anion contributions to the absolute entropy.

**Generalization of the Rule to Solvate/Parent Salts.** Although the correlation coefficients,  $r^2$ , are sometimes slightly less than those found for hydrates, other solvates also satisfy the difference rule for  $P = \Delta_f H^\circ$ ,  $S_{298}^\circ$  (and  $\Delta_f S^\circ$ ) and  $\Delta_f G^\circ$ . Details are summarized in Table 1 for a number of different

**Table 3.** Thermodynamic Data Available for SO<sub>2</sub> Solvate Parent (unsolvated) Salts

parent M <sub>p</sub> X <sub>q</sub> (s)	$\Delta_f H^\circ\{M_p X_q, s\}/\text{kJ mol}^{-1}$	$S^\circ_{298}\{M_p X_q, s\}/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta_f G^\circ\{M_p X_q, s\}/\text{kJ mol}^{-1}$
NH <sub>4</sub> CNS	-78.7 <sup>a</sup>		
AlCl <sub>3</sub>	-704.2 <sup>a,d</sup> , -705.33 <sup>b</sup> , -705.29 <sup>b</sup> , -671.78 <sup>b</sup> , -705.63 <sup>c</sup>	110.67 <sup>a</sup> , 108.8 <sup>b</sup> , 111.21 <sup>b</sup> , 114.0 <sup>b</sup> , 110.667 <sup>b</sup> , 109.3 <sup>d</sup> , 109.29 <sup>c</sup>	-628.8 <sup>a,d</sup> , -630.177 <sup>b</sup> , -630.0 <sup>c</sup>
LiI	-270.4 <sup>a,d</sup> , -271.08 <sup>b</sup> , -270.077 <sup>c</sup>	86.78 <sup>a,d</sup> , 75.7 <sup>b</sup> , 76.6 <sup>b</sup> , 73.2 <sup>b</sup> , 85.772 <sup>c</sup>	-270.29 <sup>a,d</sup> , -267 <sup>b</sup> , -268.95 <sup>b</sup> , -268.61 <sup>b</sup> , -266.92 <sup>b</sup> , -269.666 <sup>c</sup>
NaCNS	-170.50 <sup>a</sup> , -153.1 <sup>b</sup> , -174.5 <sup>b</sup>	119.2 <sup>b</sup> , 112.1 <sup>b</sup>	-359.4 <sup>b</sup> , -410.5 <sup>b</sup>
KI	-327.0 <sup>a</sup> , -327.649 <sup>b</sup> , -327.9 <sup>d</sup> , -327.900 <sup>c</sup>	106.32 <sup>a</sup> , 110.79 <sup>b</sup> , 104.2 <sup>b</sup> , 104.6 <sup>b</sup> , 107.1 <sup>b</sup> , 106.3 <sup>d</sup> , 106.387 <sup>c</sup>	-324.892 <sup>a,d</sup> , -320.1 <sup>b</sup> , -324.084 <sup>b</sup> , -323.024 <sup>c</sup>
KCNS	-200.16 <sup>a</sup>	124.26	-178.31

<sup>a</sup> Wagman et al.<sup>7a</sup> <sup>b</sup> Karapet'yants and Karapet'yants.<sup>13</sup> <sup>c</sup> Lide.<sup>17</sup> <sup>d</sup> Barin.<sup>16</sup>

**Table 4.** Calculated Difference Functions for SO<sub>2</sub> Solvate Salts

solvate M <sub>p</sub> X <sub>q</sub> ·nSO <sub>2</sub> (s)	$n$	$[\Delta_f H^\circ\{\text{solvate}, s\} - \Delta_f H^\circ\{\text{parent}, s\}]/\text{kJ mol}^{-1} = n \theta_{\text{HF}}\{\text{SO}_2, s-s\}$	$[S^\circ_{298}\{\text{solvate}, s\} - S^\circ_{298}\{\text{parent}, s\}]/\text{kJ mol}^{-1} = n \theta_S^\circ\{\text{SO}_2, s-s\}$	$[\Delta_f G^\circ\{\text{solvate}, s\} - \Delta_f G^\circ\{\text{parent}, s\}]/\text{kJ mol}^{-1} = n \theta_{\text{Gf}}\{\text{SO}_2, s-s\}$
NH <sub>4</sub> CNS·SO <sub>2</sub>	1	-334.3		
AlCl <sub>3</sub> ·SO <sub>2</sub>	1	-356.9, -355.77, -355.9, -389.32 <sup>a</sup>		
AlCl <sub>3</sub> ·1/2SO <sub>2</sub>	1/2	-186.6, -185.47, -185.51, -219.0 <sup>a</sup>		
LiI·SO <sub>2</sub>	1	-337.5, -336.82		
LiI·2SO <sub>2</sub>	2	-673.9, -673.22		
NaCNS·2SO <sub>2</sub>	2	-680.5, -440.5 <sup>a</sup> , -676.5		
KI·4SO <sub>2</sub>	4	-1349.1, -1348.5		
KCNS·1/2SO <sub>2</sub>	1/2	-171.8	49.8	-151.8
KCNS·2SO <sub>2</sub>	2	-675.9	215	-599.4

<sup>a</sup> Aberrant values, excluded from the analysis.

solvates (D<sub>2</sub>O, NH<sub>3</sub>, ND<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>O, NaOH, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, (CH<sub>2</sub>OH)<sub>2</sub> (ethylene glycol), H<sub>2</sub>S and SO<sub>2</sub>).

After the hydrates, the ammoniates,<sup>12</sup> M<sub>p</sub>X<sub>q</sub>·nNH<sub>3</sub>, possess the most extensive set of thermodynamic data (see Figure 3).

### Predictions for Hydrates, M<sub>p</sub>X<sub>q</sub>·nH<sub>2</sub>O

**Uses of the Difference Rule.** Table S2 (see Supporting Information) compares the tabulated data for hydrates with estimates of thermochemical data predicted by using eq 2 [with  $P = \Delta_f G^\circ$  and  $P = S^\circ_{298}$ ].<sup>13,14</sup> The SO<sub>2</sub> solvates<sup>15</sup> are selected to illustrate the power of the rule for estimating missing thermodynamic data, in a case where only minimal data (for Gibbs energy and entropy) are initially known, based on the example scenario presented in Table S3 in which three hydrates are listed having  $n_1$ ,  $n_2$ , and  $n_3$  molecules of water.

(12) These consist of ammoniates ( $0.5 \leq n \leq 21$ ) formed by monohalides of Li, Na, Tl, Cu, Ag, Au, Pb, and NH<sub>4</sub>; dihalides of Be, Mg, Sn, Pb, Hg, Zn, Cd, Hg, Ni, Co, Fe, Cr, Pt, Cu, and Tl; trihalides of Sb, Sn, Al, Ga, In; tetrahalides of Th; nitrates of Pb; tetrahydroborates of Li and Na; acetates of Zn and Cu; cyanides of Ag; formates of Cu; and sulfates of Pb.

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**Prediction for SO<sub>2</sub> Solvates, M<sub>p</sub>X<sub>q</sub>·nSO<sub>2</sub>.** Tables 2 and 3 list the thermodynamic information available for the solvates formed by SO<sub>2</sub> (Table 2) and their corresponding parent salts (Table 3).

Assembling a thermodynamic difference plot of  $\Delta_f H^\circ$  data (from data in Table 4) for nine SO<sub>2</sub> solvates (columns 2 and 3, Table 4) yields

$$\theta_{\text{HF}}\{\text{SO}_2, s-s\}/\text{kJ mol}^{-1} (\text{SO}_2 \text{ molecule})^{-1} = -339.7 \quad (18)$$

with a correlation coefficient of  $r^2 = 0.998$ .

Using this result (and similar results for other solvates) permits us to estimate the standard enthalpy of formation of any other SO<sub>2</sub> solvate having a different  $n$  value to a solvate already listed in the Table (including  $n = 0$ , the parent salt). We can also estimate the standard enthalpy of formation of any SO<sub>2</sub> solvate of a parent salt whose standard enthalpy is already known (and, in general, we can always estimate the standard enthalpy of formation of any parent salt from our earlier published procedures<sup>1</sup>) irrespective of whether a solvate of this parent is already known. Thus, for example,  $\Delta_f H^\circ\{\text{AlCl}_3 \cdot 2\text{SO}_2, s\}$  could be estimated either (i) from the known data for  $\Delta_f H^\circ\{\text{AlCl}_3 \cdot \text{SO}_2, s\}$  and  $\Delta_f H^\circ\{\text{AlCl}_3 \cdot 1/2\text{SO}_2, s\}$ , or (ii) from the known value of  $\Delta_f H^\circ\{\text{AlCl}_3, s\}$ , independently of the existence of other SO<sub>2</sub> solvates of AlCl<sub>3</sub>. Using  $\theta_{\text{HF}}\{\text{SO}_2, s-s\}$  (eq 18) in the two cases we have

$$\begin{aligned} \text{(i)} \quad \Delta_f H^\circ\{\text{AlCl}_3 \cdot 2\text{SO}_2, s\}/\text{kJ mol}^{-1} = \\ \Delta_f H^\circ\{\text{AlCl}_3 \cdot \text{SO}_2, s\} + \theta_{\text{HF}}\{\text{SO}_2, s-s\} = -1400.8 \quad (19) \end{aligned}$$

$$\Delta_f H^\circ\{\text{AlCl}_3 \cdot 2\text{SO}_2, \text{s}\} / \text{kJ mol}^{-1} = \Delta_f H^\circ\{\text{AlCl}_3 \cdot 1/2\text{SO}_2, \text{s}\} + 1.5 \theta_{\text{HF}}\{\text{SO}_2, \text{s}-\text{s}\} = -1400.4 \quad (20)$$

and

$$(ii) \Delta_f H^\circ\{\text{AlCl}_3 \cdot 2\text{SO}_2, \text{s}\} / \text{kJ mol}^{-1} = \Delta_f H^\circ\{\text{AlCl}_3, \text{s}\} + 2 \theta_{\text{HF}}\{\text{SO}_2, \text{s}-\text{s}\} \quad (21)$$

giving rise to further estimates of  $-1384$ ,  $-1385$ ,  $-1385$ , and  $-1385$  depending on the value of  $\Delta_f H^\circ\{\text{AlCl}_3, \text{s}\}$  (for which there are a number of values cited) which is selected from Table 3, with an average value of  $-1385$  kJ mol<sup>-1</sup>. (This illustrates the (usual) situation where there is generally plenty of data with which to confirm estimated values.) It is likely, however, that the better average is

$$\Delta_f H^\circ\{\text{AlCl}_3 \cdot 2\text{SO}_2, \text{s}\} / \text{kJ mol}^{-1} = -1401 \quad (22)$$

from eqs (19) and (20), since the formula of the reference salt is, in each case, closer to that of the predicted salt.

Similarly, for the (possibly hypothetical) solvate,  $\text{NaI} \cdot 3\text{SO}_2$ , we can write

$$\Delta_f H^\circ\{\text{NaI} \cdot 3\text{SO}_2, \text{s}\} / \text{kJ mol}^{-1} = \Delta_f H^\circ\{\text{NaI}, \text{s}\} + 3 \theta_{\text{HF}}\{\text{SO}_2, \text{s}-\text{s}\} \quad (23)$$

and taking  $\Delta_f H^\circ\{\text{NaI}, \text{s}\} / \text{kJ mol}^{-1} = -287.97^a$  we predict that

$$\Delta_f H^\circ\{\text{NaI} \cdot 3\text{SO}_2, \text{s}\} / \text{kJ mol}^{-1} = -1307 \quad (24)$$

In some cases (e.g., for the standard Gibbs energy of formation and standard entropy data for  $\text{SO}_2$  solvates) there are few data. Specifically, data have only been measured for *two solvates* ( $\text{KCNS} \cdot n\text{SO}_2$ ,  $n = 1/2, 2$ , Table 2). Nevertheless we are still able to make a (crude) estimate of  $\theta_{\text{GF}}\{\text{SO}_2, \text{s}-\text{s}\}$  and  $\theta_{\text{S}}^\circ\{\text{SO}_2, \text{s}-\text{s}\}$

$$\theta_{\text{GF}}\{\text{SO}_2, \text{s}-\text{s}\} / \text{kJ mol}^{-1} (\text{SO}_2 \text{ molecule})^{-1} = -301.7 \quad (25)$$

$$\theta_{\text{S}}^\circ\{\text{SO}_2, \text{s}-\text{s}\} / \text{J K}^{-1} \text{ mol}^{-1} (\text{SO}_2 \text{ molecule})^{-1} = 103.6 \quad (26)$$

and thereby use data for  $\Delta_f G^\circ\{\text{M}_p\text{X}_q, \text{s}\}$  and  $S_{298}^\circ\{\text{M}_p\text{X}_q, \text{s}\}$  in Table 3 to estimate the missing  $\Delta_f G^\circ\{\text{M}_p\text{X}_q \cdot n\text{SO}_2, \text{s}\}$  and  $S_{298}^\circ\{\text{M}_p\text{X}_q \cdot n\text{SO}_2, \text{s}\}$  data for most of the solvates listed in Table 2. Table S4 (see Supporting Information) lists six values of  $\Delta_f G^\circ\{\text{M}_p\text{X}_q \cdot n\text{SO}_2, \text{s}\}$  and  $S_{298}^\circ\{\text{M}_p\text{X}_q \cdot n\text{SO}_2, \text{s}\}$  estimated using  $\theta_{\text{GF}}\{\text{SO}_2, \text{s}-\text{s}\}$  and  $\theta_{\text{S}}^\circ\{\text{SO}_2, \text{s}-\text{s}\}$  above. The only exception is for  $\text{NH}_4\text{CNS} \cdot \text{SO}_2$  where prediction is hampered by the fact that neither  $\Delta_f G^\circ\{\text{NH}_4\text{CNS}, \text{s}\}$  nor  $S_{298}^\circ\{\text{NH}_4\text{CNS}, \text{s}\}$  are available. Scope for further prediction is, of course, not limited to just these solvates and is, potentially, much more extensive.

### Substitution Reactions

**Difference Rule Applied to Solvate/Hydrate Pairs.** The thermodynamic difference rule (1) applies, as we have seen, to solvates in the general form

$$P\{\text{M}_p\text{X}_q \cdot n\text{S}, \text{s}\} - P\{\text{M}_p\text{X}_q, \text{s}\} = n \cdot \theta_P\{\text{S}, \text{s}-\text{s}\} \quad (27)$$

Subtraction of (2) for hydrates from eq 27 for solvates, S, having the same parent,  $\text{M}_p\text{X}_q$ , and value of  $n$  leads to

$$P\{\text{M}_p\text{X}_q \cdot n\text{S}, \text{s}\} - P\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}, \text{s}\} = n \cdot (\theta_P\{\text{S}, \text{s}-\text{s}\} - \theta_P\{\text{H}_2\text{O}, \text{s}-\text{s}\}) = n \cdot \theta_P\{\text{S}-\text{H}_2\text{O}, \text{s}-\text{s}\} \quad (28)$$

Plots made of  $P\{\text{M}_p\text{X}_q \cdot n\text{S}, \text{s}\}$  versus  $P\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}, \text{s}\}$  ( $P = \Delta_f H^\circ$ ,  $S_{298}^\circ$ ,  $\Delta_f G^\circ$ , etc.,  $\text{S} = \text{SO}_2$ ) verify relationship (28):  $[\theta_{\text{HF}}\{\text{SO}_2-\text{H}_2\text{O}, \text{s}-\text{s}\} = -39.8$ ,  $r^2 = 0.951$ ,  $n = 8$ ;  $\theta_{\text{GF}}\{\text{SO}_2-\text{H}_2\text{O}, \text{s}-\text{s}\} = -59.4$ ,  $r^2 = 0.999$ ,  $n = 8$ ;  $\theta_{\text{S}}^\circ\{\text{SO}_2-\text{H}_2\text{O}, \text{s}-\text{s}\} = 63.6$ ,  $r^2 = 0.999$ ,  $n = 8$ ] and the values found for  $\theta_P\{\text{SO}_2-\text{H}_2\text{O}, \text{s}-\text{s}\}$  correspond reasonably well to the differences  $[\theta_P\{\text{SO}_2, \text{s}-\text{s}\} - \theta_P\{\text{H}_2\text{O}, \text{s}-\text{s}\}]$ . Thus, data from one solvent (say,  $\text{H}_2\text{O}$ ) may be used to predict results for another solvent (say,  $\text{SO}_2$ ).

**Ionic Substitution Reactions.** We will later report on the fact that ionic substitution reactions (of the type  $\text{Li}^+$  and  $\text{Na}^+$  substituting for one another) also yield thermodynamic difference relations of the kinds discussed herein.

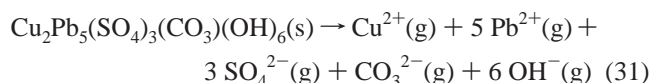
**Simple Salt Approximation for Estimation of Lattice Energies.** Yoder and Flora<sup>18</sup> have recently proposed a simple salt approximation for the estimation of lattice energies for multiple salts or for minerals,  $\text{AB} \cdot \text{CD} \cdot \text{EF}$ , whereby:

$$U_{\text{POT}}\{\text{AB} \cdot \text{CD} \cdot \text{EF}\} \approx U_{\text{POT}}\{\text{AB}\} + U_{\text{POT}}\{\text{CD}\} + U_{\text{POT}}\{\text{EF}\} \quad (29)$$

Thus, for example, for the mineral *caledonite*,  $\text{Cu}_2\text{Pb}_5(\text{SO}_4)_3(\text{CO}_3)(\text{OH})_6$  we can write several forms of eq 29, depending upon the simple salts selected to represent the structure, viz

$$\begin{aligned} U_{\text{POT}}\{\text{Cu}_2\text{Pb}_5(\text{SO}_4)_3(\text{CO}_3)(\text{OH})_6\} &= 2U_{\text{POT}}\{\text{CuSO}_4\} + \\ &U_{\text{POT}}\{\text{PbCO}_3\} + U_{\text{POT}}\{\text{PbSO}_4\} + 3U_{\text{POT}}\{\text{Pb}(\text{OH})_2\} = \\ &19\,825 \text{ kJ mol}^{-1} \\ &= U_{\text{POT}}\{\text{CuSO}_4\} + U_{\text{POT}}\{\text{CuCO}_3\} + 2U_{\text{POT}}\{\text{PbSO}_4\} + \\ &3U_{\text{POT}}\{\text{Pb}(\text{OH})_2\} = 19\,330 \text{ kJ mol}^{-1} \\ &= U_{\text{POT}}\{\text{Cu}(\text{OH})_2\} + 2U_{\text{POT}}\{\text{Pb}(\text{OH})_2\} + U_{\text{POT}}\{\text{CuSO}_4\} + \\ &U_{\text{POT}}\{\text{PbCO}_3\} + 2U_{\text{POT}}\{\text{PbSO}_4\} = 19\,367 \text{ kJ mol}^{-1} \\ &= U_{\text{POT}}\{\text{Pb}(\text{OH})_2\} + 2U_{\text{POT}}\{\text{Cu}(\text{OH})_2\} + \\ &3U_{\text{POT}}\{\text{PbSO}_4\} + U_{\text{POT}}\{\text{PbCO}_3\} = 19\,449 \text{ kJ mol}^{-1} \quad (30) \end{aligned}$$

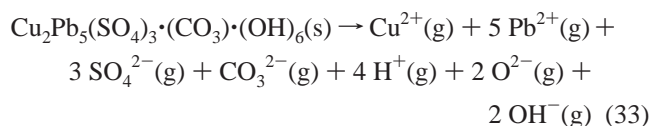
each approximating the lattice energy of the process

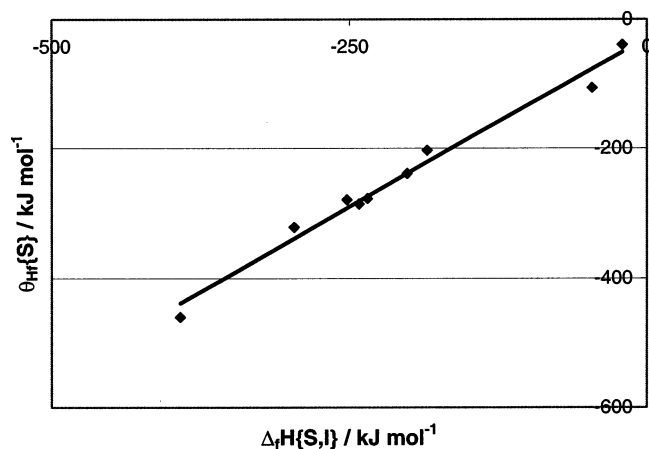


where (in kJ mol<sup>-1</sup>):  $U_{\text{POT}}\{\text{CuSO}_4\} = 3066$ ;  $U_{\text{POT}}\{\text{CuCO}_3\} = 3327$ ;  $U_{\text{POT}}\{\text{Cu}(\text{OH})_2\} = 3237$ ;  $U_{\text{POT}}\{\text{PbCO}_3\} = 2750$ ;  $U_{\text{POT}}\{\text{PbSO}_4\} = 2534$ ; and  $U_{\text{POT}}\{\text{Pb}(\text{OH})_2\} = 2623$ . And

$$\begin{aligned} U_{\text{POT}}\{\text{Cu}_2\text{Pb}_5(\text{SO}_4)_3(\text{CO}_3)(\text{OH})_6\} &= 2U_{\text{POT}}\{\text{CuO}\} + \\ &2U_{\text{POT}}\{\text{H}_2\text{O}\} + 3U_{\text{POT}}\{\text{PbSO}_4\} + U_{\text{POT}}\{\text{Pb}(\text{OH})_2\} + \\ &U_{\text{POT}}\{\text{Pb}(\text{CO}_3)\} = 21\,184 \text{ kJ mol}^{-1} \\ &= 2U_{\text{POT}}\{\text{PbO}\} + 2U_{\text{POT}}\{\text{H}_2\text{O}\} + 3U_{\text{POT}}\{\text{PbSO}_4\} + \\ &U_{\text{POT}}\{\text{CuCO}_3\} + U_{\text{POT}}\{\text{Cu}(\text{OH})_2\} = 20\,851 \text{ kJ mol}^{-1} \quad (32) \end{aligned}$$

each approximating the lattice energy of the alternative process





**Figure 4.** Plot of  $\theta_{HF}\{S, s-s\}$  versus  $\Delta_f H^\circ\{S, l\}/\text{kJ mol}^{-1}$  for the range of solvates displayed in Table 2. Values of  $\Delta_f H^\circ\{S, l\}$  not otherwise available<sup>17</sup> were obtained from ref 19. Note: data for  $(\text{CH}_3)_2\text{O}$  has been omitted.

where (in  $\text{kJ mol}^{-1}$ )  $U_{\text{POT}}\{\text{CuO}\} = 4050$ ;  $U_{\text{POT}}\{\text{PbO}\} = 3288$  (ref 18a, Table 2);  $U_{\text{POT}}\{\text{H}_2\text{O}\} = \theta_U\{\text{H}_2\text{O}, s-s\}^{1e} = 54.3 \text{ kJ mol}^{-1}$ . This approach has some broad analogies<sup>18b</sup> with the principles involved in the difference rule (as previously seen for the hydrates<sup>1e</sup>).

#### Prediction of $\theta_{HF}\{S, s-s\}$

A plot of  $\theta_{HF}\{S, s-s\}$  versus  $\Delta_f H^\circ\{S, l\}$  for liquid-state solvent, S, shows a linear correlation (Figure 4)

$$\theta_{HF}\{S, s-s\} = 1.041 \Delta_f H^\circ\{S, l\} - 9.28 \quad (34)$$

with a correlation coefficient  $r^2 = 0.995$ . Thus, we have the useful observation that the enthalpy of formation of the solvate in a crystalline environment is  $\sim 5\%$  more negative than in the liquid. Similarly, a plot of  $\theta_{HF}\{S, s-s\}$  versus  $\Delta_f H^\circ\{S, g\}$  shows the linear correlation

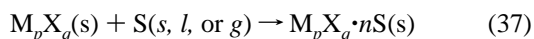
$$\theta_{HF}\{S, s-s\} = 1.087 \Delta_f H^\circ\{S, g\} - 41.72 \quad (35)$$

with a correlation coefficient  $r^2 = 0.989$ . This pair also implies the correlation

$$\Delta_f H^\circ\{S, g\} = 1.043 \Delta_f H^\circ\{S, l\} - 29.14 \quad (36)$$

with a correlation coefficient  $r^2 = 0.981$ . We prefer to use eq 34 in evaluating  $\theta_{HF}\{S, s-s\}$  because it represents data closer to the form of the solvate in the solid, and has the better correlation coefficient.

As a corollary to the above correlations, we can consider the process of incorporation of one molecule of solvate (or hydrate) in its normal physical state (solid, liquid or gas, as represented by  $s, l, \text{ or } g$ ) into the crystal structure



then the functions:  $\Delta_r H = [\theta_{HF}\{S, s-s\} - \Delta_f H^\circ\{S, s, l, \text{ or } g\}]$ ,  $\Delta_r S = [\theta_S^\circ\{S, s-s\} - S_{298}^\circ\{S, s, l, \text{ or } g\}]$ , and  $\Delta_r G =$

**Table 5.** For the Process:  $M_p X_q(s) + S(s, l, \text{ or } g) \rightarrow M_p X_q \cdot nS(s)$  [eq 37]<sup>a</sup>

solvate S	phase, p	$\Delta_r H/\text{kJ mol}^{-1}$	$\Delta_r S/\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta_r G/\text{kJ mol}^{-1}$
H <sub>2</sub> O	l	-12.8	-29.0	-5.2
D <sub>2</sub> O	l	-12.2		
NH <sub>3</sub>	g		-28.2	-4.5
Me <sub>2</sub> O	l		-125.0	
Et <sub>2</sub> O	l	-31.4		
NaOH	s	-4.4		
MeOH	l	-33.7		
EtOH	l	-23.4		
(CH <sub>2</sub> OH) <sub>2</sub>	l	-28.1		
H <sub>2</sub> S	g	-33.0		
SO <sub>2</sub>	g	-42.9	-144.6	-1.6

<sup>a</sup>  $\Delta_r H = [\theta_{HF}\{S, s-s\} - \Delta_f H^\circ\{S, p\}]/\text{kJ mol}^{-1}$ ,  $\Delta_r S = [\theta_S^\circ\{S, s-s\} - S_{298}^\circ\{S, p\}]/\text{J K}^{-1} \text{ mol}^{-1}$  and  $\Delta_r G = [\theta_{GF}\{S, s-s\} - \Delta_f G^\circ\{S, p\}]/\text{kJ mol}^{-1}$ , where  $p$  is the usual phase ( $s, l, \text{ or } g$ ) in which the solvate, S, is encountered at ambient temperature and pressure.

$[\theta_{GF}\{S, s-s\} - \Delta_f G^\circ\{S, s, l, \text{ or } g\}]$  represent the enthalpy, entropy or Gibbs energy of combination of solvate (water) molecule and salt in the above process (which should be contrasted with the interpretation of the  $\theta_P\{S, s-s\}$  value alone, which corresponds to the sum of the processes of both creation and incorporation of the solvate molecule in the crystal structure). Table 5 summarizes our data from our studies.

Equation 34 introduces a powerful extension to the difference rule since it enables us to estimate the  $\theta_{HF}\{S', s-s\}$  increment per solvate molecule for new solvates, S', for which we have insufficient data in order to make a plot of  $[\Delta_f H^\circ\{M_p X_q \cdot nS, s\} - \Delta_f H^\circ\{M_p X_q, s\}]$  versus  $n$  to obtain  $\theta_{HF}\{S', s-s\}$ , but for which we have thermodynamic data for  $\Delta_f H^\circ\{S', l\}$ . The use of eq 34 in this way is necessarily more approximate but we illustrate its use in the three examples in Table 6.

#### Discussion

The thermodynamic difference rule is exhibited by hydrate/parent, solvate/parent, hydrate/hydrate and solvate/solvate pairs as well as by solvate/hydrate, and their deuterated analogues, and beyond. The utilization of the difference rules for establishing missing thermodynamic data is powerful and has been amply illustrated in this paper.

There is further scope for employing this rule since certain types of salts can be viewed as comprised of more than one solvate. Consider, for example, the salt  $\text{ZnCl}_2 \cdot 4\text{NH}_3 \cdot 1/2\text{H}_2\text{O}$  listed in Table 2, for which we have estimated the entropy,  $S_{298}^\circ\{\text{ZnCl}_2 \cdot 4\text{NH}_3 \cdot 1/2\text{H}_2\text{O}, s\}$ , to be  $398.7 \text{ J K}^{-1} \text{ mol}^{-1}$ . This salt was considered to be the hemi-hydrate of the tetra-ammoniate salt of  $\text{ZnCl}_2 \cdot 4\text{NH}_3$  and thus

$$S_{298}^\circ\{\text{ZnCl}_2 \cdot 4\text{NH}_3 \cdot 1/2\text{H}_2\text{O}, s\}/\text{J K}^{-1} \text{ mol}^{-1} = S_{298}^\circ\{\text{ZnCl}_2 \cdot 4\text{NH}_3, s\} + 1/2\theta_S^\circ\{\text{H}_2\text{O}, s-s\} = 378.2 + 20.5 = 398.7 \quad (38)$$

using the value for  $\theta_S^\circ\{\text{H}_2\text{O}, s-s\}$  given in eq 16. Alternatively,  $\text{ZnCl}_2 \cdot 4\text{NH}_3 \cdot 1/2\text{H}_2\text{O}$  can be viewed as both a hydrate and a tetra-ammoniate of  $\text{ZnCl}_2$  and hence

$$S_{298}^\circ\{\text{ZnCl}_2 \cdot 4\text{NH}_3 \cdot 1/2\text{H}_2\text{O}, s\}/\text{J K}^{-1} \text{ mol}^{-1} = S_{298}^\circ\{\text{ZnCl}_2, s\} + 1/2\theta_S^\circ\{\text{H}_2\text{O}, s-s\} + 4\theta_S^\circ\{\text{NH}_3, s-s\} = 111.5^{7a} + 20.5 + 256.4 = 388.4 \quad (39)$$

(16) Barin, I. *Thermochemical Data for Pure Substances*, Parts I & II, 2nd ed., VCH: Weinheim, Germany, 1993.  
 (17) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 82nd ed.; CRC Press: Boca Raton, London, New York, Washington, D. C., 2001–2002.  
 (18) (a) Yoder, C. H.; Flora, N. *J. Am. Mineral.* **2005**, accepted. (b) As is acknowledged in ref 18a, we arrived at a similar conclusion concerning the existence of the additivity relationship for lattice potential energies largely as an extension of the work here presented.



**Table 6.** Estimated Enthalpies of Formation from Limited Data<sup>7a</sup>

solvate S'	$\theta_{\text{H}}\{\text{S}',\text{s}-\text{s}\}/$ kJ mol <sup>-1</sup>	solvated salt	$\Delta_f H(\text{estimate})/$ kJ mol <sup>-1</sup>	$\Delta_f H(\text{expt})/$ kJ mol <sup>-1</sup>	% error
HF	-321.5	KF·2HF	-1210	-1255.6	3.6
		KF·3HF	-1532	-1577.4	2.9
KOH	-439.9 <sup>b</sup>	KNO <sub>2</sub> ·KOH	-810	-806.3	-0.4
		KNO <sub>3</sub> ·KOH	-935	-921.3	-1.4
(CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub> O <sup>a</sup>	-375	LiBH <sub>4</sub> ·(CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub> O	-566	-563.6	-0.4

<sup>a</sup> (CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>O = diisopropyl ether. <sup>b</sup> cf. value of -430.0 for NaOH in Table 1.

where the term  $\theta_{\text{S}}^{\circ}\{\text{NH}_3,\text{s}-\text{s}\}$  is that determined for the ammoniates in Table 1 (= 64.1 J K<sup>-1</sup> mol<sup>-1</sup>). The difference between the two results, (38) and (39), is less than 3% which, in view of our comments below concerning entropy estimation, is virtually insignificant for most purposes.

There is further scope for the use of the difference rule. It can be used to compare crystal structure data when several determinations have been made for a *single* hydrate. Relationship (2) (with  $P = V_m = V_{\text{cell}}/Z$ , where  $V_{\text{cell}}$  is the unit cell volume, and  $Z$  is the number of molecules in the unit cell) can be used to identify the more reliable structural data from a choice available (on the grounds that the volume of parent and hydrate must fit the rule and be consistent with relationship (4)).

## Errors

There may sometimes be considerable discrepancies among different databases in the value assigned to a particular experimental enthalpy of formation, absolute entropy, or standard Gibbs energy of formation of a crystalline material. To cite a couple of examples, we find the following values for  $\Delta_f G^{\circ}\{\text{MgSO}_4 \cdot 6\text{H}_2\text{O},\text{s}\}/\text{kJ mol}^{-1}$ : -2603.7,<sup>13a,b</sup> -2627.1<sup>13a</sup> and -2628.64<sup>13c</sup> amounting to a 1% variation in the values, while  $S_{298}^{\circ}\{\text{BaS},\text{s}\}/\text{J K}^{-1} \text{ mol}^{-1}$  has experimental values: 78.2,<sup>8,13d,13e</sup> 87.0,<sup>13f</sup> 68.2,<sup>13g</sup> 92.0,<sup>13h</sup> 90.0,<sup>13i</sup> and 84.1<sup>13j</sup> representing a variation of *over* 25% between highest and lowest assignments. The modest “scattering” that is observed in Figures 1 and 2 is therefore quite possibly at least partially an artifact of the data employed.

**Hydrates.** We have been able to predict, in this paper, 62 values of  $\Delta_f G^{\circ}\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O},\text{s}\}$ ; fourteen values of  $\Delta_f G^{\circ}\{\text{M}_p\text{X}_q,\text{s}\}$ ; 63 values of  $S_{298}^{\circ}\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O},\text{s}\}$ ; and eleven values of  $S_{298}^{\circ}\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O},\text{s}\}$ . Where it has been possible to compare our predicted values with other tabulated data<sup>14,17</sup> for  $\Delta_f G^{\circ}$  (17 cases), 88% of the predicted values agree to within *less than* 1% with the tabulated data (and in one case we highlight there is clear doubt about the credibility of the *tabulated* value<sup>20</sup>); for  $S_{298}^{\circ}$  values (15 cases) agreement is somewhat worse, with only 30% of the predicted values lying within 1% of the tabulated value. Comparison of predicted values with Latimer estimates,<sup>8</sup> where available, increases this agreement to correspond to 47% of predicted values lying between the tabulated and the Latimer estimate. This is consistent with our impression that tabulated standard entropy data is generally somewhat less precise than other thermodynamic data. This is mitigated in use, however, by the fact that evaluation of the  $T\Delta S$  term for ambient temperature (the usual purpose of the use of entropy data)

requires multiplication of the absolute entropy values effectively by 0.298 K kJ J<sup>-1</sup>, reducing the overall effect of any error in entropy on the Gibbs energies thus derived.

**Solvates.** For most solvates, error in the listed standard thermodynamic data is likely to be somewhat greater than that seen for hydrates. This is possibly the origin of the poorer correlation coefficients seen in some of the “difference” plots reported in Table 1.

## Standard Entropy of Formation of Water of Crystallization, $\theta_{\text{sr}}\{\text{H}_2\text{O},\text{s}-\text{s}\}$

The standard entropy of formation of water of crystallization is established by considering, separately, the processes corresponding to the thermodynamic changes  $\Delta_f S^{\circ}\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O},\text{s}\}$  and  $\Delta_f S^{\circ}\{\text{M}_p\text{X}_q,\text{s}\}$ , i.e., formation from elements in their standard reference states at 101 325 Pa and 298.15 K to hydrate and parent, respectively. We have that

$$\Delta_f S^{\circ}\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O},\text{s}\} = [S_{298}^{\circ}\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O},\text{s}\} - p S_{298}^{\circ}\{\text{M},\text{s}\} - 1/2 q S_{298}^{\circ}\{\text{X}_2,\text{ss}\}] - n S_{298}^{\circ}\{\text{H}_2,\text{g}\} - 1/2 n S_{298}^{\circ}\{\text{O}_2,\text{g}\} \quad (40)$$

where ‘ss’ refers to the standard reference state of the element X<sub>2</sub>, while

$$\Delta_f S^{\circ}\{\text{M}_p\text{X}_q,\text{s}\} = [S_{298}^{\circ}\{\text{M}_p\text{X}_q,\text{s}\} - p S_{298}^{\circ}\{\text{M},\text{s}\} - 1/2 q S_{298}^{\circ}\{\text{X}_2,\text{ss}\}] \quad (41)$$

Subtraction of eq 41 from (40) leads to

$$\Delta_f S^{\circ}\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O},\text{s}\} - \Delta_f S^{\circ}\{\text{M}_p\text{X}_q,\text{s}\} = S_{298}^{\circ}\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O},\text{s}\} - S_{298}^{\circ}\{\text{M}_p\text{X}_q,\text{s}\} - n S_{298}^{\circ}\{\text{H}_2,\text{g}\} - 1/2 n S_{298}^{\circ}\{\text{O}_2,\text{g}\} \quad (42)$$

or, indicating the differences symbolically<sup>7b</sup>

$$\theta_{\text{sr}}\{\text{H}_2\text{O},\text{s}-\text{s}\} = \theta_{\text{S}}^{\circ}\{\text{H}_2\text{O},\text{s}-\text{s}\} - S_{298}^{\circ}\{\text{H}_2,\text{g}\} - 1/2 S_{298}^{\circ}\{\text{O}_2,\text{g}\} \quad (43)$$

Since:<sup>7a</sup>  $S_{298}^{\circ}\{\text{H}_2,\text{g}\}/\text{J K}^{-1} \text{ mol}^{-1} = 130.7$  and  $S_{298}^{\circ}\{\text{O}_2,\text{g}\}/\text{J K}^{-1} \text{ mol}^{-1} = 205.138$ , with  $\theta_{\text{S}}^{\circ}\{\text{H}_2\text{O},\text{s}-\text{s}\}/\text{J K}^{-1} \text{ mol}^{-1}$  (H<sub>2</sub>O molecule)<sup>-1</sup> = 40.9, therefore

$$\theta_{\text{sr}}\{\text{H}_2\text{O},\text{s}-\text{s}\}/\text{J K}^{-1} \text{ mol}^{-1} (\text{H}_2\text{O molecule})^{-1} = -192.4 \quad (44)$$

This result may be compared with the standard entropy of formation for ice of -192 J K<sup>-1</sup> mol<sup>-1</sup>, the latter being our own estimate, using tabulated data.<sup>1c</sup>

(19) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(20) Consider the experimental value listed<sup>14</sup> for  $\Delta_f G^{\circ}\{\text{CaCl}_2 \cdot 2\text{H}_2\text{O},\text{s}\} = -828$  kJ mol<sup>-1</sup>, which does not follow the trend of decreasing  $\Delta_f G^{\circ}$  value with increasing  $n$ .

Using the difference rule in the form of eq 15

$$S_{298}^{\circ}\{M_p X_q \cdot nH_2O, s\} - S_{298}^{\circ}\{M_p X_q, s\} = n \theta_S\{H_2O, s-s\} = n k \theta_V\{H_2O, s-s\} \quad (45)$$

together with the above value for  $\theta_S\{H_2O, s-s\}$ , and  $\theta_V\{H_2O, s-s\} = 0.0245 \text{ nm}^3$  (from ref 1e), we find that

$$k = \theta_S^{\circ}\{H_2O, s-s\} / \theta_V\{H_2O, s-s\} = 40.9 / 0.0245 = 1669 \text{ J K}^{-1} \text{ mol}^{-1} \text{ nm}^{-3} \quad (46)$$

This value for  $k$  agrees (to better than 4%) with the least-squares value,<sup>2a</sup>  $1606 \text{ J K}^{-1} \text{ mol}^{-1} \text{ nm}^{-3}$ , found by a linear plot through the origin of  $[S_{298}^{\circ}\{M_p X_q \cdot nH_2O, s\}]$  versus  $V_m$  for 67 hydrates.

Thus, the various independent correlations that we have established for hydrates prove to be reliably consistent.

**Supporting Information Available:** Table S1 contains a subset of the data used for this work (thermodynamic data for hydrated salts and their parent salt). Table S2 gives values of standard Gibbs energies of formation and absolute standard entropies (including values not available in the NBS tabulation<sup>7a</sup>). The latter are estimated using the difference rule and are compared with values from other literature sources (where available). The material accompanying Table S3 demonstrates estimation procedures when limited thermodynamic information is available. Table S4 estimates thermodynamic  $S_{298}^{\circ}$  and  $\Delta_f G^{\circ}$  values for  $SO_2$  solvates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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