

# Systematic Thermodynamics of Hydration (and of Solvation) of Inorganic Solids

Leslie Glasser\* and Franca Jones

Nanochemistry Research Institute, Department of Applied Chemistry, Curtin University of Technology, GPO Box U1987, Perth WA 6845, Australia

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The thermodynamics of the formation of solid and liquid inorganic hydrates and ammoniates is examined. In earlier studies, average values of the Gibbs energy of reaction,  $\Delta_r G$ , assuming a constant additivity per mole of bound water, have been obtained and have suggested that hydration is always marginally thermodynamically favorable. More detailed consideration now demonstrates that the mean value of  $\Delta_r G$  per mole of water, from anhydrous parent to hydrate within a sequence, increases consistently toward zero, becoming progressively less favorable as the degree of hydration,  $n$ , increases, and broadly independent of any structural features of the materials. Furthermore, the consistent behavior suggests that missing intermediate hydrates in hydrate sequences are likely to be thermodynamically stable, even if difficult to prepare, isolate, or measure. The behavior of ammoniates is similar but less regular, the irregularity being ascribed to a wider range of interactions within the solid ammoniates than in the hydrates. The “Ostwald Rule of Stages” suggests that the first precipitate from a supersaturated solution is usually a metastable phase, having an intermediate value of the Gibbs energy between that of the anhydrous parent and of the thermodynamically stable phase, then progressing to the stable phase with the lowest Gibbs energy, implying kinetic rather than thermodynamic control of the sequence of precipitation. The implications for hydrate formation are briefly considered.

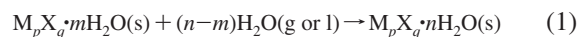
## Introduction

Materials formed in the presence of solvent may bind that solvent to form solvates, and the resulting solvates may have profoundly different physical properties from those of the parent material.<sup>1</sup> Such differences are often of significance:<sup>2</sup> for example, the stability and efficacy of pharmaceuticals<sup>2b</sup> may differ according to the extent of solvation; in mineral systems, solvation may affect the stability and processes available; in synthesis, solvation may be necessary for (or interfere with) the formation of product. By contrast, as discussed in detail below, equilibrium thermodynamic properties vary in a largely systematic fashion.

Our discussion deals only with those thermodynamic considerations which govern the formation of stoichiometric

solvates of inorganic materials. Water is the most prevalent solvent, and we direct our attention to the hydration of inorganic solids since there is much data<sup>1,3–5</sup> to support analysis of this process, but the considerations discussed below should apply generally to other solvents and to their solvation processes. We will focus on equilibrium behavior, neglecting kinetic effects. These kinetic effects may, however, be important and attention should be given to them whenever possible (see final paragraphs).

The following chemical equation represents the process of formation of a solid inorganic hydrate from a parent material and molecular water:



The thermodynamics of this reaction at temperature  $T$  and ambient pressure is represented by:

$$\Delta_r G = \Delta_r H - T \Delta_r S \quad (2)$$

where  $G$ ,  $H$ , and  $S$  are, respectively, Gibbs energy, enthalpy, and entropy. The process of hydration is thermodynamically

\* To whom correspondence should be addressed. E-mail: l.glasser@curtin.edu.au. Phone: +61 8 9266-3126. Fax: +61 8 9266-4699.

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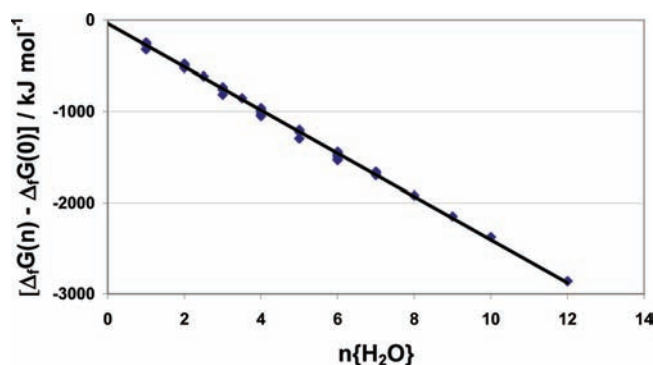
**Table 1.** Thermochemical Quantities for Water,<sup>8</sup> and Average Values for Hydration Reactions<sup>2,3</sup> at 298 K

row	standard thermodynamic parameters at 298 K	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta_f S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta_f G^\circ / \text{kJ mol}^{-1}$
1	H <sub>2</sub> O(g)	-241.826	188.834	-44.5	-228.582
2	H <sub>2</sub> O(l)	-285.830	69.950	-163.4	-237.141
3	H <sub>2</sub> O(s-metastable)	-291.8	48	-185	-236.7
row	difference quantity	$\theta_{\text{Hr}}$	$\theta_{\text{So}}$	$\theta_{\text{Sf}}$	$\theta_{\text{Gf}}$
4a <sup>b</sup>	$\theta_P\{M_P X_q \cdot n\text{H}_2\text{O}(s) - M_P X_q \cdot m\text{H}_2\text{O}(s)\}/(n-m)$	-298.6	44.8	-188.5	-242.4
4b <sup>b</sup>		-301.4 ± 10.7	40.9 ± 7.0	-192.4 ± 7.0	-241.3 ± 18
4c <sup>b</sup>		-293.6	42.1	-190.2	-236.8
4d <sup>b</sup>		-307.5 ± 15.3	42.7 ± 6.6	-190.8 ± 6.6	-250.7 ± 14.8
row	hydration reactions [condensation of H <sub>2</sub> O]	$\Delta_r H/n$	$\Delta_r S/(n-n+1)$	$\Delta_r S/n$	$\Delta_r G/n$
5a <sup>c</sup>	$n\text{H}_2\text{O}(g) \rightarrow n\text{H}_2\text{O}(l)$	-44.0		-118.9	-8.6
5b <sup>c</sup>	$n\text{H}_2\text{O}(g) \rightarrow n\text{H}_2\text{O}(s)$	-50.0		-140.5	-8.1
6a <sup>d</sup>	$n\text{H}_2\text{O}(g) + M_P X_q(s) \rightarrow M_P X_q \cdot n\text{H}_2\text{O}(s)$	-59.6	-146 ± 6.6	-144.0	-12.7
6b <sup>e</sup>	$n\text{H}_2\text{O}(l) + M_P X_q(s) \rightarrow M_P X_q \cdot n\text{H}_2\text{O}(s)$	-15.6	-27 ± 6.6	-25.1	-4.2

<sup>a</sup>  $S^\circ(\text{H}_2\text{g}) = 130.7$ ;  $S^\circ(\text{O}_2\text{g}) = 205.2 \text{ J K}^{-1} \text{ mol}^{-1}$ .  $\Delta_f S^\circ = (\Delta_f H^\circ - \Delta_f G^\circ)/T$ . <sup>b</sup> 4a: slopes of difference plots from the original reports;<sup>2,3</sup> 4b: mean values and their standard deviations, evaluated from the original data sets; 4c: slopes of difference plots, Figure 1 legend; 4d: mean values from Supporting Information, Table S1. <sup>c</sup> Condensation quantity:  $\Delta_r P/n = \Delta_f P^\circ(l) - \Delta_f P^\circ(g)$  where  $P = H, S, \text{ or } G$ ; 5a: (= row 2 - row 1); 5b: (= row 3 - row 1). <sup>d</sup> Thermochemical reaction quantity per mole of gaseous water:  $\Delta_r P/n = \theta_P - \Delta_f P^\circ(g)$  where  $P = H, S, \text{ or } G$  (= row 4a - row 1). <sup>e</sup> Thermochemical reaction quantity per mole of liquid water:  $\Delta_r P/n = \theta_P - \Delta_f P^\circ(l)$  where  $P = H, S, \text{ or } G$  (= row 4a - row 2).

favorable<sup>6</sup> at  $T$  provided that  $\Delta_r G < 0$ . Moreover, the so-called<sup>7</sup> “law of compensation” suggests that the Gibbs energy will be little altered by small changes in temperature (since enthalpy and entropy both tend to alter in the same way, increase or decrease, with temperature while their signs in eq 2 are opposite). The questions then become: what considerations apply to render the hydrated product of lower Gibbs energy than the reactants, and why are certain of the hydrates missing from hydrate sequences?

Although the general physical properties of materials may alter considerably on hydration, it has nevertheless been consistently found that the corresponding thermodynamic properties vary in a rather systematic fashion. Various authors<sup>1,3,4</sup> have evaluated the average thermodynamic contributions on binding a mole of water to materials, and Table 1 lists published results, where  $\theta_P\{\text{H}_2\text{O},\text{s-s}\}$  (in row 4a) represents<sup>1</sup> the average contribution to the general thermodynamic property,  $P$  (which may represent any of functions such as  $H, S, G, C_p$ , etc.) per mole of bound water as measured between *solid*  $n$ -hydrate and *solid*  $m$ -hydrate (thus, “s-s”), including the anhydrous parent (for which  $m$  is zero). (Note that the  $\theta_P$  values listed include the contribution from the formation of water from its constituent elements at 298 K.) Rows 5 give the properties for phase changes of pure water, while rows 6 show the reaction properties per mole of bound water,  $\Delta_r P/(n - m)$ . These values correspond to the condensation of molecular water into the hydrate. The reliability of the data in the table is exemplified by the linearity of the plot in Figure 1, of  $\Delta_r G(n)$  versus  $n\{\text{H}_2\text{O}\}$ ,



**Figure 1.**  $\Delta_r G = [\Delta_r G(n) - \Delta_r G(0)]$  versus  $n\{\text{H}_2\text{O}\}$  for 60 hydrates (Supporting Information, Table S1). Fitted line: slope =  $-236.8 \text{ kJ mol}^{-1}$ ; intercept =  $-39.3 \text{ kJ mol}^{-1}$ ;  $R^2 = 0.998$ . The corresponding difference graph for  $\Delta H$  has slope =  $-293.6 \text{ kJ mol}^{-1}$ ; intercept =  $-38.9 \text{ kJ mol}^{-1}$ ;  $R^2 = 0.999$ , while that for  $\Delta S$  has slope =  $-190.2 \text{ J K}^{-1} \text{ mol}^{-1}$ , intercept =  $-0.6 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $R^2 = 0.998$ .

which includes all 21 inorganic hydrate series with more than 3 hydrates for which thermodynamic information has been found from standard thermodynamic databases<sup>8,9</sup> (excluding only  $\text{Cr}_2(\text{SO}_4)_3$ , for which the data is inconsistent).

The values of  $\Delta_r G/(n - m)$  as reported in Table 1 (rows 6), are fixed and negative, which implies that  $\Delta_r G$  will become increasingly favorable as the extent of hydration,  $n$ , increases. However, this is clearly contrary to observation since many materials do not form hydrates at all, while no material forms indefinitely extended,  $n \rightarrow \infty$ , series of hydrates. The significant point is that the average quantity,  $\Delta_r G/(n - m)$ , is only slightly negative so that its value and even sign is vulnerable to small alterations in the internal interactions within the reactants and products of hydration. The fault in the implied assumption of general hydrate

(4) (a) Mercury, L.; Vieillard, P.; Tardy, Y. *Appl. Geochem.* **2001**, *16*, 161–181. (b) Leclaire, A.; Monier, J. C. *Acta Crystallogr.* **1982**, *B38*, 724–727.

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(6) Johnson, D. A. *Some Thermodynamic Aspects of Inorganic Chemistry*; Cambridge U. P.: Cambridge, U.K., 1968.

(7) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; J. Wiley: New York, 1976. Benson notes that the “law of compensation” relies on the observation that increased binding energy (exothermic, so negative) goes together with greater cohesion (so reducing entropy) so that the difference is little altered by (small) temperature changes, resulting in the Gibbs energy being relatively independent of temperature.

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(9) (a) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*; The NBS Tables of Chemical Thermodynamic Properties, Supp. 2, NBS, Washington, DC 20234. (b) Chase, M. W., Jr. NIST-JANAF Thermochemical Tables, 4th ed.; *J. Phys. Chem. Ref. Data*, 1998, Monograph 9, Amer. Inst. Physics, NY. (c) HSC Chemistry 6.1, Outotec Research Oy, Finland. <http://outotec.com/hsc>. Accessed Jan., 2009.

**Table 2.** Successive Gibbs Energies, Enthalpies ( $\Delta_r G$  in  $\text{kJ mol}^{-1}$ ) and Entropies ( $\Delta_r G/n$  in  $\text{J K}^{-1} \text{mol}^{-1}$ ) of Formation and their Differences for Hydration Reactions with Gaseous Water at 298.2 K, for 21 Materials with Multiple Solid Hydrates (Extract, showing Gibbs Energy Columns only, from Supporting Information, Table S1)<sup>9</sup>

material	$n\{\text{H}_2\text{O}\}$	$\Delta_r G$	$\Delta(\Delta_r G)/(n - m)^a$	$\Delta_r G/n^b$
MgSO <sub>4</sub>	0	-1174.5		
	1	-1436.5	-262.0	-33.4
	2	-1665.8	-229.3	-17.1
	4	-2150.8	-242.5	-15.5
	5	-2396.9	-246.1	-15.9
	6	-2632.2	-235.3	-14.4
	7	-2871.7	-239.5	-13.9

<sup>a</sup>  $\Delta(\Delta_r G)/(n - m) = [\Delta_r G^\circ\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}\} - \Delta_r G^\circ\{\text{M}_p\text{X}_q \cdot m\text{H}_2\text{O}\}]/[n - m]$ , i. e., the difference in  $\Delta_r G^\circ$  between successive hydrates (including the anhydrous parent, for which  $m = 0$ ), which corresponds to formation of water within the hydrated material. <sup>b</sup>  $\Delta_r G/n = [\Delta_r G^\circ\{\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}\} - \Delta_r G^\circ\{\text{M}_p\text{X}_q\}]/n - \Delta_r G^\circ\{\text{H}_2\text{O}, \text{g}\}$  where  $\Delta_r G^\circ\{\text{H}_2\text{O}, \text{g}\} = -228.6 \text{ kJ mol}^{-1}$ , i. e., the mean difference in  $\Delta_r G^\circ$  between hydrate  $n$  and the anhydrous parent, which corresponds to condensation of gaseous water into the hydrated material.

**Table 3.** Successive Gibbs Energies, Enthalpies ( $\Delta_r G$  in  $\text{kJ mol}^{-1}$ ) and Entropies ( $\Delta_r G/n$  in  $\text{J K}^{-1} \text{mol}^{-1}$ ) of Formation and their Differences for Hydration Reactions with Gaseous Water at 298.2 K, for Three Materials with Multiple Liquid Hydrates (Extract, showing Gibbs Energy Columns only, from Supporting Information, Table S2)<sup>9</sup>

material	$n\{\text{H}_2\text{O}\}$	$\Delta_r G$	$\Delta(\Delta_r G)/(n - m)^a$	$\Delta_r G/n$	
H <sub>2</sub> SO <sub>4</sub> (l)	0	-698			
	1	-950.3	-252.3	-23.7	
	2	-1199.6	-249.3	-22.2	
	3	-1443.9	-244.3	-20.1	
	4	-1685.8	-241.9	-18.4	
	6.5	-2285.6	-239.9	-15.7	
HNO <sub>3</sub> (l)	0	-80.71			
	1	-328.77	-248.1	-1.1	
	3	-811.09	-241.2	-2.7	
NaOH	0	-379.49			
	Cr	1	-629.34	-249.8	-21.3
	L	2	-873.09	-243.8	-18.2
	L	3.5	-1236.36	-242.2	-16.2
	L	4	-1356.64	-240.6	-15.7

<sup>a</sup> NaOH and NaOH·H<sub>2</sub>O are solids.

stability then lies with the fact that the tabulated difference quantity,  $\theta_{\text{Gr}}\{\text{H}_2\text{O}, \text{s-s}\}$ , has been obtained<sup>1,3,4</sup> as a simple average over many materials and with varied extents of hydration.

In Tables 2 and 3 (which are extracts from Supporting Information, Tables S1 and S2), we examine detailed values<sup>9</sup> of  $\Delta_r G$  as the extent of hydration progresses for both solid (Table 2) and liquid (Table 3) hydrates. These Tables demonstrate a general pattern of behavior (not apparently remarked on before), namely that the addition of bound water becomes progressively less thermodynamically favorable as hydration proceeds, in that the negative values of  $\Delta_r G$  per mole of bound water added tend upward toward zero as the extent of hydration,  $n$ , increases so that  $\Delta_r G$  eventually will become positive, and the corresponding hydrate unstable. These results are plotted in Figure 2, where the systematic progress from negative values of the Gibbs energy of hydration toward zero as the extent of hydration,  $n$ , increases is readily observed. There is little general evidence of any strong dependence of the thermodynamic behavior on structural features of the materials.

As noted in the legend to Figure 1, the enthalpies of formation of the hydrates, treated in the identical fashion, show similar trends to those for Gibbs energies shown in Figure 1.

Figure 3 plots the enthalpy differences for the ammoniates, corresponding to Figure 1 for hydrates (data for the Gibbs energies and entropies of the ammoniates are not available). The enthalpy data for 39 ammoniate series is listed as Supporting Information, Table S3.

The line with minimum slope in Figure 3 demonstrates that incorporation of ammonia into an ammoniate releases at least 46.4  $\text{kJ mol}^{-1}$  of enthalpy but that, when the enthalpy is more negative, the ammonia may be more strongly incorporated.

### Kinetics (see added Note in Proof)

The “Ostwald Rule of Stages” (or “Ostwald Step Rule”)<sup>11–13</sup> is based on Ostwald’s observation that the initial precipitate from a supersaturated solution is often a metastable phase, having an intermediate value of the Gibbs energy, progressing with time to the thermodynamically stable phase with the lowest Gibbs energy, implying kinetic rather than thermodynamic control of the sequence of precipitation. In the often quoted<sup>12</sup> case of sodium sulfate, the metastable heptahydrate ( $n = 7$ ) forms initially from solution before giving way in due course to the thermodynamically stable decahydrate ( $n = 10$ ). No consensus on the status of this Rule exists, although it is well recognized in geology in the phenomenon of paragenesis (that is, the sequential formation, in time, of minerals)<sup>13</sup> and elsewhere. It would be interesting to know how well the Rule applies to the formation of a sequence of crystal hydrates, each of which have negative Gibbs energies of reaction at room temperature (Tables 2 and 3).

### Discussion and Conclusion

The consistent patterns of thermodynamic behavior here observed (see figures and tables) demonstrate that the interactions within hydrates are very largely independent of the details of ion and water interactions (but somewhat more dependent in the more weakly bonded ammoniates) and that the energetics is largely associated with condensation of solvent to form bound solvate. Indeed, the mean energetics of hydrate formation matches that of metastable ice formation quite closely (compare the small  $\sim 2\%$  difference between rows 3 and 4 of Table 1). We also note that the consistency of the hydration thermodynamics in the hydration sequences reported suggests that missing intermediate hydrates in a sequence (for example,<sup>14</sup> MgSO<sub>4</sub>·3H<sub>2</sub>O in Table 2) are likely to exist, even if difficult to prepare, isolate or measure.<sup>15</sup>

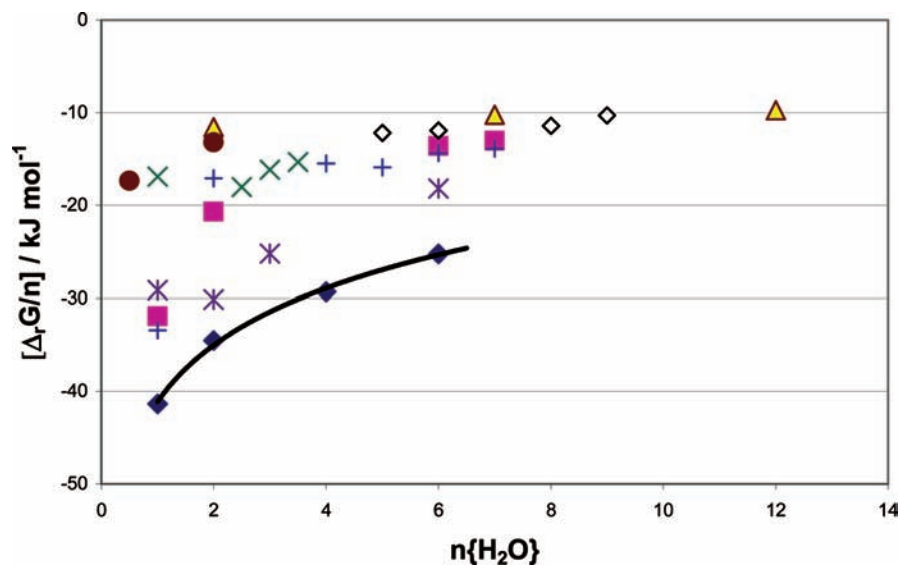
The small but decreasing Gibbs energy differences with increasing extent of hydration suggest that there are only

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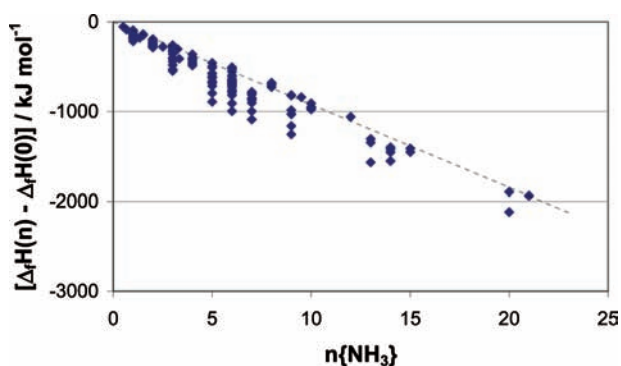
(11) Nývlt, J. *Cryst. Res. Technol.* **1995**, *30* (4), 443–449.

(12) Mullin, J. W. *Crystallization*, 3rd revised ed.; Butterworth-Heinemann: Oxford, 1997.

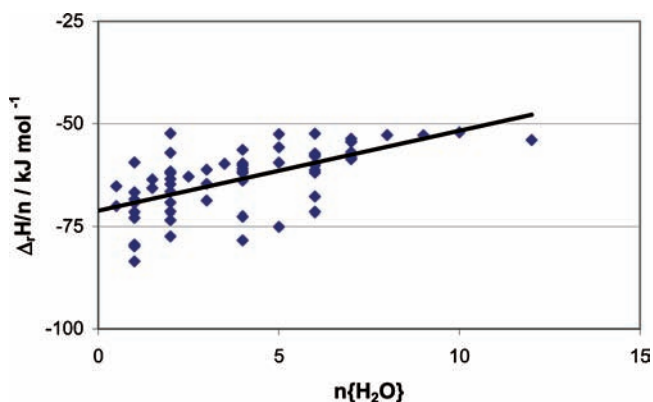
(13) Morse, J. W.; Casey, W. H. *Am. J. Sci.* **1988**, *288* (6), 537–560.



**Figure 2.**  $\Delta_r G/n$  versus  $n\{\text{H}_2\text{O}\}$ .  $\Delta_r G/n = [\Delta_r G(n) - \Delta_r G(0)]/n - \Delta_r G^\circ(\text{H}_2\text{O}, \text{g})$  for  $\text{M}_p\text{X}_q(\text{s}) + n\text{H}_2\text{O}(\text{g}) \rightarrow \text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}(\text{s})$ , which corresponds to condensation of gaseous water into the hydrated material (cf.,  $-8.1 \text{ kJ mol}^{-1}$  for condensation to metastable ice). Filled diamonds,  $\text{MgCl}_2$ ; filled squares,  $\text{ZnSO}_4$ ; triangles,  $\text{Na}_2\text{HPO}_4$ ; filled circles,  $\text{CaSO}_4$ ; crosses,  $\beta\text{-UO}_2\text{SO}_4$ ; stars,  $\text{UO}_2(\text{NO}_3)_2$ ; plus signs,  $\text{MgSO}_4$ ; diamonds,  $\text{Na}_2\text{SiO}_3$ . The curve through the  $\text{MgCl}_2$  data is shown for illustrative purposes only. Note: (i) the quantities plotted are small differences between large quantities, and so subject to the combined error in the differenced quantities; (ii) uranyl hydrates have a water molecule coordinated to the central atom (Gil, J. M.; Villa, F. M.; Gil, F. J. M. *J. Therm. Anal.* **1979**, *17*, 115–121) which may be related to the initial more positive values in the plotted uranyl sequences.



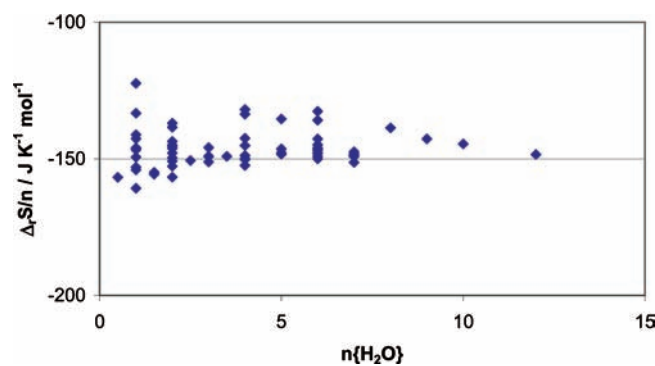
**Figure 3.**  $[\Delta_r H(n) - \Delta_r H(0)]$  versus  $n\{\text{NH}_3\}$ . The data show a minimum slope of  $-92.3 \text{ kJ mol}^{-1}$ , or  $-46.4 \text{ kJ mol}^{-1}$  for  $[\Delta_r H(n) - \Delta_r H(0)]/n - \Delta_r H^\circ(\text{NH}_3, \text{g})$ , where  $\Delta_r H^\circ\{\text{NH}_3, \text{g}\} = -45.9 \text{ kJ mol}^{-1}$ , which corresponds to condensation of ammonia into the ammoniated material.



**Figure 4.** Mean reaction enthalpy for the hydration of 21 materials (Supporting Information, Table S1). See legend to Fig. 5 for details.

small repulsive interactions between the contents of hydrates. We follow the processes more closely by examining the enthalpy and entropy changes separately below.

Figure 4 shows that the mean hydration enthalpy for a large number of materials increases systematically toward



**Figure 5.** Mean reaction entropy for the hydration of 21 materials in Supporting Information, Table S1:  $\Delta_r S/n = [\Delta_r S(n) - \Delta_r S(0)]/n - \Delta_r S^\circ(\text{H}_2\text{O}, \text{g})$  for  $\text{M}_p\text{X}_q(\text{s}) + n\text{H}_2\text{O}(\text{g}) \rightarrow \text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}(\text{s})$ , which corresponds to condensation of gaseous water into the hydrated material. Enthalpy data for  $\text{VOSO}_4 \cdot \text{H}_2\text{O}$  ( $-134.8 \text{ kJ mol}^{-1}$ ) and  $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$  ( $-87.8 \text{ kJ mol}^{-1}$ ) have been omitted as being inconsistent with the remainder of the data.  $\Delta_r S/n = [\Delta_r S(n) - \Delta_r S(0)]/n - \Delta_r S^\circ(\text{H}_2\text{O}, \text{g})$  for  $\text{M}_p\text{X}_q(\text{s}) + n\text{H}_2\text{O}(\text{g}) \rightarrow \text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}(\text{s})$  which corresponds to condensation of gaseous water into the hydrated material (cf.  $-140.5 \text{ J K}^{-1} \text{ mol}^{-1}$  for condensation into metastable ice).

zero as the extent of hydration increases; the intercept of about  $-71 \text{ kJ mol}^{-1}$  for  $n = 0$  represents the process of condensation and attraction into the structure, without water–water repulsion. Figure 5 shows that the entropy change is largely independent of the materials involved, becoming possibly more negative with increasing degree of hydration. These graphs thus confirm that the principal process at work is condensation of the water into the crystal structure. There are only minor effects from detailed interac-

(14) For example, see Polymet Commodities, Ltd.: <http://www.made-in-china.com/showroom/polymet888/product-detailnqjxRJCbLhu/China-Magnesium-Sulphate-Trihydrate.html>.

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(16) Chung, S.-y.; Kim, Y.-m.; Kim, J.-g.; Kim, Y.-j.; *Nature Phys.* **2009**, *5* (1), 68–73.

tions (such as hydrogen bonding, Coulombic interactions, and so forth) within the hydrated materials which affect the energetics; that is, the process of hydration is largely independent of structural details among these inorganic materials.

The slightly decreasing entropy difference demonstrates that the librations of the bound water molecules become slightly more constrained with degree of hydration, while the decreasingly negative enthalpies show that the additional water molecules are less easily incorporated into the crystal structures. Full elucidation of these interactions, will require detailed and individual consideration (such as modeling).

From their small negative differences of Gibbs energies of reaction from liquid water, we may infer that hydrates are only marginally thermodynamically stable species (some decomposing at temperatures not much above the boiling point of water) with respect to their less hydrated neighboring hydrate, and that hydrates only form to a limited extent. This implies that average thermodynamic values, while useful for broad generalizations,<sup>10</sup> are insufficiently accurate to make reliable predictions as to the relative stabilities of hydrates. We find the same pattern of behavior for the enthalpies of

ammoniates (for which Gibbs energies are generally unavailable) and suggest that much the same considerations apply to sequences of solvation reactions in general.

Extension of this approach can likely be made into the area of borate, silicate, and other glasses and amorphous materials, as well as in the investigation of double salt hydrates (e. g.,  $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ) and other multiple salts.

**Note Added in Proof:** Ostwald's Rule of Stages has been proved by observation during the crystallization of a metal phosphate.<sup>16</sup>

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**Supporting Information Available:** Table S1 of Gibbs energies, enthalpies and entropies for 21 sequences of solid inorganic hydrates, Table S2 for 3 sequences of liquid inorganic hydrates, and Table S3 of enthalpies only for 39 sequences of ammoniates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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