Inorg. Chem. **2007**, *46*, 9768–9778

Inorganic Chemistry
Article

The Thermodynamic *Solvate* Difference Rule: Solvation Parameters and Their Use in Interpretation of the Role of Bound Solvent in Condensed-Phase Solvates

Leslie Glasser* and H. Donald Brooke Jenkins*

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

Received June 5, 2007

Our earlier-established thermodynamic solvate difference rule encompasses thermodynamic relationships for the quantities $P = \Delta_{\mathrm{f}}H^\circ$, $\Delta_{\mathrm{f}}G^\circ$, $\Delta_{\mathrm{f}}S^\circ$, S°, V_{m}, and U_{POT} for pairs of condensed-phase solvates (including hydrates) having n and m moles, respectively, of bound solvent (including water, i.e., $\mathrm{L} = \mathrm{H_2O}$), and can be written as $P\{\mathrm{M_pX_q}\cdot n\mathrm{L,p}\} \approx P\{\mathrm{M_pX_q}\cdot m\mathrm{L,p}\} + (n\text{-}m)\cdot\theta_{\mathrm{P}}\{\mathrm{L,p–p}\}$ (with $m = 0$ for the corresponding thermodynamic quantity of the condensed-phase unsolvated parent, $P\{\mathrm{M_pX_q,p}\}$), where $\theta_{\mathrm{P}}\{\mathrm{L,p–p}\}$ is the incremental contribution per mole of the bound solvent, L, to the property, P, of the solvate in condensed phase, p (where p = solid or liquid). We find that this rule can be extended to supercooled NaOH (and, probably, even more generally). Once established, the parameter $\theta_{\mathrm{P}}\{\mathrm{L,p–p}\}$ provides approximate values of the thermodynamic property, P, for the remaining solvates (hydrates) for which data are unknown. The difference rule is here further extended to heat-capacity data, C_{p}, for both hydrates and other solvates. For solid-phase hydrates, $\theta_{C_{\mathrm{p}}}\{\mathrm{H_2O,s–s}\}$ is determined to be 42.8 J K^{-1} mol^{-1}. Further, the method is shown to apply also to the organic solvates, DMSO and DMF (the latter is based on a single example), leading to the (tentative) values $\theta_{C_{\mathrm{p}}}\{\mathrm{DMSO,s–s}\} \approx 105$ J K^{-1} mol^{-1} (at 255 K); ≈ 161 J K^{-1} mol^{-1} (at 350 K), illustrating typical temperature dependence of the θ_{Cp} values. $\theta_{C_{\mathrm{p}}}\{\mathrm{DMF,s–s}\} \approx 84$ J K^{-1} mol^{-1}. For supercooled NaOH, $\theta_{C_{\mathrm{p}}}\{\mathrm{NaOH,l–l}\} = 77$ J K^{-1} mol^{-1}. The values of the solvate difference rule parameters provide us with insight into the bonding condition of the solvent molecule, leading to the conclusion that bound solvent water in an ionic environment is ice-like. The situation is more complex within zeolites because water may enter the solvate in a variety of ways. These latter considerations are also briefly discussed with respect to fullerenes.

Introduction

The structure of a solid material influences its physical properties, and this is often of crucial importance in dealing with the material in respect of, for example, its particle size and shape, its flow and compaction properties, its solubility, or its stability under different conditions of temperature, pressure, and humidity. Two of the ways in which structures of solids may vary are through polymorphism (crystallization into different crystalline states) and through the formation of solvates (including hydrates) in different proportions and even as different polymorphs (for example, see the case[1] of the numerous calcium chloride hydrates, $\mathrm{CaCl_2}\cdot n\mathrm{H_2O}$).

Here, we concern ourselves with the thermodynamics of solvation (which includes hydration) in condensed phases. As we demonstrate, comparison of thermodynamic quantities can even provide us with information as to the state of the solvent molecule within the condensed-phase solvate. Solvation properties are not only of practical and theoretical interest[2–4] but also of considerable concern because, for

---

* To whom correspondence should be addressed. E-mail: l.glasser@curtin.edu.au. Tel: + 61 8 9266-3126. Fax: + 61 8 9266-4699 (L.G.), E-mail: h.d.b.jenkins@warwick.ac.uk. Telephone: +44 2476-523-265. Fax: + 44 2476-524-112 (H.D.B.J.).

(1) Jenkins, H. D. B.; Hirst, D. M.; Lagadianou, E.; Patel, M.; Herzig, P.; Brown, I. D. *J. Chem. Soc., Faraday Trans.* **1985**, *81* (2), 1607–1626.

(2) Glasser, L.; Jenkins, H. D. B. *Chem. Soc. Rev.* **2005**, *34*, 866–874.

10.1021/ic701105p CCC: $37.00

example, geological processes, both terrestrial and extraterrestrial,[5] are affected by the presence (or absence) of water, whereas behavior in pharmaceutical manufacture and use[6,7] may be materially altered by both the nature and extent of solvation and by possible associated polymorphisms. Such processes have deep relevance to biological processes as well.[8,9] In addition, in chemical syntheses, the solvent may be of a much wider variety than simply water. The bound solvent molecule may behave in a static, solid-state fashion, may be able to librate, rotate, or translate within the crystal structure, or even behave in a pseudo-gas phase manner, as for certain cations in weakly interacting environments.[10]

Thermodynamic (and kinetic) studies of mineral reactions[11] are significant too for processes affecting the movement of contaminants in the environment. Minerals are often effective at retarding or even preventing the movement of contaminants in groundwater by adsorption to surfaces or by intracrystalline absorption. Mineral precipitation and dissolution reactions also control rock or soil permeability,[12] thereby controlling rates of groundwater movement. The theoretical understanding of sorption processes, particularly of water in zeolites[13] (and clays), is a further area of topical interest.

Our difference rule[3,4] has already demonstrated that many thermodynamic properties, P, of solvates (where P corresponds with $\Delta_f H^\circ$, $\Delta_f G^\circ$, $\Delta_f S^\circ$, S°_{298}, V_m°, or lattice energy, U_{POT}) are additive with respect to the bound solvent. In this article, we examine further aspects of the applicability of the difference rule, in particular, extending its role to correlating heat-capacity data, C_p°, and to its applicability to condensed phases in general. Once the additive factor $\theta_P\{L\}$ for a bound solvent, L, has been established, missing thermodynamic data for solvates (and, indeed, for their corresponding parent salts) may be estimated. In addition, the approach may be used as a validation tool to test and check literature data and, in this way, highlight suspect values. Examples of these latter aspects of the rule may be seen in what follows.

Further, we demonstrate that this thermodynamic data, which is capable of providing a measure of the incremental effect of adding water (solvate), may be utilized to probe the chemical environment existing around water molecules within a variety of structures from hydrates to ice, through to cavity structures like fullerenes, zeolites, and similar minerals. The idea can be extended to solvates besides water, as is illustrated also for the case of DMSO.

The Thermodynamic Solvate Difference Rule. The thermodynamic solvate difference rule[3,4] is formulated as

$$P\{M_pX_q{\cdot}nL,s\} \approx P\{M_pX_q,s\} + n\theta_P\{L,s{-}s\} \tag{1a}$$

$$P\{M_pX_q{\cdot}nL,s\} \approx P\{M_pX_q{\cdot}mL,s\} + (n-m)\theta_P\{L,s{-}s\} \tag{1b}$$

where the thermodynamic quantity, P, can be any of $\Delta_f H^\circ$, $\Delta_f G^\circ$, $\Delta_f S^\circ$, S°_{298}, V_m°, or lattice energy, U_{POT}, and now also heat capacity, C_p°; L is a bound solvent molecule (which may be water); and s−s notes that the values derive from difference in the properties of solvate and parent, each in the solid state. The notation $\theta_P\{L,l{-}l\}$, used later in this article, refers to a case where solvated, $M_pX_q{\cdot}nL(l)$, and parent, $M_pX_q(l)$, materials are both in the liquid state. The rule, as stated above, records the average properties associated with the combined creation and incorporation of a mole of bound solvent (water) molecules into a general solvate (hydrate), through the factor $\theta_P\{L,s{-}s\}$. Values of $\theta_P\{L,s{-}s\}$ are listed in the upper portion of Table 1 for the important thermodynamic functions, P, of water listed above.

The difference rule may alternatively be considered in terms of reactions of the type

$$\underset{\text{parent}}{M_pX_q(s)} + nL(p) \rightarrow \underset{\text{solvate}}{M_pX_q{\cdot}nL(s)} \tag{2a}$$

$$\underset{\text{solvate}}{M_pX_q{\cdot}nL(s)} + mL(p) \rightarrow \underset{\text{higher solvate}}{M_pX_q{\cdot}(n+m)L(s)} \tag{2b}$$

(where L = H_2O for hydrates, and p represents the specific phase of L).

The thermodynamic reaction parameter, $\Delta_r P$, for such processes describes the change in the value of thermodynamic property, P, on the incorporation of one mole of the solvate molecule, L, from phase p (s, l, or g) into the solid solvate

$$\begin{aligned}\Delta_r P &= [P\{M_pX_q{\cdot}nL,p\} - P\{M_pX_q,p\} - nP\{L,p\}]/n \\ &= ([P\{M_pX_q{\cdot}nL,p\} - P\{M_pX_q,p\}]/n) - P\{L,p\} \\ &= [\theta_P\{L,p{-}p\} - P\{L,p\}]\end{aligned} \tag{3}$$

The essential features of the thermodynamic solvate difference rule are that, *irrespective of the nature of the parent molecule*:

- $\theta_P\{H_2O,p{-}p\}$ (or $\theta_P\{L,p{-}p\}$for a general bound solvent, L), where solvate and parent (eq 1a) or both solvate phases (eq 1b) are in phase p, is approximately constant for a family of hydrates (solvates); and, equivalently
- $\Delta_r P = [\theta_P\{L,p{-}p\} - P\{L,p\}]$ is approximately constant for a family of hydrates (solvates).

---

(3) Jenkins, H. D. B.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 4378−4388.

(4) Jenkins, H. D. B.; Glasser, L. *J. Am. Chem. Soc.* **2004**, *126*, 15809−15817.

(5) Mercury, L.; Vieillard, P.; Tardy, Y. *Appl. Geochem.* **2001**, *16*, 161−181. Bish, D. L.; Carey, J. W.; Vaniman, D. T.; Cipera, S. J. *Icarus* **2003**, *164*, 96−103.

(6) Giron, D. *Thermochim. Acta* **1995**, *248*, 1−9.

(7) Espeau, P.; Céolin, R.; Tamarit, J.; Perrin, M.; Gauchi, J.; Leveiller, F. *J. Pharm. Sci.* **2005**, *94*, 524−539.

(8) Dunitz, J. D. *Science* **1994**, *264*, 670.

(9) Prabhu, N. V.; Sharp, K. A. *Ann. Rev. Phys. Chem.* **2005**, *56*, 521−548.

(10) Krossing, I.; Reisinger, A. *Coord. Chem. Rev.* **2006**, *250*, 2721−2744.

(11) Carey, J. W.; Bish, D. L. *Am. Mineral.* **1996**, *81*, 652−962.

(12) Carey, J. W.; Robinson, B. A.; Henderson, S. *Geol. Soc. Amer. Abstracts with Programs*, 1995. Chipera, S. J.; Carey, J. W.; Bish, D. L. *Clay Miner. Soc. Meet.* 1996.

(13) Bish, D. L. In *Natural Zeolites '93*; Ming, D. W., Mumpton, F. A., Eds.; Intl. Comm. Natural Zeolites: Brockport, NY, 1995; pp 259−269.

Table 1. Experimentally Derived Thermodynamic Parameters, θ_P(L,s-s), for L = H_2O and for Nonaqueous Solvents[a]

Water as solvent, L = H_2O	**θ_V (H_2O,s−s) nm^3**	**θ_U (H_2O,s−s) kJ mol^{-1}**	**θ_{C_p} (H_2O,s−s) J K^{-1} mol^{-1}**	**θ_S (H_2O,s−s) J K^{-1} mol^{-1}**	**θ_{H_f} (H_2O,s−s) kJ mol^{-1}**	**θ_{G_f} (H_2O,s−s) kJ mol^{-1}**
hydrates	$0.0245^b \pm (0.0228)^c$	54.3^b	42.8^f	40.9^b $(40)^c$	-298.6^b	-242.4^b
hydroxides, oxyhydroxides[d]	0.02158 ± 0.0035		43.1 ± 12.6	42.5 ±17.1	−333.3 ± 63.8	−269.3 ± 55.9
sulfates, sulfites[d,e]	0.02407 ± 0.0020		39.0 ± 5.2^e	41.5 ± 6.0	−301.4 ± 7.7	−244.4 ± 7.9
chlorides, chlorates[d]	0.02341 ± 0.0038		42.0 ± 2.7	43.7 ± 5.9	−308.3 ± 8.6	−251.8 ± 8.5
nonaqueous solvent, L	**θ_V (L,s−s) nm^3**	**θ_U (L,s−s) kJ mol^{-1}**	**θ_{C_p} (L,s−s) J K^{-1} mol^{-1}**	**θ_So (L,s−s) J K^{-1} mol^{-1}**	**θ_{H_f} (L,s−s) kJ mol^{-1}**	**θ_{G_f} (L,s−s) kJ mol^{-1}**
deuterium oxide, L = D_2O					−307.8	
liquid ammonia L = NH_3				64.1	−105.5	−21.0
deuterated ammonia, L = ND_3				68.8	−103.6	−31.4
dimethyl ether, L = Me_2O				141.3	−282.1	−173.5
diethyl ether, L = Et_2O					−311.0	
sodium hydroxide, L = NaOH					−430.0	
methanol, L = MeOH					−272.3	
ethanol, L = EtOH					−301.1	
ethylene glycol, L = $(CH_2OH)_2$					−483.4	
hydrogen sulfide, L = H_2S					−53.6	
sulfur dioxide, L = SO_2					−339.7	
			θ_{C_p} (L,s−s) J K^{-1} mol^{-1}			
dimethylsulfoxide, L = Me_2SO (350 K)			160, 190^f			
N, *N*′-dimethylformamide, L = $HCONMe_2$(270 K)			$(84)^g$			

[a] Taken from References.[3−5] [b] Ref 3,4. [c] Ref 15. [d] Ref 5. the values of Mercury, Veillard and Tardy,[5] equivalent to our value of θ_P *(*H_2O*,s*-s) for oxides and oxyhydroxides, include some 'constitutive' water, such as $Mg(OH)_2 = MgO{\cdot}H_2O$, which we have generally excluded from our own hydrate analyses. [e] For sulfates alone, $\theta_{C_p}\{H_2O,s-s\} = 39.5 \pm 5.2$ J K^{-1} mol^{-1}; for other hydrates, $\theta_{C_p}\{H_2O,s-s\} = 44.3 \pm 2.7$ J K^{-1} mol^{-1}. [f] This work (cf. Figure 2). [g] This work (cf. Table 3).

According to eq 1a, the simple addition of the constant, $\theta_P\{L,p-p\}$, for each bound solvent molecule to the corresponding thermodynamic value reported for the parent (unsolvated) salt yields the corresponding property of the solvated salt, whereas the thermodynamic value of the parent may be obtained from that of a solvate by subtraction of the appropriate number of $\theta_P\{L,p-p\}$ values. The properties of the same parent with different numbers of bound solvent molecules may be derived similarly, as also solvates with differing numbers of bound solvent molecules, using eq 1b.

Using the data for the calcium chloride hydrates (for which $n = 1, 2, 4$, and 6) in Table 2 of ref 1, it is easy to verify that $[\Delta_f H°\{CaCl_2{\cdot}nH_2O,s\} - \Delta_f H°\{CaCl_2,s\}]$, is linear when plotted versus *n*, with a correlation coefficient $r^2 = 0.9998$ and gradient $\theta_{H_f}\{H_2O,s-s\} = -299.2$ kJ mol^{-1}, whereupon $\Delta_r P = [\theta_{H_f}\{H_2O,s-s\} - \Delta_f H°\{H_2O,g\}]$, the average enthalpy change per mole of (gaseous) water addition, is equal to $-299.2 - (-241.818) = -57.4$ kJ mol^{-1}. These values compare extremely closely with the overall average values of $\theta_{H_f}\{H_2O,s-s\} = -298.6$ kJ mol^{-1} and of $\Delta_r P = [\theta_{H_f}\{H_2O,s-s\} - \Delta_f H°\{H_2O,g\}] = -56.7$ kJ mol^{-1} obtained for the *entire set* of hydrates listed in the NBS thermochemical database.[14] It is therefore seen that the difference rule parameters are rather reliably transferable.

The Difference Rule Exemplified by Heat-Capacity, $C_p°$, Data for Hydrates. The equivalent of our difference rule values of $\theta_P\{H_2O,s-s\}$ have earlier been reported by Mercury, Vieillard, and Tardy[5] within groupings of 134 hydrates: for $\Delta_f H°$; $\Delta_f G°$; standard molar entropies, $S°_{298}$; heat capacities, $C_p°$; and molar volumes, $V_m°$; and by ourselves[3,4] for many hydrates and other solvates. All of these results, including our own, are collected together in Table 1.

We now also include heat-capacity data for 85 ungrouped hydrates (Table 2), and use these data to validate the difference rule for the case where $P = C_p°$. In Figure 1, we plot $[C_p°\{M_pX_q{\cdot}nH_2O,s\} - C_p°\{M_pX_q,s\}]$ versus *n* for these 85 hydrates (having values of $n = 0.5$ to 18). There is a good linear correlation, with gradient $\theta_{C_p}\{H_2O,s-s\} = 40.1 \pm 0.4$ J K^{-1} mol^{-1} and correlation coefficient, $r^2 = 0.979$. However, the frequency distribution of the values of θ_{C_p}-$\{H_2O,s-s\}$ is quite strongly negatively skewed (Figure 2), with skew = −0.13 and mode = 42.8. This suggests that the most favorable value to use for $\theta_{C_p}\{H_2O,s-s\}$ is the mode value, 42.8 J K^{-1} mol^{-1}.

To examine the difference rule as it applies to DMSO solvates (below), we require a value for $C_p\{Zn(NO_3)_2,s\}$, which does not appear in the literature. Using the ion summations for C_p listed by Spencer[16] gives a value 150.6 J K^{-1} mol^{-1}. A check on this value might also (in a procedure suggested anonymously to us) be obtained from the literature value[14] of $C_p\{Zn(NO_3)_2{\cdot}6H_2O,s\} = 323$ J K^{-1} mol^{-1}, by subtracting the bound water contribution; however, comparison with $C_p\{Ni(NO_3)_2{\cdot}6H_2O,s\} = 462$ J K^{-1} mol^{-1}, which would be expected to be closely similar in value on the basis of well-established additivity principles, demonstrates that the published heat capacities of these high

---

(14) (a) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm., R. H. NBS Technical Note 270−3, *Selected Values of Chemical thermodynamic properties, Tables for the First Thirty-Four Elements In the Standard Order of Arrangement*; U.S. Department of Commerce, National Bureau of Standards, January, 1968. (b) 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,* Suppl. 2.

(15) Helgeson, H. C.; Delany, J. M.; Nesbitt, H. W.; Bird, D. K. *Am. J. Sci.* **1978**, *278A*, 1−229, see p 49 ff.

(16) Spencer, P. J. *Thermochim. Acta* **1998**, *314,* 1−21.

Table 2. Heat-Capacity Data, $C_p^\circ\{M_pX_q.nH_2O,s\}$ for Hydrated Salts and Related Species, and Their Unhydrated Parents, $C_p^\circ\{M_pX_q,s\}$, and Individual Heat-Capacity Increments Per Mole of H_2O (cf. Figures 2 and 3)

parent	C_p° {parent} $J\ K^{-1}\ mol^{-1}$	hydrate	C_p° {hydrate} $J\ K^{-1}\ mol^{-1}$	*n*	C_p° increment $J\ K^{-1}\ mol^{-1}$	increment per H_2O $J\ K^{-1}\ mol^{-1}$
$(COOH)_2$	97.55	$2H_2O$	178.23	2	80.68	40.3
AgF	51.921	$2H_2O$	130	2	78.079	39.0
AgF	51.921	$4H_2O$	209	4	157.079	39.3
$Al_2(SO_4)_3$	259.41	$6H_2O$	492.9	6	233.49	38.9
$Al_2(SO_4)_3$	259.41	$18H_2O$	987.34	18	727.93	40.4
Al_2O_3	79	$1H_2O$	106.19	1	27.19	27.2
Al_2O_3	79	$1H_2O$	131.25	1	52.25	52.3
Al_2O_3	79	$3H_2O$	183.47	3	104.47	34.8
$AlCl_3$	91.84	$6H_2O$	296.2	6	204.36	34.1
AlF_3	80.48	$3.5H_2O$	210.45	3.5	129.96	37.1
$BaCl_2$	75.142	$2H_2O$	161.96	2	86.818	43.4
$BeSO_4$	86.008	H_2O	119.5	1	34.0	34.0
$BeSO_4$	86.008	$2H_2O$	152.844	2	66.836	33.4
$BeSO_4$	86.008	$4H_2O$	216.441	4	130.433	32.6
$CaCl_2$	76.18	$6H_2O$	293.41	6	217.23	36.2
$CaHPO_4$	110.04	$2H_2O$	197.07	2	87.03	43.5
$CaSO_4$	99.648	$0.5H_2O$	117.98	0.5	18.332	36.7
$CaSO_4$	99.648	$2H_2O$	186.02	2	86.372	43.2
$CdSO_4$	99.62	$1H_2O$	134.56	1	34.94	34.9
$CdSO_4$	99.62	$8/3H_2O$	213.26	2.67	113.64	42.6
$CoSO_4$	103.217	$6H_2O$	353.38	6	250.163	41.7
$CoSO_4$	103.217	$7H_2O$	390.49	7	287.273	41.0
$Cr_2(SO_4)_3$	282.4	$18H_2O$	933	18	650.6	36.1
$CuSO_4$	98.769	$1H_2O$	133.991	1	35.222	35.2
$CuSO_4$	98.769	$3H_2O$	205	3	106.231	35.4
$CuSO_4$	98.769	$5H_2O$	281.19	5	182.421	36.5
$DyCl_3$	97.068	$6H_2O$	346.015	6	248.947	41.5
$ErCl_3$	98.062	$6H_2O$	343.1	6	245.038	40.8
$EuCl_3$	107.013	$6H_2O$	366.909	6	259.896	43.3
$FePO_4$	93.5	$2H_2O$	180.54	2	87.04	43.5
$FeSO_4$	100.549	$7H_2O$	394.47	7	293.921	42.0
$GdCl_3$	88.003	$6H_2O$	347.3	6	259.297	43.2
H_3PO_4	106.06	$0.5H_2O$	126.02	0.5	19.96	39.9
$HoCl_3$	96.222	$6H_2O$	347.3	6	251.078	41.8
$K_4Fe(CN)_6$	332.21	$3H_2O$	482.42	3	150.21	50.1
$KAl(SO_4)_2$	192.97	$3H_2O$	314.32	3	121.35	40.5
$KAl(SO_4)_2$	192.97	$12H_2O$	651.88	12	458.91	38.2
$La(SO_4)_3$	280	$9H_2O$	636	9	356	39.6
$LaCl_3$	98.132	$7H_2O$	431	7	332.868	47.6
Li_2SO_4	117.57	$1H_2O$	151.08	1	33.51	33.5
LiOH	46.0[a]	$1H_2O$	79.5	1	33.5	33.5
$MgCl_2$	71.383	$1H_2O$	115.27	1	43.887	43.9
$MgCl_2$	71.383	$2H_2O$	159.2	2	87.817	43.9
$MgCl_2$	71.383	$4H_2O$	241.42	4	170.037	42.5
$MgCl_2$	71.383	$6H_2O$	315.06	6	243.677	40.6
$MgSO_4$	96.202	$1H_2O$	144.8	1	48.6	48.6
$MgSO_4$	96.202	$2H_2O$	175.5	2	79.5	39.8
$MgSO_4$	96.202	$4H_2O$	251	4	154.8	38.7
$MgSO_4$	96.202	$6H_2O$	348.11	6	251.908	42.0
$MgSO_4$	96.202	$7H_2O$	380.7	7	284.5	40.6
$Na_2B_4O_7$	186.77	$10H_2O$	615	10	428.23	42.8
Na_2CO_3	112.3	$1H_2O$	145.6	1	33.3	33.3
Na_2CO_3	112.3	$10H_2O$	550.32	10	438.02	43.8
$Na_2HPO_4{\cdot}7H_2O$	393.79	$+5H_2O$	642.72	5	248.93	49.8
$Na_2S_2O_3$	145.57	$5H_2O$	359.38	5	213.81	42.8
$Na_5P_3O_{10}$	327.02	$6H_2O$	573.6	6	246.58	41.1
$NaAlSi_2O_6$	164.43	$1H_2O$	209.91	1	45.48	45.5
$NaC_2H_3O_2$	116.39	$3H_2O$	195.92	3	79.53	26.5
NaOH(s)	59.54	$1H_2O$	90.17	1	30.63	30.6
NaOH(s)	59.54	$2H_2O$	120.2	2	60.66	30.3
NaOH(s)	59.54	$3.5H_2O$	190	3.5	130.46	37.3
Na_2SO_4	128.1	$10H_2O$	518.8	10	390.7	39.1
$Nd_2(SO_4)_3$	272.638	$8H_2O$	606.3	8	333.662	41.7
$NdCl_3$	99.102	$6H_2O$	360.87	6	261.768	43.6
$NH_4Al(SO_4)_2$	226.44	$12H_2O$	683.2	12	456.76	38.1
$NiSO_4$	137.999	$6H_2O$	327.86	6	189.861	31.6
$NiSO_4$	137.999	$7H_2O$	364.59	7	226.591	32.4
$SmCl_3$	99.528	$6H_2O$	361.5	6	261.972	43.7
$SrBr_2$	76.857	$1H_2O$	120.9	1	44.043	44.0
$SrBr_2$	76.857	$6H_2O$	343.5	6	266.643	44.4

Table 2 (Continued)

parent	$C_p°$ {parent} J K^{-1} mol^{-1}	hydrate	$C_p°$ {hydrate} J K^{-1} mol^{-1}	*n*	$C_p°$ increment J K^{-1} mol^{-1}	increment per H_2O J K^{-1} mol^{-1}
$SrCl_2$	75.6	$1H_2O$	120.1	1	44.5	44.5
$SrCl_2$	75.6	$2H_2O$	160.2	2	84.6	42.3
SrI_2	77.963	$1H_2O$	119.2	1	41.237	41.2
SrI_2	77.963	$2H_2O$	163.6	2	85.637	42.8
SrI_2	77.963	$6H_2O$	355.2	6	277.237	46.2
$UO_2(NO_3)_2$	187.682	$2H_2O$	278.2	2	90.518	45.3
$UO_2(NO_3)_2$	187.682	$6H_2O$	466.9	6	279.218	46.5
UO_2SO_4	145.2	$3H_2O$	282.8	3	137.6	45.9
UO_3	81.667	$1H_2O$	117.347	1	35.68	35.7
UO_3	81.667	$2H_2O$	154.405	2	72.738	36.4
$YbCl_3$	95.348	$6H_2O$	341.4	6	246.052	41.0
$ZnSO_4$	99.062	$1H_2O$	153.559	1	54.497	54.5
$ZnSO_4$	99.062	$2H_2O$	198.738	2	99.676	49.8
$ZnSO_4$	99.062	$6H_2O$	357.966	6	258.904	43.2
$ZnSO_4$	99.062	$7H_2O$	379.151	7	280.089	40.0
					Mean	40.3
					Mode	42.8

[a] *Handbook of Chemistry and Physics*, 87th ed.; Lide, D. R., ed.; CRC Press: Boca Raton, London, New York, Washington, D.C., 2006−2007; Sec. 5−4 ff.

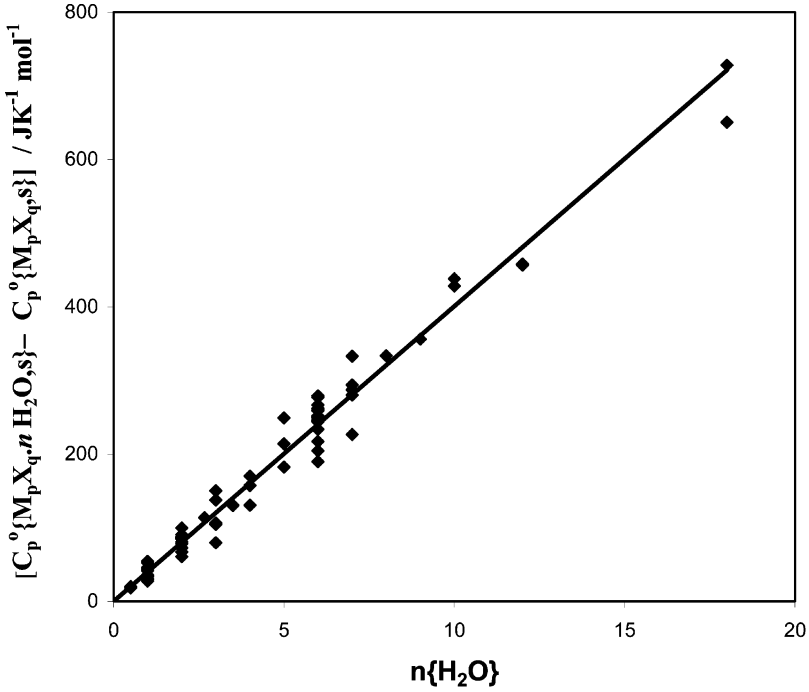

Figure 1. Plot of [$C_p°$\{hydrate,s\} − $C_p°$\{parent\}]/J K^{-1} mol^{-1} versus $n\{H_2O\}$ constrained to pass through the origin. Gradient, $\theta_{C_p}\{H_2O,s-s\} = 40.1 \pm 0.4$ J K^{-1} mol^{-1}; correlation coefficient, $r^2 = 0.978$; 85 points (but see also Figure 2).

hydrates may not necessarily be reliable. Ion summation[16] yields $C_p\{Ni(NO_3)_2,s\} = 156.5$ J K^{-1} mol^{-1}, similar to the ion summation value reported above for $Zn(NO_3)_2$. The expected heat capacities of both hexahydrates should then approximate 390 J K^{-1} mol^{-1}. This is further broadly confirmed by comparison of the heat-capacity values[14] for the sulfate hexahydrates: $ZnSO_4$, where $C_p\{ZnSO_4{\cdot}6H_2O,s\} = 357.69$ J K^{-1} mol^{-1} and α-$NiSO_4$, where $C_p\{NiSO_4{\cdot}6H_2O,s\} = 327.86$ J K^{-1} mol^{-1}.

Validation of Existing Literature Data using the Difference Rule. In Table 2, we have calculated $\theta_{C_p}\{H_2O,s-s\}$ for each of the hydrates listed. Examination of the table shows anomalously low values (when compared with the mode $\theta_{C_p}\{H_2O,s-s\}$ value of 42.8 J K^{-1} mol^{-1}) for the two lithium salts, for $NaAc{\cdot}3H_2O(s)$, and for $NaOH{\cdot}nH_2O(s)$, and a rather high value for $ZnSO_4{\cdot}H_2O(s)$. These observations suggest that these experimentally based values should be revisited. A particularly interesting case is that for $C_p°\{Al_2O_3{\cdot}H_2O,s\}$ where neither of the two values cited in Table 2, namely, 106.19 and 131.25 J K^{-1} mol^{-1}, yields a satisfactory incremental value. However, we may predict an additive difference rule value, $C_p°\{Al_2O_3{\cdot}H_2O,s\} = 79 + 42.8 = 122$ J K^{-1} mol^{-1}, which is close to the mean of the two inconsistent reported values. But, the four polymorphic forms of Al_2O_3 do further complicate matters:[17] $C_p°\{Al_2O_3$, α ≡ corundum, s\} = 79.038; $C_p°\{Al_2O_3$, γ, s\}

---

(17) Barin, I.; Sauert, F.; Schultze−Rhonof, E. W.; Sheng, S. *Thermochemical data of Pure Substances*, VCH, Weinheim, FRG, 1993.

Table 3. Heat-Capacity Data (J K^{-1} Mol^{-1}) for DMSO and DMF Solvates

T (K)	Parent	C_p\{solvate\}	C_p\{parent\}	difference	*n*-\{DMF\} n	difference/*n*	average
298	DMF(*l*)						C_p(DMF,l) = 150.6[f]
270	$AgNO_3$(*s*)	253.4[a]	87.88[d]	165.5	1.98	83.6	84
					\{*n*-DMSO\}		
255	DMSO(*s*)						C_p(DMSO,*s*) = 107.84[g]
255		239.1[b]	69.4[d]	169.7	1.38	123.0	
255		275.7[b]	69.4[d]	206.3	1.98	104.2	
255		448.5[b]	69.4[d]	379.1	2.94	128.9	
255	$ZnCl_2$(*s*)	633.6[b]	69.4[d]	564.2	4	141.1	137
255		794.0[b]	69.4[d]	724.6	5.03	144.1	
255		1041.6[b]	69.4[d]	972.2	6.02	161.5	
255		1334.2[b]	69.4[d]	1264.8	8	158.1	
255		368.0[a]	150.6[e]	217.4	2.24	97.1	
255	$Zn(NO_3)_2$(*s*)	765.2[a]	150.6[e]	614.6	6	102.4	105
255		1097.6[a]	150.6[e]	947.0	8.11	116.8	
255	$NaNO_3$(*s*)	438.9[a]	71.1[d]	367.8	2.85	129.1	129.1
270	DMSO(*s*)						C_p(DMSO,*s*) = 115.8[g]
270		245.4[b]	70.1[d]	175.3	1.38	127.0	
270		291.3[b]	70.1[d]	221.2	1.98	111.7	
270		493.6[b]	70.1[d]	423.5	2.94	144.0	
270	$ZnCl_2$(*s*)	725.7[b]	70.1[d]	655.6	4	163.9	156
270		912.8[b]	70.1[d]	842.7	5.03	167.5	
270		1248.6[b]	70.1[d]	1178.5	6.02	195.8	
270		1543.7[b]	70.1[d]	1473.6	8	184.2	
270		385.5[a]	150.6[e]	234.9	2.24	104.9	
270	$Zn(NO_3)_2$(*s*)	816.6[a]	150.6[e]	666.0	6	111.0	114
270		1178.5[a]	150.6[e]	1027.9	8.11	126.7	
270	$NaNO_3$(*s*)	481.0[a]	81.24[d]	399.8	2.85	140.3	140
290	DMSO (*s*)						C_p(DMSO,s) =125.4[g]
290	kaolinite(*s*)	341.8[c]	241.7[c]	100.1	0.94	106.5	107
350	DMSO(*l*)						C_p(DMSO,l) = 157.9[g]
350		341.1[b]	73.7[d]	267.4	1.38	193.8	
350		425.0[b]	73.7[d]	351.3	1.98	177.4	
350		685.9[b]	73.7[d]	612.2	2.94	208.2	
350	$ZnCl_2$(*s*)	775.4[b]	73.7[d]	701.7	4	175.4	190
350		1028.7[b]	73.7[d]	955.0	5.03	189.9	
350		1245.3[b]	73.7[d]	1171.6	6.02	194.6	
350		1601.3[b]	73.7[d]	1527.6	8	191.0	
350		478.9[a]	150.6[e]	328.3	2.24	146.6	
350	$Zn(NO_3)_2$(*s*)	1090.9[a]	150.6[e]	940.3	6	156.7	161
350		1610.3[a]	150.6[e]	1459.7	8.11	180.0	
350	$NaNO_3$(*s*)	705.5[a]	103.3[d]	602.2	2.85	211.3	211

[a] From Table 1 in ref 21. [b] From Table 1 in ref 22 by using the formula for $C_p\{ZnCl_2,s\} = A + BT$, where *T* is the absolute temperature. [c] Ref 23b [d] *HSC Chemistry 5.11*, Outokumpu Research: Oy, Finland, 2002. [e] Value predicted using parameters in Tables 1 and 2 of ref 16. [f] *Handbook of Chemistry and Physics*, 82nd ed.; Lide, D. R., ed.; CRC Press: Boca Raton, London, New York, Washington, D.C., 2006−2007; Sec. 5−5 ff. [g] Ref 23a.

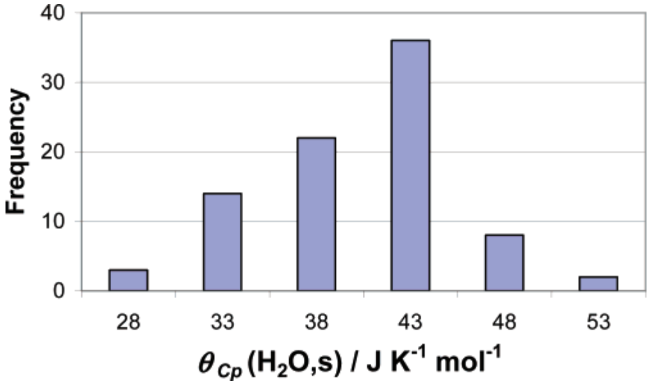

Figure 2. Frequency distribution of $\theta_{C_p}\{H_2O,s-s\}$/J K^{-1} mol^{-1} of data in Table 1, showing the non-normal distribution, with corresponding values for the distribution: mode = 42.8 and skew = −0.13.

= 82.706; $C_p°\{Al_2O_3, \delta, s\} = 81.362$, and $C_p°\{Al_2O_3, \kappa, s\} = 80.730$ J K^{-1} mol^{-1}.

The Difference Rule Applied to Heat Capacities of DMSO and DMF as Bound Solvents. The only cases for which we have found sequences of heat-capacity data for condensed-phase nonaqueous bound solvents are for DMSO (dimethylsulfoxide) solvates and for the related DMF (*N*,*N*-dimethylformamide) solvate (but having only one example, $AgNO_3$·1.98DMF, for the latter). DMSO is a colorless, odorless (when pure), and very hygroscopic stable liquid (mp 291.4 K, bp 462 K) with heat capacity,[14] $C_p°\{DMSO,l\} = 153.0$ J K^{-1} mol^{-1}. Heat-capacity data have been recorded[20,21] for the solvates of DMSO listed in Table 3. In Figure 3, we plot [$C_p°\{M_pX_q·n\mathrm{DMSO},s\}$.

In addition, Danil de Namor and her colleagues have studied the interactions of some cations with a variety of coordinating species in various solvents, yielding solid-state coordination data.[18] While thermodynamically interesting, the reported data unfortunately do not include solvate sequences;

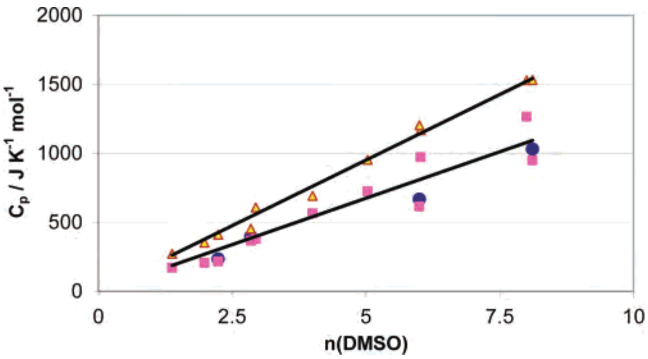

Figure 3. Plot of $[C_p°\{M_pX_q{\cdot}n\mathrm{DMSO,s}\} - C_p°\{M_pX_q\mathrm{,s}\}]$ versus $n\{\mathrm{DMSO}\}$, constrained to pass through the origin. The slope of the fitted curve is 190 at 365 K (with $r^2 = 0.99$) and 135 J K^{-1} mol^{-1} at 255 K (with $r^2 = 0.90$). The heat capacity of DMSO at 298 K is 153 J K^{-1} mol^{-1}. Circles for Zn$(NO_3)_2{\cdot}n$DMSO and $NaNO_3$·DMSO at 270 K; squares for $ZnCl_2{\cdot}n$DMSO at 255 K; and triangles for $ZnCl_2{\cdot}n$DMSO at 365 K.

Table 4. Thermodynamic Data[14] for NaOH and Its Hydrates, $NaOH{\cdot}nH_2O$

salt or hydrate, $NaOH{\cdot}nH_2O$	C_p J K^{-1} mol^{-1}	$\Delta_fH°$ kJ mol^{-1}	$\Delta_fG°$ kJ mol^{-1}	$S°$ J K^{-1} mol^{-1}
NaOH(s)	59.54	−425.609	−379.494	64.455
NaOH(l)	86.102	−418.8	−336.352	121.409
$NaOH{\cdot}H_2O$(s)	90.17	−734.543	−629.338	99.50
$NaOH{\cdot}2H_2O$(l)	239.41	−1019.076	−873.091	195.979
$NaOH{\cdot}3.5H_2O$(l)	354.43	−1459.798	−1236.356	286.089
$NaOH{\cdot}4H_2O$(l)		−1605.15	−1356.64	318.70
$NaOH{\cdot}5H_2O$(l)		−1894.31	−1596.34	386.06
$NaOH{\cdot}7H_2O$(l)		−2469.02	−2073.80	526.31

Table 5. Values of $\theta_P\{H_2O\mathrm{,s-s}\}$ and $\theta_P\{H_2O\mathrm{,l-l}\}$ for NaOH Hydrates Compared to General Values for Hydrates from Table 1

Water as solvent, L = H_2O(s)	**$\theta_{C_p}\{H_2O\mathrm{,s-s}\}$ J K^{-1} mol^{-1}**	**$\theta_S\{H_2O\mathrm{,s-s}\}$ J K^{-1} mol^{-1}**	**$\theta_{H_f}\{H_2O\mathrm{,s-s}\}$ kJ mol^{-1}**	**$\theta_{G_f}\{H_2O\mathrm{,s-s}\}$ kJ mol^{-1}**
NaOH hydrate(*s*) (single example)	(31)	(35)	(−309)	(−250)
	cf. 42.8 ± 5.5	cf 40.9[a]	cf. −298.6[a]	cf. −242.4[a]
Water as solvent, L = H_2O(l)	**$\theta_{C_p}\{H_2O\mathrm{,l-l}\}$ J K^{-1} mol^{-1}**	**$\theta_{S_o}\{H_2O\mathrm{,l-l}\}$ J K^{-1} mol^{-1}**	**$\theta_{H_f}\{H_2O\mathrm{,l-l}\}$ kJ mol^{-1}**	**$\theta_{G_f}\{H_2O\mathrm{,l-l}\}$ kJ mol^{-1}**
NaOH hydrates(l) supercooled	(76.7)	53.4	−284.8	−251.9
	(limited data set)	($r^2 = 0.9545$)	($r^2 = 0.9996$)	($r^2 = 0.9972$)

some tentative comments on the possible additive thermodynamic contributions within complexes have been made.[19]

Extension of the Solvate Difference Rule to Supercooled NaOH(l). NaOH, like many substances containing hydroxyl groups, supercools readily. The heat capacities of supercooled liquid sodium hydroxide and its liquid hydrates have been studied by Siemens and Giaque;[22] their results are reproduced in the NBS thermochemical tables[14] and appear in Table 4, where the results for NaOH hydrates and the parent salt in both solid and liquid phases are included.

In the table, several hydrates (n = 2, 3.5, 4, 5, and 7) supercooled below their freezing points and, hence, remaining as liquids, are listed. It is interesting to examine whether our difference rule applies in such cases because we anticipate that our procedures will apply generally to condensed phases.

We investigate two difference functions, namely the s−s and l−l versions $[P\{NaOH{\cdot}nH_2O\mathrm{,s}\} - P\{NaOH\mathrm{,s}\}]$ and $[P\{NaOH{\cdot}nH_2O\mathrm{,l}\} - P\{NaOH\mathrm{,l}\}]$. The quantity $[P\{NaOH{\cdot}H_2O\mathrm{,s}\} - P\{NaOH\mathrm{,s}\}]$ for the single solid-hydrate phase example for which data are available gives rise to the difference quantity $\theta_P\{H_2O\mathrm{,s-s}\}$ shown in the top half of Table 5, where it is compared to the values for $\theta_P\{H_2O\mathrm{,s-s}\}$, obtained from our previous work[3,4] for hydrates in general. On the basis of this single example, these values compare reasonably well for $P = \Delta_fH°$ and $\Delta_fG°$, but differ somewhat for $P = C_p$ and $S°$.

The l−l function, $\theta_P\{NaOH\mathrm{,l\text{-}l)}\} = [C_p\{NaOH{\cdot}nH_2O\mathrm{,l}\} - C_p\{NaOH\mathrm{,l}\}]$ can be evaluated for the larger data set consisting of five supercooled hydrates of NaOH, and gives rise to the incremental values shown in the lower half of Table 5. The difference rule holds up well for these supercooled materials (Figures in Supporting Information). Despite the phase change, the values for $\theta_P\{H_2O\mathrm{,l-l}\}$ are similar in magnitude to those established for $\theta_P\{H_2O\mathrm{,s\text{-}s)}\}$ for $P = \Delta_fH°$ and $\Delta_fG°$, although they are somewhat different (on the basis of limited data) for $P = C_p$ and $S°$ (with poorer correlation coefficients also).

Hydration/Solvation Processes. The thermodynamics of solvation in a condensed phase are described by the standard Gibbs thermodynamic relation:

$$\Delta_rG = \Delta_rH - T\Delta_rS \tag{4}$$

where Δ_rG, Δ_rH, and Δ_rS are, respectively, the Gibbs energy, the enthalpy, and the entropy of reaction at the absolute temperature, T. If the Gibbs energy is negative, then the process is thermodynamically (but not necessarily kinetically) feasible at T. Although neither Δ_rH nor Δ_rS vary much with temperature in a given phase, the feasibility will alter with temperature through the above relation and also with pressure (for which the latter most affects Δ_rS if one of the reaction components is gaseous). Thus, the prime thermodynamic requirement in attempting to establish the nature of condensed-phase solvation is to consider the enthalpy and entropy changes involved.

The Role of Thermodynamic Parameters as Indicators of the Nature of Hydrate (Solvate) Binding Interactions.[15] If we know, for example, the entropy or heat capacity of a water molecule within the environment of a crystalline hydrate, zeolite, or other material, then a low value compared to the corresponding value for ice would tend to signify a rigid, possibly restricted environment. If, on the other hand, the values for the water molecule are relatively large, then this would indicate a less-constrained environment. In general, then, by comparing $\theta_P\{\mathrm{L,s-s}\}$ with the value of $P\{\mathrm{L,s}\}$, we are able to infer something of the condition of the solvated molecule in its solid solvate.

---

(18) de Namor, A. F. D.; Cleverley, R. M.; Zapata−Ormachea, M. L. *Chem. Rev.* **1998**, *98*, 2495−2525. de Namor, A. F. D.; Kowalska, D. *J. Phys. Chem. B* **1997**, *101*, 1643−1648. de Namor, A. F. D. *Coord. Chem. Rev.* **1999**, *190−192*, 283−295.

(19) de Namor, A. F. D; Jenkins, H. D. B. *Chem. Comm.* **2005**, 3844−3846.

(20) Skokanek, M.; Slama, I. *Collect. Czech. Chem. Comm.* **1987**, *52*, 2188−2193.

(21) Skokanek, M.; Slama, I. *Collect. Czech. Chem. Comm.* **1988**, *53*, 3072−3079.

(22) Siemens, P. R.; Giaque, W. F. *J. Phys. Chem.* **1969**, *73*, 149−157.

Table 6. Average Thermodynamic Reaction Parameters for the Processes Listed

process	$[\theta_{H_f}\{H_2O,s-s\} - \Delta_f H°(H_2O,g)]$ kJ mol^{-1}	$[\theta_S\{H_2O,s-s\} - S°(H_2O,g)]$ J K^{-1} mol^{-1}	$[\theta_{G_f}\{H_2O,s-s\} - \Delta_f G°(H_2O,g)]$ kJ mol^{-1}
Average values found for process in which gaseous water is converted to hydrated water in solid hydrate at 298 K. $M_pX_q(s) + H_2O(g) \rightarrow M_pX_q·H_2O(s)$ [a]	−56.8	−147.9	−13.8 / −12.7
	$\Delta_r H$ kJ mol^{-1}	**$\Delta_r S$ J K^{-1} mol^{-1}**	**$\Delta_r G$ kJ mol^{-1}**
Thermodynamic values for process of conversion of gaseous water into metastable ice: $H_2O(g) \rightarrow$ metastable ice $H_2O(s)$ (298 K)	−50.9[b]	−140.8[b] −143.9	−8[b]
Thermodynamic values for process of conversion of gaseous water into ice: $H_2O(g) \rightarrow$ ice $H_2O(s)$ (273 K)	−51.1[c] (−50)[c]	−144[c] (−142)[c]	
Thermodynamic values for process of conversion of gaseous water into liquid water: $H_2O(g) \rightarrow H_2O(l)$ (298 K)	−44.0[b]	−118.9[b]	−8.6[b]

[a] For details of these and related calculations see the Supporting Information. [b] Obtained directly from standard thermodynamic data tables. [c] Temperature adjusted data.

Table 7. Experimental Thermodynamic Parameters for Water (H_2O) as a Gas, Liquid, and Solid, All at a Temperature of 298 K and a Pressure of 1 Bar, and in Other Environments[a]

water	V_m nm^3	$C_p°$ J K^{-1} mol^{-1}	$S°$ J K^{-1} mol^{-1}	$\Delta_f H°$ kJ mol^{-1}	$\Delta_f G°$ kJ mol^{-1}
H_2O, g, 298 K		33.590	188.834	−241.826	−228.582
H_2O, l, 298 K	0.02984	75.351	69.950	−285.830	−237.141
metastable ice (H_2O, s, 298 K)		42	48 44.92[d]	−292 −292.76[b]	−237
ice (H_2O, s, 273 K)	0.02743	38.0	41.3	−293	−240
ices[b]	0.02607 ± 0.0028	36.2 ± 5.5	45.8 ± 2.8	−291.0 ± 1.4	−235.1 ± 1.4
water in zeolites	0.0133[b]		59[c]		
water in hydrous Mg−corderite at 1 bar and 298 K	0.0	42.2 ± 2.1[e]	80.6[e]		

[a] The data for ice have been determined by interpolation and extrapolation from published data (Supporting Information). [b] Ref 5, [c] Ref 15. Note that V_m values in ref 2, in both the mineral (structural water) and zeolites (water in channels) rows were converted to nm^3 by an incorrect factor, omitting the numeric value of the Avogadro constant. [d] Ref 27. [e] Ref 31. Note that $S°$ (this table) = $[\Delta_{hyd}S°$ (Table 8) + $S°(H_2O,g)$ (first row)] = −108.2 + 188.834 = 80.6 J K^{-1} mol^{-1}.

Hydrates. Hydration water is commonly described as ice-like, that is, it is more restricted than in liquid water, but this does not imply a particular structure to the water molecules. Our parameters reflect this (Table 6 and the appendix in the Supporting Information) because comparison of the *average* parameters $[\theta_P\{H_2O,s-s\} - P\{H_2O,g\}]$, where $\theta_p \equiv \theta_{H_f} = -56.8$ kJ mol^{-1} and $\theta_p \equiv \theta_s = -147.9$ J K^{-1} mol^{-1}, corresponding to the enthalpy and entropy changes for the process where a water molecule from the gas phase is incorporated into a solid hydrate, compare most closely with the enthalpy (−51.1 kJ mol^{-1}) and entropy (−144 J K^{-1} mol^{-1}) changes needed to convert gaseous water into solid ice at 273 K and less so to the corresponding conversion to liquid water, $H_2O(l)$, at 298 K. The water vapor pressure above a hydrate is generally well below 1 atm, so that the dehydration temperature under ambient conditions is generally well above the temperature calculated from eq 4, that is, the hydrate needs to be heated well above 100 °C to promote dehydration. Basic thermodynamic parameters for various forms of water appear in Table 7 and in the Supporting Information.

Certain elements and nonpolar compounds form hydrates. These can be hydrates of gaseous substances, such as methane, in which case they are only formed under pressure, are very unstable, and have melting points close to ambient temperature. In these clathrate hydrates, the water molecules behave as though they were ice-like. At the other extreme, there are hydrates in which the water molecules reside in tunnels or cavities of a rigid framework, as in zeolites. Intermediate between these two are hydrates of acids, salts, and hydroxides in which the water, anions, and cations are packed together to form a structure characteristic of the hydrate. In most hydrates, $M_pX_q·nH_2O$, the water molecules tend to associate with the cations, M^{q+} (although not exclusively), and the nature of the coordination group around the cation can be used as a basis for classification. Whereas removal of the water in the zeolites does not result in a structural collapse, removal of the water in the hydrates generally causes such a collapse and rearrangement of the structure (thus the parent and hydrates often do not have identical structures, except in rather rare instances).

In our own hydrate analyses, we have generally excluded the presence of constitutive water from consideration, such as that found in $Mg(OH)_2 \equiv MgO·H_2O$. The Gibbs energy change for the (hypothetical) process of forming a monohydrate of magnesium oxide can be estimated from the difference rule[3,4] as follows:

$$\mathrm{MgO}(s) + \mathrm{H_2O}(g) \rightarrow \mathrm{MgO{\cdot}H_2O}(s)$$

$$\Delta_r G = [\theta_{G_f}\{\mathrm{H_2O,s{-}s}\} - \Delta_f G^\circ\{\mathrm{H_2O,g}\}]$$

$$\approx [-242.4 - (-228.6)] = -13.8\ \mathrm{kJ\ mol^{-1}} \tag{5}$$

which corresponds to the average value found for the conversion of gaseous to hydrated water in most hydrates (Table 6, column 4), whereas the constitutive process of formation of $\mathrm{Mg(OH)_2}(s)$

$$\mathrm{MgO}(s) + \mathrm{H_2O}(g) \rightarrow \mathrm{Mg(OH)_2}(s)$$

$$\Delta_r G = \Delta_f G^\circ\{\mathrm{Mg(OH)_2,s}\} - \Delta_f G^\circ\{\mathrm{MgO,s}\} - \Delta_f G^\circ\{\mathrm{H_2O,g}\}$$

$$= -833.6 - (-568.9) - (-228.6) = -36.1\ \mathrm{kJ\ mol^{-1}} \tag{6}$$

can be estimated from thermodynamic data[17] and is found to offer an additional 22 kJ $\mathrm{mol^{-1}}$ of Gibbs energy stability over that of monohydrate formation. One may conclude that hydration of the cation in the hydrate is fairly weak, whereas the water in $\mathrm{Mg(OH)_2}$ is more intimately bound. A comparison of the above value with the value of $[\theta_{G_f}\{\mathrm{H_2O,s{-}s}\} - \Delta_f G^\circ\{\mathrm{H_2O,g}\}]$ in Table 4 shows that the latter process is a very different one when compared to normal hydrate reactions. The environment of the water has clearly been altered significantly, and constitutive incorporation of water must be regarded as a separate process from simple solvation.

Dimethylsulfoxide (DMSO) Solvates. The heat capacity of pure liquid DMSO has been studied by Clever and Westrum,[23a] and is recorded at 298 K as $C_p^\circ\{\mathrm{DMSO,s}\} = 125.4$ J $\mathrm{K^{-1}\ mol^{-1}}$ and $C_p^\circ\{\mathrm{DMSO,l}\} = 153.0$ J $\mathrm{K^{-1}\ mol^{-1}}$ while at 350 K, $C_p^\circ\{\mathrm{DMSO,l}\} = 158$ J $\mathrm{K^{-1}\ mol^{-1}}$. Analysis of the heat-capacity data listed in Table 3 shows, for the $\mathrm{Zn(NO_3)_2}$ solvate, $\theta_{C_p}\{\mathrm{DMSO,s{-}s}\} = 105$ J $\mathrm{K^{-1}\ mol^{-1}}$ at 255 K, rising to 161 J $\mathrm{K^{-1}\ mol^{-1}}$ at 350 K; that is to say, the incremental increase in the heat capacity of the parent salt or existing solvate of DMSO by the further addition of a single DMSO molecule to the structure is smaller than that of solid DMSO at low temperatures but comparable to that of liquid DMSO at high temperatures. The corresponding C_p increment for DMSO in kaolinite at 290 K also has a low value.[23b] For $\mathrm{ZnCl_2}$ and $\mathrm{NaNO_3}$ solvates, the values of θ_{C_p} are much larger. DMSO acts as an electron donor to form coordination compounds with a large number of inorganic ions. In most of its complexes, the DMSO ligand is attached through the oxygen atoms, and the bond strength is found to be roughly that of the corresponding aquo ($\mathrm{H_2O}$) derivative. The values noted above suggest that DMSO is strongly constrained in the $\mathrm{Zn(NO_3)_2}$ and kaolinite solvates but is much freer in the other solvates for which we have data.

***N,N*-Dimethylformamide (DMF) Solvate.** Comparison of the heat capacity of pure liquid DMF ($C_p^\circ = 150.6$ J $\mathrm{K^{-1}\ mol^{-1}}$, Table 3) with $\theta_{C_p}\{\mathrm{DMF,s{-}s}\} = (253.4 - 87.88)/1.98 = 83.6$ J $\mathrm{K^{-1}\ mol^{-1}}$ (obtained from a C_p° value for a *single* DMF solvate, Table 3) suggests that the DMF within the $\mathrm{AgNO_3}$ solvate may behave in a solid-like manner, as with the DMSO solvates of $\mathrm{Zn(NO_3)_2}$.

Supercooled Liquid NaOH. The heat-capacity increment per water molecule in supercooled liquid NaOH, $\theta_{C_p}\{\mathrm{NaOH,l{-}l}\} = 76.7$ J $\mathrm{K^{-1}\ mol^{-1}}$, is very close to the heat capacity, $C_p^\circ\{\mathrm{H_2O,l}\}$, of liquid water at 298 K, namely 75.3 J $\mathrm{K^{-1}\ mol^{-1}}$, consistent with the water molecules being in approximately the same state as in liquid water, free to librate.

Zeolites, Layered, and Microporous Hydrous Silicate Minerals: Comparison of Binding with that in Hydrates. Zeolites[24−26] are characterized by having water molecules contained within them that show a range of behaviors, varying from having some hydrogen bonding with their crystal structure framework, intramolecular bonding between the water molecules themselves, and interaction with extraframework cations. Recent thermodynamic studies of the hydrotalcite-like layered structures[27] and of the hydrosodalite family[28] of zeolites have yielded some further information on the state of hydration waters. Average hydration enthalpies, $\Delta_{hyd}H$ of −76.7 and −37.0 ± 2.4 kJ $\mathrm{mol^{-1}}$ were obtained for the Na8 and Na6 members, respectively, of the hydrosodalite series; Table 8 gives further data, showing ranges for the compounds listed, of

$$-9.5 \geq \Delta_{hyd}G^\circ/\ \mathrm{kJ\ mol^{-1}} \geq -44.9 \tag{7}$$

$$-41.8 \geq \Delta_{hyd}H^\circ/\ \mathrm{kJ\ mol^{-1}} \geq -84.9 \tag{8}$$

$$-108.2 \geq \Delta_{hyd}S^\circ/\ \mathrm{kJ\ mol^{-1}} \geq -194.3 \tag{9}$$

which straddle the parameters given in Table 6.

$$[\theta_{G_f}\{\mathrm{H_2O,s{-}s}\} - \Delta_f G^\circ\{\mathrm{H_2O,g}\}] = -13.8\ \mathrm{kJ\ mol^{-1}} \tag{10}$$

$$[\theta_{H_f}\{\mathrm{H_2O,s{-}s}\} - \Delta_f H^\circ\{\mathrm{H_2O,g}\}] = -56.8\ \mathrm{kJ\ mol^{-1}} \tag{11}$$

$$[\theta_{Sf}\{\mathrm{H_2O,s{-}s}\} - \Delta_f S^\circ\{\mathrm{H_2O,g}\}] = -147.9\ \mathrm{J\ K^{-1}\ mol^{-1}} \tag{12}$$

The conclusion from these comparisons is that materials (e.g., Na8 or hydrosodalites) with $\Delta_{hyd}G^\circ$, $\Delta_{hyd}H^\circ$, or $\Delta_{hyd}S^\circ$ values in Table 8 that are lower (i.e., more negative) than the comparison values in eqs 10−12 all have hydration water that is more firmly bound than normally found in hydrates, whereas those that are higher (i.e., less negative, for example Na6) are more loosely bound. Similarly, the hydrotalcite hydration water is described[27] as being intermediate in character between water and ice. Again by comparison, we can see that the entropy datum[15] for zeolites of 59 J $\mathrm{K^{-1}\ mol^{-1}}$ is between a value of 69.95 found for liquid water and the values of 48 or 44.92 for metastable ice, and 41.3 J $\mathrm{K^{-1}\ mol^{-1}}$ for ice itself at 273 K. There has, in contrast,

---

(23) (a) Clever, H. L.; Westrum, E. F. Jr. *J. Phys. Chem.* **1970**, *74* (6), 1309−1317. (b) Robie, R. A.; Hemingway, B. S. *Clays Clay Miner.* **1991**, *39* (4), 362−368.

(24) Kvick, A. *Trans. Am. Crystallogr. Assoc.* **1986**, *22*, 97−105.

(25) Kolesov, B. A.; Geiger, C. A. *Am. Mineral.* **2002**, *87*, 1426−1431.

(26) Kolesov, B. A.; Geiger, C. A. *Am. Mineral.* **2006**, *91*, 1039−1048.

(27) Allada, R. K.; Navrotsky, A.; Boerio-Goates, J. *Am. Mineral.* **2003**, *90*, 329−335.

(28) Moloy, E. C.; Liu, Q.; Navrotsky, A. *Microporous Mesoporous Mater.* **2006**, *88*, 283−292.

Table 8. Data for $\Delta_{hyd}G°$, $\Delta_{hyd}H°$, and $\Delta_{hyd}S°$ Per Mole of H_2O for Various Hydration Reactions Relative to Liquid Water (taken from Table 4 of Bish and Carey[a])

material	$\Delta_{hyd}G°$ kJ mol^{-1}	$\Delta_{hyd}H°$ kJ mol^{-1}	$\Delta_{hyd}S°$ J K^{-1} mol^{-1}
Cordierite,[b] $Mg_2Al_3(AlSi_5O_{18})$	−9.5	−41.8	−108.2 ± 3.2
Analcime, $NaAlSi_2O_6 \cdot H_2O$	−44.9	−84.9	−133.2
Ca-Clinoptilolite	−36.13	−76.92	−136.8
K-Clinoptilolite	−25.53, −24.9	−67.78, −81,	−141.7, −188.3
Na-Clinoptilolite	−29.68, −26.9	−74.19, −84.8	−149.3, −194.3
NaCa-mordenite	−33.5	−73.8	−134.8
Chabazite,[c] $(Ca_{0.5},Na,K)_4Al_4Si_8O_{24} \cdot 12H_2O$		−39.65 ± 9.3 (over total water content)	

[a] Bish, D. L.; Carey, J. W. *Rev. Miner. Geochem.*, **2001**, *45*, 403−452. [b] A recent article (Paukov et al.[31]) considers the heat capacity of hydrous and anhydrous cordierite, $Mg_{1.97}Al_{3.94}Si_{5.06}O_{18} \cdot 0.645H_2O$, yielding the results shown in Table 7, which agree with the entropy data given in this Table (see footnote [e], Table 7). [c] Ref 30.

also been reported[29] a very small value for the entropy of zeolitic water, but this seems to be an extrapolated value, corresponding to a zero water content of the zeolite. Some studies on chabazite,[30] a natural hydrated zeolite, yield results of extreme complexity, suggesting that the water of hydration exists in three different environments within the hydrated chabazite.

Very recently, Paukov et al.[31] have reported a study of the condition of water in hydrous Mg−cordierite. Their study shows that here the water molecules have fairly weak interaction with the structural framework, with the consequence that the water molecule approaches a free state similar to that found in water vapor. The observation that absorption of water causes little or no change in the volume of the structure is unusual in minerals and arises here because the water molecules are absorbed into the microcavities of the structure, which is itself largely unaffected.[15] The intermediate entropy contribution of 80 J K^{-1} mol^{-1} found (Table 7), when compared with the other entries in column 4 of Table 7, specifically to that for liquid water at 69.95 and for gaseous water at 188.8 J K^{-1} mol^{-1} indicates that (i) the single hydrate water molecule in cordierite is somewhat more free than in liquid water but more constrained than in the gas phase, and (ii) because the entropy in hydrates in general (where hydrogen bonding constrains the water molecules) is as low as $\theta_{S°}\{H_2O, s{-}s\} = 42.8$ J K^{-1} mol^{-1} (Table 1, column 5), there appears to be little or no hydrogen bonding to water in cordierite.

Fullerenes. The spherical-cage fullerene molecules (the most common form of which is buckminsterfullerene, C_{60}) have carbon atoms at the corners of a polyhedral structure featuring pentagons and hexagons. It appears that fullerenes readily form solvates with organic solvents, where the solvate is held by local van der Waals forces within the crystal structure.[32] Considerable thermochemical data have been generated for such fullerene solvates.[33,34] In general, formation of C_{60} solvates with arenes is said to cause significant loss of entropy and enthalpy, with a typical reaction entropy, $\Delta_r S$, being below −50 J K^{-1} mol^{-1}, which is comparable with or more negative than the entropy of freezing of pure arenes. For comparison, for benzene itself, $\Delta_{fus}H° = +9.87$ kJ mol^{-1} at 278.5 K, leading to an entropy of freezing, $\Delta_{fus}S°$, of −35.4 J K^{-1} mol^{-1}. On the other hand, solvates with alkanes are more clathrate-like (zeolitic), where the entropy and enthalpy of the reaction may be less negative than the corresponding values for the solvent on freezing or condensation.

Céolin and colleagues[35] have noted many instances where the enthalpy of the incorporation of the solvate molecule matches the enthalpy of its condensation while, at the same time, the volume of the solvate product is less than the sum of the volumes of the fullerene and the solvent; they regard this as paradoxical. However, the paradox is readily explained away because[36] locally enhanced $C_{60}{-}C_{60}$ interactions would effect the volume decrease without increasing the interactions with the solvate molecules, often lying within their own groupings.[33]

Other Solvates. We also report thermodynamic data for other solvates for which we have found appropriate thermodynamic data (Table 1), expanding on the list previously published,[3] namely, for D_2O, NH_3, ND_3, $(CH_3)_2O$, $(C_2H_5)_2O$, NaOH(s), CH_3OH, C_2H_5OH, H_2S, and SO_2.

General. We conclude that examination of the hydration (solvation) process in each of these cases using the *thermodynamic* information assembled in Tables 1, 5, and 6 and in the Supporting Information appendix can be useful for appraising the *dynamic* situation of the water environment in these materials.

---

(29) Mizota, T.; Petrova, N. L.; Nakayama, N. *J. Therm. Anal. Calorim.* **2001**, *64*, 211−217.

(30) Fialips, C. I.; Carey, J. W.; Bish, D. L. *Geochim. Cosmochim. Acta* **2005**, *69* (9), 2293−2308.

(31) Paukov, I. E.; Kovalevskaya, Y. A.; Rahmoun, N-S.; Geiger, C. A. *Am. Mineral.* **2007**, *92*, 388−396.

(32) Ahrland, S. *Pure Appl. Chem.* **1982**, *54*, 1451−1468.

(33) Céolin, R.; Michaud, F.; Toscani, S.; Agafonov, V.; Tamarit, J. L.; Dworkin, A.; Szwarc, H. *Proc.*−*Electrochem. Soc.* **1997**, *97*−*42*, 373−381.

(34) Korobov, M. V.; Stukalin, E. B.; Mirakyan, A. L.; Neretin, I. S.; Slovokhotov, Y. L.; Dzyabchenko, A. V.; Ancharov, A. I.; Tolochko, B. P. *Carbon* **2003**, *41*, 2743−2755.

(35) Céolin, R.; Tamarit, J. L.; Barrio, M.; Lopez, D. O.; Espeau, P.; Allouchi, H.; Papoular, R. J. *Carbon* **2005**, *43*, 417−424.

(36) Céolin, R.; Lopez, D. O.; Barrio, M.; Tamarit, J. L.; Espeau, P.; Nicolai, B.; Allouchi, H.; Papoular, R. *Chem. Phys. Lett.* **2004**, *399*, 401−405.

Comments

Mercury, Vieillard, and Tardy[5] suggest that it is not useful to use thermodynamic data to express how a hydrate is structured because "the hydration phenomenon is here considered as the addition of an unmodified crystal and of hydration water, different from liquid water." We would argue that the hydration (and solvation) parameters in a series of hydrates (solvates) with a common parent are rather constant (Table 2 and Figure 2, for example), which leads one to conclude that it is, indeed, the water (solvent) in its new environment that is altered, whereas the parent is hardly changed (except for those cases involving so-called constitutive water, such as $Mg(OH)_2$, as in the calculation above).

Our belief that thermodynamic and physical studies can provide useful and complementary information on the state of bound solvent molecules within a structure is strongly corroborated by a recent extensive study[37] of hydration in macrocations with polyoxometalates, combining infrared spectroscopy, water vapor sorption, and X-ray diffraction with thermodynamic information. The thermodynamics of heat capacity effects in zeolite hydration reactions (for analcime, wairakite, and natrolite) have received very detailed attention in a current publication.[38] The important influences of temperature are emphasized.

Acknowledgment. Professor Bill Carey of Los Alamos National Laboratory, New Mexico, is thanked for providing the data in Table 8.

Supporting Information Available: Calculation of thermodynamic functions for incorporation of water into *n*-hydrates and into ice; figures for difference plots for the supercooled hydrates, $NaOH \cdot nH_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701105P

---

(37) Ogasawara, Y.; Uchida, S.; Mizuno, N. *J. Phys. Chem. C* **2007**, *111*, 8218−8227.

(38) Neuhoff, P. S.; Wang, J. *Am. Mineral.* **2007**, *92*, 1358−1367.