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Relative Packing Efficiency in Hydrates[†]

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We define two parameters, Π_{ice} and Π_{parent}, estimated from hydrate and parent volumes, to be a measure of the efficiency of the packing of molecules in a hydrate compared on the one hand to that of idealized solid ice and on the other to the parent molecule from which the hydrate is derived. The packing efficiency ratio, $\Pi_{ice}[M_p \cdot X_q \cdot nH_2O]$, is defined for a general hydrate $M_p \cdot X_q \cdot nH_2O$ containing p (complex) cations M^{q+} and q (complex) anions X^{p-} by $\Pi_{ice}[\text{hydrate}] = [V_{at}(\text{parent}) - V_{at}(\text{hydrate})]/[V_{at}(\text{parent}) - 0.0082]$ where $V_{at}(\text{parent})$ and $V_{at}(\text{hydrate})$ are the average volumes occupied per atom in the parent and hydrate structures, respectively, and 0.0082 corresponds to the average volume per atom in ice. All volumes are measured in units of nm^3. $\Pi_{par}[\text{hydrate}] + \Pi_{ice}[\text{hydrate}] = 1$. Two simpler indices are studied, Π and Π^*, and we explore the use of these as a means of categorizing hydrates and defining their domain of existence.

Introduction

Crystallization of material from a suitable solvent—a traditional method of purifying materials—may result in either pure material or a solid containing a well-defined stoichiometric amount of "solvent of crystallization". In many cases, water is that suitable solvent, and accordingly many inorganic materials, M_pX_q, form hydrates, $M_pX_q \cdot nH_2O$. Well-characterized hydrates of gaseous molecules are also known but are formed only under pressure and are excluded from the present discussion. Two extreme structural entities may be characterized. In the latter compounds (clathrates), a three-dimensional framework is built of H_2O molecules in a crystalline, icelike formation, which has cavities or tunnels in which the gaseous solute molecule can reside. At the other extreme, we have a rigid structure (e.g., as found in many aluminosilicates) in which water molecules can freely enter or leave wherein the essential framework remains intact (zeolites). Between such extremes are the hydrates of salts, $M_pX_q \cdot nH_2O$, in which M^{q+} cations, X^{p-} anions, and water molecules are cojoined, packed together, and give rise to the wealth of diverse structures and stoichiometries we call hydrates. These latter materials are discussed in this paper.

Table 1. Data from Approximate Equation 22 Showing Plots of $\Pi_{ice}(M_pX_q \cdot nH_2O)$ versus *n*

	$\Pi_{ice}(M_pX_q \cdot nH_2O)$		
n	$p = q = 1$	$p = 1; q = 2$	$p = 2; q = 2$
0	0.00	0.00	0.00
1	0.60	0.50	0.43
2	0.75	0.67	0.60
3	0.82	0.75	0.69
4	0.86	0.80	0.75
5	0.88	0.83	0.79
6	0.90	0.86	0.82
7	0.91	0.88	0.84
8	0.92	0.89	0.86
9	0.93	0.90	0.87
10	0.94	0.91	0.88
11	0.94	0.92	0.89
12	0.95	0.92	0.90
13	0.95	0.93	0.91
14	0.95	0.93	0.91
15	0.96	0.94	0.92
20	0.97	0.95	0.94
25	0.97	0.96	0.95
30	0.98	0.97	0.96
35	0.98	0.97	0.96
40	0.98	0.98	0.97
45	0.99	0.98	0.97
50	0.99	0.98	0.97
55	0.99	0.98	0.98
60	0.99	0.98	0.98
65	0.99	0.98	0.98
70	0.99	0.99	0.98
80	0.99	0.99	0.98
90	0.99	0.99	0.99
100	0.99	0.99	0.99

The most common salts that form hydrates are oxy-salts, hydroxides, and halides.[1,2a] These can range from highly hydrated salts, e.g., $Cr_2(SO_4)_3 \cdot 18H_2O$, to monohydrates or even hemihydrates, e.g., $CaSO_4 \cdot 1/2H_2O$ and $VOHPO_4 \cdot 1/2H_2O$, or give rise to stoichiometric hydrate series, e.g., $MgCl_2 \cdot nH_2O$ (n = 2, 4, 6, 8, and 12); $MgBr_2 \cdot nH_2O$ (n = 6 or 10); and $MgI_2 \cdot nH_2O$ (n = 8 or 10). In the alkali metal series, for example, Li and Na do not form $MF \cdot nH_2O$ hydrates, while K (n = 2, 4), Rb (n = 3/2), and Cs (n = 2/3, 3/2) do; $LiCl \cdot nH_2O$ (n = 1, 2, 3,5) and $NaCl \cdot nH_2O$ (n = 2) exist, while K, Rb, and Cs do not form chloride hydrates. Li_2CO_3 does not form any hydrates, whereas the remaining alkali metal carbonates Na (n = 1, 7, 10), K (n = 2, 6), Rb (n = 1, 3/2), and Cs (n = 10/3) do. In contrast, $Li_2SO_4 \cdot nH_2O$ and $Na_2SO_4 \cdot nH_2O$ (n = 1, 7, 10) hydrates are formed, while K, Rb, and Cs sulfates do not form any hydrates. Some hydrate water molecules adopt an icelike arrangement, while others cannot. Water molecules find themselves in numerous possible environments in hydrates (see, for example, Figure 15.10 in ref 2a), and attempts at classification on this basis have not proved feasible because: (i) water

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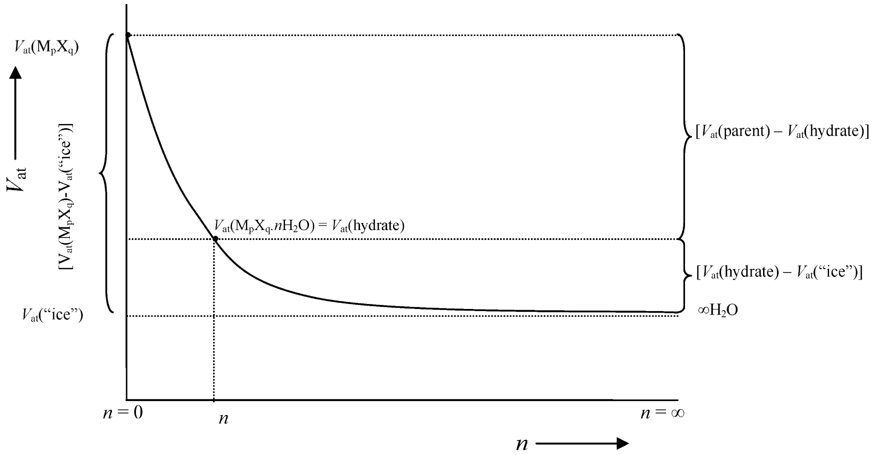

Figure 1. Plot of volume versus n. Situation for a general hydrate for which the average volume per atom, V_{at}, is plotted as a function of n, the number of hydrated water molecules present ($0 \leq n \leq \infty$).

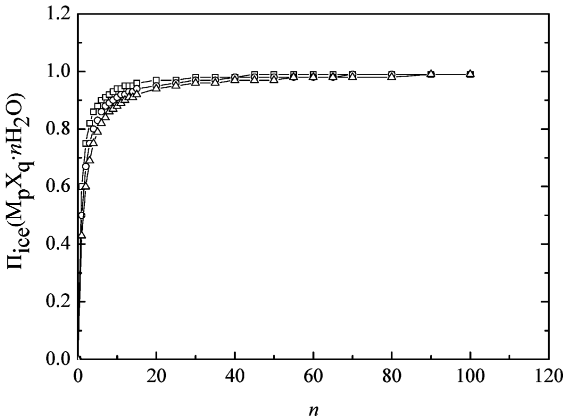

Figure 2. Approximate plot of $\Pi_{ice}(M_pX_q \cdot nH_2O)$ versus n for $p = q = 1$ (upper curve □ univalent ions); $p = 1$; $q = 2$ or $p = 2$; $q = 1$ (middle curve ○) and $p = q = 1$ (lowest curve Δ divalent ions).

molecules within hydrates may not all have identical environments and (ii) stoichiometrically similar hydrates can exhibit vastly different water environments. For example, in $FeSO_4 \cdot 7H_2O$[2b] six waters are clustered around the Fe^{2+} cation, $Fe(H_2O)_6^{2+}$—although these exhibit no fewer than four different environments—and the seventh water is not in contact with the cation at all. This nonequivalence of waters within hydrate structures is what makes classification complicated. Attempts by Wells[2a] to classify $M_pX_q \cdot nH_2O$ hydrates on the basis of the index $[n/(px)]$ where x is the coordination number exhibited by the cation, $M(H_2O)_x$, have been met with only partial success because there exists no simple relationship between $[n/(px)]$ and composition.

Recently, Glasser and Jones[3] have studied the thermodynamics of hydration concluding it to always be marginally thermodynamically favorable.

In recent work,[4−20] volume has emerged as an important measure of molecule size which is related to key thermodynamic properties. One possible solution to this problem of classification of hydrate structures might be to consider packing volumes since this takes into account some of the various environmental factors yet remains a concept which is relatively simple, and it may offer an alternative means of viewing the problem. In the present paper, we explore whether hydrate volume, in the form of the *average volume per atom*, is able to provide us with a convenient measure by which to compare to what extent the atom packing efficiency within hydrates, $M_pX_q \cdot nH_2O$,[7] resembles that of the respective "end members". The atom count is made in two alternative ways: either including ($= p + q + 3n$) or ignoring ($= p + q + 1$) the (small) hydrogen atoms present in the solvate water. The end members are either the parent salt, M_pX_q, when $n \rightarrow 0$ or that of solid water (corresponding to ∞H_2O) when $n \rightarrow \infty$, assumed here to be ice (assumed ice I, the form most stable at 1 atm pressure). The more closely packed (compacted) a crystal structure is, the lower the average volume occupied per atom will be. This principle is used, and the average volume occupied by the atoms within a hydrate, $M_pX_q \cdot nH_2O$, is compared to the average volume of the atoms found in the parent, M_pX_q, and in ice, H_2O, respectively.

The current study is limited to structural concerns rather than thermochemical ones—we have not yet attempted to relate packing efficiency with solvation enthalpies or free energies at varying solute concentrations or relate the maximum number of hydrating waters with solubility as defined by the molality of a saturated solution. What the present approach seems capable of doing is to single out discrepant values and thus lead us to inquire about errors in solute composition (e.g., degrees of hydration) and about atypical intracrystal interactions. Such is the case for $K_4Fe(CN)_6$ and its trihydrate and some strontium salts and a discussion of these species will be explicitly made in the current text.

Theory

Solid ice (which could be denoted as ∞H_2O), in which each water molecule makes four hydrogen bonds with its four nearest neighbors, could be considered to represent one limit of idealized packing which might be aspired to by a hydrate, $M_pX_q \cdot nH_2O$, especially when n becomes large (i.e., ultimately when $n \rightarrow \infty$, then $M_pX_q \cdot \infty H_2O \rightarrow \infty H_2O$, the "hydrate" to all intents and purposes becomes ice which we recognize as the crystallographically ordered, solid form of water under "conventional conditions"). Similarly, we can regard the packing found in the parent salt (denoted "∞"M_pX_q) as the limit of idealized packing in hydrates where n is very small and so approaches zero (i.e., when $n \rightarrow 0$, then $M_pX_q \cdot nH_2O \rightarrow$ "∞"M_pX_q). These conjectures provide us with the extremes of a possible comparative scale by which we might compare relative packing within the same and across different hydrate families. Figure 1 illustrates this idea. A given hydrate, $M_pX_q \cdot nH_2O$, could be considered to be positioned on a curve (by virtue of its average volume per atom, $V_{at}(M_pX_q \cdot nH_2O)$), which has as its limits $V_{at}(M_pX_q)$, the corresponding volume of the parent when $n \rightarrow 0$, and at the other limit asymptotically approaches

Table 2. Calculation of $V_{at}(M_pX_q \cdot nH_2O)$ from Crystal Structure Data for a Series of Hydrates and Their Parents Showing the Calculation of $\Pi(M_pX_q \cdot nH_2O)^{a,b}$

consecutive number	hydrate ($M_pX_q \cdot nH_2O$) or parent (M_pX_q, $n = 0$)	no. of atoms per molecule, $n_{at} = (p + q + 3n)$	volume of parent/hydrate $V_m(M_pX_q \cdot nH_2O)$/nm^3	$V_{at}(M_pX_q) = V_{att}(par)$/nm^3	$V_{at}(M_pX_q \cdot nH_2O) = V_{at}(hyd)$/nm^3	packing ratio, $\Pi_{ice} = [(V_{at}(par) - V_{at}(hyd)]/[V_{at}(par) - 0.0082]$
1	Li_2SO_4	7	0.0773	0.0110		
2	$Li_2SO_4 \cdot H_2O$	10	0.1018		0.0102	0.29
3	$NaOH$	3	0.0327	0.0109		
4	$NaOH \cdot H_2O$	6	0.0550		0.0092	0.63
5	$NaOH \cdot 2.5H_2O$	10.5	0.0880		0.0084	0.93
6	$NaOH \cdot 2.75H_2O$	11.25	0.0959		0.0085	0.89
7	$NaOH \cdot 3.5H_2O$	13.5	0.1134		0.0084	0.93
8	$NaOH \cdot 4H_2O$	15	0.1316		0.0088	0.78
9	$NaOH \cdot 5H_2O$	18	0.1567		0.0087	0.81
10	$NaOH \cdot 7H_2O$	24	0.2060		0.0086	0.85
11	Na_2SO_4	7	0.0868	0.0124		
12	$Na_2SO_4 \cdot 10H_2O$	37	0.3650		0.0099	0.60
13	Na_2CO_3	6	0.0761	0.0127		
14	$Na_2CO_3 \cdot H_2O$	9	0.1006		0.0112	0.33
15	$Na_2CO_3 \cdot 10H_2O$	36	0.3211		0.0089	0.84
16	$Na_2B_4O_7$	13	0.1627	0.0125		
17	$Na_2B_4O_7 \cdot 10H_2O$	43	0.4077		0.0095	0.70
18	$NaAlSi_2O_6$	10	0.1016	0.0102		
19	$NaAlSi_2O_6 \cdot H_2O$	13	0.1261		0.0097	0.23
20	K_2CuCl_4	7	0.1642	0.0235		
21	$K_2CuCl_4 \cdot 2H_2O$	13	0.2187		0.0168	0.43
22	KF	2	0.0382	0.0191		
23	$KF \cdot 2H_2O$	8	0.0927		0.0116	0.69
24	$KF \cdot 4H_2O$	14	0.150		0.0107	0.77
25	$K_4Fe(CN)_6$	17	0.294	0.0173		
26	$K_4Fe(CN)_6 \cdot 3H_2O$	26	0.367		0.0141	0.35
27	$MgCl_2$	3	0.0677	0.0226		
28	$MgCl_2 \cdot H_2O$	6	0.0922		0.0154	0.50
29	$MgCl_2 \cdot 2H_2O$	9	0.1167		0.0130	0.67
30	$MgCl_2 \cdot 4H_2O$	15	0.1657		0.0110	0.81
31	$MgCl_2 \cdot 6H_2O$	21	0.2147		0.0102	0.86
32	$MgCl_2 \cdot 12H_2O$	39	0.4170		0.0107	0.83
33	$MgSO_4$	6	0.068	0.0113		
34	$MgSO_4 \cdot 6H_2O$	24	0.22		0.0092	0.68
35	$CaHPO_4$	7	0.0845	0.0106		
36	$CaHPO_4 \cdot 2H_2O$	13	0.123		0.0095	0.67
37	$CaSO_4$	6	0.075	0.0125		
38	$CaSO_4 \cdot 0.5H_2O$	7.5	0.0855		0.0114	0.26
39	$CaSO_4 \cdot 2H_2O$	12	0.123		0.0103	0.51
40	CaC_2O_4	7	0.0845	0.0121		
41	$CaC_2O_4 \cdot H_2O$	10	0.109		0.0109	0.31
42	$SrCl_2$	3	0.0853	0.0284		
43	$SrCl_2 \cdot H_2O$	6	0.1213		0.0202	0.41
44	$SrCl_2 \cdot 2H_2O$	9	0.119		0.0132	0.75
45	$SrBr_2$	3	0.0968	0.0323		
46	$SrBr_2 \cdot H_2O$	6	0.111		0.0185	0.57
47	$SrBr_2 \cdot 6H_2O$	21	0.242		0.0115	0.86
48	SrI_2	3	0.122	0.0407		
49	$SrI_2 \cdot H_2O$	6	0.1465		0.0244	0.50
50	$SrI_2 \cdot 2H_2O$	9	0.171		0.0190	0.67
51	$SrI_2 \cdot 6H_2O$	21	0.269		0.0128	0.86
52	$BaCl_2$	3	0.0877	0.0292		
53	$BaCl_2 \cdot 2H_2O$	9	0.131		0.0146	0.70
54	$Ba(ClO_3)_2$	9	0.1365	0.0152		
55	$Ba(ClO_3)_2.H_2O$	12	0.161		0.0134	0.26
56	$Ba(BrO_3)_2$	9	0.1485	0.0165		
57	$Ba(BrO_3)_2 \cdot H_2O$	12	0.173		0.0144	0.25
58	$Y_2(SO_4)_3$	17	0.206	0.0121		
59	$Y_2(SO_4)_3 \cdot 8H_2O$	41	0.402		0.0098	0.59
60	$La_2(SO_4)_3$	17	0.2035	0.0120		
61	$La_2(SO_4)_3 \cdot 9H_2O$	44	0.424		0.0096	0.63
62	$Cr_2(SO_4)_3$	17	0.208	0.0122		
63	$Cr_2(SO_4)_3 \cdot 18H_2O$	71	0.649		0.0091	0.78
64	$Cr(NO_3)_3$	13	0.1475	0.0113		
65	$Cr(NO_3)_3 \cdot 9H_2O$	40	0.368		0.0092	0.68
66	$NH_4Cr(SO_4)_2$	16	0.1680	0.0105		
67	$NH_4Cr(SO_4)_2 \cdot 12H_2O$	52	0.462		0.0089	0.70
68	$MnSO_4$	6	0.0724	0.0121		
69	$MnSO_4 \cdot 5H_2O$	21	0.1949		0.0093	0.72
70	$FeBr_2$	3	0.0767	0.0256		
71	$FeBr_2 \cdot 9H_2O$	30	0.2972		0.0099	0.90
72	$FeSO_4$	6	0.069	0.0115		
73	$FeSO_4 \cdot 7H_2O$	27	0.243		0.0090	0.76

Table 2. Continued

consecutive number	hydrate ($M_pX_q \cdot nH_2O$) or parent (M_pX_q, $n = 0$)	no. of atoms per molecule, $n_{at} = (p + q + 3n)$	volume of parent/hydrate $V_m(M_pX_q \cdot nH_2O)$/nm^3	$V_{at}(M_pX_q) = V_{at}(\text{par})$/nm^3	$V_{at}(M_pX_q \cdot nH_2O) = V_{at}(\text{hyd})$/nm^3	packing ratio, $\Pi_{ice} = [(V_{at}(\text{par}) - V_{at}(\text{hyd})]/[V_{at}(\text{par}) - 0.0082]$
74	$FePO_4$	6	0.063	0.0110		
75	$FePO_4 \cdot 2H_2O$	12	0.112		0.0093	0.61
76	$CoSO_4$	6	0.069	0.0115		
77	$CoSO_4 \cdot H_2O$	9	0.093		0.0103	0.33
78	$CoSO_4 \cdot 6H_2O$	24	0.216		0.0090	0.76
79	$CoSO_4 \cdot 7H_2O$	27	0.246		0.0091	0.73
80	$Co(NO_3)_2$	9	0.109	0.0121		
81	$Co(NO_3)_2 \cdot 6H_2O$	27	0.256		0.0095	0.67
82	$NiSO_4$	6	0.0641	0.0107		
83	$NiSO_4 \cdot 6H_2O$	24	0.209		0.0087	0.80
84	$NiSO_4 \cdot 7H_2O$	27	0.244		0.0090	0.68
85	$CuSO_4$	6	0.0684	0.0114		
86	$CuSO_4 \cdot H_2O$	9	0.0846		0.0094	0.63
87	$CuSO_4 \cdot 3H_2O$	15	0.133		0.0089	0.78
88	$CuSO_4 \cdot 5H_2O$	21	0.182		0.0087	0.84
89	Na_4XeO_6	11	0.1364	0.0124		
90	$Na_4XeO_6 \cdot 2H_2O$	17	0.1854		0.0109	0.36
91	$Na_4XeO_6 \cdot 6H_2O$	29	0.2736		0.0094	0.71
92	$Na_4XeO_6 \cdot 8H_2O$	35	0.3203		0.0092	0.76
93	H_2O	3	0.0245	0.0082		

[a] N.B. hyd = hydrate; par = parent, unhydrated salt. [b] Data above is taken from refs 22 and 23. It is important to note (see Figure 1) that the relationships, $V_m(\text{hydrate}) > V_m(\text{parent})$ and $V_{at}(\text{hydrate}) < V_{at}(\text{parent})$ are always found to be true.

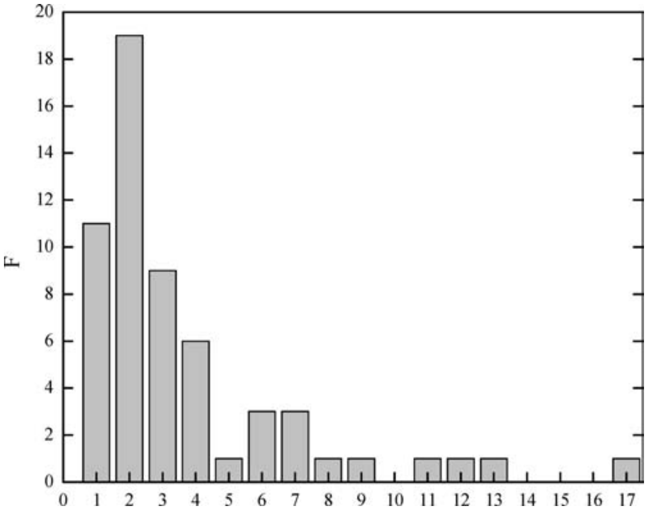

Figure 3. Showing the distribution of $V_{at}(M_pX_q \cdot nH_2O)$/nm^3 for 58 hydrates. 41 % (i.e., 24) of the hydrates listed have volumes within ± 0.0005 nm^3 of 0.0090 nm^3. Data are given in Table 2. None have $V_{at}(M_pX_q \cdot nH_2O)$/nm^3 < 0.0083. On the vertical axis, F represents the frequency of occurrence of $V_{at}(M_pX_q \cdot nH_2O)$/nm^3 in the hydrates in the numbered ranges specified as follows: 1, (0.0084 to 0.0089) nm^3; 2, (0.0090 to 0.0100) nm^3; 3, (0.0101 to 0.0110) nm^3; 4, (0.0111 to 0.0120) nm^3; 5, (0.0121 to 0.0130) nm^3; 6, (0.0131 to 0.0140) nm^3; 7, (0.0141 to 0.0150) nm^3; 8, (0.0151 to 0.0160) nm^3; 9, (0.0161 to 0.0170) nm^3; 10, (0.0171 to 0.0180) nm^3; 11, (0.0181 to 0.0190) nm^3; 12, (0.0191 to 0.0200) nm^3; 13, (0.0201 to 0.0210) nm^3; 14, (0.0211 to 0.0220) nm^3; 15, (0.0221 to 0.0230) nm^3; 16, (0.0231 to 0.0240) nm^3; and 17, (0.0241 to 0.0250) nm^3.

V_{at}("ice"). We can thus define, with reference to Figure 1, two "positional" packing parameters

$$\prod\nolimits_{\text{ice}}[\text{hydrate}] = [V_{at}(M_pX_q) - V_{at}(M_pX_q \cdot nH_2O)]/[V_{at}(\text{parent}) - V_{at}(\text{ice})] \quad (1)$$

$$\prod\nolimits_{\text{parent}}[\text{hydrate}] = [V_{at}(M_pX_q \cdot nH_2O) - V_{at}(\text{ice})]/[V_{at}(\text{parent}) - V_{at}(\text{ice})] \quad (2)$$

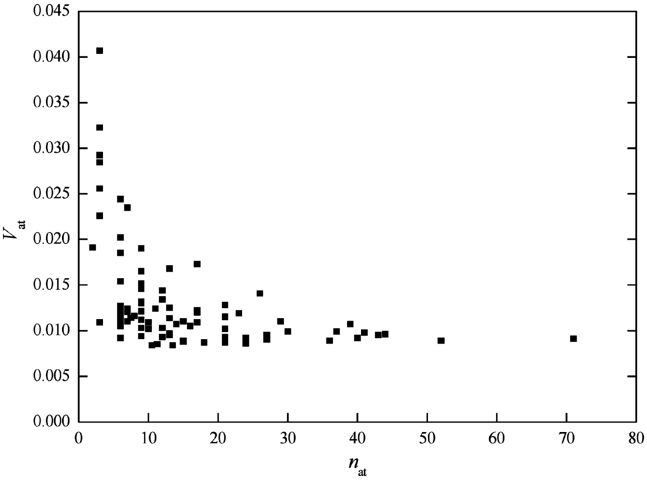

Figure 4. Plot of V_{at} and n_{at} (N.B. n_{at} is number of atoms and not n which is the number of waters) showing how, as n gets larger, $V_{at} \rightarrow V_{at}(\text{ice}) = 0.0082$ nm^3.

In fact, since

$$\prod\nolimits_{\text{parent}}[\text{hydrate}] + \prod\nolimits_{\text{ice}}[\text{hydrate}] = [V_{at}(\text{parent}) - V_{at}(\text{ice})]/[V_{at}(\text{parent}) - V_{at}(\text{ice})] = 1 \quad (3)$$

we need only concern ourselves with using one of these parameters, say Π_{ice}[hydrate]. We note also that if Π_{ice}[hydrate] → 0, then Π_{parent}[hydrate] → 1, and then the packing atoms will adopt similarities to that found in ice, or more precisely, the average space accessible per atom is similar to that found in solid ice. If, on the other hand, Π_{ice}[hydrate] → 1, then Π_{parent}[hydrate] → 0, and then the packing will closely mimic that of the parent salt, M_pX_q. Intermediate between these extremes, the index Π_{ice}[hydrate] categorizes the extent to which the water molecules of the hydrate mimic that found in ice.

For the calculation of V_{at} values the formula unit volume is divided by the total number of atoms (including hydrogen atoms) and is also extendable to other solvates (e.g., SO_2 solvate salts) with appropriate substitution (i.e., solid SO_2 for ice).

In ice, the average volume per atom, $V_{at}(H_2O)$, is given by

$$V_{at}(H_2O) = V_m(H_2O)/3 \quad (4)$$

where $V_m(H_2O)$ is the molecular (formula unit) of ice. Since we found[7] that

$$V_m(H_2O)/nm^3 = \Theta_V(H_2O, s-s) = 0.0245 \quad (5)$$

then V_{at}(ice) for ice is equal to

$$V_{at}(\text{ice})/nm^3 = V_m(H_2O)/3 = 0.0245/3 = 0.0082 \quad (6)$$

In the parent salt, the average volume per atom, V_{at}(parent), is given by

$$V_{at}(\text{parent}) = V_{at}(M_pX_q) = V_m(M_pX_q)/(p + q) \quad (7)$$

For a hydrate, $M_pX_q\cdot nH_2O$ containing pM^{q+} *monatomic* cations and qX^{p-} *monatomic* anions, the average volume per atom in the simple hydrate, V_{at}(hydrate), is given by

$$V_{at}(\text{hydrate}) = V_m(M_pX_q\cdot nH_2O)/(p + q + 3n) \quad (8)$$

For a more complicated hydrate, $M_pX_q\cdot nH_2O$ containing pM^{q+} cations where M might represent a polyatomic cation (say, EX_x^{q+} such as $Co(NH_3)_6^{3+}$) and qX^{p-} anions where X might represent a polyatomic anion (say, $E'Y_y^{p-}$ such as SO_4^{2-}), then the average volume per atom in the hydrate, V_{at}(hydrate), is given by

$$V_{at}(\text{hydrate}) = V_m((EX_x)_p\cdot(E'Y_y)_q\cdot nH_2O)/[p(x + 1) + q(y + 1) + 3n] \quad (9)$$

Thus, for example, for $MgSO_4\cdot 6H_2O$, $p = 1$, $q = 1$, $x = 0$, $y = 4$, and $n = 6$, and therefore

$$V_{at}(MgSO_4\cdot 6H_2O) = V_m(MgSO_4\cdot 6H_2O)/24 = 0.220/24 = 0.0092\ nm^3 \quad (10)$$

whether or not the "true" cation is best described as Mg^{2+} or $Mg(H_2O)_6^{2+}$· Π_{ice}[hydrate] provides a uniform quantitative scale measuring the relative packing which can be used for *any* hydrate in spite of the fact that $V_{at}(M_pX_q)$ varies from hydrate family to hydrate family. We confine ourselves to hydrates (as opposed to more general solvates) in this paper. The former being more in evidence in chemistry while the latter are much more sparsely found, although they are assuming importance in modern cutting edge synthetic chemistry.[21] Furthermore, with our explicit interest in thermochemistry, we note there are few more general solvates for which enthalpy and/or entropy data exist.

In view of the above eq 1, we have

$$\prod\nolimits_{ice}[\text{hydrate}] = [V_{at}(M_pX_q) - V_{at}(M_pX_q\cdot nH_2O)]/[V_{at}(\text{parent}) - 0.0082] \quad (11)$$

Calculations

Table 1 assembles the results for the calculation of the parameter Π_{ice}[hydrate] for a series of parent ($n = 0$) and hydrate salts. The hydrates represented (Table 2) have a limited set of values for n, and examples lie in the range

$$0.5 \le n \le 18 \quad (12)$$

where 18 is the maximum value for which crystal structures[22,23] are available. We now give some examples of the detailed calculations made for Table 2.

KF hydrates. For potassium fluoride hydrates $KF\cdot nH_2O$, two are reported:[22,23] orthorhombic $KF\cdot 2H_2O$ ($a = 0.515$ nm, $b = 0.887$ nm, $c = 0.406$ nm, $Z = 2$) and monoclinic $KF\cdot 4H_2O$ ($a = 0.680$ nm, $b = 1.329$ nm, $c = 0.664$ nm, $\beta = 90.67°$, $Z = 4$). For the cubic KF parent, $a = 0.5344$ nm and $Z = 4$,[23] and the volume is given by

$$V_m(KF)/nm^3 = a^3/Z = 0.0382 \quad (13)$$

and hence

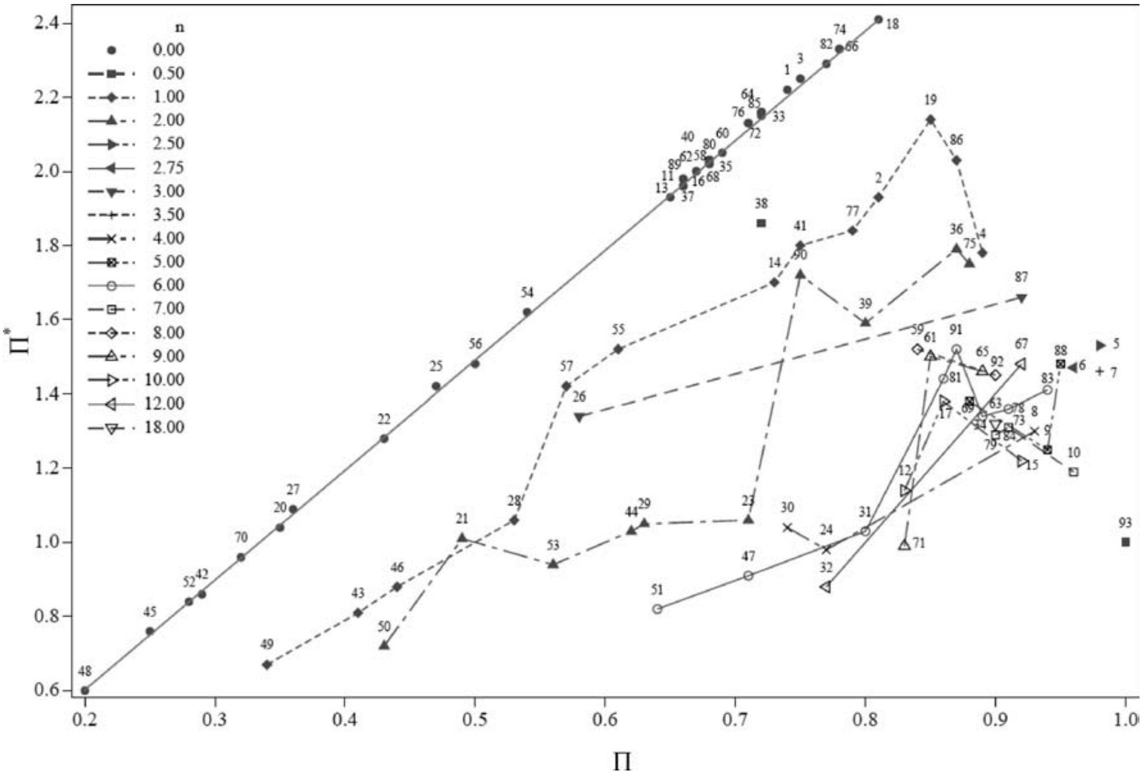

Figure 5. Plot of Π[hydrate] versus Π*[hydrate]. For each hydrate and parent salt, a consecutive number was ascribed, corresponding to those found in Table 2.

$$V_{\mathrm{at}}(\mathrm{KF})/\mathrm{nm}^3 = 0.0382/2 = 0.0191 \tag{14}$$

Using experimental data[23]

$$V_{\mathrm{m}}(\mathrm{KF{\cdot}2H_2O})/\mathrm{nm}^3 = 0.0927 \tag{15}$$

and

$$V_{\mathrm{m}}(\mathrm{KF{\cdot}4H_2O})/\mathrm{nm}^3 = 0.1500 \tag{16}$$

so that

$$V_{\mathrm{at}}(\mathrm{KF{\cdot}2H_2O})/\mathrm{nm}^3 = 0.0927/8 = 0.0116\ \mathrm{nm}^3 \tag{17}$$

and

$$V_{\mathrm{at}}(\mathrm{KF \cdot 4H_2O})/\mathrm{nm}^3 = 0.1500/14 = 0.0107\ \mathrm{nm}^3 \tag{18}$$

$\Pi_{\mathrm{ice}}(\mathrm{KF}{\cdot}n\mathrm{H_2O})$ is given by eq 11 and thus

$$\prod\nolimits_{\mathrm{ice}} (\mathrm{KF{\cdot}2H_2O})/\mathrm{nm}^3 = [V_{\mathrm{at}}(\mathrm{KF}) - V_{\mathrm{at}}(\mathrm{KF{\cdot}2H_2O})]/[V_{\mathrm{at}}(\mathrm{KF}) - 0.0082] = [0.0191 - 0.0116]/[0.0191 - 0.0082] = 0.0075/0.0109 = 0.69 \tag{19}$$

$$\prod\nolimits_{\mathrm{ice}} (\mathrm{KF{\cdot}4H_2O})/\mathrm{nm}^3 = [V_{\mathrm{at}}(\mathrm{KF}) - V_{\mathrm{at}}(\mathrm{KF{\cdot}4H_2O})]/[V_{\mathrm{at}}(\mathrm{KF}) - 0.0082] = [0.0191 - 0.0107]/[0.0191 - 0.0082] = 0.0084/0.0109 = 0.77 \tag{20}$$

thus indicating that the tetrahydrate structure is more "icelike" than the dihydrate. Equation 11 can be approximated by making the ion additive assumption

$$V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q{\cdot}n\mathrm{H_2O}) \approx V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q) + nV_{\mathrm{m}}(\mathrm{H_2O}) \tag{21}$$

so that

$$\begin{aligned}\prod\nolimits_{\mathrm{ice}} [\text{hydrate}] &= [V_{\mathrm{at}}(\mathrm{M}_p\mathrm{X}_q) - V_{\mathrm{at}}(\mathrm{M}_p\mathrm{X}_q{\cdot}n\mathrm{H_2O})]/[V_{\mathrm{at}}(\mathrm{M}_p\mathrm{X}_q) - 0.0082] \\ &= [\{V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q)/(p + q)\} - \{V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q{\cdot}n\mathrm{H_2O})/(p + q + 3n)\}]/[V_{\mathrm{at}}(\mathrm{M}_p\mathrm{X}_q) - 0.0082] \\ &\approx [\{V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q)/(p + q)\} - \{V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q)/(p + q + 3n)\} - n\{V_{\mathrm{m}}(\mathrm{H_2O})/(p + q + 3n)\}]/[V_{\mathrm{at}}(\mathrm{M}_p\mathrm{X}_q) - 0.0082] \\ &\approx [(p + q + 3n)V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q) - (p + q)V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q) - n(p + q)V_{\mathrm{m}}(\mathrm{H_2O})]/\{(p + q)(p + q + 3n)[V_{\mathrm{at}}(\mathrm{M}_p\mathrm{X}_q) - 0.0082]\} \\ &\approx \{3nV_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q) - 0.0245n(p + q)\}/\{(p + q)(p + q + 3n)[V_{\mathrm{at}}(\mathrm{M}_p\mathrm{X}_q) - 0.0082]\} \\ &\approx 3n\{V_{\mathrm{at}}(\mathrm{M}_p\mathrm{X}_q) - 0.0082\}/(p + q + 3n)[V_{\mathrm{at}}(\mathrm{M}_p\mathrm{X}_q) - 0.0082]\} \approx 3n/(p + q + 3n)\end{aligned} \tag{22}$$

so taking $V_{\mathrm{at}}(\mathrm{KF})/\mathrm{nm}^3 = 0.0191$, approximation eq 22 leads to for $\mathrm{KF{\cdot}2H_2O}$ ($p = q = 1$; $n = 2$)

$$\prod\nolimits_{\mathrm{ice}} [\mathrm{KF{\cdot}2H_2O}]_{\mathrm{fam}} \approx 6/8 = 0.75 \tag{23}$$

and for $\mathrm{KF{\cdot}4H_2O}$ ($p = q = 1$; $n = 4$), approximation eq 22 leads to

$$\prod\nolimits_{\mathrm{ice}} [\mathrm{KF{\cdot}4H_2O}]_{\mathrm{fam}} \approx 12/14 = 0.86 \tag{24}$$

The approximate eq 22, if plotted for an MX (univalent ions), $\mathrm{MX_2}$, $\mathrm{M_2X}$, or MX (divalent ions) hydrate with $0 \leq n \leq 100$, shows the characteristics of Figure 2.

Figure 2 shows a plot of $\Pi_{\mathrm{ice}}(\mathrm{M}_p\mathrm{X}_q\mathrm{Y}_r{\cdot}n\mathrm{H_2O})_{\mathrm{fam}}$ versus n for the cases $p, q, r = 1, 1, 0$ (e.g., KF); 1, 2, 0 (e.g., $\mathrm{MgCl_2}$); and 2, 4, 7 (e.g., $\mathrm{Na_2B_4O_7}$). The index r is introduced to cover the case of $\mathrm{Na_2B_4O_7}$. In this case, some (two) of the waters in this species are attached to the $\mathrm{B_4O_7}$ anion and appear as OH groups. In practice though, only small numbers of water molecules are usually involved in forming hydrates.

The asymptotic nature of the curve in which the bonding approaches that of ice as n increases is clearly seen. In practice, however, experimentally, only small values of n are usually encountered. The data taken from plotting approximate eq 22 are given in Table 1.

Values of $V_{at}(M_pX_q{\cdot}nH_2O)/nm^3$ Found in Hydrates. A cursory glance at the values of $V_{\mathrm{at}}(\mathrm{M}_p\mathrm{X}_q{\cdot}n\mathrm{H_2O})/\mathrm{nm}^3$ in Table 2 reveals, overall, a remarkable constancy, for many hydrates (having varying degrees of hydration and widely different total number of atoms) as is displayed in the histogram shown in Figure 3. Figure 4 shows how, as the number of water molecules is increased, the value of V_{at} approaches that of solid ice.

An Alternative, and Likewise Simple, Index of Packing

We can devise a simpler definition of (but nonequivalent) packing ratio for a hydrate, Π[hydrate], in which the average volume per atom in ice is compared with that for the hydrate. This too can provide a measure of the relative packing densities in a family of hydrates having different numbers of hydrated water molecules (i.e., different n values) as well as between hydrates evolved from different parents (i.e., different $\mathrm{M}_p\mathrm{X}_q$). Therefore, for the complex hydrate mentioned earlier

$$\prod [\text{hydrate}] = 0.0082/V_{\mathrm{at}}(\text{hydrate}) = 0.0082[p(x + 1) + q(y + 1) + 3n]/V_{\mathrm{m}}((\mathrm{EX}_x)_p{\cdot}(\mathrm{E'Y}_y)_q{\cdot}n\mathrm{H_2O}) \tag{25}$$

We can explore, theoretically, the dependence of Π[hydrate] on n and how this will be affected by differing $\mathrm{M}_p\mathrm{X}_q$ parents, using the difference rule (XX) to estimate V_{at}(hydrate) for model systems.

Let us consider the simplest case for a hydrate, $\mathrm{M}_p\mathrm{X}_q{\cdot}n\mathrm{H_2O}$, where M^{q+} and X^{p-} are both monatomic ions, then we can write

$$V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q{\cdot}n\mathrm{H_2O})/\mathrm{nm}^3 \approx V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q) + nV_{\mathrm{m}}(\mathrm{H_2O}) \approx V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q) + n\Theta_{\mathrm{V}}(\mathrm{H_2O}) \approx V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q) + 0.0245n \tag{26}$$

and hence that

$$V_{\mathrm{at}}(\mathrm{M}_p\mathrm{X}_q{\cdot}n\mathrm{H_2O})/\mathrm{nm}^3 \approx V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q{\cdot}n\mathrm{H_2O})/(p + q + 3n) \approx [V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q) + 0.0245n]/(p + q + 3n) \tag{27}$$

and therefore we can define Π[hydrate] to be

$$\prod [\text{hydrate}] = 0.0082/V_{\mathrm{at}}(\text{hydrate}) = 0.0082/[p + q + 3n]/[V_{\mathrm{m}}(\mathrm{M}_p\mathrm{X}_q) + 0.0245n] \tag{28}$$

and we see from eq 28 that, as conjectured earlier, as $n \to \infty$, then $\Pi[\text{hydrate}] \to 1$.

A simpler index than Π[hydrate] can be derived by ignoring the small hydrogen atoms in the atom count thereby giving rise to a modified definition, Π*[hydrate], thus

$$\Pi^*[\text{hydrate}] = 0.0245/V_{\mathrm{at}}(\text{hydrate}) = 0.0245[p(x + 1) + q(y + 1) + n]/V_{\mathrm{m}}((\mathrm{EX}_x)_p{\cdot}(\mathrm{E'Y}_y)_q{\cdot}n\mathrm{H_2O}) \tag{29}$$

and for parent salts, $\mathrm{M}_p\mathrm{X}_q$, for which $n = 0$

$$\Pi^*[M_pX_q] = 3\prod[M_pX_q] \tag{30}$$

It is found that if we plot Π^*[hydrate] versus Π[hydrate], Figure 5 results.

In Figure 5 it can be seen to be such that the (unhydrated, $n = 0$) parent salts are all grouped such as to form an upper diagonal boundary to the plot. If a fit is made to this data, we find they fit the curve ($R = 0.998$, $N = 16$)

$$\Pi^*[M_pX_q] = 2.97\prod[M_pX_q] + 0.01 \tag{31}$$

close to the theoretical relationship, eq 30.

The point (1, 1) on the graph corresponds to the case of pure ice (equivalent to ∞H_2O) and represents a lower boundary for the curves. Examination of the plot reveals that points which correspond to the monohydrates ($n = 1$) nestle approximately parallel to the diagonal line for the parent salts. Further, for increasing values of n, the hydrates form series of almost parallel areas outward from the parent line in order of increasing values of n such that the higher hydrates lie increasingly toward the lower right quadrant of the plot.

Π^* may also be understood in terms of solvent molecules being considered as pseudoatomic "clumps" in which case the three atoms in H_2O are conceptually considered as one. Numerically, this assumption results in the same relation between Π and Π^* as above. However, had we considered species in which ammonia or methanol was the solvent, with their total atom counts of 4 and 6, respectively, then this new index would differ from the earlier one. Thermochemical consequences plausibly differ, but as we said, there are almost no relevant data (structural and thermochemical[24]) for such ammoniates and methanolates to derive any meaningful consequences at this time.

Anomalies appear in the case of $K_4Fe(CN)_6$ (species #25) and of its hydrate, $K_4Fe(CN)_6 \cdot 3H_2O$ (species #26), as the volumes of both seem to be small in comparison to other salts. The structural data of $K_4Fe(CN)_6$ taken from the ref 25 published in 1947 can be however viewed with scepticism because of measurement incompleteness and low precision. The source of anomaly in the case of $K_4Fe(CN)_6 \cdot 3H_2O$ can be ascribed to disordering of water molecules.[26] Four of the remaining anomalous species (salts #43, 46, 49, 50) are strontium halide monohydrates and a dihydrate. That these species contain bifurcated hydrogen bonds[27] is a defining feature in terms of lattice structure but does not provide a reason for the exceptionally large values of the packing ratio V_{at} and correspondingly low values of Π.

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