Thermochimica Acta, 67 (1983) 167–179
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CRITICAL EXAMINATION AND EXPERIMENTAL DETERMINATION OF MELTING ENTHALPIES AND ENTROPIES OF SALT HYDRATES

J. GUION

Laboratoire de Chimie Physique, IMSP, Université de Nice, Nice (France) et Groupe d'Ecothermique Solaire du CNRS, Sophia Antipolis, BP 21, 06 562 Valbonne Cédex (France)

J.D. SAUZADE and M. LAÜGT

Groupe d'Ecothermique Solaire du CNRS, Sophia Antipolis, BP 21, 06 562 Valbonne Cédex (France)

(Received 10 February 1983)

ABSTRACT

Experimental melting enthalpies and entropies of a great number of salt hydrates ($MX \cdot n\ H_2O$) are reviewed and/or determined by differential scanning calorimetry (DSC).

Experimental and theoretical correlations and evaluations are proposed for melting entropies correlated with the number of water molecules, n.

INTRODUCTION

Full-scale utilisation of solar energy, using phase change materials, is dependent on various techniques and storage strategies, which are extensively studied in numerous research centers.

For temperatures between 10 and 100°C, storage is possible using materials with a solid–liquid phase transition. It may be accomplished essentially by hydrated salts (hereafter designated by the general formula $MX \cdot n\ H_2O$). These salts must be evaluated along several parameters: melting or crystallising temperature, enthalpy of fusion, volume change upon melting, specific heats of liquid and solid, thermal conductivity, surfusion and segregation phenomena, corrosion, prices, etc.

This paper deals with the determination of enthalpies of fusion of numerous salt hydrates.

RESULTS AND DISCUSSION

The enthalpy of fusion, ΔH_m, of a salt hydrate ($MX \cdot n\ H_2O$) defines the thermal energy which must be furnished to provoke the fusion of one mole of $(MX \cdot n\ H_2O)_s$ or, inversely, the energy recoverable during the crystallization of one mole of $(MX \cdot n\ H_2O)_l$ at a given pressure (generally, $p = 1$ atm) and, in the absence of surfusion, at a given temperature, θ_m. (ΔH_m is generally expressed in kJ mole^{-1} or in kcal mole^{-1}, and θ_m in °C).

Potentially valuable systems will be based on high values of ΔH_m, but this simple affirmation should in fact be attenuated. For practical applications, ΔH_m values, which refer to molar quantities, are generally not easily handled.

Different expressions of the expected energy released during the crystallization process of a compound $MX \cdot n\ H_2O$ will be presented: one is expressed relative to mass unit and denoted by $\Delta H_{m/M}$ in J kg^{-1}, the other is expressed relative to the volume unit, $\Delta H_{m/V}$ in kJ m^{-3}, or in terms of storage density, $\Delta H_{m/V}$ (kW h m^{-3}).

Values of fusion enthalpies and melting temperatures

A broad survey of the literature, scientific journals and contract reports (refs. 1–24), has been made. Several difficulties must be outlined.

(1) The original experimentalists are frequently not mentioned. This leads to the situation presented in Table 1, for three salt hydrates, chosen for illustration. In this table, fusion enthalpies are given relative to 1 g of salt, and are denoted by $\Delta H_{m/M}$. At first sight, one might believe that many experiments had led to these values. This is not true, and unfortunately many of the different values found in the literature are often linked with trivial errors in transcription, or in conversion between different systems of units. Most ΔH_m and θ_m values are related to quite old experimental determinations, and for a number of salts are missing altogether.

(2) The phenomenon of melting, as recorded from differential scanning calorimetry (DSC), is not always very simple. One has to be well aware of how experiments must be performed, for results from experiments open to the atmosphere may be completely different from those performed under vacuum or argon, or with tightly closed samples. Some complications may occur, such as allotropic transformations in a temperature region near the melting zone, or partial dehydration in a very narrow temperature interval, etc.

Table 2 shows some useful values for evaluating the potential applications of a number of compounds $(MX \cdot n\ H_2O)$, in relation to increasing the values of the number of water molecules, n. The molecular weight, M, of $MX \cdot n\ H_2O$ is expressed in grams, the melting temperature, θ_m, in °C, and the molar enthalpy of melting, ΔH_m, in kcal mole^{-1}. Relative errors of 10% on the most reliable values may be expected. Included in Table 2 are some recent determinations from this laboratory (DSC measurements, to be published), marked with asterisks.

From ΔH_m determinations, the molar entropies of melting, ΔS_m, were

TABLE 1

Comparative values of θ_m and ΔH_m, compiled from the literature, for three salt hydrates

Compound	θ_m (°C)	ΔH_m (cal g^{-1})	Ref.
$Ca(NO)_3)_2 \cdot 4\,H_2O$	43	39 33.4	6
	47	38.7 33.9	7
	42.6(α) 39.7(β)	33.5	14
	39–42	33.3	15
	43	37	17
	40–42	50	20
	47	34	21
	42.7	36.7	23
$KF \cdot 4\,H_2O$	18.5	55.4	16,17
	18.5	78.9	18
$CaCl_2 \cdot 6\,H_2O$	29	40.6	6
	29–39	41.7	7
	30.5	42.2	8
	29.5	40.6	15
	28.5	32	17
	29.48	40.6	18
	36 27	45.6	19
	29	50.5	20
	29	40.7	21

calculated.

$$\Delta S_m = \frac{\Delta H_m}{T_m} \tag{1}$$

where $T_m = \theta_m + 273$, and is given in K, ΔH_m is in cal mole^{-1} and ΔS_m is in cal mole^{-1} K^{-1}. The ΔS_m values are reported in Table 2.

In practical applications, the energy which may be released from the crystallization process of $MX \cdot n\, H_2O$ compounds is expressed relative either to the mass unit of the compound, $\Delta H_{m/M}$ (in kJ kg^{-1}), or to the volume unit, $\Delta H_{m/V}$ (in kJ m^{-3}). In order to calculate the latter quantity one needs to know the density, d, generally recorded for solids in scientific literature. For solar energy applications, $\Delta H_{m/V}$ is often expressed in kW h m^{-3}, with

$$\Delta H_{m/V}(\text{kW h m}^{-3}) = \Delta H_{m/M}(\text{J g}^{-1}) \times d \times 0.27778 \tag{2}$$

When expressed in kW h m^{-3}, $\Delta H_{m/V}$ is commonly designated as the storage energy density.

TABLE 2

Salt hydrate	Molar weight	θ_m (°C)	ΔH_m (kcal mole^{-1})	ΔS_m (cal. mole^{-1} K^{-1})	d_{solid}	$\Delta H_{m/M}$ (J g^{-1})	$\Delta H_{m/V}$ (MJ m^{-3})	$\Delta H_{m/V}$ (kW h m^{-3})	Ref. number in Fig. 1
*$H_3PO_4 \cdot 0.5\ H_2O$	107	29.3	3.68	8.2	1.88	143.8	270.3	75	1
*$NaHSO_4 \cdot H_2O$	138	60	4.3	12.8		129.6			2
$NaOH \cdot H_2O$	58	64.3	3.78	11.2	1.7	272	460	128	3
$HNO_3 \cdot H_2O$		−37	4.18	17.7					4
$H_2SO_4 \cdot H_2O$	116.09	8.48	4.5	16	1.788	163.5	292	81	5
$KF \cdot 2H_2O$	94.1	41.4	5.9	18.8	1.658	266	441	122	6
$Li(Ac) \cdot 2H_2O$	101.9	58	6.12	18.5		251			7
$LiNO_3 \cdot 3\ H_2O$	123	29.9	8.7	28.7	1.55	296	459	127	8
$LiClO_3 \cdot 3\ H_2O$	144.39	8	8.7	31					9
$LiClO_4 \cdot 3\ H_2O$	160.44	95	9.7	26.4	1.84	253	465	129	10
$Na(Ac) \cdot 3\ H_2O$	136.08	58	8.85	26.7	1.45	272	394	109.5	11a
*$Na(Ac) \cdot 3\ H_2O$	136.08	58	9.4	28.4		289	419	116.4	11b
$Ca(NO_3)_2 \cdot 4\ H_2O$	210	39.7β 42.7α	7.0	22.2	 1.896				12a
*$Ca(NO)_3)_2 \cdot 4\ H_2O$	210	42.7	7.1	22.6	1.82	142.1	258.6	71.8	12b
$KF \cdot 4\ H_2O$	130	18.5	10.3	35.2	1.44/1.45	330	475.2	132	13
$Zn(NO_3)_2 \cdot 4\ H_2O$	261.4	48	9	28	2.22	144	320	89	14
$Cd(NO_3)_2 \cdot 4\ H_2O$	308.4	59.5	7.8	23.5	2.455	106	26.5	74	15
$MnCl_2 \cdot 4\ H_2O$	198	58	8.4	25.4	2.01	178	357	99	16
*$CuSO_4 \cdot 5\ H_2O$	249.6	96.5	6.9	18.8	2.287	116	265	74	17
$Na_2S_2O_3 \cdot 5\ H_2O$	248	48	12.4	38.6	1.729	209	361	100	18a
*$Na_2S_2O_3 \cdot 5\ H_2O$	248	48	11.9	36.9		200	346	96	18b
$CaBr_2 \cdot 6\ H_2O$	308	38.2	8.5	27.3	2.295	116	266	74	19
$CaCl_2 \cdot 6\ H_2O$	219	29.4	8.9	29.4	1.71	170	291	81	20a
$CaCl_2 \cdot 6\ H_2O$		29	8.8	29.2		168	287	80	20b
$NaNO_3 \cdot 6\ H_2O$	193	53	7.3	22.4		158			21

$MgCl_2 \cdot 6\,H_2O$	203.3	117	8.35	21.5	1.569	171	269	75	22
$Co(NO_3)_2 \cdot 6\,H_2O$	291	57	8.9	27	1.87	128	239	66	23a
$*Co(NO_3)_2 \cdot 6\,H_2O$	291	55.5	9.9	30.3		142.9	267	74.2	23b
$Cu(NO_3)_2 \cdot 6\,H_2O$	295.6	24.4	8.7	29.2	2.074	123	255	71	24
$FeCl_3 \cdot 6\,H_2O$	279.3	37	14.4	46.6	1.6	223	357	99	25b
$*FeCl_3 \cdot 6\,H_2O$		37	12	38.8		186.2	298	83	25a
$K_2HPO_4 \cdot 6\,H_2O$	282	13	7.3	25.6		109			26
$Zn(NO_3)_2 \cdot 6\,H_2O$	297.5	36.4	9.5	30.8	2.065	134	277	77	27a
$Zn(NO_3)_2 \cdot 6\,H_2O$		42	10.45	33.1		146.7	303	84	27b
$Ni(NO_3)_2 \cdot 6\,H_2O$	290.8	56.7	11.7	35.4	2.05	168	344	96	28
$Mg(NO_3)_2 \cdot 6\,H_2O$	256.4	89	9.8	27.1	1.6363	160	262	73	29
$Mn(NO_3)_2 \cdot 6\,H_2O$	287	26	9.6	32.1	1.82s 1.881	140	255	71	30
$Fe(NO_3)_2 \cdot 6\,H_2O$	288	60	8.6	25.6		125			31
$*Mn(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$	391.2	84.8	17.8	49.7		192.8			32
$FeSo_4 \cdot 7\,H_2O$	278	64	13.3	39.4	1.89	200	378	105	33
$Na_2HPO_4 \cdot 7\,H_2O$	268	48.2	11.2	34.9	1.679	175	294	82	34a
$*Na_2HPO_4 \cdot 7\,H_2O$		48	9.2	28.7		143	240	67	34b
$*CoSO_4 \cdot 7\,H_2O$	281.1	95.2	11.4	31	1.948	170	331	92	35
$MgSO_4 \cdot 7\,H_2O$	246.5	49.2	11.9	37	1.68	201	338	94	36
$Ba(OH)_2 \cdot 8\,H_2O$	315.5	78	22.7	64.7	2.18	301	656	182	37a
$*Ba(OH)_2 \cdot 8\,H_2O$		78	22.3	63.5		295.5	644	179	37b
$LiBO_2 \cdot 8\,H_2O$	193.9	47	17.3	54	1.38	372	513	143	38
$Al(NO_3)_3 \cdot 9\,H_2O$	375.1	70	13.9	40.5	1.74(c)	155	270	75	39a
$*Al(NO_3)_3 \cdot 9\,H_2O$		74.2–76.2	15.81	45.5	1.74(c)	176.3	307	85	39b
$*Cr(NO_3)_3 \cdot 9\,H_2O$	400.15	65	18.6	55.7	1.807	194.8	352	98	40
$*Fe(NO_3)_3 \cdot 9\,H_2O$	404	48.7	18.4	57.2	1.684	190.5	320	89	41
$Na_2CO_3 \cdot 10\,H_2O$	286.1	33	17.2	56.2	1.44	251	362	100	42
$Na_2B_4O_7 \cdot 10\,H_2O$	318.4	68.1	14.5	42.5	1.705	159	271	75	43
$Na_2SO_4 \cdot 10\,H_2O$	322.2	32.38	18.8	61.5	1.464	244	357	99	44
$Na_2CrO_4 \cdot 10\,H_2O$	342.1	16	14	48.6	1.483	172	255	71	45
$*Na_4P_2O_7 \cdot 10\,H_2O$	446.07	76.3	24.5	70.2	1.82	230	419	116	46
$AlK(SO_4)_2 \cdot 12\,H_2O$	474.4	80	20.0	56.7	1.757	176	310	86	47a

TABLE 2 (continued)

Salt hydrate	Molar weight	θ_m (°C)	ΔH_m (kcal mole^{-1})	ΔS_m (cal. mole^{-1} K^{-1})	d_{solid}	$\Delta H_{m/M}$ (J g^{-1})	$\Delta H_{m/V}$ (MJ m^{-3})	$\Delta H_{m/V}$ (kW h m^{-3})	Ref. number in Fig. 1
*$AlK(SO_4)_2 \cdot 12\ H_2O$		89.2–90	27.6	76	1.757	243	426	118	47b
$Na_2HPO_4 \cdot 12\ H_2O$		37	20.5	66		187.7			48a
*$Na_2HPO_4 \cdot 12\ H_2O$	358.1	36.5	22.5	72.8	1.52	279	424	118	48b
$Na_3PO_4 \cdot 12\ H_2O$	380.1	79	20	58.3	1.62	220	356	99	49a
*$Na_3PO_4 \cdot 12\ H_2O$	380.1	71.2–76.7	17.3	50					49b
*$FeNH_4(SO_4)_2 \cdot 12\ H_2O$	482.1	36.5–29.7	22.8	73.3	1.713	197.6	338	94	50
*$CrK(SO_4)_2 \cdot 12\ H_2O$	499.3	42.7	28.4	90	1.828	237.9	435	121	51
*$Al(NH_4)(SO_4)_2 \cdot 12\ H_2O$	453.22	93.8	24.7	67.4	1.64	228	374	104	52
$Al_2(SO_4)_3 \cdot 18\ H_2O$	666.4	88	34.8	96.4	1.69	218.3	369	102	53

* Recent results from this laboratory.

All the quantities mentioned are also reported in Table 2.

In contrast to some thermodynamic functions such as C_p, $\Delta H_{\text{vaporisation}}$, etc., it is impossible to predict values of ΔH_m theoretically. Some correlations between experimental values of ΔH_m and ΔS_m and the number of water molecules in the hydrated compounds $MX \cdot n\ H_2O$, n, have been proposed by Furbo and Svendsen [6]. From fourteen determinations they proposed linear correlations (correlation coefficient = 0.944) given by

$$\Delta H_m = 1.62n + 0.41 \tag{3}$$

$$\Delta S_m = 5.48n - 1.16 \tag{4}$$

From the (more numerous) values in Table 2 (60 values) for linear correla-

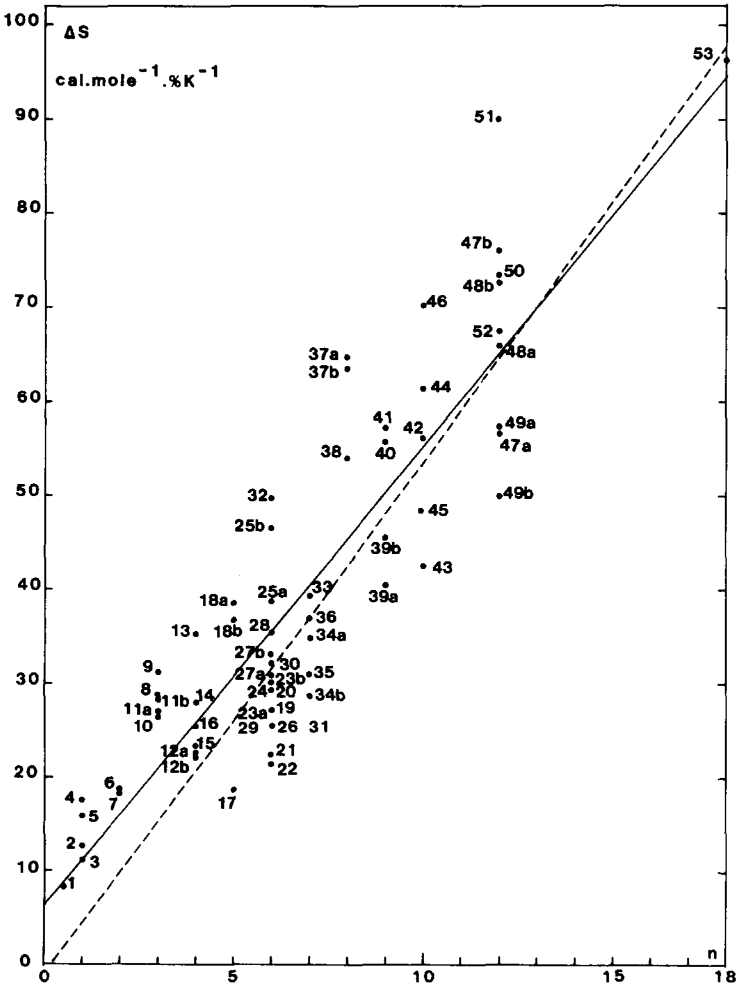

Fig. 1. Experimental values of $\Delta S_m = f(n_{H_2O})$. ——— corresponds to eqn. (6) and - - - - - - to eqn. (4).

tions (correlation coefficient = 0.911), it is found that

$$\Delta H_{m(\text{experimental})} = 1.692n + 1.314 \tag{5}$$

$$\Delta S_{m(\text{experimental})} = 4.89n + 6.35 \tag{6}$$

All the experimental values of the function $\Delta S_m = f(n_{H_2O})$ are presented in Fig. 1, where straight lines corresponding to eqns. (4) and (6) are drawn. This figure explains quite well the poor correlation coefficient obtained. This is not surprising, considering the preceding remarks about the experimental precision of ΔH_m and sometimes θ_m. Nevertheless, eqns. (5) and (6) may be considered as a good approximation to the mean values to be expected for a compound $MX \cdot n\ H_2O$, if n is known. This is noteworthy since a linear correlation cannot be expected a priori.

Equation (4) leads to an extrapolated value of ΔS_m for $n = 0$, which appears to be negative (-1.16). On the other hand, eqn. (6) leads to a positive value of 6.35. This corresponds approximately to the mean value observed for pure compounds, MX [1–3], which seems more reasonable.

Theoretical approach to fusion entropies of $MX \cdot n\ H_2O$ compounds

The fusion phenomena of a hydrated compound ($MX \cdot n\ H_2O$) may be formally described by

$$(MX \cdot n\ H_2O)_s \overset{\theta_m, \Delta H_m}{\rightleftarrows} (MX \cdot n\ H_2O)_l \tag{7}$$

where M is the metallic ion, in a definite oxidation state; X is the anion corresponding to an element in the oxidation state correlating that of the cation M, or complex anion; $(MX \cdot n\ H_2O)_s$ is the hydrated salt, with n water molecules of constitution, in the solid state; and $(MX \cdot n\ H_2O)_l$ is the same hydrated salt, in the liquid state.

It is assumed then that the melting process described in (7) corresponds to some developing degrees of freedom, e.g. vibration, translation [linked to the breaking of crystal, and suppression of long distance order in the solid state, and the subsequent formation of short-ordered aggregates symbolized by $(M \cdot x\ H_2O)_{aq}$, $(X \cdot y\ H_2O)_{aq}$], following the general scheme of eqn. (8)

$$MX_{(s)} + n\ H_2O_{(s)} \rightleftarrows MX_{(l)} + n\ H_2O_{(l)} \tag{8}$$

which might be considered as the addition of the two sub-equations (9a) and (9b)

$$MX_{(s)} \rightleftarrows MS_{(l)} \tag{9a}$$

$$n\ H_2O_{(s)} \rightleftarrows n\ H_2O_{(l)} \tag{9b}$$

In other words it is assumed that eqn. (10), reflecting simple additivities of entropies, reads

$$(\Delta S_m)_{th} = \Delta S_m(MX) + n\Delta S_m(H_2O) \tag{10}$$

TABLE 3

Theoretical values of ΔS_m, calculated from eqn. (10), for salt hydrates $MX \cdot n\ H_2O$

n								
1	NaOH	H_2SO_4	$NaHSO_4$	HNO_3				
	11.5	13.6	10.7	16.1				
2	KF	LiBr	$BaBr_2$					
	16.5	14.02	17					
3	$LiNO_3$	$ZnCl_2$	LiI	NaBr	$CaBr_2$	$LiClO_4$		
	27.1	25.8	20.5	21.9	22.7	25.4		
3,5	NaOH							
	24.6							
4	$Ca(NO_3)_2$		$MnCl_2$	KF	$CdBr_2$	$Cd(NO_3)_2$		
	26.2		30.1	26.8	30.5	28.6		
6	$MgCl_2$	$AlBr_3$	$AlCl_3$	$FeCl_3$	$NaNO_3$	$CaCl_2$	$CaBr_2$	$SrBr_2$
	42	38.9	49.6	49.4	38	37.3	38.4	37.4
	CaI_2							
	41.06							
7	$MgSO_4$	K_3PO_4						
	39.3	43.3						
8	$LiBO_2$	$Ba(OH)_2$						
	49.5	48.7						
9	Na_2SiO_3							
	56.5							
10	Na_2CO_3		$Na_2B_4O_7$	Na_2SO_4	Na_2CrO_4			
	58.8		71.7	60.6	58			

where $(\Delta S_m)_{th}$ is the fusion entropy of one mole of $MX \cdot n\ H_2O$, calculated by eqn. (10); $\Delta S_m(MX)$ is the fusion entropy of one mole of MX compound; and $\Delta S_m(H_2O)$ is the fusion entropy of one mole of water.

Equation (10) is formally analogous to eqn. (11)

$$\Delta S_m(A_pB_q) = p\Delta S_m(A) + q\Delta S_m(B) \tag{11}$$

A and B being elements of the periodic table [13,14,26]. This relation has already been used by M. Telkes et al. [26], particularly for MX salts where X = Cl, Br and I. However, this author used theoretical values, which depart significantly from experimentally measured values, for $\Delta S_m(MX)$. This point will be outlined again later.

From eqn. (10), we calculated $(\Delta S_m)_{th}$ for a number of $MX \cdot n\ H_2O$ compounds. The $\Delta S_m(H_2O)$ value is 5.26 cal $mole^{-1}$ K^{-1} and $\Delta S_m(MX)$ values are experimental determinations from the literature [1–3,9,11]. Values of $(\Delta S_m)_{th}$ are reported in Table 3, and from them, coefficients of the linear relationship $(\Delta S_m)_{th} = g(n\ H_2O)$ were determined (correlation coefficient 0.970), leading to

$$(\Delta S_m)_{th} = 5.52n + 7.03 \tag{12}$$

A number of hydrated compounds in Table 2 do not appear in Table 3. This is generally due to the absence of any experimental determination of $\Delta S_{\mathrm{m}}(\mathrm{MX})$ for the anhydrous compound. In general, the latter decomposes before melting, or its melting temperature is too high for a correct determination of ΔH_{m}. Conversely, Table 3 shows hydrated compounds which are not included in Table 2: this reflects the absence, to our present knowledge, of any ΔH_{m} determination, and/or θ_{m}.

Equation (12), considering all the previous hypotheses, may be considered as quite interesting for a qualitative evaluation of ΔS_{m} of $\mathrm{MX} \cdot n\ \mathrm{H_2O}$ compounds, and consequently of ΔH_{m}, if θ_{m} is known.

The difference between the mean values of ΔS_{m}, given by eqns. (12) and (6), i.e. between a theoretical mean value and the corresponding experimental mean value, for a given number of moles of water, for compounds $\mathrm{MX} \cdot n\ \mathrm{H_2O}$, reaches a maximum of 10%. Despite the rough simplicity of the model used, its efficiency for predictive evaluations has to be recognized. It must be noted that for $n = 0$, ΔS_{m} values are of the same order of magnitude (7.03 and 6.35).

TABLE 4

Compound	$x \to y$	$(x-y)$	ΔS^1_{m} (MX)	$\Delta S^{(x-y)}_{\mathrm{m}}$ (H_2O)	$(\Delta S^1_{\mathrm{m}})_{\mathrm{th}}$	$\Delta S^{\mathrm{exp}}_{\mathrm{m}}$	$(\Delta S^2_{\mathrm{m}})_{\mathrm{th}}$	ΔS^2_{m} (MX)
Na_2SO_4	$10 \to 0$	10	8.38	52.6	61	63.5	62.3	9.7
$Ba(OH)_2$	$8 \to 0$	8	6.65	42.08	48.07	64.5	52.8	10.7
$FeCl_3$	$6 \to 0$	6	15.4	31.56	47	47.1 38.8	46.9	15.3
$Na_2S_2O_3$	$5 \to 0$	5		26.3		37	42.3	1
NaAc	$3 \to 0$	3	7.3	15.8	23.1	26.7 28.4	26.1	10.3
$LiNO_3$	$3 \to 0$	3	12.1	15.8	27.9	28.9	29	13.2
KF	$2 \to 0$	2	6.0	10.4	16.4	18.8	15.5	5.1
NaOH	$1 \to 0$	1	11.41	5.3	16.7	11.2	16.6	11.4
$NaHSO_4$	$1 \to 0$	1	5.45	5.3	10.7	12.8	11.1	5.8
H_3PO_4	$0.5 \to 0$	0.5	10.1	2.6	12.7	8.2	20	17.4
Na_2HPO_4	$12 \to 2$	10		52.6		72.8	71.3	18.7
Na_3PO_4	$12 \to 2$	10		52.6		58	71.9	19.3
Na_2CO_3	$10 \to 1$	9	10.3	47.3	57.6	56.6	65.6	18.3
Na_2CrO_4	$10 \to 4$	6	5.5	31.6	37	48.6 46	50.4	18.9
$MgSO_4$	$7 \to 1$	6	2.5	31.6	34.1	37.5	40	8.4
$CaCl_2$	$6 \to 2$	4	6.44	21	27.5	29.4	31.2	11.1
$MgCl_2$	$6 \to 4$	2	10.44	10.5	20.9	21.6	21.7	11.2
$Ca(NO_3)_2$	$4 \to 2$	2	6.8	10.5	17.3	22.6	25.7	15.2
$MnCl_2$	$4 \to 2$	2	9.8	10.4	20.2	25.5	21.6	11.2
KF	$4 \to 2$	2	6.0	10.4	16.44	35.2	15.54	5.1
$Cd(NO_3)_2$	$4 \to 3$	1	7.6	5.3	12.9	23.5	19.3	14

A deeper examination of the fusion phenomena, for salt hydrate compounds, would have to take into account that in their melting, not only the dissolution of MX in the n moles of constitution water occurs, but often also the formation of another hydrate ($MX \cdot x\ H_2O$), with $x < n$, more or less dissolved in $(n - x)$ moles of H_2O, is observed. It is to be noted that $x = 0$ corresponds to the particular case described previously.

These facts have been more specifically studied by Telkes et al. [26]. Using their model

$$\begin{aligned}(\Delta S'_{\mathrm{m}})_{\mathrm{th}} &= \Delta S_{\mathrm{m}}[MX \cdot (n - x)\ H_2O] \\ &= \Delta S_{\mathrm{m}}(MX) + (n - x)\Delta S_{\mathrm{m}}(H_2O) \qquad (13)\end{aligned}$$

In Table 4, the theoretical values calculated from eqn. (13) which have been quoted are $(\Delta S^1_{\mathrm{m}})_{\mathrm{th}}$, when $\Delta S_{\mathrm{m}}(MX)$ experimental values are used, and $(\Delta S^2_{\mathrm{m}})_{\mathrm{th}}$, for calculations made by Telkes et al. [26], using theoretical values of $\Delta S_{\mathrm{m}}(MX)$ predicted by these authors.

Equation (13) evidently leads, for $x = 0$, to the same results for $(\Delta S^1_{\mathrm{m}})_{\mathrm{th}}$ as those already reported in Table 3 (first part of Table 4).

When comparing either $(\Delta S^1_{\mathrm{m}})_{\mathrm{th}}$ or $(\Delta S^2_{\mathrm{m}})_{\mathrm{th}}$ values with the experimentally determined ΔS_{m}, large deviations may generally be noted. For instance, for melting $KF \cdot 4\ H_2O$ which gives $KF \cdot 2\ H_2O + 2\ H_2O$, and melting $KF \cdot 2\ H_2O$ which gives $KF + 2\ H_2O$, eqn. (13) leads to identical predictions for $(\Delta S_{\mathrm{m}})_{\mathrm{th}}$. Experimentally we note a very large difference in corresponding ΔS_{m} values.

Some comments should be made on the model used by Telkes et al. [26].

(1) This type of calculation will apply only if $MX \cdot x\ H_2O$ is completely insoluble in the $(n - x)$ moles of water. This is not generally so, and a better description of the liquid phase would correspond to the mechanism symbolized by eqns. (9a) and (9b).

(2) Some calculated values of $(\Delta S^2_{\mathrm{m}})_{\mathrm{th}}$ by Telkes et al. [26] may seem to correspond quite satisfactorily with experimental determinations. This is a complete artefact, linked to the use of calculated $\Delta S_{\mathrm{m}}(MX)$ values, which may differ by a factor of 2 or even 3 from corresponding experimental $\Delta S_{\mathrm{m}}(MX)$ values.

This is particularly unfortunate, especially for predictive work, and in particular where salts with oxy anions (e.g. NO_3^-, SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, ClO_3^-, ClO_4^-) are concerned. On the other hand, it should be remembered that experimental $\Delta S_{\mathrm{m}}(MX)$ values are often unknown, or not very precisely determined.

CONCLUSIONS

The study of experimental melting enthalpies and entropies of about sixty salt hydrates ($MX \cdot n\ H_2O$) allows semi-empirical correlations, enabling the estimation, for a given value of *n* (number of moles of constituent water), of the value of the melting entropy [eqn. (6)], and melting enthalpy (if melting temperature is known), for any salt hydrate.

These correlations have been used in conjunction with a very simple model, giving a theoretical prediction, which compares (with a 10% margin of error) with experimental determinations.

This analysis will be refined using new experimental results actually performed, especially with compounds such as $CuSO_4 \cdot 5\ H_2O$, $Al(NO_3)_3 \cdot 9\ H_2O$, vitriol series $M(II)SO_4 \cdot 7\ H_2O$ (M = Mg, Fe, Ni, Co, Zn) and alums.

REFERENCES

1 Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, Cleveland, OH, 49th edn., 1968.
2 J.A. Dean (Ed.), Lange's Handbook of Chemistry, McGraw-Hill, New York, 12th edn., 1979.
3 J.H. Perry (Ed.), Chemical Engineers' Handbook, McGraw-Hill, New York, 4th edn., 1950.
4 D.V. Hale, M.J. Hoover and M.J. O'Neill, Phase Change Materials Handbook, N.A.S.A. Contractor Report 61363, 1971.
5 G. Belton and F. Ajami, N.S.F. Rep. RANN/SE/GAZ7979/TR/73/4, University of Pennsylvania.
6 S. Furbo and S. Svendsen Heat Storage in a Solar Heating System using Salt Hydrates, Thermal Insulation Laboratory Report, Den Polytekniske Laereanstatt, Copenhagen, 1977.
7 Proceedings of the Workshop on Solar Energy Storage Subsystems for the Heating and Cooling of Buildings, American Society of Heating, Refrigerating and Air-Conditioning Engineers Inc., Charlottesville, Virginia, April 1975. (a) M. Telkes, pp. 17–23; (b) G.A. Lane, S.W. Quigley, D.N. Glen, S.S. Drake, E.C. Clarke, J.S. Best and H.E. Rossow, pp. 43–56.
8 M. Telkes, in F. Daniels and J.A. Duffie (Eds.), Solar Energy Research, University of Wisconsin Press, 1955.
9 F.D. Rossini, D.D. Wagman, W.H. Evans, S. Levine and I. Jaffe, Natl. Bur. Stand., U.S., Circ. 500, 1952.
10 M. Telkes, ASME 64-WA/SOL, 1964, p. 9.
11 JANAF Thermochemical Tables, U.S. Dept. Commerce, N.B.S., Clearing, 1966.
12 R.L. Magin, B.W. Mangum, J.A. Statler and D.D. Thornton, J. Res. Natl. Bur. Stand., 86 (1981) 181.
13 S. Procopiu, C.R. Acad. Sci., 224 (1947).
14 M. Telkes, Phase change thermal storage, Monegon Ltd. Reprint, Gaitherburg, MD, 1980.
15 M. Farge-Coulombier, private communication.
16 K. Gawron and S. Schroder, Energy Res., 1 (1977) 351.
17 J.L. Chevalier and H. Sallee, (a) Communications Stockage de l'Energie solaire Appliquée au Bâtiment, Villeurbanne, 21st Jan., 1981; (b) Note d'information technique C.S.T.B. No. 26, Déc., 1978.
18 B. Carlsson, H. Stymne and G. Wettermark, Storage of Low-Temperature Heat in Salt-Hydrate Melts, Royal Institute of Technology, S-100 44, Stockholm.

19 G. Lane, J. Best, E. Clarke, D. Glen, G. Karris, S. Quigley and H. Rossow, NSF Contract -C906, Dow Chemical Company, Midland, MI 48640, U.S.A. and SARNSA, Ontario, Canada.

20 J. Lammers, International seminar on Future Energy Production, Heat and Mass Transfer Problems, Dubrovnik, 1975.

21 H.G. Lorsch, K.N. Kauffman and J.C. Denton, Energy Convers., 15 (1975) 1.

22 A.P. King, CH 1 6ES/ECRC/M893, The Electricity Council Research Center, Capenhurst, Chester, 1976.

23 K.K. Pillai and G.J. Brinkworth, Appl. Energy, 2, (3) (1976) 205.

24 J.W. Mullin, Crystallisation, Chemical and Engineering Series, Butterworths, London, 2nd edn., 1972, p. 453.

25 K. Kauffmann and I.C. Pan, NSF/RANN/SE/GI 27976/TR 73/5, 1973.

26 M. Telkes, P.F. Kando and P.H. Grambs, Rep. M 105, Monegon Ltd., Gaitherburg, MD, 1980.