[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNIVERSITY OF CALIFORNIA]

Specific Heats at Low Temperatures of Hydrates of Magnesium Chloride[1]

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Recent publications of the Pacific Experiment Station of the Bureau of Mines have dealt with the specific heat of anhydrous magnesium chloride at both low[4] and high[5] temperatures and with the heats of formation[6] at 298.16° K. of magnesium chloride and its hydrates. The present paper deals with low-temperature specific-heat and entropy data for hydrated magnesium chlorides, thus completing the basic data required for thermodynamic considerations of reactions and processes into which these substances enter.

Four hydrates are considered, the mono-, di-, tetra- and hexahydrates. The last three materials have been recognized generally as definite hydrates for some time. The monohydrate apparently was reported first by Moldenhauer.[7] The best evidence for its identification as a definite hydrate probably is the decomposition isobars established by Grube and Bräuning[8] and the heat of formation measurements of Shomate and Huffman.[6] The latter are particularly significant when considered jointly with the method of preparation used by these investigators. Further evidence also is afforded by the dehydration experiments of Treadwell and Zürrer.[9]

Materials[10]

The materials used in the present work were similarly prepared and in all cases virtually identical with the substances employed by Shomate and Huffman.

Merck's reagent-grade magnesium chloride hexahydrate, which contained some excess water, was stored over 80% sulfuric acid for seven days at room temperature and used without further purification. Analyses gave 34.81% Cl and 12.05% Mg, as compared with the theoretical values, 34.88 and 11.96%, respectively. No MgO, Ca^{++}, Fe^{+++}, or SO$_4^{--}$ were detected. A 97.10-g. sample was used in the measurements.

Magnesium chloride tetrahydrate was prepared from the hexahydrate by heating in air in an oven at 100–103° for six days. Analyses gave 42.39% Cl and 14.61% Mg, the theoretical figures being, respectively, 42.39% and 14.54%. The MgO content was found to be 0.012%. The calorimeter was filled with 95.97 g. of this material.

Magnesium chloride dihydrate was made from the tetrahydrate by heating in a stream of dry hydrogen chloride at temperatures gradually increasing from 170 to 220° until the required amount of water was removed. Actually, a small deficiency of water was found on analysis. This deficiency was made up by diffusing, at room temperature, the calculated amount of water into the sample. The material was then transferred to a Kjeldahl flask, evacuated and sealed, and aged for seven hours at 103°. The resulting product analyzed 54.04% Cl and 18.62% Mg (theoretical, 54.03 and 18.53%). The MgO content was determined as 0.01%. The sample used in the measurements contained 104.05 g.

To prepare magnesium chloride monohydrate, stoichiometric quantities of dihydrated and anhydrous magnesium chloride were mixed, placed in a flask which was then evacuated and sealed, and heated for sixteen hours at 120–140°. The anhydrous chloride used was that previously prepared by Kelley and Moore.[4] The product resulting from this process contained 62.44% Cl (calcd. 62.62%) and 21.57% Mg (calcd., 21.47%). The MgO content was determined as 0.14%. It required 90.61 g. of the monohydrate to fill the calorimeter.

Specific Heats

The previously described methods[11] and apparatus again were employed. The specific-heat results, expressed in defined calories (1 calorie = 4.1833 int. joules), are given in Table I and shown graphically in Fig. 1. Molecular mass figures, shown in the headings of Table I, accord with the 1941 International Atomic Weights.

The monohydrate results have been corrected for the 0.14% magnesia content. This correction varied from zero to 0.12%, depending on the temperature. The magnesia content of the other materials was insignificantly small.

As may be seen from Fig. 1, the specific-heat curves of the mono-, di- and tetra-hydrates are normal and require no discussion. The hexahydrate curve, however, exhibits a curious and unexpected maximum or transition with the peak at 136.7° K. The specific heat in the region of this maximum appeared to be perfectly reproducible. Two sets of measurements, labeled "a" and "b" in Table I, were made throughout the transition range, but under conditions involving considerable difference in heat treatment of the sample. The "a"-results were obtained after cooling from room temperature to 78.9° K. during a period of four hours and holding at 78.9° K. for one hour. During the course of the measurements, seven hours were required in raising the temperature from 78.9° K. to the peak. The "b"-results were obtained after cooling in a virtually identical manner, but the subsequent treatment was different. After the hydrates stood one hour at 78.9° K., measurements were started and carried up to 115.9° K. over a period of four and one-half hours. At this point the substance was allowed to stand fifteen hours, then measurements were started again and an additional eight hours were consumed in reaching the peak temperature. No difference is observable between these two sets of results. The third series of

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[4] Kelley and Moore, THIS JOURNAL, **65**, 1264 (1943).

[5] Moore, *ibid.*, **65**, 1700 (1943).

[6] Shomate and Huffman, *ibid.*, **65**, 1625 (1943).

[7] Moldenhauer, *Z. anorg. Chem.*, **51**, 369 (1906).

[8] Grube and Bräuning, *Z. Elektrochem.*, **44**, 134 (1938).

[9] Treadwell and Zürrer, *Helv. chim. acta*, **15**, 1271 (1932).

[10] These materials were prepared and analyzed by Dr. E. H. Huffman, Pacific Experiment Station, Bureau of Mines. The authors gratefully acknowledge this assistance.

[11] Kelley, THIS JOURNAL, **63**, 1137 (1941).

TABLE I

SPECIFIC HEAT OF $MgCl_2 \cdot H_2O$ (MOL. WT. 113.25 G.)

T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
53.5	6.452	105.3	14.84	216.4	24.28
56.9	7.068	114.8	16.06	226.3	24.83
60.5	7.710	125.6	17.34	236.3	25.30
64.6	8.490	135.7	18.41	246.2	25.75
69.1	9.317	145.7	19.34	256.3	26.18
74.1	10.22	157.2	20.38	266.4	26.64
81.7	11.43	166.0	21.10	275.9	27.04
81.9	11.45	175.8	21.78	285.9	27.27
86.7	12.22	185.6	22.49	295.7	27.51
87.0	12.25	196.3	23.22	298.2	27.48
95.7	13.57	206.0	23.72		

SPECIFIC HEAT OF $MgCl_2 \cdot 2H_2O$ (MOL. WT. 131.27 G.)

T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
54.1	8.521	104.7	18.77	206.1	31.37
57.6	9.342	114.4	20.35	215.9	32.15
62.1	10.38	124.7	22.00	225.8	33.01
66.8	11.53	134.8	23.46	236.2	33.81
70.8	12.37	145.3	24.84	246.2	34.70
75.1	13.27	155.2	26.10	256.2	35.39
81.2	14.44	165.6	27.36	266.3	36.12
85.6	15.31	175.4	28.40	276.3	36.84
90.2	16.22	185.7	29.46	285.7	37.40
94.9	17.08	195.9	30.51	295.0	37.90

SPECIFIC HEAT OF $MgCl_2 \cdot 4H_2O$ (MOL. WT. 167.30 G.)

T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
54.1	12.69	114.2	28.99	216.0	47.61
57.5	13.71	124.6	31.35	225.9	49.02
61.8	15.05	135.2	33.66	236.4	50.40
66.4	16.55	145.1	35.67	246.1	51.74
70.3	17.73	155.6	37.68	255.9	52.99
74.9	19.05	165.3	39.53	265.9	54.29
81.0	20.70	175.6	41.28	276.0	55.55
85.4	21.80	185.4	42.95	285.7	56.56
94.5	24.26	196.0	44.73	295.5	57.43
104.5	26.69	205.8	46.12		

SPECIFIC HEAT OF $MgCl_2 \cdot 6H_2O$ (MOL. WT. 203.33 G.)

T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
54.1c	18.90	123.8b	44.50	155.3a	50.51
56.9c	20.09	124.4a	44.66	159.0b	51.50
60.6c	21.66	126.4b	45.28	165.7a	53.00
64.7c	23.51	128.3b	45.87	169.6b	53.85
68.6c	25.15	130.3b	46.46	175.5a	55.07
73.1c	26.98	132.2b	46.98	179.7b	56.24
80.9a	29.88	134.0b	47.53	185.8a	57.37
80.9b	29.90	134.9a	47.60	195.9a	59.40
85.2a	31.49	135.9b	47.86	205.7a	61.10
85.2b	31.49	137.6b	47.86	216.1a	62.99
94.7a	34.94	139.4b	47.26	226.1a	64.64
94.7b	34.93	141.2b	47.31	235.9a	66.38
104.3b	38.14	142.9b	47.64	245.8a	68.16
104.4a	38.15	144.6b	48.01	255.5a	69.92
114.1b	41.31	145.5a	48.24	265.9a	71.21
115.0a	41.60	146.2b	48.40	276.2a	72.84
117.4b	42.43	147.8b	48.79	285.8a	73.92
120.7b	43.47	149.4b	49.12	295.8a	75.16
		151.0b	49.56		

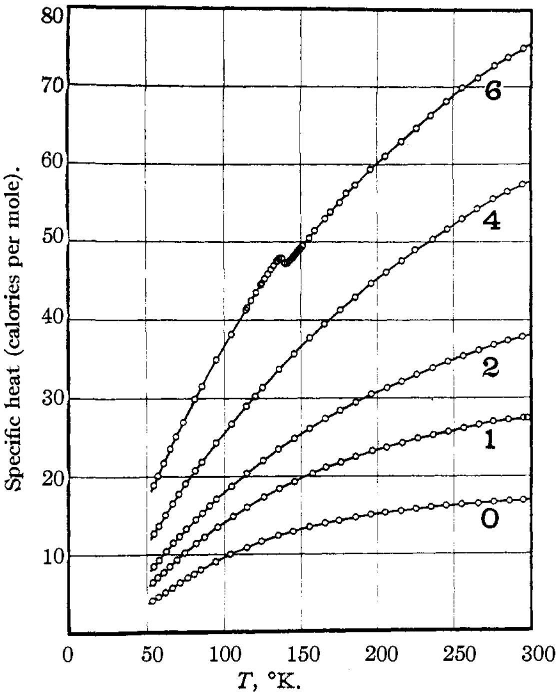

Fig. 1.—Specific heats of the hydrates of magnesium chloride. Figures indicate the number of moles of water of crystallization.

measurements, labeled "c," were obtained after cooling to 52.5° K. from room temperature during a period of eight hours and are seen to join nicely with the other two series.

It is to be noted also that the tetra- and dihydrates were prepared from the same batch of hexahydrate that was used in the measurements and 50 mole per cent. of the monohydrate also came from this source. The complete absence of any irregularity in the specific-heat curves of these other substances appears to preclude the possibility of the hexahydrate maximum being attributable to an impurity. In this connection it is significant to recall that the only operation in preparing the tetrahydrate from the hexahydrate was merely heating at 100–103°. Moreover, the marked difference in slope at temperatures above and below the maximum would indicate that the phenomenon is not the result of a minor impurity even though the height of the maximum above the adjacent portions of the curve is small.

Consequently, it is our considered opinion that this specific heat anomaly represents an energy change in the hexahydrate itself.

Entropies at 298.16° K.

The entropies were calculated in the usual manner, the portions between 50.12 and 298.16° K. being obtained by graphical integration under C_p against T curves and the portions lying below 50.12° K. being extrapolated. In determining the extrapolated portions the method of Kelley,

TABLE II

ENTROPIES AT 298.16° K. (CAL. PER DEG. MOLE)

	$MgCl_2 \cdot H_2O$	$MgCl_2 \cdot 2H_2O$	$MgCl_2 \cdot 4H_2O$	$MgCl_2 \cdot 6H_2O$
0–50.12°K. (extrap.)	2.80	3.75	5.73	8.76
50.12 to 298.16°K. (graph.)	30.05	39.27	57.35	78.75
$S^0_{298.2}$	32.8 ± 0.5	43.0 ± 0.5	63.1 ± 0.7	87.5 ± 1.0

TABLE III

FREE ENERGIES AT 298.16° (CAL. PER MOLE)

Substance	$\Delta Hf_{298.16}$ (1)	$\Delta Hf_{298.16}$ (2)	$\Delta S^0_{298.16}$ (1)	$\Delta S^0_{298.16}$ (2)	$\Delta F^0_{298.16}$ (1)	$\Delta F^0_{298.16}$ (2)
$MgCl_2$	−153,220 ± 110	0	−39.7 ± 0.2	0	−141,380 ± 130	0
$MgCl_2 \cdot H_2O$	−230,970 ± 110	−9,430 ± 30	−84.0 ± 0.5	−5.3 ± 0.5	−205,920 ± 190	−7,850 ± 150
$MgCl_2 \cdot 2H_2O$	−305,810 ± 110	−15,950 ± 30	−129.6 ± 0.5	−11.9 ± 0.5	−267,170 ± 190	−12,400 ± 150
$MgCl_2 \cdot 4H_2O$	−453,820 ± 110	−27,330 ± 45	−221.0 ± 0.7	−25.3 ± 0.7	−387,930 ± 240	−19,790 ± 210
$MgCl_2 \cdot 6H_2O$	−597,240 ± 120	−34,110 ± 60	−308.0 ± 1.0	−34.3 ± 1.0	−505,410 ± 320	−23,880 ± 310

The columns marked "(1)" refer to formation from the elements; those marked "(2)" refer to formation from anhydrous magnesium chloride and liquid water. The values of $\Delta H_{298.16}$ are from the paper of Shomate and Huffman (ref. 6). The entropies of the elements and of liquid water are from the compilation of Kelley, Bureau of Mines Bulletin 434, 1941.

Parks and Huffman[12] was employed, anhydrous magnesium chloride[4] being taken as the "standard" substance. The entropy figures are given in Table II.

In the case of the hexahydrate, the graphical integration between 133 and 140° K. was checked by the summation, $\sum_i \frac{C_{pi}\Delta T_i}{T_i}$, of the individual specific-heat determinations. It was possible to evaluate this sum accurately because the "b"-series of determinations was made with small temperature rises and without skipping any temperature gaps, the initial temperature of each determination being within 0.007° of the final temperature of the preceding determination. This calculation gave $S^0_{140} - S^0_{133} = 2.444$, while a similarly computed result for the total heat, $\sum_i C_{pi}\Delta T_i$, gave 333.47 calories per mole. The mean temperature for entropy calculation for this region is, therefore, 136.47° K., about 0.2° lower than the actual peak temperature. This indicates what may be seen readily on a larger-size plot of the data, namely, that the specific heat drops away from the maximum more sharply on the high-temperature side. Such behavior is characteristic of low-temperature specific-heat maxima.

Comparison of the present entropy results with the previously determined value for anhydrous magnesium chloride,[4] $S^0_{298.16} = 21.4 \pm 0.2$, yields the differences 11.4, 10.8, 10.4 and 11.0 per mole of water. These are fairly constant and in line with the differences between anhydrous and decahydrated sodium sulfate[13,14] and between anhydrous and dihydrated calcium sulfate,[14,15] which are 10.5 and 10.4 per mole of water, respectively. It would thus appear that, as a first approximation, the entropy of a hydrated salt may be computed from that of the anhydrous salt by adding about 10.8 units per mole of water of crystallization.

Related Thermal Data

A complete portrayal of the applications of these data to the various reactions occurring in the magnesium chloride–water system is beyond the scope of this paper and will be presented elsewhere. It may be well, however, to list values of the free energies of formation of these compounds at 298.16° K., computed from the present results and the data of Shomate and Huffman[6] in conjunction with the relationship $\Delta F^0 = \Delta H^0 - T\Delta S^0$. This is done in Table III.

Summary

Specific-heat measurements are reported of the mono-, di-, tetra- and hexahydrates of magnesium chloride in the temperature range 52 to 298° K. An anomaly was found in the specific heat of the hexahydrate with a peak temperature of 136.7° K.

The entropies at 298.16° K. were computed to be, respectively, 32.8 ± 0.5, 43.0 ± 0.5, 63.1 ± 0.7 and 87.5 ± 1.0 cal. per deg. mole.

Free energies of formation of the hydrates from the elements and from anhydrous magnesium chloride and liquid water are listed.

BERKELEY, CALIFORNIA RECEIVED AUGUST 25, 1943

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[12] Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

[13] Pitzer and Coulter, THIS JOURNAL, **60**, 1310 (1938).

[14] Kelley, Bureau of Mines Bulletin 434, 1941, 115 pp.

[15] Kelley, Southard and Anderson, Bureau of Mines Technical Paper 625, 1941, 73 pp.