[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY OF THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Cadmium Sulfate and its Hydrates. Heat Capacities and Heats of Hydration. Application of the Third Law of Thermodynamics[1]

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The heat capacities of $CdSO_4$, $CdSO_4 \cdot H_2O$ and $CdSO_4 \cdot 8/3H_2O$ have been measured from 15 to 315°K. The entropies are 29.41, 36.82 and 54.89 cal. deg.$^{-1}$ mole^{-1}, respectively, at 298.16°K. Tables of thermodynamic properties have been prepared for each of these substances. Their molal heats of solution in 400 moles of water are −10,977, −6095 and −2899 cal. mole^{-1}, respectively, at 298.16°K. For the reaction $CdSO_4 \cdot H_2O + 5/3H_2O(g) = CdSO_4 \cdot 8/3H_2O$, $\Delta H_{298.16}$ was calculated from the above entropy values and available dissociation pressures over a range of temperature. This value, −20,738 cal. mole^{-1}, obtained from the third law of thermodynamics is in excellent agreement with the calorimetric result −20,729. A similar calculation for the reaction $CdSO_4 + H_2O(g) = CdSO_4 \cdot H_2O$ utilizing a single available value of the dissociation pressure gives $\Delta H_{298.16} = -15{,}451$ cal. mole^{-1}. This agrees with the calorimetric value, −15,402 within the limit of error of the dissociation pressure. It is concluded that cadmium sulfate and its two hydrates approach zero entropy at limiting low temperatures.

The research reported in this paper is one of a series in this Laboratory on a variety of hydrated substances. The purpose is to find if possible disorder, particularly of the type due to hydrogen bonding, remains at limiting low temperatures. In the present case the compound $CdSO_4 \cdot 8/3H_2O$ is also of special interest because it is a product of the reaction in the Weston standard cell. The thermodynamics of this cell will be considered in another paper.

The reactions to be considered are

$$CdSO_4 \cdot H_2O(s) + 5/3H_2O(g) = CdSO_4 \cdot 8/3H_2O(s) \quad (1)$$

and

$$CdSO_4(s) + H_2O(g) = CdSO_4 \cdot H_2O(s) \quad (2)$$

$$\Delta H = \Delta F + T\Delta S$$

In each case ΔF, the free energy change, may be calculated from available dissociation pressures of the hydrate systems. The entropy values obtained by means of the third law of thermodynamics and the present heat capacity measurements can be used to calculate ΔS and thus ΔH, for each reaction. These results may then be compared with calorimetric determinations of ΔH to be given below.

Apparatus.—The low temperature heat capacities were measured by means of a calorimeter described by Kemp and Giauque,[2] except that Gold Calorimeter IV was replaced by a copper calorimeter with a gold resistance thermometer-heater. This was similar to the copper calorimeter described by Giauque and Archibald.[3]

Laboratory Standard Copper Constantan Thermocouple No. 105, which was used, was compared with several fixed points. It was found to be 0.01° high at both the triple point (13.94°K.) and the boiling point (20.36°K.) of hydrogen. It was correct at the triple point (63.15°K.) of nitrogen and read 0.01° high at the boiling point (77.34°K.) of nitrogen.

One defined calorie was taken as 4.1840 absolute joules and 0°C. = 273.16°K.

The heat of solution measurements were made in a calorimeter recently described by Kunzler and Giauque,[4] for the heats of dilution of sulfuric acid, except that the solid samples were introduced as described by Giauque and Archibald.[3] Water-proof plastic adhesive tape was used to fasten the Pyrex sample tube, which was approx. 7 cm. long and 2 cm. in diam., to a Pyrex rod. Gold foil, 0.025 mm. thick, was sealed to the flat ends of the sample tube with a very small amount of paraffin wax, and the plunger, for breaking the seals, was designed so that it would penetrate the top and push the sample through the bottom. The lower gold seal assembly was broken off intact from the wax rim by this process, which facilitated rapid solution of the sample. However, this had an unexpected result, which was not understood until a run was simulated with an unsilvered Dewar vessel to enable visual observation. It had been shown in preliminary experiments that the rate of heat introduction due to stirring was a constant. After the samples were dissolved the rate of heat introduction due to stirring changed in some samples. Visual observation showed that the loose piece of gold foil sometimes became attached to the stirrer and changed the rate of heat introduction. The data enabled correction for this effect but we recommend that no gold foil should be allowed to come loose and thus change stirring characteristics.

The average equilibrium times were 4, 8, 12 and 30 minutes for KCl, $CdSO_4 \cdot 8/3H_2O$, $CdSO_4 \cdot H_2O$ and $CdSO_4$, respectively, although observations were continued over considerably longer periods.

All instruments involving accuracy of the heat of solution measurements were checked against standards calibrated at the National Bureau of Standards.

The temperature of the calorimeter was kept below the thermostated bath temperature at all times to avoid possible distillation of water to the surroundings.

The temperature of the thermostat was obtained by means of a Bureau of Standards thermometer graduated at 0.02° intervals. A Beckmann thermometer showed that the thermostat stayed constant within 0.002° for the heat capacity and heat of solution runs for each sample. The temperature difference between the thermostat and the calorimeter was measured by means of a single copper-constantan thermocouple. A copper resistance thermometer heater was used in the calorimeter for the high precision needed.

The solution experiments were arranged to give the same final concentration and essentially the same water level in the calorimeter in all cases. The amount of water was determined by weight.

When it was necessary to cool the calorimeter, this was done by means of cold nitrogen as described in detail by Kunzler and Giauque.[4]

Several heat capacity measurements were made before and after solution in order to obtain the electrical equivalent of the heat of solution and to enable correction over a 1.5° interval to 25°. This was a straightforward procedure except that the plunger used to break the seals was above the liquid before solution and was left in it afterwards. This correction was only about 0.5 cal. mole^{-1} in the final value of the heat of solution at 25°.

Preparation and Analysis of Samples.—Pure cadmium metal (J. T. Baker Analyzed, total impurities 0.008%) was oxidized with excess HNO_3. Excess H_2SO_4 was then added, dropwise, and the crystals and liquid were heated to and held in the temperature range 130–150° for 36 hr. The mixture was then placed in an oven and the temperature was raised slowly to 300° and finally to 500°, and kept at that temperature for several days. The anhydrous, rhom-

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[1] This research was supported in part by the Office of Naval Research, United States Navy, and the United States Atomic Energy Commission.

[2] J. D. Kemp and W. F. Giauque, THIS JOURNAL, **59**, 79 (1937).

[3] W. F. Giauque and R. C. Archibald, *ibid.*, **59**, 561 (1937).

[4] J. E. Kunzler and W. F. Giauque, *ibid.*, **74**, 3472 (1952).

bic, $CdSO_4$ crystals were white, lustrous, well-formed and averaged 0.2 mm. in size.

As a check on the above procedure five samples were given a similar treatment on an analytical scale. The $Cd/CdSO_4$ ratios were found to be 0.53924, 0.53924, 0.53914, 0.53917, 0.53929, compared to the theoretical value 0.53921.

To ensure that all excess H_2SO_4 was removed by heating, a *p*H meter was used in a 0.1 molal solution of the $CdSO_4$. The value 5.12 obtained corresponds to that given by Latimer[5] for the pure salt.

$CdSO_4 \cdot 8/3H_2O$ was prepared by dissolving some of the anhydrous salt to form a nearly saturated solution. This was thermostated at 35 ± 0.1° and water was pumped off for 12 days. Crystals which started at the surface level were shaken to the bottom so that they were kept covered by the solution. After pumping was stopped they were allowed to stand at 35° for two weeks.

The preparation was drained on a Buchner funnel. The material was polycrystalline, opalescent, white and ranged in size from 0.5 to 5 mm. The crystals were cracked to an average size of 0.5 mm. and were cooled in liquid nitrogen in the hope of fracturing any crystal that had a solution inclusion. Final drying was accomplished by means of a stream of dry oxygen, which happened to be conveniently available.

Analysis for water content was effected by heating to a constant weight at 500°. Preliminary heating was carried out slowly until most of the water was removed slowly at relatively low temperatures. The material used for the heat capacity and solution experiments contained 99.69 mole % $CdSO_4 \cdot 8/3H_2O$ and 0.31 mole % $CdSO_4 \cdot H_2O$ as calculated from the hydrate–anhydrous ratio equivalent to $CdSO_4 \cdot 2.6615H_2O$.

One of the difficulties in working with hydrated crystals is the prevalence of solution inclusion, "brine holes." The presence of solution inclusion is made evident by eutectic melting superimposed on heat capacity measurements below 0°. This is a very sensitive test. Heat capacity measurements over the range 250 to 280°K. showed no evidence of brine holes in $CdSO_4 \cdot 8/3H_2O$, nor were any found in the monohydrate.

TABLE I

HEAT CAPACITY OF ANHYDROUS $CdSO_4$

Cal. deg.$^{-1}$ mole^{-1}, 0°C. = 273.16°K., mol. wt. $CdSO_4$ = 208.470, 1.5687 moles in calorimeter.

$T_{\text{ave.}}$, °K.	C_p	$T_{\text{ave.}}$, °K.	C_p
Series 1		150.03	16.39
15.22	0.595	156.72	16.83
17.07	0.785	163.49	17.27
19.06	1.056	170.54	17.72
21.97	1.466	177.73	18.14
25.49	1.947	184.79	18.56
28.52	2.464	192.07	18.97
31.13	2.903	199.44	19.34
34.27	3.451		
38.19	4.148	Series 2	
42.70	4.955	181.56	18.37
47.36	5.730	187.92	18.76
52.12	6.520	194.65	19.12
56.73	7.212	201.64	19.52
56.28	7.172	208.85	19.93
61.52	7.956	215.95	20.22
66.84	8.708	222.84	20.63
72.32	9.454	229.19	20.97
78.59	10.23	243.91	21.63
84.58	10.88	250.85	21.92
90.49	11.50	257.49	22.19
96.84	12.13	264.54	22.48
103.08	12.70	272.17	22.78
109.35	13.27	279.68	23.02
115.93	13.82	286.48	23.34
122.64	14.36	293.26	23.58
129.72	14.93	300.01	23.86
136.61	15.45	306.71	24.16
143.35	15.92	312.81	24.29

The α form of $CdSO_4 \cdot H_2O$ is stable in contact with saturated solution over the range 45 to 75°. The preparation was similar to that of $CdSO_4 \cdot 8/3H_2O$ except that the solution was thermostated at 68° during evaporation. The crystals were filtered and broken to an average size of 0.2 mm. in a box thermostated at 65°. Final drying was carried out at 68° in a thermostated flask by means of a pump.

Analysis for water by heating to 500° gave the hydrate/anhydrous ratio equivalent to $CdSO_4 \cdot 1.0011H_2O$ corresponding to 99.934 mole % $CdSO_4 \cdot H_2O$ and 0.066 mole % $CdSO_4 \cdot 8/3H_2O$.

The heat of solution measurements on the hydrates utilized the same samples as those used for the low temperature heat capacities. A new batch of well-formed anhydrous $CdSO_4$ crystals, averaging 0.2 mm. in size was prepared for the heat of solution experiments. The *p*H test gave 5.2 for a 0.1 *M* solution.

Low Temperature Heat Capacity Measurements.—The heat capacity observations are given in Tables I, II and III. Smoothed values of the thermodynamic properties are given in interpolation Tables IV, V and VI. The heat capacities of the two hydrates were each corrected for the small amount of the other one present. A smooth curve through the data should be accurate to 3% at 15°K., 1% at 20°K. and 0.1% above 35°K.

TABLE II

HEAT CAPACITY OF $CdSO_4 \cdot 1.0011H_2O$

Cal. deg.$^{-1}$ mole^{-1}, mol. wt. $CdSO_4 \cdot H_2O$ = 226.486, 0°C. = 273.16°K. (1.11279 moles $CdSO_4 \cdot H_2O$ + 0.00078 mole $CdSO_4 \cdot 8/3H_2O$) in calorimeter.

$T_{\text{ave.}}$, °K.	C_p	$T_{\text{ave.}}$, °K.	C_p
Series 1		158.08	21.43
253.07	29.20	166.20	22.20
259.99	29.66	174.52	22.94
267.57	30.16	182.79	23.67
274.26	30.61	190.78	24.37
		199.34	25.13
Series 2		208.79	25.88
14.88	0.632	216.98	26.62
17.02	0.895	225.61	27.20
18.58	1.138	234.01	27.75
20.04	1.369	242.50	28.45
21.71	1.669	251.15	29.04
23.47	2.044	259.99	29.68
25.72	2.375	268.85	30.25
28.62	2.988	277.66	30.81
32.04	3.761	287.05	31.41
36.04	4.510		
40.69	5.458	Series 3	
46.14	6.527	305.25	32.50
52.00	7.516	317.40	33.36
57.75	8.692	329.16	34.14
64.43	9.845	314.92	33.25
71.20	10.98	322.74	33.72
78.02	12.05		
85.09	13.07	Series 4	
92.16	14.04	118.75	17.33
98.72	14.90	126.02	18.15
105.03	15.70	128.67	18.44
111.69	16.52	231.82	27.64
118.71	17.34	240.08	28.26
126.16	18.18	286.69	31.40
134.01	19.02	296.44	32.04
141.97	19.85	306.40	32.67
150.01	20.64	316.75	33.36

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(5) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," 2nd Ed., Prentice–Hall, New York, N. Y., 1952, p. 172.

TABLE III

HEAT CAPACITY OF $CdSO_4 \cdot 2.6615H_2O$

Cal. deg.$^{-1}$ mole^{-1}, mol. wt. $CdSO_4 \cdot 8/3H_2O$ = 256.513, 0°C. = 273.16°K. (1.09059 moles $CdSO_4 \cdot 8/3H_2O$ + 0.00339 mole $CdSO_4 \cdot H_2O$) in calorimeter.

$T_{ave.}$, °K.	C_p	$T_{ave.}$, °K.	C_p
Series 1		102.21	22.73
256.21	45.73	107.43	23.66
261.92	46.43	112.81	24.66
268.10	47.17	118.31	25.67
274.28	47.92	123.87	26.64
		129.54	27.63
Series 2		135.23	28.57
		140.94	29.53
15.50	0.857	146.68	30.43
17.41	1.213	152.62	31.35
18.92	1.544	158.60	32.32
20.57	1.898	164.92	33.25
22.25	2.266	171.59	34.26
23.84	2.672	178.43	35.30
25.95	3.198	185.21	36.26
28.68	3.940	191.66	37.23
31.56	4.764	198.14	38.07
34.74	5.688	204.67	38.97
38.36	6.766	211.23	39.89
42.31	7.961	218.10	41.16
46.40	9.165	225.20	41.80
50.94	10.50	232.44	42.77
55.75	11.87	239.83	43.77
60.05	13.05	247.27	44.60
64.31	14.20	254.86	45.68
69.23	15.50	262.26	46.53
74.70	16.87	269.58	47.44
80.42	18.17	277.07	48.37
86.25	19.43	284.55	49.23
91.74	20.57	291.97	50.16
96.97	21.65	299.39	51.17

TABLE IV

THERMODYNAMIC PROPERTIES OF $CdSO_4$, CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K.	$C_p{}^0$	S^0	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$
15	0.570	0.190	0.143	0.047
20	1.180	0.433	0.321	.112
25	1.899	0.771	0.563	.208
30	2.712	1.188	0.853	.335
35	3.581	1.671	1.180	.491
40	4.474	2.207	1.536	.671
45	5.344	2.785	1.911	.874
50	6.173	3.391	2.296	1.095
55	6.969	4.017	2.685	1.332
60	7.724	4.656	3.074	1.582
70	9.149	5.956	3.842	2.114
80	10.384	7.260	4.585	2.675
90	11.451	8.546	5.290	3.256
100	12.420	9.804	5.955	3.849
110	13.316	11.031	6.585	4.446
120	14.151	12.227	7.182	5.045
130	14.937	13.391	7.749	5.642
140	15.679	14.526	8.290	6.236
150	16.381	15.632	8.806	6.826
160	17.049	16.710	9.300	7.410
170	17.687	17.761	9.775	7.986
180	18.297	18.787	10.230	8.557
190	18.880	19.791	10.669	9.122
200	19.438	20.774	11.094	9.680
210	19.972	21.736	11.504	10.232
220	20.482	22.678	11.902	10.776
230	20.969	23.600	12.286	11.314
240	21.434	24.503	12.659	11.844
250	21.879	25.388	13.020	12.368
260	22.306	26.254	13.369	12.885
270	22.717	27.103	13.706	13.397
280	23.115	27.935	14.034	13.901
290	23.500	28.752	14.353	14.399
298.16	23.806	29.408	14.605	14.803
300	23.875	29.554	14.663	14.891
310	24.240	30.342	14.965	15.377
320	24.596	31.116	15.260	15.856

TABLE V

THERMODYNAMIC PROPERTIES OF $CdSO_4 \cdot H_2O$ CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K.	$C_p{}^0$	S^0	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$
15	0.638	0.216	0.150	0.066
20	1.370	0.491	0.372	.119
25	2.269	0.890	0.659	.231
30	3.266	1.391	1.009	.382
35	4.297	1.972	1.405	.567
40	5.318	2.612	1.830	.782
45	6.314	3.296	2.273	1.023
50	7.277	4.008	2.724	1.284
55	8.206	4.741	3.176	1.565
60	9.099	5.490	3.628	1.862
70	10.779	7.016	4.527	2.489
80	12.328	8.560	5.409	3.151
90	13.745	10.095	6.258	3.837
100	15.065	11.612	7.073	4.539
110	16.307	13.107	7.857	5.250
120	17.482	14.577	8.611	5.966
130	18.597	16.021	9.336	6.685
140	19.658	17.436	10.034	7.402
150	20.672	18.827	10.709	8.118
160	21.644	20.190	11.360	8.830
170	22.597	21.528	11.990	9.538
180	23.479	22.842	12.601	10.241
190	24.346	24.131	13.194	10.937
200	25.183	25.400	13.771	11.629
210	25.991	26.648	14.334	12.314
220	26.771	27.875	14.881	12.994
230	27.525	29.082	15.415	13.667
240	28.254	30.269	15.934	14.335
250	28.962	31.438	16.441	14.997
260	29.651	32 588	16.936	15.652
270	30.324	33.720	17.420	16.300
280	30.984	34.835	17.892	16.943
290	31.634	35.933	18.354	17.579
298.16	32.157	36.815	18.724	18.091
300	32.275	37.014	18.807	18.207
310	32.910	38.081	19.251	18.830
320	33.541	39.133	19.687	19.446

The heat capacity measurements were continuous in the sense that each one started where the previous one ended, thus there were no uninvestigated intervals.

The values of $\int_0^{298.16} C_p/T\,dT$ for $CdSO_4$, $CdSO_4 \cdot H_2O$ and $CdSO_4 \cdot 8/3H_2O$ were found to be 29.41, 36.82 and 54.89 cal. deg.$^{-1}$ mole^{-1}, including extrapolated amounts of 0.19, 0.22 and 0.26 cal. deg.$^{-1}$ mole^{-1}, respectively, below 15°K. The heat capaci-

TABLE VI

THERMODYNAMIC PROPERTIES OF $CdSO_4 \cdot 8/3H_2O$, CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K.	C_p^0	S^0	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$
15	0.776	0.259	0.194	0.065
20	1.770	0.612	0.459	.153
25	2.958	1.132	0.839	.293
30	4.302	1.789	1.305	.484
35	5.754	2.564	1.838	.726
40	7.254	3.431	2.422	1.009
45	8.755	4.373	3.045	1.328
50	10.221	5.372	3.690	1.682
55	11.662	6.416	4.353	2.063
60	13.048	7.490	5.019	2.471
70	15.710	9.704	6.358	3.346
80	18.080	11.964	7.681	4.283
90	20.258	14.220	8.959	5.261
100	22.292	16.458	10.189	6.269
110	24.209	18.670	11.375	7.295
120	26.027	20.852	12.517	8.335
130	27.756	23.002	13.621	9.381
140	29.420	25.117	14.688	10.429
150	31.025	27.199	15.722	11.477
160	32.581	29.249	16.726	12.523
170	34.094	31.269	17.702	13.567
180	35.568	33.258	18.652	14.606
190	37.005	35.218	19.579	15.639
200	38.411	37.150	20.484	16.666
210	39.789	39.055	21.367	17.688
220	41.137	40.936	22.234	18.702
230	42.458	42.794	23.086	19.708
240	43.758	44.630	23.922	20.708
250	45.031	46.443	24.741	21.702
260	46.282	48.235	25.546	22.689
270	47.520	50.005	26.337	23.668
280	48.750	51.754	27.115	24.639
290	49.975	53.485	27.881	25.604
298.16	50.972	54.886	28.500	26.386
300	51.197	55.201	28.639	26.562
310	52.417	56.899	29.390	27.509
320	53.637	58.582	30.134	28.448

ties between 0 and 15°K. were estimated by plotting C_p/T^2 *vs.* T. The curves approached linearity below 15°K. since the C_p's were nearing the T^3 limiting law.

The Heat of Hydration of Cadmium Sulfate.—The ΔH for the process

$$CdSO_4 \cdot xH_2O + yH_2O = (CdSO_4 \cdot [x + y]H_2O) \text{ soln.}$$

was obtained for each of the three samples. The data relating to the solution of the several substances are given in Table VII. Several measurements on KCl are included as a check. The C.P. KCl used in the experiments was dried by heating at about 130° for 36 hours.

The average result for the reaction

$$KCl + 200H_2O = \text{soln. } \Delta H_{25°} = 4188 \pm 4 \text{ cal. mole}^{-1}$$

may be compared with a value 4192 ± 3 cal. mole^{-1} obtained by Cohen and Kooy.[6] The value of C. and K. has been corrected to the defined calorie.

The results in Table VII have been corrected for the small amount of $CdSO_4 \cdot 8/3\ H_2O$ in the $CdSO_4 \cdot H_2O$ and for the presence of monohydrate in the $CdSO_4 \cdot 8/3\ H_2O$.

TABLE VII

HEAT OF SOLUTION DATA

ΔH in cal. mole^{-1} at 25°

KCl, moles	$KCl \cdot 200H_2O$ ΔH	$CdSO_4$, moles	$CdSO_4 \cdot 400H_2O$ ΔH
0.20727	4194	0.103532	−10,978
.20721	4184	.102421	−10,979
.20723	4186	.106332	−10,973
Av.	4188 ± 4	Av.	−10,977 ± 2

$CdSO_4 \cdot 2.6615H_2O$, moles	$CdSO_4 \cdot 400H_2O$ ΔHcor. to $CdSO_4 \cdot 8/3H_2O$	$CdSO_4 \cdot 1.0011H_2O$, moles	$CdSO_4 \cdot 400H_2O$ ΔHcor. to $CdSO_4 \cdot H_2O$
0.102919	−2901	0.10499	−6098
.104919	−2899	.104701	−6084
.104881	−2898	.104967	−6096
		.104964	−6100
Av.	−2899 ± 1	Av.	−6095 ± 5

The difference in total heat capacities before and after solution permitted a rough evaluation of $\bar{C}_{p2}$ for $CdSO_4$ at the concentration $CdSO_4 \cdot 400H_2O$. The values obtained from $CdSO_4$, $CdSO_4 \cdot H_2O$ and $CdSO_4 \cdot 8/3H_2O$ were, respectively, −51.2, −51.2 and −52.7; average −52 cal. deg.$^{-1}$ mole^{-1}.

Cohen, Helderman and Moesveld[7] measured the heat of solution of $CdSO_4 \cdot 8/3\ H_2O$ in 400 moles of water at 18°. This may be corrected to 25° by means of the temperature coefficient from the present work. Their value is −2918 ± 6 cal. mole^{-1} compared to the present value −2899. They also measured the heat of solution of $CdSO_4$ which was obtained by heating the hydrate at 200°. Their value, corrected to 25°, is −11220 cal. mole^{-1} compared to the present value −10977. The difference may possibly be attributed to the presence of some microscopic material in their sample due to the method of dehydration.

$$CdSO_4 \cdot H_2O(s) + 5/3H_2O(l) = CdSO_4 \cdot 8/3H_2O(s) \quad (3)$$

$$\Delta H_{25°} = -6095 + 2899 = -3196 \text{ cal. mole}^{-1}$$

$$CdSO_4(s) + H_2O(l) = CdSO_4 \cdot H_2O \quad (4)$$

$$\Delta H_{25°} = -10{,}977 + 6095 = -4882 \text{ cal. mole}^{-1}$$

For the heat of vaporization of water at 25° Osborne, Stimson and Ginnings[8] give ΔH = 10514 cal. mole^{-1}.

Keyes[9] gives an equation for the gas imperfection of water which leads to $H_2O(g)$sat. = $H_2O(g)$ideal, ΔH = 6 cal. mole^{-1}. Combining the above two results the ideal heat of vaporization, $H^0(g) - H(l)$ = 10520 cal. mole^{-1}. Combining the ideal heat of vaporization with equations 3 and 4

$$CdSO_4 \cdot H_2O(s) + 5/3H_2O(g) = CdSO_4 \cdot 8/3H_2O(s) \quad (1)$$

$$\Delta H^0_{298.16} = -20{,}729 \text{ cal. mole}^{-1}$$

$$CdSO_4(s) + H_2O(g) = CdSO_4 \cdot H_2O(s) \quad (2)$$

$$\Delta H^0_{298.16} = -15{,}402 \text{ cal. mole}^{-1}$$

The entropy values obtained by means of the third law of thermodynamics may be tested by combining them with free energy data, to calculate the heats of hydration at 25°, and comparing these results with the calorimetrically measured values.

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$$\Delta H^0_{298.16°\text{K.}} = \Delta F^0_\text{T} + T\,\Delta S^0_{298.16°\text{K.}} - \int_{298.16}^{T} \Delta C_\text{p}\,\text{d}T + T\int_{298.16}^{T} \Delta C_\text{p}\,\text{d}\ln T$$

The free energy of reaction 1 may be calculated from data of Carpenter and Jette,[10] and Ishikawa and Murooka.[11] Carpenter and Jette measured the dissociation pressure over $CdSO_4 \cdot H_2O(s) - CdSO_4 \cdot 8/3H_2O(s)$. Ishikawa and Murooka measured the pressure of water vapor over saturated solutions of cadmium sulfate hydrates. At 316.76°K., $CdSO_4 \cdot 8/3H_2O$ undergoes a transition to α-$CdSO_4 \cdot H_2O$, thus we may use I. and M.'s value at the transition temperature.

The free energy of formation of $CdSO_4 \cdot 8/3H_2O$ from liquid water and $CdSO_4 \cdot H_2O$ is given by the expression $\Delta F^0 = 5/3\, RT \ln P_{H_2O}(\text{atm.})$.

The heat capacity and entropy of water were based on spectroscopic data.[12] $H_2O(g)$, $S^0_{298.16} = 45.106$. This was combined with the heat of vaporization of Osborne, Stimson and Ginnings[8] and the vapor pressure and gas imperfection equations of Keyes[9] to give $H_2O(l)$, $S^0_{298.16} = 16.71$.

$$CdSO_4 \cdot 8/3H_2O,\ S_{298.16} = 54.89 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$
$$CdSO_4 \cdot H_2O,\ S_{298.16} = 36.82 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$
$$CdSO_4,\ S_{298.16} = 29.41 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

TABLE VIII

HEAT OF THE REACTION $CdSO_4 \cdot H_2O(s) + 5/3H_2O(g) = CdSO_4 \cdot 8/3H_2O(s)$ FROM THE THIRD LAW OF THERMODYNAMICS

Units are cal. mole^{-1}

T, °K.	ΔF_T	Ref.	$T\Delta S_{298.16}$	$-\int_{298.16}^{T}\Delta C_\text{p}\text{d}T$	$\int_{298.16}^{T}\Delta C_\text{p}\text{d}\ln T$	$\Delta H_{298.16}$
298.15	−3719	C. and J.	−17027	0	0	−20746
298.16	−3708	C. and J.	−17028	0	0	−20736
303.33	−3411	C. and J.	−17323	−31	38	−20727
308.33	−3144	C. and J.	−17609	−62	79	−20736
313.28	−2871	C. and J.	−17891	−94	115	−20740
313.41	−2852	C. and J.	−17899	−95	116	−20740
316.76	−2674	I. and M.	−18090	−118	144	−20738

Av. from third law = −20738

Isothermal calorimetric measurement = −20729

The results are summarized in Table VIII.

The lack of trend in the values of $\Delta H_{298.16}$ in Table VIII supports the accuracy of the third law values although the individual values deviate appreciably from the average due to the limitations of the dissociation pressure data. However, the agreement of the calorimetric and third law values of the heat of reaction within 9 cal. mole^{-1} shows a consistency in terms of entropy of 0.03 cal. deg.$^{-1}$ mole^{-1}

For the reaction

$$CdSO_4(s) + H_2O(g) = CdSO_4 \cdot H_2O$$
$$\Delta F^0 = RT \ln P_{H_2O}(\text{atm.})$$

there is only one observation due to Ishikawa and Murooka[13] who give

$$P_{H_2O} = 0.62 \text{ mm. at } 25°,\ \Delta H^0 = \Delta F^0 + T\Delta S^0$$
$$\Delta H_{298.16} = -4210 + 298.16\,(36.82 - 29.41 - 45.11)$$
$$= -15451 \text{ cal. mole}^{-1}.$$

This is in satisfactory agreement with the more reliable calorimetric value, −15,402 cal. mole^{-1}, especially considering that each 0.01 mm. error in p_{H_2O} represents 10 cal. mole^{-1}.

The two third law agreements presented above indicate that $CdSO_4$, $CdSO_4 \cdot H_2O$ and $CdSO_4 \cdot 8/3H_2O$ all approach zero entropy at limiting low temperatures.

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[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Vapor Pressure of Water Over Aqueous Sulfuric Acid at 25°[1]

BY E. W. HORNUNG AND W. F. GIAUQUE

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Direct observations of the vapor pressure of water over $H_2SO_4 \cdot 4H_2O$, $H_2SO_4 \cdot 3H_2O$ and $H_2SO_4 \cdot 2H_2O$ have been made over a range of temperatures above 25°. These results with available partial molal heat content and heat capacity data have been used to calculate accurate values of the partial pressure of water at 25°. These results confirm the accuracy of the direct pressure observations of Shankman and Gordon, and of Stokes, and reinforce the earlier conclusion of Stokes that the cells H_2, H_2SO_4, $PbSO_4$, PbO_2, Pt and H_2, H_2SO_4, Hg_2SO_4, Hg have not given accurate activities of water or of sulfuric acid in the more concentrated range.

In connection with our series of investigations on the thermodynamics of the sulfuric acid–water system, from 15 to 300°K., accurate data on the free energy of dilution at 25° are essential. In much of the range below 20 molal H_2SO_4 the most effective methods appear to be either the direct measurement of the vapor pressure of water over the solutions, or measurements with some cell involving sulfuric acid, *e.g.*

$$Hg_2SO_4 + H_2 = H_2SO_{4(xm)} + 2Hg$$

Both types of measurement have been made by several observers. Results calculated from cell measurements by means of the Duhem equation fail to agree with the direct measurements within the expected limits of error. Our problem was to extend the data to a somewhat higher concentra-

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