

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

The Heat of Hydration of Sodium Sulfate. Low Temperature Heat Capacity and Entropy of Sodium Sulfate Decahydrate¹

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The heat capacity of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ has been measured from 15 to 300°K. The $\int_0^{298.15^\circ\text{K.}} C_p d \ln T$ has been found to be 139.95 ± 0.1 cal. deg.⁻¹ mole⁻¹ in comparison with the entropy value 141.46 obtained with the assistance of the heat and free energy of hydration. The residual entropy of 1.51 cal. deg.⁻¹ mole⁻¹ in the decahydrate, confirms the similar result reported by Pitzer and Coulter, and indicates disorder of about $R \ln 2 = 1.38$ cal. deg.⁻¹ mole⁻¹ in the crystal. The heat of solution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in an infinite amount of water was found to be $18,989 \pm 20$ cal. mole⁻¹. The heat of transition at 32.384° for the reaction $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(\text{s}) = (A - 10)/A \text{Na}_2\text{SO}_4(\text{s}) + 10/A \text{Na}_2\text{SO}_4 \cdot A\text{H}_2\text{O}(\text{liq. soln.})$ was determined to be $18,873 \pm 20$ cal. mole⁻¹. $A = \text{moles H}_2\text{O}/\text{mole Na}_2\text{SO}_4$ for saturation at the transition.

A considerable number of hydrated crystalline substances has been investigated in this Laboratory to find out whether any residual entropy remained at low temperatures, as in the case of ice where disordered hydrogen bonding² leads to this effect.³

No residual entropy has been found in hydrates except in the single case of sodium sulfate decahydrate where a residual entropy of 1.7 cal. deg.⁻¹ mole⁻¹ has been reported.⁴

During our work with various hydrates we have found that over-all analysis is not a sufficient criterion to prove that all of the material is in the desired hydrate form. For example, it has been shown that it is impracticable to prepare such hydrates as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ by crystallization from aqueous solution without some solution inclusions. These are not easy to detect by visual observation. Attempts to eliminate the excess water by preparing samples with the exact amount required for the particular hydrate also are impracticable since one ends up with a sample containing a lower hydrate plus solution inclusion. This maldistribution of water can be proved by means of measurements in a low temperature type calorimeter at the eutectic point between ice, the hydrate and the resulting solution, and sometimes at temperatures above the eutectic by means of the heat of solution. This type of error is not easy to detect if such a calorimeter is not used and we once asked the late Dr. F. R. Bichowsky who had made essentially complete surveys of existing heat of solution data on hydrates in connection with the International Critical Tables, and his well known book on Thermochemistry with Dr. F. D. Rossini, if he had found any case where an experimenter had evaluated such an error. His answer was no. Although the opportunities for obtaining equilibrium distribution of water in sodium sulfate decahydrate are probably much greater than with hydrates in general, it seemed worthwhile to subject the case of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to a re-examination, especially with respect to the heat of solution, and incidentally to remeasure the low temperature heat capacity. There is no reason to question the accuracy of the existing measurements on anhydrous

sodium sulfate which are necessary in connection with the test.

Heats of Dilution and Solution of Sodium Sulfate Decahydrate.—In order to avoid any possibility of the presence of anhydrous Na_2SO_4 in the samples, the heat of solution was measured on material with about 10% more water than corresponded to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Since we also suspect that it is difficult to take representative samples of the decahydrate both for analysis and experiment, the composition of the sample was determined by means of its original weight and analytical evaluation of the total Na_2SO_4 in the calorimeter after each heat of solution determination. A series of measurements on the heat of solution for concentrations near saturation was made in order to correct for the heat effect of the excess solution during the solution of the solid. A point was obtained with a supersaturated solution so that extrapolation was avoided.

The material used for the experiments was prepared from Baker and Adamson Reagent grade sodium sulfate, which was stated to have a total maximum impurity of 0.013%. This was recrystallized twice before use. The analyses for Na_2SO_4 were made by evaporating known fractions of the solution to dryness and heating the residue to about 850° (m.p. 884°) in a platinum crucible as recommended by Richards and Yngve.⁵

The heats of dilution and solution were measured in a calorimeter described by Kunzler and Giauque.⁶ The samples were enclosed in small glass cylinders, with thin glass cover plates cemented over the ends by means of Araldite 101 cement. The cover plates could be broken by means of a glass plunger to start the solution process. The total volume of the calorimeter was about 1 liter. The results for the dilution of the several solutions are given in Table I. The corrections from the final concentrations to infinite dilution were made by means of the data of Lange and Streack.⁷

TABLE I
HEAT OF DILUTION OF Na_2SO_4 SOLUTIONS
 $A = \text{moles H}_2\text{O}/\text{mole Na}_2\text{SO}_4$

Run	Na_2SO_4 , g.	t dilution, °C.	A	Mo-lar-ity final soln.	ΔH 25° cal. mole ⁻¹	ΔH_m final to ∞ dil., cal. mole ⁻¹	ΔH 25° to ∞ dil., cal. mole ⁻¹
1	6.2276	25.00	26.226	0.04756	1706	-239	1467
Interpolated	(25.00)	(28.365)		Satd. soln.			(1400)
2	5.6190	24.99	30.807	.04238	1562	-237	1325
3	5.0505	25.00	33.810	.03823	1481	-234	1247
4	4.4363	25.02	38.884	.03329	1311	-230	1081

The heats of solution of the samples of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ plus excess saturated solution are given in Table II.

The present value 18989 cal. mole⁻¹ for the heat of solution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in an infinite amount of water may be compared with the value 18840

(1) This work was supported in part by the National Science Foundation. The U. S. Government may reproduce this article.

(2) L. Pauling, *THIS JOURNAL*, **57**, 2680 (1935).

(3) W. F. Giauque and J. W. Stout, *ibid.*, **58**, 1144 (1936).

(4) K. S. Pitzer and L. V. Coulter, *ibid.*, **60**, 1310 (1938).

(5) T. W. Richards and V. Yngve, *ibid.*, **40**, 164 (1918).

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

(7) E. Lange and H. Streack, *Z. physik. Chem.*, **A157**, 1 (1931).

TABLE II
HEAT OF SOLUTION OF $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
 $A = \text{moles H}_2\text{O}/\text{mole Na}_2\text{SO}_4$

Run	Sample, g.	A av.	t soln., °C.	A sat.	Molarity final soln.
1	27.0515	15.188	25.00	28.368	0.070066
2	23.6197	11.741	25.01	28.346	.072371
3	25.5263	11.845	25.00	28.368	.076476

Run	$\Delta H_{\text{meas. total}}$	$\Delta H_{\text{dil. sat. soln.}}$	$\frac{\Delta H_{\text{soln. deca.}}}{\text{cal. mole}^{-1}}$	$\frac{\Delta H_{\text{final soln. to } \infty \text{ dil.}}}{\text{cal. mole}^{-1}}$	$\frac{\Delta H_{\text{deca. to } \infty \text{ dil.}}}{\text{cal. mole}^{-1}}$
1	927.71	30.15	19227	-240	18987
2	1173.04	10.41	19234	-240	18994
3	1253.73	11.84	19227	-240	18987

Av. 18989 \pm 20

obtained by Pitzer and Coulter. We have no reason to doubt that the difference is due to the maladjustment of water in the sample used by Pitzer and Coulter, since they depended on an over-all analysis for water as the criterion for pure decahydrate. We have calculated what the composition of their sample would have to be to give exact agreement of the heats of solutions. The result is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 0.99211$ mole; $\text{Na}_2\text{SO}_4 = 0.00278$ mole, $\text{Na}_2\text{SO}_4 \cdot 28.368\text{H}_2\text{O} = 0.00511$ mole in sat. soln. The heat of solution -560 cal. mole $^{-1}$ for anhydrous Na_2SO_4 was taken from Pitzer and Coulter⁴ in making the above calculation. It is, of course, possible that the discrepancy has some other origin.

Apparatus for Low Temperature Calorimetry.—The low temperature measurements were made in a copper calorimeter similar to one described by Giauque and Archibald.⁸ One defined calorie was taken as 4.1840 absolute joules and 0°C. = 273.15°K. Laboratory Thermocouple W-26 was used as a reference for the non-strain-free gold resistance thermometer-heater. The thermocouple had recently been

TABLE III

HEAT CAPACITY OF $\text{Na}_2\text{SO}_4 \cdot 9.601\text{H}_2\text{O}$, CAL. DEG. $^{-1}$ MOLE $^{-1}$
1 "mole" = 0.9601 mole $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ + 0.0399 mole Na_2SO_4 ; 0°C. = 273.15°K.

T , °K.	C_p	T , °K.	C_p	T , °K.	C_p
Series I					
252.57	115.98	81.28	44.33	238.58	110.69
264.97	120.49	89.05	48.67	246.80	113.80
271.12	122.73	97.05	52.88	254.71	116.65
278.07	125.64	104.66	56.64	262.54	119.49
		112.57	60.32	270.37	123.05
Series II					
13.14	1.09	120.42	63.92	278.00	125.41
15.16	1.91	127.69	67.12	285.59	128.40
18.15	3.21	135.14	70.73	293.03	130.99
Series III					
21.61	4.95	143.05	74.10	274.36	124.03
24.96	6.89	151.14	77.47	286.79	129.36
29.19	9.66	159.09	80.66	297.44	132.88
33.91	12.84	166.92	83.88	302.90	136.65
38.51	15.98	175.15	87.16	Transition	
43.41	19.47	183.23	90.29	313.06	223.58
49.07	23.49	191.50	93.40	319.17	246.46
54.85	27.68	199.42	96.39		
60.71	31.99	206.94	99.04		
67.24	36.18	214.70	101.68		
74.21	40.26	222.39	104.82		
		230.35	107.58		

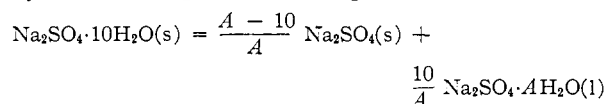
(8) W. F. Giauque and R. C. Archibald, THIS JOURNAL, 59, 561 (1937).

checked against the triple and boiling points of hydrogen and nitrogen with excellent agreement. For the present work the calorimeter was moved to a new laboratory and a new potentiometer was used. In the case of an accurate thermocouple the potentiometer is an essential part of the system calibrated, so a recomparison was made against the triple (13.94°K.) and boiling (20.36°K.) points of hydrogen and the triple (63.15°K.) and boiling (77.34°K.) points of nitrogen after assembly in the new laboratory. The new values of the microvoltages were about 0.02–0.03% higher than the previous ones which is within the relative limits of accuracy of the potentiometers. Appropriate corrections were made.

The Sample of "Sodium Sulfate Decahydrate."—No attempt was made to prepare a sample corresponding exactly to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and a 140.736 g. sample with an average composition $\text{Na}_2\text{SO}_4 \cdot 9.601\text{H}_2\text{O}$ was used. There was no appreciable heat effect at the eutectic so that 1 "mole" of sample contained 0.9601 mole of decahydrate and 0.0399 mole of Na_2SO_4 . Each run started where the previous one terminated so that there were no unexplored temperature intervals.

The Heat Capacity and Entropy of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.—The experimental heat capacity results are given in Table III.

The Heat of Transition.—Sodium sulfate decahydrate decomposes according to the reaction



where $A =$ the moles H_2O per mole of Na_2SO_4 in the saturated solution at the transition temperature.

A single measurement of the heat of this transition gave $18,873 \pm 20$ cal. mole $^{-1}$ of decahydrate at the transition temperature. This value was not utilized in the entropy considerations in this work but is included as a matter of record. The temperature of the transition was accepted as the accurately known value $32.384^\circ\text{C.} = 305.534^\circ\text{K.}$

The molal heat capacity of sodium sulfate decahydrate is given in Table IV. The data of Pitzer and Coulter⁴ on anhydrous sodium sulfate were used to correct the amount of Na_2SO_4 in the sample.

TABLE IV

MOLAL HEAT CAPACITY OF $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, CAL. DEG. $^{-1}$ MOLE $^{-1}$

Molecular weight = 322.22, 0°C. = 273.15°K.					
T , °K.	C_p	T , °K.	C_p	T , °K.	C_p
15	1.87	90	50.56	210	103.25
20	4.26	100	55.93	220	107.08
25	7.14	110	60.91	230	110.89
30	10.55	120	65.67	240	114.71
35	14.02	130	70.31	250	118.57
40	17.58	140	74.89	260	122.44
45	21.21	150	79.31	270	126.33
50	24.90	160	83.55	280	130.24
55	28.64	170	87.69	290	134.14
60	32.41	180	91.75	300	138.06
70	38.98	190	95.67		
80	44.91	200	99.48		

The $\int_0^{298.15} C_p d \ln T$ for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was found

to be 139.95 ± 0.10 cal. deg. $^{-1}$ mole $^{-1}$. This included an extrapolated amount of 0.28 cal. deg. $^{-1}$ mole $^{-1}$ below 15°K.

The Entropy of Hydration of Na_2SO_4 .—Pitzer and Coulter⁴ have summarized the available dis-

sociation pressure data of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. It has been very accurately measured by a number of observers and the value 19.19 cm. Hg = 0.02525 atm. is probably accurate to 0.1%. Thus for hydration

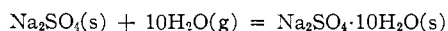
$$\Delta F = 10RT \ln P \text{ dissoci.}$$

$$\Delta F_{298.15^\circ\text{K.}} = -21,795 \text{ cal. mole}^{-1}$$

The heat of hydration may be obtained from the heat of solution data including the value $-560 \text{ cal. mole}^{-1}$ for Na_2SO_4 to infinite dilution obtained by Pitzer and Coulter.⁴ Their value is supported by the more recent work of Coughlin,⁹ who made solution measurements at 30° . Coughlin's result calculated to 25° is $-541 \pm 35 \text{ cal. mole}^{-1}$ in satisfactory agreement with the result of Pitzer and Coulter.

The heat of vaporization of water¹⁰ is taken as $10,520 \text{ cal. mole}^{-1}$ when the ideal gas is the final state. The entropy of water¹¹ in the ideal gas state is available from spectroscopic data. $S_{298.15} = 45.106 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ on the scale $0^\circ\text{C.} = 273.16^\circ\text{K.}$ When this is corrected to the new scale, $0^\circ\text{C.} = 273.15^\circ\text{K.}$, $S_{298.15^\circ\text{K.}} = 45.104 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

The above values give for the entropy of hydration



$$\Delta S = \frac{\Delta H - \Delta F}{T} = \frac{-124,749 + 21,795}{298.15}$$

$$= -345.31 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$S \text{ deca.} = S \text{ anh.} + 10S_{\text{H}_2\text{O}(\text{g})} - 345.31$$

$$= 35.73 + 451.04 - 345.31$$

$$= 141.46$$

The $\int_0^T C_p \, d \ln T$ given above for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was found to be $139.95 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. The discrepancy indicates that $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ retains $141.46 - 139.95 = 1.51 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ of residual entropy. This confirms the result obtained by Pitzer and Coulter.⁴ Pitzer and Coulter used earlier values of the entropy and heat of vaporization of water. Correction of their results by

(9) J. P. Coughlin, *THIS JOURNAL*, **77**, 868 (1955).

(10) M. N. Papadopoulos and W. F. Giauque, *ibid.*, **77**, 2740 (1955).

(11) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular No. 500, issued 1952.

means of the values used here yields a discrepancy of $1.54 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. However, as noted above, their values of the heat of hydration and entropy vary by substantial amounts from the ones determined here. The agreement results partly from inherent cancellation of some of the errors due to maldistribution of water in their samples and partly due to chance cancellation within about their estimated $0.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ error on their value of $\int_0^T C_p \, d \ln T$. Pitzer and Coulter placed their data books at our disposal and it was of interest to check some preliminary data obtained near the eutectic region shortly after the sample had been placed in the calorimeter. This showed a heat absorption of $127 \text{ cal. mole}^{-1}$ at the eutectic. After standing for 17 days the heat absorption at the eutectic had decreased to $23.5 \text{ cal. mole}^{-1}$ showing that water was reaching the anhydrous portion and converting it to the decahydrate. This contributes evidence in line with the earlier statement above to the effect that the samples used in the heat of solution measurements of P. and C. may have had some incomplete adjustment of the water content. Additional evidence may be noted from the fact that the heat capacities of P. and C. above the eutectic temperature are considerably higher than the present results due to a heat of solution effect. Our experience with other hydrates leads us to conclude that this particular hydrate system can distribute water at a much greater rate than is possible in most other cases many of which might require years. Within the limits of accuracy the disorder effect of $1.51 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ is equivalent to $R \ln 2 = 1.38 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ which could result from one water molecule with a double choice of position or a grouping with multiple choice of orientation. It seems highly probable that most of the water molecules are held in definitely ordered arrangement by the attracting ions. In general the orienting forces between ions and water molecules are so great that in nearly all cases order will be produced at the temperatures where the hydrates are formed from solution. Cases where two or more positions of nearly equal energy exist, leading to the persistence of disorder to temperatures so low that an ordering mechanism cannot operate, are likely to occur very rarely.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Vapor Pressure and Heat of Vaporization of Some Simple Molten Electrolytes

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The vapor pressures of the molten electrolytes NaBr, AgCl, AgBr, ZnCl₂, ZnBr₂, CdBr₂, CdI₂ and PbBr₂ have been measured over a pressure range of 2 to 600 mm. by a boiling point method. Heat and entropy of vaporization, and normal boiling point have been calculated for each electrolyte.

Introduction

Investigation of vapor pressure of molten electrolytes is beset with considerable experimental difficulty which has led to the publication of

numerous, widely varying results for many individual substances. Kelley¹ has coordinated and assessed the best available information on vapor

(1) K. K. Kelley, U. S. Bureau of Mines Bulletin No. 383, 1935.