

Thermodynamic Investigation of Disorder in the Hydrates of Sodium Carbonate

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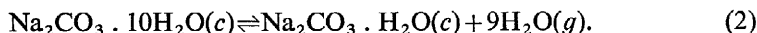
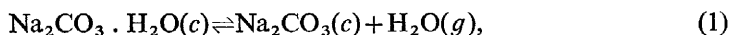
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Received 16th October, 1967

Measurements have been made of the molar heat capacity of crystalline anhydrous sodium carbonate and of the monohydrate and decahydrate from ~ 15 to $\sim 300^\circ\text{K}$, of the integral heat of solution in water at 25°C of these three salts, and of the water vapour dissociation pressure at 25°C for the salt pairs, anhydrous salt+monohydrate and monohydrate+decahydrate. The calorimetric entropies at 25°C have been compared with the values obtained from the experimental entropy changes for the two equilibria and the calorimetric entropy of the anhydrous salt. For the monohydrate, the calorimetric entropy is $40.19 \pm 0.2 \text{ cal deg}^{-1} \text{ mole}^{-1}$ and the entropy derived from the equilibrium study is $40.16 \pm 0.1 \text{ cal deg}^{-1} \text{ mole}^{-1}$, implying that the monohydrate achieves a state of perfect order at 0°K . For the decahydrate, however, the calorimetric entropy is less than the value derived from the equilibrium study by $1.5 \pm 0.5 \text{ cal deg}^{-1} \text{ mole}^{-1}$, this entropy difference being the same as that found for sodium sulphate decahydrate. The disorder persisting in both salts at 0°K probably derives from the same cause, randomness in some of the hydrogen bonding.

Some dissociation pressure measurements have been made using anhydrous sodium carbonate in a finely divided form. The values differ appreciably from those obtained using the macro-crystalline salt. Reasons are given for believing that previous dissociation pressure measurements made on systems involving the metastable heptahydrate are not reliable.

Thermodynamic studies, mostly by Giauque and his co-workers, have shown that of about 20 hydrates so far examined, only two are disordered at the absolute zero. These are sodium sulphate decahydrate^{1, 2} and disodium hydrogen phosphate dodecahydrate.³ We report here the results of an investigation of the monohydrate and decahydrate of sodium carbonate. This has involved (a) heat capacity measurements on these two hydrates and the anhydrous salt down to low temperatures, to give the apparent calorimetric entropy of each salt at 25°C , (b) the indirect determination of the entropies of the two hydrates at 25°C by studying the equilibria:



The data needed for (b) are the integral heats of solution of the three salts, preferably to give a very dilute aqueous solution of a particular concentration, and the water-vapour dissociation pressure at 25°C for the reactions (1) and (2). We have measured all of these quantities. No heat capacity measurements appear to have been made on the hydrates of sodium carbonate. Anderson⁴ determined C_p for the anhydrous salt, but only down to $\sim 54^\circ\text{K}$.

EXPERIMENTAL

The heat capacities were measured with the two adiabatic calorimeters previously described,³ except for C_p for the two hydrates from the lowest temperatures to 50°K , which were determined with an earlier calorimeter in which adiabatic conditions were maintained

by manual, and not automatic, control. The measurements started at 9°K for the anhydrous salt and at ~14°K for the two hydrates. The heats of solution of the three salts were found with the calorimeter used in our work on the disodium hydrogen phosphate system, the concentration of the final sodium carbonate solution being 1 mole of Na_2CO_3 to 2,400 moles of water. Likewise, the same technique as before was used to measure the water-vapour dissociation pressure at $25.00 \pm 0.01^\circ\text{C}$ for the reactions (1) and (2). The water-vapour dissociation pressure values used to estimate the entropy changes in these reactions were obtained when both solids in the vapour-pressure apparatus were in a definite crystalline form. But some dissociation pressure measurements were also made on systems in which one of the two solid phases was in a less well-defined state, and the results of these are briefly reported below, as they give some indication of the effect which the method of preparation of a solid phase can have on its Gibbs energy.

Macrocrystalline anhydrous sodium carbonate was prepared by melting A.R. Na_2CO_3 in a platinum boat in a stream of carbon dioxide. It was allowed to cool overnight, then stored over P_2O_5 . Jaffray and Martin⁵ have reported that anhydrous sodium carbonate has a second-order phase transition at 359°C and a first-order transition at 481°C, and the existence of these transitions has been confirmed by Brouns *et al.*⁶ To reduce the possibility of the sample containing a supercooled high-temperature phase, the crystalline mass was roughly ground and maintained for 6 h at 310°C (i.e., 50° below the temperature of the lowest transition).

$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ crystallizes out of solution as the stable phase above ~36°C. It was prepared⁷ by isothermal crystallization at 75°C followed by rapid filtration, keeping the temperature above 40°C. A stream of dry air was passed over the crystals for 30 min after which they were dried over anhydrous Na_2CO_3 . We shall refer to attempts to measure water vapour dissociation pressures at 25°C in systems involving the metastable heptahydrate, and for these this salt was prepared in a similar manner except that the crystallization was carried out in a thermostatically controlled tank at 34.0°C. Analyses of specimens of the decahydrate prepared on a laboratory scale convinced us that they were more likely to contain occluded mother liquor than the commercially available A.R. material, and our experiments were therefore carried out with the latter.

The water content of the hydrates was determined by heating *in vacuo* to constant weight. The decahydrate used in the C_p and heat of solution measurements analyzed as $\text{Na}_2\text{CO}_3 \cdot 9.988 \text{ H}_2\text{O}$, and the monohydrate used in the C_p determinations as $\text{Na}_2\text{CO}_3 \cdot 1.000 \text{ H}_2\text{O}$. Heat-of-solution measurements on the monohydrate were made on this sample and also on samples analyzing as $\text{Na}_2\text{CO}_3 \cdot 1.014 \text{ H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 1.018 \text{ H}_2\text{O}$. Values of the heat of solution obtained on the last two samples and on the decahydrate were corrected to give the value for the stoichiometric solid assuming that they contained the small amount of decahydrate or monohydrate appropriate to the overall composition.

RESULTS

For none of the three salts was there any sign of any transition or thermal anomaly. Values of C_p at regular temperature intervals are given in table 1, with derived thermodynamic quantities. The experimental C_p values were smoothed graphically up to ~50°K, and from there to room temperature on a least-squares basis by fitting them to six-term polynomials with a KDF9 computer. Increasing the number of terms produced no significant improvement in the residuals. The extrapolations to 0°K needed to complete the evaluation of the calorimetric entropies at 25°C were effected by fitting the three or four lowest heat capacity values to a Debye function. As far as we are aware, the only C_p determinations made on any of these salts are those of Anderson⁴ on the anhydrous carbonate from ~55 to 290°K. He used a commercial sample, which was presumably finely divided. His results from 55 to 255°K are higher than ours by about 1 %, but from 255°K upwards his values fall below ours, the discrepancy reaching about 1 % at 290°K.

The heats of solution, which are recorded in table 2, cannot profitably be compared

TABLE 1.—MOLAR THERMODYNAMIC PROPERTIES OF SODIUM CARBONATE AND ITS HYDRATES.
(1 cal = 4.1840 abs. J)

Na ₂ CO ₃				
T°K	C _p cal/deg.	S cal/deg.	(H-H ₀ ^o) cal	-(G-H ₀ ^o)/T cal/deg.
10	0.135	0.045	0.36	0.01
20	0.675	0.275	4.05	0.07
30	1.870	0.755	16.04	0.22
40	3.610	1.525	42.84	0.45
50	5.660	2.555	88.7	0.78
60	7.820	3.78	156.3	1.18
70	9.79	5.14	244.5	1.65
80	11.56	6.56	351.4	2.17
90	13.14	8.02	475.1	2.74
100	14.54	9.47	613.6	3.33
110	15.78	10.92	765.3	3.96
120	16.86	12.34	928.7	4.60
130	17.83	13.73	1102	5.25
140	18.68	15.08	1285	5.90
150	19.45	16.40	1476	6.56
160	20.15	17.67	1674	7.21
170	20.79	18.92	1878	7.87
180	21.39	20.12	2089	8.51
190	21.96	21.29	2306	9.15
200	22.49	22.43	2528	9.79
210	23.01	23.54	2756	10.42
220	23.50	24.63	2988	11.05
230	23.97	25.68	3226	11.65
240	24.42	26.71	3468	12.26
250	24.85	27.72	3714	12.86
260	25.27	28.70	3965	13.45
270	25.67	29.66	4220	14.03
280	26.09	30.60	4478	14.61
290	26.53	31.52	4741	15.17
300	27.03	32.43	5009	15.73
298.15	26.84	32.26	4959	15.63
Na ₂ CO ₃ · H ₂ O				
10	(0.08)	0.03	0.20	0.01
20	0.62	0.21	3.15	0.06
30	2.14	0.71	16.55	0.16
40	4.28	1.60	48.15	0.40
50	6.87	2.83	103.9	0.75
60	9.50	4.32	186.0	1.22
70	11.90	5.97	293.2	1.78
80	14.09	7.70	423.4	2.41
90	16.06	9.48	574.3	3.10
100	17.83	11.26	743.9	3.82
110	19.42	13.04	930.4	4.58
120	20.84	14.79	1132	5.36
130	22.19	16.51	1347	6.15
140	23.26	18.19	1574	6.95
150	24.31	19.83	1812	7.75
160	25.26	21.43	2060	8.56
170	26.15	22.99	2317	9.36

TABLE 1.—*continued*

$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$				
$T^\circ\text{K}$	C_p cal/deg.	S cal/deg.	$(H-H_0^\circ)$ cal	$-(G-H_0^\circ)/T$ cal/deg.
180	26.99	24.51	2582	10.17
190	27.80	25.99	2856	10.96
200	28.60	27.44	3138	11.75
210	29.38	28.85	3428	12.53
220	30.16	30.24	3726	13.30
230	30.93	31.59	4031	14.06
240	31.70	32.93	4345	14.83
250	32.44	34.24	4665	15.58
260	33.14	35.52	4993	16.32
270	33.76	36.78	5328	17.05
280	34.28	38.02	5668	17.78
290	34.65	39.23	6013	18.50
300	34.81	40.41	6360	19.21
298.15	34.80	40.19	6296	19.07

$\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$				
$T^\circ\text{K}$	C_p cal/deg.	S cal/deg.	$(H-H_0^\circ)$ cal	$-(G-H_0^\circ)/T$ cal/deg.
10	(0.46)	0.15	1.15	0.03
20	3.25	1.17	17.3	0.30
30	9.17	3.50	76.8	0.94
40	15.88	7.04	203.1	1.96
50	23.25	11.45	397.4	3.50
60	30.48	16.34	666.8	5.23
70	36.95	21.53	1004	7.19
80	42.80	26.86	1404	9.31
90	48.14	32.21	1859	11.56
100	53.09	37.54	2365	13.89
110	57.73	42.82	2919	16.28
120	62.16	48.04	3519	18.71
130	66.44	53.18	4162	21.17
140	70.64	58.26	4847	23.64
150	74.80	63.27	5575	26.10
160	78.97	68.23	6343	28.59
170	83.16	73.15	7154	31.07
180	87.40	78.02	8007	33.54
190	91.68	82.86	8902	36.01
200	96.01	87.67	9840	38.47
210	100.35	92.46	10822	40.93
220	104.69	97.23	11847	43.38
230	108.97	101.98	12916	45.82
240	113.15	106.71	14027	48.26
250	117.17	111.41	15179	50.69
260	120.95	116.08	16370	53.12
270	124.41	120.71	17597	55.54
280	127.44	125.29	18856	57.95
290	129.95	129.81	20144	60.35
300	131.82	134.25	21453	62.74
298.15	131.53	133.43	21210	62.29

with the values of previous workers, since none of these was determined for such a low concentration of the final solution, and any attempt to allow for dilution involves a considerable and uncertain correction due to the changing degree of hydrolysis.

In the measurements of the equilibrium pressure $p_{10/1}$ for the dissociation of the decahydrate to the monohydrate (reaction (2)), equilibrium was fairly rapidly established, and the steady pressure measured when the system was brought up to 25°C and held at this temperature was later exactly reproduced when the salt mixture was warmed and then cooled at 25°C. Two separate series of measurements, lasting several months, each gave $p_{10/1} = 16.46 \pm 0.02$ int. mm Hg. This quantity does not seem to have been measured before, but values have been published for the dissociation pressures $p_{10/7}$ and $p_{7/1}$ for the two possible reactions involving the metastable heptahydrate. We therefore prepared a sample of the heptahydrate (which at atmospheric pressure is strictly only stable between ~32 and 35°C), and used it mixed with either decahydrate or monohydrate in attempts to measure $p_{10/7}$ and $p_{7/1}$. It took appreciably longer to reach reasonably constant values of the water-vapour dissociation pressure than in the decahydrate + monohydrate system, and individual values showed a larger deviation from the mean. However, $p_{10/7}$ was 18.24 ± 0.05 mm and $p_{7/1}$ was 16.89 ± 0.06 mm; Baxter and Cooper⁸ reported

TABLE 2.—INTEGRAL MOLAR HEATS OF SOLUTION OF SODIUM CARBONATE AND ITS MONOHYDRATE AND DECAHYDRATE IN 2,400 MOLES OF WATER AT 25°C (1 cal = 4.1480 abs. J).

The experimental values refer to the stoichiometric solids, having been corrected for any slight departure of the sample used from the exact stoichiometric composition.

salt	expt. value	mean
anhydrous	-5,415; -5,429; -5,419	-5,421 ± 10
monohydrate	-1,897; -1,909; -1,899; -1,910	-1,901 ± 10
decahydrate	+16,633; 16,625; 16,646; 16,640; 16,624	+16,634 ± 15

a value of 18.01 mm for $p_{10/7}$ at 25°C. Andreae⁹ measured the difference between $p_{10/7}$ and $p_{7/1}$, and if his results¹⁰ are combined with those of Baxter and Cooper, they give 16.5 mm for $p_{7/1}$ at 25°C. There should be a simple relation between $p_{10/1}$, $p_{10/7}$, and $p_{7/1}$ at a given temperature, viz.,

$$3 \log p_{10/1} = 2 \log p_{10/7} + \log p_{7/1}. \quad (3)$$

If our values of $p_{7/1}$ and $p_{10/7}$ are inserted in (3) they give $p_{10/1} = 17.34$ mm; if the literature values are used, $p_{10/1}$ is 17.0 mm. Neither of these figures for $p_{10/1}$ agrees with our experimental value of 16.46 mm. This is not surprising, since at room temperature the heptahydrate visibly decomposes in a few days, presumably into the decahydrate and monohydrate in an ill-defined condition (or at least in the form of very small particles). Baxter and Cooper measured $p_{10/7}$ by a dynamic method and obtained the same value whether the air-stream before reaching the hydrate mixture was under-saturated or over-saturated with water vapour.

Four separate runs were carried out to determine $p_{1/0}$ at 25°C, using a mixture of the monohydrate and the crystalline anhydrous salt. Each run gave the same value within the experimental error, the weighted mean for all four runs being 5.28 ± 0.03 mm. The values obtained by warming the salt mixture to 25°C did not differ from those recorded after cooling the mixture to this temperature. Some measurements were also made with mixtures of the crystalline monohydrate with one of two other samples of the anhydrous carbonate, namely (a) A.R. Na_2CO_3 , dried at 300°C, (b) the salt obtained by decomposing A.R. NaHCO_3 at 240°C. With either of these samples, it took longer (sometimes a week or more) for a steady pressure to be established, and several runs from both directions had to be performed before the

final pressures became more or less the same, regardless of whether 25°C had been reached by warming or cooling the salt mixture. With sample (a), the final value of $p_{1/0}$ was 4.3 ± 0.1 mm and with (b) 4.8 ± 0.1 mm. These lower pressures are consistent with the finely divided anhydrous carbonate samples having higher Gibbs energies than the macrocrystalline form. These two pressures correspond to molar Gibbs energy differences between the finely divided and crystalline salts of ~ 120 cal and ~ 50 cal respectively.

Caven and Sand⁷ measured $p_{1/0}$ over a range of temperature by a static method. They do not state how the anhydrous carbonate was prepared. Their values for a given temperature differ by several mm, according to whether the sample had been heated or cooled to that temperature.

DISCUSSION

From data on solutions of comparable electrolytes, it appears that the relative partial molal heat content of the water in the dilute solution formed in the heat of solution experiments is so small that the error involved in taking it as zero is insignificant. From the results recorded above, and taking $10,519.5$ cal mole⁻¹ for the heat of vaporization of water,¹¹ we obtain the following thermodynamic parameters for reaction (1) at 298.15°K:

$$\Delta G_{1/0}^\circ = 2,944 \pm 3 \text{ cal}; \quad \Delta H_{1/0}^\circ = 14,037 \pm 15 \text{ cal}; \quad \Delta S_{1/0}^\circ = 37.21 \pm 0.06 \text{ cal deg.}^{-1} \text{ mole}^{-1}$$

The molar entropy of water as an ideal gas at 1 atm at 298.16°K is 45.104 cal deg.⁻¹ mole⁻¹.¹² If we assume that crystalline anhydrous sodium carbonate is completely ordered at 0°K, then from the calorimetric entropy of this salt at 298.15°K and the value of $\Delta S_{1/0}$ we obtained 40.16 cal deg.⁻¹ mole⁻¹ for the molar entropy of the monohydrate at this temperature, in agreement with the calorimetric value of 40.19 ± 0.2 cal deg.⁻¹ mole⁻¹. It seems certain, therefore, that the monohydrate achieves a state of perfect order at 0°K.

For reaction (2) at 298.15°K we find

$$\Delta G_{10/1}^\circ = 20,435 \pm 8 \text{ cal}; \quad \Delta H_{10/1}^\circ = 113,218 \pm 20 \text{ cal}; \quad \Delta S_{10/1}^\circ = 311.20 \pm 0.1 \text{ cal deg.}^{-1} \text{ mole}^{-1}$$

This value of $\Delta S_{10/1}$, together with a value of 40.19 cal deg.⁻¹ mole⁻¹ for the molar entropy of the monohydrate gives a value of 134.93 ± 0.3 cal deg.⁻¹ mole⁻¹ for the molar entropy of the decahydrate. This exceeds the calorimetric entropy of 133.43 ± 0.2 cal deg.⁻¹ mole⁻¹ by 1.50 ± 0.5 cal deg.⁻¹ mole⁻¹, which is the same within experimental error as the corresponding discrepancy of 1.51 cal deg.⁻¹ mole⁻¹ for sodium sulphate decahydrate found by Brodale and Giauque.² Sodium carbonate decahydrate therefore provides a third example of a salt hydrate in which some disorder persists to the absolute zero.

A thorough study of the structure of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ has yet to be made, but probably the origin of the disorder is essentially the same as in $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. In other words, it may be expected that most of the water molecules are involved in an ordered hydrogen-bonded arrangement, but that there is one unit per formula weight made up of water molecules and the oxygen atoms of the carbonate ions for which there are two possible arrangements of the hydrogen bonds. Utilization of both possible arrangements down to 0°K would confer residual entropy of $R \ln 2$ per mole on the crystal, which within experimental error agrees with the observed value of 1.5 cal deg.⁻¹ mole⁻¹.

We thank Mr. N. F. Mable and Mr. H. R. Harper for assistance with the experimental work, and Imperial Chemical Industries Ltd. for financial help. One of us (C. G. W.) thanks Messrs. Albright and Wilson for a Research Grant.

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