It has been shown that the density of saturated carbon dioxide vapor is the same in the presence or absence of water within the experimental error. Assuming applicability of Raoult's law and direct proportionality between vapor pressure and vapor density, it may be calculated that the solubility of water in liquid carbon dioxide is less than about 0.05% by weight over the temperature range of this investigation. Attention has been called to qualitative evidence of the formation of a solid hydrate of carbon dioxide at about 4°.

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# THE SYSTEM POTASSIUM CARBONATE, SODIUM CARBONATE AND WATER AT 40° AND THE TRIHYDRATE OF SODIUM CARBONATE

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An investigation of this system has been proceeding in this Laboratory for a number of years and brief statements of progress have appeared elsewhere.[1] The excellent investigations of Hill and Miller[2] have thrown a flood of light upon the various phases which exist between 20 and 40° and have explained some of the difficulties encountered in the work here; conflicting results which were met with early in our study have focused attention on the isotherm of 40°. This communication gives additional data which had escaped the notice of previous investigators.

At the outset of our work a number of determinations confirmed the accuracy of the results of Osaka[3] and of Kremann and Zitek[4] regarding the composition of the saturated solution; the residues were not analyzed and the existence of the double salt $K_2CO_3.Na_2CO_3.12H_2O$ was assumed, instead of the solid solution $(K_2Na_2)CO_3.6H_2O$ found by Hill and Miller. In order to be well beyond the transition point of the supposed double salt, the temperature of 40° was selected for the next isotherm. An inspection of the solubility curves for potassium and sodium carbonates showed that there was only a slight variation in solubility in both cases with a change of temperature of several degrees, and for this reason an ordinary thermometer divided to single degrees was considered sufficiently accurate to show the temperature of the bath; this choice gave much trouble subsequently.

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[1] (a) Bain and Oliver, *Trans. Roy. Soc. Canada*, **10**, III, 65–66 (1916); (b) Bain, **18**, III, 273–274 (1924).

[2] Hill and Miller, This Journal, **49**, 669 (1927).

[3] Osaka, *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, **3**, 51 (1911).

[4] Kremann and Zitek, *Monatsh.*, **30**, 323 (1909).

## Experimental Methods

The carbonates used were of C. P. quality and each lot was analyzed before use; the samples conformed to the usual standards. Weighed quantities of the components were placed in L-shaped glass tubes which were rocked to and fro in the bath, the movement of a large bubble of air producing a stirring action. From time to time the tubes were removed and shaken vigorously to break up crusts, and in some instances the solid phase was filtered off, ground in a mortar and returned to the tube. The samples were withdrawn by a weighing pipet and, after dilution, the sodium and potassium were determined as chlorides in one portion, an operation in which wide glass tubes with bent-up, drawn-out ends[5] were almost indispensable; in another portion potassium was determined as perchlorate. All determinations were made in duplicate and the agreement was excellent.

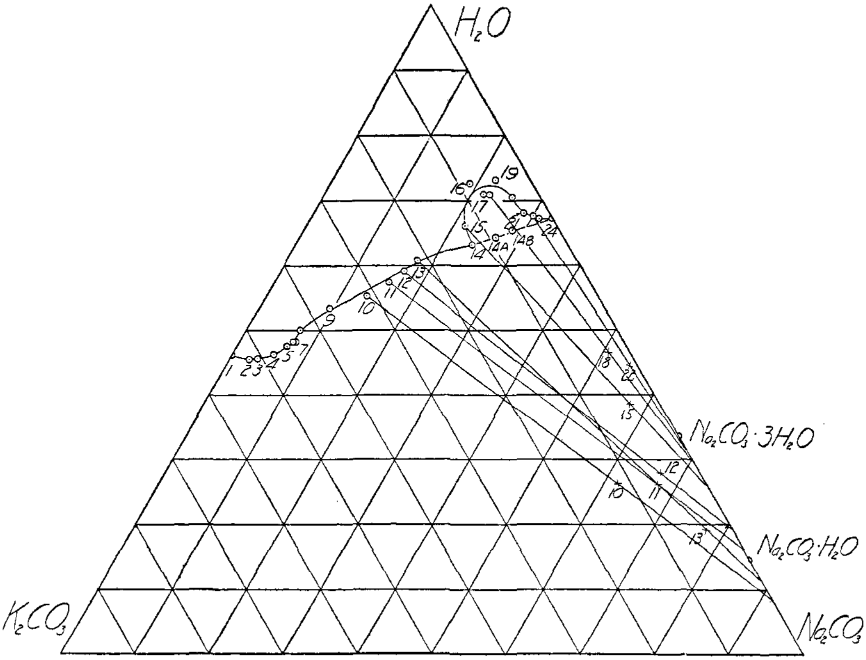

Fig. 1.

The solid phases were filtered off, sucked dry, dissolved and analyzed as above. Hill and Miller's method of centrifuging, which was only published toward the conclusion of our work, has been tried and is undoubtedly a great improvement. During the course of the investigation sixty-seven separate experiments have been carried out, the large number being due to the difficulty in securing solutions in equilibrium with a stable phase; from these the following results have been selected; temperature, 40°.

The curves lying to the left of Point 14 were thoroughly established by April, 1924, but no concordant results could be obtained in the remainder of the field. Variable results from solutions of the same composition led to the conclusion that equilibrium was only very slowly attained and,

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[5] Ostwald-Luther, "Physiko-chemischer Messungen," 4th edition, p. 309.

TABLE I

RESULTS OF EXPERIMENTS

| No. | Solution | | Residue | | Sp. gr., | Days | Solid |
|---|---|---|---|---|---|---|---|
| | $K_2CO_3$ | $Na_2CO_3$ | $K_2CO_3$ | $Na_2CO_3$ | 40°/20° | shaken | phase[a] |
| 1 | 53.9 | .. | ... | ... | ... | ... | $K_{3/2}$ |
| 2 | 51.9 | 2.7 | ... | ... | 1.582 | 7 | $K_{3/2}$ |
| 3 | 50.7 | 3.8 | ... | ... | 1.581 | 7 | $K_{3/2}$ + KN |
| 4 | 48.1 | 5.6 | ... | ... | 1.586 | 5 | KN |
| 5 | 45.8 | 6.8 | ... | ... | 1.563 | 15 | KN |
| 6 | 44.7 | 7.2 | ... | ... | 1.557 | 89 | KN + $N_1$ |
| 7 | 44.2 | 7.2 | ... | ... | 1.567 | 6 | KN + $N_1$ |
| 8 | 42.8 | 7.2 | ... | ... | 1.550 | 6 | $N_1$ |
| 9 | 37.1 | 9.5 | ... | ... | 1.508 | 56 | $N_1$ |
| 10 | 31.1 | 13.6 | 11.8 | 62.0 | 1.496 | 58 | $N_1$ |
| 11 | 27.1 | 15.5 | 6.6 | 67.5 | 1.451 | 61 | $N_1$ |
| 12 | 24.3 | 16.7 | 5.0 | 67.2 | 1.424 | 94 | $N_1$ |
| 13 | 21.6 | 17.8 | 3.6 | 77.3 | 1.447 | 99 | $N_1$ |
| 14 | 12.9 | 24.0 | ... | ... | 1.387 | 91 | $N_1$ + $N_3$ |
| 14A | 9.1 | 26.6 | ... | ... | 1.374 | 15 | $N_1$ |
| 14B | 6.2 | 28.5 | ... | ... | 1.366 | 47 | $N_1$ |
| 15 | 12.2 | 21.6 | 4.0 | 57.5 | 1.341 | 104 | $N_3$ |
| 16 | 8.4 | 19.0 | ... | ... | 1.441 | 107 | $N_3$ |
| 17 | 7.4 | 21.6 | ... | ... | 1.290 | 111 | $N_3$ |
| 18 | 6.6 | 22.5 | 2.6 | 50.7 | 1.291 | 113 | $N_3$ |
| 19 | 4.8 | 22.1 | ... | ... | 1.272 | 113 | $N_3$ |
| 20 | 3.7 | 25.8 | ... | ... | 1.292 | 115 | $N_3$ |
| 21 | 3.6 | 28.6 | ... | ... | ... | 34 | $N_3$ |
| 22 | 2.3 | 30.0 | 0.8 | 54.6 | 1.328 | 120 | $N_3$ |
| 23 | 1.8 | 31.1 | ... | ... | 1.326 | 12 | $N_3$ |
| 24 | .. | 32.8 | ... | ... | ... | ... | $N_3$ |

[a] For convenience, the symbols of Hill and Miller have been used. $K_{3/2} = K_2CO_3.3/2H_2O$; KN = $K_2CO_3.Na_2CO_3$; $N_1 = Na_2CO_3.H_2O$; $N_3 = Na_2CO_3.3H_2O$. The solid phases in Nos. 3 to 7 were not determined and are assigned on the basis of Hill and Miller's isotherm at 36°.

consequently, the period of shaking was increased first to a fortnight and then to greater lengths as indicated in the table. The conclusion was finally reached that the temperature of the bath oscillated about the temperature of a transition point, and that a new hydrate of sodium carbonate was present. It is very easy to obtain solutions supersaturated with respect to the monohydrate and of the numerous results which were obtained in consequence, numbers 14A and 14B are placed on the diagram upon a dotted line indicating the metastable prolongation of the curve stretching from 7 to 14.

As is shown in the diagram, the projection of the tie lines between the points 14, 18 and 22, indicating the composition of the solution and of the moist residue, intersect the side of the triangle at very obtuse angles and consequently little reliance can be placed upon them. It was, therefore, necessary to investigate the composition of the solid phase in equilibrium with solutions lying to the right of point 14 by some other method.

A sample of sodium carbonate which had been shaken with an amount of water sufficient only to partially dissolve it, was filtered in a tube with a Jena glass disk surrounded by water at 42°; after a few moments' suction the moist salt was washed with a very small quantity of ether, poured on dropwise, and was then rapidly removed to a stoppered weighing bottle.

*Anal.* 1.0702 g. titrated with 0.9562 *N* HCl, using methyl orange, required 14.0 cc., = 0.7102 g. $Na_2CO_3$, whence $Na_2CO_3:H_2O = 1:2.98$. 0.6768 g. heated at 270–300° gave 0.4507 g. $Na_2CO_3$, whence $Na_2CO_3:H_2O = 1:2.95$.

To confirm this result, 50.0 g. of $Na_2CO_3$, 4.0 g. of NaCl and 60.18 g. of $H_2O$ were shaken for a number of days at 41°; in the filtered solution there were found: 0.6771 g. of NaCl = 0.5045 g. of $Na_2CO_3$ + 0.1202 g. of NaCl in 1.9355 g. of solution, on the assumption that all the NaCl present was in solution; the NaCl alone = 0.1202 g.; $H_2O$ as solution = 43.64 g.; $Na_2CO_3$ in solid phase, 33.20 g.; hence $Na_2CO_3:H_2O = 1:2.93$.

Samples of the solid phase were also centrifuged as suggested by Hill and Miller and it was found after a number of trials that great care had to be taken to prevent the sample from falling below 40°, since otherwise the results were unsatisfactory.

*Anal.* 0.5479 g. of the centrifuged salt lost on heating 0.1850 g. of $H_2O$, whence $Na_2CO_3:H_2O = 1:3.02$.

The results of these independent methods, taken together with the intersections of the tie lines on the $Na_2CO_3.H_2O$ side of the triangle, are evidence of the existence of a trihydrate of sodium carbonate, the solubility of which is represented by the curve from Points 14 to 24. Solutions prepared by agitating sodium carbonate for a few hours at 40° or over are saturated with respect to the metastable monohydrate but are supersaturated with respect to the stable trihydrate; since the change from one form to the other is slow, the investigators of the solubility of this salt, even such careful and experienced workers as Wells and McAdam,[6] have overlooked the existence of the trihydrate. The present data on solubility above 40° are undoubtedly in error and will be further investigated in this Laboratory.

It is not yet possible to state definitely how long a sample must be shaken at 41° or slightly higher in order that the complete conversion to the trihydrate may be assured, but at present it is believed that not less than six days should be allowed.

An attempt was made to determine with some precision the transition point by the thermal method, using the procedure of Richards.[7] A series of runs was made with slowly rising and falling temperatures which yielded

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[6] Wells and McAdam, THIS JOURNAL, **29**, 721 (1907).

[7] Richards, *Am. J. Sci.*, [4] **6**, 201 (1898).

definite indications of a transition point although the constancy of temperature lasted only for a few minutes. The change of one hydrate into the other proceeds slowly, and the existence of the monohydrate above the transition point for days as a metastable form is indicative of this sluggishness; the trihydrate appears to pass over into the monohydrate more rapidly but the rate is still low. The transition of the trihydrate into the monohydrate is accompanied by the evolution of heat. When these difficulties had developed during the first few runs, attempts were made to obtain more favorable conditions, that is, the monohydrate prepared at 37° was added to the trihydrate at 41° and the mixture slowly cooled and then heated again. The converse procedure was also tried but no method of accelerating the change from one hydrate to the other could be found. In all, seventeen runs were made; the arrests with rising temperature occurred from 39.60 to 39.98° and on cooling at 39.97 to 39.85°. The transition temperature is, therefore, assumed for the present to be 39.8° ± 0.1°.

The compound $Na_2CO_3.3H_2O$ has not been previously described except as associated with the efflorescent soda in the dried river beds of the Cordilleras,[8] and as a deposit from hot springs near Saxby River, Queensland.[9]

The greater portion of the experimental work in this investigation has been carried out by a number of students, whose assistance is gratefully acknowledged.

## Summary

1. The system $K_2CO_3 + Na_2CO_3 + H_2O$ has been studied at 40°.

2. The existence of the trihydrate of sodium carbonate has been proved.

3. The transition point in the system $Na_2CO_3.3H_2O - Na_2CO_3.H_2O$ is 39.8 ± 0.1°.

4. The solubility data for sodium carbonate at 40° and for some unknown higher range in temperature, as at present recorded, refer to the composition of solutions in equilibrium with the metastable monohydrate and require revision.

TORONTO, CANADA

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[8] Schickendantz, *Ann.*, **155**, 359 (1870).

[9] Daintree, *Quart. J. Geol. Soc.*, **28**, 285 (1872).