[Contribution from the Havemeyer Chemical Laboratory, New York University]

TERNARY SYSTEMS. VI. SODIUM CARBONATE, SODIUM BICARBONATE AND WATER

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It has been known for a very long time that solutions of carbonate and bicarbonate of sodium may precipitate the double salt Trona as well as the two simple salts. The concentrations and temperatures at which these compounds separate have not, however, been investigated except in a single instance; McCoy and Test[2] have studied the three-component isotherm at 25°, giving the results in terms of volume concentration. We have here studied the system at the temperatures 25, 30 and 50°, determining the composition of the saturated solutions by weight and their density.

Experimental Methods.—The sodium carbonate and bicarbonate used were Kahlbaum's "zur Analyse" preparations; the former was found to be 100% in purity, and was kept constantly in an electric oven at 100° until removed for use. The samples of bicarbonate were found to contain from 1.30 to 3.16% of normal carbonate and from 0.33 to 0.70% of water. Because the conditions for keeping the bicarbonate from change are not known, the samples were used without removing the carbonate, making proper corrections for their actual composition in the various experiments.

Solubilities were obtained in thermostats, using 50 cc. glass-stoppered Pyrex tubes, the stoppers being wired in to prevent loss of carbon dioxide during stirring. Rotation was continued until equilibrium was obtained, the usual period being about fifteen hours. Samples for analysis were removed with a pipet fitted with a filter, and weighed to give a fairly accurate density determination. The loss of carbon dioxide, which Dibbits[3] points out as considerable for solutions saturated with sodium bicarbonate, is very little in the presence of even small amounts of the normal carbonate; no especial precautions were necessary on this account. One sample of filtrate was titrated with 0.5 *N* hydrochloric acid, using methyl orange as indicator, to determine the total base; a second sample was analyzed for carbon dioxide content by absorption in soda lime in a Morgan bottle, thus permitting calculation of the concentration of both normal salt and acid salt. The thermometers were compared with a standard thermometer.

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[1] The material of this paper is part of a thesis presented by Leslie R. Bacon in partial fulfilment of the requirements for the degree of Doctor of Philosophy, at New York University.

[2] McCoy and Test, This Journal, **33**, 473 (1911).

[3] Dibbits, *J. prakt. Chem.*, **10**, 417 (1874).

The Binary Systems.—For the two binary systems, only the eutectics were determined, as the solubility data in the literature appear to be accurate. In the case of the bicarbonate, the usual method of lengthy stirring in open vessels was found to result in considerable loss of carbon dioxide and the formation of normal carbonate. To avoid this error, washed carbon dioxide was passed into the solution during the determination of the eutectic in the Beckmann apparatus; the correction for freezing-point depression caused by saturation with the gas is only a few hundredths of a degree. The results are given in the following table.

TABLE I

BINARY EUTECTICS FOR Na_2CO_3 AND $NaHCO_3$ WITH H_2O

Point in Fig. 4	Eutectic temp.	Solution			Solid phases
		Wt. %, Na_2CO_3	Wt. %, $NaHCO_3$	Density	
B	−2.05	5.71	..	1.056	$Na_2CO_3.10H_2O$ + ice
M	−2.33	..	6.26	1.046	$NaHCO_3$ + ice

The eutectic for the bicarbonate we have not found in the earlier literature. That determined by us for the normal carbonate is slightly lower in temperature and concentration than that given by Guthrie[4] (—2.0° and 5.97%) and is higher in concentration than the value given by de Coppet[5] (—2.1° and 5.03%); it is much closer to the extrapolated solubility curve than either of these earlier results.

The Ternary Isotherms.—In Tables II, III and IV are given the data for the ternary system at 24.87, 30.0 and 50.0°. The water in the saturated solutions may be calculated by subtracting the sum of Cols.

TABLE II

ISOTHERM AT 24.87° FOR $Na_2CO_3+NaHCO_3+H_2O$

Point in figs.	Solution			Original complex		Solid phases
	Wt. %, Na_2CO_3	Wt. %, $NaHCO_3$	Density	Wt. %, Na_2CO_3	Wt. %, $NaHCO_3$	
A	0.0	(9.3)	...	...	...	N_{bi}
	0.2	9.11	1.065	...	...	N_{bi}
	2.10	8.21	1.076	1.91	17.29	N_{bi}
	8.11	6.13	1.125	7.45	14.05	N_{bi}
	10.88	5.50	1.152	10.08	12.46	N_{bi}
	13.61	4.90	1.179	12.57	12.41	N_{bi}
K	17.85	4.00	1.216	...	...	N_{bi} + T
	18.66	3.57	1.225	21.26	6.46	T
	19.31	3.18	1.228	21.17	6.54	T
	20.90	2.49	1.240	23.30	6.12	T
C	22.10	2.09	1.250	...	...	T + N_{10}
	22.15	1.59	1.247	26.31	1.23	N_{10}
	22.26	1.09	1.243	26.03	1.04	N_{10}
	22.20	0.86	1.238	26.06	0.51	N_{10}
D	22.45	.00	...	...	...	N_{10}

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[4] Guthrie, *Phil. Mag.* [4] **49,** 269 (1875).

[5] De Coppet, *Z. physik. Chem.*, **22,** 240 (1897).

Table III

Isotherm at 30.00°

Point in figs.	Solution			Original complex		Solid phases
	Wt. %, Na_2CO_3	Wt. %, $NaHCO_3$	Density	Wt. %, Na_2CO_3	Wt. %, $NaHCO_3$	
A	0.0	(9.8)	...	...	...	N_{bi}
	0.25	9.71	1.068	...	...	N_{bi}
	6.06	7.30	1.112	5.38	18.03	N_{bi}
	11.84	5.67	1.160	10.33	17.68	N_{bi}
K	17.52	4.45	1.216	...	...	N_{bi} + T
	18.43	3.92	1.225	19.98	5.87	T
	18.54	3.91	1.226	20.09	5.66	T
	21.00	2.65	1.239	22.45	4.80	T
	23.39	1.79	1.256	24.01	2.95	T
	24.30	1.47	1.269	25.88	4.32	T
	27.52	0.82	1.301	29.06	3.91	T
C	28.09	.76	1.307	...	...	T + N_{10}
D	28.24	.00	1.296	...	...	N_{10}

Table IV

Isotherm at 50.00°

Point in figs.	Solution			Original complex		Solid phases
	Wt. %, Na_2CO_3	Wt. %, $NaHCO_3$	Density	Wt. %, Na_2CO_3	Wt. %, $NaHCO_3$	
A	...	(12.40)	...	...	...	N_{bi}
	0.27	12.22	1.078	...	...	N_{bi}
	1.08	11.68	1.079	...	...	N_{bi}
	4.78	9.93	1.112	...	...	N_{bi}
	10.04	8.27	1.152	9.20	17.10	N_{bi}
	14.90	6.80	1.196	13.39	15.73	N_{bi}
K	16.97	6.28	1.214	...	...	N_{bi} + T
	23.79	2.40	1.260	25.59	5.21	T
C	31.92	0.48	1.337	...	...	T + N_1
D	32.16	.00	1.331	...	...	N_1

2 and 3 from 100%. As abbreviations for the compositions of the solid phases given in the last column, N_{10}, N_7 and N_1 are used for the decahydrated, heptahydrated and monohydrated sodium carbonate, respectively, N_{bi} for the bicarbonate and T for the double salt, Trona, $NaHCO_3 . Na_2CO_3 . 2H_2O$. Figs. 1, 2 and 3 represent the results graphically.

Lines drawn through the two points representing the saturated solution and the original complex can be extrapolated to pass through the point representing the saturating solid phase with sufficient accuracy.

From the foregoing data, it can be shown that the solubility of the normal carbonate is increased slightly by the addition of bicarbonate, if calculated as referred to a constant amount of water; this is the case for the course of the short solubility curve DC. The solubility of the bicarbonate, however, as indicated by the curve AK, shows the more usual behavior of a marked decrease in solubility upon the addition of the carbonate. The solubility of the pure bicarbonate, given at A in the three isotherms, has been obtained by graphic extrapolation of the curve KA. It is believed that the figures obtained are closer to the truth than those obtained by the direct measurements of Dibbits,[3] who found it necessary to make a correction for the loss of carbon dioxide during the removal of the sample for analysis. The bicarbonate solutions which contain normal carbonate, on the line KA, have a pressure of carbon dioxide so low that the loss is not appreciable.

The three isotherms studied in complete form show the decahydrated and the monohydrated sodium carbonate as solid phases but do not show the heptahydrated carbonate. It is of course obvious that at some intermediate temperatures that hydrate must be a stable phase. The temperature range within which the heptahydrate is the solid phase in equilibrium with solutions along the line CD is from 31.98°, shown later in Table IV, to its transition temperature 35.27°; but as the temperature range is short, and the solubility on the line CD at this temperature varies only slightly from that at 30° (Table III), the separate measurements were not made.

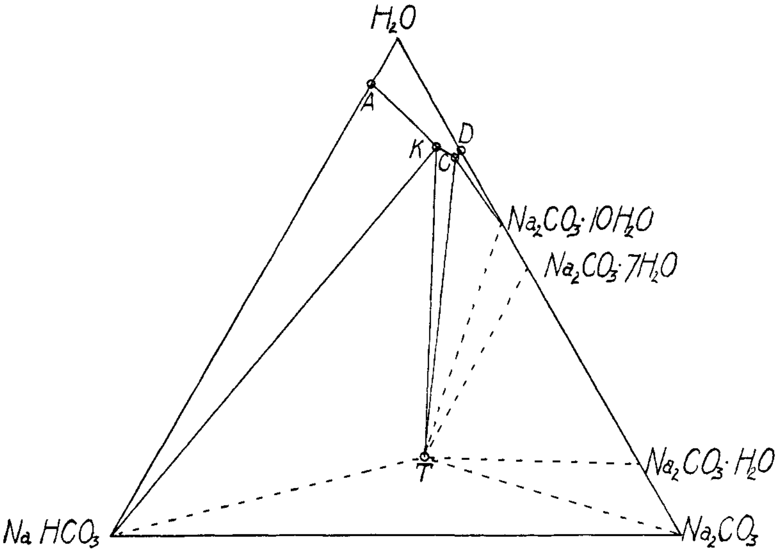

Fig. 1.—Isotherm for $Na_2CO_3.NaHCO_3.H_2O$ at 24.87°.

The chief interest in the system is in the double compound Trona, which is found to be a stable phase throughout the temperature range of Tables II–IV. Its composition, represented by the point T, is given by the formula $NaHCO_3.Na_2CO_3.2H_2O$, as first found by Laurent,[6] and confirmed by Chatard,[7] McCoy and Test[2] and others. We have

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[6] Laurent, *Ann. chim. phys.* [3] **36**, 348 (1852).

[7] Chatard, *U. S. Geol. Survey Bull.*, **60**, 27 (1887); *Am. J. Sci.*, **38**, 59 (1889).

satisfied ourselves as to the correctness of this formula by two independent methods. The first consisted in a slow isothermal evaporation over sulfuric acid at about 30°, using a solution represented by a point on the solubility curve CK, discontinuing before the total composition of the system had moved outside the triangle TCK; the slow procedure gave relatively distinct crystals (although we have not been able to obtain them of any large dimensions) which could be well centrifuged. Analysis of three samples gave the water content 1.43% too great, the bicarbonate 1.05% too small and the carbonate 0.38% too small for the above formula. The second method consisted in preparing two saturated solutions, to one of which the three components were added in the molecular ratio $NaHCO_3 + Na_2CO_0 + 3H_2O$ and to the second in the ratio $NaHCO_3 + Na_2CO_3 + H_2O$; in the first experiment the composition of the saturated solution moved in the direction toward K, and in the second toward C, indicating that the first addition contained water in excess and the second in deficit.

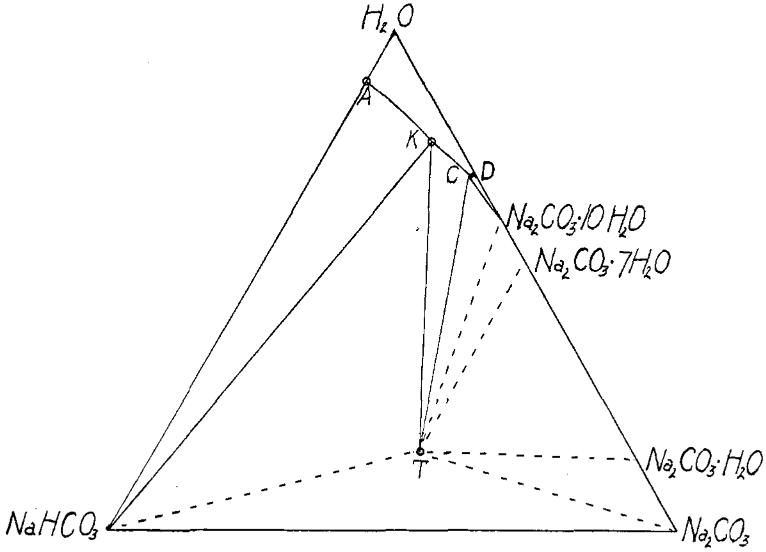

Fig. 2.—Isotherm for $Na_2CO_3.NaHCO_3.H_2O$ at 30°.

The range of concentrations within which Trona is stable varies widely with the temperature. At 25° the triangle TKC is quite narrow, indicating that the compound is here but slightly above its temperature of formation; the determination of that temperature is given later in the paper. The points C and K agree with those of McCoy and Test[2] within less than 0.2%, the comparison being made possible by the density data contained in our tables. At 30° the triangle TKC has extended considerably, and at 50° is still larger. It seems probable, therefore, that Trona may be stable up to considerably higher temperatures, provided the pressure is kept high enough to prevent the loss of carbon dioxide. The salt shows incongruent solubility throughout the temperature range studied; but it should be observed that with increasing temperature there is a continuous movement of the point K toward A, and it is not by any means excluded that at sufficiently high temperature and pressure it may move far enough to bring the salt into congruent saturation, so that it might be recrystallized from water.

The point C represents solutions isothermally saturated with Trona and with sodium carbonate decahydrate in Tables II and III, and with Trona and sodium carbonate monohydrate in Table IV; at temperatures between 31.98 and 35.27°, as shown later in this paper, the two salts will be Trona and sodium carbonate heptahydrate. In every case the point is close to the H_2O-Na_2CO_3 axis, its farthest removal being 3.74% at 21.26° and its closest approach being 0.16% at 31.98°. It is apparent from these figures that a comparatively small addition of bicarbonate to normal carbonate will result in the precipitation of Trona, and that pure carbonate cannot be prepared by recrystallization if the excess of carbon dioxide is more than a very small amount.

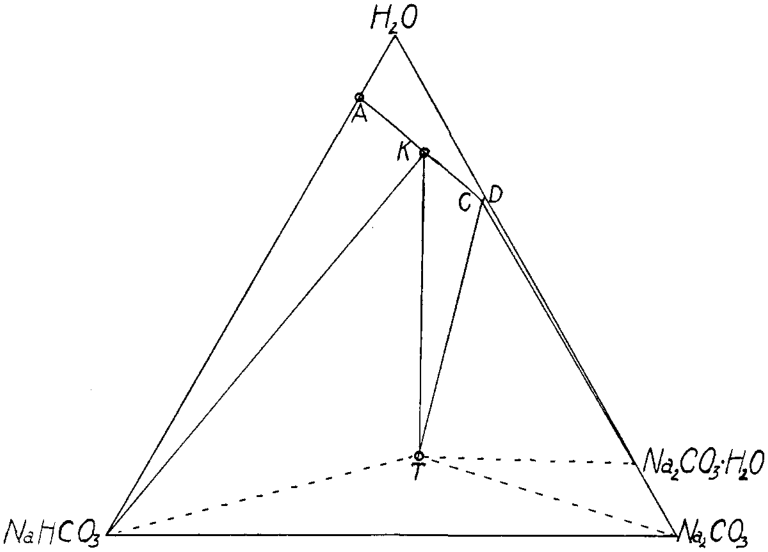

Fig. 3.—Isotherm for $Na_2CO_3.NaHCO_3.H_2O$ at 50°.

The Invariant Points (Quintuple Points).—With the number of possible solid phases at moderate temperatures so large ($Na_2CO_3.H_2O$, $Na_2CO_3.7H_2O$, $Na_2CO_3.10H_2O$, $NaHCO_3$, Trona and ice) it is obvious that several invariant (quintuple) points might be expected. Investigation from the temperature of the ternary eutectic up to 50° has given four such invariant points, the data for which are in Table V. L stands for the saturated liquid phase. The phase reaction, read from left to right, represents the change occurring upon addition of heat.

TABLE V

INVARIANT POINTS IN THE SYSTEM Na_2CO_3–$NaHCO_2$–H_2O

Point in Fig. 4	Temp., °C.	Liquid phase Wt. %, Na_2CO_3	Liquid phase Wt. %, $NaHCO_3$	Density	Phase reaction
E	−3.32±0.05	4.41	4.64	1.078	$N_{10} + N_{bi} + \text{ice} \leftrightarrows L$
H	+21.26± .10	18.15	3.74	1.220	$N_{10} + N_{bi} \leftrightarrows T + L$
N	31.98± .05	31.32	0.16	1.334	$N_{10} + T \rightleftarrows N_7 + L$
O	35.17± .05	33.08	.19	1.350	$N_7 + T \rightleftarrows N_1 + L$

The invariant temperature of Line 1 was determined with the usual Beckmann apparatus; the heat of the reaction is large and if vigorous stirring and a slow drop of temperature are maintained, the transition temperature is reproducible with satisfactory accuracy. In the other experiments, however, each of which involves the formation or decomposition of Trona, special precautions were necessary to avoid considerable variations in the transition temperature. This was especially true of the experiment of Line 2, which is the temperature of formation of Trona from its components previously referred to, and found to be at 21.26°. The temperature found is in agreement with the finding of McCoy and Test[2] that Trona is a stable phase at 25°, and with that of Applebey and Lane[8] that the compound is non-existent at 18°. The use of the ordinary Beckmann apparatus, however, gave no satisfactory determination of the temperature; cooling curves and heating curves showed arrests differing a degree or more from each other, and yielding no truly invariant temperature, from which it may be deduced that the heat of the reaction is small or that the rate of formation and decomposition of the double salt is slow, or possibly that both statements may be true. In order to obtain a satisfactory curve, it was necessary to carry on the experiments in a small Dewar flask, surrounded by water at a temperature only a degree or two above the invariant temperature, and to carry on mechanical stirring over a period approximating a day, seeding the mixture with the necessary salts. With the exceedingly slow change in temperature thus produced, a constant temperature was obtained over a period of several hours; the average of four such determinations is given. The determinations of Lines 3 and 4 were somewhat less troublesome but the use of the Dewar flask as a container was found necessary. Since in these two latter cases the concentration of bicarbonate in the solution is very small, it is clear that the transition points can vary only slightly from the two-component transition temperatures of the heptahydrated and decahydrated carbonates. These two-component temperatures were therefore redetermined by us so that

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[8] Applebey and Lane, *J. Chem. Soc.*, 113, 609 (1918).

our three-component temperatures should express a difference brought about by the presence of the bicarbonate rather than a variation between the work of different investigators. By our experiment the transition temperature of sodium carbonate decahydrate was found to be 32.08°,[9] making the depression by the bicarbonate 0.1°, and that of the heptahydrate was found at 35.27°, making the depression by the bicarbonate again 0.1°.

From the solubility data and the invariant points it is possible to construct a space model showing relationships in the ternary system from —3.32° to +50°. This is shown in perspective in Fig. 4, which is drawn approximately to scale. The usual triangular prism has been cut off at the composition of 55% water, which is below the composition of any of the saturated solutions. The surface EMAKH represents solutions saturated with sodium bicarbonate, HKCON those saturated with Trona, EHNSB those saturated with decahydrate, NORS those saturated with heptahydrate and OCDR those saturated with monohydrate. The four invariant points given in Table V are represented by E, H, N and O. E is the ternary eutectic of Table V and B and M are the binary eutectics of Table I. The dotted lines GA″K″C″D″ and FA′K′C′D′ represent the temperatures of the isotherms at 25 and 30°, and the upper surface of the figure represents the isotherm at 50°.

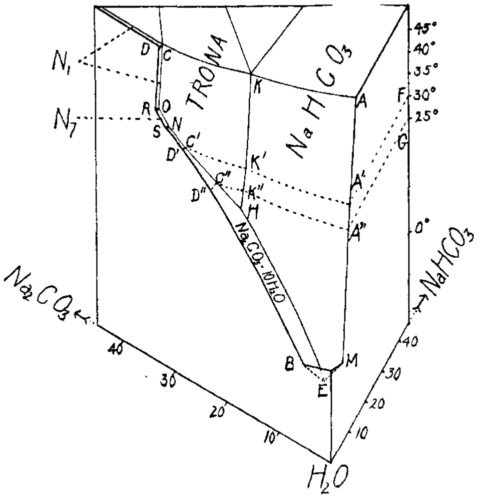

Fig. 4.—Space model of the system Na_2CO_3.-$NaHCO_3$.H_2O.

Summary

1. Isotherms of the system: Na_2CO_3–$NaHCO_3$–H_2O at 25, 30 and 50° have been studied.

2. The double salt Trona, $NaHCO_3 . NaCO_3 . 2H_2O$, is stable in contact with saturated solutions from 21.26°, the temperature of its formation, up to at least 50°. It shows incongruent solubility throughout this entire range of temperatures. The range of concentrations within which it may be prepared increases gradually with increase in temperature. The salt forms a stable phase from solutions containing as little as 0.16%

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[9] Wells and McAdam (This Journal, 29, 721 (1907)) found 32.00° at 31.34% and 35.37° at 33.19% as the two transition temperatures and concentrations.

of bicarbonate at 31.98°, and nowhere requires for its formation more than 3.74% of bicarbonate in the solution.

3. Four invariant temperatures for the ternary system have been found between the temperature of the ternary eutectic at —3.32 and 35.27°.

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[Contribution from the Kent Chemical Laboratory of the University of Chicago]

PHOTOCHEMICAL STUDIES. V. THE PHOTOCHEMICAL DECOMPOSITION OF AMMONIA BY RELATIVELY SHORT WAVE LENGTHS

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Very few photochemical studies in the far ultraviolet have been carried out. In a previous paper[1] a report was made of a study of the photochemical decomposition of anhydrous oxalic acid in the far ultraviolet. It was found, qualitatively, that the decomposition proceeded more rapidly with light transmitted by fluorite than with light transmitted by quartz.

The present work was undertaken with the object of determining the quantum efficiency of the decomposition of ammonia in the region of wave lengths below that transmitted by quartz.

I. Experimental Method and Results

It is possible to use fluorite windows for studies of the effects of radiations of slightly shorter wave lengths than those transmitted by quartz. Quartz may be said to transmit, under ideal conditions and in thin layers, as far as 185mμ. Fluorite is considerably more variable in its characteristics and the data on its transmission do not agree among themselves. Fluorite transmits relatively well to about 150mμ and some authors report transmission as far as 100mμ.

Many authors have made spectroscopic investigations in the far ultraviolet. Methods of detection of the radiation were available which were far more sensitive than the ordinary methods which may be used in photochemical studies.

In the case of gas reactions, the rate of reaction can be determined by measurements of the pressure change. It is far more difficult to find a suitable light source, since the sources of light used by spectroscopists for studies in this region are usually too feeble to produce measurable photochemical effects unless the quantum efficiency of the reaction is high. In the present work two sources of light were tried. The first was a discharge tube of the type described by Hopfield.[2] This tube was used with both nitrogen and hydrogen, but the light emitted was found to be too feeble to produce

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[1] Noyes and Kouperman, This Journal, **45**, 1398 (1923).

[2] Hopfield, *Phys. Rev.*, **20**, 573 (1922).