entropy of vaporization of 21.8 cal. per degree, indicating that *iso*propyl acetate is a normal liquid.

Following Hildebrand,[9] we have also calculated the molal entropy of vaporization at that temperature (35.0° in the case of *iso*propyl acetate) at which the concentration of the vapor is 0.00507 mole per liter and obtained a value of 27.6 cal. per degree. As 27.4 cal. per degree is the mean value obtained by Hildebrand for normal liquids, this value also indicates that *iso*propyl acetate is a normal liquid.

Summary

Vapor pressure measurements have been made on *iso*propyl acetate from 0 to 90°, inclusive.

An equation has been obtained for the vapor pressure curve from which the boiling point has been determined.

From this equation the molal heat of vaporization has been determined.

The molal entropy of vaporization has been determined at the boiling point and also at that temperature at which the vapor concentration is 0.00507 mole per liter.

These molal entropies indicate that *iso*propyl acetate is a normal liquid.

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EQUILIBRIUM BETWEEN THE CARBONATES AND BICARBONATES OF SODIUM AND POTASSIUM IN AQUEOUS SOLUTION AT 25°

BY ARTHUR E. HILL AND STERLING B. SMITH[1]

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A phase-rule study of the reactions between the carbonates and bicarbonates of sodium and potassium does not appear to have been published heretofore. Such a study may be regarded as including the more important part of the possible reactions of the two bases with carbonic acid, between the limits in which the carbonic acid varies from an amount just sufficient to form normal carbonates with all the base present and an amount sufficient to form bicarbonates with all the base present. For such a four-component study, four three-component studies are a preliminary essential; these are listed below. Three of them have been studied with more or less completeness at a number of times and places, and more recently at this

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[9] Hildebrand, "Solubility," American Chemical Society Monograph, Chemical Catalog Company, New York, **1924**, p. 94.

[1] The material of this paper was presented by Sterling B. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1927.

Laboratory with a special view toward their use in the four-component study here reported; the fourth has been studied elsewhere, the results not yet being published.

Na_2CO_3-K_2CO_3-H_2O[2] K_2CO_3-$KHCO_3$-H_2O[4]
Na_2CO_3-$NaHCO_3$-H_2O[3] $KHCO_3$-$NaHCO_3$-H_2O[5]

Data from these studies, recalculated so as to be of use in the four-component study, will be introduced later.

Experimental Methods.—The four salts used were Kahlbaum's preparations "zur Analyse." These were found by analysis, after drying, to be pure up to the limit of our most careful standardization, with the exception of the sodium bicarbonate, which showed decomposition into carbonate in amount varying from 0.5 to 3% in various samples. Since sodium carbonate is one of the components of the systems studied, it was necessary merely to correct the weights taken in some cases; in others the correction is wholly unnecessary.

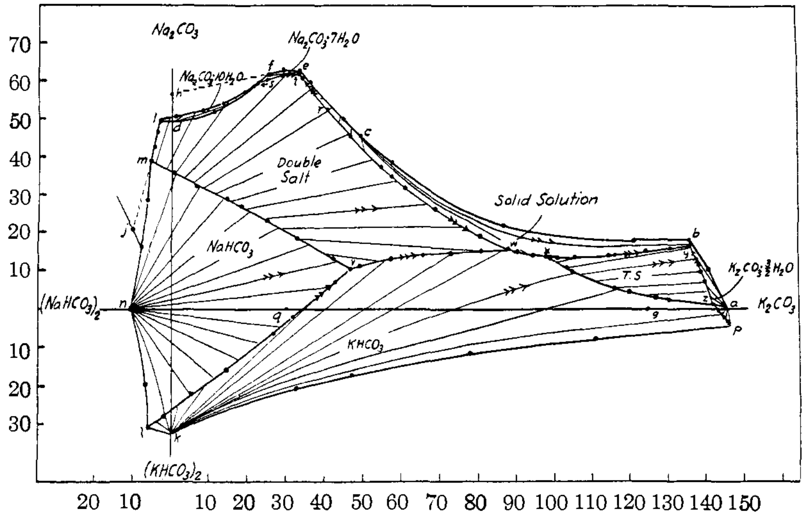

Fig. 1.—K_2CO_3-$NaHCO_3$-Na_2CO_3-$KHCO_3$-H_2O at 25°.

In carrying out the solubility experiments, which were intended to give us the lines for saturation with respect to two solid phases later shown in Fig. 1, solutions were prepared corresponding to the isothermally invariant points in the three-component systems (Points l, m, i, etc., in Fig. 1) or in the four-component system (Points v, w, etc.), with a small excess of the two solid phases present. To each of these was added a small amount of the necessary fourth component, the whole complex being contained in a 50-cc. glass-stoppered Pyrex test-tube. The solubility tubes were then rotated,

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[2] (a) Kremann and Zitek, *Monatsh.*, **30**, 323 (1909); (b) Osaka, *Mem. Coll. Sci. Eng., Kyoto*, **3**, 51 (1911); (c) Blasdale, THIS JOURNAL, **45**, 2935 (1923); (d) Hill and Miller, *ibid.*, **49**, 669 (1927).

[3] McCoy and Test, *ibid.*, **33**, 473 (1911); (b) Freeth, *Phil. Trans. Roy. Soc.*, **223**, 35 (1922); (c) Hill and Bacon, THIS JOURNAL, **49**, 2487 (1927).

[4] Hill and Hill, *ibid.*, **49**, 967 (1927).

[5] N. E. Oglesby, University of Virginia (unpublished).

with suitable protection against entrance of water, in a thermostat at 25 ± 0.1°; sixteen hours sufficed for the attainment of equilibrium in the majority of cases, but from thirty-six to forty-eight hours were required where one of the phases is a solid solution. For the analysis of the saturated solutions, three samples were withdrawn by pipet in each instance, using a small filter of linen in cases where the liquid did not settle clear, and their weights ascertained. One sample was titrated for total alkali, using hydrochloric acid with methyl orange as indicator; by the use of a color blank for matching end-points, of a constant volume in the titration, and of sodium carbonate as the ultimate standard for the hydrochloric acid, errors in this titration were reduced to a minimum. The second sample was weighed into a platinum dish and evaporated under reduced pressure of about $^1/_6$ atmosphere in a vacuum oven at 80°; after apparent completion of the evaporation, the sample was heated to incipient fusion over a Bunsen burner and brought to a constant weight; the residue gives the total carbonates of the two metals obtained from the solution of carbonates and bicarbonates. The third sample was analyzed for its carbon dioxide content by acidification with sulfuric acid in a suitable train, the gas finally being absorbed by soda lime in a Morgan bottle. From these three operations the complete composition of the solution can be calculated, to be expressed in terms of whatever four components may be most convenient. It is estimated that the errors in the individual analyses are not greater than 0.1%, but the method of indirect calculation multiplies these errors to what may be as great as 1%; the smoothness of the curves, however, indicates that the total errors are less than this amount. Densities of the solutions were known from the weights of the pipetted samples, usually 5 or 10 cc. in volume.

The analysis of a series of solutions by the above method gives a saturation curve for solutions saturated with two solid phases, such as the line m–v in Fig. 1. The terminus of such a curve, detected experimentally by a break in the course of the curve, represents an isothermally invariant point, at which a third solid phase has appeared. Such points were determined from the analysis of two or more solutions obtained by following the curves leading to that point. In all such cases except the Points x, y and z, where one of the solid phases cannot be prepared pure, the invariant composition was checked further by preparing a solution of the composition found, adding the three solid phases believed to be in equilibrium with the solution and rotating the system in the thermostat; if the analysis of the solution was found unchanged after forty-eight hours' rotation of the sample, the point was considered definitely fixed.

Experimental Results

In Table I are given the data for the four three-component systems, recalculated from the original papers so as to show composition in terms of moles of the components per 1000 moles of water. These data appear in part in Fig. 1 upon the boundary lines of the drawing. The abbreviations used to indicate the more complex solid phases are indicated at the head of the table. In accordance with custom, the two bicarbonates are assigned a double molecular weight.

The figures for the fourth of the systems ($NaHCO_3$–$KHCO_3$–H_2O) in Table I have been newly determined here and are in fair agreement with those reported to us privately by Mr. Oglesby.[5]

In Table II are given the data found for the four-component system. The three components necessary (with water) to define the composition are arbitrarily chosen so as to be of greatest convenience for the part of the complete diagram represented. An additional abbreviation for a new tetragene salt, described later in the paper, is included in the table.

TABLE I

THE FOUR THREE-COMPONENT SYSTEMS AT 25°

D.S. = Double salt, Trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$; S.S. = Solid solution, $(K_2.Na_2)CO_3 \cdot 6H_2O$

System $Na_2CO_3–K_2CO_3–H_2O$ (Ref. 2d)

Point in Fig. 1	Moles of Na_2CO_3	Moles of K_2CO_3	Solid phases
a	0.0	145.8	$K_2CO_3 \cdot 3/2H_2O$
	10.2	141.0	$K_2CO_3 \cdot 3/2H_2O$
b	18.3	136.0	$K_2CO_3 \cdot 3/2H_2O$ + S.S.
	18.4	121.6	S.S.
	20.1	95.6	S.S.
	22.0	86.8	S.S.
	33.5	65.3	S.S.
	38.6	57.7	S.S.
	49.8	44.8	S.S.
	59.5	36.3	S.S.
e	62.7	33.5	S.S. + $Na_2CO_3 \cdot 7H_2O$
	62.9	29.3	$Na_2CO_3 \cdot 7H_2O$
f	61.7	25.4	$Na_2CO_3 \cdot 7H_2O$ + $Na_2CO_3 \cdot 10H_2O$
	58.7	21.2	$Na_2CO_3 \cdot 10H_2O$
	52.0	11.1	$Na_2CO_3 \cdot 10H_2O$
d	49.2	0.0	$Na_2CO_3 \cdot 10H_2O$

System $Na_2CO_3–NaHCO_3–H_2O$ (Ref. 3c)

Point in Fig. 1	Moles of Na_2CO_3	Moles of $(NaHCO_3)_2$	Solid phases
n	0.0	10.99	$NaHCO_3$
	3.98	9.82	$NaHCO_3$
	16.07	7.66	$NaHCO_3$
	22.11	7.05	$NaHCO_3$
	28.39	6.45	$NaHCO_3$
m	38.79	5.49	$NaHCO_3$ + D.S.
	40.78	4.92	D.S.
	42.34	4.40	D.S.
	46.37	3.49	D.S.
	49.52	2.97	D.S. + $Na_2CO_3 \cdot 10H_2O$
	49.37	2.24	$Na_2CO_3 \cdot 10H_2O$
	49.36	1.52	$Na_2CO_3 \cdot 10H_2O$
	49.04	1.20	$Na_2CO_3 \cdot 10H_2O$
d	49.20	0.0	$Na_2CO_3 \cdot 10H_2O$

System $K_2CO_3–KHCO_2–H_2O$ (Ref. 4)

Point in Fig. 1	Moles of K_2CO_3	Moles of $(KHCO_3)_2$	Solid phases
a	145.8	0.0	$K_2CO_3 \cdot 3/2H_2O$
p	146.8	4.32	$K_2CO_3 \cdot 3/2H_2O$ + $KHCO_3$
	110.8	7.70	$KHCO_3$
	78.1	11.41	$KHCO_3$
	47.3	17.02	$KHCO_3$
	32.8	20.57	$KHCO_3$
k	0.0	32.53	$KHCO_3$

TABLE I (*Concluded*)

System $NaHCO_3$–$KHCO_3$–H_2O

Point in Fig. 1	Moles of $(NaHCO_3)_2$	Moles of $(KHCO_3)_2$	Solid phases
k	0.0	32.53	$KHCO_3$
l	6.17	31.05	$KHCO_3 + NaHCO_3$
	7.60	19.4	$NaHCO_3$
n	10.99	0.0	$NaHCO_3$

TABLE II

EQUILIBRIUM $K_2CO_3 + 2NaHCO_3 \rightleftharpoons 2KHCO_3 + Na_2CO_3$ IN WATER AT 25°

T.S. = Tetragene salt, $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$

Point in Fig. 1	Density	Moles of Na_2CO_3	Moles of $(NaHCO_3)$	Moles of K_2CO_3	Moles of $(KHCO_3)_2$	Solid phases
m	1.216	38.79	5.49	...	...	$NaHCO_3$ + D.S.
	1.236	35.89	6.21	6.82	...	$NaHCO_3$ + D.S.
	1.256	32.38	7.25	13.66	...	$NaHCO_3$ + D.S.
	1.279	28.95	8.26	22.62	...	$NaHCO_3$ + D.S.
	1.297	26.91	9.06	27.21	...	$NaHCO_3$ + D.S.
	1.314	23.39	10.30	35.23	...	$NaHCO_3$ + D.S.
	1.345	18.52	12.07	44.86	...	$NaHCO_3$ + D.S.
	1.375	13.50	14.08	56.61	...	$NaHCO_3$ + D.S.
v	1.390	10.70	15.40	62.18	...	$NaHCO_3$ + D.S. + $KHCO_3$
l	1.196	...	6.17	...	31.05	$NaHCO_3 + KHCO_3$
	1.208	4.62	2.05	...	32.55	$NaHCO_3 + KHCO_3$
	1.232	8.85	...	5.07	30.95	$NaHCO_3 + KHCO_3$
	1.264	11.23	...	14.52	27.07	$NaHCO_3 + KHCO_3$
	1.310	15.80	...	26.93	22.21	$NaHCO_3 + KHCO_3$
	1.331	18.34	...	31.95	20.23	$NaHCO_3 + KHCO_3$
	1.378	23.88	...	42.98	16.64	$NaHCO_3 + KHCO_3$
v	1.390	10.70	15.40	62.18	...	$NaHCO_3 + KHCO_3$ + D.S.
p	1.558	...	...	146.8	4.32	$K_2CO_3 \cdot 3/2H_2O + KHCO_3$
	1.56	4.22	...	143.8	4.73	$K_2CO_3 \cdot 3/2H_2O + KHCO_3$
z	1.559	1.35	4.71	146.9	...	$K_2CO_3 \cdot 3/2H_2O + KHCO_3$ + T.S.
i	...	49.52	2.97	...	...	D.S. + $Na_2CO_3 \cdot 10H_2O$
	1.262	50.46	2.59	3.48	...	D.S. + $Na_2CO_3 \cdot 10H_2O$
	1.294	52.08	2.11	10.22	...	D.S. + $Na_2CO_3 \cdot 10H_2O$
	1.310	54.04	1.65	15.03	...	D.S. + $Na_2CO_3 \cdot 10H_2O$
	1.334	57.27	1.05	20.02	...	D.S. + $Na_2CO_3 \cdot 10H_2O$
	1.347	58.56	1.00	22.35	...	D.S. + $Na_2CO_3 \cdot 10H_2O$
s	1.358	59.20	0.78	23.40	...	D.S. + $Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O$
s	1.358	59.20	0.78	23.40	...	D.S. + $Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O$
	1.365	60.40	0.82	25.69	...	D.S. + $Na_2CO_3 \cdot 7H_2O$
	1.381	61.37	0.51	29.59	...	D.S. + $Na_2CO_3 \cdot 7H_2O$
t	1.396	61.77	0.37	34.01	...	D.S. + $Na_2CO_3 \cdot 7H_2O$ + S.S.
t	1.396	61.77	0.37	34.01	...	D.S. + $Na_2CO_3 \cdot 7H_2O$ + S.S.
	1.403	60.95	0.52	34.74	...	D.S. + S.S.
	1.396	56.53	0.60	38.32	...	D.S. + S.S.
	1.396	52.56	0.84	41.70	...	D.S. + S.S.
	1.399	45.51	1.36	48.16	...	D.S. + S.S.
	1.410	37.58	2.36	57.15	...	D.S. + S.S.
	1.414	34.86	2.92	60.11	...	D.S. + S.S.

TABLE II (*Concluded*)

Point in Fig. 1	Density	Moles of Na_2CO_3	Moles of $(NaHCO_3)$	Moles of K_2CO_3	Moles of $(KHCO_3)_2$	Solid phases
	1.422	32.15	3.38	64.21	...	D.S. + S.S.
	1.434	26.04	4.84	73.65	...	D.S. + S.S.
	1.458	19.27	7.03	87.65	...	D.S. + S.S.
w	1.481	15.90	8.23	96.45	...	D.S. + S.S. + $KHCO_3$
w	1.481	15.90	8.23	96.45	...	D.S. + S.S. + $KHCO_3$
	1.484	15.10	8.17	98.78	...	S.S. + $KHCO_3$
	1.490	14.13	7.87	102.5	...	S.S. + $KHCO_3$
x	1.496	13.73	7.46	105.8	...	S.S. + $KHCO_3$ + T.S.
v	1.390	10.70	15.40	62.18	...	$NaHCO_3$ + D.S. + $KHCO_3$
	1.391	11.56	14.71	63.92	...	D.S. + $KHCO_3$
	1.413	13.24	12.79	70.18	...	D.S. + $KHCO_3$
	1.433	14.11	11.30	76.92	...	D.S. + $KHCO_3$
	1.446	14.80	10.15	83.35	...	D.S. + $KHCO_3$
	1.462	15.17	9.19	90.18	...	D.S. + $KHCO_3$
w	1.481	15.90	8.23	96.45	...	D.S. + $KHCO_3$ + S.S.
x	1.496	13.73	7.46	105.8	...	S.S. + $KHCO_3$ + T.S.
	1.497	13.57	6.85	107.9	...	S.S. + T.S.
	1.507	13.89	5.83	111.7	...	S.S. + T.S.
	1.521	14.03	4.25	118.8	...	S.S. + T.S.
	1.524	14.42	3.94	120.2	...	S.S. + T.S.
	1.542	15.43	2.71	127.3	...	S.S. + T.S.
	1.550	15.96	2.04	133.1	...	S.S. + T.S.
y	1.563	16.66	1.68	137.7	...	S.S. + T.S. + $K_2CO_3.3/2H_2O$
x	1.496	13.73	7.46	105.8	...	$KHCO_3$ + S.S. + T.S.
	1.501	13.30	7.38	106.8	...	$KHCO_3$ + T.S.
	1.502	10.92	7.23	111.0	...	$KHCO_3$ + T.S.
	1.504	9.98	7.36	112.4	...	$KHCO_3$ + T.S.
	1.517	5.62	6.87	122.9	...	$KHCO_3$ + T.S.
	1.531	4.63	6.61	126.8	...	$KHCO_3$ + T.S.
	1.536	3.42	6.12	133.0	...	$KHCO_3$ + T.S.
	1.543	2.49	6.35	136.8	...	$KHCO_3$ + T.S.
z	1.559	1.35	4.71	146.9	...	$K_2CO_3.3/2H_2O$ + $KHCO_3$ + T.S.
y	1.563	16.66	1.68	137.7	...	S.S. + T.S. + $K_2CO_3.3/2H_2O$
	1.560	11.73	2.30	140.8	...	T.S. + $K_2CO_3 \cdot 3/2H_2O$
	1.558	10.04	2.70	141.7	...	T.S. + $K_2CO_3 \cdot 3/2H_2O$
	1.560	7.38	3.22	143.3	...	T.S. + $K_2CO_3 \cdot 3/2H_2O$
z	1.559	1.35	4.71	146.9	...	T.S. + $K_2CO_3 \cdot 3/2H_2O$ + $KHCO_3$

Discussion of the 25° Isotherm

The preceding table gives the eleven curves for solubility equilibria with two and with three solid phases. In addition there are the three curves b–y, e–t and f–s which are so short that only their end-points could be determined. All fourteen are shown in Fig. 1, together with the fields representing saturation with respect to a single solid phase; the results are plotted according to the conventional method of Löwenherz.[6] The points

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[6] Löwenherz, *Z. physik. Chem.*, **13**, 459 (1894).

s, t, v, w, x, y and z represent the seven isothermally invariant points, at which the solution is in equilibrium with three solid phases.

Of the eight fields of saturation with a single salt, seven represent salts found in the four three-component systems. Of these the field bounded by the lines b–e–t–w–x–y–b represents the phase recently shown[2d] to be a solid solution, of the formula $(K_2,Na_2)CO_3 \cdot 6H_2O$, and previously thought to be a definite compound of the formula $KNaCO_3 \cdot 6H_2O$. The field for the decahydrated sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, is bounded by the lines i–d–f–s–i; its apparent extension beyond the boundary line for the three-component system (d–f) is, of course, wholly a matter of the Löwenherz method of representation. The eighth field, x–y–z, represents a new tetragene salt, $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, which does not occur in any of the three-component systems at this temperature.

The Tetragene Salt.—Upon finding the existence of the field x–y–z, experiments were conducted to determine the composition of the salt which crystallized out within that area. A number of isothermal evaporations of such solutions were carried out, for the purpose of studying the crystallization paths described later. The crystals thus obtained were filtered off, centrifuged at a rate of 1000 r.p.m., which unfortunately was too slow to secure very complete expulsion of the mother liquor, and analyzed in this slightly moist condition. The results of the analysis are given in Table III.

TABLE III

ANALYSIS OF TETRAGENE SALT

Calculated for the formula $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$: $K_2CO_3 = 53.52$; $NaHCO_3 = 32.53$; $H_2O = 13.95\%$

Wt. % K_2CO_3	Wt. % $NaHCO_3$	Wt. % H_2O	Wt. % Na_2CO_3	Wt. % K_2CO_3	Wt. % $NaHCO_3$	Wt. % H_2O	Wt. % Na_2CO_3
52.80	31.17	15.17	0.90	54.32	32.05	14.68	−1.05
52.87	31.24	15.24	0.65	55.49	33.29	14.90	−3.68
52.39	28.49	18.48	0.64	55.29	29.86	14.79	0.06
54.17	32.66	14.37	−1.20	53.54	30.19	16.82	−0.55
53.80	32.34	15.05	−1.19	53.63	36.55	14.63	−4.81

In the above table the fourth column is included to represent the actual results as calculated for a possible four-component body. The variations from the composition assumed are not inconsiderable. How far they may be due to occlusion of mother liquor or to precipitation of metastable salts we are not in a position to estimate, but the evidence seems to us convincing that the salt has the formula $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. This would put the compound in the comparatively small class of salts built up of two cations and two anions, to which Meyerhoffer[7] has given the name of "tetragene salts." It is perhaps also worthy of note that the composition of the salt is that of the well-known double salt Trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), with

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[7] Meyerhoffer, *Z. anorg. Chem.*, **34**, 147 (1902).

the substitution of a molecule of potassium carbonate for one of sodium carbonate.

In order to verify the formula by a different method, 200 g. of solution was prepared of a composition known to fall in the desired area. A small amount of the solid was added and the mixture rotated in the thermostat at 25° for 120 hours. At the end of that time the solid phase had not disappeared, indicating that equilibrium existed between the solid and liquid phases. The crystals were then allowed to settle and the liquid was analyzed. The composition of this solution is represented by a point within the field x–y–z and is as follows: Na_2CO_3 = 3.26; $NaHCO_3$ = 1.87; K_2CO_3 = 46.62; H_2O = 48.25. To the above equilibrium mixture was added 13.82 g. of K_2CO_3, 8.4 g. of $NaHCO_3$ and 3.6 g. of H_2O, corresponding to the composition of the alleged salt, $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. The mixture was again rotated in the thermostat for forty-eight hours and the solution analyzed. This solution gave the following analysis: Na_2CO_3 = 3.30; $NaHCO_3$ = 1.85; K_2CO_3 = 46.71; H_2O = 48.14. Since the analyses of these two solutions agree within a small experimental error, the composition of the liquid phase may be regarded as unchanged and the solid phase is shown to have the composition $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$.[8]

Crystallization Paths.—In Fig. 1 the lines drawn within the fields represent crystallization paths of solutions undergoing isothermal evaporation. Except for the field x–y–z, for which experimental data will be given later, these lines have been drawn according to the conventional *a priori* reasoning, assuming that solid phases are withdrawn as formed; they therefore can represent only in a qualitative way the course of such evaporations. In the case of the four salts $Na_2CO_3 \cdot 10H_2O$, $K_2CO_3 \cdot 3/2H_2O$, $KHCO_3$ and $NaHCO_3$, the solubilities in water are represented by the four points d, a, k and n, falling on the respective axes; the crystallization paths for these salts are therefore drawn as radiating from these points. The heptahydrate, $Na_2CO_3 \cdot 7H_2O$, is not stable in water at this temperature, but its solubility may be estimated by extrapolation of its solubility curve e–f to the point h, from which center its crystallization paths radiate. The point for the crystallization paths of the double salt Trona also has to be found by extrapolation of its solubility curve i–m to a point on a line representing its molecular composition, namely, the point j. For the solid

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[8] Since this paper was written there has appeared Teeple's "The Industrial Development of Searles Lake Brines," Chemical Catalog Company, New York, **1929**, in which appears (p. 132) a study of this four component system at 35°, carried out by Harald de Ropp. The field which we assign at 25° to the tetragene salt $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ is assigned by them at 35° to a potassium sesquicarbonate, $K_2CO_3 \cdot 2KHCO_3 \cdot 3H_2O$. Without raising any question as to the correctness of de Ropp's findings at 35°, we have not found the potassium sesquicarbonate at 25°, and are sure that the salt found by us is a sodium–potassium salt in the atomic ratio of 1:2, as we have reaffirmed by repeated analyses.

solution $(Na_2,K_2)CO_3{\cdot}6H_2O$ we cannot speak of a definite solubility in water, for the solid phase has a varying composition; the crystallization paths therefore will radiate not from a single point but from a series of points. By drawing lines from the origin in the coördinate system so as to represent the atomic ratios of sodium to potassium in the extreme compositions found for the solid solution, it was found that the two lines intersect the solubility curve e–b close to the point e and at c; the crystallization paths will therefore radiate from a series of points between e and c. These lines are drawn in this area with a considerable curvature, to correspond with the curvature of the line e–b; elsewhere in the diagram they are drawn arbitrarily as straight lines, or lines with but a slight curvature.

The crystallization paths for the remaining phase, the tetragene salt, were investigated experimentally; *a priori* it could only be deduced that the center of the radiating lines would fall somewhere between the point representing the composition of the salt and the origin of the coördinate system. For the experiments large quantities of solutions were prepared of compositions lying near to the line x–z. Each of these was inoculated with a

TABLE IV

CRYSTALLIZATION PATHS IN THE AREA X–Y–Z–(TETRAGENE SALT)

		Initial solution				Final solution	
		Wt. %	Moles per 1000 of H_2O	Wt. %	Moles per 1000 of H_2O	Wt. %	Moles per 1000 of H_2O
Curve 1	Na_2CO_3	3.63	12.43	3.70	12.80	4.11	14.43
	$(NaHCO_3)_2$	2.62	5.66	2.08	4.54	1.55	3.43
	K_2CO_3	44.11	115.8	45.11	119.7	45.95	123.8
	H_2O	49.64	....	49.11	....	48.39	....
Curve 2	Na_2CO_3	2.97	10.15			3.42	12.61
	$(NaHCO_3)_2$	2.82	6.08			1.15	2.68
	K_2CO_3	44.50	116.7			49.33	139.5
	H_2O	49.71	....			46.10	....
Curve 3	Na_2CO_3	2.72	9.35			3.10	10.89
	$(NaHCO_3)_2$	2.70	5.85			1.86	4.12
	K_2CO_3	45.13	119.0			46.67	125.8
	H_2O	49.45	....			48.37	....
Curve 4	Na_2CO_3	2.43	8.31			3.23	11.85
	$(NaHCO_3)_2$	3.27	7.05			0.88	2.04
	K_2CO_3	44.57	116.8			49.58	139.6
	H_2O	49.73	....			46.31	....
Curve 5	Na_2CO_3	2.28	7.78			3.25	11.86
	$(NaHCO_3)_2$	3.49	7.51			1.17	2.69
	K_2CO_3	44.43	116.3			49.03	137.3
	H_2O	49.80	....			46.55	....
Curve 6	Na_2CO_3	1.95	6.72			2.67	9.84
	$(NaHCO_3)_2$	3.33	7.25			1.20	2.79
	K_2CO_3	45.44	120.2			50.01	141.4
	H_2O	49.28	....			46.12	....

small amount of crystalline tetragene salt and rotated in the thermostat for forty-eight hours to secure equilibrium; after being allowed to settle, the clear liquid was analyzed. The remaining material was then placed in an evaporating dish in a desiccator over concentrated sulfuric acid and maintained in an air thermostat at 25°. The solutions were stirred from day to day and were weighed at frequent intervals to follow the rate of evaporation. In the course of three weeks about 20 g. of water was lost by each and a quantity of solid phase obtained sufficient for analysis. The mixtures were then again rotated in the thermostat at 25° for forty-eight to seventy-two hours to secure equilibrium and the solid phase was filtered off; the analysis of ten such samples has been given previously in Table III. The liquid phases were then analyzed. The results of the initial and final analysis for six such experiments are given in Table IV and shown in Fig. 2 by the points within the area x–y–z; connecting these by straight lines (as the simplest assumption) we obtain a series of crystallization paths for the tetragene salt.

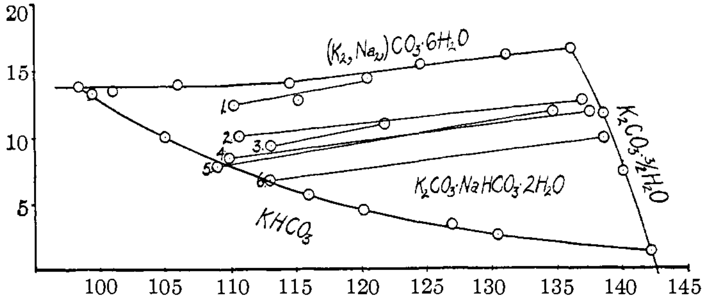

Fig. 2.—Crystallization paths for the tetragene salt, $K_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$ at 25°.

If the crystallization paths thus found and shown in Fig. 2 be extrapolated, they will fall close to the point in Fig. 1 represented by q.

With the crystallization paths for the eight single solids determined, the direction of the crystallization paths along the lines for two-solid equilibrium follows. Of these fourteen curves for isothermally univariant equilibrium, only three are not crystallization paths; these are the Curves m–v, s–f and x–z. At each of these curves resorption of the solid phase present takes place, with separation of a new solid phase; the changes represented are, respectively

$$NaHCO_3 \longrightarrow NaHCO_3{\cdot}Na_2CO_3{\cdot}2H_2O \text{ (Trona)}$$
$$Na_2CO_3{\cdot}10H_2O \longrightarrow Na_2CO_3{\cdot}7H_2O$$
$$KHCO_3 \longrightarrow K_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O \text{ (Tetragene salt)}$$

Isothermally Invariant Points.—The fourteen isothermally univariant curves meet at seven points, which represent saturation with respect to three solid phases in each case and are therefore isothermally invariant.

Inspection of the curves meeting at these points shows, however, that in only two of the seven cases are the points the termini of three crystallization lines; these are the points t and y, which are therefore crystallization end-points or drying-up points. Solutions of any possible composition will, therefore, under isothermal evaporation, go to dryness at one or another of these two points, with the precipitation of the three salts indicated, namely at t, $Na_2CO_3 \cdot 7H_2O$, Trona and the solid solution, and at y, $K_2CO_3 \cdot 3/2H_2O$, solid solution and the tetragene salt. The other five points are not points of congruent saturation.

There is also in the system a single point of congruent saturation with respect to two solid phases, namely, Trona and the solid solution; the point has been set arbitrarily, without experimental confirmation, at r. This point represents the position for dividing the possible solutions of the system into two classes: those falling to the right of the crystallization paths leading to r will dry up at the point y, and those to the left will dry up at t, the division depending chiefly upon the total amounts of sodium salts and of potassium salts which are present.

Summary

1. The 25° isotherm has been studied for the quaternary system made up from sodium carbonate, potassium bicarbonate and water, and the results have been plotted according to the method of Löwenherz.
2. The system has been found to contain eight fields of isothermally bivariant equilibrium, fourteen lines of isothermally univariant equilibrium and seven isothermally invariant points.
3. There is no "stable pair" in this system at this temperature; *i. e.*, neither Na_2CO_3 and $KHCO_3$ nor $NaHCO_3$ and K_2CO_3 can be in equilibrium as solid phases.
4. A new tetragene salt has been found, of the formula $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, not occurring in any of the three-component systems.
5. The crystallization paths for the tetragene salt have been studied experimentally, and the paths for the other salts have been deduced *a priori*.
6. There exist in the system at this temperature two crystallization end-points and one two-solid congruent point.

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