

Our experiments at 20° agree very closely for both chlorides with the exact results of Richards and his collaborators for 20°, but when our experiments at other temperatures are compared with them with the aid of temperature coefficients, the agreement is poor. The concentrations at which the discrepancies are significant are rather low, and it appears that the temperature coefficients are not known at sufficiently low concentrations to establish the extrapolated value at zero concentration.

CAMBRIDGE, MASSACHUSETTS

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

## DOUBLE SALT FORMATION AMONG THE CARBONATES AND BICARBONATES OF SODIUM AND POTASSIUM

By ARTHUR E. HILL

RECEIVED JUNE 2, 1930

PUBLISHED OCTOBER 6, 1930

When aqueous solutions of the carbonates and bicarbonates of sodium and potassium are brought to crystallization, five solid phases of the general nature of double salts have been found and identified with certainty. The best known of these is Trona,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , which has been known for a long period of time and which has been studied from its lower temperature of formation, 21.26°, up to 50° by Hill and Bacon,<sup>1</sup> and more recently up to 89° by Wegscheider and Mehl;<sup>2</sup> at this temperature the latter investigators also believe that two new double salts are formed, for which the evidence is, however, less conclusive than for the five here under discussion. Known also for a long time, but incorrectly classed as a definite compound in the earlier literature, is the hydrated solid solution  $(\text{K}_2, \text{Na}_2)\text{CO}_3 \cdot 6\text{H}_2\text{O}$ , which was shown by Hill and Miller<sup>3</sup> to exist in contact with alkali carbonate solutions over a rather wide range of concentrations, from 34° downward. The anhydrous double carbonate  $\text{KNaCO}_3$  has been shown<sup>3</sup> to be stable in contact with solution from 25.12° upward to at least 50°, and probably much higher. Recently, in a study of the reciprocal salt pair  $\text{K}_2\text{CO}_3 + 2\text{NaHCO}_3 \rightleftharpoons \text{Na}_2\text{CO}_3 + 2\text{KHCO}_3$ , Hill and S. B. Smith<sup>4</sup> found a new double salt of the formula  $\text{K}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , belonging to the class of double salts without common ion which Meyerhoffer<sup>5</sup> has called tetragene salts. This salt was found only in four-component solutions, and its occurrence and the limits of its field were determined, it was thought, with surety. At the same time that this paper was published, there appeared the valuable and comprehensive work of Teeple upon the

<sup>1</sup> Hill and Bacon, *THIS JOURNAL*, **49**, 2487 (1927).

<sup>2</sup> Wegscheider and Mehl, *Monatsh.*, **49**, 283 (1928).

<sup>3</sup> Hill and Miller, *THIS JOURNAL*, **49**, 669 (1927).

<sup>4</sup> Hill and Smith, *ibid.*, **51**, 1626 (1929).

<sup>5</sup> Meyerhoffer, *Z. anorg. Chem.*, **34**, 147 (1902).

Searles Lake deposits; in this there is given<sup>6</sup> a 35° isotherm by de Ropp for the same system, in which our tetragene salt does not appear, but its place is given over to a potassium salt,  $K_2CO_3 \cdot 2KHCO_3 \cdot 3H_2O$ , which we had not found in our work. and which is the fifth of the double salts which have been claimed for the system. As it was considered necessary to clear up this contradiction, the four-component work has been repeated at the two temperatures in question, 25 and 35°, with the resulting conclusion that both earlier publications contained an error of omission; as will be shown below, both the tetragene salt and the potassium sesquicarbonate (though with a different degree of hydration, as will be shown in the paper following this) occur at both temperatures, with a division of the disputed field between them.

**Experimental Methods.**—The experiments at the two temperatures have been carried out as in the previous work of Hill and Smith.<sup>4</sup> Pure specimens of the carbonates and bicarbonates of sodium and potassium, in suitable weighed amounts, have been treated with weighed amounts of water and tumbled in a thermostat usually for two days before pipetted samples of the saturated solutions were withdrawn and analyzed. Attainment of saturation with respect to two salts on the lines of isothermally univariant equilibrium, and with respect to three salts at the isothermally invariant points, was proved in every case by the method of adding the components necessary to give the composition of the saturating salts, tumbling the mixture for another day, and again analyzing the solution; where it remained unaltered within the errors of the analysis, equilibrium was assured. For the analysis, one sample of solution was titrated for total alkali with standard hydrochloric acid, using methyl orange as indicator; a second sample was evaporated to constant weight to give total potassium and sodium as carbonate; a third sample was analyzed for total carbon dioxide by adding sulfuric acid and absorbing the evolved gas in soda lime in a Flemming bottle. From these data the composition of the solution was calculated. The samples were weighed from volumetric pipets, from which data densities can be calculated, but not with a high degree of accuracy.

**The 25° Isotherm.**—The data at 25° are given in Table I and reproduced graphically in Fig. 1. In the table, the abbreviation T. S. is used for the tetragene salt  $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ , and D. S. for the double salt  $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$ .

It will be seen from Fig. 1, which reproduces on a large scale a part of the four-component diagram previously given<sup>4</sup> in full, that the double salt  $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$  found by Teeple at 35° has an existence in this system, but is stable only over a small range of concentrations.

<sup>6</sup> Teeple, "The Industrial Development of Searles Lake Brines," The Chemical Catalog Co., Inc., New York, 1929.

TABLE I

THE DATA AT 25°

Point in Fig. 1	Weight %, satd. soln.				Moles per 1000 moles of H <sub>2</sub> O				Solid phases	
	Density	K <sub>2</sub> CO <sub>3</sub>	KHCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	(KHCO <sub>3</sub> ) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>		(NaHCO <sub>3</sub> ) <sub>2</sub>
A	1.559	52.77	0.0	...	...	145.6	...	...	...	K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O
B	1.563	51.23	2.64	...	...	144.8	5.2	...	...	K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O + D. S.
	1.562	50.77	2.85	...	...	142.8	5.5	...	...	D. S.
	1.554	50.28	3.02	...	...	140.4	5.8	...	...	D. S.
	1.549	49.77	3.22	...	...	138.0	6.2	...	...	D. S.
C	1.545	49.48	3.33	...	...	136.4	6.4	...	...	D. S. + KHCO <sub>3</sub>
	1.556	49.90	2.19	...	1.00	138.7	4.2	...	2.3	D. S. + KHCO <sub>3</sub>
	1.552	50.06	1.26	...	1.85	139.4	2.4	...	4.2	D. S. + KHCO <sub>3</sub>
Q	1.553	50.05	...	0.38	2.73	139.3	...	1.4	6.3	D. S. + KHCO <sub>3</sub> + T. S.
	1.557	50.55	...	.34	2.52	141.5	...	1.2	5.8	D. S. + T. S.
	1.560	50.91	...	.24	2.44	143.0	...	0.9	5.6	D. S. + T. S.
Z	1.566	51.80	...	.15	2.10	147.0	...	.5	4.9	D. S. + T. S. + K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O
	1.567	51.82	0.44	...	1.79	147.0	0.9	...	4.2	D. S. + K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O
	1.565	51.64	1.46	...	0.87	146.0	2.9	...	2.0	D. S. + K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O
B	1.563	51.23	2.64	...	...	144.8	5.2	...	...	D. S. + K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O

The 35° Isotherm.—The data at 35° are given in Table II and shown in Fig. 2.

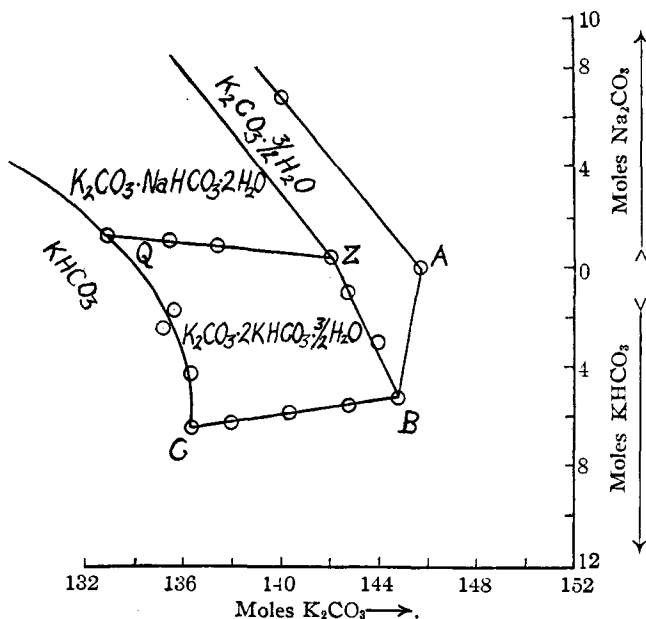


Fig. 1.—System K<sub>2</sub>CO<sub>3</sub>-NaHCO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-KHCO<sub>3</sub>-H<sub>2</sub>O at 25°.

Comparing Fig. 2 with the comparable part of de Ropp's isotherm at the same temperature, the present work establishes the existence of the isothermally invariant points Q and Z and the existence of separate fields for

TABLE II  
THE DATA AT 35°

Point in Fig. 2	Weight %, satd. soln.					Moles per 1000 moles of H <sub>2</sub> O					Solid phases
	Density	K <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	KHCO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	(NaHCO <sub>3</sub> ) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	(KHCO <sub>3</sub> ) <sub>2</sub>		
X	1.571	50.07	..	4.19	..	142.7	...	15.6	...	K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O + KNaCO <sub>3</sub>	
A	1.580	53.56	..	..	..	150.4	...	..	...	K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O	
B	1.573	51.68	..	..	3.26	149.5	...	..	6.5	K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O + D. S.	
	1.563	50.99	..	..	3.48	146.0	...	..	6.9	D. S.	
	1.564	50.58	..	..	3.62	144.0	...	..	7.0	D. S.	
	1.556	50.00	..	..	3.92	141.5	...	..	7.6	D. S.	
C	1.556	49.51	..	..	4.27	139.6	...	..	8.3	D. S. + KHCO <sub>3</sub>	
	1.557	49.96	1.26	..	2.69	141.2	2.9	..	5.2	D. S. + KHCO <sub>3</sub>	
	1.558	50.02	1.93	..	2.01	141.6	4.5	..	3.9	D. S. + KHCO <sub>3</sub>	
	1.557	50.37	2.90	..	0.53	142.1	6.7	..	1.0	D. S. + KHCO <sub>3</sub>	
	1.553	49.81	3.54	0.25	..	139.9	8.2	0.9	..	D. S. + KHCO <sub>3</sub>	
	1.551	49.20	3.49	.64	..	137.4	8.0	2.3	..	D. S. + KHCO <sub>3</sub>	
Q	1.547	48.42	3.58	1.12	..	134.7	8.2	4.1	..	D. S. + KHCO <sub>3</sub> + T. S.	
	1.552	48.52	3.11	1.66	..	135.4	7.1	6.0	..	D. S. + T. S.	
	1.562	48.54	2.05	3.10	..	136.7	4.7	11.4	..	D. S. + T. S.	
Z	1.568	48.62	1.38	4.25	..	138.6	3.3	15.8	..	D. S. + T. S. + KNaCO <sub>3</sub>	
Y	1.576	50.37	1.19	3.28	..	145.4	2.8	12.4	..	D. S. + KNaCO <sub>3</sub> + K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O	
	1.574	51.20	1.37	2.20	..	147.5	3.2	8.3	..	D. S. + K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O	
	1.573	51.12	1.75	0.99	..	150.6	4.2	3.7	..	D. S. + K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O	
	..	52.54	2.17	.17	..	151.8	5.2	0.6	..	D. S. + K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O	
	1.573	52.57	1.95	..	0.49	152.4	4.6	..	1.0	D. S. + K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O	
	1.573	52.15	1.17	..	1.82	151.6	2.8	..	3.6	D. S. + K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O	
B	1.573	51.68	..	..	3.26	149.5	...	..	6.5	D. S. + K <sub>2</sub> CO <sub>3</sub> ·3/2H <sub>2</sub> O	

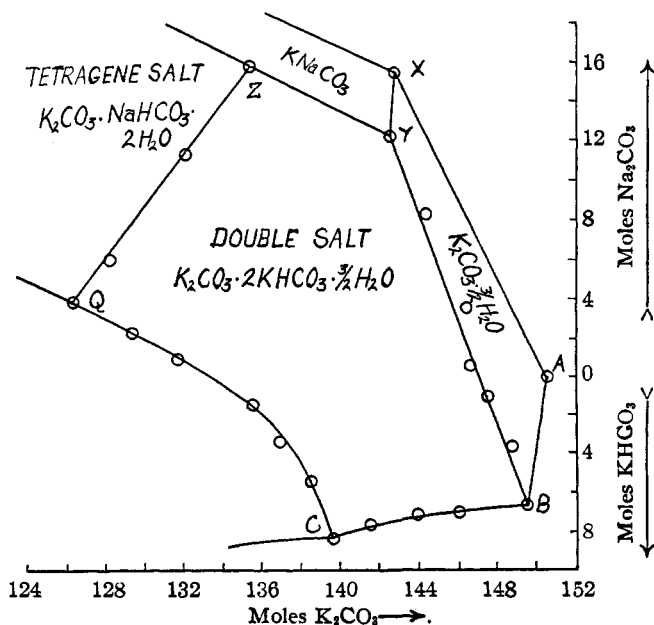


Fig. 2.—System  $K_2CO_3$ - $NaHCO_3$ - $Na_2CO_3$ - $KHCO_3$ - $H_2O$  at 35°.

the double salt and the tetragene salt; this was confirmed by preparing the single salts, each within the concentration range indicated, and subjecting each to an analysis which confirmed its composition beyond doubt. The other points in the diagram were found to be in qualitative agreement with de Ropp's findings, but varying from his by several per cent. in composition. As compared with the 25° isotherm, the figure shows that a rise of temperature increases the range of concentrations within which the double salt can form and decreases the range for the tetragene salt.

### Summary

Partial isotherms at 25° and at 35° for the four component system  $K_2CO_3 + 2NaHCO_3 \rightleftharpoons Na_2CO_3 + 2KHCO_3$  in water have shown that at both temperatures there exist as solid phases the double salt  $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$  and the tetragene salt  $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ .

NEW YORK, N. Y.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

## HYDRATED POTASSIUM SESQUICARBONATE, $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$

BY ARTHUR E. HILL

RECEIVED JUNE 2, 1930

PUBLISHED OCTOBER 6, 1930

The existence of a sesquicarbonate of potassium, intermediate in composition between the normal carbonate and the bicarbonate, has been claimed frequently over a long period of time, and at least as frequently disputed. It appears to have been mentioned first by Berthollet,<sup>1</sup> who obtained it by boiling and cooling a solution of the bicarbonate, and also by cooling a solution of equimolecular proportions of the carbonate and bicarbonate; it is obvious that these operations gave partial decomposition of the bicarbonate into carbonate and that therefore the composition of the solutions was unknown. The only known analyses of the salt were performed by Flückiger,<sup>2</sup> who used an incrustation found upon an earthenware jar containing crude potash, and by Bauer<sup>3</sup> and by Rammelsberg,<sup>4</sup> who prepared their specimen by evaporation and crystallization of a bicarbonate solution; Flückiger assigned to the salt the formula  $K_2CO_3 \cdot 2KHCO_3 \cdot 5H_2O$  and Bauer and Rammelsberg gave it the formula  $K_2CO_3 \cdot 2KHCO_3 \cdot 3H_2O$ ; these formulas will be discussed later in this paper. The salt has also been reported more recently by Appleby and Lane,<sup>5</sup> incidental

<sup>1</sup> Berthollet, *Mem. Arcueil*, **2**, 475 (1809).

<sup>2</sup> Flückiger, *Ber.*, **16**, 1143 (1883).

<sup>3</sup> Bauer, *Monatsh.*, **4**, 341 (1883).

<sup>4</sup> Rammelsberg, *Ber.*, **16**, 273 (1883).

<sup>5</sup> Appleby and Lane, *J. Chem. Soc.*, **113**, 609 (1918).