

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 $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$.

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

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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,¹ 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,² who used an incrustation found upon an earthenware jar containing crude potash, and by Bauer³ and by Rammelsberg,⁴ 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,⁵ incidental

¹ Berthollet, *Mem. Arcueil*, **2**, 475 (1809).

² Flückiger, *Ber.*, **16**, 1143 (1883).

³ Bauer, *Monatsh.*, **4**, 341 (1883).

⁴ Rammelsberg, *Ber.*, **16**, 273 (1883).

⁵ Appleby and Lane, *J. Chem. Soc.*, **113**, 609 (1918).

to a study of a four-component system, and by de Ropp,⁶ in these two publications no analytical data are given, and the formula of Bauer and Rammelsberg is used. A large number of investigators have failed to find this salt upon studying carbonate-bicarbonate solutions, justifying the comment of Mellor,⁷ "there is room for doubting the existence of these salts as chemical individuals until the systems have been explored by the aid of the phase rule." Having been among those who failed to find the compound at one time⁸ and found it at another,⁹ I have thought it well to make a systematic study, to determine the temperature range and concentration range within which the compound has stable existence, and to determine as correctly as possible its true composition.

Experimental Methods.—Solubility measurements have been made for the three-component system K_2CO_3 - $KHCO_3$ - H_2O at four temperatures. The potassium carbonate, a Kahlbaum preparation which showed as high purity as the sodium carbonate used as the ultimate standard, was first heated over a burner for several hours and then stored in an electric oven at 110° ; attempts to dehydrate the sesquihydrate $K_2CO_3 \cdot 3/2H_2O$ at this temperature are likely to be futile, unless very long periods of time are used. The pure bicarbonate was stored over sulfuric acid in an atmosphere of carbon dioxide. Weighed amounts of these salts, with weighed amounts of water, were put into 40-cc. glass-stoppered pyrex tubes and revolved in a water thermostat; although twenty-four hours were allowed for the attainment of equilibrium in nearly all cases, it is certain that equilibrium with the liquid is attained in a much shorter time, even when the double salt has to crystallize out as solid phase; an important point, however, is the necessity for adding the carbonate first and insuring that it is well broken up and brought to complete solution before the bicarbonate is added, to prevent the formation of hard lumps of the hydrated carbonate which may remain incompletely changed for long periods. The high heat of hydration of the anhydrous salt makes it easy to bring it completely into solution. After attainment of equilibrium, two 5-cc. samples were withdrawn from each tube; one was titrated for total alkali by hydrochloric acid solution, using methyl orange as indicator, and the second was treated with sulfuric acid in a suitable train and the carbon dioxide absorbed by soda lime in a Flemming bottle. Tests showed that these two determinations were accurate to within 0.1%; the calculation of the carbonate-bicarbonate ratio from them includes a multiplication which would make errors in the total composition of the order of 0.5%, but the smoothness of the curves obtained

⁶ De Ropp, see Teeple, "Industrial Development of Searles Lake Brines." The Chemical Catalog Co., Inc., New York, 1929, p. 132.

⁷ Mellor, "Comprehensive Treatise," Vol. II, London, 1922, p. 779.

⁸ Hill and Hill, *THIS JOURNAL*, 49, 967 (1927).

⁹ See previous paper, Hill, *ibid.*, 52, 3813 (1930).

indicates that the actual errors were much less. The weights of solution delivered by the volumetric pipets gave rough figures for the densities of the solutions.

The Isotherms.—The solubility measurements, which were carried out at four temperatures, from 5 to 50°, are given in the following table. Columns 5 and 6 give the composition of the mixture weighed into the tubes; Cols. 3 and 4 give the composition of the saturated solutions. The

TABLE I
TERNARY SYSTEM, K_2CO_3 - $KHCO_3$ - H_2O

Point in Fig. 1	Satd. solution			Orig. complex		Solid phases
	Density	K_2CO_3	$KHCO_3$	K_2CO_3	$KHCO_3$	
5° Isotherm						
A	1.543	51.53	..	55.0	0.0	$K_2CO_3 \cdot 3/2H_2O$
B	1.155	50.59	1.72	$K_2CO_3 \cdot 3/2H_2O$ + D. S.
	...	50.03	1.77	49.2	6.0	D. S.
	1.543	49.91	1.90	49.0	6.0	D. S.
C	1.542	49.65	1.96	D. S. + $KHCO_3$
	1.509	46.38	2.55	44.0	8.0	$KHCO_3$
D	1.137	...	20.15	...	30.0	$KHCO_3$
25° Isotherm						
A	1.559	52.77	..	57.0	..	$K_2CO_3 \cdot 3/2H_2O$
B	1.563	51.23	2.64	$K_2CO_3 \cdot 3/2H_2O$ + D. S.
	1.562	50.77	2.85	49.16	7.99	D. S.
	1.554	50.28	3.02	48.95	8.03	D. S.
	1.549	49.77	3.22	48.48	7.92	D. S.
C	1.545	49.48	3.33	D. S. + $KHCO_3$
	1.538	48.14	3.56	46.41	7.03	$KHCO_3$
	1.526	47.20	3.51	45.04	7.98	$KHCO_3$
	1.484	43.89	4.41	38.00	17.00	$KHCO_3$
	1.485	42.82	4.67	41.63	7.41	$KHCO_3$
	1.402	34.71	7.35	30.00	20.00	$KHCO_3$
	1.316	23.36	12.19	20.00	25.00	$KHCO_3$
	1.272	16.98	15.45	15.00	25.00	$KHCO_3$
	1.228	10.00	19.31	9.00	28.00	$KHCO_3$
D	1.187	0.00	26.78	$KHCO_3$
35° Isotherm						
A	1.560	53.56	0.0	56.0	54.0	$K_2CO_3 \cdot 3/2H_2O$
B	1.573	51.68	3.26	$K_2CO_3 \cdot 3/2H_2O$ + D. S.
	1.563	50.99	3.48	49.96	7.00	D. S.
	1.564	50.58	3.62	50.00	7.00	D. S.
	1.556	50.00	3.92	48.52	9.00	D. S.
C	1.556	49.51	4.27	48.08	7.99	D. S. + $KHCO_3$
	1.548	48.93	4.27	46.96	8.00	$KHCO_3$
	1.441	37.73	7.50	34.97	13.99	$KHCO_3$
	1.329	23.04	14.21	20.00	24.98	$KHCO_3$
	1.252	10.04	22.10	8.98	29.99	$KHCO_3$
	1.208	0.97	28.82	$KHCO_3$
D	1.200	0.00	29.60	$KHCO_3$

TABLE I (Concluded)

Point in Fig. 1	Satd. solution		Orig. complex		Solid phases	
	Density	K_2CO_3	$KHCO_3$	K_2CO_3		$KHCO_3$
50° Isotherm						
A	...	54.8	0.0	$K_2CO_3 \cdot 3/2H_2O$
B	1.584	52.85	3.83	$K_2CO_3 \cdot 3/2H_2O$ + D. S.
	1.581	51.97	4.40	D. S.
	1.569	50.92	4.97	50.01	7.01	D. S.
C	1.565	49.65	5.77	D. S. + $KHCO_3$
D	...	0.0	34.2	$KHCO_3$ (Dibbetts)

abbreviation D. S. is used for the double salt as solid phase, $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$.

At each of these four temperatures, there is clear proof of the existence of three solubility curves, one each for $K_2CO_3 \cdot 3/2H_2O$, for $KHCO_3$, and for the double salt; the isothermal invariance of the points marked B and C was established by analyses of two or three solutions in each case, made up

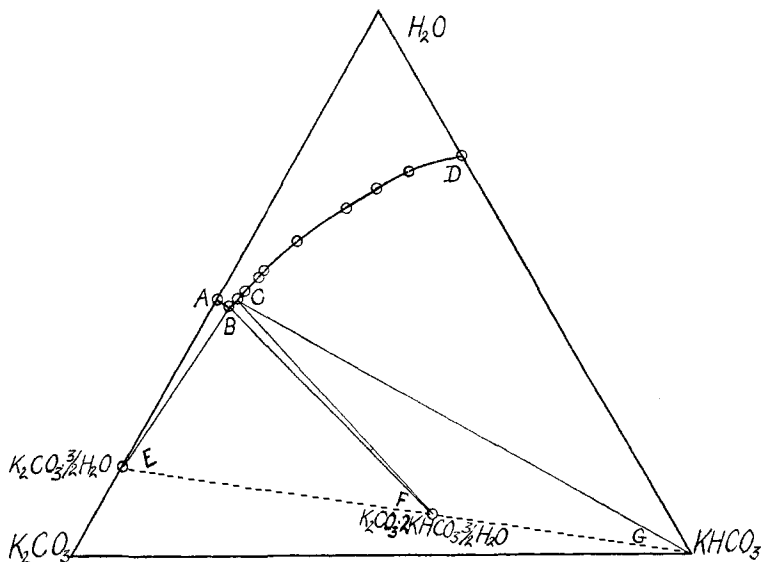


Fig. 1.—25° Isotherm for system K_2CO_3 - $KHCO_3$ - H_2O .

from varying ratios of the three components. The solubility curve for the compound is very short, covering only a concentration range of 1 to 2%, as shown by the curve BC in Fig 1, the isotherm for 25°; the narrow limits of this concentration give the explanation as to why the salt has been overlooked on so many occasions. Figure 2 has been drawn so as to show these solubility curves on a much larger scale, from which it appears that the range of stable existence for the double salt, always narrow, becomes more and more restricted as the temperature falls; a rough graphic extrapolation of the curves drawn through the B and C values indicates that the

salt must cease to have stable existence at some temperature not greatly below 5° . It was possible, however, to draw some *a priori* conclusions as to this lower ternary transition temperature of the salt, by means of thermochemical considerations. Since the salt exists only above this temperature, it follows by application of the van't Hoff law of mobile equilibrium that the phase reaction by which it is formed from solution and the solid salts adjacent to it in the diagram must be an endothermal reaction. If it were formed from the bicarbonate and the sesquihydrate $K_2CO_3 \cdot 3/2H_2O$, its formation would in all probability be exothermal, since

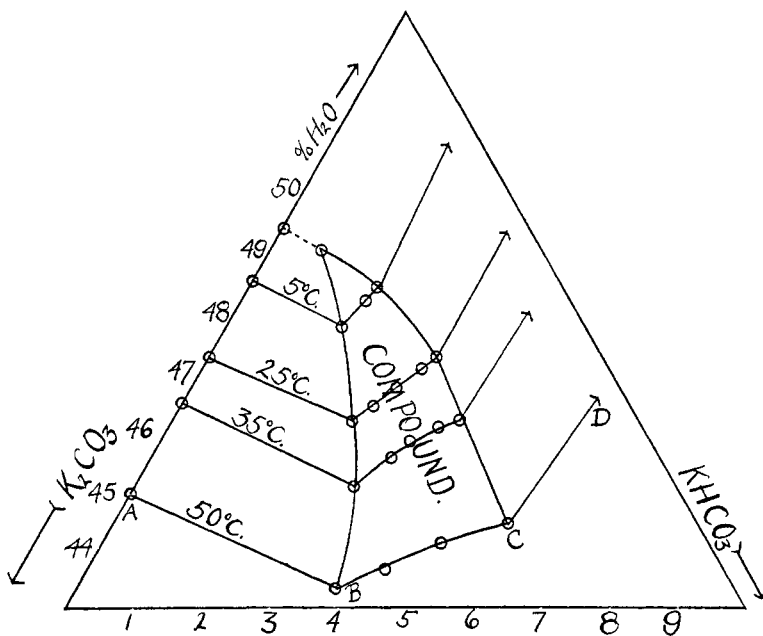
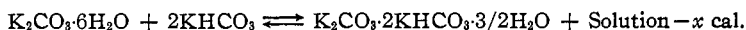


Fig. 2.—System K_2CO_3 - $KHCO_3$ - H_2O ; partial isotherms.

the reaction would be a simple additive reaction of the two salts. In order to have the reaction endothermal, the compound would have to be formed from compounds of a higher degree of hydration; of such compounds, only one is known, the hexahydrate $K_2CO_3 \cdot 6H_2O$, which Hill and Miller¹⁰ have shown to exist only below -6.2° ; it may be concluded, therefore, that the ternary transition temperature of the compound is below -6.2° , and that the phase reaction is



Experimental confirmation of this reasoning was had by means of cooling curves of complexes made up to fall within the proper range at low temperatures; they were first cooled to about -8° and seeded with the compound

¹⁰ Hill and Miller, *THIS JOURNAL*, 49, 669 (1927).

$K_2CO_3 \cdot 6H_2O$ which can be secured only by undercooling potassium carbonate solution to below -20° .¹⁰ The temperature then rose nearly to -6.2° , indicating that the transition temperature of hydrated potassium carbonate is but slightly affected by the small amount of bicarbonate in the solution. On being subjected to the temperature of an ice-salt bath, the solution could be undercooled a few tenths of a degree but showed a long continued halt at -9.2° , this being taken as the decomposition temperature of the compound. Efforts to secure a halt in the warming curve were all fruitless, indicating that the formation of the compound is not a rapid reaction. Inasmuch as the ternary transition temperature could not be confirmed on rise of temperature, the best approximation is the temperature -9.2° , which is the highest temperature obtained on the cooling curve.

Composition of the Compound.—Early in the work it became apparent that the compound could not possibly have the composition assigned to it by Flückiger or by Bauer and Rammelsberg; the tie lines in the area for the compound showed at each temperature a much steeper inclination toward the base line of Fig. 1 than could be made to pass through the alleged composition of the salt. This indicated that the compound must contain either more potassium carbonate than assigned to it previously, or less water; a decision could not be arrived at through this means alone, for the extrapolation of lines so nearly parallel as are the tie lines in this narrow area would require an accuracy of analysis which is not attainable. Inspection of the original analytical data of the three authors mentioned showed that their agreement with the proposed formulas was really a fictitious one; arranged by them in terms of percentage of K_2O and CO_2 found, the agreement with the formulas did not look bad, but when recalculated to the ratio of K_2CO_3 to $KHCO_3$ the disagreement is startling. The results of the calculation are given in Table II, together with the critical analysis discussed later in this paper.

TABLE II
COMPOSITION OF DOUBLE SALT

		Ratio	$\frac{\text{Moles } K_2CO_3}{\text{Moles } KHCO_3}$	Proposed formula
Rammelsberg	1883	1.00:	2.57	$K_2CO_3 \cdot 2KHCO_3 \cdot 3H_2O$
Bauer	1883	1.00:	2.27	$K_2CO_3 \cdot 2KHCO_3 \cdot 3H_2O$
Flückiger	1883	1.00:	2.08	$K_2CO_3 \cdot 2KHCO_3 \cdot 5H_2O$
Hill	1930	1.00:	1.94	$K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$

Examination of these figures makes it problematical why Rammelsberg should assign the formula for a 1:2 ratio when the ratio found is less than 2:5. The results of Bauer and Flückiger, while nearer to the 1:2 ratio, are still distinctly high, and the water content given is very much higher in all three cases than I have found it to be. The explanation is not hard to give for all three cases; the solids used for analysis in every instance

must have contained as impurity solid KHCO_3 and solution, the latter tending to give a high value for water and (by its high K_2CO_3 content) tending also to give a high figure for K_2CO_3 and thus to counteract the effect of the first impurity. Since the ratios are nevertheless high in KHCO_3 content, the samples must have contained very large amounts of solid KHCO_3 .

Although the necessary conditions for obtaining a pure specimen of a salt showing incongruent solubility follow quite directly from phase-rule considerations, these conditions do not appear to have been stated often and have been observed still less often. A brief discussion of them is not out of place. The first necessary condition is that the compound be isolated after a complete phase-rule study at the temperature decided upon, to insure that it has been precipitated as the *one* solid phase in equilibrium with its saturated solution and not as one of the *two* phases precipitated from isothermally invariant mixtures, such as those covering the large areas BEF and GCF of Fig. 1. Second, comes the trying question of the mother liquor, which in all cases of incongruent solubility is different in composition from the salt and in this case is very widely different. Recrystallization from water is, of course, out of the question, since water brings about the decomposition of an incongruently soluble salt. Removal of as much mother liquor as possible, by mechanical means such as centrifuging, is highly desirable; but the essential point is that, inasmuch as mother liquor is necessarily present, its amount shall be definitely known, so that a correction of the final analysis may be made. The practice of allowing the moist crystals to undergo air-drying before analysis is entirely useless, except in so far as it reduces the water content to a closer approximation to the truth; the salt is then contaminated by the residuum from the evaporated mother liquor, the amount of that contamination being entirely unknown and not capable of being allowed for in the calculation. To determine the amount of such mother liquor, the well-separated crystals may be placed in a desiccator over the next lower hydrate and brought to constant weight; the loss of water corresponds to a definite precipitation of salts, known in amount and character from the analysis of the solution, which quantities may then be introduced into the subsequent analysis as a perfectly definite and reliable correction. Such a procedure will give material which may be analyzed with confidence as to its composition in respect to salts and also as to water of crystallization.

Preliminary examination by this method showed that the double salt of this discussion contained K_2CO_3 and KHCO_3 in ratio close to 1.00 to 2.00, and that the water content is between 7 and 8%. The water of crystallization, as reported by Rammelsberg, Bauer and Flückiger, is of the order of 15 to 20%, showing the presence of a very large amount of mother liquor in the moist crystals; such large amounts are inevitable if simple filtration is

used with so highly concentrated a solution as exists in this case. The clear deduction as to these three analyses is that those investigators analyzed very wet samples, and therefore found the apparent water of hydration much too high. This large amount of mother liquor would give the crystals a large excess of K_2CO_3 over the true ratio; to account for the fact that the analyses show, on the contrary, too much $KHCO_3$, we must believe that the systems, at the time the samples were taken, were represented by complexes within the isothermally invariant triangle FCG and that the solid was, therefore, a mixture of the double salt with excess $KHCO_3$. This accords wholly with Rammelsberg's and Bauer's method of preparation by partial decomposition of a solution saturated with $KHCO_3$.

For a final analysis, a large sample of double salt was prepared from a solution analyzing as containing 49.96% K_2CO_3 , 1.93% $KHCO_3$ and 48.11% H_2O , falling on the solubility curve for the double salt at 5° . The sample was centrifuged for two minutes at 4000 r. p. m., and brought to constant weight over double salt partially dehydrated by sulfuric acid. The water lost as water of solution for two samples was, respectively, 2.7 and 5.65% of the wet solid. Table III gives the results for the two samples.

TABLE III
ANALYSIS OF DOUBLE SALT

	Analysis of dried sample, %	Corrected, %	Molar ratio	2d cor- rection, %	Molar ratio	% Calcd. for $K_2CO_3 \cdot$ $2KHCO_3 \cdot 3/2H_2O$
Sample 1						
K_2CO_3	40.45	38.60	1.00	38.47	1.00	37.82
$KHCO_3$	51.21	53.41	1.91	54.13	1.94	54.78
H_2O	8.34	7.99	1.59	7.40	1.48	7.40
Sample 2						
K_2CO_3	42.21	38.99	1.00	38.60	1.00	37.82
$KHCO_3$	46.78	52.28	1.85	54.00	1.93	54.78
H_2O	11.01	8.73	1.71	7.40	1.47	7.40

In Col. 2 are given the results of the analyses of the samples as brought to constant weight. Column 3 gives the results corrected for the loss of 2.7 and 5.65% of water of solution from the wet samples. These corrected results show, by the molar ratio of Col. 4, that the two salts approximate a 1:2 ratio, and that the water of hydration is distinctly less than two moles. From this it may be assumed that the water of hydration is probably 1.5 moles, corresponding to that of the sesqui-hydrated potassium carbonate. On that basis a further correction may be made, namely, that the slight excess of water found (0.59 and 1.33%) represents mother liquor enclosed by the process of drying, and not given up during the drying periods, which were ten and thirty days, respectively. We can then determine algebraically the excess solution still present and correct for its presence, as in the former case. Correcting so as to bring the water content

down to the assumed value of 7.40%, we have the figures of Col. 5 and the molar ratio of Col. 6, which agree with the calculated values as closely as may be expected. The formula of the salt is thereby established as $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$, an addition compound of $K_2CO_3 \cdot 3/2H_2O$ and $KHCO_3$ without change in hydration.

Summary

1. Isotherms have been constructed for the ternary system K_2CO_3 - $KHCO_3$ - H_2O at 5, 25, 35 and 50°.

2. The double salt first observed by Berthollet has been found to have a stable existence in contact with solution from -9.2°, its lower transition temperature, to something above 50°, but always within a very narrow range of concentrations.

3. A critique is offered of the methods for preparing incongruently soluble double salts for analysis.

4. The formula of the double salt is found to be $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$.

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THE QUENCHING OF MERCURY RESONANCE RADIATION. I. THE SATURATED HYDROCARBONS

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The reactions of the saturated hydrocarbons under the influence of excited mercury atoms have been studied by Taylor and Hill,¹ who found that, with the exception of methane, they are all decomposed to give hydrogen, methane and high-boiling mixtures such as are obtained in the thermal "cracking" of hydrocarbons. This behavior, which is analogous to that observed in the presence of hydrogen atoms,² seemed worthy of further study to determine whether the inactivity of methane arose from its inability to receive the energy of the mercury atom or whether it was similar to the case of hydrogen and excited cadmium atoms,³ where the energy is transferred, but no reaction results.

Measurements have therefore been made of the quenching of mercury resonance radiation by the four hydrocarbons—methane, ethane, propane and butane—which make quite clear the reasons for the results obtained by Taylor and Hill and also furnish values for the collision radii for collisions of the second kind between excited mercury atoms and the hydro-

¹ Taylor and Hill, *THIS JOURNAL*, **51**, 2922 (1929).

² Bonhoeffer and Harteck, *Z. physik. Chem.*, **139**, 64 (1928).

³ Bates, *Proc. Nat. Acad. Sci.*, **14**, 849 (1928).