[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

TERNARY SYSTEMS. V. POTASSIUM BICARBONATE, POTASSIUM CARBONATE AND WATER

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As part of a complete investigation of the aqueous solutions of the carbonates and bicarbonates of sodium and potassium,[1] solubility measurements of the mixed potassium salts in water have been conducted in this Laboratory. Previous determinations appear to have been made in one instance only; Engel[2] has made measurements at 0°, but the solubility curve as drawn shows no break and gives no indication as to the solid phases present. We have, therefore, investigated the system at two temperatures, 25° and 36°, and determined the nature of the solid phases formed.

The two salts used were of Kahlbaum's preparation, marked "zur Analyse." Analyses after dehydration (the carbonate at 100° in an oven, and the bicarbonate at room temperature over sulfuric acid in an atmosphere of carbon dioxide) established the purity of both within a few hundredths of one per cent. For the solubility experiments, weighed quantities of the two salts were introduced into glass-stoppered tubes with measured quantities of water, and turned in a thermostat for several hours. Samples of the saturated solutions were then withdrawn by a volumetric pipet, weighed in order to afford a rough measurement of density, and analyzed; the total alkali was determined by titration with standard hydrochloric acid, using methyl orange as indicator, and the carbon dioxide determined by absorption in soda lime in a Fleming bottle. The solid phases were analyzed after filtration in a few instances, but in the majority of cases that procedure was omitted, as the line drawn on triangular coördinates through the composition of the original complex and that of the saturated solution gave the composition of the solid phase without possibility of misinterpretation. The results are given in Table I. The percentage of water may be obtained by subtracting the sum of the two salts from 100.

As has been shown by Dibbits,[3] the carbon dioxide pressure of saturated solutions of the bicarbonate is very high. In transferring the sample of such solutions for analysis there is, therefore, a loss of weight. However, as the total alkali was obtained by titration and calculated as bicarbonate, this error is reduced to about one-fourth when the result is expressed in percentage of bicarbonate, and is probably of small magni-

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[1] See Hill and Miller, THIS JOURNAL, 49, 669 (1927).

[2] Engel, *Ann. chim. phys.*, [6] 13, 348 (1888).

[3] Taken from Dibbits, *J. prakt. Chem.*, [2] 10, 417 (1874).

TABLE I

K_2CO_3, $KHCO_3$ AND H_2O

Saturated solution			Original complex		
$KHCO_3$, %	K_2CO_3, %	Density	$KHCO_3$, %	K_2CO_3, %	Solid phases
25° Isotherm					
26.55	0.00	1.180	..	..	$KHCO_3$
19.31	10.00	1.228	28.0	9.0	$KHCO_3$
15.45	16.98	1.272	25.0	15.0	$KHCO_3$
12.19	23.36	1.316	25.0	20.0	$KHCO_3$
7.35	34.71	1.402	20.0	30.0	$KHCO_3$
4.44	43.89	1.484	17.0	38.0	$KHCO_3$
2.21	51.79	1.558	15.0	50.0	$KHCO_3 + K_2CO_3.{}^3/_2H_2O$
0.00	52.74	1.555	..	..	$K_2CO_3.{}^3/_2H_2O$
36° Isotherm					
29.9[3]	0.00	...	..	..	$KHCO_3$
14.83	22.92	1.325	25.0	20.0	$KHCO_3$
7.86	37.57	1.437	19.0	33.0	$KHCO_3$
3.88	51.44	1.565	7.0	53.0	$KHCO_3 + K_2CO_3.{}^3/_2H_2O$
0.00	53.66	1.557	..	..	$K_2CO_3.{}^3/_2H_2O$

tude. This source of error, however, affects only the solubility results for the pure bicarbonate; upon the addition to the solution of any appreciable amount of carbonate, the pressure becomes too small to be observed as loss of weight, and the results in the ternary system may be looked upon as free from that error.

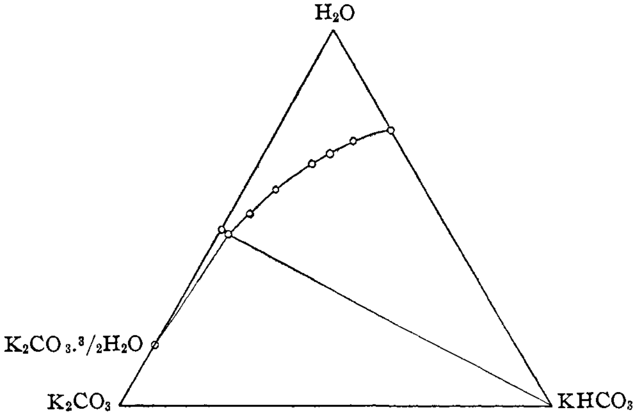

Fig. 1.

The isotherms are shown in Fig. 1, which represents either temperature rather closely, as the solubilities do not differ greatly and the solid phases do not differ at all. It will be seen that there is no evidence of compound formation or of solid solution at these temperatures; the two solids are, respectively, the anhydrous bicarbonate and the sesquihydrated carbonate,[1] $K_2CO_3 . {}^3/_2H_2O$. The isothermally invariant point is close to the K_2CO_3-H_2O

axis at both temperatures; that is, the normal carbonate cannot be precipitated from solutions containing more than a very few per cent. of the bicarbonate. However, the point moves with increasing temperature toward the $KHCO_3$-H_2O axis, which follows from the fact that the solubility of the bicarbonate increases with temperature rise more rapidly than that of the normal carbonate.

Summary

1. Solubility measurements of systems consisting of potassium bicarbonate, potassium carbonate and water have been made at 25° and at 36°.
2. The only solid phases found in equilibrium with saturated solution at these temperatures are the anhydrous bicarbonate and the sesquihydrated carbonate.
3. Solutions at these two temperatures will not precipitate the normal carbonate if the saturated solution contains more than 2.21 and 3.88%, respectively, of the bicarbonate.

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STRUCTURE OF A PROTECTIVE COATING OF IRON OXIDES

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Introduction

In 1877, F. S. Barff[1] described a process by which a smooth, adherent rust- and wear-resisting coat of iron oxide or oxides was produced on the surface of iron objects. A few years later the process was improved and developed by G. Bower,[2] and since that time many modifications have been proposed. In preparing the sample used in this investigation, the iron was heated to 730° in an air-tight furnace and brought into contact with steam for about an hour, cooled slightly in the air, reheated to 715° with steam again for another hour and cooled in the air. This method produced a coating 0.1 to 0.3 mm. thick. Chemical analysis of this coating cannot determine definitely the amount of any phase because it cannot determine what phases exist. The x-ray analysis described below, however, cannot only distinguish between the three oxides and give a means for estimating roughly the amounts of each present, but can also determine the position of any phase relative to the other phases

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[1] Barff, *J. Soc. Arts*, **25**, 254 (1877); **27**, 390 (1879).

[2] Bower, *Trans. Soc. Eng.*, **23**, 59 (1883). Thwarte, *Proc. Inst. Civil Eng.*, **74**, 215 (1883). For a description of the original method and its many modifications see Pollitt, "The Causes and Prevention of Corrosion," D. Van Nostrand Co., New York, **1924**, p. 136.