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A STUDY OF THE SYSTEM SODIUM BICARBONATE–POTASSIUM BICARBONATE–WATER

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I. Introduction and Survey of Previous Work

Although studies have been made of the systems sodium bicarbonate–ammonium bicarbonate–water,[1] of sodium bicarbonate–sodium carbonate–water,[2] of potassium carbonate–sodium carbonate–water, including a very thorough investigation of the solid phases,[3] and of potassium bicarbonate–potassium carbonate–water,[4] no real investigation of the system sodium bicarbonate–potassium bicarbonate–water has been found in the literature.

The writer first became interested in this system during 1920, when it was suggested by Mr. W. D. Mount, Consulting Engineer of Lynchburg, Virginia, that he determine the practicability of developing commercially a process of obtaining soda ash as a by-product in the purification of potassium salts from Nebraska brines. A search of the literature at that time failed to disclose any study of the system sodium bicarbonate–potassium bicarbonate–water but the relative solubilities of sodium carbonate, potassium carbonate, sodium bicarbonate and potassium bicarbonate indicated that carbonating a saturated brine to convert the carbonates to bicarbonates, thereby precipitating the less soluble sodium bicarbonate, and then fractionally crystallizing the salts in solution, might offer a practical means of separating the salts commercially.

Dibbits has shown that solutions of sodium bicarbonate and of potassium bicarbonate lose appreciable quantities of carbon dioxide at even comparatively low temperatures, and that definite solubilities of the bicarbonates will only be found with definite partial pressures of carbon dioxide.[1,2,5] Since many investigators failed to consider loss of carbon dioxide from bicarbonate solutions, the solubility data given in the literature for pure $NaHCO_3$ and $KHCO_3$ are not always consistent. Of the references given, Fedotieff,[1] McCoy and Test,[2] Hill and Hill[4] and Dibbits[5] have taken into consideration the loss of carbon dioxide.

Since definite solubilities of the bicarbonates will be obtained only with

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[1] Fedotieff, *Z. physik. Chem.*, **49**, 162 (1904).

[2] McCoy and Test, THIS JOURNAL, **33**, 476 (1911).

[3] Hill and Miller, *ibid.*, **49**, 669 (1927).

[4] Engel, *Ann. chim. phys.*, [6] **13**, 366–369 (1888); Hill and Hill, THIS JOURNAL, **49**, 967 (1927).

[5] Dibbits, *J. prakt. Chem.*, [2] **10**, 417 (1874); Bodländer, *Z. physik. Chem.*, **35**, 32 (1900).

a definite partial pressure of carbon dioxide, and since practical application of the present study to the separation of sodium and potassium carbonates would be by passing a stream of carbon dioxide through the carbonates, it was decided to study the system $NaHCO_3$–$KHCO_3$–H_2O under the fixed condition that the partial pressure of carbon dioxide plus the partial pressure of water is equal to one atmosphere in the same way that Fedotieff[1] studied $NaHCO_3$–NH_4HCO_3–H_2O.

II. Theoretical Considerations

Since the restriction has been made that the partial pressure of carbon dioxide plus the partial pressure of water is equal to one atmosphere, carbon dioxide is not a component in the system. The components, therefore, can be considered as sodium bicarbonate, potassium bicarbonate and water. In the presence of one vapor and one liquid phase, three solid phases are required to make the system invariant. In the experimental work it has been found that at 20, 25 and 30° neither sodium bicarbonate nor potassium bicarbonate exists as a hydrate. Also, it has been found that at these temperatures solid solutions and double salts do not exist in equilibrium with solutions of any concentrations. Since only two solid phases have been found to separate from the solutions at these three temperatures, a quintuple point does not exist between the temperatures taken and the system cannot, therefore, become invariant between these temperatures. If the temperature is held constant, the system is fixed when the two phases sodium bicarbonate and potassium bicarbonate are present.

III. Apparatus and Procedure

The thermostat used was provided with a special shaker. The thermometer was graduated in tenths of a degree and was calibrated by the Bureau of Standards. Ordinary 300-cc. Erlenmeyer flasks were used to hold the solution and solids which were to be brought to equilibrium. These flasks were closed with two-holed rubber stoppers. A glass tube passed through one hole of the rubber stopper to well down into the solution in the flask, and when the flask was placed on the shaker in the thermostat, this glass tube was connected to a combination trap and carbon dioxide distributor by means of a light rubber tube. For the greater part of the run this glass dip-tube was raised above the solution. A second glass tube, about three inches in length, was placed in the second hole of the rubber stopper, flush with the bottom of the stopper and extending about two inches above the top of the stopper to prevent the possible entry of water from the thermostat. The combination trap and carbon dioxide distributor was connected to a cylinder of compressed carbon dioxide by means of a rubber tube.

In the earlier runs at 25° carbon dioxide was allowed to bubble through the solution for a considerable part of the run while the temperature was maintained at about 0.1° above the desired equilibrium temperature. It was later found that all the points determined with this procedure gave low solubility values, due to the temperature depression caused by bubbling carbon dioxide through the solution. It was also found, however, that unless carbon dioxide was bubbled through the solution for an appreciable time, considerable time would be required to convert the small amount of carbonate present to bicarbonate. The final procedure was to bubble carbon dioxide through the solutions for from two to four hours prior to starting the accurate temperature control, while holding the temperature 0.5 to 1° above the desired equilibrium temperature. In order to determine whether or not carbonates had been removed from the solutions, a small portion of the solution was, in some cases, removed from the flask and tested with phenolphthalein, which reacts approximately neutral to bicarbonate solution. The dip-tubes extending into the solution were then raised above the surface of the liquid, the carbon dioxide outlets on the Erlenmeyer flasks were capped and a slow stream of carbon dioxide was allowed to escape through a vent attached to the rubber tube leading to one of the Erlenmeyer flasks. By this method a pressure of carbon dioxide equal to the atmospheric pressure was maintained within the flasks, but carbon dioxide was not allowed to pass freely over the solution so as to cause a temperature depression. When the dip-tubes had been raised and the outlets capped, the temperature was adjusted to the equilibrium temperature and shaking continued to the first sampling period.

After the samples were taken, the air that had entered the Erlenmeyer flasks was displaced with carbon dioxide, the carbon dioxide outlets were again capped and carbon dioxide again was allowed to escape from the vent until the next sampling period.

For analysis of the solution and identification of the solid phases, the following determinations were in general made: (1) determination of the density of the solution at the equilibrium temperature by means of a pycnometer which had been standardized with distilled water at the equilibrium temperature; (2) determination of the total alkali in the solution by the titration of a 10-cc. sample with approximately normal hydrochloric acid, using methyl orange as an indicator; (3) determination of potassium present in the solution by means of the perchloric acid method; (4) determination of the total alkali bicarbonate in the solid phase which had been quickly washed and sucked fairly dry in a Büchner filter and then dried between folds of filter paper, or which had been whizzed until dry in a basket-type centrifuge; (5) determination of the ratio of sodium bicarbonate to potassium bicarbonate in the solid phase by heating the washed solid to a constant weight as carbonates and determining potassium by the perchloric acid method.

Due to the fact that the work had to be carried out in an atmosphere of carbon dioxide, an effort was made to shorten the runs as much as possible. Actually, much time was lost by trying to obtain consistent values after very short times (three or four hours) in the thermostat. Although the titration checks were fairly close (0.1 cc.) for an interval of about one hour, it was found that still better checks could be obtained. It would appear that the final rate at which equilibrium is obtained in the apparatus used is fairly slow, although equilibrium is approached very closely within a comparatively short time. Slight but consistent variations in the analyses established the greater certainty of the values obtained in longer runs. Equilibrium was considered to have been established when titrations separated by a two- or three-hour interval checked within 0.05 cc.

All pipets used in sampling were calibrated for delivery at each equilibrium temperature and the proper corrections for this delivery were made in the calculations.

IV. Materials

Merck's C. P. sodium bicarbonate was purified by dissolving in warm distilled water and recrystallizing with a stream of carbon dioxide passing through the solution.

The potassium bicarbonate employed was also a Merck product and was labeled "U. S. P. IX—Highest Purity—C. P." Before use it was dissolved in warm water and recrystallized with a stream of carbon dioxide passing through the solution.

V. Probable Errors in the Procedure

The temperature was maintained constant to 0.01° at 19.97°, to 0.03° at 25° and to 0.04° at 30.01°. The maximum variation at 30° would affect the solubility of pure sodium bicarbonate, or of pure potassium bicarbonate, by about 1 part in 2000 and is therefore negligible.

In the analysis of the samples taken there was in no case a difference of over 0.1 cc. between check titrations. For most of the points at 19.97° and at 30.01°, the difference did not exceed 0.05 cc. In many cases the difference was not over 0.03 cc. Check potassium determinations did not differ more than 1 part in 350, except in one or two cases. Potassium checks of 1 in 1000 were not unusual and for most of the points variations not to exceed 1 part in 700 can be assumed.

The density determination was one of the most consistently reproducible determinations made. It is true that solutions of the bicarbonates tend to lose carbon dioxide, but the transfer to the pycnometer could be made quickly and the pycnometer sealed. The pycnometer was always brought to within 0.2° of the equilibrium temperature before being filled. The density determinations invariably checked in the third decimal place, while checks of 3 in the fourth decimal place were not unusual.

All of the above errors may, of course, be slightly increased by errors in taking the samples. Care was exercised, however, in keeping the pipets clean and in sampling, so that such errors were reduced to a minimum. It must be admitted that any difference method of analysis in which the combined errors may possibly all be thrown on that material present in the smallest percentage may result in comparatively large errors in the values found for the latter material. However, such a difference method of analysis is more accurate than the indirect determination of sodium and potassium bicarbonates by titrating, weighing as carbonates and solving a simultaneous equation for the quantities of sodium and potassium bicarbonates present. With the balance and compensation of errors that is obtained by plotting a curve from the data obtained, values read from the curve should be considerably more accurate than the maximum probable error for a single point.

At 25° the determinations of potassium by the perchloric acid method were made according to the procedure recommended by Scott,[6] with one exception. The procedure of Smith[7] was followed in all determinations at 19.97 and at 30.01°. In one case at 25° the two methods were run in

[6] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, **1920.**

[7] Smith, THIS JOURNAL, **47,** 780 (1925).

parallel. A weight of 2.0771 g. of $KClO_4$ was obtained by the method of Scott and a weight of 2.0742 g. by the method of Smith. This is a variation of about 1 in 700, with the method of Smith giving a slightly lower value. In general, the procedure of Scott gave as good checks as the procedure of Smith, but the latter is decidedly smoother from the standpoint of manipulation and probably gives more accurate results, as claimed by Smith.

VI. Experimental Details and Tabulation of Results

A. Study of the System at a Temperature of 19.97 ± 0.01°.—The work at approximately 20° was carried out after the procedure at 25° had been well developed and checked. For some reason solutions at 19.97°, fairly high in potassium, gave in two successive runs points which did not fit all of the curves, the deviations being comparatively large in some cases. The slowness with which equilibrium appeared to be reached suggested the possibility of solid solutions.

Analyses of the solid phases from runs which were continued considerably longer than usual established definitely that no solid solution or double salt existed along that portion of the curve where erratic results were obtained in the shorter runs. The longer runs with concentrations lying

TABLE I

DATA OBTAINED (EXCLUDING THE ERRATIC VALUES IN TWO RUNS)

No.	Density	G. per 100 g. of H_2O $NaHCO_3$	G. per 100 g. of H_2O $KHCO_3$	G. per 100 g. of soln. $NaHCO_3$	G. per 100 g. of soln. $KHCO_3$	Solid phases
1	1.0625	9.55	0.00	8.72	0.00	$NaHCO_3$
2	1.0954	8.15	7.46	7.05	6.45	$NaHCO_3$
3	1.1309	7.03	15.60	5.73	12.72	$NaHCO_3$
4	1.1519	6.55	20.52	5.16	16.15	$NaHCO_3$[a]
5	1.1637	6.33	23.31	4.88	17.98	$NaHCO_3$[a]
6	1.1803	6.11	27.34	4.58	20.48	$NaHCO_3$[a]
7	1.1968	6.07	31.54	4.41	22.93	$NaHCO_3$–$KHCO_3$
8	1.1965	5.97	31.36	4.34	22.84	$NaHCO_3$–$KHCO_3$[b]
9	1.1897	3.85	32.05	2.84	23.58	$KHCO_3$
10	1.1830	1.86	32.74	1.38	24.32	$KHCO_3$
11	1.1777	0.00	33.30	0.00	24.98	$KHCO_3$[a]

[a] The solid phase was identified by analysis for all points except 11. Since hydrates of $KHCO_3$ had been found not to exist at Points 7, 8, 9 and 10, analysis of the solid at Point 11, other than a microscopic examination, was not considered necessary. Results of solid phase analyses are given for Points 4, 5 and 6, since it was in this area that solid solutions were suspected. A 0.6647-g. sample of solid from 4 that had been quickly washed and sucked fairly dry in a Büchner filter did not give a weighable quantity of $KClO_4$. Solid phases centrifuged but not washed from 5 and 6 gave the following analyses: 5, $NaHCO_3$, 99.25%; $KHCO_3$, 0.75%; 6, $NaHCO_3$, 98.99%; $KHCO_3$, 1.01%. In the solid phase from both 5 and 6 a few minute crystals of $KHCO_3$ that formed during centrifuging could be identified with the microscope.

[b] With the aid of a reading glass and a small pair of tweezers a mechanical separation of the two solid phases was made. One analyzed 95.89% $KHCO_3$ and the other 94.80% $NaHCO_3$.

along the curve where erratic results had been previously obtained gave values which fitted closely into a smooth curve with the other points. No explanation can be offered for the comparative slowness with which equilibrium was reached.

B. Study of the System at a Temperature of 25 ± 0.03°.—The work at 25° was carried out first and it was during these runs that the technique was improved. While the values obtained at 25° are hardly, as a whole, as accurate as the values obtained on the 19.97° curves, and on the 30.01° curves, nevertheless, a very accurate check was made of the solubility of the pure sodium and potassium bicarbonates and of the solution composition at the break in the curve where both sodium and potassium bicarbonates are present as solid phases. Also, in plotting the values on the curve slightly greater weight was given to the later results.

TABLE II

DATA OBTAINED AT 25 ± 0.03°

No.	Density	G. per 100 g. of H_2O $NaHCO_3$	G. per 100 g. of H_2O $KHCO_3$	G. per 100 g. of soln. $NaHCO_3$	G. per 100 g. of soln. $KHCO_3$	Solid phases
1	1.0648	10.31	0.00	9.34	0.00	$NaHCO_3$
2	1.0857	9.36	4.82	8.20	4.23	$NaHCO_3$
3	1.1035	8.72	8.98	7.41	7.63	$NaHCO_3$
4	1.1282	7.83	14.85	6.38	12.10	$NaHCO_3$
5	1.1547	7.21	21.12	5.62	16.46	$NaHCO_3$
6	1.1746	6.88	26.03	5.18	19.59	$NaHCO_3$
7	1.1732	6.81	25.69	5.14	19.39	$NaHCO_3$
8	1.1903	6.76	29.92	4.94	21.89	$NaHCO_3$
9	1.2087	6.58	34.59	4.66	24.50	$NaHCO_3$–$KHCO_3$[a]
10	1.2087	6.50	34.42	4.61	24.43	$NaHCO_3$–$KHCO_3$[b]
11	1.2042	5.24	34.95	3.74	24.93	$KHCO_3$
12	1.1998	3.77	35.08	2.72	25.27	$KHCO_3$
13	1.1977	3.32	35.48	2.39	25.56	$KHCO_3$
14	1.1927	1.55	35.93	1.12	26.13	$KHCO_3$
15	1.1884	0.00	36.57	0.00	26.78	$KHCO_3$
16	1.1882	0.00	36.56	0.00	26.77	$KHCO_3$[a]
17	1.1879	0.00	36.58	0.00	26.78	$KHCO_3$[a]

[a] The solid phases were not analyzed in these runs, since they were all check runs and the solid phases were identified by the other runs at these same points. Runs 16 and 17 were made because it was realized that 15 did not check the values given in the literature to within the experimental errors.

[b] A rough mechanical separation of the two solid phases was made. One part analyzed 93.63% $NaHCO_3$ and 6.37% $KHCO_3$; the other, 95.86% $KHCO_3$ and 4.14% $NaHCO_3$.

C. Study of the System at a Temperature of 30.01 ± 0.04°.—Due to the impossibility of keeping the room temperature within over 4 to 7° of the bath temperature, there was a tendency for crystals to separate out in the pipets. It was found advisable to warm the pipets slightly and then bring them to approximately the solution temperature by sucking up some of the solution, discarding it and then taking the sample. This same procedure was used in calibrating the pipets. This procedure in sampling is considered rapid and satisfactory.

All except two points on the curves were determined after the desirability of long runs was established, and from this standpoint the values for 30.01 ± 0.04° may be slightly superior to those on the 25° curves and some points on the 19.97° curves.

Table III

Data Obtained

No.	Density	G. per 100 g. of H_2O		G. per 100 g. of soln.		Solid phases
		$NaHCO_3$	$KHCO_3$	$NaHCO_3$	$KHCO_3$	
1	1.0673	11.05	0.00	9.95	0.00	$NaHCO_3$
2	1.0973	9.61	7.22	8.22	6.18	$NaHCO_3$
3	1.1196	8.90	12.39	7.34	10.22	$NaHCO_3$
4	1.1543	8.02	20.69	6.23	16.08	$NaHCO_3$
5	1.1887	7.48	29.26	5.47	21.40	$NaHCO_3$
6	1.2189	7.01	37.61	4.85	26.01	$NaHCO_3$–$KHCO_3$[a]
7	1.2189	6.97	37.64	4.82	26.03	$NaHCO_3$–$KHCO_3$[b]
8	1.2145	5.13	38.22	3.58	26.66	$KHCO_3$
9	1.2077	2.92	38.90	2.06	27.43	$KHCO_3$
10	1.1986	0.00	39.91	0.00	28.52	$KHCO_3$
11	1.1988	0.00	39.95	0.00	28.52	$KHCO_3$[a]
12	1.1990	0.00	39.92	0.00	28.53	$KHCO_3$[a]

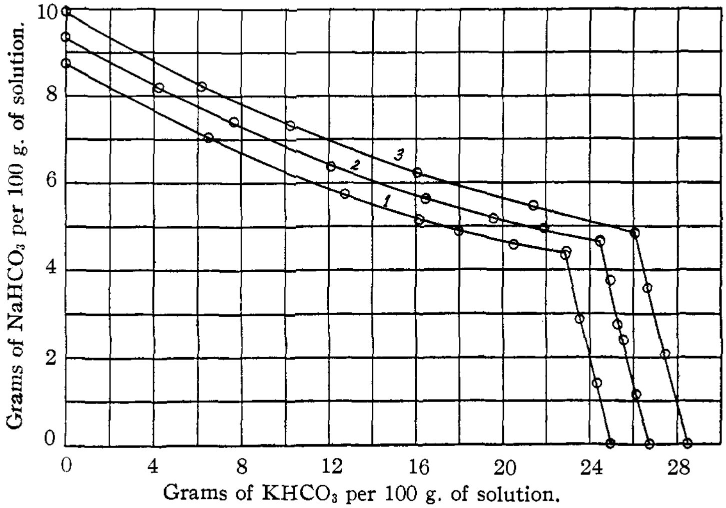
[a] Analysis of the solid phase was not made since these were check runs. Runs 11 and 12 were made after it was realized that the values found in 10 did not check to values found in the literature to within the experimental errors.

[b] A rough mechanical separation of the two solid phases was made. One gave an analysis of 91.74% $NaHCO_3$ and 8.26% $KHCO_3$. The other gave an analysis of 92.55% $KHCO_3$ and 7.45% $NaHCO_3$.

VII. Graphical Representation of Results

The triangular coördinate method of graphically representing results for ternary systems is particularly well adapted to those systems which show more than two solubility curves. Also, in general, lines drawn through the composition of the solution and the composition of the original complex can be made to give very definite indications of the composition of the solid phase.

In the present study an accurate knowledge of the exact composition of the original complex was somewhat difficult to obtain, (1) because the two salts used have a decided tendency to lose carbon dioxide and often contain appreciable quantities of carbonate, and (2) because bubbling carbon dioxide through the solution removed some water. In view of these facts, and the fact that there appeared to be only two solubility curves in the system at the temperatures chosen, it was felt that it would be more advisable to plot the weight of sodium bicarbonate against the weight of potassium bicarbonate while holding the weight of water or weight of solution constant. Curves constructed in this way can be plotted on a scale that makes them suitable for reading off interpolated values.

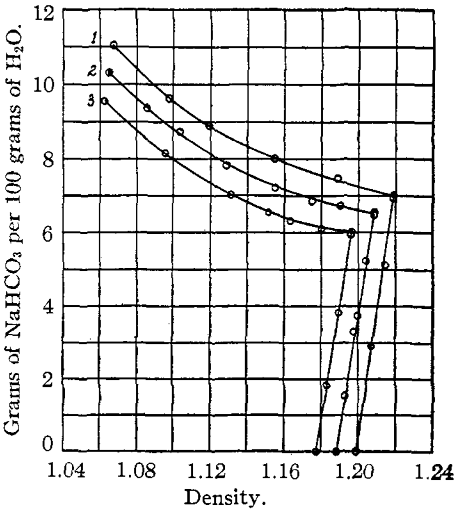


1, 19.97 ± 0.01°C.; 2, 25 ± 0.03°C.; 3, 30.01 ± 0.04°C.

Fig. 1.

Figures 1 and 2 are shown as illustrations of the curves plotted. Figure 1 shows the weight in grams of $NaHCO_3$ per 100 g. of solution plotted against the weight in grams of $KHCO_3$ per 100 g. of solution. Figure 2 shows the weight in grams of $NaHCO_3$ per 100 g. of water plotted against the density of the solution.

Various other smooth curves were plotted from the data obtained but are not considered worth reproducing as they can be readily made up from the tables. It may be of interest to note that when the grams of $KHCO_3$ per 100 g. of water are plotted against the density of the solution, points for the three temperatures all fall on approximately the same curve so long as $NaHCO_3$ is the solid phase.



1, 19.97 ± 0.01°C.; 2, 25 ± 0.03°C.; 3, 30.01 ± 0.04°C.

Fig. 2.

VIII. Comparison of Solubilities Found for Sodium Bicarbonate and Potassium Bicarbonate with Those Given in the Literature

The values found for the solubilities in water of pure sodium bicarbonate and pure potassium bicarbonate may be compared with values previously reported by other investigators, to whose work references have already been made.

TABLE IV

SODIUM BICARBONATE SOLUBILITY IN GRAMS PER 100 GRAMS OF WATER

	20°	25°	30°
Dibbits	9.6	10.35	11.1
Fedotieff	..	...	11.02
Tables I, II, III	9.55	10.31	11.05

McCoy and Test report 98.7 g. per liter for the solubility of sodium bicarbonate at 25°. The values given in Table II are equivalent to 99.4 g. per liter.

On the whole the values found check the better values given in the literature very closely. This is particularly true for values given by Fedotieff for 30°. Fedotieff did his work with the partial pressure of carbon dioxide plus the partial pressure of water vapor equal to the atmospheric pressure, and the values found in the two cases should check very closely.

TABLE V

POTASSIUM BICARBONATE—SOLUBILITY IN GRAMS PER 100 GRAMS OF WATER

	20°	25°	30°
Dibbits	33.2	36.1	39.0
Tables I, II, III	33.3	36.57	39.92

Hill and Hill find the solubility of potassium bicarbonate at 25° to be 26.55 g. per 100 g. of saturated solution, while the solubility given in Table II is 26.78 g. per 100 g. of saturated solution.

It is evident that the values found for the solubility of potassium bicarbonate are higher than the values given in the literature. However the results found, particularly those for 25 ± 0.03° and for 30.01 ± 0.04°, have been thoroughly checked and it has been found that they can be consistently duplicated with carefully calibrated volumetric apparatus, acid standardized at different times and chemicals crystallized separately from different packages. The values reported are consistently reproducible and, therefore, are offered as correct for the conditions under which the study was made.

A study of the work of Dibbits indicates that he made every effort to secure accuracy. Certain criticisms of his technique, however, may be made. Most important of these criticisms is the fact that he used a water-bath for temperature control and states, that, to avoid supersaturation, care was taken that the temperature should rise somewhat rather than drop. This procedure would certainly tend to give low results. According to Dibbits, loss of carbon dioxide at 30° might make a difference of about 0.3 in the values found. Such a difference would not account for the 0.92 variation between the value of Dibbits and that given in Table III. However, Dibbits' calculations of the extent to which loss of carbon dioxide might change the results probably did not represent equilibrium, and, therefore, may have indicated a smaller variation than would have been found at equilibrium.

The value obtained by Hill and Hill for the solubility of potassium bicarbonate at 25° is in good agreement with that of Dibbits, the value of Hill and Hill being equivalent to 36.15 g. per 100 g. of water. The value given in Table II, solubility of potassium bicarbonate in grams per 100 g. of solution, is 0.23 higher than the value of Hill and Hill. Such a variation is well outside of the experimental errors of the work recorded in this paper and, therefore, is significant. That the results found for sodium bicarbonate check the better values in the literature, while the results found for potassium bicarbonate are higher than the better values in the literature, is in agreement with the observation of Dibbits that the partial pressure of carbon dioxide is considerably higher over solutions of potassium bicarbonate than over solutions of sodium bicarbonate.

From the above comparison of results with the results of other investigators, it is indicated that the partial pressure of carbon dioxide over saturated solutions of potassium bicarbonate slightly exceeds the partial pressure of carbon dioxide maintained in the flasks during the experiments. Under such conditions, there would be present in the solutions a small amount of potassium carbonate. The carbonate content was not, however, sufficient to cause the solutions to react alkaline to phenolphthalein.

Even if the solubilities for potassium bicarbonate found in this study are higher than the results in the literature, because of the presence of a small amount of potassium carbonate, the results may be accepted as those that would be obtained when mixed solutions of the carbonates of sodium and potassium are treated at atmospheric pressure with a stream of carbon dioxide gas so as to convert the carbonates to bicarbonates and thereby effect a partial separation by precipitating one of the pure bicarbonates (usually sodium bicarbonate).

IX. Summary

1. The ternary system $NaHCO_3$–$KHCO_3$–H_2O has been studied at temperatures of 19.97 ± 0.01, 25 ± 0.03 and 30.01 ± 0.04° under the fixed condition that the sum of the partial pressures of carbon dioxide and of water vapor is equal to the atmospheric pressure.

2. The only solid phases that exist at these temperatures are $NaHCO_3$ and $KHCO_3$. The absence of hydrates, of solid solutions and of double salts at these temperatures has been definitely established.

3. The values found for the solubility of sodium bicarbonate check very closely the best values given in the literature.
4. The values found for the solubility of potassium bicarbonate, especially at 25 and at 30°, are higher than the best values found in the literature.
5. The composition of the solutions found in the ternary system, and the absence of complicating double salts and solid solutions, indicate that the present study might be of value in the commercial separation of sodium and potassium carbonates.

University, Virginia

[Contribution from the Physikalisches Institut, Leipzig, and the Department of Chemistry, Duke University]

THE DETERMINATION OF THE SOLUBILITY OF SLIGHTLY SOLUBLE LIQUIDS IN WATER AND THE SOLUBILITIES OF THE DICHLORO-ETHANES AND -PROPANES

By Paul Gross

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In order to make some measurements of the salting out effect of salts in water on the slightly soluble dichloro-ethanes and propanes, it became necessary to develop a method for determining their solubility in water and salt solutions. As this method is capable of considerable precision and as Hill[1] has pointed out that the methods for determining the solubility of liquids in liquids are in general very unsatisfactory, it is described here, together with the results of some solubility determinations made by its use.

The principle of the method is to prepare saturated solutions of the substance in water by shaking in a thermostat in the usual way. These solutions are then analyzed by the use of a liquid interferometer. The interferometer scale is calibrated by dissolving weighed amounts of the substance in weighed quantities of water.

Experimental

The instrument available was a Zeiss portable water interferometer with a glass comparison chamber 40 mm. in length with two cells, in one of which a sample of the solution to be analyzed was placed and in the other the comparison or reference liquid. The general procedure and precautions to be observed in the use of the interferometer have been described in a number of places,[2] so it is unnecessary to repeat them here.

The scale readings on the compensator drum of the interferometer are not directly proportional to the number of interference bands it is necessary to shift to return the displaced upper bands to zero setting. The relation of bands shifted to scale divisions for different parts of the range of the instrument (which has a total of 3000 scale di-

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[1] Hill, This Journal, **45**, 1143 (1923).

[2] See, for example, L. H. Adams, *ibid.*, **37**, 1181 (1915).