structures, the lead and low-temperature thallium types, respectively. This can be seen to agree fairly well with the phase diagram reproduced in Fig. 1.

The atomic spacing in the alloys having the lead structure varies with the composition, being decreased by the addition of thallium nearly linearly up to 80% of thallium, which is about the limit of its solubility.

## Summary

Powder photographs of the system lead-thallium have been taken at room temperature. These give no evidence whatever of the existence of a compound $PbTl_2$, but agree with the assumption that at this temperature two solid solutions exist, one having the low-temperature structure of thallium and the other the structure of lead.

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# TERNARY SYSTEMS. IV. POTASSIUM CARBONATE, SODIUM CARBONATE AND WATER

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## Introduction

Aqueous solutions of sodium and potassium carbonate have naturally received attention over a considerable period of time, and the composition of solid phases obtained at room temperature has been frequently the subject of discussion. The greater part of such work was done prior to the enunciation of the phase rule or, when later, without its use; as a consequence the evidence assembled is contradictory and unconvincing. Mellor[1] cites a large number of papers on the topic in which claims are made that the solid phase obtained from mixed solutions of the two carbonates is a solid solution or that it is a hydrated double salt, for which varying formulas are proposed; the one point of general agreement is that the solid obtained at room temperatures is hydrated and that it is intermediate in composition between the two carbonates. Two investigations have been made according to phase-rule methods, but in both cases, as will be shown, with erroneous result; Kremann and Zitek[2] show on the basis of analysis that the solid phase at 24.8° is a compound of the formula $K_2CO_3.Na_2CO_3.12H_2O$,[3] and Osaka,[4] working at 25°, decides that the solid is without doubt

[1] Mellor, "Comprehensive Treatise," Longmans, Green and Co., London, **1922**, vol. 2, p. 768.

[2] Kremann and Zitek, *Monatsh.*, **30**, 323 (1909).

[3] The formula given is $K_2CO_3.Na_2CO_3.6H_2O$, but the analysis indicates that it is a typographical error for $K_2CO_3.Na_2CO_3.12H_2O$.

[4] Osaka, *Mem. Coll. Sci. Eng. Kyoto*, **3**, 51 (1911).

of the formula given, on the basis of extrapolation of tie-lines to a supposed intersection; as a matter of fact, Osaka's tie-lines do not intersect at any one point, and there is every evidence in his experiments that the systems were not at equilibrium.

The clarification of these contradictory results having been suggested by the National Research Council,[5] we have studied the system at six temperatures between 20° and 50°, and have attempted to obtain evidence that should not be open to question. As will appear in the body of the paper, it is established that at no temperature within these limits is a hydrated double carbonate formed, but that the material which was obtained by practically all investigators is a hydrated *solid solution*, the composition of which can vary over a considerable range. At temperatures above 25° and within limited concentrations there is formed a completely anhydrous compound of the formula $K_2CO_3.Na_2CO_3$. The composition of the hydrates of potassium carbonate has also been studied.

## Experimental Methods

The carbonates used were Kahlbaum's preparations "zur Analyse," which after drying were found to be entirely pure. To insure complete dryness the materials were kept continuously in an electric oven at 105°. For each experiment the dry carbonates in selected quantity were weighed into glass-stoppered, 50cc. Pyrex test-tubes, and the water was measured volumetrically; total weights of 33 to 50 g. were used, and the quantities, expressed in percentages, are recorded under the heading "original complex" in each of the succeeding tables. Because of the slowness with which equilibrium is reached in all cases in which the solid solution is formed, it was found advisable to add the sodium carbonate to the water first and to stir (taking advantage of the heat of hydration) until the solid was completely dissolved; the potassium carbonate was then added and the samples were stirred while quite hot. An excess of the latter salt is much more quickly converted to the equilibrium solid than is the sodium carbonate which, if left in excess, may delay the attaining of equilibrium very greatly. In only a few cases was it impossible, on account of the solubility relations, to dissolve the sodium salt completely before addition of the potassium salt. The complex thus made up was allowed to stand in the thermostat until it had reached constant temperature, and was then seeded with the solid known to be the equilibrium phase at that temperature. The tube was then covered with a glass cap and rotated in the thermostat until equilibrium was attained.

Experience obtained in the usual costly manner showed that the time required for equilibrium must not be underestimated. External equilibrium between liquid and solid is doubtless quite rapidly attained—

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[5] Zanetti, *Ind. Eng. Chem.*, **16**, 304 (1924).

probably in a fraction of an hour, if the stirring is good—but internal equilibrium within the solid solution or within the anhydrous double compound is attained very much more slowly. One can understand that a process in which solid $K_2CO_3.3/2H_2O$, for example, must dissolve and dissolved sodium carbonate combine with the residual $K_2.CO_3.3/2H_2O$ and with water to produce a new solid of probably different crystalline form, must be a change occurring at a reduced speed, since the change is largely within and upon the solid phase. In practice, we found it necessary to arrange the complexes so that the total solid phase to be formed was relatively small (about 10% of the whole complex) and to continue the rotation for 48 hours; when larger amounts of solid were present or when the rotation was interrupted earlier, we found by analysis that the solid was still undergoing change in composition. Where the solid phase was a simple salt we reduced the time of rotation to 18–24 hours.

Equilibrium having been attained, the tubes were set upright in the thermostat; the solids were crystalline and settled quickly in all cases except that of $Na_2CO_3.H_2O$ in solutions containing much $K_2CO_3$, and that of the anhydrous compound $Na_2CO_3.K_2CO_3$. In the more usual cases, liquid was drawn up in a 5cc. pipet (warmed when necessary), run into a platinum dish and weighed; we thus obtained data for a rough density determination which is, of course, much less accurate than the analysis which followed. Where the solid did not settle well, in the cases mentioned, the pipet was fitted with a small filtering wad of cotton cloth or of absorbent cotton. The weighed sample was covered to prevent loss by spattering and evaporated to dryness in a vacuum oven at 80° and a pressure of about $^1/_6$ of an atmosphere. The residue was finally heated to incipient fusion over a burner, and from the total loss in weight the water content of the solution became known. The same residue was then dissolved in water and titrated with 1 *N* hydrochloric acid, using methyl orange as an indicator. With the weight of the mixed carbonates known, the titration made possible a calculation of the per cent. of each salt in the mixture and hence in the pipetted solution. In the indirect determination of the two carbonates by titration, the errors are multiplied by three; but as the titration could be performed with an error not greater than 0.1 to 0.2%, we feel sure that the analyses are correct to within 0.5%, in all cases, and the error is usually much smaller.

In order to determine the solid phase from the solubility experiments, we have endeavored to secure it as such instead of resorting to the method of analyzing wet residues, as suggested by Schreinemakers[6] and by Bancroft.[7] This latter method not infrequently may lead to erroneous conclusions, as in the work of Osaka on this system. We have therefore put

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[6] Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893).

[7] Bancroft, *J. Phys. Chem.*, **6**, 178 (1902).

the solids in a hand-driven centrifuge and have centrifuged them one to two minutes at 3000–4000 r.p.m. The outer basket of the centrifuge was treated with some of the mother liquor to prevent dehydration of the solid by evaporation, and the whole centrifuge was enclosed in a box and heated to the equilibrium temperature by an electric lamp. The crystals were then analyzed in the manner previously described for analysis of solution. This method of treatment was entirely satisfactory for the solids which came out in good crystalline form, and particularly for the crystalline solid solution, but failed for those which appeared in very fine crystals; in these latter cases the solids were filtered on a Monroe crucible in an oven regulated to the necessary temperature and were taken off the filter in a pasty condition, so that they are to be regarded as wet residues.

The foregoing method gave us three sets of analytical data for each experiment—the composition of the saturated solution, that of the original complex and that of the solid phase (or of a wet residue), as shown in Tables I to VI. When plotted on triangular coördinate paper, these three points should fall upon a straight line, and they have done so here usually within a few tenths of a per cent.; the exceptions are in the cases of the finely crystalline materials mentioned above, where slower filtration or possible evaporation in the centrifuge has altered the composition of the residue slightly.

## Experimental Results

**Hydrates of Potassium Carbonate.**—While the composition, solubility and transition temperatures of the hydrated carbonates of sodium are known beyond question, the same cannot be said for the hydrates of potassium carbonate. Mellor[8] again lists a series of investigations in which the hydrate stable at room temperature is given formulas ranging from $K_2CO_3.H_2O$ to $K_2CO_3.4H_2O$. In the present day literature, about equal weight seems to be given to the formula $K_2CO_3.2H_2O$ and to Städeler's[9] formula $K_2CO_3.3/2H_2O$. It seemed desirable to settle the question by a phase-rule study that should not leave the formula in doubt. Accordingly a solution was allowed to crystallize slowly at room temperature, and the crystals were filtered off and rapidly centrifuged. Thus prepared, the crystals were found to contain distinctly less than the 20.6% of water necessary for the composition of the dihydrate. We are unable, therefore, to find evidence for the existence of a dihydrate, or higher hydrate, at room temperature. These crystals were put in a desiccator over anhydrous potassium carbonate, and after becoming superficially dry were coarsely powdered. They were then allowed to remain in the desiccator until their weight became constant, except for fluctuations of a few hundredths of a

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[8] Ref. 1, p. 754.

[9] Städeler, *Ann.*, **133**, 371 (1865).

per cent. which we believe may be due to adsorption upon the containers or upon the crystals. On the fourth day the water content was obtained by ignition, and found to be 16.50% ± 0.03%; the formula $K_2CO_3.3/2\ H_2O$ requires 16.36%. Crystals left in the desiccator for several months did not lose further amounts of water; the small excess is doubtless held interstitially. The preceding experiments seem to prove definitely that the lowest hydrate has the formula $K_2CO_3.3/2H_2O$; the solubility curve given in Seidell[10] indicates that this is the hydrate stable in contact with solution from room temperature to above 100°.

The solubility curve given in Seidell's tables[10] shows a transition point at —6.8°; the same temperature is given in the Landolt-Börnstein "Tabellen" from an unpublished result by Meyerhoffer. We have redetermined this transition temperature, and have found the composition of this higher hydrate. The transition temperature was determined by cooling curve and warming curve in the Beckmann apparatus, with the following result: transition temperature, by cooling curve, —6.3° (corr.); by warming curve, —6.1° (corr.); av., —6.2° ± 0.1°. The lack of closer agreement is probably due to the viscous nature of the solution at this temperature, acting to prevent both an equalization of temperature and the attainment of saturation. The solution showed upon analysis a content of 51.47% of potassium carbonate. The solution shows obstinate supersaturation, requiring from 10° to 20° of undercooling to produce the hydrate.

A direct analysis of the hydrate stable below —6.2° is not easily possible. We have therefore determined its composition by indirect analysis in a three-component system at a constant temperature, choosing potassium hydroxide as the third component both because of its high solubility and also because the formation of double compounds is unlikely. Complexes were made up of such composition that they could be cooled to a temperature of —18° with the precipitation of a minimum quantity of the metastable solid phase, $K_2CO_3.3/2H_2O$. They were put in a Dewar flask in ice and salt at this temperature, seeded with a fragment of the higher hydrate obtained by cooling a solution in a bath of solid carbon dioxide and alcohol, and stirred for about one hour; the temperature fluctuations were very small. By choosing the compositions as given above, the presence of unchanged lower hydrate was kept at a minimum. Samples of liquid phase were filtered from the vessel under suction and analyzed for total alkali by titration and for carbon dioxide by absorption in soda lime; from these data the composition of the liquid phase was calculated. By plotting the composition of the original complex and of the solution upon triangular coördinates and extrapolating the line to the $K_2CO_3.H_2O$ axis, the composition of the solid phase was determined, as given in the last column of the formula table.

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[10] Seidell, "Solubilities," Van Nostrand Company, New York, 1919, p. 508.

| | Original complex $K_2CO_3$, % | Original complex KOH, % | Solution $K_2CO_3$, % | Solution KOH, % | $H_2O$ in solid phase, % |
|---|---|---|---|---|---|
| 1 | 43.14 | 5.70 | 36.11 | 8.80 | 43.93 |
| 2 | 43.16 | 5.72 | 36.89 | 8.49 | 43.89 |

The formula $K_2CO_3.6H_2O$ requires 43.87% of water; we may therefore conclude that the solid phase below —6.2° has that composition.

**The 20° Isotherm.**—The solubility curve at 20°, shown in Fig. 1, contains three parts, corresponding to three solid phases. The sesquihydrated potassium carbonate is the solid phase in solutions containing less than 3% of sodium carbonate (Point *b*); in the presence of larger proportions of the sodium salt the solid phase is the solid solution shown on the line *no*, which will be discussed in the next section. This is the dominating phase throughout the greater part of the isotherm, and is stable until the solution contains 19% of sodium carbonate (Point *c*), at which point the decahydrated sodium carbonate $Na_2CO_3.10H_2O$ becomes the stable phase. It was found possible, however, to carry the solubility curve *bc* for the solid solution over into the metastable region for a considerable distance. The solubility curve for the decahydrate is indicated by the line *cd*. The measurements are given in Table I; the percentage of water and of sodium carbonate are given, and that of potassium carbonate may be obtained by subtracting the sum of the former two from 100%. Data are given for the saturated solution, for the original complex and for the solid residue. In the last column are indicated the saturating solid phases; as abbreviations in Tables I to Table VI the following are used: $K_{3/2}$ for $K_2CO_3.3/2H_2O$; S for the solid solution $(Na_2, K_2)CO_3.6H_2O$; $N_{10}$ for $Na_2CO_3.10H_2O$; $N_7$ for $Na_2CO_3.7H_2O$; $N_1$ for $Na_2CO_3.1H_2O$; KN for the compound $Na_2CO_3.K_2CO_3$.

TABLE I

20° ISOTHERM, $Na_2CO_3 + K_2CO_3 + H_2O$

| Point in Fig. 1 | Solution $H_2O$, % | Solution $Na_2CO_3$, % | Solution Density | Original complex $H_2O$, % | Original complex $Na_2CO_3$, % | Residue $H_2O$, % | Residue $Na_2CO_3$, % | Solid phases |
|---|---|---|---|---|---|---|---|---|
| *a*[a] | 47.4 | 0.0 | ... | .. | .. | .. | .. | $K_{3/2}$ |
| *b* | 47.1 | 3.0 | ... | 42.0 | 9.0 | .. | .. | $K_{3/2}$ + S |
| | 47.4 | 3.6 | 1.545 | 47.3 | 6.0 | 47.0 | 22.3 | S |
| | 48.2 | 3.6 | 1.541 | 48.0 | 7.0 | 46.9 | 22.2 | S |
| | 58.8 | 7.6 | 1.417 | 57.0 | 10.0 | 47.2 | 23.5 | S |
| | 63.6 | 19.0 | 1.373 | 58.0 | 22.0 | 47.9 | 27.1 | S |
| | 63.6 | 21.1 | 1.375 | 60.0 | 23.0 | 48.4 | 28.7 | S (metastable) |
| | 63.6 | 22.5 | 1.372 | 62.5 | 23.0 | 48.5 | 31.6 | S (metastable) |
| *c* | 63.6 | 19.2 | 1.371 | 58.0 | 30.0 | 55.8 | 34.2 | S + $N_{10}$ |
| | 65.3 | 18.7 | 1.352 | 65.0 | 21.0 | 62.5 | 37.0 | $N_{10}$ |
| *d*[a] | 82.2 | 17.8 | ... | .. | .. | .. | .. | $N_{10}$ |

[a] The solubilities of the pure salts in water are taken from the average curve calculated by Seidell (see Ref. 10).

In Fig. 1, the numbered triangles represent isothermally invariant systems (four phases, including vapor), which will be discussed later. The triangle *noq*, however, is an area representing equilibrium between monohydrated sodium carbonate and the solid solution *no;* any complex taken within this area will, at equilibrium, consist of solid $Na_2CO_3.H_2O$ mixed with solid solution of a composition shown by the intersection of *no* with prolongation of the tie-line drawn from *q* through the complex. As both phases are solids, presumably equilibrium would be reached only after a very long time, and presumably by the same mechanism as is reached in systems consisting of three solid phases (such as Equilibrium 16). That the phase in equilibrium with the solid solution is $Na_2CO_3.H_2O$ and not some other solid cannot, we believe, be foretold *a priori* from the figure alone, but appears as a necessity from the study of the quintuple points given later.

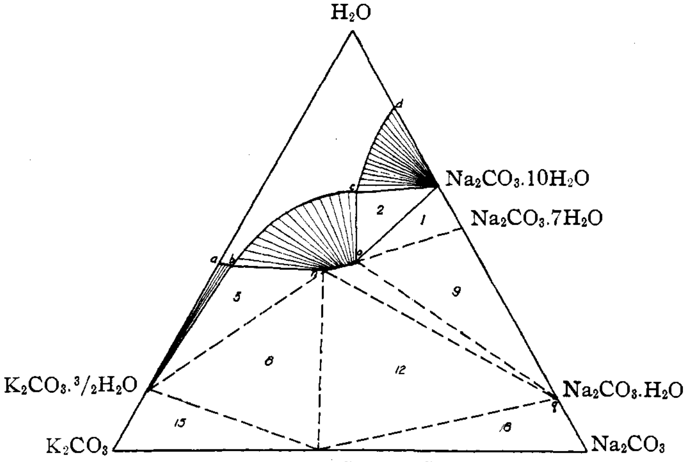

Fig. 1.—20° isotherm.

**The Solid Solution.**—It will be seen that the solid phase in equilibrium with the saturated solution *bc* has a varying composition falling upon the straight line *no*, as established by the direct analysis of the solid residues in Lines 3 to 6 of Table I. The same evidence appears in Figs. 2, 3 and 6. This establishes that the solid phase is a ternary solution, and in no sense a single compound as concluded by Kremann and Zitek and by Osaka. The analyses of ordinary centrifuged residues showed that the sodium carbonate content varies from 21.7% (Table III, Line 11) to 31.6% (Table I, Line 8), while the water content varies only from 46.3% near the point *n* (Table II, Line 4) to 48.5% near the point *o* (Table I, Line 8). The points fall quite well upon a straight line with the water content increasing slightly from *n* to *o*. The variation from the straight line for all points on *no* in Tables I to IV is less than 1%, and is probably due to the presence of mother liquor upon the crystals, or possibly to unchanged

$Na_2CO_3.H_2O$. In order to obtain crystals as free as possible from these errors, two crystallizations were conducted by making up saturated solutions of compositions close to the points *b* and *c*, which were allowed to evaporate very slowly in a desiccator over sulfuric acid; the temperature being between 21° and 25°. The crystals thus produced were about 3 mm. in diameter and regular in form; it is believed that the slow building up of the crystals reduced the interstitial liquor to a minimum. They were then well centrifuged, with mother liquor in the outer basket to prevent loss of water by evaporation. The analyses follow.

| | $H_2O$, % | $Na_2CO_3$, % | $K_2CO_3$, % |
|---|---|---|---|
| Crystals near Point *n* | 47.23 | 22.77 | 30.00 |
| Crystals near Point *o* | 48.30 | 29.14 | 22.56 |

By extrapolation of the line drawn between these two points, or of the line *no* in any of the diagrams, an understanding of the nature of this ternary solid solution may be had. The extrapolated line ends with the composition $K_2CO_3.6H_2O$ upon the left, and with $Na_2CO_3.6H_2O$ upon the right. The former is the higher hydrate of potassium carbonate previously discussed, while the latter has no independent existence; our efforts to prepare such a hydrate by desiccation of the heptahydrate over the monohydrate gave no evidence of any hydrate of intermediate composition. The simplest explanation of the composition of the solid solution, based upon these facts, is that the hexahydrated potassium carbonate, metastable above —6.2° if in contact with its own saturated solution, can exist at much higher temperatures in contact with solution saturated with both carbonates as a result of the lowering of its vapor tension by substitution of sodium atoms for potassium, giving rise to a solid solution which we may formulate $(K_2, Na_2)CO_3.6H_2O$; it is also possible that the mixed liquid solution has a higher vapor tension than the saturated solution of the pure potassium salt, which would be favorable to the existence of the solid solution. At room temperature, the range of concentrations in which this solid solution can exist is limited, on the one hand (the left of the diagram) by the fact that as the sodium content becomes less the vapor tension of the solid becomes greater, and on the other hand (the right of the diagram) by the fact that replacement of potassium atoms by sodium cannot proceed beyond a fixed ratio without too great distortion of the crystal lattice.

From the above analytical data it becomes clear that the view of Kremann and Zitek and of Osaka that the solid phase is a compound $K_2CO_3.Na_2CO_3.12H_2O$ is erroneous, although the composition given by them is close to the line of solid solutions established by us; the molecular ratio of potassium carbonate to sodium carbonate we have found to vary continuously from 1:0.88 to 1:2.07 in the various solids analyzed. The solid solutions appear to extend only a short distance in the direction of excess of potassium carbonate over the 1:1 ratio, but a long distance in the direction of excess of sodium carbonate. There is, accordingly, no evidence whatever for the existence of any compound in this area.

The crystals of the solid solution obtained in the various experiments are rhombic in shape and usually well formed; a single crystal obtained by chance in one experiment measured 9.5 mm. in its maximum dimension. Crystals high in sodium carbonate content were always found to be well formed and of considerable size; those rich in potassium carbonate, however, were invariably smaller, and at points near *n* appeared usually as a fine crystalline meal. We have found that all of the solids containing sodium carbonate tend to appear in very small crystals when precipitated from a solution high in potassium carbonate.

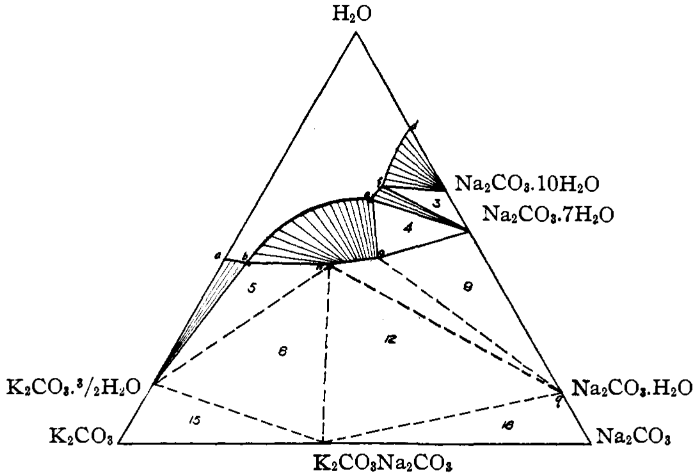

Fig. 2.—25° isotherm.

**The 25° Isotherm.**—The isotherm at 25° is shown in Fig. 2. This is the temperature at which Osaka's[4] measurements were made, and Kremann and Zitek's[3] were but slightly lower (24.8°). In both of these investigations error was made by omission of the solid solution *no*, as previously pointed out, and also by omission of the curve *ef*, for which the solid phase is the heptahydrate $Na_2CO_3.7H_2O$. In our experiments we were able not only to establish the existence of stable, saturated solutions with this salt as saturating phase (curve *ef*), but also were able to carry the curve into the metastable region as far as *p* (Table II). The data are given in Table II.

The analyses of the residues are omitted from Table II in a number of cases. These experiments were conducted before our experience had shown that equilibrium is but slowly attained in the solid solutions; as a result of the failure to obtain equilibrium, the tie-lines cross in the same irregular fashion found by Osaka.[4] The liquid solutions, however, fall upon the same solubility curve *be* within the errors of analysis and we have, therefore, included the composition of the liquid phase in order to establish more fully the course of the solubility curve. The equilibrium solids obtained all fell quite close to the line *no*.

TABLE II

25° ISOTHERM, $Na_2CO_3$-$K_2CO_3$-$H_2O$

| Point in | Solution | | | Original complex | | Residue | | Solid |
|---|---|---|---|---|---|---|---|---|
| Fig. 2 | $H_2O$, % | $Na_2CO_3$, % | Density | $H_2O$, % | $NaC_2O_3$, % | $H_2O$, % | $Na_2CO_3$, % | phases |
| *a* | 47.2 | 0.0 | ... | .. | .. | ... | .. | $K_{3/2}$ |
| | 46.7 | 2.8 | 1.561 | 40.0 | 2.5 | 19.68 | .. | $K_{3/2}$ |
| *b* | 46.6 | 5.0 | 1.555 | 30.0 | 18.0 | .. | .. | $K_{3/2}$ + S |
| | 47.6 | 4.9 | 1.551 | 46.2 | 7.8 | 46.3 | 21.8 | S |
| | 49.0 | 5.3 | 1.552 | 47.9 | 10.9 | .. | .. | S |
| | 54.0 | 6.4 | ... | 50.9 | 14.0 | .. | .. | S |
| | 55.7 | 7.2 | ... | 49.9 | 18.5 | .. | .. | S |
| | 58.9 | 11.6 | 1.471 | 50.5 | 20.3 | 46.8 | 24.3 | S |
| | 59.9 | 13.6 | 1.471 | 55.1 | 18.0 | .. | .. | S |
| | 60.1 | 13.7 | 1.406 | 58.0 | 15.3 | 47.3 | 26.0 | S |
| | 61.1 | 17.9 | 1.404 | 54.0 | 22.5 | .. | . | S |
| | 61.4 | 21.5 | 1.404 | 57.5 | 23.3 | .. | .. | S |
| | 61.5 | 22.1 | 1.399 | 59.0 | 23.2 | 48.2 | 29.4 | S |
| *e* | 61.5 | 22.7 | 1.395 | 59.0 | 26.0 | .. | .. | S + $N_7$ |
| | 62.7 | 23.2 | ... | 60.0 | 30.0 | .. | .. | $N_7$ |
| | 64.1 | 23.3 | 1.404 | 62.8 | 26.1 | .. | .. | $N_7$ |
| *f* | 64.2 | 23.3 | 1.368 | 63.0 | 28.0 | .. | .. | $N_7$ + $N_{10}$ |
| | 65.6 | 24.3 | 1.368 | 62.9 | 29.1 | .. | .. | $N_7$ (metastable) |
| | 66.4 | 24.3 | 1.369 | 65.0 | 27.0 | .. | .. | $N_7$ (metastable) |
| *p* | 69.5 | 26.1 | 1.335 | 63.2 | 33.8 | .. | .. | $N_7$ (metastable) |
| | 66.3 | 22.9 | 1.317 | 65.9 | 24.1 | .. | .. | $N_{10}$ |
| | 71.9 | 22.0 | ... | 70.0 | 25.0 | .. | .. | $N_{10}$ |
| | 75.0 | 22.4 | 1.263 | 73.4 | 24.1 | .. | .. | $N_{10}$ |
| *d* | 77.8 | 22.5 | ... | .. | .. | .. | .. | $N_{10}$ |

**The 30° Isotherm.**—The isotherm at 30° (Fig. 5) shows a number of features not present at 25°. There are present three new sectors of the solubility curve. In the sector *ij* the saturating phase is a new anhydrous double compound, $K_2CO_3.Na_2CO_3$, discussed in the following section of the paper; in the very short sector *jk* the saturating phase is the monohydrate $Na_2CO_3.H_2O$, and in the longer sector *hg*, on the further side of the solubility curve for the solid solution, the solid phase is again the same monohydrated sodium carbonate. As will be shown in the latter part of the paper, the sector *ij* first appears at 25.12°, *hg* appears at 26.76° and *jk* at 29.6°. The curve for the heptahydrate $Na_2CO_3.7H_2O$ has gained in length (*gf*), and that for the decahydrate $Na_2CO_3.10H_2O$ has become much shorter (*fd*). The results at 30° are given in Table III.

Figs. 3 and 4, at temperatures between the measurements made at 25° and at 30°, represent schematically the form of the isotherm at intermediate temperatures at which the solubility curve has been added to by the appearance of the new solid phases, the anhydrous compound $K_2CO_3$.-

TABLE III

30° ISOTHERM, $NaCO_3 + K_2CO_3 + H_2O$

| Point in Fig. 5 | Solution $H_2O$, % | Solution $Na_2CO_3$, % | Solution Density | Original complex $H_2O$, % | Original complex $Na_2CO_3$, % | Residue $H_2O$, % | Residue $Na_2CO_3$, % | Solid phases |
|---|---|---|---|---|---|---|---|---|
| *a* | 46.8 | 0.0 | ... | .. | .. | .. | .. | $K_{3/2}$ |
| | 46.3 | 3.5 | 1.561 | 40.0 | 3.0 | .. | .. | $K_{3/2}$ |
| *i* | 46.1 | 4.0 | 1.561 | 40.0 | 5.5 | .. | .. | $K_{3/2}$ + KN |
| | 46.3 | 4.7 | 1.554 | 40.0 | 10.0 | .. | .. | KN |
| | 46.6 | 5.4 | 1.558 | 42.0 | 9.0 | 10.9 | 34.5 | KN |
| | 46.8 | 5.3 | 1.553 | 43.0 | 8.8 | 13.5 | 33.1 | KN |
| | 47.2 | 6.6 | 1.551 | 43.0 | 10.0 | .. | .. | KN |
| *j* | 47.4 | 6.8 | 1.547 | 40.0 | 15.0 | 14.6 | 44.5 | KN + $N_1$ |
| | 47.6 | 7.3 | 1.545 | 42.2 | 20.0 | 28.9 | 53.5 | $N_1$ |
| *k* | 47.85 | 7.3 | 1.543 | 46.0 | 14.0 | 42.4 | 27.6 | $N_1$ + S |
| | 48.6 | 7.3 | 1.530 | 48.0 | 11.0 | 46.4 | 21.7 | S |
| | 55.5 | 11.1 | 1.451 | 53.0 | 15.0 | 47.6 | 23.0 | S |
| | 58.5 | 18.5 | 1.422 | 57.0 | 19.0 | 47.8 | 26.7 | S |
| *h* | 58.8 | 19.1 | 1.419 | 56.0 | 22.4 | .. | .. | S + $N_1$ |
| | 59.2 | 19.6 | 1.414 | 58.0 | 21.4 | .. | .. | $N_1$ |
| | 61.2 | 22.6 | 1.398 | 57.7 | 27.5 | .. | .. | $N_1$ |
| | 62.0 | 24.5 | 1.390 | 60.5 | 26.5 | .. | .. | $N_1$ |
| *g* | 63.2 | 26.6 | 1.378 | 60.7 | 30.9 | .. | .. | $N_1$ + $N_7$ |
| | 65.5 | 27.8 | 1.354 | 64.0 | 30.3 | 54.4 | .. | $N_7$ |
| *f* | 67.4 | 28.6 | 1.330 | 64.8 | 33.0 | .. | .. | $N_7$ + $N_{10}$ |
| *d* | 72.0 | 28.0 | ... | .. | .. | .. | .. | $N_{10}$ |

$Na_2CO_3$ and the monohydrate $Na_2CO_3.H_2O$; Fig. 5 shows the addition of the second sector taken up by the monohydrate (*jk*).

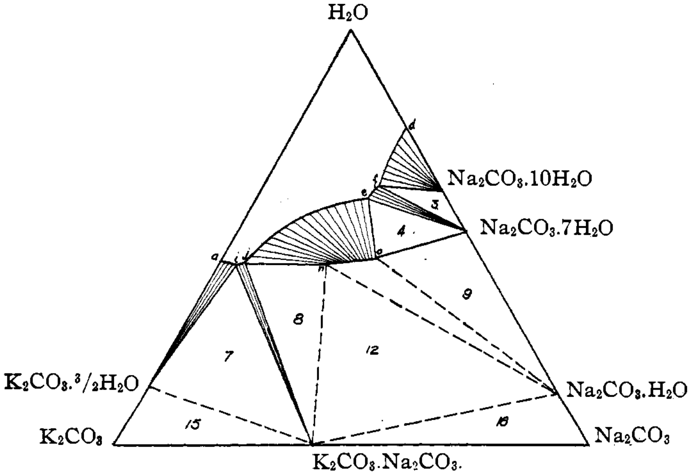

Fig. 3.—Isotherm above 25.12°.

**The Anhydrous Double Salt, $K_2CO_3.Na_2CO_3$.**—The measurements at 30° showed that the tie-lines emanating from the solubility curve *ij* converge toward a point on the base line, indicating that the solid phase is an anhydrous double salt. Moreover, the water content of the centrifuged residues in Lines 5 and 6 of Table III is distinctly lower than that found when $Na_2CO_3.H_2O$ or $K_2CO_3.3/2H_2O$ was the solid, notwithstanding that the crystals were much the smallest found in our work and were therefore the hardest to free from superficial mother liquor. In order to prove beyond question, however, that the solid is anhydrous, it was necessary to prepare the salt in as large crystals as possible, so that the centrifuging might be most effective. This was accomplished by preparation of a solution represented by a point on the line *ij* near to *j*, which was allowed to

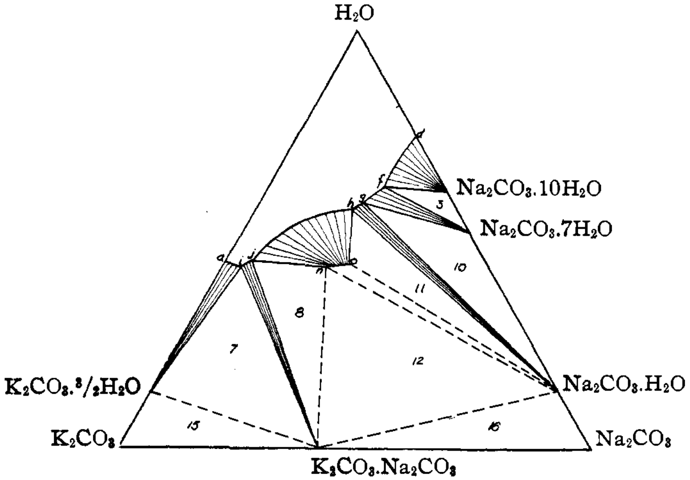

Fig. 4.—Isotherm above 26.76°.

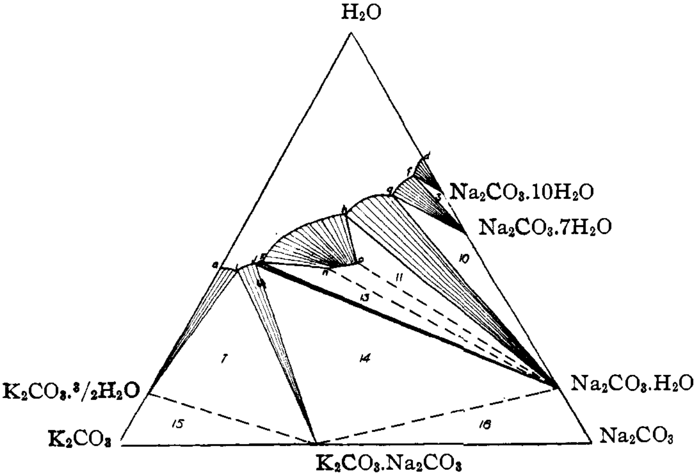

Fig. 5.—30° isotherm.

evaporate slowly over sulfuric acid at temperatures between 31° and 34°; the evaporation was interrupted before the loss of water brought the total composition into Triangle 7 of Fig. 5, at which point $K_2CO_3.3/2H_2O$ also should begin to precipitate. About 6 g. of crystals was obtained, about 3 mm. in diameter; they were well centrifuged, and gave the following results upon analysis.

*Anal.* Calcd. for $K_2CO_3.Na_2CO_3$: $H_2O$, 0; $Na_2CO_3$, 43.41; $K_2CO_3$, 56.59. Found: $H_2O$, 0.25; $Na_2CO_3$, 44.40; $K_2CO_3$, 55.35.

The analysis establishes that the compound is anhydrous, and that it is within 1% of the composition of the 1:1 ratio. We are not prepared to affirm, however, that there is no possibility of solid solution of anhydrous sodium carbonate in this compound. Not only did this especially prepared sample show a small excess of sodium carbonate, but the extrapolation of tie-lines emanating from the curve *ij* at various temperatures frequently met the base line of the triangle from 1 to 2% toward the sodium carbonate apex. Whether these results are to be attributed to the formation of a solid solution or to the presence of sodium carbonate through failure to obtain equilibrium we cannot tell, but in either case the amount of the variation is not more than 2% at any of the temperatures used in this investigation.

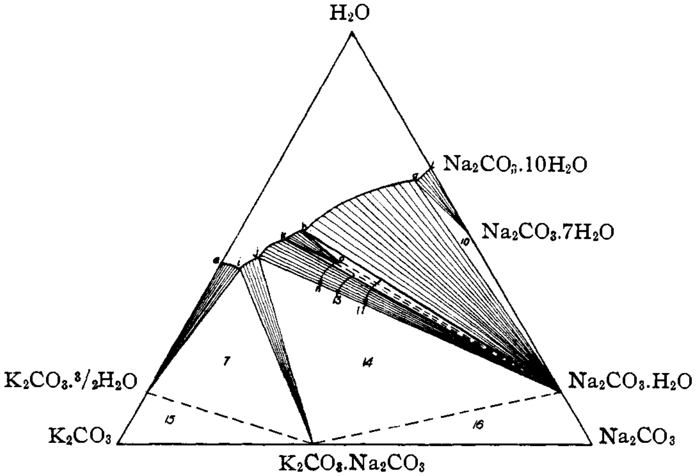

Fig. 6.—33° isotherm.

**The 33° Isotherm.**—The results at 33° were carried out in order to determine as nearly as possible the upper temperature limit for the existence of the solid solution. Beginning at 20°, at which temperature the solubility curve for the solid solution dominates the system, the curve becomes progressively smaller as the temperature rises, and was found to be wholly absent at 36°. At 33° the conditions are as shown in Fig. 6; the solubility curve has been reduced to a variation in composition of only about 2% (*kh* in Fig. 6), and the line of the solid solution *no* is correspondingly shorter. It can be estimated that the phase ceases to exist at a temperature of about 34°. Other changes in the diagram, as compared with Fig. 5, are the extension of the solubility curve *jk* for $Na_2CO_3.H_2O$, and the complete absence of the solubility curve for the decahydrate; this has, of course, disappeared at the temperature of the transition of the decahydrate to the heptahydrate, 32.0°.[11] The solubility curve *gl* for the heptahydrate has become shortened through the extension of the curve *hg* for the monohydrate. The results are given in Table IV.

TABLE IV

33° ISOTHERM, $Na_2CO_3 + K_2CO_3 + H_2O$

| Point in Fig. 6 | Solution | | | Original complex | | Residue | | Solid phases |
|---|---|---|---|---|---|---|---|---|
| | $H_2O$, % | $Na_2CO_3$, % | Density | $H_2O$, % | $Na_2CO_3$, % | $H_2O$, % | $Na_2CO_3$, % | |
| *a* | 46.8 | 0.0 | ... | .. | .. | .. | .. | $K_{3/2}$ |
| *i* | 45.9 | 4.3 | ... | 39.0 | 7.0 | 23.7 | 13.4 | $K_{3/2}$ + KN |
| | 46.8 | 5.7 | 1.555 | 40.0 | 11.0 | 17.5 | 30.8 | KN |
| *j* | 48.2 | 6.7 | ... | 40.0 | 15.0 | 14.3 | 43.3 | KN + $N_1$ |
| | 50.4 | 8.9 | 1.510 | 49.0 | 12.0 | 29.0 | 54.0 | $N_1$ |
| | 52.0 | 10.0 | 1.498 | 49.3 | 16.0 | 29.9 | 53.9 | $N_1$ |
| *k* | 52.4 | 10.6 | 1.479 | 50.4 | 16.0 | 46.5 | 25.5 | $N_1$ + S |
| | 53.0 | 11.5 | 1.454 | 51.0 | 16.0 | .. | .. | S |
| | 53.8 | 12.0 | 1.455 | 51.6 | 16.0 | 47.1 | 24.3 | S |
| *h* | 54.3 | 12.8 | 1.454 | 52.0 | 17.0 | 36.4 | 43.6 | S + $N_1$ |
| | 55.4 | 14.0 | 1.457 | 52.0 | 20.0 | 25.5 | 64.9 | $N_1$ |
| | 56.6 | 15.6 | 1.440 | 54.0 | 20.0 | 29.0 | 59.6 | $N_1$ |
| | 62.2 | 24.0 | 1.377 | 53.0 | 36.0 | 27.8 | 68.0 | $N_1$ |
| *g* | 65.4 | 29.9 | 1.354 | 56.4 | 41.4 | 49.4 | 50.1 | $N_1$ + $N_7$ |
| *l* | 68.4 | 31.6 | ... | .. | .. | .. | .. | $N_7$ |

**The 36° Isotherm.**—At 36°, as shown in Fig. 7, heptahydrated sodium carbonate has ceased to exist (having passed through its transition to the

TABLE V

36° ISOTHERM, $Na_2CO_3 + K_2CO_3 + H_2O$

| Point in Fig. 7 | Solution | | | Original complex | | Residue | | Solid phases |
|---|---|---|---|---|---|---|---|---|
| | $H_2O$, % | $Na_2CO_3$, % | Density | $H_2O$, % | $Na_2CO_3$, % | $H_2O$, % | $Na_2CO_3$, % | |
| *a* | 46.4 | 0.0 | ... | .. | .. | .. | .. | $K_{3/2}$ |
| | 45.6 | 3.5 | ... | 40.0 | 3.0 | 22.0 | 0.5 | $K_{3/2}$ |
| *i* | 45.6 | 4.0 | 1.545 | 41.0 | 6.0 | .. | .. | $K_{3/2}$ + KN |
| | 46.4 | 4.9 | 1.552 | 43.0 | 8.0 | .. | .. | KN |
| | 47.8 | 5.7 | ... | 40.0 | 12.0 | 23.9 | 25.4 | KN |
| *j* | 47.4 | 7.2 | 1.532 | 45.0 | 10.0 | 22.2 | 35.3 | KN + $N_1$ |
| | 50.9 | 9.6 | 1.503 | 49.0 | 14.0 | 27.5 | 58.5 | $N_1$ |
| | 54.7 | 12.9 | 1.461 | 52.0 | 18.0 | 30.2 | 57.2 | $N_1$ |
| | 58.4 | 18.2 | 1.421 | 55.0 | 23.0 | 18.6 | 77.7 | $N_1$ |
| | 60.9 | 21.5 | 1.392 | 55.0 | 30.0 | 19.4 | 78.2 | $N_1$ |
| *m* | 66.8 | 33.2 | ... | .. | .. | .. | .. | $N_1$ |

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[11] Wells and McAdam, THIS JOURNAL, **29**, 721 (1907).

monohydrate at 35.37°)[11] the solid solution is no longer found, and the two parts of the solubility curve of Fig. 6 (*jk* and *hg*) have joined in the one curve *jm*. The data are given in Table V.

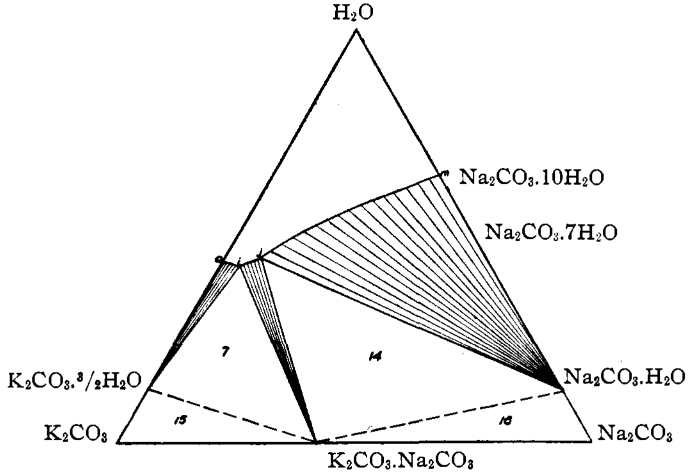

Fig. 7.—36° isotherm.

**The 50° Isotherm.**—A few determinations were carried out at 50°, not with the expectation of observing any new phase relations, but in order to determine which of the three solubility curves may be expected to enlarge their dimensions. The results are shown in Table VI. In interpreting the data, Fig. 7 may be used, since the changes are slight.

Table VI

50°; $Na_2CO_3 + K_2CO_3 + H_2O$

| Point in Fig. 7 | Solution | | | Original complex | | Residue | | Solid phases |
|---|---|---|---|---|---|---|---|---|
| | $H_2O$, % | $Na_2CO_3$, % | Density | $H_2O$, % | $Na_2CO_3$, % | $H_2O$, % | $Na_2CO_3$, % | |
| *a* | 45.2 | 0.0 | ... | .. | .. | .. | .. | $K_{/2}$ |
| *i* | 44.4 | 3.3 | 1.574 | 41.0 | 6.0 | 18.1 | 25.0 | $K_{3/2}$ + KN |
| *j* | 47.5 | 8.0 | 1.530 | 44.0 | 11.0 | 18.0 | 33.0 | KN + N |
| | 48.9 | 8.5 | 1.523 | 46.0 | 15.0 | 32.2 | 47.2 | $N_1$ |
| *m* | 67.8 | 32.2 | ... | .. | .. | .. | .. | $N_1$ |

The monohydrated sodium carbonate still dominates the system, but with a slightly shorter solubility curve; the curve for the double salt on the other hand is slightly longer, while that for the sesquihydrated potassium carbonate is somewhat shorter. We may expect Fig. 7 to show the relationship qualitatively over a considerable increase of temperature, but with a gradual extension of the curve *ij* for the double salt.

## The Quintuple Points and the Isothermally Invariant Equilibria

Inspection of Figs. 1 to 6 shows that four quintuple points may be expected, at the temperatures at which, with increase in temperature, new solid phases become stable and take a place upon the solubility curve. Each of these new solid phases obtrudes itself into a system already containing vapor, liquid solution and two solid phases, thus giving rise to an invariant system with five phases present. In addition to these four fixed points, there is a fifth unique temperature, slightly above that of Fig. 6, at which the two isothermally invariant liquids *k* and *h* become identical and at which also the two solid solutions *n* and *o* become identical. This point may be looked upon as a consolute point for the two liquids and two solids, or as an incongruent melting point of the solid solution, but as there appears to be no method for determining it by thermal methods we have been content to estimate it as at about 34°. The four quintuple points, however, have been determined by the usual method; cooling curves were drawn as properly chosen complexes were stirred in a Beckmann freezing-point tube.

Choosing a mixture of the components represented by a point in Fig. 1, within the triangle marked 2 and near to the point *c*, an invariant temperature of 22.02° was obtained. This we have called Quintuple Point A. Using the customary method of reasoning, we may deduce the phase reaction which occurs at this temperature to be the following, indicating the change which occurs upon addition of heat by the arrow pointing toward the right, and *vice versa*: Quintuple Point A, 22.02°; $S + N_{10} \rightleftarrows N_7 + L$. The symbol L indicates the liquid phase, which was analyzed and found to contain water, 62.7%; sodium carbonate, 21.3%. This is not far from the composition of the point *c*, Fig. 1.

At each quintuple point there originate four isothermally invariant equilibria, represented in the figures as triangles. Giving to each of these a number, used in the figures, we tabulate those originating at Quintuple Point A, and add the data as to the temperatures at which each equilibrium ceases to exist: at lower temps., (1) $S + N_{10} + N_7$, to below 20° (3 solids); (2) $S + N_{10} + L_1$, to below 20°; at higher temps., (3) $N_7 + L + N_{10}$, to the transition $N_{10} \longrightarrow N_7$, 32°; (4) $N_7 + L + S$, to Quin. Pt. C.

The second quintuple point occurs slightly above the temperature of Fig. 2, namely, at 25.12°, and is caused by the formation of the double salt from solutions saturated with hydrated potassium carbonate and the solid solution. Using a complex in Triangle 5, near the point *b* of Fig. 2, and chosen to fall within Triangle 7 of Fig. 3, the constant temperature was obtained. Quintuple Point B, 25.12°; $S + K_{3/2} \rightleftarrows L + KN$; composition of L: $H_2O$ 46.4%, $Na_2CO_3$ 4.8%; at lower temps., (5) $S + K_{3/2} + L$, to below 20°; (6) $S + K_{3/2} + KN$, to below 20° (3 solids); at higher temps., (7) $L + KN + K_{3/2}$, to above 50°; (8) $L + KN + S$, to Quin. Pt. D.

The third quintuple point occurs, with rising temperature, upon the first appearance of the monohydrate $Na_2CO_3.H_2O$ as a solid stable in contact with solution, as known in Fig. 4. The experiment was conducted with a complex of salts falling within Triangle 4 of Fig. 3 and Triangle 10 of Fig. 4. Quintuple Point C, 26.76°; $S + N_7 \rightleftarrows N_1 + L$; composition of L: $H_2O$ 60.8%, $Na_2CO_3$ 22.3%; at lower temps., (4) $S + N_7 + L_1$ to Quin. Pt. A; (9) $S + N_7 + N_1$, to below 20° (3 solids); at higher temps., (10) $N_1 + L + N_7$, to transition $N_7 \longrightarrow N_1$, at 35.37°; (11) $N_1 + L + S$, to consolute point $L_1 = L_2$ and $S_1 = S_2$, 34°.

Equilibrium 11, given above, comes to its end at a temperature of about 34°, slightly above that of Fig. 6, when the area of solid solution *no* becomes reduced to a point and the solubility curve *kh* has likewise shrunk to a point. This is an unusual type of phase reaction, in which the coalescence of two liquids occurs through the juncture of two monovariant equilibria (11 and 13); ordinarily coalescence occurs when two liquids which coexist in equilibrium with one solid are brought to the same composition by rise in temperature. Such instances have been noted, however, by Schreinemakers,[12] in the case of water, phenol and aniline, and by Hill and Macy[13] in the case of silver perchlorate, aniline and water. In neither of these cases, however, is a solid solution one of the phases concerned.

The fourth quintuple point, marking the second entrance of the monohydrate $Na_2CO_3.H_2O$ into a place on the solubility curve (Fig. 5), could not be determined with the same accuracy as in the preceding determinations. The phase reaction, as given below, shows that on falling temperature the phases formed are the solid solution and the double compound; the formation of each of these is a relatively slow process and the evolution of heat is not sufficient to hold the temperature constant. In each of the preceding cases, it will be observed, there is a simple hydrate formed in addition to the solid solution, and the formation of this compound was rapid enough to give a temperature about as constant as is usually found in determining invariant points by cooling curves; but in the case of Quintuple Point D we were not able to secure a constant temperature. There was however a sharp break in the cooling curve, which enables us to set the temperature as 29.6° without any considerable error. Quintuple Point D, 29.6°; $KN + S \rightleftarrows L + N_1$; composition of L: $H_2O$ 47.5%, $Na_2CO_3$ 6.9%; at lower temps., (8) $KN + S + L$, to Quin. Pt. B; (12) $KN + S + N_1$, to below 20° (3 solids); at higher temps., (13) $L + N_1 + S$, to consolute point $L_1 = L_2$ and $S_1 = S_2$; (14) $L + N_1 + KN$, to above 50°.

The establishment of this quintuple point and the diagram at 30° make possible a train of reasoning as to the solid solution *no*. Above 29.6° this area of solid solution is bounded by Equilibria 11 and 13; it follows necessarily therefore that the only solid phase with which it can stand in equilibrium is the monohydrate $Na_2CO_3.H_2O$, giving an isothermally univariant area *noq*, the selection of any other point than *q* would involve contra-

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[12] Schreinemakers, *Z. physik. Chem.*, **30**, 479 (1899).

[13] Hill and Macy, THIS JOURNAL, **46**, 1149 (1924).

dictions with the phase rule. It has been stated earlier that *a priori* reasoning could not lead to a conclusion as to the correct phase; the rather tempting guess that it might be $K_2CO_3.Na_2CO_3$ forming the solid solution by becoming hydrated, is clearly wrong. The correct conclusion can be arrived at only through knowledge of the quintuple points and isothermally invariant equilibria which are characteristic of the system.

Equilibrium 13 has the same apparent constitution as Equilibrium 11, previously discussed, but the solid solution has the composition designated by *n* in 13 and *o* in 11, and the liquid solution that of *k* in 13 and *h* in 11. In addition to the 14 equilibria indicated above, there exist two others drawn in the figures, but not having origin or termination within the temperature ranges here studied. They are: (15) $K_{3/2}$ + KN + $K_2CO_3$ (3 solids); (16) $N_1$ + KN + $Na_2CO_3$ (3 solids).

## Summary

1. The system consisting of $K_2CO_3 + Na_2CO_3 + H_2O$ has been studied at temperatures from 20° to 50°, and solubility determinations have been made and the phases studied at six intermediate temperatures.

2. The formula of the hydrated potassium carbonate stable at room temperatures is $K_2CO_3.3/2H_2O$. There is no monohydrate at any temperature. At temperatures below —6.2° the stable hydrate has the formula $K_2CO_3.6H_2O$.

3. From 20° to 34° there exists, in contact with liquid solutions of certain concentrations, a continuous series of ternary solid solutions of the formula $(K_2, Na_2) CO_3.6H_2O$, in which the atomic ratio of potassium to sodium varies from 1:0.88 to 1:2.07.

4. From 25.12° upward there exists, in contact with solutions rather high in potassium carbonate, an anhydrous 1:1 double salt of the formula $K_2CO_3.Na_2CO_3$, which is stable over increasing ranges of concentration with increasing temperature.

5. Between the temperatures taken there exist four quintuple points at which three solid phases, a liquid solution and vapor are present. From these quintuple points there originate 14 monovariant (four-phase) equilibria. There exists also a consolute temperature at which two liquid solutions become identical and two solid solutions become identical.

The work reported above is part of an investigation of the phase relations in aqueous solutions of potassium carbonate and bicarbonate and of sodium carbonate and bicarbonate, which includes a study of the reciprocal salt pairs $K_2CO_3 + NaHCO_3 \rightleftarrows KHCO_3 + Na_2CO_3$.

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