[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

EQUILIBRIA IN SOLUTIONS CONTAINING MIXTURES OF SALTS[1]

III. THE SYSTEM, WATER AND THE CHLORIDES AND CARBONATES OF SODIUM AND POTASSIUM AT 25°

IV. THE SYSTEM, WATER AND THE SULFATES AND CARBONATES OF SODIUM AND POTASSIUM AT 25°

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Although the system composed of water and the chlorides and carbonates of sodium and potassium should find important applications in dealing with the problem of separating the salts of potassium from certain brines of both natural and artificial origin, it does not appear to have been investigated. The work here reported upon is limited to a single temperature, but much information relating to the system at both higher and lower temperatures has been accumulated and will form the subject of subsequent papers. The writer is indebted to Dr. Harry East Miller for assistance in carrying out a part of the analytical work which the investigation demanded.

The Solid Phases Concerned

The solid phases found to be concerned in this system are the chlorides of sodium and potassium, the decahydrate, heptahydrate and five-halves hydrate of sodium carbonate, the three-halves hydrate of potassium carbonate and a hydrated double carbonate of sodium and potassium. The identification of these salts by means of the microscope formed an important part of the work here described and it was found necessary to make many preparations of them and ascertain some of their more important crystallographic and optical properties.

The difficulties encountered in preparing such hydrates free from occluded mother liquor and in drying them without loss of combined water are very great. Large crystals, whose surfaces were perfectly dry, almost invariably gave appreciable amounts of a saturated solution when crushed in an agate mortar and although smaller crystals yielded less, it was difficult to eliminate it entirely. Since the vapor tensions of most of these hydrates have not been determined, it is not possible to define with accuracy the proper conditions for drying them. The procedure usually adopted was to prepare fine crystals by rapid cooling, through a few degrees, of a saturated solution, separate these on a coarse filter as rapidly as possible, wash with solutions of alcohol of increasing concentration and allow to dry spontaneously until the odor of alcohol could no longer be recognized.

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[1] The preceding articles of this series will be found in *J. Ind. Eng. Chem.*, **10,** 334 (1918) and **12,** 164 (1920).

The Decahydrate of Sodium Carbonate.—Although this hydrate is the one usually obtained at ordinary temperatures, the available data regarding its crystallography are rather meager. This is probably due to the fact that it loses water under ordinary atmospheric conditions so rapidly that accurate measurements of the interfacial angles are difficult to obtain. A limited number of such measurements were made by means of a reflecting goniometer. They showed that the crystals were monoclinic; the value found for the β angle was 122° 42′ instead of 122° 20′, as calculated by Mohs.[2] Adopting the axial ratios found by him, the only planes found in the prismatic zone were (110), (100) and (010). The most conspicuous terminal planes observed were (001), (101) and (111). When the crystals were caused to separate rapidly, columnar prisms terminated by the basal plane were obtained. When they were grown more slowly, tabular forms flattened parallel to (010) and terminated by (001) and (101) were formed. Under the microscope, such crystals gave a hexagonal figure with angles of 122° 42′ (100):(001), of 115° 50′ (001):(101), and of 121° 28′ (101):(001).

The birefringence is strong and extinction is parallel to (100) and hence divides almost equally the 115° 50′ angle. The three indices of refraction reported by Larson,[3] namely, 1.405, 1.425 and 1.440, do not differ sufficiently from those of the related hydrates to make identification by means of these constants certain.

The Heptahydrate of Sodium Carbonate.—The crystallography of this salt has been investigated by Rammelsberg[4] and others. It readily forms perfect crystals of good size which assume the form of tabular prisms of easily recognizable orthorhombic symmetry. From measurements of angles in the prismatic zone, assuming the axial ratios calculated by Rammelsberg, it was found that the faces usually present were (010), (230) and (100). Similarly, it was found that the predominant terminal planes were (111) and (021). As the crystals are usually flattened parallel to the brachypinacoid the usual outline presented on the stage of the microscope was that of a 6-sided figure showing angles of 128° 40′ and 115° 40′, or of an 8-sided figure showing angles of 154° 40′ and 115° 40′, or still more rarely, of a 4-sided rectangle. The extinction is parallel to (100) and bisects the 128° 40′ angle. This serves to distinguish it from the usual forms of the decahydrate.

Under ordinary atmospheric conditions, the salt readily loses water of crystallization and when heated forms a liquid and a new solid phase, probably the monohydrate.

The Five-halves Hydrate.—This salt usually separates in the form

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[2] Mohs, *Pogg. Ann.*, **5**, 369 (1825).

[3] Larson, *U. S. Geol. Survey Bull.*, **679**, 114 (1921).

[4] "Hand. d. kryst. Chemie," Suppl., Leipzig, **1857**, p. 75.

of needles, but occasionally as long, 4-sided or flattened 8-sided prisms, terminated by a single pair of planes intersecting at 134°. The birefringence is strong and the extinction parallel. The percentages of water found in different preparations of it were 31.04, 31.30, 32.10, 31.54, 29.90, and 30.46. Many samples contained potassium in the form of carbonate from negligible amounts to as much as 4%. The theoretical percentage of water should be 29.80 and it is believed that the variations in its composition are due to a limited amount of solid solution formation.

The Double Carbonate of Sodium and Potassium.—The formation of a double carbonate of these elements was noted by Fehling,[5] and somewhat later by Stolba,[6] both of whom reported a composition corresponding to $NaKCO_3.6H_2O$. Marguerite[7] has also reported a salt of the composition $2Na_2CO_3.K_2CO_3.18H_2O$, and still more recently, Hugounenq and Morel[8] reported that the double salt which separated from solutions containing large amounts of potassium iodide varied greatly in its composition and concluded that the hexahydrates of the two carbonates formed a series of isomorphous mixtures.

Many samples obtained from solutions, which varied greatly as to the relative amounts of the two carbonates, were submitted to analysis during the course of this work. Some of these are as follows.

	A	B	C	D	Calculated ($NaKCO_3.6H_2O$)
H_2O	48.10	47.69	47.09	46.65	46.96
CO_3	26.04	25.90	25.94	26.83	26.06
K	13.80	14.78	16.66	13.46	16.99

These figures seem to justify the statement that there is a certain amount of solid solution formation represented in this solid.

Perfect crystals of short columnar or tabular habit, 3 cm. in length, were easily obtained, especially when the solution contained an excess of potassium carbonate. Measurement of the more important interfacial angles of 9 well-formed crystals gave values differing but slightly from the values reported by Marignac.[9] The most strongly developed planes were (110), (010), (100), (011), (101) and (111).

When examined on the stage of the microscope, they usually lie on the prismatic face, and in this position give an extinction angle of 25°. The indices of refraction, determined in directions parallel and perpendicular to extinction by the embedding method, were 1.428 and 1.440. When heated slowly, the salt shows a clearly defined transition temperature of 34.5°, but it is readily formed at temperatures as low as zero.

[5] Fehling, *Ann. Chem. Pharm.*, **130**, 247 (1864).

[6] Stolba, *J. prakt. Chem.*, **94**, 409 (1865).

[7] Marguerite, *Ann. Chem. Pharm.*, **56**, 220 (1845).

[8] Hugounenq and Morel, *Compt. rend.*, **106**, 1158 (1888).

[9] Marignac, *Ann. Mines*, [5] **12**, 55 (1857).

The Three-halves Hydrate of Potassium Carbonate.—Analyses and microscopic examination of several preparations of this salt obtained during the course of the work showed that the only hydrate formed at 25° was the three-halves hydrate.

The Vapor and Liquid Phases

In addition to the seven solids named above, this system is concerned with a solution phase and a vapor phase composed of water vapor plus the components of the atmosphere. Variation in the composition of the liquid phase must produce corresponding variations in the partial pressure of the water vapor in equilibrium with it, and these in turn must affect the partial pressures of the oxygen, nitrogen, etc., in the vapor phase. Although these variations affect the concentrations of the gases dissolved in the liquid phase, since the values concerned are too small when calculated in weight units to be classed as important constituents of the solution phase, they produce only insignificant effects upon the solubility of the solids concerned. Probably a much greater variation can be attributed to variations in the composition of the solids, due to solid solution formation and to occlusion. The partial pressure of the carbon dioxide normally present in the atmosphere is too small to affect, to a recognizable degree, the concentration of the acid carbonate, which results from hydrolysis of the soluble carbonates. Hence, the nature of the entire system is established with a high degree of accuracy by the composition of the liquid phase.

Composition of the Liquid Phase

No essential departures were made from the procedure outlined in the former papers of this series in determining the composition of solutions

Table I

Composition in Moles per 1000 Moles of Water of Solutions Saturated at 25°

	Saturated with	Na_2CO_3	K_2CO_3	Na_2Cl_2	K_2Cl_2
A	$Na_2CO_3.10H_2O$	50.63	....	...	...
B	NaCl	...	....	54.90	...
C	KCl	...	....	...	44.62
D	$K_2CO_3.{}^3/_2H_2O$	...	147.93	...	...
E	$K_2CO_3.{}^3/_2H_2O$; $NaKCO_3.6H_2O$	18.50	135.70	...	...
F	$Na_2CO_3.7H_2O$; $NaKCO_3.6H_2O$	60.40	39.70	...	...
G	$Na_2CO_3.10H_2O$; $Na_2CO_3.7H_2O$	60.50	24.70	...	...
H	$Na_2CO_3.10H_2O$; NaCl	44.10	....	36.20	...
I	NaCl; KCl	...	....	46.04	19.66
J	$K_2CO_3.{}^3/_2H_2O$; KCl	...	144.16	...	2.50
P	$Na_2CO_3.10H_2O$; NaCl; KCl	46.61	....	24.33	16.64
Q	$Na_2CO_3.10H_2O$; $Na_2CO_3.7H_2O$; KCl	45.90	33.60	16.30	...
R	$Na_2CO_3.7H_2O$; $NaKCO_3.6H_2O$; KCl	47.33	38.79	13.17	...
S	$NaKCO_3.6H_2O$; $K_2CO_3.{}^3/_2H_2O$; KCl	18.72	133.50	...	2.22
T	$NaKCO_3.6H_2O$	47.25	47.25	...	...
U	$NaKCO_3.6H_2O$; KCl	43.80	43.80	...	11.80
O	$Na_2CO_3.10H_2O$; KCl	65.63	....	...	26.64

in equilibrium with the various solid phases. The thermostat used was kept constant to 0.1°. All determinations of potassium were made by separating and weighing as the chloroplatinate. Changes in the solid phases present were followed by a study of the crystal form and optical properties.

The composition of the saturated solutions finally obtained were calculated in terms of the number of grams per 100 g. of water and of moles per 1000 moles of water of the salts necessary to express its composition. The results are given in Tables I and II.

TABLE II

COMPOSITION IN GRAMS PER 100 GRAMS OF WATER OF SOLUTIONS SATURATED AT 25°

	Saturated with	Na_2CO_3	K_2CO_3	Na_2Cl_2	K_2Cl_2
A	$Na_2CO_3.10H_2O$	29.78	....	...	...
B	$NaCl$	...	....	35.66	...
C	KCl	...	....	...	36.97
D	$K_2CO_3.{}^3/_2H_2O$	...	113.57	...	...
E	$K_2CO_3.{}^3/_2H_2O$; $NaKCO_3.6H_2O$	10.89	104.18	...	...
F	$Na_2CO_3.7H_2O$; $NaKCO_3.6H_2O$	35.57	30.48	...	...
G	$Na_2CO_3.10H_2O$; $Na_2CO_3.7H_2O$	35.63	18.96	...	...
H	$Na_2CO_3.10H_2O$; $NaCl$	25.97	....	23.51	...
I	$NaCl$; KCl	...	....	29.88	16.29
J	$K_2CO_3.{}^3/_2H_2O$; KCl	...	110.68	...	2.07
P	$Na_2CO_3.10H_2O$; $NaCl$; KCl	27.45	....	15.81	13.78
Q	$Na_2CO_3.10H_2O$; $Na_2CO_3.7H_2O$; KCl	27.03	25.79	10.59	...
R	$Na_2CO_3.7H_2O$; $NaKCO_3.6H_2O$; KCl	27.86	29.78	8.55	...
S	$NaKCO_3.6H_2O$; $K_2CO_3.{}^3/_2H_2O$; KCl	11.02	102.50	...	1.82
Y	$NaKCO_3.6H_2O$	27.82	36.29	...	...
U	$NaKCO_3.6H_2O$; KCl	25.79	33.64	...	9.78
O	$Na_2CO_3.10H_2O$; KCl	38.65	....	...	22.08

Graphical Representation of the System

Since the system represents a reciprocal salt pair, it can be represented graphically by the method of Löwenhertz as modified by van't Hoff, in which the composition expressed in terms of moles of Na_2Cl_2, K_2CO_3, K_2Cl_2 and Na_2CO_3 is plotted on two lines intersecting at 90°. The resulting diagram based upon the data of Table I is shown in Fig. 1, in which the letters represent "significant points." The positions of these points were fixed by averaging two or more results.

A large number of determinations, which are shown on the diagram as crosses, of points on the lines connecting significant points were found to be necessary to locate the course of these lines accurately. The departures from linear relations are in some cases surprisingly large.

As the hydrates here concerned readily form greatly supersaturated solutions and as long continued stirring was necessary to destroy this condition of supersaturation, great difficulty was found in correctly locating the limits of the fields on the left side of the diagram. The general course

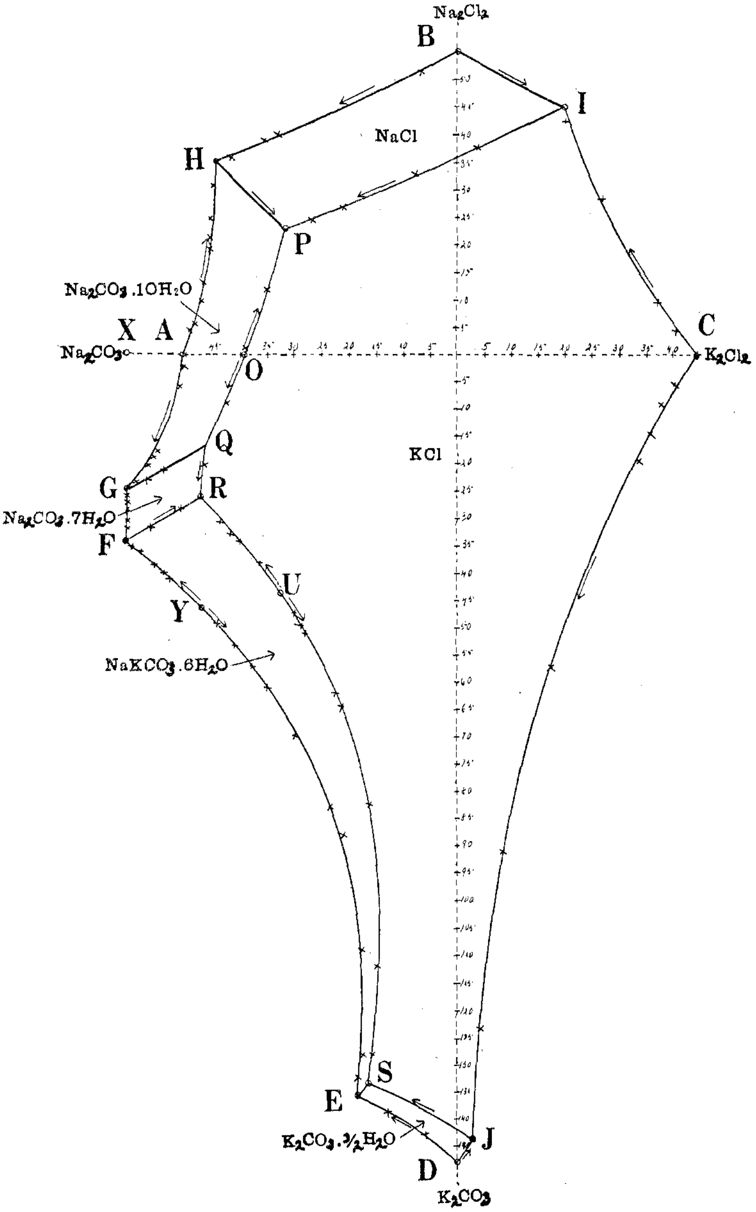

Fig. 1.—Equilibria between water and the carbonates and chlorides of sodium and potassium at 25°

of the broken line A-G-F-E shows a satisfactory degree of agreement with a similar line determined by Kremann and Zitek[10] at a temperature of

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[10] Kremann and Zitek, *Ber. Vinnee Akad.*, **11B**, 118 (1909).

24.2° as part of their work on the system, sodium carbonate-potassium nitrate. Since the solubility of the double salt is very greatly affected and that of the two hydrates of sodium carbonate is affected to a large extent by temperature changes, only rough agreement with their work in the location of the points G and F could be expected.

Although the five-halves hydrate frequently separated in solutions whose composition was represented by points along and beyond the limits of the line EF, no indications of a further break between A and E could be found in spite of the large number of determinations made. This salt also appeared in solutions corresponding to points in portions of the decahydrate, the heptahydrate, the double salt and the potassium chloride fields, but no definite limits within which it separated could be established, and the conclusion was reached that it was always metastable at this temperature.

The lines representing the changes in the composition of solutions which would result from evaporation at 25°, that is, the crystallization paths, have not been shown on the diagram, but their location can be indicated at least approximately with but little difficulty. For the fields representing solutions saturated with respect to $Na_2CO_3.10H_2O$, NaCl, KCl and $K_2CO_3.{}^3/_2H_2O$, these lines must radiate from the points A, B, C and D respectively: for the heptahydrate field they must radiate from the point X, at the intersection of the lines CA and the prolongation of FG; for the double salt field they must radiate from Y, at the intersection of EF and the line bisecting the angle between AC and BD.

Each of the points A, B, C, D and Y represents a solution congruently saturated with respect to a single salt, and each of the points H, I, J, E and F a solution congruently saturated with respect to a pair of salts, but G is not congruently saturated. The points P, R and S represent solutions congruently saturated with respect to three salts, but Q is not a congruent solution although saturated with respect to three salts. Another congruent solution which is saturated with respect to the double salt and potassium chloride must be located on the line RS not far from Y. Its location can be fixed by the following procedure. From a study of the figures representing the composition of solutions on RS in the neighborhood of Y it can be estimated that the point in question should contain K_2Cl_2 to the extent of 11.8 moles. Starting at a point 11.8 units directly to the right of Y, and moving in a direction parallel to the diagonal bisecting the angle between AC and BD, the point at which RS is intersected, that is, the point U, will represent the one desired. Its composition, namely, 11.8 K_2Cl_2, 43.8 K_2CO_3, and 43.8 Na_2CO_3, is such that when evaporated it can lose double salt and potassium chloride in such proportions as to cause no change in its composition.

Still another congruent solution, which is saturated with respect to

$Na_2CO_3.10H_2O$ and KCl, must be represented by a point on the line PQ. Since this solution must contain Na, CO_3, K and Cl in the same proportions as a solution prepared by dissolving sodium carbonate and potassium chloride in water, it must lie on the line AC. The point O therefore possesses the desired properties.

After having ascertained the locations of all the possible congruent solutions it can be predicted that all solutions represented by points lying above AC, except those on the periphery, will when evaporated ultimately attain the composition represented by P: solutions represented by points below YUC will reach S and those between these lines will reach R.

In conclusion it might be noted that this diagram illustrates the behavior of two kinds of congruent solutions. Those represented by H, I, J, E, F, P, R and S indicate the limiting values which can be attained in the composition of certain solutions when they are evaporated. They are crystallization end-points. Those represented by A, B, C, D, Y, U and O indicate points at which the character of the change in the composition of the solution resulting from evaporation changes abruptly. They are points from which certain crystallization paths take their origin.

The System, Water and the Carbonates and Sulfates of Sodium and Potassium at 25°

The solid phases found to be concerned in the system, water and the carbonates and sulfates of sodium and potassium are, in addition to the carbonates described in discussing the chloride-carbonate system, potassium sulfate, the decahydrate of sodium sulfate and glaserite, a salt usually represented by the formula, $3K_2SO_4.Na_2SO_4$, but known to vary slightly as to the relative amounts of the two sulfates owing to the formation of a solid solution. The absence of anhydrous sodium sulfate from the entire system is worthy of comment. Possibly its absence is due to the formation of the sulfate carbonate of sodium to which the name "burkeite"[11] has been given, which was found to separate at slightly higher temperatures. This salt may exist potentially in the form of complex ions at 25°, thereby reducing the concentration of the simple sodium ions and increasing the vapor pressure of the solution to such an extent as to prevent saturation with respect to the anhydrous salt. As in the former system, the five-halves hydrate of sodium carbonate appears as a metastable phase only.

The composition of solutions saturated with respect to one or more of these solids is given in Tables III and IV, and a diagram based upon the data of Table III is given in Fig. 2. Very great difficulty was found in locating the line separating the potassium sulfate and glaserite fields, owing to the extreme slowness with which equilibrium was established in solutions whose composition corresponded to points near this line.

[11] Teeple, *J. Ind. Eng. Chem.*, **13**, 251 (1921).

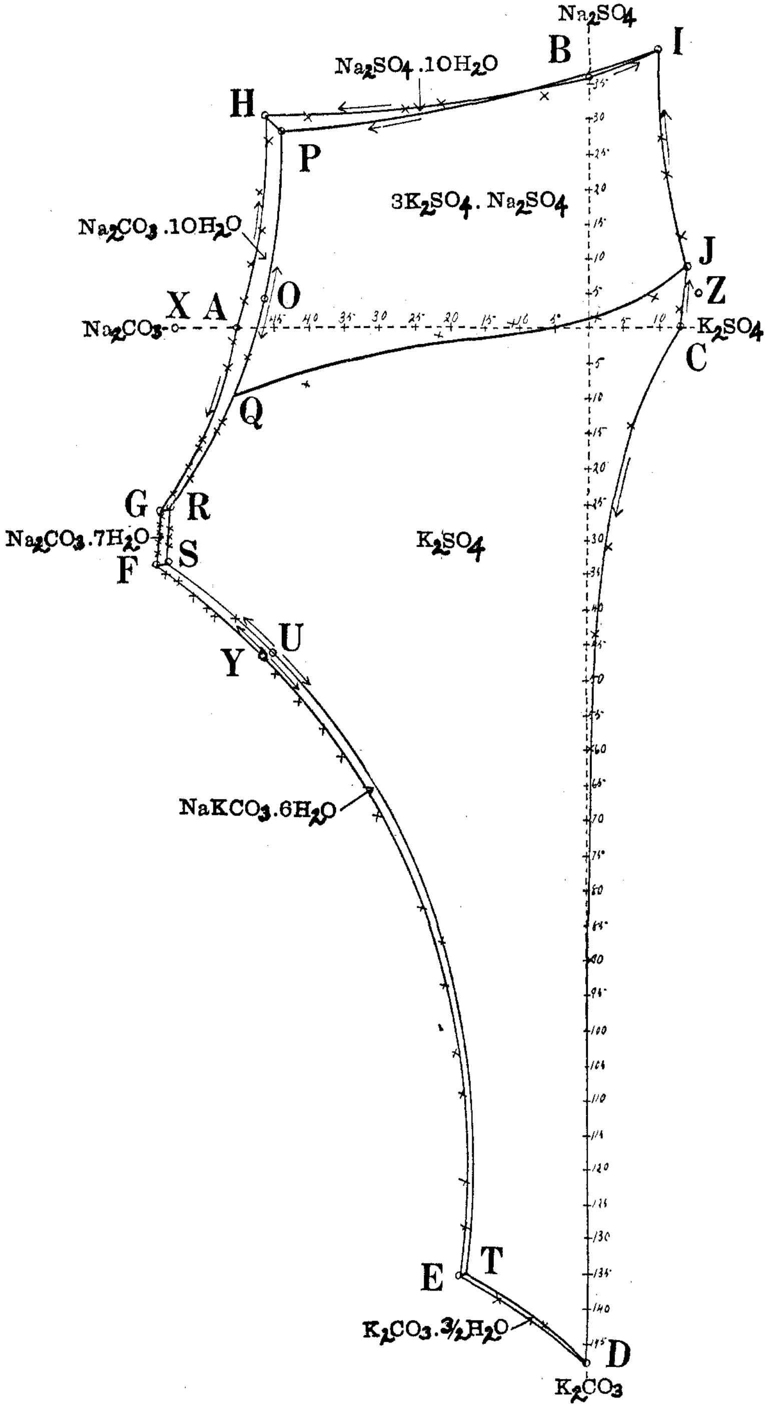

Fig. 2.—Equilibria between water and the carbonates and sulfates of sodium and potassium at 25°

TABLE III

COMPOSITION IN MOLES PER 1000 MOLES OF WATER OF SOLUTIONS SATURATED AT 25°

	Saturated with	Na_2CO_3	K_2CO_3	Na_2SO_4	K_2SO_4
A	$Na_2CO_3.10H_2O$	50.63	....	...	...
B	$Na_2SO_4.10H_2O$	...	....	35.41	...
C	K_2SO_4	...	....	...	12.46
D	$K_2CO_3.{}^3/_2H_2O$	...	147.93	...	...
E	$K_2CO_3.{}^3/_2H_2O$; $NaKCO_3.6H_2O$	18.50	135.70	...	...
F	$NaKCO_3.6H_2O$; $Na_2CO_3.7H_2O$	60.4	39.70	...	...
G	$Na_2CO_3.10H_2O$; $Na_2CO_3.7H_2O$	60.50	24.70	...	...
H	$Na_2CO_3.10H_2O$; $Na_2SO_4.10H_2O$	46.60	....	30.50	...
I	$Na_2SO_4.10H_2O$; $K_3Na(SO_4)_2$	...	....	39.27	9.36
J	K_2SO_4; $K_3Na(SO_4)_2$	...	....	8.70	13.72
P	$Na_2CO_3.10H_2O$; $Na_2SO_4.10H_2O$; $K_3Na(SO_4)_2$	44.30	3.69	32.28	...
Q	$Na_2CO_3.10H_2O$; K_2SO_4; $K_3Na(SO_4)_2$	57.30	9.60	...	6.50
R	$Na_2CO_3.10H_2O$; $Na_2CO_3.7H_2O$; K_2SO_4	60.50	24.10	...	1.50
S	$Na_2CO_3.7H_2O$; $NaKCO_3.6H_2O$; K_2SO_4	60.04	35.26	1.28	...
T	$NaKCO_3.6H_2O$; $K_2CO_3.{}^3/_2H_2O$; K_2SO_4	18.40	135.10	...	1.40
Y	$NaKCO_3.6H_2O$	47.25	47.25	...	...
U	$NaKCO_3.6H_2O$; K_2SO_4	46.50	46.50	...	1.30
O	$Na_2CO_3.10H_2O$; $K_3Na(SO_4)_2$	59.50	....	4.20	12.60

TABLE IV

COMPOSITION IN GRAMS PER 100 GRAMS OF WATER OF SOLUTIONS SATURATED AT 25°

	Saturated with	Na_2CO_3	K_2CO_3	Na_2SO_4	K_2SO_4
A	$Na_2CO_3.10H_2O$	29.78	....	...	...
B	$Na_2SO_4.10H_2O$	...	....	27.94	...
C	K_2SO_4	...	....	...	12.08
D	$K_2CO_3.{}^3/_2H_2O$	...	113.57	...	....
E	$K_2CO_3.{}^3/_2H_2O$; $NaKCO_3.6H_2O$	10.89	104.18	...	...
F	$NaKCO_2.6H_2O$; $Na_2CO_3.7H_2O$	35.57	30.48	...	...
G	$NaCO_3.10H_2O$; $Na_2CO_3.7H_2O$	35.63	18.96	...	...
H	$Na_2CO_3.10H_2O$; $Na_2SO_4.10H_2O$	27.44	....	24.06	...
I	$Na_2SO_4.10H_2O$; $K_3Na(SO_4)_2$	...	....	30.98	9.34
J	K_2SO_4; $K_3Na(SO_4)_2$	...	....	6.86	13.31
P	$Na_2CO_3.10H_2O$; $Na_2SO_4.10H_2O$; $K_3Na(SO_4)_2$	26.09	3.58	25.46	...
Q	$Na_2CO_3.10H_2O$; K_2SO_4; $K_3Na(SO_4)_2$	33.74	7.37	...	6.30
R	$Na_2CO_3.10H_2O$; $Na_2CO_3.7H_2O$; K_2SO_4	35.63	18.50	...	1.45
S	$Na_2CO_3.7H_2O$; $NaKCO_3.6H_2O$; K_2SO_4	35.35	27.07	1.01	...
T	$NaKCO_3.6H_2O$; $K_2CO_3.{}^3/_2H_2O$; K_2SO_4	10.83	103.72	...	1.36
Y	$NaKCO_3.6H_2O$	27.82	36.29	...	...
U	$NaKCO_3.6H_2O$; K_2SO_4	27.38	35.71	...	0.97
O	$Na_2CO_3.10H_2O$; $K_3Na(SO_4)_2$	41.65	....	3.31	9.40

The crystallization paths for fields representing solutions saturated with respect to $Na_2CO_3.10H_2O$, $Na_2SO_4.10H_2O$, K_2SO_4, and $K_2CO_3.{}^3/_2H_2O$ must radiate from the points A, B, C and D. The form of the field for the solid $Na_2SO_4.10H_2O$ is difficult to visualize without a space model of which Fig. 2 is only a projection. The paths for the heptahydrate of sodium carbonate and the double carbonate fields must radiate from the points X and Y, whose positions are located by the construction indicated in the preceding system. Assuming that glaserite has a constant composition indicated by the formula given, the crystallization paths for the glaserite field must radiate from the point Z, obtained by prolonging IJ until it intersects a line representing solutions containing three times as many moles of potassium as of sodium sulfate. Owing to variations in the composition of this solid the directions of these paths can only be indicated with approximate accuracy.

The points A, B, C, D and Y must represent solutions congruently saturated with respect to a single salt and the points **H**, I and E with respect to two salts, but G and J are not congruently saturated. There must also be a point on the line connecting C and D representing a solution congruently saturated with respect to potassium sulfate and the three-halves hydrate of potassium carbonate, but its position is so near to D that it cannot be indicated properly on the diagram. Expressed otherwise the solubility of potassium sulfate in solutions saturated with potassium carbonate is negligible.

From a study of the directions of the crystallization paths it becomes obvious that the points P, S and T represent solutions congruently saturated with respect to three salts, but Q and R are not congruently saturated.

Another congruent solution, which is saturated with respect to potassium sulfate and the double carbonate, must be located on the line ST not far from Y. Its position can be fixed by the following procedure. Solution S contains 1.28 moles of potassium sulfate and T 1.4 moles; therefore a point on the line ST not far from Y might be expected to contain 1.3 moles. Starting from a point located 1.3 units to the right of Y and moving along a line parallel to the line bisecting the angle between AC and BD, the line ST will be intersected at U, which will represent the desired point. It contains in addition to 1.3 moles of K_2SO_4, 46.5 of K_2CO_3 and 46.5 of Na_2CO_3.

Still another congruent solution must be located on the PQ line. Its composition can be established roughly by a series of approximations to be 59.5 Na_2CO_3, 4.2 Na_2SO_4, and 12.6 K_2SO_4. The point in question must be located not far from A but slightly above AC. The number of moles of sodium carbonate present can be estimated to be 59.5, basing the estimate upon the rate at which sodium carbonate changes between P and Q. Starting on AC at a point 59.5 units to the right of the origin and proceeding therefrom in a line parallel to the line which represents three times as many moles of potassium as of sodium sulfate it will be found that PQ is intersected at **O**. This point corresponds to the composition indicated above, and contains that number of moles of sodium carbonate and a total number of moles which its position with respect to

P and Q requires. This procedure involves rather large errors and assumes that the rate at which the composition of the solution changes along the line PQ is uniform as to sodium carbonate and the total number of moles present.

Having fixed the position of O it can be predicted that all solutions represented by points above AOZ except those on the periphery must finally attain the composition P when evaporated. Further owing to the fact that certain crystallization paths pass into the glaserite field from the potassium sulfate field there will be a small triangular area limited by the point C, the intersection of OZ and QJ and the line OZ representing solutions which have the same crystallization end-point. In a like manner it can be predicted that that portion of the diagram limited by the two areas already defined and the line YUC represents solutions for which the crystallization end-point is S, and those portions below the last named line represent solutions for which T is the crystallization end-point.

Summary

1. Certain optical and crystallographic properties of the hydrates of sodium carbonate and of the hydrate of the double sodium-potassium carbonate have been ascertained, which can be used in identifying these compounds by means of the microscope.

2. The solubility data necessary for the preparation of complete phase-rule diagrams for the systems H_2O-Na_2CO_3-KCl and H_2O-Na_2CO_3-K_2SO_4 at 25° have been determined.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, NO. I, 37]

STUDIES RELATING TO METALLO-ORGANIC COMPOUNDS. IV. THE CONDUCTANCE OF TRIMETHYL STANNYL CHLORIDE IN MIXED SOLVENTS

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In preceding numbers of this series it has been shown that the alkyl tin halides are non-conductors when dissolved in solvents of the non-basic type and conductors in solvents of the basic type,[1] such as the amines and the alcohols. It has further been shown that the alkyl metal halides exhibit a marked tendency to combine with ammonia and the amines to form compounds having markedly higher melting points than either of the constituents.[2] While in some instances two molecules of ammonia or amine may combine with an alkyl metal halide, in by far the greater number of instances only a single molecule is involved. Where two molecules of am-

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[1] Kraus and Callis, THIS JOURNAL, **45**, 2624 (1923).

[2] Kraus and Greer, *ibid.*, **45**, 3078 (1923).