

EQUILIBRIA IN AQUEOUS SYSTEMS CONTAINING Sr^{2+} , K^+ , Na^+ AND Cl^-

BY GUNNAR O. ASSARSSON

*Chemical Laboratory of the Geological Survey of Sweden, Stockholm, Sweden**Received April 25, 1952*

The univariant equilibria of the binary system $\text{SrCl}_2\text{-H}_2\text{O}$ and of the ternary systems $\text{SrCl}_2\text{-KCl-H}_2\text{O}$ and $\text{SrCl}_2\text{-NaCl-H}_2\text{O}$ as well as of the quaternary system $\text{SrCl}_2\text{-KCl-NaCl-H}_2\text{O}$ have been examined, and isotherms at 18, 60 and 100° obtained. Only the already known hexahydrate and dihydrate of strontium chloride occur in equilibrium with the solutions between 18 and 115° . The transition temperatures of strontium chloride hexahydrate-dihydrate in the systems mentioned are, respectively, 61.3 , 58.5 ± 0.5 , 59.5 ± 0.5 , $56.0 \pm 0.5^\circ$. No double salt exists in equilibrium with the solutions within the temperature interval $18\text{--}115^\circ$.

In an earlier paper¹ the crystallization of aqueous solutions containing calcium chloride and alkali chlorides was described, giving particular consideration to the isolation of salts from some kinds of brine. As such brines often contain a not insignificant amount of strontium chloride² it seems to be necessary in certain cases to know in what way this component influences the crystallization of the solids. No investigations concerning this topic have been published. Moreover the earlier investigated system calcium chloride-potassium chloride-water contains a double salt, $\text{CaCl}_2\cdot\text{KCl}$, so that it is also of particular interest to know, whether an analogous compound containing strontium chloride and alkali chloride can exist under similar conditions. The literature on strontium is reported in Gmelin's "Handbuch der anorganischen Chemie," system nr 29, in which book all investigations up to 1931 are taken into consideration.

Experimental

The experiments were carried out as described in the earlier paper. The methods for determination of strontium earlier published were critically reviewed and tested. The method which worked most accurately and rapidly was found to be the precipitation of strontium as carbonate with ammonium carbonate. After heating the sample of strontium chloride solution with ammonium carbonate on the steam-bath for about one hour and cooling down to room temperature the precipitate formed was filtered off, washed with water containing a little ammonium carbonate, and then with alcohol, dried by heating to 550° and weighed. It is not convenient to dry the precipitate at 120° , as it contains 1.5–2.0% humidity which can only be removed at higher temperature. Temperatures higher than 650° should not be employed if the precipitate is weighed in a porcelain filter crucible as the filter is easily attacked at high temperatures. When 0.5 g. of substance was used for the analysis the error of this determination method of strontium chloride was found to be within 0.05%. In the filtered solutions the other components of the systems in question were determined by standard methods. The strontium chloride used in the experiments was obtained from Baker ("Baker's Analyzed"), the impurities being about 0.1%, chiefly alkali chlorides.

The figures in the tables are weight per cent.

The Binary System $\text{SrCl}_2\text{-H}_2\text{O}$.—As the earlier investigations on the binary system are not quite complete and diverge in some points concerning the observations between 15 and 115° , the solubility of strontium chloride in pure water was re-examined. In the literature the determinations by Mulder³ and by Tilden⁴ are usually cited. The

system contains a hexahydrate and a dihydrate; the transition temperature was very carefully determined by Richards and Yngve⁵ as 61.341° . Moreover, Hüttig and Slonim,⁶ working with an eudiotensimeter, found a break on the $t\text{-}p$ curve, from which they concluded that there should exist a monohydrate of strontium chloride at temperatures higher than 93° . The equilibrium between this suggested hydrate and its solutions is not known. Some dehydration curves are determined by Lescoeur,⁷ and Etard⁸ the curves show that a dihydrate and perhaps also a monohydrate exist, the equilibrium conditions of the monohydrate being not exactly defined.

TABLE I

THE BINARY SYSTEM $\text{SrCl}_2\text{-H}_2\text{O}$

Solid phases: B, $\text{SrCl}_2\cdot 6\text{H}_2\text{O}$; C, $\text{SrCl}_2\cdot 2\text{H}_2\text{O}$. Wet residues: (1) 56.4; (2) 57.9; (3) 74.2; (4) 75.6.

Composition of the saturated solutions between 18 and 114°			Temp., $^\circ\text{C}$.			Solution SrCl_2			Solid phase		
Temp., $^\circ\text{C}$.	Solution SrCl_2	Solid phase	Temp., $^\circ\text{C}$.	Solution SrCl_2	Solid phase	Temp., $^\circ\text{C}$.	Solution SrCl_2	Solid phase	Temp., $^\circ\text{C}$.	Solution SrCl_2	Solid phase
18.0	34.15	B	65.0	46.95	C						
30.0	37.00	B	70.0	47.30	C						
40.0	39.45	B	80.0	48.30	C						
50.0	42.20	B	90.0	49.35	C						
60.0	46.10	B (1)	100.0	50.80	C						
60.8	46.50	B (2)	110.0	52.20	C						
61.3	46.65	C (3)	114.0	53.0	C						
62.0	46.75	C (4)	Transition point								
			61.3	46.65	B, C						

Figure 1 and Table I give the composition of the saturated solutions between 18 and 115° . The transition temperature hexahydrate-dihydrate was found to be 61.3° . In the diagram there are also plotted the determinations by Mulder and by Tilden as well as the solubility figures from "Handbook of Chemistry and Physics" (1947). Both these series of figures diverge sometimes by more than 0.5% from the values found in this investigation.

Solids in equilibrium with the solutions have been prepared with the greatest carefulness in order to make it possible to study the properties of the crystals. Large and apparently completely homogeneous crystals were prepared according to the methods of Wulff and Heigl,⁹ Wulff,¹⁰ Schub-

(1) G. O. Assarsson, *J. Am. Chem. Soc.*, **72**, 1433 (1950).

(2) Cf., e.g., W. Stout, K. E. Lamborn and D. Schaaf, "Brines of Ohio," Geol. Survey of Ohio, Ser. 4, Bull. 37. Some Swedish brines, too, contain sometimes a not insignificant amount of Sr.

(3) G. J. Mulder, "Scheik. Verhandelingen," Vol. III, Rotterdam, 1864, p. 118.

(4) W. A. Tilden, *J. Chem. Soc.*, **45**, 269 (1884).

(5) T. W. Richards and V. Yngve, *J. Am. Chem. Soc.*, **40**, 89 (1918).

(6) G. F. Hüttig and Ch. Slonim, *Z. anorg. Chem.*, **181**, 76 (1929).

(7) H. Lescoeur, *Ann. chim. phys.*, [6] **19**, 538 (1890).

(8) A. L. Etard, *Compt. rend.*, **113**, 864 (1891).

(9) P. Wulff and A. Heigl, *Z. Krist.*, **77**, 111 (1931).

(10) L. Wulff, *ibid.*, **14**, 552 (1882).

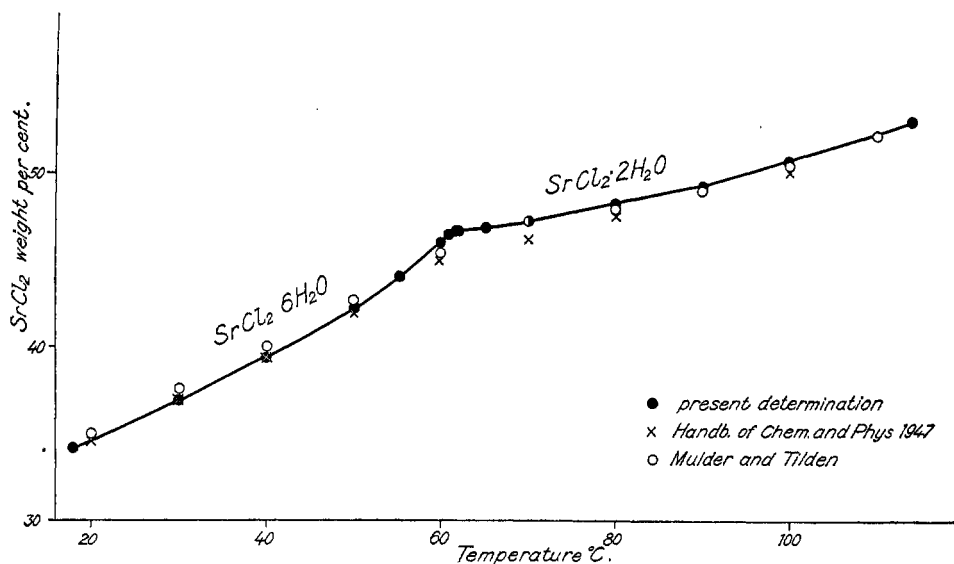


Fig. 1.—Solubility of strontium chloride in water 18–114°.

nikow,¹¹ and others with moving or stationary solutions. The crystals formed were rapidly removed from the mother liquor, washed with alcohol and ether, dried between paper and taken for the analyses. Three of these analyses are listed below.

Crystn. temp., °C.	Molar compn. $\text{SrCl}_2:\text{H}_2\text{O}$
64	1:2.22
84	1:2.22
105	1:2.28

The crystals analyzed seemed to be quite perfect, having the optical properties known from Wulff and Heigl⁹ (α 1.594, γ 1.617); no interpositional liquid drops or lamellar liquid layers could be observed. Observations in a polarizing microscope with an electrically heated stage have confirmed that no transformation of the dihydrate takes place between 62 and 110°.

Further in order to decide if there could exist a lower hydrate than dihydrate in equilibrium with the saturated solution three other methods have been used: the determination of the cubic heat expansion with a dilatometer, the method of differential thermal analysis, and the examination of the solids by the aid of X-ray diffraction (powder diagrams).

The determination of the cubic heat expansion gave a straight line between 66 and 102°. The value of the heat expansion per degree was found to be 8×10^{-5} .

The differential thermal analysis was performed in an oil thermostat. The sample of strontium chloride was previously dried at 55° to about 81% water-free salt, and carefully mixed with a fifth of the hexahydrate. Sodium chloride was used as neutral substance. The vessels (test-tubes) were closed with a piece of asbestos. The only reaction which could be observed between 50 and 115° was the peak of the endothermic transformation of the present hexahydrate into dihydrate at 61°.

To confirm the results a sample of the fine-

pulverized mixture of dihydrate and hexahydrate mentioned above was exposed in a Unicam-heat camera to $\text{CuK}\alpha$ radiation at a temperature of 110°. The reflections measured at the exposure were those of the dihydrate, the structure of which is known from the investigations by Tovborg-Jensen.¹²

The Ternary System $\text{SrCl}_2\text{--KCl--H}_2\text{O}$.—In this system three isotherms have been worked out: 18, 60 and 100° (Table II, Fig. 2). They show only the hydrates of strontium chloride already known and pure potassium chloride.

The composition of the solutions at the isothermally invariant equilibria have been examined. In Table IV (Fig. 2) part of the determinations are listed. The concentration of potassium chloride changes very insignificantly between 18 and 58.5°, which is the transition temperature hexahydrate–dihydrate in this system. At higher temperatures the solubility of the potassium chloride at the equilibria increases appreciably, obviously as a result of the formation of strontium chloride dihydrate. No solids of the character of a double salt, however, could be found up to 114°.

TABLE II

THE TERNARY SYSTEM $\text{SrCl}_2\text{--KCl--H}_2\text{O}$

Solid phase: A, KCl; B, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$; C, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$.
Wet residues: (1) 10.0, 77.0; (2) 58.0, 0.6; (3) 11.4, 70.7; (4) 78.0, 1.4; (5) 73.8, 0.9; (6) 60.8, 0.7; (7) 57.9, 0.7; (8) 25.5, 55.5; (9) 69.6, 4.8; (10) 47.9, 8.0.

Isotherm, 18°			Isotherm, 60°			Isotherm, 100°		
SrCl ₂	KCl	Solid phase	SrCl ₂	KCl	Solid phase	SrCl ₂	KCl	Solid phase
..	25.4	A	..	31.3	A	..	36.2	A
14.2	15.7	A	18.5	18.1	A	16.9	24.7	A
24.8	9.8	A	29.3	12.3	A	28.9	17.4	A
30.5	7.5	A (1)	39.9	8.0	A (3)	35.9	13.8	A
31.0	7.2	A, B	43.5	7.2	A, C	44.2	11.1	A
32.0	4.6	B (2)	43.8	6.7	C (4)	46.5	10.9	A (8)
34.3	..	B	45.1	3.7	C	46.7	10.8	A, C
			45.2	3.3	C (5)	46.9	10.1	C (9)
			45.6	2.7	B, C (6)	47.9	8.0	C (10)
			45.7	2.6	B (7)	50.8	..	C
			46.2	..	B			

(11) A. Schubnikow, *Z. Krist.*, **50**, 20 (1912). The book "Crystal Growth," H. E. Buckley, appeared in 1951 after the completion of the work here recorded.

(12) A. Tovborg-Jensen, *Kgl. Danske Videnskab. Selskab. Mat. fys. Medd.*, Bd XX, nr 5. (1942).

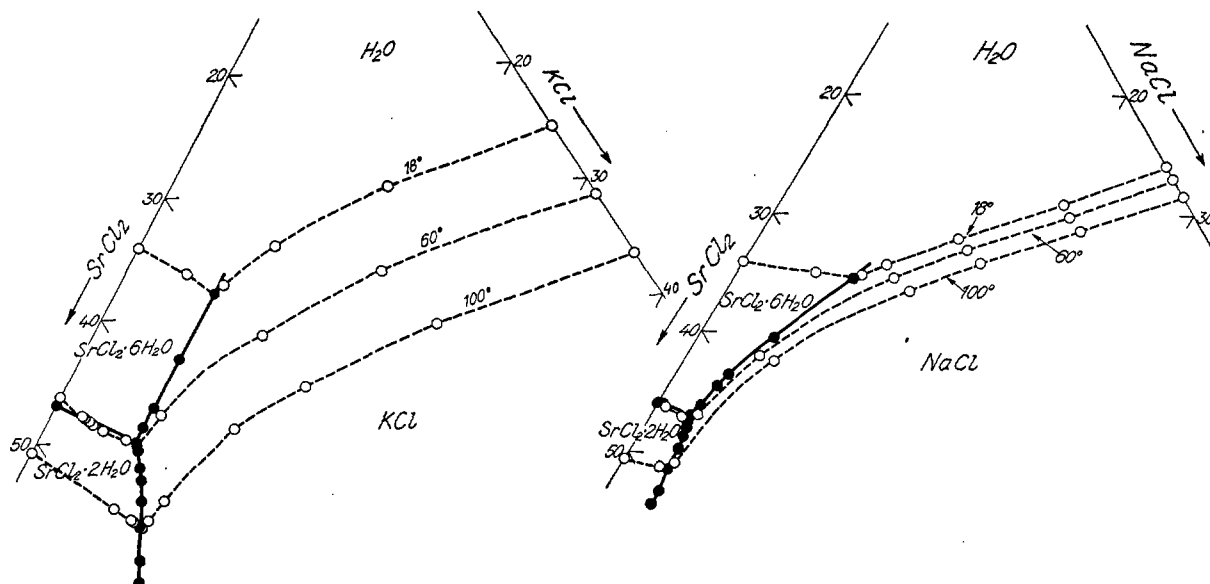


Fig. 2.—The ternary systems $\text{SrCl}_2\text{-KCl-H}_2\text{O}$ and $\text{SrCl}_2\text{-NaCl-H}_2\text{O}$, 18–114°: isotherms (dashed lines), isothermally invariant points (full-drawn lines).

The thermal examination of the system showed only the transition point hexahydrate-dihydrate ($58.5 \pm 0.5^\circ$), and the X-ray investigation at 110° only the interferences of the ordinary dihydrate.

The Ternary System $\text{SrCl}_2\text{-NaCl-H}_2\text{O}$.—This system has the same character as the system strontium chloride-potassium chloride-water. The isotherms at 18, 60 and 100° have been worked out (Table III, Fig. 2). The curves are regular and have a break only at the isothermally invariant points strontium chloride hexahydrate-dihydrate or the strontium chloride hydrates-sodium chloride. The solubility of sodium chloride at the isothermally invariant points (Table IV, Fig. 2) decreases slowly from 18° to the invariant point (59.5°). At higher temperatures the concentration of sodium chloride in these solutions is nearly constant. No compounds of double salt type were found.

TABLE III

THE TERNARY SYSTEM $\text{SrCl}_2\text{-NaCl-H}_2\text{O}$

Solid phase: B, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$; C, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$; D, NaCl. Wet residues: (1) 56.0, 2.8; (2) 12.0, 72.0; (3) 71.7, 0.7; (4) 71.4, 0.3; (5) 56.6, 0.2; (6) 15.0, 70.0; (7) 69.0, 1.4.

Isotherm, 18°			Isotherm, 60°			Isotherm, 100°		
SrCl ₂	NaCl	Solid phase	SrCl ₂	NaCl	Solid phase	SrCl ₂	NaCl	Solid phase
..	26.0	D	..	27.0	D	..	28.5	D
9.0	20.1	D	8.9	21.2	D	8.8	22.5	D
18.0	14.2	D	17.8	15.2	D	17.5	17.2	D
24.3	10.1	D	24.0	11.6	D	23.6	13.1	D
26.7	8.7	D	36.9	5.1	D	36.4	6.6	D
27.1	8.6	B, D	44.0	3.0	D (2)	48.0	3.8	D (6)
28.0	7.2	B (1)	44.3	2.9	C, D	48.2	3.6	C, D
29.6	5.5	B	44.8	2.2	C (3)	48.7	3.5	C (7)
34.3	..	B	45.8	0.9	C (4)	50.8	..	C
			46.1	0.5	B (5)			
			46.2	..	B			

The Quaternary System $\text{SrCl}_2\text{-KCl-NaCl-H}_2\text{O}$

—The isotherms at 18, 60 and 100° have been obtained (Tables V, VI). The composition of the solutions at the isothermally invariant equilibria have been determined (Table VI). The system contains no binary or ternary compounds, only the single salts and the hydrates of strontium chloride

TABLE IV

ISOTHERMALLY INVARIANT EQUILIBRIA IN THE TERNARY SYSTEMS BETWEEN 18 AND 114°

Solid phases: A, KCl; B, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$; C, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$; D, NaCl. Wet residues: (1) 55.0, 2.6; (2) 57.5, 2.2; (3) 63.2, 3.6; (4) 56.1, 1.0; (5) 68.6, 1.1.

$\text{SrCl}_2\text{-KCl-H}_2\text{O}$				$\text{SrCl}_2\text{-NaCl-H}_2\text{O}$			
Temp., $^\circ\text{C}$.	SrCl ₂	KCl	Solid phase	Temp., $^\circ\text{C}$.	SrCl ₂	NaCl	Solid phase
18.0	31.0	7.2	A, B	18.0	27.1	8.6	B, D
40.0	36.4	7.1	A, B	40.0	35.2	5.1	B, D
50.0	40.1	7.0	A, B	50.0	39.3	3.9	B, D
54.7	42.1	7.1	A, B (1)	55.0	41.5	3.4	B, D
57.5	43.1	7.2	A, B (2)	58.7	43.6	3.1	B, D (4)
58.7	43.3	7.2	A, C (3)	59.6	44.2	2.9	C, D (5)
60.0	43.5	7.2	A, C	60.0	44.3	2.9	C, D
70.0	43.9	8.2	A, C	70.0	44.9	3.1	C, D
80.0	44.5	8.9	A, C	80.0	45.9	3.3	C, D
90.0	45.4	9.8	A, C	90.0	46.6	3.4	C, D
100.0	46.7	10.8	A, C	100.0	48.2	3.6	C, D
110.0	48.7	11.9	A, C	110.0	49.8	3.7	C, D
114.0	49.4	12.4	A, C	114.0	50.1	3.8	C, D

mentioned earlier. The invariant point alkali chlorides-strontium chloride hexahydrate-dihydrate was found to be at $56.0 \pm 0.5^\circ$. The

TABLE V

THE QUATERNARY SYSTEM $\text{SrCl}_2\text{-KCl-NaCl-H}_2\text{O}$

Solid phases: A, KCl; B, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$; C, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$; D, NaCl. Wet residues: (1) 56.0, 0.7, 0.9; (2) 16.4, 70.0, 1.0; (3) 18.2, 4.4, 59.0; (4) 67.5, 2.7, 1.0.

Isotherm at 18°				Isotherm at 60°			
SrCl ₂	KCl	NaCl	Solid phase	SrCl ₂	KCl	NaCl	Solid phase
..	..	26.0	D	27.0	D
..	25.4	..	A	..	31.3	..	A
..	10.1	20.9	A, D	..	16.1	18.7	A, D
7.7	9.0	16.4	A, D	8.2	15.1	13.9	A, D
25.1	6.3	7.5	A, D	16.2	12.6	10.6	A, D
26.1	6.1	7.4	A, D	22.0	10.8	8.2	A, D
26.2	6.0	7.3	A, B, D	34.3	7.9	4.0	A, D
26.5	5.8	7.4	A, B, D (1)	41.6	8.4	1.2	A, D (2)
27.1	..	8.6	B, D	41.4	6.9	2.5	A, D, (3)
31.0	7.2	..	A, B	41.5	7.0	2.6	A, C, D
34.2	B	41.6	7.1	2.6	A, C, D (4)
				43.3	7.2	..	A, C
				44.3	..	2.9	C, D
				45.7	B

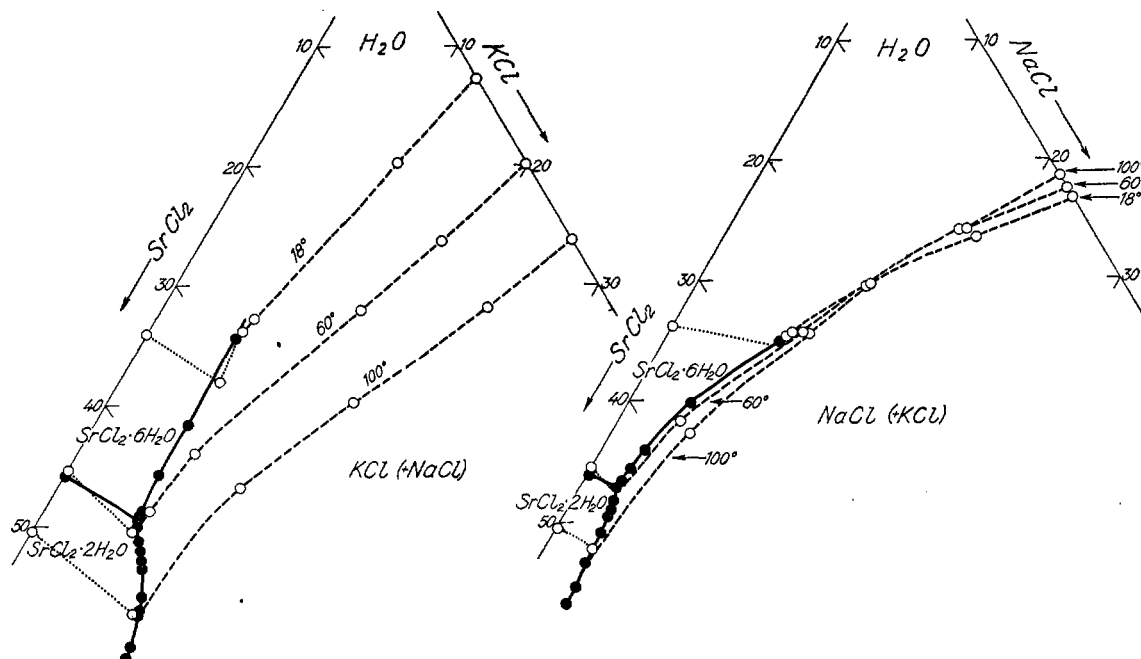


Fig. 3.—The quaternary system $\text{SrCl}_2\text{--KCl--NaCl--H}_2\text{O}$, 18–114°, projections on the $\text{SrCl}_2\text{--KCl--H}_2\text{O}$ plane and on the $\text{SrCl}_2\text{--NaCl--H}_2\text{O}$ plane: isothermally invariant points, full-drawn lines; isotherms, dashed lines, solid alkali chlorides present; dotted lines, solid potassium chloride and strontium chloride present, or solid sodium chloride and strontium chloride present.

dilatometrical and thermal analysis methods gave no reason to presume the presence of hydrates or crystal forms between 18 and 114° other than those already mentioned.

chloride does exist. Some experiments of this kind have been made in connection with the determinations above. The strontium chloride dihydrate is transformed into a monohydrate in an air-

TABLE VI

THE QUATERNARY SYSTEM $\text{SrCl}_2\text{--KCl--NaCl--H}_2\text{O}$

Solid phases: A, KCl; B, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$; C, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$; D, NaCl. Wet residues: (1) 15.0, 65.2, 2.5; (2) 16.2, 2.2, 67.4; (3) 65.2, 4.2, 1.7; (4) 55.0, 1.6, 1.0; (5) 55.1, 1.8, 1.0; (6) 62.6, 3.2, 1.5; (7) 63.0, 3.0, 1.4.

Isotherm at 100°				Isothermally invariant equilibria 18–114°				
SrCl_2	Solution KCl	NaCl	Solid phase	SrCl_2	Solution KCl	NaCl	Solid phase	Temp., °C.
..	..	28.3	D	26.2	6.0	7.3	A, B, D	18.0
..	36.0	..	A	33.5	6.5	7.2	A, B, D	40.0
..	21.8	16.8	A, D	38.4	6.7	3.0	A, B, D	50.0
7.6	20.1	13.8	A, D	40.8	6.8	2.6	A, B, D (4)	54.7
20.8	15.7	8.3	A, D	41.5	6.9	2.5	A, B, D (5)	55.8
32.4	12.2	5.1	A, D	41.3	6.8	2.6	A, C, D (6)	56.5
44.6	10.1	2.9	A, D (1)	41.3	6.7	2.5	A, C, D (7)	57.0
44.2	9.9	3.1	A, D (2)	41.5	7.0	2.6	A, C, D	60.0
44.8	10.3	2.9	A, C, D	42.0	7.8	2.8	A, C, D	70.0
44.9	10.2	2.7	A, C, D (3)	42.6	8.6	2.8	A, C, D	80.0
46.7	10.8	..	A, D	43.4	9.2	2.8	A, C, D	90.0
48.2	..	3.6	C, D	46.9	11.4	2.9	A, C, D	110.0
50.8	C	47.6	11.8	2.9	A, C, D	114.0

The possibility of the occurrence of other crystalline forms has been examined circumstantially because of the existence of a monohydrate mentioned by Lescoeur and by Hüttig and Slonim. It is very easy to control with the aid of thermal dehydration that a monohydrate of strontium

current with about 5 mm. tension pressure of water vapor at a temperature between 53 and 59°. At higher temperature (100°) the last traces of water of crystallization are slowly lost. As shown above, these transformations cannot, however, take place in saturated solutions up to 115°.