

EQUILIBRIA BETWEEN 18 AND 114° IN THE AQUEOUS TERNARY SYSTEM CONTAINING Ca^{2+} , Sr^{2+} AND Cl^-

BY GUNNAR O. ASSARSSON AND AINO BALDER

Chemical Laboratory of The Geological Survey of Sweden, Stockholm

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The system strontium chloride–calcium chloride–water has been investigated between 18 and 114°. No double salt has been found within this temperature range. The hexahydrates of the chlorides form solid solution crystals of complete miscibility belonging to Roozeboom's type I, the cell axes of these crystals being slightly shorter than those calculated from Vegard's law. The dehydrating properties of the concentrated calcium chloride solutions cause an appreciable lowering of the transition temperature strontium chloride hexahydrate–dihydrate so that the field of stable existence of strontium chloride dihydrate overlaps the region of stability of the solid solution of the hexahydrates. In this way a new type of isothermal solid solution diagram appears: a continuous miscibility of the end phases is interrupted by a gap within which the stable phase is a compound not belonging to the end phases. The boundary curve between strontium calcium chloride hexahydrate (solid solution) and strontium chloride dihydrate has a temperature minimum at $28.2 \pm 0.2^\circ$. The invariant point at which strontium calcium chloride hexahydrate (solid solution) is in equilibrium with α -calcium chloride tetrahydrate, strontium dihydrate and liquid is at $29.4 \pm 0.1^\circ$. Another invariant point occurs at $44.9 \pm 0.2^\circ$ at which temperature α -calcium chloride tetrahydrate may exist in equilibrium with calcium chloride dihydrate, strontium chloride dihydrate and liquid. At higher temperatures strontium chloride monohydrate is deposited, its lowest formation temperature being at $76 \pm 1^\circ$. The X-ray interferences of this new compound are given. The observations on the system are combined in a synopsis diagram.

In an earlier paper,¹ the results were reported of an investigation on the equilibrium between strontium chloride and alkali chlorides in aqueous solutions, with regard to the crystallization of salt from certain brines. Calcium chloride is also a usual component of such brines. Among the crystalline phases in salt deposits strontium chloride should occur either as a pure compound or in phases in which it could be combined with other components, although these phases have not yet been observed and recorded. It may be suggested that the phases containing strontium chloride could be utilized as temperature indicators for the crystallization of the salt deposits and it would therefore be of considerable interest to know the equilibria in the systems containing the chlorides of the alkalies as well as those of calcium and strontium.

Experimental

The experiments were performed as described in the earlier papers. Some difficulty was encountered in finding a rapid and accurate method for the determination of calcium and strontium chloride when occurring together. An indirect physical chemical method, based on the electrical conductivity of the aqueous solutions, was tried and worked out; it is described elsewhere.² For the elucidation of the character of the crystal phases the methods of optical microscopy, of thermal analysis, and of X-ray identification were used. In this work the equilibria between 18 and 114° were studied.

In the tables all determinations are given as weight per cent.

Discussion of the Results

It can be expected that the calcium chloride in the solutions will depress the solubility of strontium chloride. This appears in fact in the isotherms; the solubility of strontium chloride in concentrated calcium chloride solutions is very low (about 1–2%). As the water of crystallization of strontium chloride hexahydrate is partly loosely bound, the transition temperature of strontium chloride hexahydrate–dihydrate should be lowered appreciably with increasing calcium chloride content.

The transition temperature strontium chloride hexahydrate–dihydrate is at 61.3° in the binary

system strontium chloride–water, and in the present ternary system the strontium chloride dihydrate has its lowest formation temperature at 28.2° . The transition temperature of calcium chloride α -tetrahydrate–dihydrate is insignificantly affected by the presence of strontium chloride; the temperatures are 45.3 and 44.9° , respectively, in the binary system calcium chloride–water and in the present ternary system (Table I, point E).

The equilibria in which the hexahydrates of calcium and strontium chlorides are present have a certain interest. Eppler³ has shown by goniometrical measurements that the hexahydrates are isomorphous and trigonal. Herrmann⁴ and later Tovborg-Jensen⁵ have recorded that the two phases mentioned have a unit cell of almost the same dimensions. Because the hexahydrates are isomorphous and there is no considerable difference between the ionic radii of Ca^{2+} and Sr^{2+} , they should be able to form solid solution (mixed crystals). The study of the isothermal equilibria in the present investigation has shown the conditions for the formation of the solid solution. The isotherms between 18.0 and 28.0° have no breaks indicating isothermal invariant points. Instead of the break there is a flexure on the curves, which are S-shaped close to the calcium chloride axis of the diagrams (see Table I and Fig. 1, the isotherms at 18.0 and 28.0°), and the composition of the solid phase changes successively with the concentration of the mother liquor, two characteristic phenomena shown when a solid solution crystallizes. It can be estimated from the tie-lines of Fig. 1 that a solid solution containing equal parts of the two hexahydrates requires a mother liquor containing 1.4–2.1% strontium chloride and 39–42% calcium chloride between 18.0 and 28.0° . The distribution diagram according to Roozeboom (Fig. 2, 28.0°) illustrates the dependence of the composition of the solid solution on the concentration of the solutions. As the curve first follows very close to one of the axes of the distribution

(3) A. Eppler, *Z. Krist.*, **30**, 149 (1899).(4) L. Herrmann, *Z. anorg. allgem. Chem.*, **197**, 212 (1931).(5) A. Tovborg-Jensen, *Danske Videnskab. Selskab. Mat.-fys. Medd.*, **XVII**, 9 (1940), (Copenhagen) (English).(1) G. O. Assarsson, *This Journal*, **57**, 207 (1953).(2) G. O. Assarsson and A. Balder, *Anal. Chem.*, **24**, 1679 (1952)

TABLE I

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

Symbols for the solid phases, used in the tables: a, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$; b, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$; c, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$; d, $\alpha\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$; e, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; f, solid solution of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$; g, $\text{SrCl}_2 \cdot \text{H}_2\text{O}$. Some isotherms between 18 and 45°.

Solution		Wet residue		Solid phase	Solution		Wet residue		Solid phase
SrCl ₂	CaCl ₂	SrCl ₂	CaCl ₂		SrCl ₂	CaCl ₂	SrCl ₂	CaCl ₂	
18°									
34.15	a	1.7	44.3	54.6	15.5	b
26.9	6.6	f	1.6	44.6	9.6	41.2	f
18.0	14.6	f	1.4	45.2	8.2	42.6	f
4.0	31.2	42.0	10.5	f	1.4	45.8	5.8	44.8	f
3.0	33.3	41.2	12.2	f	1.1	46.8	2.6	47.2	f
2.1	35.5	40.3	13.6	f	0.9	47.7	1.9	48.7	f
1.9	37.7	27.6	22.4	f	0.2	48.7	0.5	49.0	f
1.4	38.7	22.5	28.4	f	...	49.2	..	49.8	c
1.1	39.7	18.9	31.2	f	29.3°				
0.7	40.4	10.0	40.6	f	3.7	38.5	41.5	14.2	f
0.5	40.6	5.0	43.0	f	3.5	39.9	35.9	18.3	f
0.4	41.2	1.5	46.0	f	3.4	40.2	50.0	11.6	b + f
0.3	41.4	1.0	48.9	f	2.7	41.6	55.3	14.3	b
...	42.05	c	2.5	42.4	54.7	15.1	b
28.0°					2.3	42.8	55.5	14.9	b
36.6	a	1.9	44.8	54.5	16.0	b
17.6	17.2	44.8	6.3	f	1.7	46.5	9.0	42.0	f
6.0	30.7	39.0	7.0	f	1.4	47.4	4.5	46.7	f
3.4	35.4	35.7	16.0	f	0.7	48.7	1.8	48.7	f
2.7	40.1	34.6	19.0	f	0.3	49.1	0.9	49.6	f
2.2	41.7	20.4	31.4	f	...	49.6	..	49.8	c
2.1	42.3	15.9	35.4	f	29.7°				
1.7	43.6	11.1	39.4	f	37.0	a
1.5	44.3	5.3	44.0	f	28.7	7.5	57.0	1.0	f
1.0	45.2	5.7	44.7	f	13.5	21.9	56.3	1.6	f
1.1	45.9	2.9	47.1	f	7.4	29.5	42.0	10.6	f
1.0	46.1	2.4	47.3	f	3.1	39.4	35.5	19.0	f
0.6	46.6	1.6	48.3	f	3.0	40.4	48.4	11.2	b + f
...	47.2	c	2.0	42.2	54.1	14.9	b
28.5°					1.4	44.6	52.7	16.9	b
2.6	40.3	33.6	20.3	f	1.3	46.6	54.8	16.2	b
2.6	40.9	22.8	29.0	f	1.4	46.9	47.0	21.4	b
2.4	42.2	52.9	16.1	b	1.2	47.7	47.0	21.7	b
2.3	42.7	52.5	17.0	b	1.2	48.2	47.5	22.0	b
1.7	44.1	52.1	17.6	b	1.0	49.2	6.0	49.0	b + d
1.6	44.2	8.7	41.1	f	1.0	49.0	0.7	57.4	d
1.3	44.6	8.2	42.1	f	0.8	49.2	0.5	57.7	d
1.2	45.2	6.6	43.9	f	...	50.2	..	56.7	d
1.0	46.0	3.5	46.0	f	44.3°				
0.8	46.9	2.9	47.1	f	9.6	31.6	45.7	10.4	f
...	47.9	..	49.5	c	7.2	34.4	53.5	13.5	b
29.0°					1.0	55.2	0.4	59.7	d
29.0°					44.7°				
36.8	a	44.7°				
20.0	16.0	55.0	2.0	f	1.0	55.0	35.1	31.9	b
6.4	30.6	39.1	12.0	f	0.9	55.6	0.4	59.0	d
2.8	39.1	34.9	19.1	f	45.3°				
2.9	40.6	33.0	21.0	f	0.9	56.0	34.0	33.6	b
2.9	41.6	58.7	13.1	b	0.9	56.3	0.1	69.2	e
2.5	42.0	55.0	15.0	b	For the invariant points (C, D, E, in Fig. 5)				
2.5	42.5	57.7	14.5	b	Solution				
1.7	44.0	59.7	11.7	b	SrCl_2 CaCl_2				
					C 28.2 ± 0.2°	2.0	42.2	b + f	
					D 29.4 ± 0.1°	1.0	48.5	b + d + f	
					E 44.9 ± 0.2°	1.0	55.7	b + d + e	

diagram up to a very high concentration of one of the components, and then follows the direction of the other axis, it can be concluded that the forma-

tion of the solid phase is connected with extraordinary properties of the liquid phase. Other plotting methods point to the same conclusion.

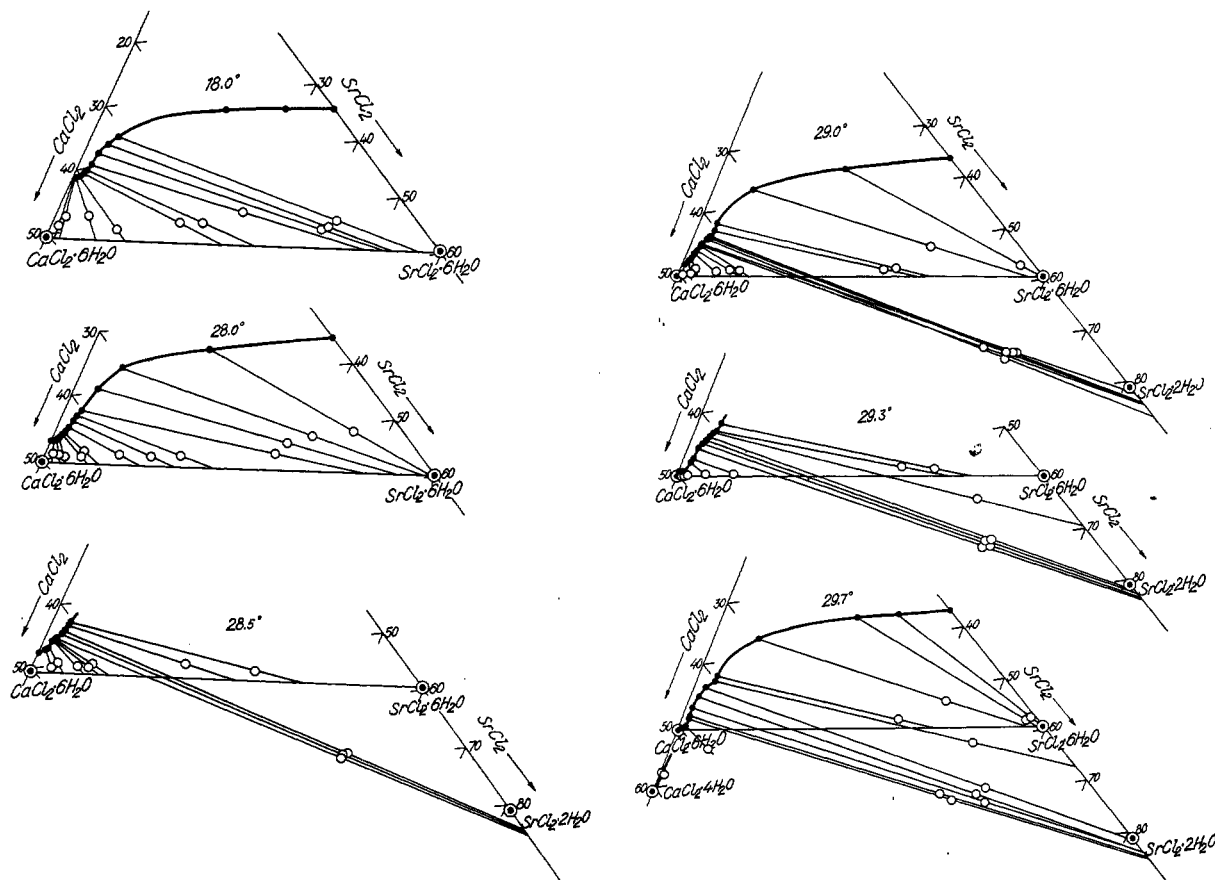


Fig. 1.—Some isotherms between 18.0 and 29.7°.

The plot of $\log R_1$ against R_s (R_1 = mole ratio of the dissolved salts, R_s = mole ratio of the solid phase) and the plot of $\log (R_1/R_s)$ against the mole fraction in the solid are not linear, so that the distribution coefficient is not constant and the solid

TABLE II

CALCULATED AND OBSERVED INTERFERENCES IN POWDER DIAGRAMS OF $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, AND A SOLID SOLUTION CONTAINING 50% OF EACH; $\text{CuK}\alpha$ RADIATION

Int.	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$		Solid solution ($\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Cl}_2 \cdot 6\text{H}_2\text{O}$)		$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$		Miller indices
	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.	
s	0.0127	0.0130	0.0127	0.0127	0.0128	0.0130	100
s	.0375	.0375	.0380	.0380	.0380	.0382	110
s	.0474	.0477	.0496	.0500	.0513	.0509	101
w	.0500	..	.0507	..	.0510	..	200
m	.0725	.0727	.0750	.0751	.0767	.0760	111
s	.0843	.0850	.0876	.0875	.0895	.0894	201
w	.0878	..	.0887	..	.0893	..	210
s	.1124	.1125	.1140	.1140	.1148	.1154	300
s	.1224	.1229	.1256	.1260	.1277	.1280	211
w-m	.1397	.1400	.1477	.1480	.1538	.1536	002
w	.1474	.1480	.1509	..	.1533	..	301
m	.1504	.1510	.1520	..	.1531	..	220
w-m	.1626	.1625	.1647	.1620	.1659	.1662	310
w-m	.1771	.1775	.1858	.1860	.1920	.1921	112
w	.1897	.1900	.1989	.1980	.2048	.2045	202
m	.1971	.1972	.2016	.2011	.2044	..	311
w	.2000	..	.2027	..	.2045	..	400
m	.2267	.2270	.2364	.2363	.2432	.2431	212
m	.2348	.2350	.2396	..	.2426	..	401
m	.2519	.2519	.2618	.2610	.2688	.2683	302
m	.2622	.2626	.2661	.2672	.2681	..	410
m	.2726	.2726	.2777	.2794	.2809	.2806	312

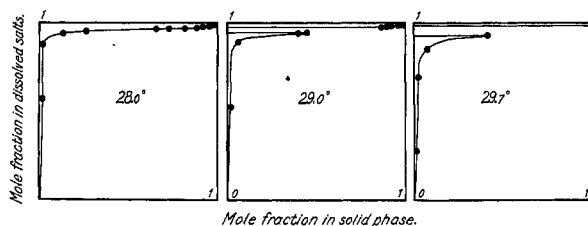


Fig. 2.—Distribution diagrams according to Roozeboom: in solid solution ($\text{CaSr})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ and mother liquor mole fraction 1 = 100% CaCl_2 .

solution is not "regular."⁶ It can hardly be expected that the concentrated solutions in which the solid solution in question is formed, would correspond to the more "ideal" solution presumed in such calculations, since the reactions of concentrated calcium chloride solutions obviously indicate that the solutions contain hydrated aggregates.

The relation between the cell dimensions of the solid solution crystals and their composition could be of some interest. X-Ray photographs (powder) of some preparations were made. The samples were exposed to $\text{CuK}\alpha$ radiation and the cameras used had a diameter of 114.7 mm. The interference measurements of a preparation containing 50% of each component are listed in Table II together with the measurements for the pure hexahydrates: these last are calculated from measurements earlier

(6) J. E. Ricci and J. Fischer, *J. Am. Chem. Soc.*, **74**, 1443 (1952), and their cited literature.

published.⁵ The calculated axial lengths of two other preparations are listed in Table III together with those above mentioned. The hexahydrates

TABLE III
RELATION BETWEEN THE UNIT CELL DIMENSIONS AND THE COMPOSITION OF THE SOLID SOLUTION $(\text{CaSr})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, Å. UNITS

Content of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	100	78	50	33	0
a-axis	7.880	7.890	7.905	7.920	7.960
c-axis	3.930	3.970	4.010	4.045	4.130

form solid solution crystals, with axes slightly shorter than those calculated on the assumption that they depend only on the relative length of the integral components, represented in Fig. 3 by the tie-line between the values of the pure phases (Vegard's law). The largest negative deviation appears to be shown by the crystals containing equal parts of the components.

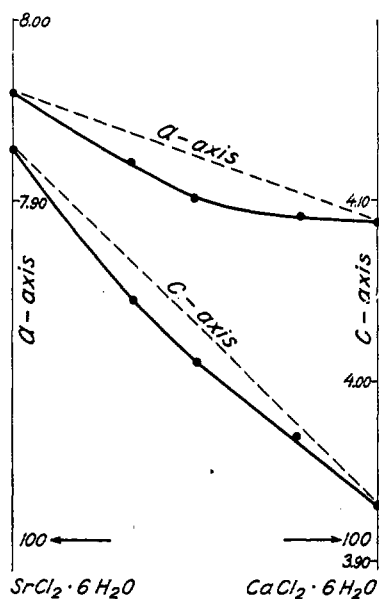


Fig. 3.—The relation between the axial lengths of the unit cells and the composition of the solid solution $(\text{CaSr})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$.

Between 28.0 and 30.0° the system shows some interesting traits. In the binary system calcium chloride–water the transition temperature calcium chloride hexahydrate– α -tetrahydrate is at 29.5°. In the present ternary system, however, the dihydrate of the strontium chloride is the stable phase in saturated calcium chloride solution at this temperature. This dihydrate is monoclinic and α -calcium chloride tetrahydrate is triclinic.⁸ The hexahydrates of calcium and strontium chlorides are isomorphous and form crystals of complete miscibility as shown above. Therefore, the stability area of strontium chloride dihydrate overlaps the area of solid solution of the hexahydrates.

When studying in more detail the isotherms from

(7) H. W. B. Roozeboom, *Z. physik. Chem.*, 4, 31 (1889), has recorded 29.8°. A. Lannung, *Z. anorg. allgem. Chem.*, 228, 1 (1936), reports 29.5° as transition temperature, which value has been confirmed and will be used here.

(8) H. Basset, H. F. Gordon and J. Heinschall, *J. Chem. Soc.*, 972 (1937).

28.0 to 29.7°, the following observations can be made (see Table I and Fig. 1). The isotherm at 28.0° shows the hexahydrates forming solid solution continuously without any gap. Between 28.5 and 29.3°, when the solutions contain pure calcium chloride, the solid phase is the hexahydrate. On adding small quantities of strontium chloride, solid solution of the two hexahydrates is deposited, the crystals being rich in calcium chloride. As the proportion of strontium chloride is further increased, the solid phase undergoes continuous change in composition, the crystals containing successively more strontium chloride and less calcium chloride. The calcium chloride concentration can be lowered in this way to a certain value, after which the solid phase suddenly changes its character. A deposition of strontium chloride dihydrate now begins. The transition concentration, however, is not discernible as a break in the isotherm. As the calcium chloride concentration is lowered still further, deposition of strontium chloride dihydrate continues. During the first part of this crystallization the strontium chloride concentration of the solutions is almost constant and during the later part the concentration increases. With continued decrease in calcium chloride content the solid phase again changes its character and the solid solution is formed once more. Here the curves show a distinct break. The crystals are now poorer in calcium chloride than those formed within the solid solution zone immediately before the described transition to strontium dihydrate. As the curves representing the solutions in equilibrium are S-shaped and have no discernible break where the solutions are very rich in calcium chloride, it is to be suggested that the transition of the solid phase in this case is caused by only a small change of entropy of the system compared with the change in concentration. At that part of the curves where the break is distinct the entropy change must be greater. If the isotherms are compared it is apparent that the higher the temperature, the higher the calcium chloride content in the solutions at the isothermal invariant point strontium dihydrate–solid solution of the hexahydrates rich in calcium chloride. The solid solution occurs in this part of the 29.3° isotherm but cannot occur in the same part of the 29.7° isotherm containing the transition point calcium chloride hexahydrate– α -tetrahydrate in pure water, therefore the invariant point strontium chloride dihydrate– α -calcium chloride tetrahydrate–solid solution of the hexahydrates is estimated to be at 29.4°. As the dihydrate crystallizes in the described way along the isotherm at 28.5° but does not do so along the isotherm 28.0°, the lowest temperature of its formation is estimated to be $28.2 \pm 0.2^\circ$.

The solid solution of the hexahydrates formed at both sides of the dihydrate interval, changes in composition in the same continuous way as already described for temperatures lower than 28.0°. In the distribution diagrams (Fig. 2) the change in composition of the solids [solid solution (hexahydrate)–strontium chloride dihydrate–solid solution (hexahydrate)] appears as a continuous curve

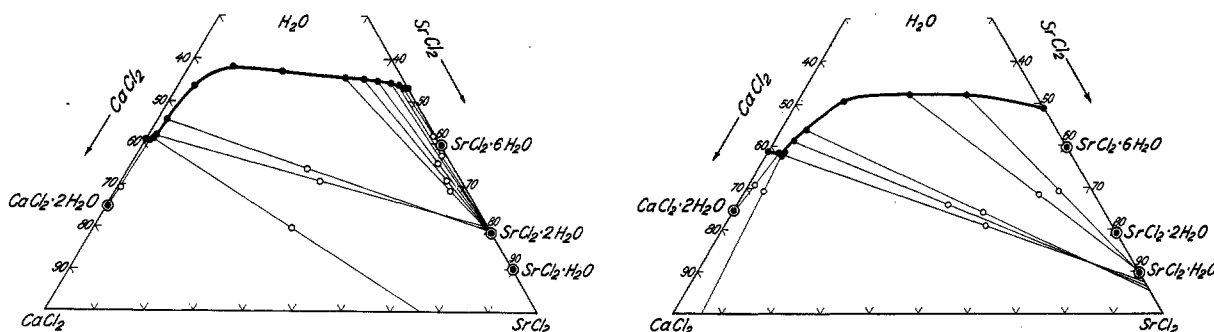


Fig. 4. Isotherms at 60 and 100°.

representing solid solution, interrupted by a gap corresponding to the dihydrate. Thus, the formation of solid solution mentioned above is characterized by the fact that a continuous crystallization occurs, having the behavior of a solid solution with complete miscibility of the end phases, but showing a gap in which there crystallizes out a new phase not belonging to the miscible phases. This type of crystallization of a solid solution with a gap in which is deposited another compound has not been described before, as far as is known to the authors. It could perhaps be classified as a seventh type of system forming solid solutions after Roozeboom,—a sixth type has been recorded by Ricci⁹—but in the authors' opinion the case described above should be considered as an infrequent and special one of Roozeboom's type I, as the solid solution shows a continuous miscibility and the intermediate phase does not contain the end phases.

At higher temperatures, too, the system shows some interesting characteristics. The isotherm at 60° (Table IV, Fig. 4) shows no double salt but it is noteworthy that even a small amount of calcium chloride (1.4%) in the solution causes a transition of the strontium chloride hexahydrate into the dihydrate.

It is known from some earlier investigations, that strontium chloride monohydrate is formed above 100° (Etard,¹⁰ Hüttig and Slonim¹¹). Benrath¹² has determined the transition temperature of this reaction in the binary system chloride–water and found it to be at as high a temperature as 230°. The very strongly dehydrating properties of saturated calcium chloride solutions must influence the transition temperature considerably. For the 100° isotherm (Table IV, Fig. 4) it is shown that the solid phase is the monohydrate over the greater part of the strontium chloride branch. Because of the experimental conditions it is difficult to determine the calcium chloride concentration at which the transformation of the di- and monohydrate takes place at 100°; it has no special significance in the present investigation but it must have a low value. In order to determine the invariant point in the ternary system some other isotherms were investigated. An extract of the observations are listed in Table V. The lowest formation temperature of strontium chloride mono-

TABLE IV
THE TERNARY SYSTEM SrCl_2 – CaCl_2 – H_2O

SrCl_2	Solution CaCl_2	Wet residue SrCl_2	Wet residue CaCl_2	Solid phase
Isotherm at 60.0°				
46.2	a
45.5	0.8	58.0	0.2	f
45.0	1.4	62.4	0.2	f + b
43.3	2.9	72.1	0.5	b
40.0	5.6	62.0	2.6	b
37.0	8.0	66.0	2.5	b
33.0	11.4	68.2	3.3	b
18.8	23.7	b
8.5	34.3	b
3.3	43.2	b
1.7	52.5	36.0	30.0	b
1.0	57.0	39.9	29.0	b
1.0	57.1	38.2	40.6	b + e
0.8	57.6	0.6	70.3	e
..	58.2	..	69.7	e
Isotherm at 100°				
50.8	b
33.7	15.2	63.8	7.0	g
22.4	26.0	60.2	11.2	g
9.5	39.8	g
5.1	51.0	51.3	25.2	g
3.9	54.4	42.6	31.1	g
2.9	58.7	53.1	26.2	g
2.7	59.1	3.6	67.1	e + g
2.5	59.4	1.4	68.1	e
..	61.3	..	70.0	e

TABLE V
THE TERNARY SYSTEM SrCl_2 – CaCl_2 – H_2O ; SOME EQUILIBRIA
BETWEEN 50 AND 114°

Temp., °C.	Solution SrCl_2	Solution CaCl_2	Wet residue SrCl_2	Wet residue CaCl_2	Solid phase
50	0.9	56.7	b + e
60	1.0	57.0	b + e
70	1.5	57.0	b + e
75	2.6	56.5	46.4	26.0	b
	2.5	56.8	2.0	66.5	e
77	3.0	55.6	47.2	25.7	b
	2.9	56.1	36.5	35.4	g
	2.4	57.1	1.6	57.1	e
90	2.5	58.2	e + g
100	2.7	59.1	e + g
114	3.5	59.6	e + g

For the invariant point (I, Fig. 5)

76	2.5	57.0	b + e + g
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(9) J. E. Ricci, *J. Am. Chem. Soc.*, **57**, 805 (1935).(10) A. L. Etard, *Ann. chim. phys.*, [7] **2**, 533 (1894).(11) G. I. Hüttig and Chr. Slonim, *Z. anorg. allgem. Chem.*, **181**, 66 (1929).(12) A. Benrath, *ibid.*, **247**, 147 (1941).

hydrate was found to be 76° . The univariant curve as defined by the series of isothermal invariant points is drawn in Fig. 5, but no distinct break can be observed in this curve at 76° .

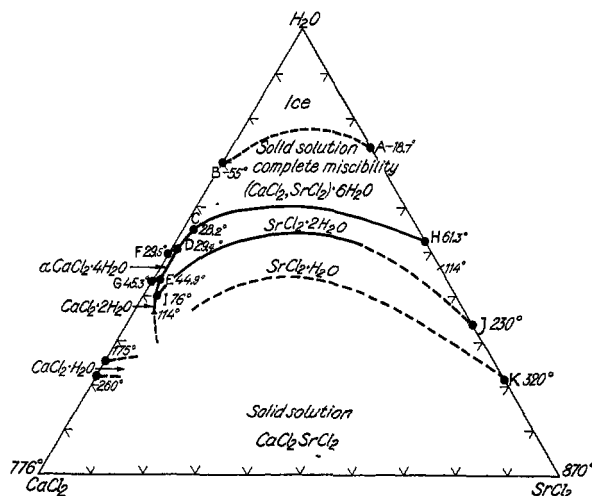


Fig. 5.—Synopsis of the composition of the solutions at the invariant and univariant equilibria of the ternary system $\text{SrCl}_2\text{--CaCl}_2\text{--H}_2\text{O}$.

Some other experiments were performed in order to determine the character of the solid phase. The direct preparation of pure solid phase according to a method earlier used,¹ was not successful because of the necessity of working at high temperatures and with mother liquors rich in calcium chloride. Differential thermal analysis, mentioned in the earlier paper¹ was performed on a mixture of three parts strontium chloride dihydrate and two parts calcium chloride tetrahydrate and showed a distinctly marked endothermic peak beginning at about 80° . As the transition takes place slowly, it was of importance to conduct the analysis under conditions of very slowly increasing temperature, which resulted in the heat absorption being delayed.

A preparation of strontium chloride dihydrate was mixed with 10% α -calcium chloride tetrahydrate and exposed in a Lindemann glass capillary in a heat X-ray camera at 110° . At another preparation strontium chloride hexahydrate was dried in an air-bath at 95° to constant weight (89.5% chloride) and exposed in a common X-ray camera of 114.7 mm. diameter. The interference measurements of both preparations are listed in Table VI and agree very well with one another and are quite different from those of strontium chloride dihydrate.¹³ As the preparation at the heat camera

(13) A. Tovborg-Jensen, *Kgl. Danske Videnskabs Selskab. Mat.-fys. Medd.*, XX, nr 5, Copenhagen 1942 (English).

corresponds to the solid phases precipitated from the saturated calcium chloride solutions at 110° , both of the preparations contain the same phase, which must be a monohydrate. An examination of the crystals in a polarization microscope with heated stage was not successful because of the difficulty in handling the solutions.

TABLE VI

X-RAY INTERFERENCES OF $\text{SrCl}_2\cdot\text{H}_2\text{O}$; $\text{Cu K}\alpha$ RADIATION

Preparation: a, $\text{SrCl}_2\cdot 6\text{H}_2\text{O}$, dried in an air-bath at 95° , 89.5% SrCl_2 ; b, $\text{SrCl}_2\cdot 2\text{H}_2\text{O}$, containing 10% $\text{CaCl}_2\cdot 4\text{H}_2\text{O}$, exp. at 110° in X-ray heat camera.

Int.	Prep. a \sin^2	Prep. b \sin^2	d , Å.	Int.	Prep. a \sin^2	Prep. b \sin^2	d , Å.
s	0.0119	0.0119	7.00	s	0.0716	0.0714	2.882
m-w	.0130	.0130	6.74	m	.0771	.0769	2.774
w	.0150	..	6.27	m	.0820	.0813	2.696
m	.0199	.0198	5.47	m	.0870	.0865	2.615
w	.0225	..	5.11	w	..	.0895	2.572
w	.0247	..	4.88	m	.0995	.0981	2.456
m	.0275	.0273	4.62	m	.1050	.1042	2.384
m-w	..	.0288	4.518	s	.1124	.1118	2.301
w	.0340	.0347	4.132	m	.1154	.1151	2.259
m	.0366	.0360	4.047	w	.1186	..	2.228
w	.0428	.0427	3.721	m	.1240	.1233	2.191
m	.0483	.0478	3.526	w	.1285	.1273	2.156
w	.0535	.0535	3.325	m	.1393	.1391	2.062
w	.0580	.0576	3.202	w	.1510	.1501	1.986
w	.0640	.0627	3.066				

The only observation which was made concerning the crystallographic properties was that the monohydrate crystallizes in plates and needles of apparently low degree of symmetry. As the strontium chloride monohydrate is formed at 230° in the binary system¹² and its lowest formation temperature in present ternary system is at 76° (Table V) the saturated calcium chloride solution lowers the transition temperature 154° .

Figure 5 is intended to give a synopsis of the univariant and invariant equilibria of the system. The equilibria at low temperature with ice as one of the solid phases are known only in the case of the binary systems, where the second phase is the respective hexahydrate. It is evident, however, that in the present ternary system the other solid phase must be solid solution of the hexahydrates. The bivariant equilibria containing the solid solution cover the area up to the line FDCH (Fig. 5), bounding the area within which strontium chloride dihydrate is a stable phase. Strontium chloride monohydrate crystallizes at temperatures higher than 76° (boundary I-J) and at very high temperatures, at which the mother liquor is very poor in water, a solid solution of anhydrous calcium and strontium chloride must crystallize.^{12,14}

(14) C. Sandonnini, *Atti Acad. Lincei.*, [5] 20, II, 497 (1911).