Equilibria in Aqueous Systems Containing K^+, Na^+, Ca^{+2}, Mg^{+2} and Cl^-. I. The Ternary System $CaCl_2$-KCl-H_2O[1]

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In the year 1943 the Geological Survey of Sweden started a deep boring at Höllviken in Scania, Southern Sweden. At the depths 1200–1800 m. brines of very good supply were found in Cretaceous rocks. As the chemical industry might benefit by the salt occurring in the brine, it was evident that some research work on the systems of ions, occurring in the brines, should be carried out. Earlier investigations were reviewed and critically examined. A very good survey of the literature is found in Gmelin's "Handbuch der anorganischen Chemie," System-Nummer 22: Kalium, Anhangsband: Die Salze der ozeanischen Ablagerungen und ihre Lösungen (Berlin, 1942), where the literature up to the 1st of January 1940 is taken into consideration. Later, when the parts of the present investigation corresponding to the title of this paper had been completed, two investigations were published by Lightfoot and Prutton, dealing with the systems mentioned. The results had no influence on the conclusions of the present paper. As the results published here have been retested very carefully, an account of the investigations of the Laboratory of the Geological Survey of Sweden may be of interest.

Experimental

The experiments were carried out as is customary in equilibrium investigations. Samples were prepared by mixing the individual salts and water in suitable proportions in bottles. The bottles were shaken in an air-bath, which was electrically heated and carefully insulated. The air of the bath was vigorously stirred by means of a fan. The temperature was constant within 0.1°. After a time—two or three days as a rule—the sample was passed through a glass filter, without taking the bottle containing the sample, or the filter, out of the thermostat. Small amounts of the solid phase and of the solution were immediately weighed for analysis. To the pure filtered solution was added a small quantity of one of the components, and the experiment was repeated as before. The solid phase now formed corresponded to a very small part of the isotherm. This precaution was absolutely necessary because of the frequent occurrence of interpositions of undissolved added compound.

The composition of the solid phase was determined by Schreinemakers' residue method. The solid phases were also identified microscopically.

Earlier Investigations; Some Conclusions.—

Investigations of the ternary system $CaCl_2$-

KCl-H_2O have been published by Igelsrud and Thompson (0°),[2] by Lee and Egerton (25°),[3] by Barbaudy (30°),[4] and later by Lightfoot and Prutton (35°),[5] and (75°).[6] Generally, the determinations of the solubility agree well. However, the present investigation and the summary of the results hitherto published disclose some interesting points. The univariant equilibria, when potassium chloride, hydrates of calcium chloride, or a double salt of potassium chloride and calcium chloride as solid phases are in equilibrium with solutions at various temperatures, show some special properties. Figure 1 shows those parts of the solubility curves which correspond to solutions rich in calcium chloride. At a lower temperature (0°),[2] the solubility of potassium chloride decreases up to the univariant equilibrium. At 18° and 25°[3] the contents of potassium chloride in the solutions are almost constant between about 30% calcium chloride and the univariant points. At 30°[4] and of higher temperatures the solubility of potassium chloride increases between about 40% calcium chloride and the univariant point. In view of these conditions, it was supposed that complex ions are present in the solutions (Gmelin's Handbuch, Kalium, Anhangsband, p. 177). It will be shown below that a double salt of the composition $CaCl_2 \cdot KCl$ exists. Its existence may be connected with these ions.

The Composition of the Double Salt and Some Isotherms.—

The experimental conditions at the formation of the double salt can cause some discrepancies in the calculation of the composition. Two isothermal solubility curves will be published here to illustrate the equilibrium conditions at 50 and 95° (Figs. 2–3, Tables I–II).

The double salt required special precautions. When the samples were treated without precautions within the stability limits of the double salt, by mixing calculated amounts of the components, the compositions of the solid phases often showed very poor agreement, even when the experimental conditions seemed to be alike. However, a systematic examination disclosed that a solid phase of theoretical composition $CaCl_2 \cdot KCl$ resulted when calcium chloride, in the form of finely powdered suitable hydrate, was added in small amounts to solutions of a composition within the stability area of the double salt. When the experiments were started with pure solutions, and calcium chloride was added

(1) Some problems connected with the Swedish brines will be published in the Year Book of the Geological Survey of Sweden (Ser., nr. 501).
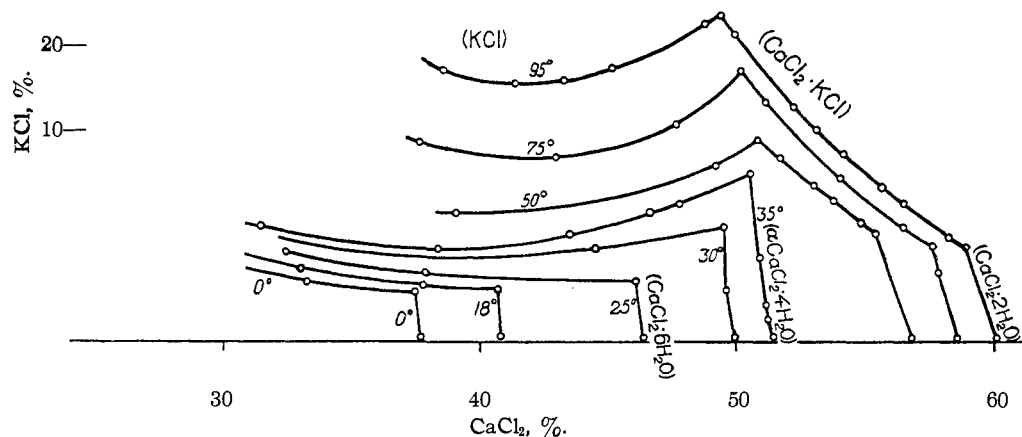
(2) I. Igelsrud, T. G. Thompson, THIS JOURNAL, **58**, 318 (1936).

(3) W. B. Lee, A. C. Egerton, J. Chem. Soc., **123**, 707 (1923).

(4) J. Barbaudy, Rec. Trav. Chim., **42**, 639 (1932).

(5) W. L. Lightfoot and C. F. Prutton, THIS JOURNAL, **68**, 1001 (1946).

(6) W. L. Lightfoot and C. F. Prutton, ibid., **69** 2098 (1947).

Fig. 1.—The ternary system $CaCl_2$–KCl–H_2O. Equilibria in solutions rich in $CaCl_2$.

in this way, it was possible to follow the isotherm, step by step, within the existence area of the double salt by analyzing the solid phase in equilibrium. The extrapolation of the tie-lines, according to Schreinemakers, always showed the constant composition $CaCl_2$·KCl. On the other hand, when the solid phases were prepared by adding some small amount of potassium chloride its composition was so changed that a solution rich in calcium chloride gave a double salt containing an excess of potassium chloride. The richer in calcium chloride the solution had been at the beginning of the experiment, the greater the excess. The composition of the solid phase was also influenced by the size of the potassium chloride crystals. Finely powdered preparation gave more correctly composed double salt. The solubility curves were quite identical when potassium chloride, or calcium chloride, was added. It is evident that it is difficult for the potassium chloride to react with the viscous, highly concentrated calcium chloride solutions, especially as

its solubility decreases rapidly with increasing content of calcium chloride of the solutions. Similar conditions are known in many other cases, e. g., in the crystallization of carnallite and tachydrite. Correctly composed double salt was also obtained when solutions were saturated at a high temperature and then cooled down to a suitable one, a condition being that the solutions were within the stability area of the double salt. Of course, other means may also be used, e. g., pure solutions mixed in suitable proportions yield perfectly composed double salt. All the solid phases in Tables I–II and Figs. 2–3 were prepared by adding calcium chloride dihydrate—the most suitable hydrate at these temperatures—to prepared solutions.

Some samples of the double salt which had an incorrect composition were studied microscopically. It was not possible to distinguish any interpositions of potassium chloride in the double salt as the crystals originating from the residue of the mother liquid disturbed the determination.
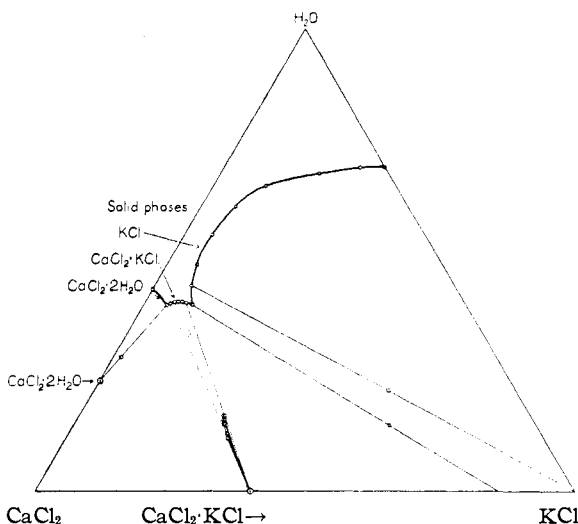

Fig. 2.—The ternary system $CaCl_2$–KCl–H_2O at 50°.

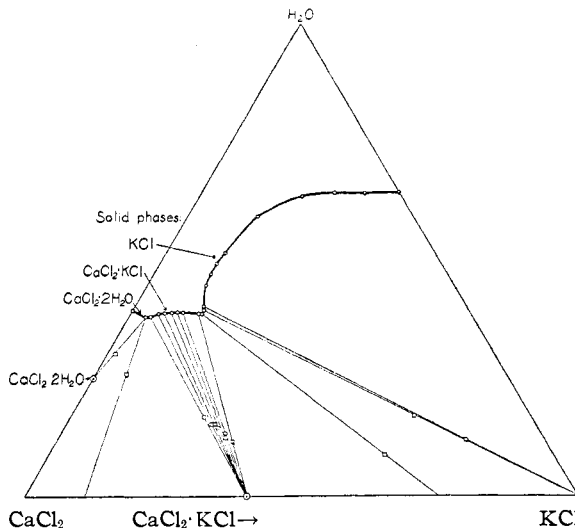Fig. 3.—The ternary system $CaCl_2$–KCl–H_2O at 95°.

TABLE I

THE TERNARY SYSTEM CaCl₂–KCl–H₂O, ISOTHERM AT 50°

Solution		Wet residue		
CaCl₂	KCl	CaCl₂	KCl	Solid phase
...	29.9	Not determ. anal.		KCl
5.9	24.9	Not determ. anal.		KCl
12.7	18.1	Not determ. anal.		KCl
23.8	9.8	Not determ. anal.		KCl
30.9	6.1	Not determ. anal.		KCl
39.0	4.8	Not determ. anal.		KCl
45.7	5.7	Not determ. anal.		KCl
48.9	6.6	24.0	54.0	KCl
50.85	8.60	26.1	58.0	KCl + CaCl₂·KCl
50.75	8.65	26.8	59.0	KCl + CaCl₂·KCl
51.6	7.1	56.5	26.8	CaCl₂·KCl
52.1	6.6	56.9	28.0	CaCl₂·KCl
52.9	6.0	56.8	26.8	CaCl₂·KCl
53.8	5.6	57.5	27.8	CaCl₂·KCl
54.8	4.6	58.4	30.5	CaCl₂·KCl
55.51	4.10	68.9	7.6	CaCl₂·KCl + CaCl₂·2H₂O
55.58	4.09	69.2	1.3	CaCl₂·2H₂O
56.54	...	..	..	CaCl₂·2H₂O
56.58	...	..	..	CaCl₂·2H₂O

TABLE II

THE TERNARY SYSTEM CaCl₂–KCl–H₂O, ISOTHERM AT 95°

Solution		Wet residue		
CaCl₂	KCl	CaCl₂	KCl	Solid phase
...	36.2	Not determ. anal.		KCl
6.4	29.2	Not determ. anal.		KCl
11.3	24.2	Not determ. anal.		KCl
18.0	18.6	Not determ. anal.		KCl
28.0	12.7	Not determ. anal.		KCl
38.4	10.5	Not determ. anal.		KCl
41.3	10.3	Not determ. anal.		KCl
43.2	10.2	Not determ. anal.		KCl
45.3	10.5	Not determ. anal.		KCl
48.0	11.9	22.0	62.0	KCl
48.6	12.2	15.0	74.1	KCl
49.6	12.4	29.8	60.6	KCl + CaCl₂·KCl
49.9	12.1	57.3	32.2	CaCl₂·KCl
52.2	9.3	57.8	30.2	CaCl₂·KCl
53.0	8.0	58.0	30.0	CaCl₂·KCl
54.0	7.2	58.0	27.6	CaCl₂·KCl
55.6	5.9	58.3	27.9	CaCl₂·KCl
56.4	5.3	59.0	27.4	CaCl₂·KCl
58.3	3.9	59.6	24.1	CaCl₂·KCl
59.6	2.9	68.3	5.3	CaCl₂·KCl + CaCl₂·2H₂O
59.8	2.5	68.6	1.0	CaCl₂·2H₂O
60.20	..	69.2	..	CaCl₂·2H₂O

A mineralogical note may be added in this connection. The double salt described above is obviously identical with the mineral mentioned in the literature as "hydrophilite," "chlorocalcite" and "baeumlerite." Probably, it is also identical with the binary compound CaCl₂·KCl formed in the anhydrous system CaCl₂–KCl and melting at 754°. These compounds, however, may be investigated further.

The Invariant Points of the System CaCl₂–KCl–H₂O.

—The binary system CaCl₂–H₂O has four invariant equilibria of stable hydrates: CaCl₂·6H₂O + αCaCl₂·4H₂O (29.8°), αCaCl₂·4H₂O + CaCl₂·2H₂O (45.3°), CaCl₂·2H₂O + CaCl₂·H₂O (175.5°), and CaCl₂·H₂O + CaCl₂.[7] When potassium chloride is added to the system, a certain change of these temperatures appears.

The invariant equilibrium CaCl₂·6H₂O + KCl + αCaCl₂·4H₂O is at 27.00 ± 0.05°, determined dilatometrically. The compositions of the solutions belonging to the univariant equilibria around the invariant equilibrium are listed in Table III.

TABLE III

THE SYSTEM CaCl₂–KCl–H₂O, EQUILIBRIA AROUND THE INVARIANT POINTS E, G AND H (FIG. 4)

	Temperature, °C.	Solution		Wet residue		Solid phase
		CaCl₂	KCl	CaCl₂	KCl	
	26.50	45.40	3.90	Not determ.		KCl + CaCl₂·6H₂O
E	27.00	47.20	4.50	Not determ.		CaCl₂·6H₂O + αCaCl₂·4H₂O + KCl
		47.75	4.40	50.4	1.2	CaCl₂·6H₂O + αCaCl₂·4H₂O
	27.60	48.10	4.30	Not determ.		αCaCl₂·4H₂O + KCl
	28.00	48.40	4.65	17.0	56.0	KCl
		48.55	4.65	Not determ.		αCaCl₂·4H₂O + KCl
		47.75	4.50	57.5	0.9	αCaCl₂·4H₂O
G	37.75	51.40	7.30	24.7	57.9	KCl
		51.50	7.30	33.0	56.6	KCl + αCaCl₂·4H₂O
		51.90	7.35	59.0	1.2	αCaCl₂·4H₂O
	38.00	51.50	7.35	22.7	60.4	KCl
		51.60	7.20	56.5	28.3	CaCl₂·KCl
		51.70	7.15	57.7	2.2	αCaCl₂·4H₂O
		52.00	7.00	58.9	1.8	αCaCl₂·4H₂O
H	43.25	54.70	4.55	58.6	30.4	CaCl₂·KCl
		54.90	4.50	59.1	4.6	CaCl₂·KCl + αCaCl₂·4H₂O
		55.15	4.25	59.0	1.9	αCaCl₂·4H₂O
	43.50	54.45	4.40	58.7	26.6	CaCl₂·KCl
		55.10	4.20	68.1	10.0	CaCl₂·KCl + CaCl₂·2H₂O
		55.20	4.00	69.0	0.7	CaCl₂·2H₂O

Calculated for the invariant equilibria E, G and H

E	27.00	27.20	4.50	(CaCl₂·6H₂O + αCaCl₂·4H₂O + KCl)
G	37.80	51.45	7.30	(αCaCl₂·4H₂O + CaCl₂·KCl + KCl)
H	43.40	55.05	4.30	(αCaCl₂·4H₂O + CaCl₂·KCl + CaCl₂·2H₂O)

The lowest formation temperature of the double salt was determined graphically from the analysis (Table III); it is at 37.8°. The dilatometric determination gave 37.80 ± 0.05°. At this temperature the double salt is in equilibrium with the solid phases KCl and αCaCl₂·4H₂O.

The temperature of the transition αCaCl₂·4H₂O + CaCl₂·2H₂O in presence of the double salt was determined in the same way; graphically it was found to be at 43.25–43.50° (Table III); dilatometric determination gave 43.70 ± 0.05°.

Calcium chloride tetrahydrate, however, is trimorphic. The properties of the three crystal forms complicate the crystallization of the solutions between 37 and 44°. In further more detailed investigations of this temperature interval, some methods other than those mentioned in this paper will be used to obtain reliable results.
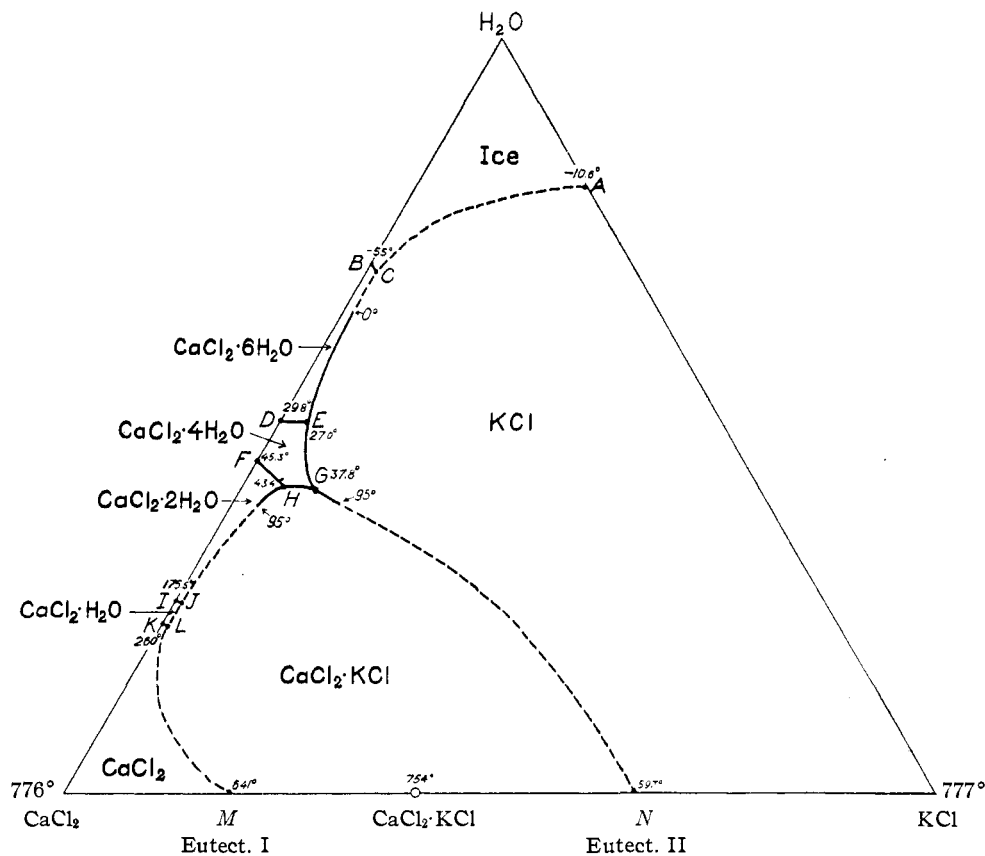
(7) B. Roozeboom, Z. physik. Chem., 4, 31 (1889).

Fig. 4.—The ternary system CaCl₂–KCl–H₂O; synopsis of the composition of the solutions for the invariant and the univariant equilibria.

At higher temperatures the double salt must be in equilibrium with CaCl₂·H₂O as well as with CaCl₂, as the double salt contains no water. These two invariant equilibria have not been determined here; their temperatures however, are supposed to be just below those of the binary system. A synopsis of the composition of the solutions for the invariant and univariant equilibria is presented in Fig. 4. The determinations at the invariant equilibria of the two-component systems are given by Roozeboom[7] and Menge.[8]

At the lowest temperatures the univariant equilibria are unknown; they are plotted in the diagram on supposition. As the temperature rises, the univariant equilibria have solutions in which the CaCl₂ and KCl contents increase.

The great change appears in the diagram when the double salt is formed at 37.80°. From this point the stability area of the double salt extends very rapidly when the temperature rises. One of the branches of the curve limiting the double salt must pass the two invariant equilibria containing CaCl₂·H₂O and CaCl₂. As the double

salt contains no crystal water, this branch must end in the eutectic of the anhydrous salts, where the double salt is in equilibrium with CaCl₂ (641°, O. Menge).[8] The other branch must pass unchanged through the area and end in the other eutectic where the double salt and KCl are in equilibrium (597°).[8]

Summary

1. Some isotherms (50°, 95°) of the ternary system are given.

2. A double salt CaCl₂·KCl occurs; its lowest formation temperature is 37.80 ± 0.05°.

3. The composition of the double salt has been examined in some detail and the conditions prerequisite for a correctly composed solid phase are discussed.

4. The transition temperatures of CaCl₂·6 H₂O + αCaCl₂·4H₂O + KCl and that of αCaCl₂·4H₂O + CaCl₂·KCl + CaCl₂·2H₂O were found to be at 27.00° and at 43.40 ± 0.05°, respectively.

(8) Menge, Z. anorg. Chem., 72, 162 (1911).