[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE GEOLOGICAL SURVEY OF SWEDEN]

Equilibria in Aqueous Systems Containing K^+, Na^+, Ca^{+2}, Mg^{+2} and Cl^-. II. The Quaternary System $CaCl_2$–KCl–NaCl–H_2O

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Earlier Investigations.—In the previous paper[1] the general properties of the system calcium chloride–potassium chloride were outlined. A knowledge of this system is important for various practical reasons, especially between 0 and 150°. As sodium chloride also belongs to the ions occurring in brines, investigations of the four-component system calcium chloride–potassium chloride–sodium chloride–water should be of interest.

The three-component system calcium chloride–sodium chloride–water was investigated at 0° by Igelsrud and Thompson,[2] at 25° by van't Hoff and Lichtenstein,[3] at 50° by Cameron, Bell and Robinson[4] and at 94.5° by Pelling and Robertson.[5] Some discrepancies occur especially in the case of solutions rich in calcium chloride, but in general the results agree satisfactorily. The new determinations of the present investigation are not discussed here. The system contains only the forms of the single salts known from the binary systems. No double salts are to be found.

The other three-component system sodium chloride–potassium chloride–water, which belongs to the four-component system in question, has been very carefully investigated and is described in most hand-books.

Experimental.—In the present investigation the solubility curves were carried out with two of the solid compounds always in equilibrium with the solutions. The solid phases were removed at suitable points, and a small amount of one of the compounds was then added to the solution and the new solid phase was analyzed after equilibrium, as usual.

Some Isotherms.—Three complete isotherms will be mentioned here (Figs. 1, 2, 3) at 18, 50 and 95°. They show the general shapes of the solubility curves.

The isotherms of the quaternary system are similar in their general character to those of the ternary system calcium chloride–potassium chloride–water, if the sum of the dissolved alkali chlorides is one of the variables. However, the alkali chlorides dissolve differently. As the calcium content increases, the sum of the alkali chlorides decreases to about 35% calcium chloride and then increases up to the univariant points. The sodium chloride decreases more than the potassium chloride, so that the solutions at the univariant points contain only small amounts of sodium chloride compared with potassium chloride. The isotherms indicate the existence of no previously known double salt other than $CaCl_2 \cdot KCl$.

The solid phases show no sodium chloride contents other than those deriving from the adhering mother liquor.

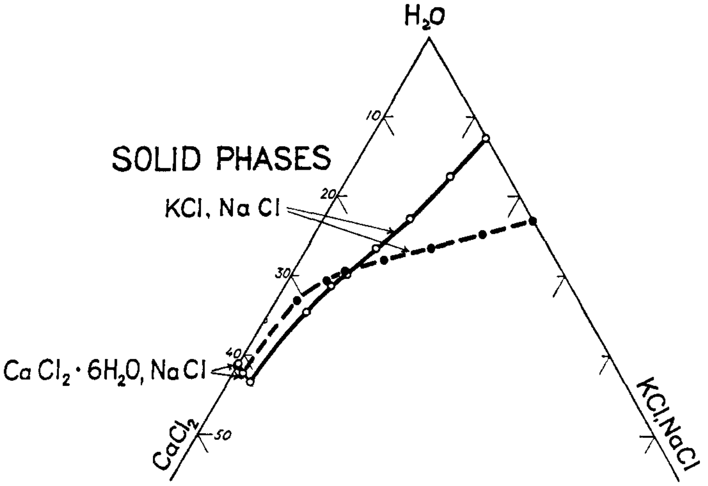

Fig. 1.—The quaternary system $CaCl_2$–KCl–NaCl–H_2O at 18°: ordinary line, projection on the $CaCl_2$–KCl–H_2O plane; dotted line, projection on the $CaCl_2$–NaCl–H_2O plane.

The double salt $CaCl_2 \cdot KCl$ has the properties

TABLE I

THE QUATERNARY SYSTEM $CaCl_2$–KCl–NaCl–H_2O AT 18°

Weight per cent. Solution $CaCl_2$	KCl	NaCl	Solid phase
...	...	26.5	NaCl
...	25.1	...	KCl
...	10.0	20.8	KCl + NaCl
6.0	9.3	16.0	KCl + NaCl
11.8	8.1	12.4	KCl + NaCl
17.6	6.8	8.4	KCl + NaCl
22.7	5.5	5.4	KCl + NaCl
25.3	4.8	4.0	KCl + NaCl
29.7	3.7	2.1	KCl + NaCl
40.80	2.65	0.45	KCl + NaCl + $CaCl_2 \cdot 6H_2O$
41.60	...	0.42	$CaCl_2 \cdot 6H_2O$ + NaCl
40.95	2.70	...	$CaCl_2 \cdot 6H_2O$ + KCl
42.05	...	...	$CaCl_2 \cdot 6H_2O$

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(1) Assarsson, THIS JOURNAL, **72**, 1431 (1950).

(2) Igelsrud and Thompson, *ibid.*, **58**, 321 (1936).

(3) J. H. van't Hoff and L. Lichtenstein, *Ber. Berl. Akad.*, 233 (1905).

(4) F. K. Cameron, J. M. Bell and W. O. Robinson, *J. Phys. Chem.*, **11**, 399 (1907).

(5) J. Pelling, J. B. Robertson, *South African J. Sci.*, **20**, 239 (1923).

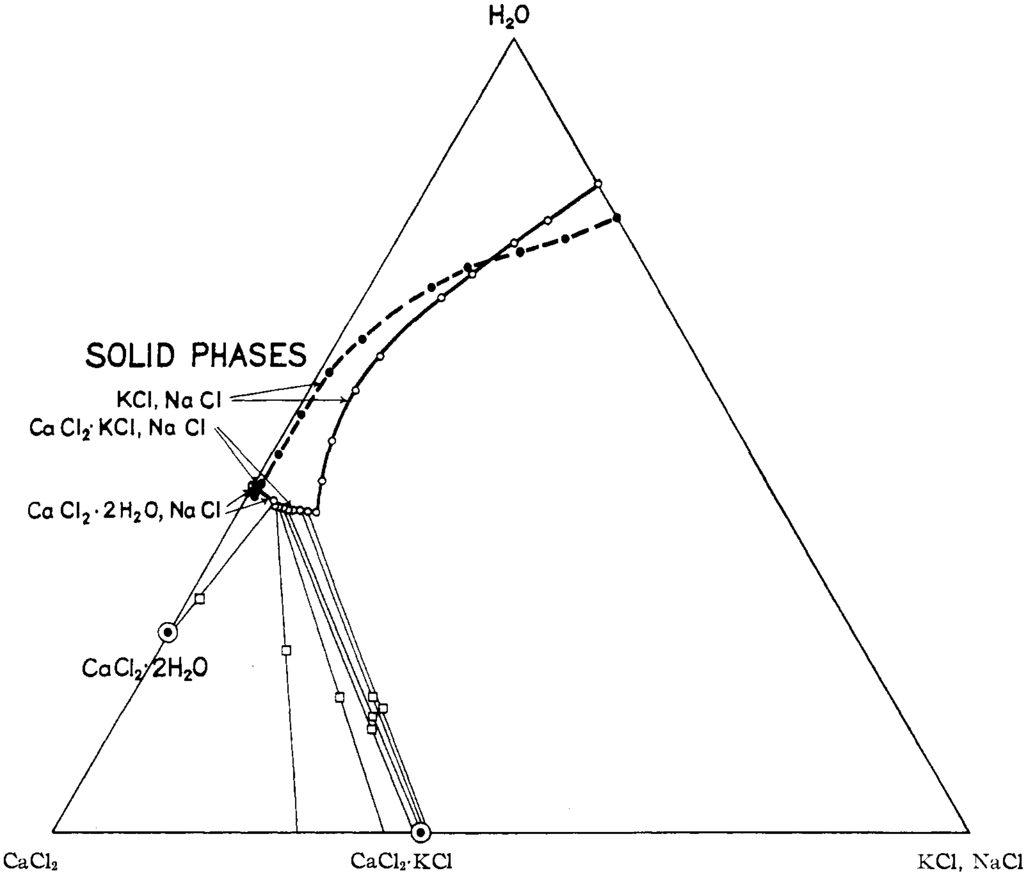

Fig. 2.—The quaternary system $CaCl_2$–KCl–NaCl–H_2O at 50°: ordinary line, projection on the $CaCl_2$–KCl–H_2O plane dotted line, projection on the $CaCl_2$–NaCl–H_2O plane.

TABLE II

THE SYSTEM $CaCl_2$–KCl–NaCl–H_2O ISOTHERM AT 50°

Weight per cent.						
Solution			Wet residue			
$CaCl_2$	KCl	NaCl	$CaCl_2$	KCl	NaCl	Solid phase
...	...	27.0	Not determined			NaCl
...	31.6	...	Not determined			KCl
...	14.7	19.1	Not determined			KCl + NaCl
6.0	13.0	16.0	Not determined			KCl + NaCl
11.6	11.2	11.9	Not determined			KCl + NaCl
17.6	9.5	8.5	Not determined			KCl + NaCl
22.7	7.8	6.0	Not determined			KCl + NaCl
33.9	5.5	2.2	Not determined			KCl + NaCl
39.2	5.0	0.7	Not determined			KCl + NaCl
44.8	5.6	.5	Not determined			KCl + NaCl
48.5	7.1	.5	Not determined			KCl + NaCl
51.00	8.25	.49	Not determined			KCl + $CaCl_2\cdot KCl$ + NaCl
50.90	8.45	.47	Not determined			KCl + $CaCl_2\cdot KCl$ + NaCl
51.70	7.45	.46	56.3	28.0	0.3	$CaCl_2\cdot KCl$ + NaCl
52.65	6.50	.45	56.5	26.4	.3	$CaCl_2\cdot KCl$ + NaCl
53.85	5.35	.45	57.6	27.5	.3	$CaCl_2\cdot KCl$ + NaCl
54.25	4.85	.44	57.9	28.7	.2	$CaCl_2\cdot KCl$ + NaCl
55.30	4.20	.44	60.6	22.8	.2	$CaCl_2\cdot KCl$ + $CaCl_2\cdot 2H_2O$ + NaCl
55.35	4.10	.44	63.4	13.9	.2	$CaCl_2\cdot KCl$ + $CaCl_2\cdot 2H_2O$ + NaCl
55.50	4.10	...	68.9	7.6	...	$CaCl_2\cdot KCl$ + $CaCl_2\cdot 2H_2O$
55.40	4.05	.44	69.6	1.3	.2	$CaCl_2\cdot 2H_2O$ + NaCl
56.45	...	.64	Not determined			$CaCl_2\cdot 2H_2O$ + NaCl
56.40	...	.61	Not determined			$CaCl_2\cdot 2H_2O$ + NaCl
56.55	...	...	.	..	...	$CaCl_2\cdot 2H_2O$

TABLE III

THE SYSTEM $CaCl_2$–KCl–NaCl–H_2O ISOTHERM AT 95°

Weight per cent.						
Solution			Wet residue			
$CaCl_2$	KCl	NaCl	$CaCl_2$	KCl	NaCl	Solid phase
...	..	28.3	Not determined			NaCl
...	37.6	...	Not determined			KCl
...	21.0	17.0	Not determined			KCl + NaCl
4.7	18.5	14.2	Not determ. anal.			KCl + NaCl
9.7	15.3	13.3	Not determ. anal.			KCl + NaCl
14.5	13.0	11.0	Not determ. anal.			KCl + NaCl
19.4	10.6	8.2	Not determ. anal.			KCl + NaCl
24.3	9.3	4.9	Not determ. anal.			KCl + NaCl
33.8	8.4	2.3	Not determ. anal.			KCl + NaCl
37.7	8.0	1.8	Not determ. anal.			KCl + NaCl
41.4	8.0	1.6	Not determ. anal.			KCl + NaCl
48.8	12.1	1.2	20.8	68.3	0.6	KCl + NaCl
49.4	12.5	1.1	Not determined			KCl + $CaCl_2\cdot KCl$ + NaCl
49.9	12.1	1.1	57.5	32.3	.4	$CaCl_2\cdot KCl$ + NaCl
50.3	11.4	1.1	58.5	35.1	.4	$CaCl_2\cdot KCl$ + NaCl
51.9	9.1	1.0	58.9	33.9	.4	$CaCl_2\cdot KCl$ + NaCl
52.9	8.2	0.9	58.5	30.6	.4	$CaCl_2\cdot KCl$ + NaCl
53.6	7.4	.9	58.9	30.4	.3	$CaCl_2\cdot KCl$ + NaCl
55.6	5.7	.9	59.4	28.1	.3	$CaCl_2\cdot KCl$ + NaCl
57.4	4.6	.9	59.6	26.0	.3	$CalC_2\cdot KCl$ + NaCl
58.1	3.9	.9	59.0	27.0	.3	$CaCl_2\cdot KCl$ + NaCl
58.8	3.2	.9	Not determined			$CaCl_2\cdot KCl$ + $CaCl_2\cdot 2H_2O$ + NaCl
59.6	2.9	...	68.8	5.3	...	$CaCl_2\cdot KCl$ + $CaC_2\cdot 2H_2O$
58.9	2.8	.9	70.5	1.1	.3	$CaCl_2\cdot 2H_2O$ + NaCl
60.10	..	.98	Not determined			$CaCl_2\cdot 2H_2O$ + NaCl
60.20	..	...	69.2	..	...	$CaCl_2\cdot 2H_2O$

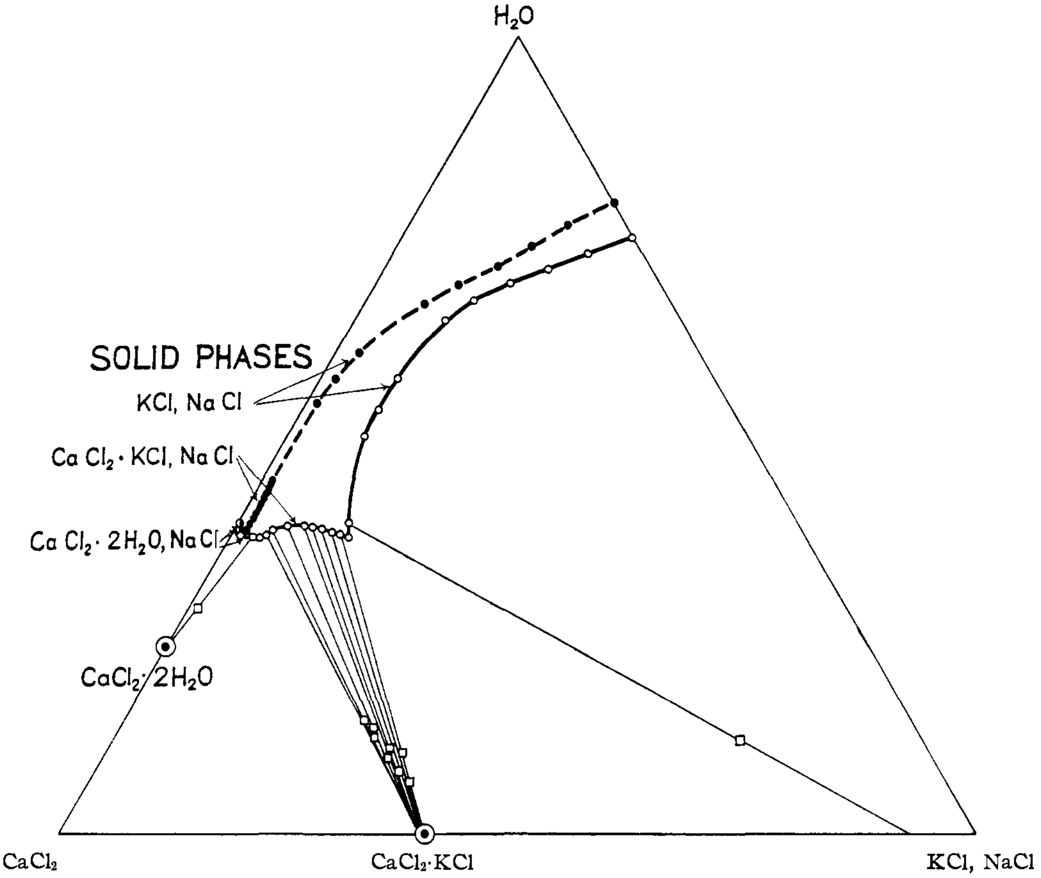

Fig. 3.—The quaternary system $CaCl_2$–KCl–NaCl–H_2O at 95°: ordinary line, projection on the $CaCl_2$–KCl–H_2O plane; dotted line, projection on the $CaCl_2$–NaCl–H_2O plane.

mentioned in the earlier paper. The transition temperature of the double salt in the presence of sodium chloride (point G, Table IV) was determined dilatometrically; it was found to be at 37.70 ± 0.05°.

The temperatures of the two invariant equilibria, $CaCl_2 \cdot 6H_2O + \alpha CaCl_2 \cdot 4H_2O$ + KCl + NaCl (point E, Table IV) and $\alpha CaCl_2 \cdot 4H_2O + CaCl_2 \cdot 2H_2O + CaCl_2 \cdot KCl$ + NaCl (point H, Table IV), are very close to those found in the system without sodium chloride. The dilatometric determinations of the transition temperatures in the presence of sodium chloride gave 26.90 ± 0.05° and 43.3 ± 0.1%, respectively. The composition of the solid phases was confirmed analytically (Table IV). In the investigation of the transition temperature last mentioned (point H) it was found analytically that calcium chloride dihydrate also occurs as solid phase at lower temperatures than 43.3°. When the transition was followed dilatometrically, a faint but quite definite rise in the level of the dilatometer liquid took place between 42.8 and 43.2°. The real expansion of the substance, however, began at 43.4°. The analyses of the solid phases formed at these temperatures show that dihydrate as well as tetrahydrate can occur as solid phases simultanously with the double salt. The presence of the two hydrates apparently in equilibrium with the double salt, can probably be attributed to the tendency of the calcium chloride solutions to form supersaturated solutions. The conditions mentioned are observed only in the four-component system calcium chloride–potassium chloride–sodium chloride–water. In the three-component system calcium chloride–potassium chloride–water such phenomena could not be detected.

The difference between the concentrations of sodium chloride + potassium chloride and potassium chloride at the univariant equilibria is very insignificant. At higher temperatures this difference increases. At 18 and 95° the solubility of sodium chloride in solutions saturated with respect to potassium chloride and calcium chloride hydrates or with respect to potassium chloride and the double salt calcium chloride–potassium chloride, is only 0.44% and 0.9–1.0% sodium chloride, respectively. Some other determinations of the concentration in solutions at univariant equilibria between 26 and 44° are given in Table IV.

Some Properties of the Solutions.—The solubility of the alkali chlorides in the solutions rich in calcium chloride is of interest.

TABLE IV

THE SYSTEM $CaCl_2$–KCl–NaCl–H_2O: UNIVARIANT EQUILIBRIA AROUND THE INVARIANT POINTS E, G AND H

Temp., °C.		Solution			Wet residue			Solid phase
		$CaCl_2$	KCl	NaCl	$CaCl_2$	KCl	NaCl	
E	26.90	47.95	4.30	0.38	Not determined			$CaCl_2\cdot 6H_2O + KCl + NaCl$
		48.20	4.15	.37	49.6	1.1	0.2	$CaCl_2\cdot 6H_2O + NaCl$
	27.50	48.10	4.30	.37	Not determined			$\alpha CaCl_2\cdot 4H_2O + KCl + NaCl$
		48.35	4.25	.38	58.6	0.8	0.1	$\alpha CaCl_2\cdot 4H_2O + NaCl$
		48.40	4.50	.39	57.2	1.2	0.1	$\alpha CaCl_2\cdot 4H_2O + NaCl$
G	37.00	50.75	6.80	.37	16.0	69.3	0.1	$KCl + NaCl$
		50.80	6.60	.36	Not determined			$\alpha CaCl_2\cdot 4H_2O + KCl + NaCl$
		51.05	6.55	.39	57.9	2.2	0.2	$\alpha CaCl_2\cdot 4H_2O + NaCl$
	37.75	51.15	7.15	.39	Not determined			$\alpha CaCl_2\cdot 4H_2O + KCl + NaCl$
		51.65	6.50	.37	58.6	2.0	0.1	$\alpha CaCl_2\cdot 4H_2O + NaCl$
	38.00	51.25	7.40	.37	19.2	66.0	.3	$KCl + NaCl$
		51.85	6.95	.38	58.4	26.3	.2	$CaCl_2\cdot KCl + NaCl$
		52.00	6.80	.36	59.3	8.0	.1	$CaCl_2\cdot KCl + \alpha CaCl_2\cdot 4H_2O + NaCl$
	38.25	51.20	7.20	.40	18.7	66.0	.5	$KCl + NaCl$
		51.35	7.40	.36	35.7	53.6	.4	$CaCl_2\cdot KCl + KCl + NaCl$
		51.55	7.15	.38	56.6	26.0	.3	$CaCl_2\cdot KCl + NaCl$
		51.65	7.05	.40	59.1	4.4	.2	$\alpha CaCl_2\cdot 4H_2O + CaCl_2\cdot KCl + NaCl$
H	42.55	54.85	4.25	.38	Not determined			$CaCl_2\cdot KCl + \alpha CaCl_2\cdot 4H_2O + NaCl$
	42.60	54.15	4.60	.38	58.0	22.0	0.2	$CaCl_2\cdot KCl + NaCl$
		54.50	4.20	.39	57.3	24.0	.1	$CaCl_2\cdot KCl + NaCl$
		55.00	3.95	.38	56.8	4.3	.1	$CaCl_2\cdot KCl + \alpha CaCl_2\cdot 4H_2O + NaCl$
		55.10	3.90	.38	Not determined			$CaCl_2\cdot KCl + \alpha CaCl_2\cdot 4H_2O + NaCl$
		55.10	3.70	.39	58.8	1.1	0.1	$\alpha CaCl_2\cdot 4H_2O + NaCl$
	42.85	52.50	6.30	.39	57.9	29.5	.1	$CaCl_2\cdot KCl + NaCl$
		53.25	5.50	.38	57.5	28.6	.1	$CaCl_2\cdot KCl + NaCl$
		54.95	4.20	.40	61.5	14.8	.2	$CaCl_2\cdot KCl + CaCl_2\cdot 2H_2O + NaCl$
		55.05	4.25	.40	Not determined			$CaCl_2\cdot KCl + CaCl_2\cdot 2H_2O + NaCl$
		55.00	4.20	.40	58.8	2.0	0.2	$\alpha CaCl_2\cdot 4H_2O + NaCl$
	43.00	54.25	4.45	.39	57.9	28.0	.1	$CaCl_2\cdot KCl + NaCl$
		54.90	4.20	.40	62.0	6.2	.1	$CaCl_2\cdot KCl + CaCl_2\cdot 2H_2O + NaCl$
		55.05	4.15	.40	Not determined			$CaCl_2\cdot KCl + \alpha CaCl_2\cdot 4H_2O + NaCl$
		54.80	4.20	.39	58.8	2.2	0.1	$\alpha CaCl_2\cdot 4H_2O + NaCl$
H	43.00	55.00	4.00	.39	58.8	0.8	0.1	$\alpha CaCl_2\cdot 4H_2O + NaCl$
	43.35	54.50	4.55	.40	58.3	29.0	.2	$CaCl_2\cdot KCl + NaCl$
		54.90	4.20	.39	65.5	8.6	.1	$CaCl_2\cdot KCl + CaCl_2\cdot 2H_2O + NaCl$
		54.95	4.15	.40	67.9	0.8	.1	$CaCl_2\cdot 2H_2O + NaCl$
		55.20	4.10	.40	68.0	0.8	.1	$CaCl_2\cdot 2H_2O + NaCl$
					Calculated for the invariant equilibria E, G and H			
E	26.90	47.95	4.30	0.38	$(CaCl_2\cdot 6H_2O + \alpha CaCl_2\cdot 4H_2O + KCl + NaCl)$			
G	37.70	51.15	7.20	.39	$(\alpha CaCl_2\cdot 4H_2O + CaCl_2\cdot KCl + KCl + NaCl)$			
H	43.30	54.90	4.20	.40	$(\alpha CaCl_2\cdot 4H_2O + CaCl_2\cdot KCl + CaCl_2\cdot 2H_2O + NaCl)$			

When the calcium chloride content increases in the solutions at isotherms below 37.7°, sodium chloride decreases up to the univariant point. At a still greater concentration of calcium chloride the sodium chloride content is almost constant. This is also the case when the isotherm cuts the stability area of the double salt; the sodium chloride content of the solutions is almost constant up to the point $CaCl_2$–hydrate + NaCl.

These relations have some practical consequences, in that they may be used for the refining of alkali chlorides in a cyclic process. An example will be given here.

Figure 4 superposes the isotherms at 18 and at 95° (Cartesian coördinates). The alkali chlorides, powdered crystals, are treated with a solution containing about 56% calcium chloride at 95°. The solution dissolves potassium chloride and the composition changes in the direction A–B–C toward pure potassium chloride. When C is reached, the solution is saturated with respect to potassium chloride and sodium chloride. If the proportion between the solution and the alkali chlorides is correct (about 13 g. potassium chloride per 100 g. solution A), all the potassium chloride will be dissolved. The solution at C contains 49.5% calcium chloride, 12.5% potassium chloride and 1.0% sodium chloride. The sodium chloride not dissolved is removed, the solution is diluted (*e. g.*, with water) to 38% calcium chloride and then would contain 9.6% potassium chloride and 0.8% sodium chloride.

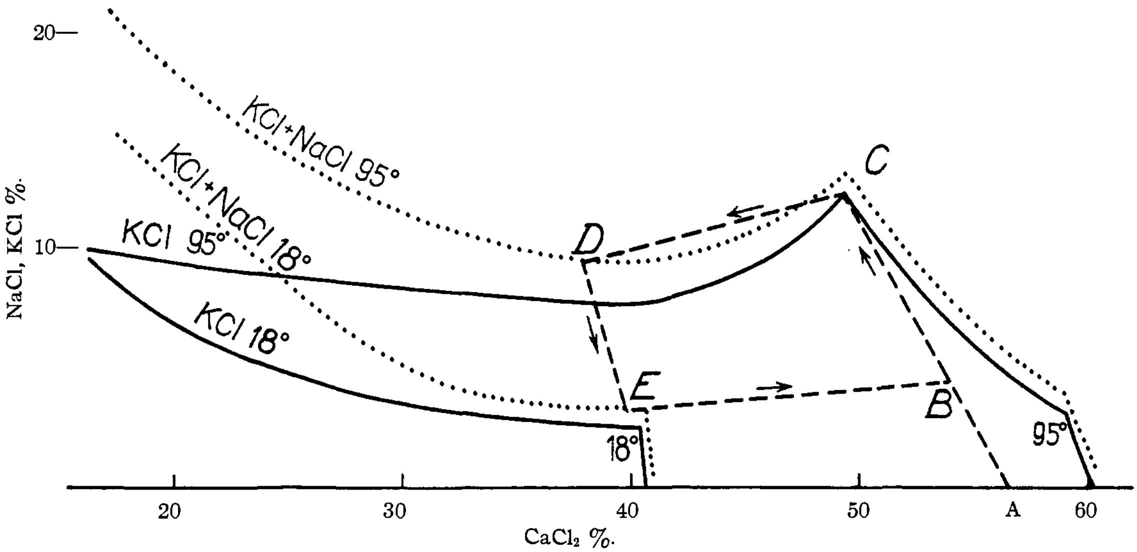

Fig. 4.—A cyclic process for extraction of potassium chloride between 18 and 95° from mixed alkali chlorides (Cartesian coördinates).

This solution is cooled down to 18°, a part of the dissolved alkali chlorides is deposited, and the solution changes its composition in the direction D–E, as the solution at E can contain only 40% calcium chloride, 2.5% potassium chloride and 0.3% sodium chloride. After removal of the precipitated alkali chlorides the solution at E is evaporated. The composition of the solution changes in the direction E–B; and the solution at B, containing the rest of the dissolved alkali chlorides, is ready for a new extraction, in this case starting at B. Per 100 g. of the solution at A or at B, 7.6 g. of alkali chlorides is precipitated as solid salt, containing 93% potassium chloride and 7% sodium chloride, theoretically.

Other starting-points may be chosen, *e. g.*, other temperatures as well as concentrations. In principle, the cyclic process is always similar in character. The practical use of the process is limited by the properties of the solutions. Calcium chloride solutions are difficult to handle at very high temperatures, especially when they are very rich in calcium chloride.

Double salt may also be used in order to extract potassium chloride from mixed alkali chlorides. This process, too, is of a cyclic type (Swedish patent). The solution at C (Fig. 4) is concentrated at a higher temperature; the double salt yielded is filtered off and decomposed at a low temperature (*e. g.*, 15°) by a solution containing a calculated amount of calcium chloride. In this way the potassium chloride will be deposited as a crystal powder of a low sodium chloride content.

Summary

1. Some isotherms (18, 50 and 95°) of the quaternary system are given.

2. Only one double salt occurs, $CaCl_2 \cdot KCl$; its lowest formation temperature is 37.70 ± 0.05°.

3. The two invariant equilibria $CaCl_2 \cdot 6H_2O + \alpha CaCl_2 \cdot 4H_2O + KCl + NaCl$ and $\alpha CaCl_2 \cdot 4H_2O + CaCl_2 \cdot KCl + CaCl_2 \cdot 2\,H_2O + NaCl$ are at 26.90 ± 0.05° and at 43.3 ± 0.1°, respectively.

4. Two cyclic processes to win potassium chloride from mixed alkali chlorides are described.

STOCKHOLM 50, SWEDEN
RECEIVED MARCH 28, 1949