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

Equilibria in Aqueous Systems Containing K^+, Na^+, Ca^{+2}, Mg^{+2} and Cl^-. III. The Ternary System $CaCl_2$–$MgCl_2$–H_2O[1]

BY GUNNAR O. ASSARSSON

Earlier Investigations.—The system has been investigated by van't Hoff and Kenrick[2] who determined the lowest temperature for the formation of the double salt tachydrite $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ (21.95°). Prutton and Tower[3] determined the invariant equilibria at low temperature: $MgCl_2 \cdot 12H_2O$ + $CaCl_2 \cdot 6H_2O$ + ice (−52.2), $MgCl_2 \cdot 12H_2O$ + $\alpha MgCl_2 \cdot 8H_2O$ + $CaCl_2 \cdot 6H_2O$ (−20.7), $\alpha MgCl_2 \cdot 8H_2O$ + $MgCl_2 \cdot 6H_2O$ + $CaCl_2 \cdot 6H_2O$ (−6.7). Later, Coolings and Shafer,[4] and Smith and Prutton[5] mentioned a new double salt, $2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$, with a transition temperature at 93°. Lightfoot and Prutton[6] also determined isotherms at 35 and 75°. At these temperatures the only double salt is tachydrite.

Some other conditions in the system will be of interest. The present investigation aims at giving a synopsis of the univariant equilibria, as new isotherms are necessary only at certain temperatures.

The Univariant Equilibria; Some Properties of the Solution.—The curves of the composition of the solutions surrounding the univariant points are plotted in the diagram, Fig. 1. The results of investigations published by other authors are also used. Some of the experimental results of the present investigation are presented in Table I, and deal chiefly with the determinations between 30 and 115°.

Two curve branches are of interest for common

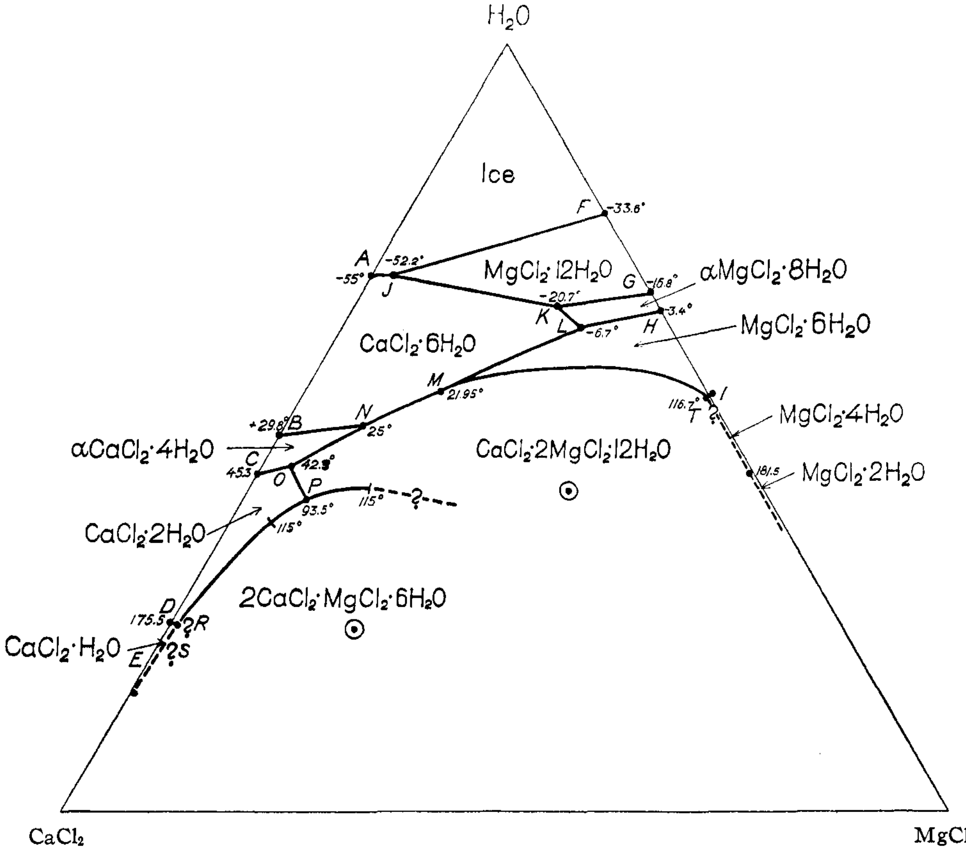

Fig. 1.—The ternary system $CaCl_2$–$MgCl_2$–H_2O: synopsis of the composition of the solutions for the invariant and univariant equilibria.

(1) Previous paper, THIS JOURNAL, **72**, 1437 (1950).

(2) J. H. van't Hoff and F. B. Kenrick, *Ber. Berl. Akad.*, 568 (1897).

(3) C. F. Prutton and O. F. Tower, THIS JOURNAL, **54**, 3046 (1932).

(4) W. R. Coolings and J. J. Shafer, U. S. Patent 1,738,492 (1923).

(5) A. K. Smith snd C. F. Prutton, U. S. Patents 1,768,797 and 1,780,098 (1923).

(6) W. J. Lightfoot and C. F. Prutton, THIS JOURNAL, **68**, 1001 (1946); **69**, 2098 (1947).

TABLE I

THE SYSTEM $CaCl_2$–$MgCl_2$–H_2O: EQUILIBRIA BETWEEN 40 AND 115°

Temperature, °C.	Solution CaCl₂ (weight per cent.)	Solution MgCl₂	Wet residue CaCl₂	Wet residue MgCl₂	Solid phase
40.0	48.9	4.5	Not determined		$\alpha CaCl_2 \cdot 4H_2O$ + tachydrite
42.0	52.0	3.5	59.4	0.4	$\alpha CaCl_2 \cdot 4H_2O$
42.5	52.4	3.2	67.7	0.9	$CaCl_2 \cdot 2H_2O$
44.0	52.5	3.2	64.1	1.5	$CaCl_2 \cdot 2H_2O$
46.5	52.6	3.6	65.0	1.7	$CaCl_2 \cdot 2H_2O$
50.0	52.3	3.9	Not determined		$CaCl_2 \cdot 2H_2O$ + tachydrite
60.0	52.4	4.3	Not determined		$CaCl_2 \cdot 2H_2O$ + tachydrite
80.0	52.6	5.4	53.5	11.9	$CaCl_2 \cdot 2H_2O$ + tachydrite
90.0	52.5	5.9	Not determined		$CaCl_2 \cdot 2H_2O$ + tachydrite
92.0	52.6	6.0	26.1	31.4	Tachydrite
	52.7	5.9	45.1	17.1	Tachydrite + $CaCl_2 \cdot 2H_2O$
	52.7	6.0	69.0	1.0	$CaCl_2 \cdot 2H_2O$
93.0	52.3	6.5	32.8	28.2	Tachydrite
	52.3	6.3	65.0	2.5	$CaCl_2 \cdot 2H_2O$
94.0	52.5	6.0	53.1	17.0	$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$
	52.4	6.3	64.4	2.8	$CaCl_2 \cdot 2H_2O$
96.5	51.5	7.1	53.0	16.7	$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$
	53.2	6.0	62.6	3.1	$CaCl_2 \cdot 2H_2O$
110.0	55.7	4.7	64.0	11.5	$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$ + $CaCl_2 \cdot 2H_2O$
	49.0	9.5	51.0	17.7	$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$ + tachydrite
115.0	58.2	4.0	63.0	10.0	$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$ + $CaCl_2 \cdot 2H_2O$
	47.0	11.5	48.0	26.0	$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$ + tachydrite
50.0	18.1	24.6	Not determined		Tachydrite + $MgCl_2 \cdot 6H_2O$
60.0	14.0	28.2	Not determined		Tachydrite + $MgCl_2 \cdot 6H_2O$
80.0	7.8	34.5	Not determined		Tachydrite + $MgCl_2 \cdot 6H_2O$
95.0	5.1	37.9	Not determined		Tachydrite + $MgCl_2 \cdot 6H_2O$
110.0	2.0	41.4	Not determined		Tachydrite + $MgCl_2 \cdot 6H_2O$
Calculated for the invariant equilibria O and P (Fig. 2)					
O 42.3	52.2	3.4	..	..	$\alpha CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 2H_2O$ + tachydrite
P 93.5	52.4	6.3	..	..	$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$ + $CaCl_2 \cdot 2H_2O$ + tachydrite

practical purposes; one limiting the stability area of tachydrite, the other limiting the area of the double salt $2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$.

The univariant equilibria, $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ + $MgCl_2 \cdot 6H_2O$ + solution, change their positions along the line M–T (Fig. 1) gradually until the invariant point T is reached (116.7°). At higher temperatures there are no determinations. This branch of the curve probably ends in the eutectic of the anhydrous system after decomposition of the double salt. The decomposition of magnesium chloride into hydrochloric acid and basic chlorides complicates the determinations. Along the other branch of the curve M–N–O, limiting the area for tachydrite, the solutions of the univariant equilibria change their compositions rather rapidly, so that the invariant equilibrium $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ + $\alpha CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 2H_2O$ is reached at 42.3°. Dilatometric determination of this transition point gave 42.3 ± 0.1°.

Simultaneously with the appearance of the calcium chloride dihydrate the curve changes its direction very strikingly, and the rising temperature causes an increase in the magnesium chloride content of the solutions only, while the calcium chloride content is constant. When 93.5° is reached, the new solid phase $2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$ appears. Isotherms at 70, 80, and 90°, cutting the boundary between the stability areas of tachydrite and of $CaCl_2 \cdot 2H_2O$ close to the transition point of the double salt $2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$ have been determined but are not given here. The curves show only faint breaks

TABLE II

THE SYSTEM $CaCl_2$–$MgCl_2$–H_2O, ISOTHERM AT 110°

Solution CaCl₂ (weight per cent.)	Solution MgCl₂	Wet residue CaCl₂	Wet residue MgCl₂	Solid phase
..	42.8	..	..	$MgCl_2 \cdot 6H_2O$
2.0	41.4	8.0	42.0	$MgCl_2 \cdot 6H_2O$ + tachydrite
13.6	30.8	18.8	34.3	Tachydrite
18.2	28.0	20.9	34.1	Tachydrite
26.9	21.2	23.2	31.4	Tachydrite
40.0	14.0	33.1	22.0	Tachydrite
47.8	10.0	31.2	26.6	Tachydrite
49.0	9.5	51.0	19.6	Tachydrite + $2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$
51.0	8.0	52.2	18.6	$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$
53.5	6.2	53.0	17.7	$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$
55.7	4.7	61.0	11.5	$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$ + $CaCl_2 \cdot 2H_2O$
56.8	4.0	70.0	1.0	$CaCl_2 \cdot 2H_2O$
62.3	..	69.0	..	$CaCl_2 \cdot 2H_2O$

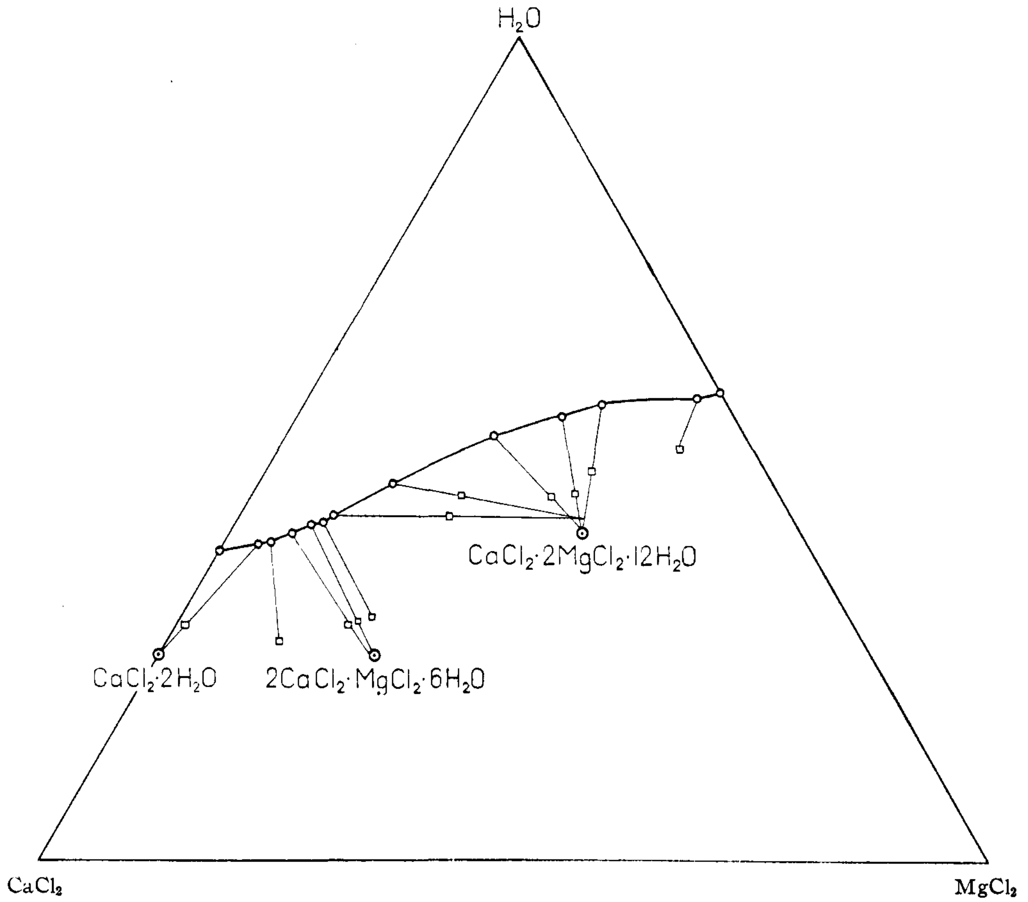

Fig. 2.—The ternary system $CaCl_2$–$MgCl_2$–H_2O at 110°.

at the boundary. No properties differing from those usually occurring in the system have been observed.

An isotherm at 110° cutting the stability area of the double salt $2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$ is given in Table II and Fig. 2. The isotherm shows only the properties usually connected with the formation of a double salt. For the univariant equilibria the slope of the curve shows only faint breaks.

On the one hand, the stability area of the double salt $2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$ borders on that of $CaCl_2 \cdot 2H_2O$ up to a temperature of about 170°, where the invariant equilibrium between this salt and $CaCl_2 \cdot 2H_2O$ and $CaCl_2 \cdot H_2O$ must lie. The properties of the solutions at still higher temperatures are not known.

On the other hand, the univariant equilibria, where the two double salts are present, have been followed up to 115°. It is not known in what way the two double salts decompose when the temperature rises still further.

Summary

Some isothermal equilibria between 30 and 115° are discussed.

1. The univariant equilibria have been determined and the results have been included in a synopsis showing the composition of the solutions for the univariant and the invariant equilibria.

2. The invariant equilibria $\alpha CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 2H_2O$ + tachydrite and $CaCl_2 \cdot 2H_2O$ + tachydrite + $2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$ have been determined at 42.2 ± 0.1° and 93.5 ± 0.5°, respectively.

STOCKHOLM 50, SWEDEN RECEIVED MARCH 28, 1949