

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF CASE SCHOOL OF APPLIED SCIENCE]

Equilibria in Saturated Salt Solutions. II. The Ternary Systems $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$, $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ and $\text{MgCl}_2\text{-KCl-H}_2\text{O}$ at 75°

BY WILLIAM J. LIGHTFOOT AND CARL F. PRUTTON

In a previous paper,¹ the three isotherms for the systems, $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$, $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ and $\text{MgCl}_2\text{-KCl-H}_2\text{O}$ at 35° were reported.

Experimental Method

The methods were similar to those used at the lower temperature where solutions were brought to equilibrium at $75 \pm 0.02^\circ$ with the exception that the saturated solution was filtered through cotton in a preheated capillary tube directly into a weighing bottle. Six to eight hours were found to be sufficient for equilibrium. However, the samples were agitated for several days before sampling.

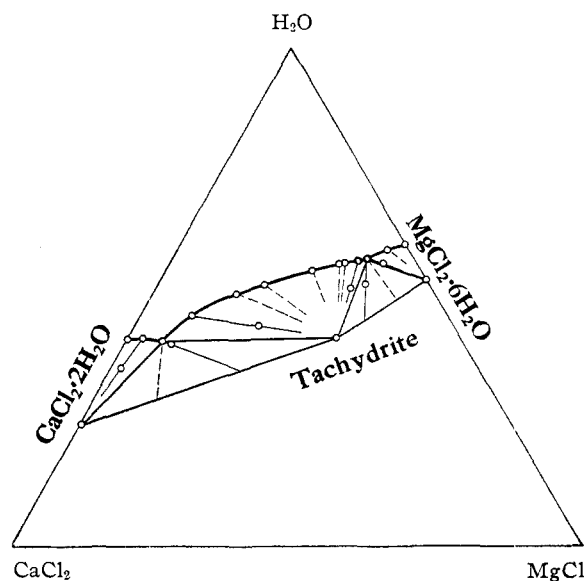


Fig. 1.—The ternary system: $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ at 75° .

All wet residues were examined microscopically and the solid phases identified by Schreinemaker's method. In examining a sample, saturated solution together with some of the crystalline solid phase were removed with a stirring rod and placed on a microscope cover glass. When samples of the mixtures from the studies at 35° were placed on the slide, very little subsequent crystallization took place except when dealing with the metastable forms of $\text{CaCl}_2\cdot 4\text{H}_2\text{O}$. To prevent crystallization of the samples taken at 75° , a small electrically heated microscope stage as described by Chamot and Mason² was used.

(1) Lightfoot and Prutton, *THIS JOURNAL*, **68**, 1001 (1946).

(2) Chamot and Mason, "Handbook of Chemical Microscopy," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1938.

The Ternary System $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$

Table I, Fig. 1.—In the temperature interval from 35 to 75° the isotherm for this system has gone through some marked changes. While there

TABLE I

THE TERNARY SYSTEM $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ AT 75°

Saturated solution		Wet residue		Solid phase
CaCl_2	MgCl_2	CaCl_2	MgCl_2	
58.58	0	$\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
55.76	2.53	62.72	1.65	$\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
52.59	5.27	51.38	7.99	$\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ + Tachydrite
52.57	5.28	$\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ + Tachydrite
45.01	8.74	34.12	21.42	Tachydrite
34.97	14.70	Tachydrite
29.15	18.63	Tachydrite
19.28	25.55	Tachydrite
13.83	29.65	Tachydrite
12.52	30.59	Tachydrite
10.15	32.39	Tachydrite
9.97	32.59	14.09	34.06	Tachydrite
8.31	33.90	Tach. + $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$
8.31	33.91	11.06	36.22	Tach. + $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$
8.04	34.07	6.00	37.27	$\text{MgCl}_2\cdot 6\text{H}_2\text{O}$
3.84	36.62	$\text{MgCl}_2\cdot 6\text{H}_2\text{O}$
0	39.12	$\text{MgCl}_2\cdot 6\text{H}_2\text{O}$

has been only a small change in the extent of the saturation curve for calcium chloride in the ternary system, the range of existence of tachydrite has opened so much that it occupies a major portion of the entire diagram. Where at 35° tachydrite incongruently saturated the solution, at 75° it shows congruent solubility. The field of existence of $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ now only covers a fraction of what it had covered at the lower temperature.

The Ternary System $\text{CaCl}_2\text{-KCl-H}_2\text{O}$

Table II, Fig. 2.—The diagram again shows the retrograde solubility of potassium chloride which was present at 35° . A new ternary compound $2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ has appeared which is incongruently soluble at 75° . In order to establish more completely the identity of this salt, a series of tests were run at 95° to see if its area of existence could be opened. The data are given in Table III. Since little could be gained by going to 95° as the compound still showed incongruent solubility, no further work was done at this temperature.

No information was available on the crystal structure and optical properties of $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ and $2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$. It was found that CaCl_2

TABLE II
 THE TERNARY SYSTEM $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ AT 75°

Saturated solution		Wet residue		Solid phase
Weight per cent.	Weight per cent.	Weight per cent.	Weight per cent.	
CaCl_2	KCl	CaCl_2	KCl	
0	33.16	KCl
11.73	21.62	KCl
18.27	16.00	KCl
28.47	9.62	KCl
37.65	6.77	KCl
42.84	6.97	KCl
47.64	8.43	37.52	27.17	KCl
50.19	10.32	39.68	35.30	$\text{KCl} + 2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
50.18	10.31	41.80	30.92	$\text{KCl} + 2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
50.21	10.36	$\text{KCl} + 2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
50.22	10.32	44.18	30.07	$\text{KCl} + 2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
50.34	10.36	45.68	25.97	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
50.92	9.36	48.56	16.92	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
53.85	6.21	50.14	18.25	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
54.03	6.08	45.58	30.75	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
54.52	5.45	51.21	14.67	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
54.79	5.55	51.40	14.40	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
56.33	4.51	54.85	7.92	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
56.28	4.33	52.72	13.22	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
56.57	4.20	45.58	30.41	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
56.79	4.00	47.99	24.15	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
57.00	3.92	47.67	26.22	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
57.62	3.60	44.64	34.09	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O} + \text{CaCl}_2\cdot 2\text{H}_2\text{O}$
57.64	3.58	52.79	20.47	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O} + \text{CaCl}_2\cdot 2\text{H}_2\text{O}$
57.69	3.58	57.93	5.59	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O} + \text{CaCl}_2\cdot 2\text{H}_2\text{O}$
57.68	3.60	54.80	11.95	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O} + \text{CaCl}_2\cdot 2\text{H}_2\text{O}$
57.77	2.56	63.80	1.57	$\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
58.58	0	$\text{CaCl}_2\cdot 2\text{H}_2\text{O}$

$2\text{H}_2\text{O}$ is probably orthorhombic, biaxial. It crystallized out on the largest face, a basal pina-

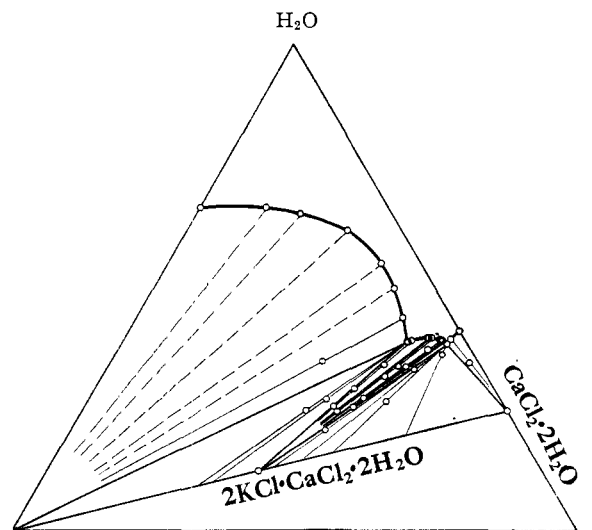

 Fig. 2.—The ternary system: $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ at 75° .

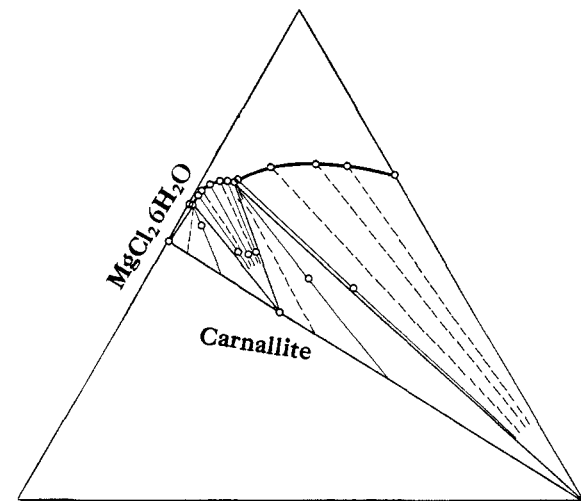
 TABLE III
 THE TERNARY SYSTEM $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ AT 95°

Saturated solution weight per cent.		Solid phase
CaCl_2	KCl	
49.47	12.42	$\text{KCl} + 2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
49.40	12.44	$\text{KCl} + 2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
52.47	7.25	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$
58.26	3.93	$2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O} + \text{CaCl}_2\cdot 2\text{H}_2\text{O}$

loid, the edges forming a rhomboid. It shows symmetrical extinction with low birefringence. $2\text{KCl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ is probably orthorhombic, biaxial negative with an index of refraction greater than 1.49. It crystallizes out in large rectangular plates or in small, well-defined cubes having a face across opposite corners, the usual form being in plates with the optic axis steeply inclined to the plate, about 20° from vertical. Depending on the development of the crystal, it will show either

 TABLE IV
 THE TERNARY SYSTEM $\text{MgCl}_2\text{-KCl-H}_2\text{O}$ AT 75°

Saturated solution		Wet residue		Solid phase
Weight per cent.	Weight per cent.	Weight per cent.	Weight per cent.	
MgCl_2	KCl	MgCl_2	KCl	
0	33.16	KCl
7.51	23.98	KCl
12.65	18.36	KCl
20.95	10.73	KCl
28.43	5.88	18.85	37.23	KCl
29.26	5.57	$\text{KCl} + \text{Carnallite}$
29.25	5.57	25.54	28.73	$\text{KCl} + \text{Carnallite}$
30.08	4.54	32.49	16.46	Carnallite
31.75	3.00	Carnallite
33.57	1.73	33.83	15.16	Carnallite
35.84	0.81	Carnallite
37.04	0.58	35.62	13.20	Carnallite
38.85	0.32	39.33	4.29	$\text{Carn.} + \text{MgCl}_2\cdot 6\text{H}_2\text{O}$
38.86	0.32	$\text{Carn.} + \text{MgCl}_2\cdot 6\text{H}_2\text{O}$
39.12	0	$\text{MgCl}_2\cdot 6\text{H}_2\text{O}$


 Fig. 3.—The ternary system: $\text{MgCl}_2\text{-KCl-H}_2\text{O}$ at 75° .

parallel or symmetrical extinction. There is a tendency to form twins. It has low birefringence, less than 0.01 and a positive sign of elongation.

The Ternary System $\text{MgCl}_2\text{-KCl-H}_2\text{O}$

Table IV, Fig. 3.—Even with increased temperature the area of existence of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ has not increased appreciably. It still represents a very small portion of the entire diagram. Since potassium chloride was determined directly on a sample of saturated solution, the values obtained for the isothermally invariant composition of solutions in equilibrium with carnallite and $\text{MgCl}_2 \cdot$

$6\text{H}_2\text{O}$ are slightly lower than those reported at nearby temperatures.

Acknowledgment.—The authors wish to thank Dr. R. L. Barrett for his assistance in the identification of the crystalline and optical properties of the substances encountered in the experimental portion of the study.

Summary

1. The isotherms for the ternary systems at 75° are given.
2. The ternary compound $2\text{KCl} \cdot \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ has been found to exist at 75° .

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The Vapor Pressure of Liquid Titanium Tetraiodide

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The literature is fairly complete with respect to the vapor pressures of zirconium,¹ thorium,² and tin³ tetraiodides. However, no data are available for titanium tetraiodide. All references to its volatility and boiling point stem from the original work of Hautefeuille,⁴ who simply states that it has a sensible vapor pressure at room temperature, melts at 150° and boils at a little above 360° , distilling without decomposition.

The present work represents the first determination of its vapor pressure. Titanium tetraiodide is extremely hygroscopic as well as being easily oxidized in air. Hence a suitable technique was developed for its preparation, purification, and transfer *in vacuo*.

Materials and Procedure

Titanium tetraiodide was prepared by the direct iodination of crude titanium (98%) containing 1.6% iron and some calcium as the principal impurities. Twenty grams of titanium (100% excess), having been previously washed with dilute hydrofluoric acid, distilled water, and absolute alcohol and dried, was placed in the middle bulb e of the glass apparatus in Fig. 1 which was sealed at f, stoppered at a, evacuated with flaming to 10^{-3} mm., and then let down to dry air. One hundred grams of dry resublimed iodine was liquefied in the funnel at a and allowed to run into the end bulb at c. A seal was made at b and the funnel was pulled off at that point. With bulb c cooled in Dry Ice, the system was again evacuated and sealed off at i. The middle bulb was maintained at 525° while the end bulbs were alternately heated and cooled in air in such a way as to drive the iodine slowly back and forth across the hot titanium.



Fig. 1.

- (1) Rahlfs and Fischer, *Z. anorg. allgem. Chem.*, **211**, 349 (1933).
- (2) Fischer, Gewehr and Wingschen, *ibid.*, **242**, 161 (1939).
- (3) Negishi, *THIS JOURNAL*, **58**, 2293 (1936).
- (4) Hautefeuille, *Bull. Soc. Chim.*, [2] **7**, 202 (1867).

After three passes, the conversion was apparently complete. With bulb c cooled in Dry Ice, about one-half of the titanium tetraiodide in h was distilled into c which was then sealed off at d. One-third of the remaining material was distilled in a like manner into e, a seal made at g and bulb h pulled off. This left about 30 g. of iodine-free titanium tetraiodide in bulb h. To provide for the breaking of this ampoule, the flame of an oxygen torch was touched to the glass wall, whereupon a concave thin glass "bubble" was formed. This operation required some care and practice. The ampoule containing the titanium tetraiodide was sealed into the vapor-pressure apparatus as indicated in Fig. 2.

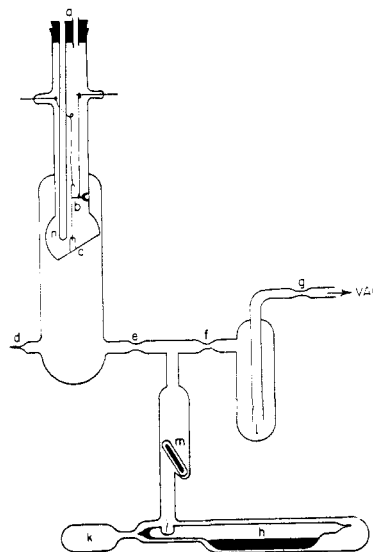


Fig. 2.

The differences in the boiling points of iodine (b. p. 184°), titanium tetraiodide (b. p. 377°), and calcium iodide (b. p. 718°) are such as to permit separation by distillation. A qualitative thiocyanate test for iron in the sample used was negative.

The vapor-pressure measurements were carried out in an all-glass manometer of the type described by Daniels⁵

- (5) F. Daniels, *THIS JOURNAL*, **50**, 1115 (1928).