[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF CASE INSTITUTE OF TECHNOLOGY]

Equilibria in Saturated Salt Solutions. IV. The Quaternary System $CaCl_2$–$MgCl_2$–KCl–H_2O at 75°

BY WILLIAM J. LIGHTFOOT AND CARL F. PRUTTON

In previous papers[1,2,3] the isotherms for the ternary systems at 35 and 75° and for the quaternary system at 35° were reported for the system $CaCl_2$–$MgCl_2$–KCl–H_2O.

Experimental Method

The experimental methods used were identical with those employed in the earlier papers. Temperature at which solutions and solid phases were brought into equilibrium was 75 ± 0.02°. The three methods of identification for the solid phases employed in the earlier work[3] were used.

The Quaternary System.—The data for the quaternary system at 75° are given in Table I. In Fig. 1 the upper portion of the quaternary tetrahedral figure is shown schematically. The relative proportions of the saturation surfaces are indicated. The same characteristic of magnesium chloride solutions that was noted in the ternaries and quaternary at 35° is found here: carnallite remains almost insoluble in solutions saturated for $MgCl_2\cdot6H_2O$. Tachydrite solutions dissolve considerably more carnallite, particularly as the saturated solution becomes richer in calcium chloride. This ability of tachydrite solutions to dissolve more carnallite is more pronounced than at 35°. The presence of the field of a new compound, $2KCl\cdot CaCl_2\cdot2H_2O$, decreases the range of existence of carnallite appreciably.

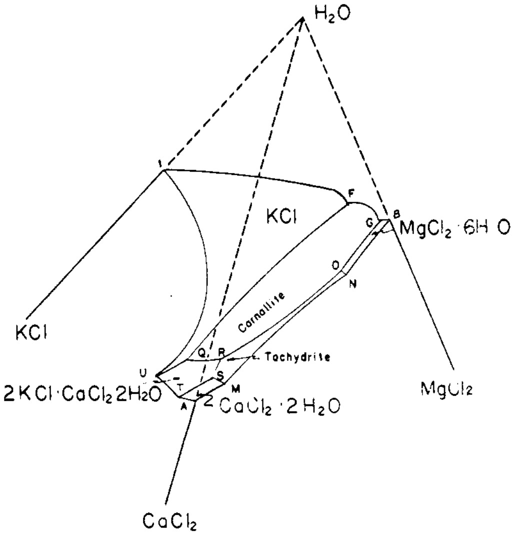

Fig. 1.—The system $CaCl_2$–$MgCl_2$–KCl–H_2O at 75°, upper portion of tetrahedron.

(1) Lightfoot and Prutton, THIS JOURNAL, **68**, 1001 (1946).
(2) Lightfoot and Prutton, *ibid.*, **69**, 2098 (1947).
(3) Lightfoot and Prutton, *ibid.*, **71**, 1236 (1949).

The saturation surface of $MgCl_2\cdot6H_2O$ has been reduced so that it now covers a very small part of the diagram. The area of saturation of $CaCl_2\cdot2H_2O$ is the second smallest with tachydrite and $2KCl\cdot CaCl_2\cdot2H_2O$ coming next in size, each with about the same area. Again KCl and carnallite occupy the largest areas in the diagram. However, the field of carnallite no longer extends from one side almost to the other.

With the introduction of a new solid phase, $2KCl\cdot CaCl_2\cdot2H_2O$, the relationships in the quaternary diagram have been altered considerably. Where at lower temperatures, $CaCl_2\cdot4H_2O$ and carnallite were in equilibrium along a portion of the isotherm, the presence of the new phase completely separates $CaCl_2\cdot2H_2O$ from carnallite. No formation of a quaternary compound was found at 75°.

In Fig. 2 the quaternary isotherm has been projected on the $MgCl_2$–KCl–H_2O plane. Points F, G, M, N, T, and U are the respective invariant points of the associated ternary systems. Area IFQU, is the saturation surface of KCl; FGORQ, that of carnallite, $KCl\cdot MgCl_2\cdot6H_2O$; NOGB, that of $MgCl_2\cdot6H_2O$; MNORS, that of tachydrite, $CaCl_2\cdot2MgCl_2\cdot12H_2O$; AMST, that of $CaCl_2\cdot2H_2O$; and RSTUQ, that of $2KCl\cdot CaCl_2\cdot2H_2O$.

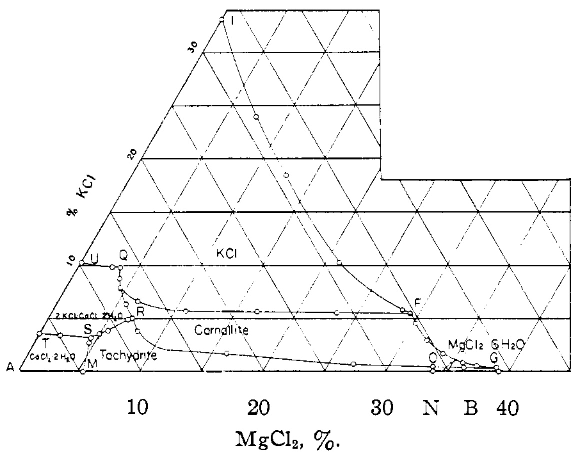

Fig. 2.—Equilibria in the quaternary system $CaCl_2$–$MgCl_2$–KCl–H_2O at 75°, projection on the $MgCl_2$–KCl–H_2O plane.

The curve FQ is the intersection of the KCl surface with the carnallite surface, and all points on it represent equilibrium between the two solid phases, KCl and carnallite, and saturated solution. GO represents solutions saturated with carnallite

TABLE I

THE QUATERNARY SYSTEM $MgCl_2$–$CaCl_2$–KCl–H_2O AT 75°

Point or line	Saturated solution $MgCl_2$ (Weight per cent.)	Saturated solution $CaCl_2$	Saturated solution KCl	Wet residue $MgCl_2$	Wet residue $CaCl_2$	Wet residue KCl	Jänecke projection weight, % $MgCl_2$	Jänecke projection weight, % $CaCl_2$	Solid phase
F	29.26	...	5.57				84.01	...	Carnallite + KCl
FQ	23.14	8.56	5.56				62.10	22.97	Carnallite + KCl
FQ	16.71	18.07	5.61				41.37	44.74	Carnallite + KCl
FQ	10.89	27.57	5.85				24.58	62.22	Carnallite + KCl
FQ	6.39	36.76	6.73	12.99	21.46	25.80	12.81	73.70	Carnallite + KCl
FQ	4.48	41.95	7.81				8.26	77.34	Carnallite + KCl
FQ	3.85	44.63	8.80				6.72	77.92	Carnallite + KCl
Q	3.49	46.28	9.70						Carnallite + KCl + $2KCl\cdot CaCl_2\cdot 2H_2O$
Q	3.44	46.34	9.70						Carnallite + KCl + $2KCl\cdot CaCl_2\cdot 2H_2O$
Q	3.49	46.32	9.70	6.83	33.82	26.93			Carnallite + KCl + $2KCl\cdot CaCl_2\cdot 2H_2O$
Q mean	3.47	46.31	9.70				5.83	77.86	Carnallite + KCl + $2KCl\cdot CaCl_2\cdot 2H_2O$
G	38.86	...	0.32				99.18	...	Carnallite + $MgCl_2\cdot 6H_2O$
GO	36.20	4.26	0.38	37.18	3.03	4.37	88.64	10.43	Carnallite + $MgCl_2\cdot 6H_2O$
O	33.64	8.38	0.40						Carnallite + $MgCl_2\cdot 6H_2O$ + Tachydrite
O	33.69	8.40	0.38						Carnallite + $MgCl_2\cdot 6H_2O$ + Tachydrite
O	33.66	8.42	0.39	36.16	6.29	4.11			Carnallite + $MgCl_2\cdot 6_2HO$ + Tachydrite
O mean	33.68	8.40	0.39				79.30	19.78	Carnallite + $MgCl_2\cdot 6H_2O$ + Tachydrite
OR	26.95	16.96	0.67				60.45	38.04	Carnallite + Tachydrite
OR	16.12	32.00	1.58	19.73	28.15	3.75	32.43	64.39	Carnallite + Tachydrite
OR	7.92	44.90	3.68				14.02	79.47	Carnallite + Tachydrite
R	6.76	46.44	5.11						Carnallite + Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
R	6.73	46.46	5.12	16.19	31.25	14.98			Carnallite + Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
R	6.79	46.40	5.11						Carnallite + Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
R mean	6.76	46.43	5.11				11.60	79.64	Carnallite + Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
RQ	5.58	46.69	6.25	11.51	31.19	25.95	9.54	79.78	Carnallite + $2KCl\cdot CaCl_2\cdot 2H_2O$
T	...	57.66	3.59				...	94.14	$CaCl_2\cdot 2H_2O$ + $2KCl\cdot CaCl_2\cdot 2H_2O$
TS	1.85	55.23	3.35	1.08	59.95	6.83	3.06	91.40	$CaCl_2\cdot 2H_2O$ + $2KCl\cdot CaCl_2\cdot 2H_2O$
M	5.28	52.58	...				9.13	90.87	$CaCl_2\cdot 2H_2O$ + Tachydrite
MS	4.66	52.47	2.65	9.21	53.02	1.54	7.80	87.77	$CaCl_2\cdot 2H_2O$ + Tachydrite
S	4.56	52.45	3.08						$CaCl_2\cdot 2H_2O$ + Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
S	4.54	52.54	3.06						$CaCl_2\cdot 2H_2O$ + Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
S	4.54	52.55	3.06	9.63	46.60	6.65			$CaCl_2\cdot 2H_2O$ + Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
S mean	4.55	52.51	3.07				7.57	87.33	$CaCl_2\cdot 2H_2O$ + Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
SR	4.51	52.29	3.19				7.52	87.16	Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
SR	4.97	51.21	3.44	6.55	45.18	15.19	8.34	85.89	Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
SR	5.44	50.06	3.81				9.17	84.40	Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
SR	6.68	46.63	5.02				11.45	79.94	Tachydrite + $2KCl\cdot CaCl_2\cdot 2H_2O$
U	...	51.20	10.33				...	83.21	KCl + $2KCl\cdot CaCl_2\cdot 2H_2O$
UQ	2.71	47.32	9.84	1.49	39.94	32.06	4.53	79.04	KCl + $2KCl\cdot CaCl_2\cdot 2H_2O$
N	33.91	8.31	...				80.32	19.68	Tachydrite + $MgCl_2\cdot 6H_2O$

and $MgCl_2\cdot 6H_2O$; RQ, carnallite and $2KCl\cdot CaCl_2\cdot 2H_2O$; UQ, KCl and $2KCl\cdot CaCl_2\cdot 2H_2O$; TS, $CaCl_2\cdot 2H_2O$ and $2KCl\cdot CaCl_2\cdot 2H_2O$; SR, tachydrite and $2KCl\cdot CaCl_2\cdot 2H_2O$; MS, $CaCl_2\cdot 2H_2O$ and tachydrite; and NO, $MgCl_2\cdot 6H_2O$ and tachydrite.

There are four isothermal invariant points in the system, R, S, Q, and O. The three solid phases in equilibrium with saturated solution at each point are: at Q, KCl, carnallite and $2KCl\cdot CaCl_2\cdot 2H_2O$; at S, $CaCl_2\cdot 2H_2O$, tachydrite, and $2KCl\cdot CaCl\cdot 2H_2O$; and at O, $MgCl_2\cdot 6H_2O$, tachydrite, and carnallite.

In Figs. 3 and 4, the quaternary relationships have been projected on the $CaCl_2$–KCl–H_2O and the $CaCl_2$–$MgCl_2$–H_2O planes respectively. In the projection on the $CaCl_2$–KCl–H_2O face there appears to be an overlapping of the KCl and carnallite surfaces. This is due only to the method of projection. The saturation curves can be readily distinguished from one another. The projection on the $CaCl_2$–$MgCl_2$–H_2O plane is perhaps the clearest in that there is no overlapping or superimposing of the different curves.

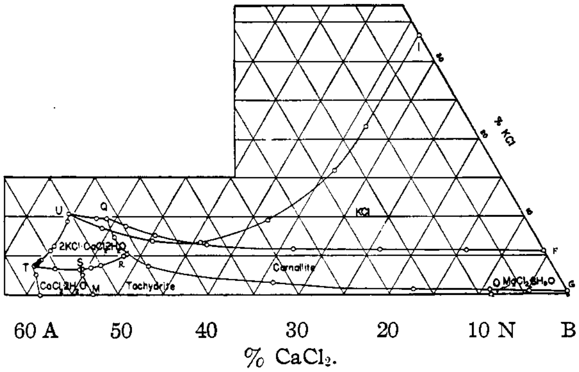

Fig. 3.—Equilibria in the system $CaCl_2$–$MgCl_2$–KCl–H_2O at 75° projected on the $CaCl_2$–KCl–H_2O plane.

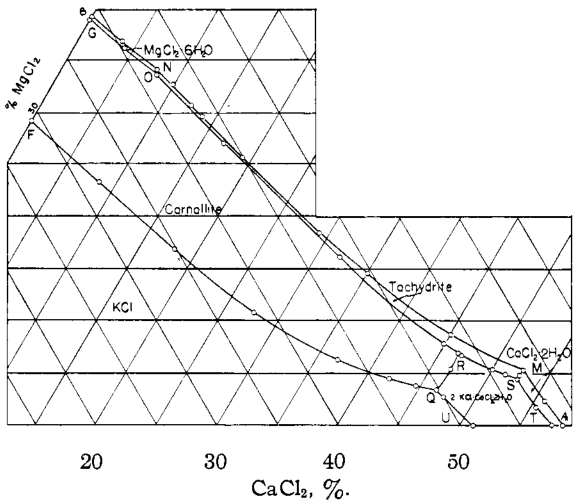

Fig. 4.—Equilibria in the quaternary system $CaCl_2$–$MgCl_2$–KCl–H_2O at 75°, projection on the $CaCl_2$–$MgCl_2$–H_2O plane.

The data on the quaternary system at 75° are given in Table I on a water free basis, and have been plotted in Figure 5, which gives the Jänecke projection. The coexistent solid phases are connected by straight lines, the triangles formed represent the three solid phases which are in equilibrium at the invariant points. The notations are consistent with those used in the other projections. Comparison with the similar type of diagram at 35° shows that all areas in general have increased except $MgCl_2 \cdot 6H_2O$. The main difference is that saturated solutions dissolve more KCl.

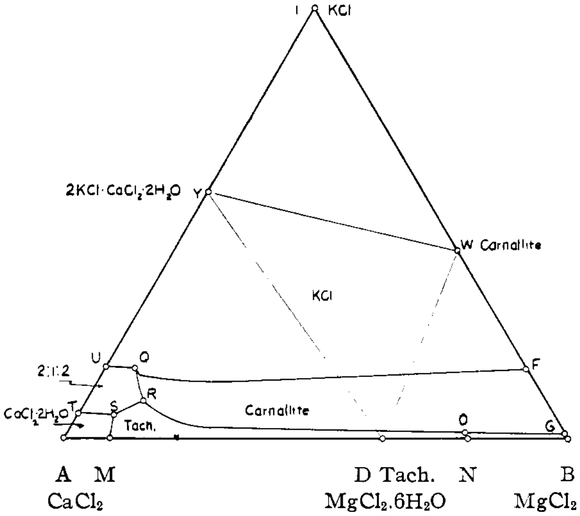

Fig. 5.—Quaternary system $CaCl_2$–$MgCl_2$–KCl–H_2O at 75°, Jänecke projection.

Summary

1. The isotherm for the quaternary system $CaCl_2$–$MgCl_2$–KCl–H_2O at 75° has been determined.

CLEVELAND HEIGHTS, OHIO RECEIVED AUGUST 25, 1948