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

Equilibria in Saturated Salt Solutions. V. The Quinary System $CaCl_2$–$MgCl_2$–KCl–NaCl–H_2O at 35°

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Invariant points in the quinary system $CaCl_2$–$MgCl_2$–KCl–NaCl–H_2O; in the quaternary systems $CaCl_2$–KCl–NaCl–H_2O, $MgCl_2$–KCl–NaCl–H_2O and $CaCl_2$–$MgCl_2$–NaCl–H_2O; and in the ternary systems $CaCl_2$–NaCl–H_2O, $MgCl_2$–NaCl–H_2O and KCl–NaCl–H_2O were determined at 35° to supplement the existing data. Data for the remaining associated ternary systems and quaternary system are found in the papers of Lightfoot and Prutton.[1,2] Seidell[3] gives references to most of the other published data on these systems

Experimental Method

Calcium chloride tetrahydrate was made by neutralizing C. P. hydrochloric acid with C. P. calcium carbonate and subsequent crystallization at 35°. Magnesium chloride hexahydrate was made by reaction of C. P. hydrochloric acid with distilled magnesium and the crystallization of the chloride at room temperature. A. C. S. grade potassium and sodium chlorides were used without further purification.

Samples of different over-all composition were made up for each invariant point, and it was possible to obtain analyses of fixed composition on these separate solutions that were within the limits for the experimental methods involved. Solid phases were checked by microscopic examination.

The samples were agitated three to five days in the usual manner in bottles in a thermostat maintained at 35 ± 0.02° to attain equilibrium. Each sample was seeded with the appropriate solid phase. Sampling and analytical methods for the determination of total chloride, calcium and potassium contents were identical with those used by Lightfoot and Prutton.[1] Magnesium was calculated by difference in all cases. Sodium was determined as uranyl zinc sodium acetate on a separate sample of saturated solution.

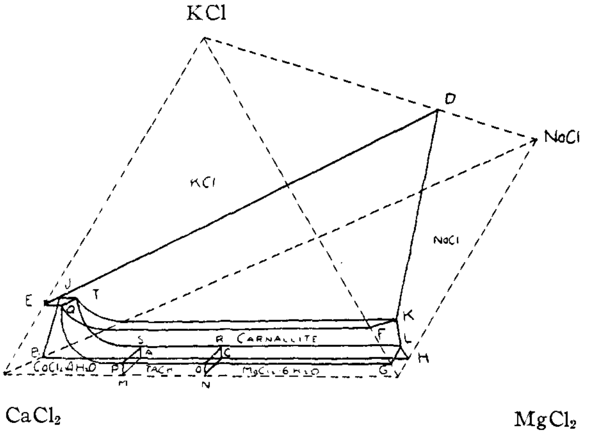

Fig. 1.—The quinary system $CaCl_2$–$MgCl_2$–KCl–NaCl–H_2O at 35°.

Experimental Results

Table I gives the data for the quinary system $CaCl_2$–$MgCl_2$–KCl–NaCl–H_2O at 35°. As it becomes increasingly difficult to graphically represent phase equilibria as the number of components increases, a schematic three dimensional figure probably offers the clearest conception of the relationships existing. In Fig. 1 the three dimensional model for the quinary system is shown schematically as a regular tetrahedron.

Each line forming the sides of the tetrahedron represents equilibria in the ternary system composed of the two salts at the ends of the line and water. Each face represents the equilibria in a given quaternary system. This last face is a projection by the Jänecke method of the equilibria in a quaternary tetrahedron on the base of the tetrahedron. Unfortunately in such a projection, there is no satisfactory method for representing water content of the saturated solutions and everything must be dealt with on a zero per cent. water basis. Each Jänecke projection of the quaternary systems forms the sides of the quinary tetrahedron. Equilibria in the quinary system are represented by points within the body of the tetrahedron.

A point on the line joining potassium chloride and magnesium chloride would represent a saturated solution of magnesium chloride and potassium chloride in equilibrium with one or two solid phases. At point F the two solid phases would be potassium chloride and carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$. At a point between F and G there would be only one solid phase, carnallite.

Within the area bounded by potassium chloride, F, K and D, a point would represent a saturated solution containing potassium chloride, magnesium chloride, and sodium chloride in equilibrium with potassium chloride as the solid phase. Along the line DK, the solid phases potassium chloride and sodium chloride would be present. At point K, a quaternary isothermal invariant point, the three phases, carnallite, potassium chloride and sodium chloride would exist. This same relationship holds true for the other quaternary faces.

In the quinary system, a point within the volume bounded by FGLKTQPOSR, the carnallite volume, would be a saturated solution containing potassium chloride, magnesium chloride, sodium chloride, calcium and chloride in equilibrium with one solid phase, carnallite. A point

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

(2) Lightfoot and Prutton, *ibid.*, **70**, 4112 (1948).

(3) Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, third ed., D. Van Nostrand, New York, N. Y., 1940.

TABLE I

THE QUINARY SYSTEM $CaCl_2$–$MgCl_2$–KCl–NaCl–H_2O AT 35°

Point	Saturated solution Weight % $MgCl_2$	$CaCl_2$	KCl	NaCl	Solid phase
D	...	...	12.35	19.93	KCl + NaCl
D	...	...	12.34	19.88	KCl + NaCl
H	35.96	...	...	0.33	$MgCl_2 \cdot 6H_2O$ + NaCl
H	35.93	...	...	0.33	$MgCl_2 \cdot 6H_2O$ + NaCl
G	36.17	...	0.14	...	$MgCl_2 \cdot 6H_2O$ + carnallite[a]
F	27.33	...	3.81	...	KCl + carnallite
N	18.18	26.68	...	...	$MgCl_2 \cdot 6H_2O$ + tachydrite[b]
M	6.20	45.03	...	...	$CaCl_2 \cdot 4H_2O\alpha$ + tachydrite
B	...	51.33	...	0.33	$CaCl_2 \cdot 4H_2O\alpha$ + NaCl
B	...	51.31	...	0.33	$CaCl_2 \cdot 4H_2O\alpha$ + NaCl
E	...	50.45	6.48	...	$CaCl_2 \cdot 4H_2O\alpha$ + KCl
K	27.87	...	1.98	1.45	Carnallite + KCl + NaCl
K	27.88	...	2.02	1.45	Carnallite + KCl + NaCl
L	35.88	...	0.09	0.33	$MgCl_2 \cdot 6H_2O$ + carnallite + NaCl
L	35.86	...	0.09	.33	$MgCl_2 \cdot 6H_2O$ + carnallite + NaCl
Q	1.02	49.76	6.46	...	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\alpha$
P	5.91	45.30	0.99	...	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$ + tachydrite
O	18.07	26.74	0.23	...	Carnallite + $MgCl_2 \cdot 6H_2O$ + tachydrite
J	...	49.75	6.77	.33	$CaCl_2 \cdot 4H_2O\alpha$ + KCl + NaCl
J	...	49.69	6.79	.33	$CaCl_2 \cdot 4H_2O\alpha$ + KCl + NaCl
A	6.53	44.67	...	.28	$CaCl_2 \cdot 4H_2O\alpha$ + tachydrite + NaCl
A	6.48	44.73	...	.28	$CaCl_2 \cdot 4H_2O\alpha$ + tachydrite + NaCl
C	18.46	26.52	...	.32	$MgCl_2 \cdot 6H_2O$ + tachydrite + NaCl
C	18.51	26.45	...	.32	$MgCl_2 \cdot 6H_2O$ + tachydrite + NaCl
T	1.41	48.83	6.28	.32	$CaCl_2 \cdot 4H_2O\alpha$ + carnallite + KCl + NaCl
T	1.34	48.77	6.25	.32	$CaCl_2 \cdot 4H_2O\alpha$ + carnallite + KCl + NaCl
R	17.41	27.18	0.21	.26	$MgCl_2 \cdot 6H_2O$ + carnallite + tachydrite + NaCl
R	17.50	27.10	.21	.26	$MgCl_2 \cdot 6H_2O$ + carnallite + tachydrite + NaCl
S	6.17	44.70	.97	.28	$CaCl_2 \cdot 4H_2O\alpha$ + carnallite + tachydrite + NaCl
S	6.21	44.72	.97	.28	$CaCl_2 \cdot 4H_2O\alpha$ + carnallite + tachydrite + NaCl

[a] Carnallite = $KCl \cdot MgCl_2 \cdot 6H_2O$. [b] Tachydrite = $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$.

on the three dimensional surface within the tetrahedron bounded by FKTQ would have the solid phases, carnallite and potassium chloride. Along the line KT the solid phases would be carnallite, potassium chloride, and sodium chloride; along JT, $CaCl_2 \cdot 4H_2O\alpha$, potassium chloride, and sodium chloride; along QT, $CaCl_2 \cdot 4H_2O\alpha$, carnallite, and potassium chloride. These three lines join at point T, a quinary isothermal invariant point, where the four solid phases, carnallite, $CaCl_2 \cdot 4H_2O\alpha$, potassium chloride and sodium chloride are co-existent.

The same relationships can be reasoned for the other volumes, surfaces, lines and points in the quinary figure.

Literature values for the sodium chloride content of the invariant points of the systems studied are not in good agreement with each other and, in general, are higher than the values given in Table I. This might be explained by the fact that many of these investigations were carried out prior to the development of the zinc uranyl acetate method for sodium.

The most striking feature of the data of this investigation is the constancy of the sodium chloride values at the invariant points in which $CaCl_2 \cdot 4H_2O\alpha$ or $MgCl_2 \cdot 6H_2O$ appear as solid phases. These values range from 0.26 to 0.33%. Concentration of sodium chloride at other points is significantly higher.

Summary

1. The isothermal invariant points in the quinary system $CaCl_2$–$MgCl_2$–KCl–NaCl–H_2O were determined at 35°.
2. The isothermal invariant points in the quaternary systems $CaCl_2$–KCl–NaCl–H_2O and $CaCl_2$–$MgCl_2$–NaCl–H_2O were determined at 35°.
3. The isothermal invariant points in the ternary systems $CaCl_2$–NaCl–H_2O, $MgCl_2$–NaCl–H_2O and KCl–NaCl–H_2O were determined at 35°.

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