and 10. The others are the results of substitution in equations 7 and 8 of the data listed in Columns 2 and 3.

Lewis and Randall's[16] calculations of the activity coefficients of sodium chloride depended upon the classic $\bar{L}_1$ data of Randall and Bisson. The data of Table II, together with the new heat capacity data of Randall and Rossini and of Lipsett, Johnson and Maass, were employed in a recalculation of activity coefficients. In spite of important differences between the above and the original values of $\bar{L}_1$ the results of the new calculations differ so little from the original ones that we refrain from giving them.

It seems probable however that work now being performed at other temperatures will introduce more important corrections. Some preliminary measurements[17] indicate that the variation of $\phi H - \phi H°$ between 25 and 0° is much larger than is indicated by heat capacity data at 25°.

Summary

Data applicable to the calculation of the relative heat contents of the constituents of aqueous sodium chloride solutions have been assembled. They have been critically examined by a method convenient for their inter-comparison and for differentiation. The collected information has been supplemented by new measurements.

From all of the available data, the relative partial molal heat contents have been calculated for 25°. Activity coefficients calculated with the aid of these values are not very different from those originally calculated by Lewis and Randall.

[16] Ref. 14, p. 351.

[17] J. F. Chittum, Dissertation, University of Chicago.

CHICAGO, ILLINOIS

THE SYSTEM CALCIUM CHLORIDE–MAGNESIUM CHLORIDE–WATER[1] AT 0, −15 AND −30°

BY C. F. PRUTTON AND O. F. TOWER

Introduction

Sodium, calcium and magnesium chlorides occur together in sea water, most salt brines and salt deposits, and provide a commercial source of the above chlorides. In connection with the separation of these chlorides, data on the quaternary system calcium chloride–magnesium chloride–sodium chloride–water are of importance.

[1] Presented by C. F. Prutton in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Western Reserve University, 1928.

This work is a study in the ternary system calcium chloride–magnesium chloride–water, undertaken as a preliminary study to the quaternary system. The only data available on this ternary system is that of Lee and Egerton,[2] who give the 25° isotherm, and Smith and Prutton[3] who verified the existence of tachydrite—$CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$—and also found a second double salt at higher temperatures—$2CaCl_2 \cdot MgCl_2 \cdot 6H_2O$. The data of Van't Hoff, Kenrick and Dawson[4] were obtained in solutions saturated with sodium chloride. The occurrence of this second double salt suggested the possibility of still other double salts at temperatures below those investigated. The exact freezing points of solutions of calcium and magnesium chlorides are of interest in refrigeration where some use is made of the mixed chlorides for refrigerating brines.

Experimental

A. Materials Used.—Pure calcium chloride was obtained by dissolving c. p. calcium carbonate in c. p. hydrochloric (1 to 1) acid and precipitation of any magnesium present by boiling this solution with an excess of calcium oxide made by ignition of part of the calcium carbonate. The filtered solution was neutralized, concentrated by evaporation, and then cooled to 20° for about one day. Large crystals of the hexahydrate of calcium chloride separated. This crystallization was repeated six times.

Magnesium chloride was prepared by the solution of distilled magnesium metal (American Magnesium Corporation) in (1 to 2) c. p. hydrochloric acid. The slight excess acidity in solution was neutralized with c. p. magnesium oxide. The solution was filtered, concentrated and cooled to obtain crystals of the hexahydrate of magnesium chloride. The crystals were recrystallized twice from distilled water.

Both chlorides met with all tests on these salts as specified by Murray[5] for chemically pure reagents.

B. Method.—Solubilities were determined by the usual saturation method; samples of the saturated solutions and of the residues were taken for analysis. The residue method of Schreinemakers[6] was used to identify the solid phase present. All isothermal invariant points were approached from both sides of the equilibrium, and it was found that eight hours' agitation, in all cases, was sufficient time for equilibrium to be reached.

The cryostat used was a modification of that of Sinozaki and Hara.[7] Liquid ammonia was used as the cooling agent for temperatures down

[2] Lee and Egerton, *J. Chem. Soc.*, **123**, 711 (1923).

[3] Smith and Prutton, U. S. Patent 1,627,068.

[4] Van't Hoff, Kenrick and Dawson, *Z. physik. Chem.*, **39**, 27 (1902).

[5] Murray, "Standards and Tests for Reagent and C. P. Chemicals," 1927.

[6] Schreinemakers, *Z. physik. Chem.*, **11**, 75 (1893).

[7] Sinozaki and Hara, *J. Soc. Chem. Ind. Japan*, **29**, 262 (1926); *Tech. Rpts. Tôhoku Imp. Univ.*, Vol. VI, 2, 121 (1926).

to −30° and liquid air for the lower temperatures. The cryostat bath was a four-liter Pyrex thermos silvered vacuum flask, 15 cm. in diameter and about 25 cm. deep. This was filled with a 50% ethyl alcohol–water mixture.

Temperature control of the bath could be automatically maintained at ±0.1° for about twelve hours. With this variation in bath temperature, the temperature inside the solubility tube was maintained within ±0.03° of the desired temperature.

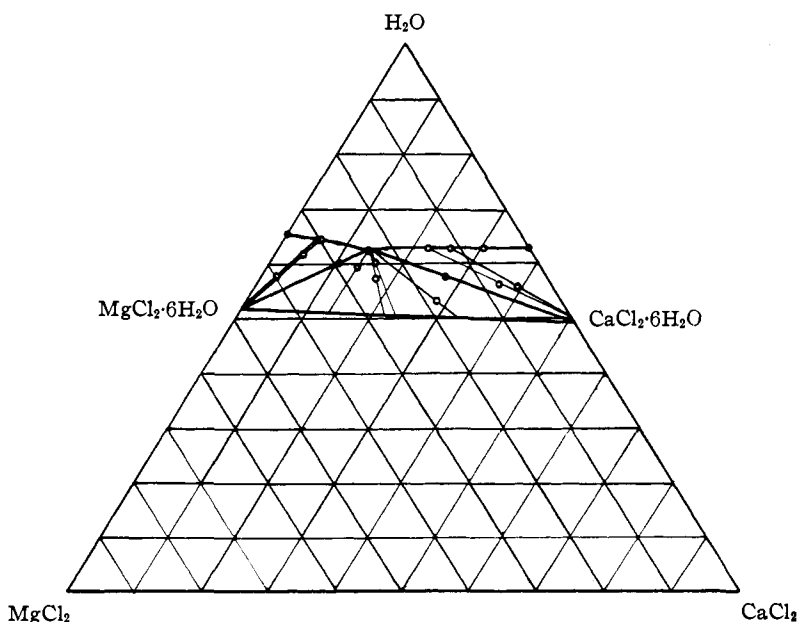Fig. 1.—0° isotherms.   System: $CaCl_2$–$MgCl_2$–H_2O.

The solubility tube was a large Pyrex test-tube (6 × 22 cm.) similar to that used by the Earl of Berkeley.[8] This tube was immersed in the cryostat bath to a depth of about 18 cm. and contained sufficient solution and crystals to fill the tube to a depth of about 7 cm.

Temperatures were measured by a multiple (six) junction copper-constantan thermocouple, inside the solubility tube, using a Leeds-Northrup portable potentiometer pyrometer. The uniformity of the wire used in the couple was checked and the couple calibrated in place; at the ice point, the freezing points of mercury and carbon tetrachloride, and the vaporizing temperature of solid carbon dioxide.

In the solutions and residues, calcium and total chloride were determined volumetrically, and the amounts of the two chlorides present cal-

8 Earl of Berkeley, *Trans. Roy. Soc. (London)*, **A203**, 189–215 (1904).

culated.   The method of Blasdale[9] was used for precipitation of calcium oxalate and the precipitated calcium oxalate titrated by the well-known method using standard potassium permanganate.   Mohr's method was used for the volumetric determination of total chlorides.
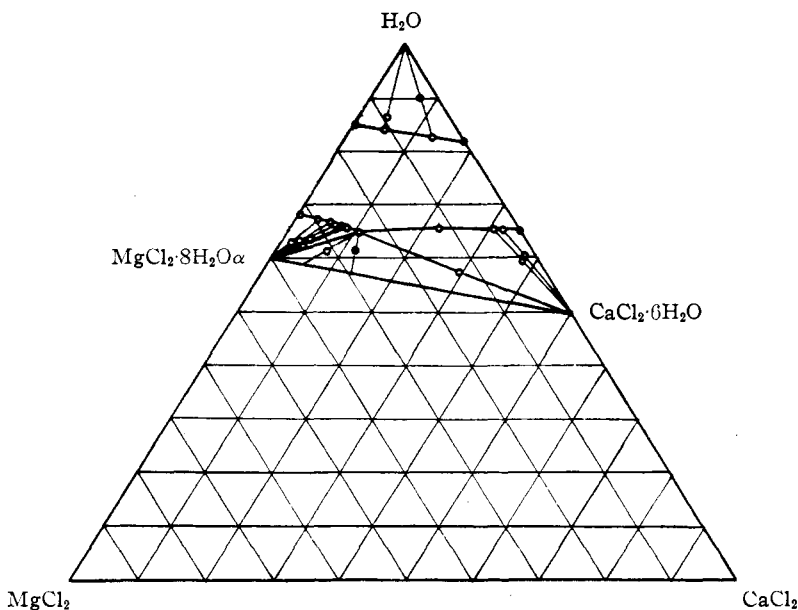

Fig. 2.—15° isotherms.   System: $CaCl_2$–$MgCl_2$–H_2O.

The potassium permanganate solution used was standardized against Bureau of Standards sodium oxalate.   The silver nitrate solution was

TABLE I

SOLUBILITY DATA AT 0°

	Solution Grams/100 g. of solution		Residue Grams/100 g. of residue	
Solid phase	$MgCl_2$	$CaCl_2$	$MgCl_2$	$CaCl_2$
$CaCl_2 \cdot 6H_2O$	0	37.32		
$CaCl_2 \cdot 6H_2O$	6.82	30.22		
$CaCl_2 \cdot 6H_2O$	11.95	25.10	5.01	37.42
$CaCl_2 \cdot 6H_2O$	14.94	22.12	7.60	36.02
$CaCl_2 \cdot 6H_2O$	22.83	14.89	14.96	27.47
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$	23.86	13.82	27.54	13.69
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$	23.78	13.90	26.17	15.44
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$	23.81	13.81	19.15	28.47
$CaCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 6H_2O$	23.70	13.78		
$MgCl_2 \cdot 6H_2O$	23.91	13.87	29.34	10.62
$MgCl_2 \cdot 6H_2O$	29.91	5.84	33.59	4.52
$MgCl_2 \cdot 6H_2O$	30.04	5.70	39.64	2.60
$MgCl_2 \cdot 6H_2O$	34.61	0.00		

[9] Blasdale. THIS JOURNAL, 31, 918 (1909). ·

standardized using c. p. dry sodium chloride and also checked against standard ammonium thiocyanate solution which was compared with pure silver. Isothermal solubility curves at 0, −15 and −30° were determined. These solubilities are given in Tables I, II and III and shown graphically in Figs. 1, 2 and 3.

Figure 2a shows metastable solubility curves for calcium chloride hexahydrate and magnesium chloride hexahydrate at −15°.

TABLE II

SOLUBILITY DATA AT −15°

Solid phase	Solution Grams/100 g. of solution		Residue Grams/100 g. of residue	
	$MgCl_2$	$CaCl_2$	$MgCl_2$	$CaCl_2$
$CaCl_2 \cdot 6H_2O$	0	34.78		
$CaCl_2 \cdot 6H_2O$	0	34.77		
$CaCl_2 \cdot 6H_2O$	2.83	31.92	1.73	37.54
$CaCl_2 \cdot 6H_2O$	3.05	31.63		
$CaCl_2 \cdot 6H_2O$	3.90	30.50	2.56	37.81
$CaCl_2 \cdot 6H_2O$	11.97	22.42		
$CaCl_2 \cdot 6H_2O + MgCl_2 \cdot 8H_2O\alpha$	24.21	10.78	30.47	7.95
$CaCl_2 \cdot 6H_2O + MgCl_2 \cdot 8H_2O\alpha$	24.07	10.68	26.86	11.68
$CaCl_2 \cdot 6H_2O$ (metastable)	25.71	9.43	12.37	30.40
$CaCl_2 \cdot 6H_2O$ (metastable)	26.58	8.58	24.49	11.97
$CaCl_2 \cdot 6H_2O + MgCl_2 \cdot 6H_2O$ (metastable)	28.06	7.64	16.85	25.64
$CaCl_2 \cdot 6H_2O + MgCl_2 \cdot 6H_2O$ (metastable)	28.11	7.41	32.75	11.81
$CaCl_2 \cdot 6H_2O + MgCl_2 \cdot 6H_2O$ (metastable)	28.05	7.50	29.55	13.64
$MgCl_2 \cdot 6H_2O$ (metastable)	29.98	5.11	33.87	3.95
$MgCl_2 \cdot 6H_2O$ (metastable)	29.53	5.78		
$MgCl_2 \cdot 6H_2O$ (metastable)	33.86	0.00		
$MgCl_2 \cdot 8H_2O\alpha$	25.68	8.67	32.84	4.35
$MgCl_2 \cdot 8H_2O\alpha$	26.15	7.70	34.01	3.31
$MgCl_2 \cdot 8H_2O\alpha$	27.17	6.46	32.04	4.04
$MgCl_2 \cdot 8H_2O\alpha$	28.70	4.42	35.68	1.66
$MgCl_2 \cdot 8H_2O\alpha$	31.85	0.00		
Ice	0	12.23		
Ice	14.69	0		
Ice	10.85	5.00	9.16	4.27
Ice	4.01	13.35	2.50	7.40

The octahydrate of magnesium chloride obtained as the solid phase in the above solubility determinations is evidently the stable alpha form of this salt reported by Van't Hoff and Meyerhoffer,[10] as the solubility of the octahydrate in water at −15° agrees closely with the value reported by these workers.

There was no evidence of the metastable beta form of magnesium chloride octahydrate as reported by Van't Hoff and Meyerhoffer.

Magnesium chloride hexahydrate will not change to the octahydrate at −15° even when agitated for twenty-four hours with the solution.

[10] Van't Hoff and Meyerhoffer, Z.·physik. Chem., 27, 75 (1898).
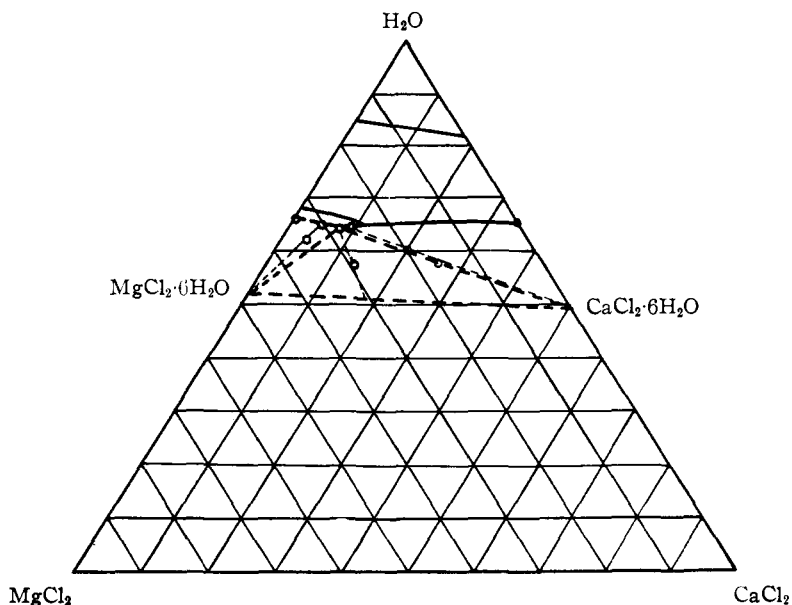
Fig. 2a.—15° isotherms, showing metastable equilibria.

This transition takes place rapidly when the solution is "seeded" with octa-hydrate crystals obtained by freezing a solution containing about 30% magnesium chloride at −30° or lower and then raising the temperature to −15°.

TABLE III

SOLUBILITY DATA AT −30°

| | Solution Grams/100 g. of solution | | Residue Grams/100 g. of residue | |
Solid phase	MgCl$_2$	CaCl$_2$	MgCl$_2$	CaCl$_2$
CaCl$_2$·6H$_2$O	0	32.92		
CaCl$_2$·6H$_2$O	2.50	30.07	0.78	42.24
CaCl$_2$·6H$_2$O	5.49	27.04	1.97	40.73
CaCl$_2$·6H$_2$O + MgCl$_2$·12H$_2$O	8.51	23.76	10.85	26.50
CaCl$_2$·6H$_2$O + MgCl$_2$·12H$_2$O	8.72	23.34	18.09	14.98
CaCl$_2$·6H$_2$O (metastable)	12.26	19.78	10.73	23.65
CaCl$_2$·6H$_2$O (metastable)	16.76	15.23		
CaCl$_2$·6H$_2$O (metastable)	25.55	7.40	15.16	24.77
CaCl$_2$·6H$_2$O (metastable)	27.20	6.14	18.59	20.01
MgCl$_2$·12H$_2$O	22.19	0.00		
MgCl$_2$·12H$_2$O	16.99	7.63	26.72	2.26
MgCl$_2$·12H$_2$O	14.65	11.27	24.10	4.70
MgCl$_2$·12H$_2$O	14.70	11.39	24.86	4.10
MgCl$_2$·12H$_2$O	10.20	19.44		
MgCl$_2$·12H$_2$O	9.94	19.81	21.12	9.05
Ice	20.47	0		
Ice	16.45	4.83	13.72	3.96
Ice	17.16	6.18	5.34	13.57
Ice	0.00	25.03		

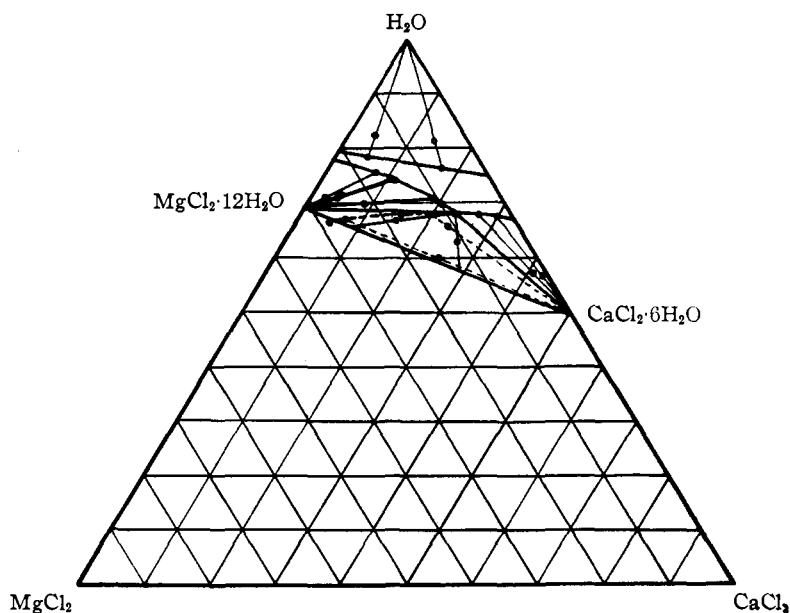Fig. 3.—30 isotherms.   System: $CaCl_2$–$MgCl_2$–H_2O.

Determination of Monovariant Points.—The following monovariant points were determined.   Temperatures were determined by the thermometric method and compositions by the saturation method.

Phases in equilibrium	Temperature, °C.	Composition
1. $MgCl_2 \cdot 6H_2O$		26.40 $MgCl_2$
$MgCl_2 \cdot 8H_2O\alpha$	-6.7	9.90 $CaCl_2$
$CaCl_2 \cdot 6H_2O$		
Satd. soln.		
2. $MgCl_2 \cdot 12H_2O$		23.23 $MgCl_2$
$MgCl_2 \cdot 8H_2O\alpha$	-20.7	10.56 $CaCl_2$
$CaCl_2 \cdot 6H_2O$		
Satd. soln.		
3. $CaCl_2 \cdot 6H_2O$		2.93 $MgCl_2$
$MgCl_2 \cdot 12H_2O$	-52.2	27.40 $CaCl_2$
Ice		
Satd. soln.		

Figure 4 shows the completed ternary diagram plotted on triangular coördinates.

The curves for temperatures above 0°, from data of Van't Hoff, are shown by broken lines, as these results were obtained in solutions saturated with sodium chloride.

Points B, C and F are the monovariant points at -6.7, -20.7 and $-52.2°$, respectively.   Points A, D, E and point between B and C, are isothermal monovariant points at 0, -24.0, -30 and $-15°$, respectively.

The light lines with arrows in the various areas indicate the direction in which the composition of a solution changes, on progressive cooling, due to separation of crystals of the stable solid phase in the given area.

Arrows on heavy lines between phase areas indicate how the solution changes when two solids separate from solutions on cooling.
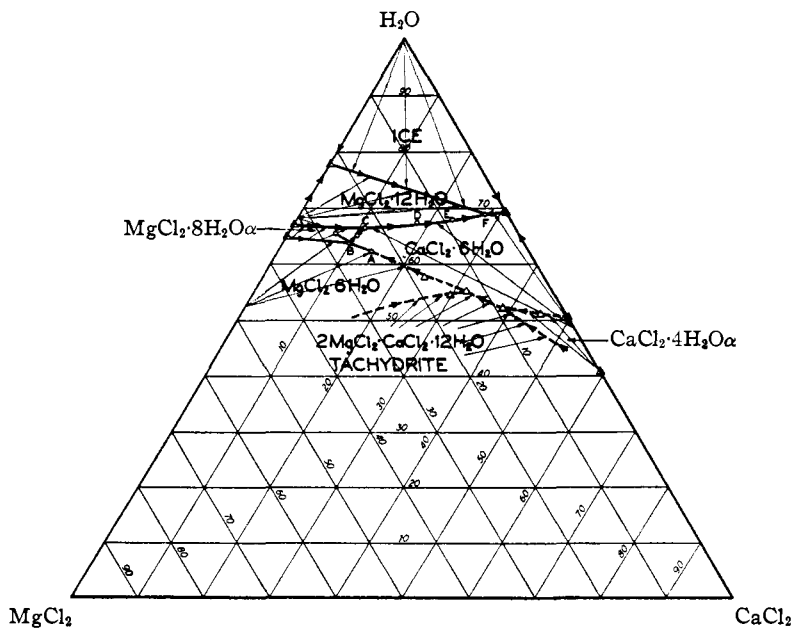

Fig. 4.—Crystallization paths. System: CaCl₂–MgCl₂–H₂O.

Summary

1. The solubility relations of the ternary system, calcium chloride–magnesium chloride–water, at 0, −15 and −30° have been determined.

2. There is no evidence of double salt formation in this system at the temperatures studied.

3. Temperatures and compositions of ternary monovariant points have been determined.

4. The existence of $MgCl_2 \cdot 8H_2O\beta$ reported by Van't Hoff and Meyerhoffer, was not detected.

CLEVELAND, OHIO