[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY AND THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

TERNARY SYSTEMS[1]

$CaCl_2$–$Ca(NO_3)_2$–H_2O (25°), $CaCl_2$–$Ca(ClO_3)_2$–H_2O (25°) $SrCl_2$–$Sr(NO_3)_2$–H_2O (25°), KNO_3–$Pb(NO_3)_2$–H_2O (0°)

BY WILLIAM F. EHRET

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The chemical literature abounds with references[2] to double and complex salts of the type RX—R′X where R and R′ are two different simple or complex radicals and the common radical, X, is Cl^-, $(CN)^-$, $(NO_2)^-$, Br^-, $(NO_3)^-$, $(SO_4)^=$, etc. Much fewer and more isolated are records of salts of the type RX—RX′. It was with the hope of discovering additional compounds of this type that the present work was begun. The systems chosen for study were selected because of the interest centering in the question of whether complex compounds are formed in solutions of very soluble, highly ionized alkaline earth salts containing anions both of which are strongly negative in character. Recent measurements of migration numbers in similar solutions,[3] but of the type RX + R′X + H_2O, indicate that rather extensive complex ion formation takes place. The study of the system KNO_3–$Pb(NO_3)_2$–H_2O (type RX—R′X) was undertaken for reasons mentioned later in connection with the isotherms.

Experimental Details

The systems at 25° were run in a water thermostat of the Freas type, the temperature being kept constant at 25.0 ± 0.01°. "Non-Sol" glass bottles, containing the salt solutions, were rotated in the thermostat. The temperature of the 0° thermostat was kept constant to ±0.05° by means of felt insulation and an ice-water mixture.

In all the systems the various mixtures of salts and water were made by starting with a bottle containing only one salt and water and in each subsequent run more of the second salt was added to the solution and solid left from the previous run. In the systems $CaCl_2$–$Ca(NO_3)_2$–H_2O and $CaCl_2$–$Ca(ClO_3)_2$–H_2O it was frequently necessary to add the dehydrated salts, since, as will be seen from the isotherms, certain mixtures of the hydrated salts will dissolve completely in their own water of hydration. Two days of rotation in the bath was found by experience to be the minimum length of time necessary to bring the solution and the crystalline residues to equilibrium. In establishing the composition of the new double salt in the system $CaCl_2$–$Ca(NO_3)_2$–H_2O, the bottles containing the saturated solutions in contact with the double salt were kept in the

[1] The greater portion of the experimental work for this paper was conducted at Columbia University and was submitted there in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The remainder of the work was carried out at the Washington Square College of New York University.

[2] Kendall, Crittenden and Miller, THIS JOURNAL, **45**, 993 (1923); Jones and Ota, *Am. Chem. J.*, **22**, 15 (1899); **22**, 110 (1899); Wells, *ibid.*, **26**, 389 (1901) (this paper mentions nearly 500 double halides); Jänecke, *Z. anorg. allgem. Chem.*, **100**, 161 (1917); **100**, 176 (1917).

[3] McBain and Van Rysselberge, THIS JOURNAL, **50**, 3009 (1928).

thermostat for over six months and then re-rotated to ensure equilibrium conditions. It was found by experiment that exactly the same points of equilibrium were reached whether the solutions in contact with the solids were heated to 25° in the bath or whether solutions saturated at a higher temperature were cooled to 25° while turning in the bath. The latter method was found to be quicker, since the dehydrated salts were brought into solution much more readily. In all cases the bottles were re-opened, after they had reached the temperature of the bath, and inoculated with the crystal variety that was thought to be the one which would exist in stable equilibrium with the solution at that temperature.

After the mixtures had come to equilibrium and while still in the bath, samples of the liquid were withdrawn by means of a pipet provided with a folded filter paper at its lower end. When the solutions were viscous, suction, approaching within 2–3 mm. of complete vacuum, was necessary to suck up a sufficient amount of the solution. The latter was immediately deposited in a specific gravity bottle, brought to 25°, and weighed. At the same time about 10–15 g. of the crystals from the same bottle were weighed as quickly as possible to prevent evaporation or absorption of moisture. The weighed samples were diluted in a volumetric flask and aliquots taken for analysis. In the case of the $Pb(NO_3)_2$–KNO_3–H_2O system the samples were not diluted, but were weighed and then dried. The $Pb(NO_3)_2$ and KNO_3 were determined by a method used by Glasstone and Saunders.[4] In the $SrCl_2$–$Sr(NO_3)_2$–H_2O system, strontium was determined as carbonate, and chlorine, volumetrically, by Mohr's method. The nitrate was determined by difference. The method used in the $CaCl_2$–$Ca(NO_3)_2$–H_2O and $CaCl_2$–$Ca(ClO_3)_2$–H_2O systems was as follows: calcium was first precipitated as the oxalate and then determined volumetrically with potassium permanganate. Chlorine was determined volumetrically and the nitrate or chlorate radical by difference. The composition of the solid phases in equilibrium with saturated solutions was determined by the indirect[5] or "residue" method. Results of the analyses are plotted as weight percentages on the triangular diagrams.

The salts used were prepared or purified as follows.

$CaCl_2 \cdot 6H_2O$ was at first obtained by three successive recrystallizations of C. P. $CaCl_2 \cdot 6H_2O$. This method resulted in the loss of about one-quarter to one-half of the material, due to the extreme solubility and the deliquescent character of the crystals. Later the salt was obtained pure by a more economical method due to Morgan[6] in which the salt is melted in its own water of crystallization and then recrystallized. $CaCl_2$ was prepared from the pure hexahydrate by heating in a Freas electrically heated air oven to 110° for several days. A test run, covering a period of nine hours, showed that during this interval no hydrolysis of the $CaCl_2$ had occurred. The salt was kept in a vacuum desiccator. $Ca(NO_3)_2 \cdot 4H_2O$ was prepared by triple recrystallization of C. P. crystals. Later an improved method similar to that given under $CaCl_2 \cdot 6H_2O$ was used. $Ca(NO_3)_2$ was made by heating the purified hydrated salt in an air oven as under $CaCl_2$. During the process of dehydration tufts of anhydrous $Ca(NO_3)_2$ grew up out of the liquefied salt; these were easily removed and the process amounted to a recrystallization as well as a dehydration. The anhydrous salt was tested as was the $CaCl_2$ and then stored in vacuum desiccators. $Ca(ClO_3)_2 \cdot 2H_2O$.—This salt as purchasable is an imported product and the small quantity kept in stock by a large retailer of chemicals was found to be so impure as to make many crystallizations, with consequent losses, necessary. It was thought best to prepare the salt in large enough quantity in the laboratory and for this purpose a new method of preparation was devised. Previous methods,

[4] Glasstone and Saunders, *J. Chem. Soc.*, **123**, 2134 (1923).

[5] Bancroft, *J. Phys. Chem.*, **6**, 179 (1902).

[6] Morgan, THIS JOURNAL, **29**, 1168 (1907).

although they furnished valuable ideas for the new method, were either not considered to yield a pure enough product or were considered too dangerous to work with. The method devised is as follows.

Eight hundred and fifty grams of C. P. barium chlorate crystals is dissolved in two liters of distilled water. About a liter of boiling hot solution of ammonium sulfate, containing enough salt to precipitate almost all the barium, is added, with stirring, to the barium chlorate solution. The remaining barium ion is precipitated with a dilute solution of ammonium carbonate. Complete removal of the barium is tested for with the sulfate test. The precipitated sulfate and carbonate are allowed to settle and the solution of ammonium chlorate removed by filtration. To the solution is added, with stirring, a calcined lime paste containing sufficient chemically pure lime to release all the ammonia and a slight excess. The mixture is then boiled until no more ammonia is driven off. After cooling and filtering, the slight excess of lime is neutralized by means of chloric acid using phenolphthalein as indicator. The resulting solution containing calcium chlorate is boiled down until a drop crystallizes. The crystals obtained by recrystallization contain no impurities except a trace of chloride ion which is not detrimental to the work in hand. $SrCl_2 \cdot 6H_2O$, $Sr(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$ and KNO_3 were obtained by recrystallizing the so-called chemically pure crystals of the salts from distilled water.

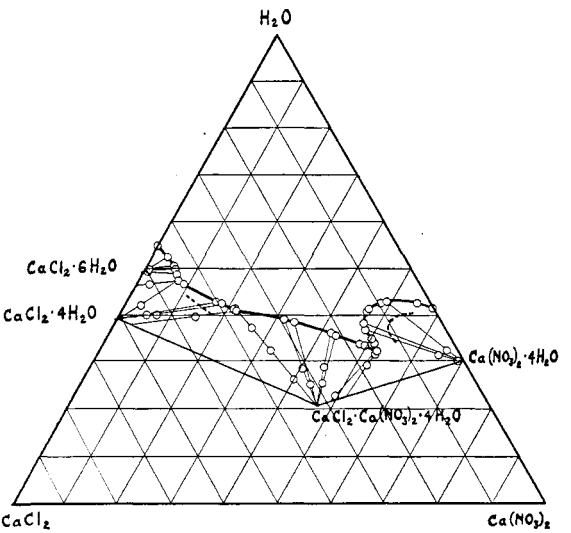

Fig. 1.—The system $CaCl_2$–$Ca(NO_3)_2$–H_2O at 25°.

Experimental Results

The System $CaCl_2$–$Ca(NO_3)_2$–H_2O at 25° (Fig. 1 and Table I).—It will be seen from Fig. 1 that the solid phase in equilibrium with saturated solutions along the first branch of the curve, beginning at the left, is $CaCl_2 \cdot 6H_2O$. Along the next branch, the crystals in equilibrium with the saturated solution are $CaCl_2 \cdot 4H_2O$. They are the alpha modification of the tetrahydrate. At 20.55% $Ca(NO_3)_2$, three phases, namely, double salt, $CaCl_2 \cdot 4H_2O$, and saturated solution, exist together. Then follows the curve

for solutions saturated with double salt ($CaCl_2 \cdot Ca(NO_3)_2 \cdot 4H_2O$) and the right branch of the solubility curve passes through solutions saturated with $Ca(NO_3)_2 \cdot 4H_2O$.

TABLE I

THE SYSTEM $CaCl_2$–$Ca(NO_3)_2$–H_2O AT 25°.

Solution			Residue		
Wt. % $CaCl_2$	Wt. % $Ca(NO_3)_2$	Density	Wt. % $CaCl_2$	Wt. % $Ca(NO_3)_2$	Solid phase
0.00	58.35	1.579			$Ca(NO_3)_2 \cdot 4H_2O$
2.26	55.08	1.581			
7.78	48.88	1.588	2.06	65.59	$Ca(NO_3)_2\ 4H_2O$
8.24	48.93	1.590			
9.19	48.72	1.595			
12.02	46.17	1.616			
12.91	46.45	1.625			
14.57	46.94	1.655	1.20	69.21	$Ca(NO_3)_2\ 4H_2O$
15.06	48.01	1.696	4.22	64.46	$Ca(NO_3)_2\ 4H_2O$
14.73	50.11				
14.45	51.30	1.713			
15.75	50.86	1.790			
15.20	52.21	1.749	18.33	51.91	$Ca(NO_3)_2\ 4H_2O$ + D. S.
16.00	52.29	1.755	27.80	49.12	
16.92	49.28	1.733	23.57	49.02	$Ca(NO_3)_2\ CaCl_2\ 4H_2O$
17.17	48.37				
21.10	43.02	1.700	26.74	44.18	$Ca(NO_3)_2 \cdot CaCl_2\ 4H_2O$
21.75	41.92	1.692	28.82	45.54	$Ca(NO_3)_2\ CaCl_2\ 4H_2O$
27.57	34.20	1.660	31.68	43.07	$Ca(NO_3)_2\ CaCl_2\ 4H_2O$
29.01	31.63	1.651	30.71	40.54	$Ca(NO_3)_2\ CaCl_2\ 4H_2O$
37.04	22.29	1.623	33.95	39.88	$Ca(NO_3)_2\ CaCl_2 \cdot 4H_2O$
36.80	21.80	1.624			
36.87	21.15	1.630	34.57	32.77	$Ca(NO_3)_2\ CaCl_2\ 4H_2O$
37.36	20.94	1.630	36.16	26.17	$Ca(NO_3)_2\ CaCl_2 \cdot 4H_2O$
37.73	20.55	1.630	46.47	14.69	$CaCl_2 \cdot 4H_2O$ + D. S.
39.75	18.07	1.630	52.75	7.64	$CaCl_2\ 4H_2O$
40.35	16.86	1.619	54.67	5.48	$CaCl_2\ 4H_2O$
43.78	9.03	1.556	54.56	3.01	$CaCl_2 \cdot 4H_2O$
44.98	7.60	1.541	50.47	2.62	$CaCl_2\ 6H_2O$ + $CaCl_2\ 4H_2O$
44.24	6.74	1.523	50.06	0.95	$CaCl_2\ 6H_2O$
44.19	5.77	1.524	50.57	0.00	$CaCl_2\ 6H_2O$
44.14	5.43	1.524	50.17	0.00	$CaCl_2 \cdot 6H_2O$
44.75	2.95	1.474	48.99	1.54	$CaCl_2 \cdot 6H_2O$
44.92	0.00	1.453			$CaCl_2\ 6H_2O$

An interesting property of this system is that crystals of $CaCl_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$, when brought together, often yielded a completely liquid mixture. That this must be so can be seen from Fig. 1. A line joining the points marked $CaCl_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ represents all possible mixtures of the solid salts, and this line would cut the ternary solubility curve in two places and for a considerable space run through the field of

unsaturated solutions. Mixtures of the two salts along this part of the line will liquefy with the formation of unsaturated solutions.

Below the portions of the ternary solubility curve in equilibrium with $CaCl_2 \cdot 4H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ will be found the incomplete solubility curves (broken lines) in this system at 30° as found by Barbaudy.[7] Because of the extreme viscosity of the saturated solutions formed, he obtained no further data. However, the slope of the curves agrees with the slope at 25° and it is therefore very likely that the double salt exists also at 30° and possibly over an even greater range of concentrations.

According to Fig. 1, a solution containing the two salts in approximately the ratio of 60 g. of $Ca(NO_3)_2$ to 40 g. of $CaCl_2$ should upon isothermal evaporation at 25° yield only crystals of the double salt. Furthermore, the double salt, if brought into contact with water at this temperature, will not be decomposed but will continue to dissolve until a saturated solution is formed. The solubility, as estimated from the diagram, is 168 ± 3 g. of anhydrous salt per 100 g. of water.

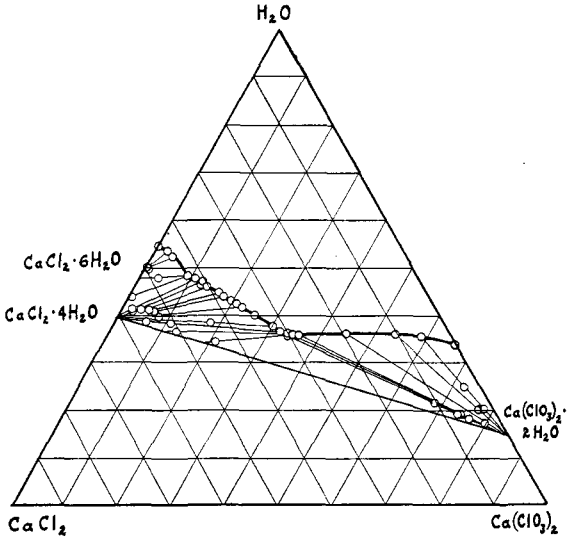

Fig. 2.—The system $CaCl_2$–$Ca(ClO_3)_2$–H_2O at 25°.

The System $CaCl_2$–$Ca(ClO_3)_2$–H_2O at 25° (Fig. 2 and Table II).—The solubility curve of this system has three branches and shows the absence of any double salt at this temperature. The first branch is in equilibrium with $CaCl_2 \cdot 6H_2O$. The middle branch of the curve represents solutions in equilibrium with $CaCl_2 \cdot 4H_2O$ and the right branch those in equilibrium with $Ca(ClO_3)_2 \cdot 2H_2O$.

[7] Barbaudy, *Rec. trav. chim.*, **42**, 638 (1923).

TABLE II

THE SYSTEM $CaCl_2$–$Ca(ClO_3)_2$–H_2O AT 25°

Solution Wt. % $CaCl_2$	Solution Wt. % $Ca(ClO_3)_2$	Density	Residue Wt. % $CaCl_2$	Residue Wt. % $Ca(ClO_3)_2$	Solid phase
0.00	66.05	1.781			$Ca(ClO_3)_2 \cdot 2H_2O$
5.86	58.65	1.767	1.96	77.89	$Ca(ClO_3)_2 \cdot 2H_2O$
10.31	53.45	1.751	3.08	77.07	$Ca(ClO_3)_2 \cdot 2H_2O$
19.19	44.59	1.731	3.70	79.75	$Ca(ClO_3)_2 \cdot 2H_2O$
28.15	36.02	1.730	7.49	73.56	$Ca(ClO_3)_2 \cdot 2H_2O$
29.21	34.71	1.733	6.77	74.20	$Ca(ClO_3)_2 \cdot 2H_2O$
30.83	33.35	1.733	5.87	76.32	$Ca(ClO_3)_2 \cdot 2H_2O$
30.43	33.01	1.735	10.35	68.20	$Ca(ClO_3)_2 \cdot 2H_2O$
30.56	34.21	1.743	44.65	20.80	$Ca(ClO_3)_2 \cdot 2H_2O$ + $CaCl_2 \cdot 4H_2O$
30.69	32.99	1.742	50.47	12.44	$Ca(ClO_3)_2 \cdot 2H_2O$ + $CaCl_2 \cdot 4H_2O$
30.70	32.81	1.748	50.83	12.78	$Ca(ClO_3)_2 \cdot 2H_2O$ + $CaCl_2 \cdot 4H_2O$
31.49	32.01	1.725	50.86	10.79	$CaCl_2 \cdot 4H_2O$
31.51	30.11	1.718	43.79	18.15	$CaCl_2 \cdot 4H_2O$
34.69	25.20	1.659	53.56	9.44	$CaCl_2 \cdot 4H_2O$
35.59	22.14	1.641	52.40	8.03	$CaCl_2 \cdot 4H_2O$
36.91	21.52	1.625			
36.89	21.02	1.629	55.20	6.09	$CaCl_2 \cdot 4H_2O$
37.75	19.65	1.618	53.99	7.29	$CaCl_2 \cdot 4H_2O$
38.16	17.85	1.606	52.87	6.24	$CaCl_2 \cdot 4H_2O$
38.17	17.69	1.607			
37.92	16.91	1.614	57.59	2.02	$CaCl_2 \cdot 4H_2O$
38.82	16.55	1.603	52.87	6.85	$CaCl_2 \cdot 4H_2O$
40.15	12.29	1.578	56.67	2.18	$CaCl_2 \cdot 4H_2O$
40.53	13.41	1.580	53.91	5.25	$CaCl_2 \cdot 4H_2O$
41.70	12.12	1.565	55.05	3.87	$CaCl_2 \cdot 4H_2O$
41.22	10.70	1.570	56.25	1.81	$CaCl_2 \cdot 4H_2O$
42.82	8.70	1.562	55.19	0.81	$CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 6H_2O$
42.41	9.01	1.526	48.18	3.64	$CaCl_2 \cdot 4H_2O$ + $CaCl_2 \cdot 6H_2O$
44.06	3.85	1.480	49.22	1.21	$CaCl_2 \cdot 6H_2O$
43.26	2.36	1.490	49.23	0.63	$CaCl_2 \cdot 6H_2O$
44.92	0.00	1.453			$CaCl_2 \cdot 6H_2O$

The System $SrCl_2$–$Sr(NO_3)_2$–H_2O at 25° (Fig. 3 and Table III).—The solubility curve in this system is again one with three branches, a simple dehydration occurring as in the previous system. No double salt is formed. The left branch of the curve represents solutions in equilibrium with $SrCl_2 \cdot 6H_2O$. The central portion represents solutions in equilibrium with anhydrous $Sr(NO_3)_2$, and the right branch those in equilibrium with $Sr(NO_3)_2 \cdot 4H_2O$.

The System KNO_3–$Pb(NO_3)_2$–H_2O at 0° (Fig. 4 and Table IV).—After the work on the alkaline earth systems was well under way, the system KNO_3–$Pb(NO_3)_2$–H_2O was brought to the attention of the author. Glasstone and Saunders[4] have determined the isotherms at 25, 50 and 100°. Their reason for investigating the system was their belief in the existence of

a complex compound of lead nitrate and potassium nitrate in water solution. Several previous investigations had shown that the solubility of

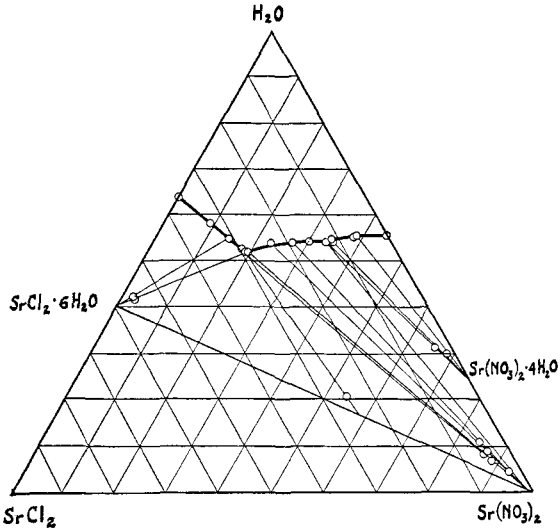

Fig. 3.—The system $SrCl_2$–$Sr(NO_3)_2$–H_2O at 25°.

lead nitrate in water was markedly increased by the addition of potassium nitrate. The increase was attributed to the formation of double molecules

TABLE III

THE SYSTEM $SrCl_2$–$Sr(NO_3)_2$–H_2O AT 25°

Solution Wt. % $Sr(NO_3)_2$	Solution Wt. % $SrCl_2$	Density	Residue Wt. % $Sr(NO_3)_2$	Residue Wt. % $SrCl_2$	Solid phase
44.28	0.00	1.476			$Sr(NO_3)_2 \cdot 4H_2O$
48.69	6.32	1.492			
38.57	5.54	1.488	68.70	1.87	$Sr(NO_3)_2 \cdot 4H_2O$
35.14	10.79	1.508			
34.29	10.87	1.510	65.71	2.97	$Sr(NO_3)_2 \cdot 4H_2O$
33.71	12.11	1.513			$Sr(NO_3)_2$
33.72	12.04	1.513	93.26	2.25	$Sr(NO_3)_2$
30.15	15.10	1.515			
27.25	18.83	1.523	88.45	4.50	$Sr(NO_3)_2$
22.75	23.07	1.537	87.00	4.11	$Sr(NO_3)_2$
19.62	28.45	1.565	86.43	5.06	$Sr(NO_3)_2$
18.91	29.01	1.571			
18.79	28.97	1.568	54.11	24.91	$Sr(NO_3)_2 + SrCl_2 \cdot 6H_2O$
18.07	29.27	1.559			$SrCl_2 \cdot 6H_2O$
18.00	29.23	1.563			
14.10	30.75	1.526	2.99	55.09	$SrCl_2 \cdot 6H_2O$
9.07	32.51	1.483			$SrCl_2 \cdot 6H_2O$
0.00	35.82	1.403			$SrCl_2 \cdot 6H_2O$

in solution, and cryoscopic measurements by Leblanc and Noyes[8] seemed to support this view. They found that mixtures of potassium nitrate and lead nitrate did not depress the freezing point of water as low as would

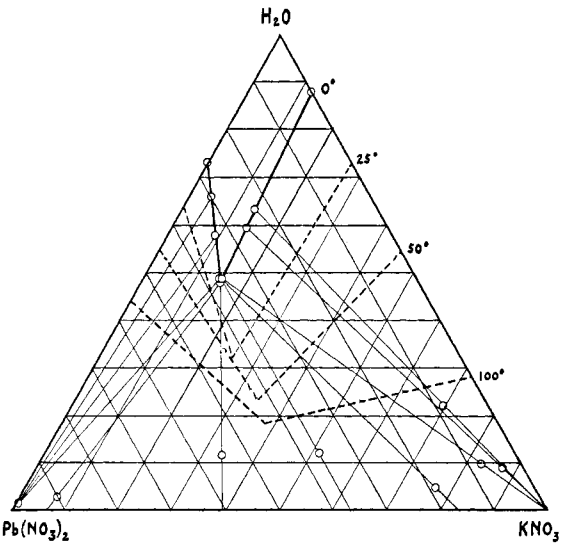

Fig. 4.—The system KNO_3–$Pb(NO_3)_2$–H_2O at 0° (broken curves show results obtained by Glasstone and Saunders).

be expected taking into consideration the common ion effect. Lewis[9] concluded from electromotive force measurements that complexes must be formed upon adding the aforementioned salts to water, for he found a

TABLE IV

THE SYSTEM KNO_3–$Pb(NO_3)_2$–H_2O AT 0°

Solution		Residue		
Wt. % $Pb(NO_3)_2$	Wt. % KNO_3	Wt. % $Pb(NO_3)_2$	Wt. % KNO_3	Solid phase
26.66	0.00			$Pb(NO_3)_2$
29.63	4.15	97.56	0.75	$Pb(NO_3)_2$
32.94	8.95	97.76	0.66	$Pb(NO_3)_2$
37.37	14.20	98.70	0.16	$Pb(NO_3)_2$
37.12	14.74	89.86	7.08	$Pb(NO_3)_2$ + KNO_3
37.14	14.81	54.94	33.29	$Pb(NO_3)_2$ + KNO_3
36.98	15.22	36.25	51.36	$Pb(NO_3)_2$ + KNO_3
37.33	14.66	18.29	76.87	$Pb(NO_3)_2$ + KNO_3
36.27	14.89	7.55	82.87	KNO_3
26.05	14.33	3.92	87.06	KNO_3
22.95	13.67	8.82	69.60	KNO_3
0.00	12.24			KNO_3

[8] Leblanc and Noyes, *Z. physik. Chem.*, **6**, 385 (1890).

[9] Lewis, Dissertation, Breslau, 1908.

diminution of lead ion concentration whenever potassium nitrate was added to a solution of lead nitrate. Although Glasstone and Saunders found no stable double salt in the system at 25, 50 and 100°, the character of their isothermal solubility curves (see dotted curves, Fig. 4) showed distinctly that the solubility influence exerted by potassium nitrate upon lead nitrate was the more decided, the lower the temperature, *i. e.*, the complex, if such exists, is more stable at lower temperatures. Later work, by Glasstone and Riggs,[10] indicated that a double salt, $2KNO_3 \cdot Pb(NO_3)_2$, separated as a solid solution along with $2KNO_3 \cdot Ba(NO_3)_2$ from solutions in the quarternary system KNO_3–$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 25°.

These considerations led the author to believe that a solubility determination at 0° over the whole range of concentrations would establish the existence of an addition compound of the two salts. The system was therefore investigated and the results are given in Table IV and Fig. 4. The solubility curve is composed of only two branches and no double salts are formed. Along the left branch will be found solutions in equilibrium with lead nitrate and along the right branch those in equilibrium with potassium nitrate. It will be noted that the relative increase in solubility of lead nitrate upon addition of potassium nitrate is greatest at 0°. The same may be said about the effect of the presence of lead nitrate upon the solubility of potassium nitrate. Although these are strong indications of the formation of complexes in the solution, a definite compound was not isolable. A number of additional experiments were carried out at −10° with mixtures of lead nitrate, potassium nitrate and water calculated to yield the complex if it exists. No solid phase, different from those already observed at 0°, was found.

The author wishes to take this opportunity to thank Professor James Kendall of the University of Edinburgh for the many valuable suggestions made during the course of the work.

Summary

1. The solubility relations have been determined in the following ternary systems: (I) $CaCl_2$–$Ca(NO_3)_2$–H_2O at 25°, (II) $CaCl_2$–$Ca(ClO_3)_2$–H_2O at 25°, (III) $SrCl_2$–$Sr(NO_3)_2$–H_2O at 25°, (IV) KNO_3–$Pb(NO_3)_2$–H_2O at 0°.

2. The existence of a new, stable double salt whose empirical formula is $CaCl_2 \cdot Ca(NO_3)_2 \cdot 4H_2O$ has been established.

3. A new method for the preparation of pure $Ca(ClO_3)_2 \cdot 2H_2O$ is described.

NEW YORK, N. Y.

[10] Glasstone and Riggs, *J. Chem. Soc.*, **127**, 2846 (1925).