

Caley for their interest and suggestions in this work.

Conclusions

1. Solutions of quinquivalent molybdenum are sufficiently stable in air at room temperature to be employed in any analytical procedure which is complete in a few hours time.

2. Molybdic acid solutions may be quantitatively reduced to the quinquivalent state by shaking with metallic mercury for five minutes if the hydrochloric acid concentration of the solu-

tion is between 2 and 3.5 *N*.

3. Quinquivalent molybdenum may be titrated with ceric sulfate at room temperature using the *o*-phenanthroline ferrous complex indicator if certain critical conditions are observed.

4. The mercury reduction method for determining molybdenum is rapid and accurate. The presence of considerable quantities of phosphate, arsenate or of ammonium salts is without effect upon the accuracy of the molybdenum determination.

PRINCETON, N. J.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

The Systems Lithium Chloride-Water-Ethyl Alcohol and Lithium Bromide-Water-Ethyl Alcohol^{1,2}

BY JOHN P. SIMMONS, HENRY FREIMUTH AND HARRY RUSSELL

The lithium halides show a marked tendency to dissolve in organic liquids, particularly the alcohols,³ and to form addition products with them. The systems lithium chloride-water and lithium bromide-water have been carefully explored and the existence of four hydrates of each halide has been shown.⁴ A study based on the phase rule of the ternary systems, lithium chloride-water-ethyl alcohol and lithium bromide-water-ethyl alcohol has not been attempted, the only related work being that of Santiago Pina de Rubies⁵ which consisted of solubility measurements of lithium chloride in mixtures of water and ethyl alcohol and analyses of the solid phases.

The following data are the experimental results of a phase rule study of the two systems lithium chloride-water-ethyl alcohol and lithium bromide-water-ethyl alcohol.

Preparation of Materials

Anhydrous Lithium Chloride and Lithium Bromide.—Hydrated lithium chloride or bromide dried by heating under ordinary conditions suffers some hydrolysis, giving products which contain about 98.50% lithium salt and 1.50% lithium hydroxide. Drying these salts in an

atmosphere of hydrogen chloride or hydrogen bromide was avoided because of the special apparatus required and because but small amounts of the salt could be made at a time. Drying by heating a mixture of lithium salt and corresponding ammonium salt did not give a product sufficiently free of lithium hydroxide. The method finally adopted consisted in drying triply recrystallized hydrated lithium chloride and bromide in an electric oven at 110°. The residue was treated with absolute alcohol whereupon the lithium salt dissolved, giving a turbid solution due to the presence of lithium hydroxide in suspension. This solution was filtered until clear and the filtrate evaporated to dryness. Analyses of the residue gave for lithium chloride 99.90% purity and for lithium bromide a purity of 99.88%. These products were considered of sufficient purity for the purpose desired and were stored in an oven at 110° until needed.

Ethyl Alcohol.—Absolute ethyl alcohol was prepared by refluxing laboratory absolute alcohol with freshly ignited lime for twelve hours. The alcohol was then distilled off, again refluxed with lime and again distilled. The product obtained gave a boiling point of 78.2°. The alcohol was stored in a bottle from which it could be siphoned and which was equipped with a phosphorus pentoxide guard tube.

Experimental Part

Ten solutions of alcohol and water were prepared, varying in composition from 7.53 to 94.43% alcohol by weight. These with pure water and absolute alcohol were used with anhydrous lithium chloride and bromide in this investigation. Complexes of known content of lithium chloride, water and alcohol and of lithium bromide, water and alcohol were placed in solubility tubes and allowed to come to equilibrium at 25.00 ± 0.02°.

(1) The investigation of the system lithium bromide-water and ethyl alcohol was offered as partial fulfillment of the requirements for the degree of Master of Science by Mr. Henry Freimuth.

(2) The investigation of the system lithium chloride-water and ethyl alcohol was offered as partial fulfillment of the requirements for the degree of Master of Science by Mr. Harry Russell.

(3) Turner and Bissett, *J. Chem. Soc.*, **105**, 1783 (1914); J. Simon, *J. prakt. Chem.*, **20**, 371 (1879).

(4) Hüttig and Steudemann, *Z. physik. Chem.*, **126**, 105 (1927).

(5) S. Pina de Rubies, *Anal. soc. españ. fis. quim.*, **11**, 422 (1912); **13**, 343 (1914).

A known weight of solution was then taken and the lithium salt determined by Mohr's volumetric method. The alcohol in the liquid phases was determined by taking a known quantity of the latter

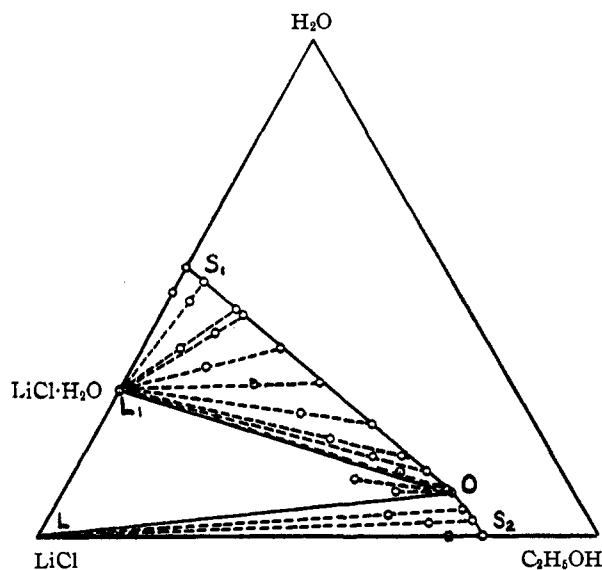


Fig. 1.

and distilling to dryness. The residue was twice moistened with water and the distillation repeated after each moistening in order to ensure as complete driving off of the alcohol as possible. The tube of the condenser was washed out several times with water, the total distillate and washings collected and made up to an exactly known volume. From density determinations the percentage of alcohol in the liquid phase was calculated. Preliminary investigation indicated that this distillation method for alcohol was accurate to about 1%. The percentage of water was obtained by difference. If the data obtained are plotted on triangular coordinate paper Figs. 1 and 2 result. A tie-line drawn through the known composition of the complex and the composition of the solution, when equilibrium is reached, will terminate at a point on the triangle which will indicate the composition of the solid phase present. As pointed out above, however, the method of analysis of the solution is liable to be in error to the extent of about 1% and thus may result in a composition of the solid phase slightly in error. The result obtained, however, will be sufficiently correct so that the exact composition of the solid phase may be determined by inspection. Knowing now the exact composition of the solid phase

and of the complex, an exact method of plotting should enable us to arrive at a more accurate composition of the liquid phase than could be reached by the above method of direct analysis on the assumption that the analysis is correct with respect to lithium chloride and lithium bromide. As Hill and Ricci⁶ have pointed out, this method of extrapolation is subject to error due to mechanical difficulties of exact plotting.

In this work the direct analysis of the liquid phase has been used to establish the composition of the solid phase and also as a check on results obtained by the Hill-Ricci method of extrapolation for the composition of the liquid phase. In the plotting of the results, Figs. 1 and 2, therefore, the composition of the solid phase has been determined by extrapolation using the known composition of the complex and the composition of the solution in equilibrium, determined by direct analysis, while the points representing the compositions of the solutions have been obtained by the Hill-Ricci method. The concentration of water and alcohol in the two transition complexes was determined from the intersection of the two curves checked by direct analyses using the distillation method for the alcohol. Tables I and II contain the data of these experiments.

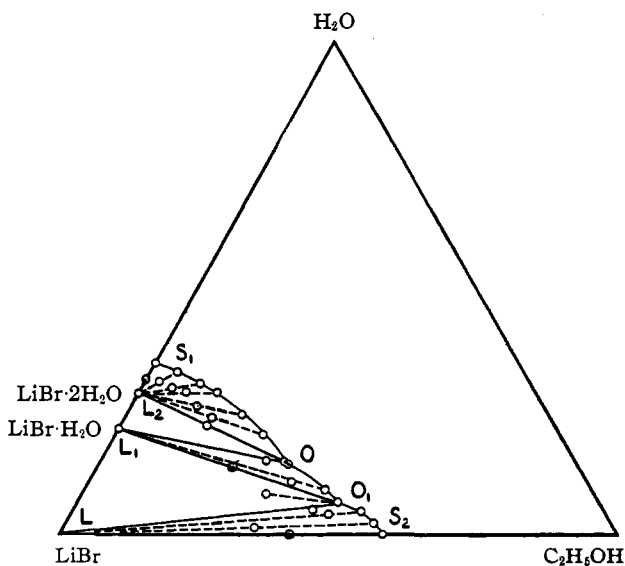


Fig. 2.

Discussion of Results

In Fig. 1, S_1OL_1 represents a divariant area which, with the fixing of the temperature at 25° , becomes univariant. Similarly the area LOS_2 is

(6) A. E. Hill and J. E. Ricci, *THIS JOURNAL*, **53**, 4305 (1931).

TABLE I
TABULATION OF DATA FOR THE SYSTEM LITHIUM CHLORIDE-WATER-ALCOHOL AT 25°

Composition of complex		Solid phase	LiCl, %	Composition of solution		Alcohol by Hill-Ricci method
LiCl, %	C ₂ H ₅ OH, %			Direct analysis	Alcohol, %	
50.01	0.00	LiCl·H ₂ O	45.94	0.00		
47.94	3.92	LiCl·H ₂ O	44.90	4.45		
54.87	6.99	LiCl·H ₂ O	41.88	12.92		13.05
47.03	11.36	LiCl·H ₂ O	40.65	14.49		
52.60	12.93	LiCl·H ₂ O	37.02	24.39		23.91
45.17	23.78	LiCl·H ₂ O	34.17	34.24		
41.06	34.39	LiCl·H ₂ O	30.02	47.43		47.70
37.64	42.71	LiCl·H ₂ O	27.19	56.42		
31.68	51.73	LiCl·H ₂ O	25.43	60.24		
28.44	59.18	LiCl·H ₂ O	23.09	66.77		65.93
37.41	50.23	LiCl·H ₂ O + LiCl	22.41	69.04		
30.92	58.88	LiCl·H ₂ O + LiCl	22.41	68.86		
35.28	60.10	LiCl	22.18	72.98		
28.27	68.56	LiCl	22.13	74.24		74.02
24.60	75.40	LiCl	20.18	79.82		

TABLE II
TABULATION OF THE DATA FOR THE SYSTEM LITHIUM BROMIDE-WATER-ETHYL ALCOHOL AT 25°

Composition of complex		Solid phase	LiBr, %	Composition of solution		Hill-Ricci method
LiBr, %	C ₂ H ₅ OH, %			Direct analysis	C ₂ H ₅ OH, %	
68.21	0.00	LiBr·2H ₂ O	65.31	0.00		
66.22	2.53	LiBr·2H ₂ O	62.08	4.88		
64.43	5.50	LiBr·2H ₂ O	59.06	10.23		
62.10	8.85	LiBr·2H ₂ O	56.68	14.44		13.52
61.53	11.91	LiBr·2H ₂ O	55.24	20.09		
60.09	15.91	LiBr·2H ₂ O	52.98	26.59		25.63
62.05	15.33	LiBr·2H ₂ O-LiBr·H ₂ O	52.07	33.05		
61.66	23.33	LiBr·H ₂ O	50.79	35.43		
53.27	36.34	LiBr·H ₂ O	47.63	43.28		
62.62	25.20	LiBr·H ₂ O	46.70	47.57		46.59
57.89	33.85	LiBr·H ₂ O-LiBr	46.63	46.53		
52.02	42.93	LiBr	46.51	47.86		
49.78	46.44	LiBr	44.13	51.66		50.72
62.59	35.91	LiBr	42.45	55.24		
56.23	43.77	LiBr	41.22	58.78		

isothermally univariant. The solid phases resulting from complexes represented by points in these areas are lithium chloride monohydrate and anhydrous lithium chloride, respectively. The compositions of the liquid phases in equilibrium with the monohydrate are the points on the line S₁O while those in equilibrium with anhydrous lithium chloride are the points on line OS₂. The area L₁OL, since it gives a system of *four phases*, exhibits one degree of freedom and with the temperature fixed becomes isothermally invariant. A complex taken in this area will give a system containing two solid phases, monohydrated lithium chloride and the anhydrous salt, and a liquid phase having the composition represented by O.

In the case of the system lithium bromide-water-ethyl alcohol three isothermally univariant areas exist, S₁OL₂, L₁OO₁ and LO₁S₂, the solid

phases present at equilibrium being lithium bromide dihydrate, lithium bromide monohydrate and anhydrous lithium bromide, respectively. The area L₂OL and L₁O₁L are isothermally invariant and complexes having the compositions represented by points in these areas will give at equilibrium, in the former a mixture of lithium bromide dihydrate and monohydrate and a liquid phase having the composition represented by O, while in the latter a mixture of lithium bromide monohydrate and anhydrous lithium bromide will be in equilibrium with a liquid phase having the composition represented by O₁.

Summary

1. A convenient and satisfactory method for preparing anhydrous lithium chloride and lithium bromide has been devised.

2. A phase rule study of the systems lithium chloride-water-ethyl alcohol and lithium bromide-water-ethyl alcohol at 25° has been completed.

3. In the case of the lithium chloride system at 25°, two solid phases, the monohydrate and anhydrous salt, or a mixture of the two, exist in equilibrium with the liquid phase.

4. In the case of the lithium bromide system the dihydrate, the monohydrate, or the anhydrous salt, or a mixture of the dihydrate and monohydrate or monohydrate and anhydrous salt may be the solid phases present.

5. No alcoholates were found in either system.

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[CONTRIBUTION FROM THE DEVELOPMENT AND RESEARCH LABORATORY, PENNSYLVANIA SALT MANUFACTURING CO.]

Equilibrium in Fluoride Systems. I. Solubility of Cryolite in Aqueous Solutions of Iron and Aluminum Salts at 25°

BY FRANCIS J. FRERE

The solubility of cryolite in aqueous solutions of aluminum chloride has been long known, although it has never been generally recognized. More than thirty years ago the laboratories of the Oresunds Chemiske Fabriker, in Denmark, employed this reaction as the basis of a determination of quartz in cryolite. Although there is no record to be found in the literature of these results, it is presumed that the work was carried out either by or under the supervision of Julius Thomsen.

Recently the author had occasion to investigate the solvent action of a great many salt solutions on cryolite. It was found that cryolite was appreciably soluble in all aluminum salt solutions as well as those of iron. Qualitative tests also indicated a moderate degree of solubility in chromium and uranium salts. Except in limiting cases, this is not in general a characteristic property of sparingly soluble salts. Indeed, such abnormalities are quite generally accepted as being typical of a double salt formation.

In view of these facts, therefore, it seems quite appropriate and desirable that an investigation be made of the mechanism of the reaction involved. Obviously, the most suitable means of obtaining the necessary data is by an investigation of the ternary systems of the various salts of iron and aluminum and their respective fluorides. This phase of the problem is now in progress and some of the results will be reported in this Journal within a short time.

It is felt that these data on the solubility measurements as well as those which are to be presented on the ternary systems will be of special interest by reason of the fact that these systems have not been heretofore thoroughly investigated.

Experimental

Materials Used.—The salts used in the solubility measurements were obtained by recrystallization of analytical reagent grade chemicals. Analysis showed these materials to be of excellent quality and that the ions were present in the correct stoichiometric ratio to conform to the normal salts. Sodium, the most objectionable impurity, was in no case found to exceed 0.01%.

Natural cryolite obtained from Greenland was used in these experiments. It was very carefully selected by hand and was found to be free of impurities.

Procedure.—The bottles containing the solutions to be saturated were treated with an excess of finely-divided cryolite, stoppered with pure gum stoppers, sealed, and rotated from seventeen to twenty-one days in a thermostatically controlled bath. The bath temperature was maintained at $25 \pm 0.02^\circ$. In order to establish the reliability of using stoppered bottles, several duplicate experiments were made in which the solutions were placed in sealed tubes and saturated. The results by the two methods checked within the error of the determination.

After saturation had been attained, the solutions were allowed to settle while standing in the bath and portions were drawn out of each bottle through a cotton filter, transferred to a tared weighing bottle and reweighed. The samples were washed into platinum dishes, treated with perchloric acid, and decomposed by evaporating to fumes of the latter. The solutions were then diluted to the desired volume and reserved for analysis.

Sodium was determined by precipitating with zinc uranyl acetate according to Barber and Kolthoff.¹

Aluminum was determined by precipitating with 8-hydroxyquinoline and weighing as the oxime salt after drying at 130 to 140°.

Iron was determined by reducing in a Jones reductor and titrating with potassium permanganate.

Results and Discussion

The data on these solubility measurements are contained in Table I. Column 1 represents the salt concentration, columns 2 and 3 represent the

(1) H. H. Barber and I. M. Kolthoff, *THIS JOURNAL*, **50**, 1625 (1928).