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 ± 0.02°. 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

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

cryolite concentration on the basis of the aluminum and sodium, respectively, and column 4 represents the average cryolite concentration.

TABLE I

SOLUBILITY OF CRYOLITE IN AQUEOUS SOLUTIONS OF IRON AND ALUMINUM SALTS AT 25°

Concentrations Expressed in Moles of Salt Per 1000 Moles of Water

Salt concn., moles	Na_3AlF_6 on basis Al moles	Na_3AlF_6 on basis Na moles	Na_3AlF_6 average, moles
	2 [$Al(NO_3)_3$]		
...	0.34	0.34	0.34
0.49	.65	.65	.65
.96	1.10	1.11	1.11
3.05	2.92	2.89	2.91
5.09	4.39	4.35	4.37
7.06	5.67	5.71	5.69
10.03	7.75	7.69	7.72
12.12	9.00	9.02	9.01
14.37	10.66	10.57	10.62
19.76	14.30	14.41	14.36
	Al_2Cl_6		
0.50	0.67	0.65	0.66
1.02	1.14	1.14	1.14
3.23	2.95	2.93	2.94
5.12	4.10	4.14	4.12
7.22	5.40	5.37	5.39
9.25	6.57	6.57	6.57
12.03	7.93	7.90	7.92
15.27	9.56	9.50	9.53
20.28	11.42	11.40	11.41
	$Al_2(SO_4)_3$		
0.40	0.56	0.55	0.56
.74	.87	.87	.87
1.56	1.60	1.58	1.59
3.33	2.84	2.83	2.84
5.08	4.03	4.01	4.02
7.59	5.56	5.52	5.54
10.50	7.15	7.11	7.13
13.72	8.66	8.60	8.63
17.04	10.04	9.96	10.00
	2[$Fe(NO_3)_3$]		
0.99	0.81	0.81	0.81
3.09	1.88	1.85	1.87
4.90	2.50	2.49	2.50
6.98	3.16	3.19	3.17
9.80	3.93	3.93	3.93
14.90	5.06	4.99	5.03
19.82	6.05	5.98	6.02
24.88	6.88	6.84	6.86
	2($FeCl_3$)		
1.00	0.72	0.74	0.73
2.94	1.55	1.55	1.55
4.90	1.99	1.99	1.99
7.44	2.18	2.22	2.20
10.19	2.25	2.28	2.27
14.94	2.22	2.23	2.23
19.70	2.03	2.06	2.05
25.28	1.89	1.87	1.88
	$Fe_2(SO_4)_3$		
1.02	0.59	0.57	0.58
3.04	1.14	1.12	1.13
5.13	1.59	1.55	1.57
7.04	1.81	1.81	1.81
9.95	2.23	2.23	2.23
14.82	2.86	2.90	2.88
19.16	3.21	3.22	3.22
24.55	3.68	3.71	3.70

From the data presented, the most obvious assumption is that there is some chemical reaction taking place by which a considerable amount of some new substance is formed by combination of the ions present in the solution. In the case of the aluminum salts, the most probable explanation of the mechanism involved would seem to be one in which there is a complete exchange of ions resulting in the formation of aluminum fluoride and the sodium salt of the solvent anion, the aluminum fluoride in turn combining with the aluminum salt present to form a double salt.

This inference seems to be amply justified by the following facts. When solutions of three aluminum salts were saturated with cryolite at an elevated temperature, no reprecipitation of cryolite occurred upon cooling or even after the addition of the respective sodium salts to the point of saturation. If, on the other hand, the sodium salt was added to the solution at the start it exerted a depressing effect upon the solubility due to the action of the common ion. The rate of decrease in solubility increased quite rapidly with increasing concentration of the added salt. From the foregoing, it is clear that the reaction is not reversible and, hence, true equilibrium is not attained.

Upon plotting the solubility data, a slight irregularity in the curves will be noted which might indicate the presence of a second solid phase. An examination of the residues, however, showed them to consist only of unchanged cryolite. The most reasonable explanation for these irregularities seems to be that equilibrium is very slowly attained after the solutions have become nearly saturated.

Apparently, a similar mechanism is involved for the iron salts. The presence of a fourth ion, however, gives rise to a more complicated system and as a result may require a knowledge of the quaternary as well as the ternary system in order to establish definitely the identity of the final reaction product.

It will be noted from the data that the solubility of cryolite in the different salt solutions in all cases, excepting ferric chloride, follows in the order of the solubility of the corresponding sodium salts. Ferric chloride solutions act normally in concentrations up to 10.0 molar, at which point the solubility reaches a maximum then falls below that of the sulfate and continues to decrease with any further increase in concentration. This difference in behavior is in accord with the facts of the case and may be readily interpreted by a consideration of the ferric chloride–sodium chloride system.

It will be seen also that cryolite dissolves to a greater extent in aluminum salt solutions and that the amount dissolved is practically the same for the different iron and aluminum salts at the lower concentrations. Undoubtedly, in these dilute solutions a considerable portion of the cryolite is dissolved at the expense of the free acid resulting from the hydrolysis of the salts.

Summary

The solubility of cryolite has been determined at 25° over a wide range of concentrations in aqueous solutions of iron and aluminum chloride, nitrate and sulfate. It has been found that the solubility was greatest in the aluminum salt solutions, and that the amount dissolved by the different salts was in all cases, excepting ferric chloride, in the order of the solubility of the corresponding sodium salt.

An explanation of the mechanism of the reaction has been offered based on the formation of a double salt.

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Condensations by Sodium. VII. A General Method for Stopping the Wurtz Reaction at the Intermediate Organo-Metallic Stages

BY AVERY A. MORTON AND INGENUIN HECHENBLEIKNER

Previous work[1] has revealed that alkyl sodium compounds, if formed as intermediates in the Wurtz synthesis, are stable only at low or moderate temperatures. Their great reactivity enables the final stage of reaction with more alkyl chloride to be completed easily. Such considerations suggested that a Wurtz synthesis might be stopped at this intermediate point if the reaction were carried out at low temperatures in the presence of excess sodium. Experiments have amply confirmed this conclusion. When *n*-amyl chloride was added gradually with stirring to a suspension of sodium sand in pentane or ligroin, the mixture stirred until after no more evolution of heat occurred, and the product carbonated, there was obtained both caproic and butylmalonic acids. The yield of combined acids, around 50% in many experiments, was sufficiently high to remove any suspicion that they were formed because of a concurrent reaction during carbonation. The general application of this method for obtaining organo-metallic compounds was demonstrated by runs with butyl halides (chloride, bromide and iodide), and a secondary, a tertiary and an aromatic chloride.

So far the best yield, 57% of total carboxylic acids, has been obtained with *n*-amyl chloride. Other chlorides in order of decreasing yield are *n*-hexyl chloride, chlorobenzene, *n*-butyl chloride, *t*-amyl chloride, 2-chloro-3-methylbutane and *n*-propyl chloride. Factors such as the temperature at which the reagents could be induced to react, the thermal stability of the resulting organometallic compound, and the readiness with which the product reacts with more organic chloride to complete a Wurtz synthesis, must be considered in each case. The first attempts were unsuccessful because the importance of these factors was not recognized. Subsequent experiments with amyl chloride demonstrated the possibilities under controlled conditions and the preliminary test with other halides confirmed the conclusion that the proper factors for preparation of organometallic compounds by direct action of sodium on the chloride had indeed been recognized.

An earlier discovery of an organo-metallic compound in a Wurtz synthesis has been recorded in some interesting work by Gilman and Wright,[2] who studied the action of sodium–potassium alloy on 3-iodofuran. A very small yield, 0.5%, of 3-

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(1) Morton and Hechenbleikner, THIS JOURNAL, **58**, 1024 (1936).

(2) Gilman and Wright, *ibid.*, **55**, 2893 (1933).