whose normal boiling point is T, it follows that for "related liquids," *i. e.*, those whose entropy of vaporization is the same, at the same vapor pressure

$$T_1/T_2 = T_1'/T_2' = \text{constant}$$

which is the empirical rule of Ramsay and Young.

Dühring's rule also follows from IVc, for considering a given pressure we write

$$\left(\frac{T_1'}{T_1}\right)^{\Delta H_1'/RT_1'} = \left(\frac{T_2'}{T_2}\right)^{\Delta H_1'/RT_2'}$$

and for "related liquids"

$$T_1' = T_1/T_2T_2' = \Delta H_1'/\Delta H_2' \times T_2'$$

which is the equation for the Dühring line. It also indicates that the slope of the Dühring line is the ratio of the absolute boiling temperatures or the heat of vaporization of the liquids chosen.

It is also possible to give some basis to Guldberg's empirical rule that for many liquids the normal boiling point is two-thirds of the absolute critical temperature. Thus, denoting the values of the quantities at the boiling point and critical point by the subscripts b and c, it can be shown on the basis of IVc that $T_b/T_c = (^1/P_c)^{-\Delta H_b/RT_b}$ Since P_c for most liquids is of the order of magnitude of 60 atmospheres, and by Trouton's rule, $-\Delta H_b/RT_b = -11$, the ratio T_b/T_c is roughly 0.7.

Summary

By a simple transformation the equations relating the change of solubility with temperature can be changed into an approximate form which is in many cases more convenient for interpolation or extrapolation than the original equations. Thus it is shown that experimental values of these quantities fall on a straight line when plotted against the temperature, or the reduced temperature, on double logarithmic coördinates. The approximate equation for vapor pressure leads directly to the rules of Ramsay and Young and of Dühring.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. JOHN'S UNIVERSITY]

The Formation and Composition of Lithium Aluminate

BY HAROLD A. HORAN AND JOHN B. DAMIANO

Introduction

According to Allen and Rogers,[1] an insoluble aluminate of lithium is formed when aluminum is dissolved in a solution of lithium hydroxide. Analysis of the air-dried substance for alumina and water led them to assign the formula, $LiH(AlO_2)_2 \cdot 5H_2O$. As a result of conductometric measurements on the saturated solution of the substance, similarly prepared, Prociv[2] concluded lithium and aluminum were present in the ratio of 0.8Li:2Al, which, he says, is an atomic ratio of approximately 1Li:2Al. According to him lithium aluminate may also be precipitated by the addition of a solution of lithium hydroxide to a solution of an aluminum salt or by adding a solution of a lithium salt to a solution of an alkali aluminate. On ignition, he claims, the compound is converted into $Li_2O \cdot 2Al_2O_3$. Dobbins and Sanders[3] describe the formation of lithium aluminate by the addition of dilute ammonia to a solution containing a lithium and an aluminum salt, in the presence of phenolphthalein as an indicator. However, they claim the compound contains lithium and aluminum in atomic ratio of 2Li:5Al and, as a result of a series of ignitions assign the formula, $2Li_2O \cdot 5Al_2O_3$, for the ignited product.

Thus there is disagreement as to the composition of lithium aluminate prepared by different methods. This might be attributed to a variation of conditions, *i. e.*, alkalinity, relative ionic concentrations or temperature, in the different methods used. Concerning temperature, Allen and Rogers[1] and Heyrovsky[4] suggest precipitation at low temperatures, (near 0°), to prevent decomposition of the aluminate.

Since the compound has not been extensively studied, this investigation was undertaken in order, (1) to determine conditions for the precipitation of lithium aluminate from a solution of an aluminum salt, (2) to determine, by analytical means, the atomic proportions of lithium to aluminum in the substance precipitated, (3) to

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(1) Allen and Rogers, *Am. Chem. J.*, **24**, 304 (1900).

(2) Prociv, *Collection des Travaux Chimique de Tchecoslovaquie*, **1**, 95 (1929).

(3) Dobbins and Sanders, THIS JOURNAL, **54**, 178 (1932).

(4) Heyrovsky, *J. Chem. Soc.*, **117**, 1013 (1920).

determine the behavior of the substance on ignition.

Materials

Aluminum Ammonium Sulfate.—The c. p. substance was recrystallized twice from water. Solutions were made up and standardized by the oxine method.[5]

Acetic Acid.—A good grade, practically free of nonvolatile matter, was used.

Ammonia.—This was freshly distilled and made up to approximately 0.5 molar concentration.

Ammonium Acetate.—An approximately 2 molar solution was prepared by mixing the proper amounts of acetic acid, ammonia and water.

8-Hydroxyquinoline.—This was the Eastman Kodak Co. product.

Lithium Chloride.—This was purified by the usual method of precipitating the carbonate and evaporation with hydrochloric acid. An approximately 5% solution was made up and standardized by evaporating a known volume to dryness, in the presence of a little sulfuric acid, gently igniting and weighing the residue.

Experimental

To solutions containing known amounts of aluminum and having volumes of 100 cc., lithium chloride solution was added in amounts to provide an excess (approx. 10%), over the calculated amount, assuming for calculations 1Li:2Al. The solutions were cooled to approximately 5° and maintained at that temperature until after filtration. Dilute ammonia was added, with stirring, to effect precipitation. The amounts added varied in several cases. In some, just enough was added to give the solution a faint yellow color in the presence of neutral red as an indicator. In others, phenolphthalein was used as an indicator and a faint pink color established, while still in others a deep pink color was established by the addition of larger amounts of ammonia. The precipitates which formed were allowed to settle, filtered and washed with cold water (approx. 5°), until washings showed no test for chlorides with silver nitrate solution. To ensure proper washing and prevent "channeling" the precipitates were stirred while washing. The precipitates were analyzed as outlined below.

Another series of precipitations was carried out in solutions where the amounts of aluminum were held constant and the lithium chloride added was varied over a considerable range. Dilute ammonia was added to these solutions, in the presence of phenolphthalein, until the solutions had a definite pink color. The solutions and precipitates were handled as described above.

For the analyses of the freshly precipitated aluminates, most of the precipitate was washed from the paper, with water, into a clean beaker. The filter paper was then boiled up with sulfuric acid (1:6) to dissolve the remaining aluminate, and extracted several times with small portions of boiling water. The sulfuric acid solution and water extractions were filtered into the beaker containing the bulk of the precipitate, which dissolved upon heating. The solution was diluted to 100 cc. with water and almost neutralized with ammonia. The aluminum was then determined by the oxine[5] method. To recover the lithium sulfate, the filtrate and washings were carefully evaporated in platinum to approximately 10 cc. Concentrated nitric acid was added, in small increments, while the evaporation was continued. After destruction of most of the ammonium salt, acetic acid and organic matter, the solution was evaporated to incipient dryness. The residue was transferred with hot water to a platinum crucible. The crucible and contents were heated in an air-bath until dry. The excess sulfuric acid was carefully expelled and the crucible heated to constant weight at about 600°. Several blanks were run on solutions containing the same amounts of aluminum but no lithium. The lithium sulfate weights were then corrected. These corrections never amounted to more than 0.6 mg. The residues from the blank determinations revealed a trace of aluminum, probably due to the solubility of the quinolate.

The results of the two series of analyses are given in Tables I and II. The lithium–aluminum ratios are also given.

TABLE I

Expt.	Al_2O_3 (taken), g.	Al_2O_3 (found), g.	Li_2SO_4 (found), g.	Li/Al
1	0.0987	0.0982	0.0519	0.490
2	.0987	.0983	.0516	.488
3	.0987	.0984	.0522	.492
4	.1043	.1038	.0540	.483
5	.1043	.1041	.0544	.485
6	.1043	.1039	.0547	.489
7	.0554[a]	.0551	.0286	.487
8	.0554[a]	.0548	.0290	.491
9	.1264[b]	.1262	.0670	.492
10	.1264[b]	.1260	.0674	.494
11	.1407[b]	.1402	.0748	.494
12	.1407[b]	.1403	.0743	.491
13	.1562[b]	.1556	.0827	.490
14	.1635[b]	.1630	.0860	.488
15	.1635[b]	.1627	.0854	.487

Expts. 1, 6, 7, 10, 11, 15 were done using neutral red as an indicator. Expts. 2, 4, 12, 14, were done using phenolphthalein as an indicator until a faint pink color resulted. Expts. 3, 5, 8, 9, 13, were done using phenolphthalein as an indicator until a very deep pink color resulted.

[a] The volume of the solution for analysis was 60 cc.

[b] Aliquot portions sufficient to give approximately 0.1 g. of Al_2O_3 per 100 cc. were taken for analysis.

TABLE II

Expt.	Al_2O_3 (taken), g.	Li_2SO_4 (taken), g.[a]	Al_2O_3 (found), g.	Li_2SO_4 (found), g.	Li/Al
16	0.1043	0.0735	0.1040	0.0542	0.485
17	.1043	.1508	.1039	.0545	.487
18	.1264[b]	.0735	.1262	.0670	.492
19	.1264[b]	.1053	.1258	.0667	.490
20	.1264[b]	.1800	.1257	.0666	.490
21	.1407[b]	.0817	.1402	.0748	.494
22	.1407[b]	.1800	.1403	.0740	.490

[a] Actually LiCl, but calculated as Li_2SO_4. [b] Aliquot portions sufficient to give approximately 0.1 g. of Al_2O_3 per 100 cc. were taken for analysis.

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(5) Kolthoff and Sandell, THIS JOURNAL, 50, 1900 (1928).

Several samples were precipitated using various amounts of lithium chloride solution and varying the alkalinity over the range indicated above. They were filtered, washed and transferred to silica crucibles. The precipitates were dried and the paper burned off at a low temperature. The temperature was gradually increased, the final ignitions to constant weight being made in a muffle at about 1050°. Some of the results are given in Table III. The calculated values, using formulas $Li_2O \cdot 2Al_2O_3$ and $2Li_2O \cdot 5Al_2O_3$ are also given.

TABLE III

Expt.	Al_2O_3 (taken), g.	Ignited residue, g.	$Li_2O \cdot 2Al_2O_3$ (calcd.), g.	$2Li_2O \cdot 5Al_2O_3$ (calcd.), g.
23	0.1154	0.1317	0.1324	0.1289
24	.1154	.1318	.1324	.1289
25	.1154	.1320	.1324	.1289
26	.0987	.1130	.1132	.1103
27	.0987	.1127	.1132	.1103
28	.0554	.0631	.0636	.0619
29	.0554	.0632	.0636	.0619

Expts. 25, 29 were done using neutral red as an indicator. Expts. 23, 24, 27 were done using phenolphthalein as an indicator until a faint pink color resulted. Expts. 26, 28 were done using phenolphthalein as an indicator until a very deep pink color resulted.

Discussion

The results in Table I show that within limits of experimental error the same results are obtained whether the solution is made faintly or definitely alkaline (pH 7.5–10.5). Thus there is no need for careful adjustment of alkalinity as suggested by Dobbins and Sanders.[3] Large excess of hydroxide should be avoided, as this causes slow solution of the precipitate.

As shown in Table II, the lithium chloride concentration has been varied over a considerable range without effect on the composition of the precipitate. It is not desirable to have too large a concentration of lithium chloride present, since this would entail prolonged washing of the precipitates to render them free of the excess, with consequent losses due to solubility and hydrolysis.

The lithium sulfate values given in Tables I and II are slightly lower than predicated by a 1Li:2Al ratio. This is undoubtedly due to loss of lithium in the solution and washings, for we have found more than traces removed if the washing is prolonged. The values are higher by some 25% than demanded by a 2Li:5Al ratio, making certain that the components are not present in that ratio.

In Table III the weights of the ignited residues, though slightly lower than expected, indicate that the ignition product is better represented by the formula $Li_2O \cdot 2Al_2O_3$ than by $2Li_2O \cdot 5Al_2O_3$. The percentage differences are only some 2.5% and, were it not for the large differences in lithium sulfate values mentioned above, one might not be justified in assigning a ratio of 1Li:2Al.

In assigning a 2Li:5Al ratio, Dobbins and Sanders[3] were led to this conclusion by (1), a series of ignitions of precipitates formed in solutions containing known amounts of aluminum and (2), Prociv's 0.8Li:2Al ratio, determined conductometrically. Concerning the first, it should be pointed out that precipitations and washings were made at room temperature where losses due to decomposition and solubility probably amount to at least 1%. In addition, no analysis of un-ignited precipitates was made prior to assignment of the formula. These points are important since the percentage difference in the weight of an ignited residue as calculated by one formula and the other is only 2.5%. Concerning Prociv's value, it is according to himself only approximate. It is an isolated value and not the result of a series of measurements. Other values obtained by Prociv[2] were quite close to a 1Li:2Al ratio.

Conclusions

1. An insoluble aluminate of lithium is precipitated, practically quantitatively, when a solution of an aluminum salt containing sufficient lithium salt, is made alkaline with ammonia.
2. Analysis shows that the substance contains lithium and aluminum in atomic ratio of 1Li:2Al.
3. Upon ignition at a high temperature the substance becomes constant in weight. The weight of the residue, obtained from a precipitate containing a known amount of aluminum, suggests the formula $Li_2O \cdot 2Al_2O_3$ for the residue.

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