The solubility curve shows three distinct breaks, at B, C, and D. The solid along the portion A B was shown by the triangular diagram to consist of the hydrate $La(C_2O_4)_3.8H_2O$. Under slightly different conditions, the length of that portion of the curve B C was increased and the lanthanum oxalate along this branch was found to contain five molecules of water of crystallization. The dotted line does not represent the true direction of the curve of this hydrate. From C to D, the lanthanum compound was found to be in a still lower state of hydration, *viz.*, $La_2(C_2O_4)_3.3H_2O$. It was observed that along D E, the curve showed a slight increase in the solubility of lanthanum nitrate.

Summary.

The above work indicates that at 25°:

1. $La_2(C_2O_4)_3.11H_2O$ is not stable in contact with lanthanum nitrate solution.

2. The following hydrates also exist:
$La_2(C_2O_4)_3.8H_2O$, $La_2(C_2O_4)_3.5H_2O$ and $La_2(C_2O_4)_3.3H_2O$.

3. No oxalo-nitrate exists, although it may possibly be found at higher temperatures.

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THE QUANTITATIVE SEPARATION OF LANTHANUM FROM YTTRIUM.

BY C. JAMES AND T. O. SMITH.

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Hitherto the only method employed for the separation of the cerium earths from the yttrium earths has been the potassium sulfate treatment. This separation is based upon the fact that lanthanum forms a double sulfate with potassium which is insoluble in saturated potassium sulfate solution, while the corresponding yttrium compound is fairly soluble.

In addition to the above, Urbain has shown that by fractionally crystallizing the rare earth magnesium nitrates in the presence of bismuth magnesium nitrate the latter inserts itself between samarium magnesium nitrate and europium magnesium nitrate, dividing these elements quantitatively at this point.

He also states that by treating yttrium earth nitrates containing some cerium earth nitrates with magnesium nitrate and bismuth magnesium nitrate the separation of the two groups was effected.

Among other compounds which show diverging solubilities for these two groups are the sodium double sulfates, the formates, and the cacodylates.

For the quantitative study it was considered that the completeness of the separation could be better shown by employing lanthanum and yttrium which approach the extremes of the series.

Solutions of the pure nitrates of lanthanum and yttrium were prepared and standardized by precipitation with oxalic acid in hot neutral solution. One cubic centimeter of the lanthanum nitrate solution contained 0.003570 gram of La_2O_3. The yttrium nitrate solution contained 0.003482 gram of Y_2O_3 per cc.

Fifty cubic centimeter portions of each solution were placed in a 250 cc. beaker and crystals of potassium sulfate added in excess. The solution was well stirred and allowed to stand twelve hours, again stirred and set aside for a like period.

The precipitate of lanthanum potassium sulfate was filtered and washed with saturated potassium sulfate solution. The yttrium was precipitated from the cold filtrate by pouring it into a dilute solution of boiling sodium hydroxide. After filtering and washing the yttrium hydroxide with boiling water, it was dissolved in hydrochloric acid, an excess being avoided, and the resulting chloride solution precipitated with oxalic acid. The oxalate was washed, dried, ignited and weighed as Y_2O_3. The results were as follows:

No.	Y_2O_3 taken.	La_2O_3 taken.	Y_2O_3 found.
1	0.1741	0.1785	0.1516
2	0.1741	0.1785	0.1517

These figures show that yttrium potassium sulfate is carried down along with lanthanum potassium sulfate. In the absence of lanthanum and under similar conditions no yttrium would be precipitated.

Sodium Double Sulfates.—Usually the sodium double sulfates are more soluble than the double sulfates of potassium. This fact seemed to present an advantage in this case. The solutions were measured out as in the previous instance, and because of the greater solubility of sodium sulfate this salt was added until the solution contained approximately ten per cent. After standing 24 hours the lanthanum sodium sulfate was filtered off and washed with a 10% sodium sulfate solution. The yttrium in the filtrate was determined as before. The results were as follows:

No.	Y_2O_3 taken.	La_2O_3 taken.	Y_2O_3 found.
1	0.1741	0.1785	0.2646
2	0.1741	0.1785	0.2613
3	0.1741	0.1785	0.2600

The conclusions, drawn from these results, appear to indicate that an excess of sodium sulfate should have been used. However, even under these conditions, the whole of the lanthanum was not precipitated as the figures below show:

No.	Y_2O_3 taken.	La_2O_3 taken.	Y_2O_3 found.
1	0.1741	0.1785	0.2570
2	0.1741	0.1785	0.2583

Formates.—The next compounds possessing favorable properties were the formates. According to previous workers lanthanum formate dissolves in 420 parts of water while the corresponding yttrium salt dissolves in less than half its weight. By working with alcoholic solutions it was thought that the difference in solubilities might be considerably increased.

The mixture of standard nitrate solutions was precipitated with a slight excess of hot dilute sodium hydroxide. The hydroxides obtained in this way were washed with hot water and dissolved in diluted formic acid. The solution was evaporated until nearly all the water was removed. The residue was treated with 95% alcohol, filtered and washed with the same reagent. The formate was ignited to the oxide and weighed.

While lanthanum formate is practically insoluble in 95% alcohol and yttrium formate fairly soluble, the analytical results show that yttrium is inclined to accompany the lanthanum.

Cacodylates.—The cacodylates were examined and, although their solubilities differ widely, were found unsatisfactory, owing to the following facts: lanthanum cacodylate has a tendency to become colloidal and yttrium cacodylate is not quite insoluble in water. The use of alcohol does not improve the conditions.

Bismuth Magnesium Nitrate.—Urbain has stated, as previously mentioned, that lanthanum magnesium nitrate is insoluble in bismuth magnesium nitrate, and since yttrium forms no double nitrate it was assumed that a quantitative method might be obtained.

First of all, a qualitative test was made with regard to the solubility of the lanthanum double salt in concentrated nitric acid (sp. gr. 1.42) containing an excess of bismuth magnesium nitrate. It was found that the lanthanum was entirely insoluble. After this point had been proved a mixture of 50 cc. of each standard solution was taken, evaporated to dryness, treated with 25 cc. of concentrated nitric acid saturated with bismuth magnesium nitrate, to which was added ten grams of bismuth magnesium nitrate and one gram of magnesium nitrate. The mixture was warmed and stirred, when a considerable amount of the bismuth magnesium nitrate went into solution. The beaker was then set aside for 24 hours. The crystallin deposit was removed on a Gooch filter and washed with concentrated nitric acid saturated with bismuth magnesium nitrate.

The filtrate containing yttrium nitrate, together with some bismuth magnesium nitrate, was evaporated to dryness to remove all free acid. The residue was treated with 200 cc. cold water and the bismuth precipitated with hydrogen sulfide. The bismuth sulfide was filtered off and washed with cold water. The filtrate was boiled to expel the excess of hydrogen sulfide, cooled, treated with ammonium chloride, made nearly neutral by means of ammonium hydroxide, and precipitated with oxalic acid. The oxalate was ignited to the oxide and weighed.

The Gooch crucible containing the lanthanum together with the excess of bismuth magnesium nitrate was washed into a beaker, saturated with hydrogen sulfide to remove the bismuth and treated similarly to the yttrium. The results were as follows:

No.	Y_2O_3 taken.	Y_2O_3 found.	La_2O_3 taken.	La_2O_3 found.
1.	0.08705	0.0892	0.08925	0.0883
2.	0.08705	0.0876	0.1785	0.1782
3.	0.1741	0.1752	0.1785	0.1731
4.	0.1741	0.1758	0.1783	0.1779
5.	0.1741	0.1767	0.1785	0.1764
6.	0.1741	0.1735	0.1785	0.1791

This method is not all that could be desired either in point of accuracy or ease of manipulation, but is offered because of its superiority over the older potassium sulfate method. For separating holmium, dysprosium, etc., from lanthanum the error would probably be greater, owing to the fact that these elements have a slight tendency to form double magnesium nitrates. On the other hand, the separation should be much more perfect for the elements of the yttrium group possessing greater solubilities than yttrium itself.

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RARE EARTH REACTIONS IN NON-AQUEOUS SOLVENTS

BY O. L. BARNEBEY.

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1. Introduction.

Very little systematic general analytical work has been done in solvents other than water. Only isolated cases are to be noticed in a review of the subject where application of some non-aqueous solvent has facilitated analytical separations. Among these might be mentioned the ether extraction of iron, the ether extraction of uranium, the separation of barium, strontium and calcium with alcohol, the ether separation of beryllium and aluminium, the pyridine and the amyl alcohol separation of lithium chloride from sodium chloride. Naumann[1] has studied several reactions, notably the action of hydrogen sulfide and ammonia with most of the common members of the second and third analytical groups in ethyl acetate, methyl acetate, pyridine and acetone, obtaining very interesting results. The solubility tables of Naumann have been found serviceable, but in error in a number of cases. A new enlarged solubility list will be published in future papers dealing with the analytical chemistry

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[1] Naumann, *Ber.*, **32**, 999; **37**, 3600, 4328, 4609; **42**, 3789.