

This investigation was undertaken at the suggestion of Professor Lenher, and the author takes this opportunity to express his gratitude for the many gracious and helpful suggestions tendered throughout the course of the work.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

YTTRIUM SODIUM SULFATE.

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The separation of the cerium and yttrium earths is usually effected by adding potassium or sodium sulfate to a sulfate solution of the rare earths, the whole being thoroughly stirred and allowed to stand for some time. Some writers state that potassium sulfate is the better, while others recommend sodium sulfate. The authors, who always employ sodium sulfate, at first obtained varying results, which led to the investigation of the system yttrium sulfate, sodium sulfate and water.

At an early stage of the work, it was found that sodium hydroxide was not an ideal reagent for the quantitative precipitation of yttrium, since the results came a little high and did not check well. The work upon the sebacates¹ showed that ammonium sebacate was well adapted for this purpose.

Twenty-four bottles of 100 cc. capacity were made up containing varying amounts of yttrium sulfate, sodium sulfate and water. The greatest amount of yttrium sulfate added to any one was nine grams. It was found that even eight grams were too much when added to bottles of greater concentration. The bottles were sealed and placed in a thermostat on November 25, 1911. They were rotated at 25° until March 29, 1912, when the first analyses were made. From the results obtained, it was evident that the system was not yet in equilibrium, and accordingly the bottles were re-sealed and returned to the thermostat. From about the middle of June to the first of September, the bottles were allowed to stand at ordinary temperatures. At the latter date the rotation was recommenced and allowed to proceed until January 18, 1913. At this time the bottles were again opened and the solutions submitted to analysis. Even after this extra period it was found that four bottles were, apparently, still in a metastable condition, as can be readily seen from an observation of the curve.

It might be interesting to mention that, when the mixtures were first placed in the thermostat, the solid phase disappeared in most of the bottles; and that they remained perfectly clear for some weeks, after which the double salt was very slowly deposited.

¹ THIS JOURNAL, 34, 772.

The analysis of the liquid phase was carried out in the following manner: About ten grams of the liquid were weighed out and diluted to 200 cc., 50 cc. were measured out, diluted, heated to boiling and precipitated by ammonium sebacate. This was allowed to stand in an oven at 100° for a few hours, and when the supernatant liquid had become clear, the precipitate was filtered off, washed, dried and ignited, and the resulting yttrium oxide weighed. The SO_3 was determined by using 25 cc. of the prepared solution, which was acidified and precipitated by adding a slight excess of barium chloride.

The figures given in Table I are the results of a study of a metastable condition.

TABLE I.

Serial No.	Per cent. of $\text{Y}_2(\text{SO}_4)_3$.	Per cent. of Na_2SO_4 .	Parts of $\text{Y}_2(\text{SO}_4)_3$ per 100 parts H_2O .	Parts of Na_2SO_4 per 100 parts H_2O .
1	5.25	1.21	5.61	1.29
2	5.79	3.50	6.38	3.85
3	6.25	5.47	7.40	6.21
4	7.21	7.29	8.43	8.53
5	7.31	7.90	8.62	9.31
6	7.47	9.49	9.00	11.43
7	7.61	10.96	9.34	13.47
8	5.58	10.70	6.69	12.77
9	4.14	13.68	4.92	14.04
10	3.67	12.79	4.39	15.31
11	2.94	13.86	3.53	16.65
12	3.47	16.80	4.35	21.07
13	4.56	16.64	5.79	21.12
14	6.05	17.46	7.92	22.85
15	3.93	21.34	5.26	28.56
19	1.17	21.75	1.52	28.22
21	2.29	21.65	3.01	28.46
23	4.37	21.20	5.87	28.48
24	5.02	...	5.38	...

The data of the final analyses are given in Table II.

TABLE II.

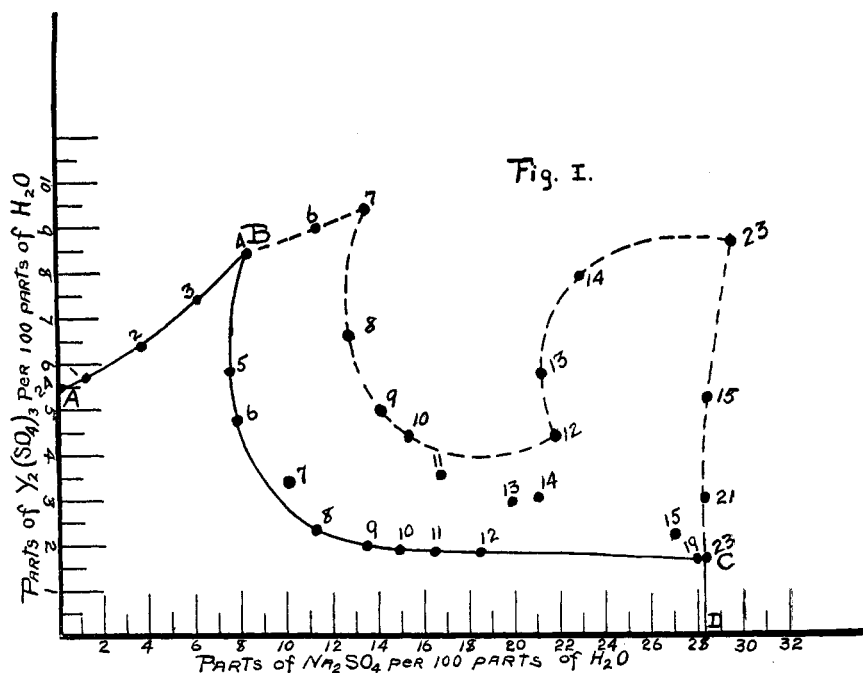
Serial No.	Per cent. of $\text{Y}_2(\text{SO}_4)_3$.	Per cent. of Na_2SO_4 .	Parts of $\text{Y}_2(\text{SO}_4)_3$ per 100 parts H_2O .	Parts of Na_2SO_4 per 100 parts H_2O .
1	5.25	1.21	5.61	1.29
2	5.79	3.50	6.38	3.85
3	6.52	5.47	7.40	6.21
4	7.21	7.29	8.43	8.53
5	5.16	6.67	5.86	7.57
6	4.23	6.87	4.75	7.72
7	3.01	8.93	3.42	10.14
8	2.07	9.99	2.36	11.36
9	1.75	11.62	2.02	13.42
10	1.63	12.79	1.90	14.89
11	1.51	13.96	1.79	16.51
12	1.54	15.33	1.86	18.44

TABLE II (continued).

Serial No.	Per cent. of $Y_2(SO_4)_3$.	Per cent. of Na_2SO_4 .	Parts of $Y_2(SO_4)_3$ per 100 parts H_2O .	Parts of Na_2SO_4 per 100 parts H_2O .
13	2.33	16.25	2.99	19.96
14	2.45	16.96	3.04	21.05
15	1.75	20.97	2.27	27.14
19	1.17	21.75	1.52	28.22
23	1.24	21.68	1.61	28.13
24	5.02	...	5.38	...

It will be observed that certain bottles are missing from the series. This is due to the fact that they were used in previous work and were broken. Bottle 24 was used for the determination of the solubility of yttrium sulfate. The solubility of sodium sulfate was taken from Seidel's tables.

The results given in Tables I and II are plotted in Fig. 1.



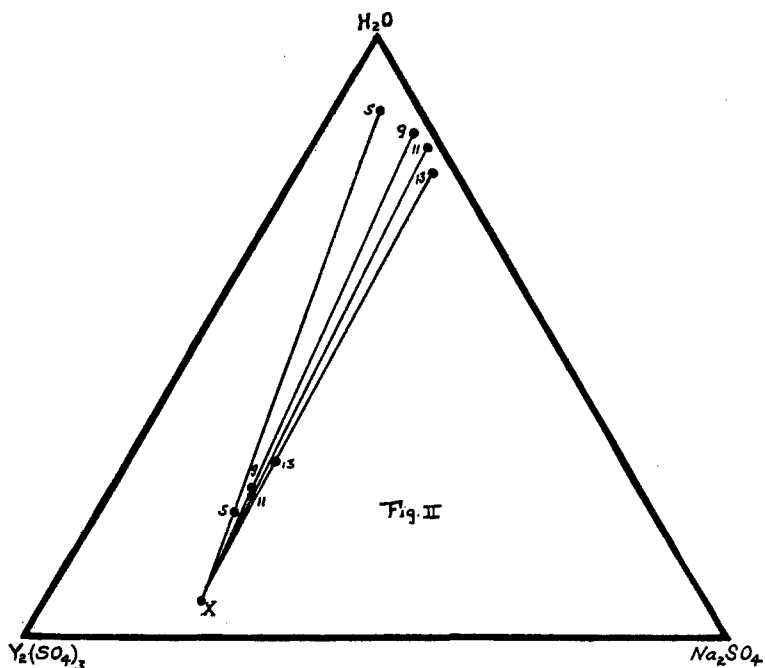
The above figure indicates that the curve consists of three sections—AB, BC and CD. The solid phase along AB was very crystallin and looked like yttrium sulfate. An analysis showed that this was the case. From B to C the solid phase consisted of the double compound, yttrium sodium sulfate. This was proved by analyses and the plotting of the results upon a triangular diagram.

The analysis of the solid phase was carried out in the following manner: The solid was removed by means of a platinum spoon, pressed between

filter paper, placed in a weighing bottle and thoroughly mixed. Two portions were then weighed out, one for the determination of yttrium oxide and the other for sulfur trioxide. They were easily dissolved by stirring with water, after which they were brought to boiling. The yttrium was precipitated by means of ammonium sebacate, while the sulfur trioxide was thrown down in the form of barium sulfate by adding barium chloride to the second portion, acidified with hydrochloric acid.

The results of the analyses of the solid phase are given in Table III and plotted in Fig. 2:

Serial No.	Liquid.		Solid.	
	Per cent. of $Y_2(SO_4)_3$.	Per cent. of Na_2SO_4 .	Per cent. of $Y_2(SO_4)_3$.	Per cent. of Na_2SO_4 .
5	5.16	6.67	59.40	19.95
9	1.75	11.62	55.85	19.80
11	1.51	13.96	56.33	20.21
13	2.33	16.25	49.99	20.72



The lines joining the points shown in the triangular diagram meet at a common point X, corresponding to a double salt possessing the composition $Y_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$, which has been previously described by Cleve. The composition of this substance was confirmed by taking the solid phase from bottle No. 6, washing with water, carefully drying, and analyzing after the method described above.

Calculated: Y_2O_3 , 35.08; SO_3 , 49.71. Found: Y_2O_3 , 34.98; SO_3 , 49.73.

Summary.

1. Only one yttrium sodium sulfate exists at 25°.
2. There is a great tendency for the solution to remain in a metastable condition for many months.
3. The efficacy of sodium sulfate for the separation of the cerium and yttrium earths depends upon the concentration. If the solution be too concentrated the yttrium earths will be precipitated to a very great extent.

DURHAM, N. H., February 8, 1913.

SOME QUANTITATIVE SEPARATIONS OF NEODYMIUM.

BY T. O. SMITH AND C. JAMES.

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During the separation of the crude rare earths as oxalates from acid solutions of minerals, it has been observed that varying amounts of other elements, such as titanium, uranium, etc., accompany the precipitate. It, therefore, seemed advisable to study this matter from the quantitative standpoint. Neodymium was chosen, because it so happened that plenty of pure material was at hand; and also, because of its position in the series, it would seem to give results that would be in accord with the other members of the group.

A standard neodymium chloride solution was prepared from the pure oxalate in the following manner: The oxalate was ignited to the oxide, Nd_2O_3 , in a weighed platinum dish and the exact weight of the oxide found. It was then carefully dissolved in a slight excess of hydrochloric acid and the excess of the latter removed by gentle evaporation to dryness. The salt so obtained was dissolved in water, diluted to a known volume and the strength of the solution calculated.

This standard solution was then further checked by measuring out 50 cc., diluting, heating to boiling, and precipitating with oxalic acid. The precipitated oxalate was allowed to stand an hour, washed with cold water, dried and ignited to the oxide. This showed that the solution contained 0.002876 gram Nd_2O_3 per cc. It was found to check perfectly with the calculated result. A standard neodymium chloride solution might therefore be prepared by simply dissolving a known weight of the oxide in the required amount of hydrochloric acid and diluting to the desired volume.

Separation of Titanium.

To prepare a standard titanium solution, dry titanium dioxide was treated with hot sulfuric acid, forming basic titanium sulfate, $(\text{TiO})\text{SO}_4$. Any considerable excess of acid was evaporated off. The granular white mass of basic sulfate was put into solution by repeated decantations with dilute sulfuric acid. The final solution contained about 4 cc. of con-