No.	% $Sa_2(SO_4)_3$.	% $(NH_4)_2SO_4$.	% H_2O.
5	61.7	13.0	25.3
9	55.9	15.2	28.9
10	57.0	13.7	29.3
13	55.1	17.9	27.1

From these results and from the corresponding liquid phase the triangular plot shown in Fig. 3 was made.

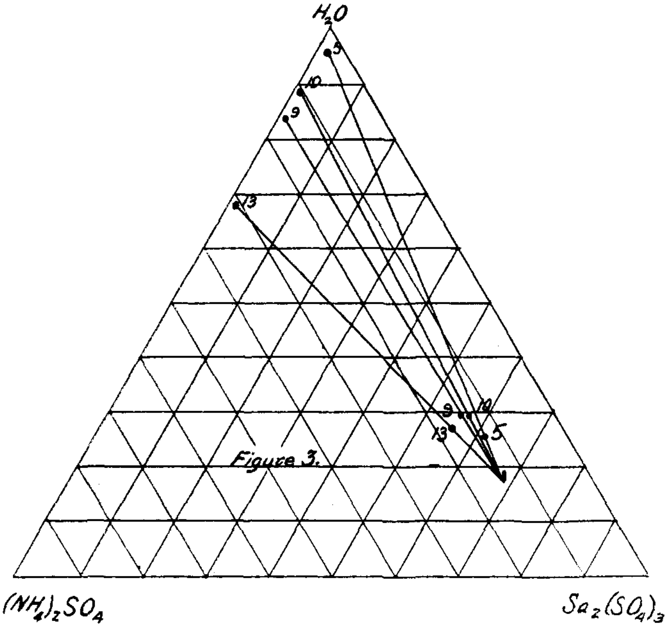

Figure 3.

It will be observed that the lines intersect at a common point corresponding with the formula $Sa_2(SO_4)_3.(NH_4)_2SO_4.7H_2O$.

Some of the pure compound was prepared by washing away the ammonium sulfate from some of the solid phase from bottle 5. Analysis showed that the composition agreed well with that indicated above. This formula is similar to the one given by Cleve, with the exception of the amount of water of crystallization.[1]

DURHAM, N. H.

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

THE SEPARATION OF YTTRIUM FROM THE YTTRIUM EARTHS.

PART I.

BY H. C. HOLDEN AND C. JAMES.

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Although the rare earth oxides obtained from minerals such as gadolinite, fergusonite, euxinite, samarskite and xenotine carry a large percentage of

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[1] *Bull. soc. chim.*, 43, 162.

yttrium, it has been found by many chemists that to obtain pure yttrium oxide involves a long and intricate process. In view of this fact, the authors have begun a systematic study of various methods in hope of finding one which will give pure material, with the greatest efficiency.

The material used in the first part of this work consisted mainly of yttrium oxide, together with some erbium oxide, the determination of the equivalent of which gave an atomic weight of 94.7. The method used in the determination of the equivalent was as follows: About 0.1500 g. of oxide was dissolved by heating in 50 cc. of carefully standardized, approximately *N*/10, sulfuric acid, after which about 8 cc. of *N*/5 potassium oxalate was added and the resulting product brought to the boiling point. This was cooled, phenolphthalein added and the excess of sulfuric acid titrated by means of approximately *N*/10 sodium hydroxide. Since the amount of acid used by the oxide was known, the equivalent could easily be determined.

(*A*) *Fractional Precipitation by Means of Hypophosphorous Acid.*—About 10 g. of the mixed oxides were dissolved in formic acid and diluted to about one liter. This solution was then boiled and stirred by means of steam, while a sufficient amount of a 5% solution of hypophosphorous acid was added to form a fair sized precipitate. The precipitate thus obtained was washed with water and dissolved in hydrochloric acid, reprecipitated with oxalic acid and ignited. On ignition, phosphine was noticed to be given off and the volume increased about three times the original. The oxide thus obtained was dissolved in hydrochloric acid and again precipitated with oxalic acid. This was washed, ignited and weighed. A portion of this was redissolved in hydrochloric acid, precipitated as oxalate, washed, ignited to constant weight and the equivalent determined. Fraction 4 was obtained from the filtrate of fraction 3 by means of oxalic acid and did not show the peculiar action on ignition of the three previous fractions. A noticeable change of color could be seen going from fraction 1, which was light pink, to fraction 4 which was nearly white.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	96.15	2.2
2	95.20	2.0
3	93.50	2.0
4	88.30	2.5

(*B*) *Fractional Precipitation by Means of the Dimethyl Phosphates.*—Between 7 and 8 g. of the mixed oxides were dissolved in hydrochloric acid and diluted with water to about 750 cc. This was boiled and stirred as in the previous fractionations, and a dilute solution of sodium dimethyl phosphate added until sufficient precipitate was obtained for fraction 1. As the dimethyl phosphates are more soluble in cold than in hot water, the solutions had to be filtered rapidly. Three fractions were obtained in this manner. The filtrate from fraction 3 was placed in a casserole and boiled. Since an excess of sodium dimethyl phosphate was present, the remaining fractions were obtained by evaporation. The various fractions were then dissolved in hydrochloric acid and precipitated as oxalates, dried, ignited and weighed. A portion was then redissolved in hydrochloric acid, filtered, reprecipitated as oxalate, dried, ignited to constant weight and the equivalent determined. Fraction 6 was obtained by adding oxalic acid to the filtrate from fraction 5. The oxalate was ignited, dissolved in hydrochloric acid and precipitated with ammonium hydroxide. The hydroxide was filtered off, dissolved in hydrochloric acid and precipitated as the oxalate, ignited and then subjected to the same treatment as the previous fractions.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	96.60	1.09
2	95.60	1.25
3	94.70	2.40
4	94.60	1.23
5	92.50	0.80
6	91.90	0.10

(*C*) *Fractional Precipitation by Means of the Cacodylates.*—A small quantity of the mixed oxides was dissolved in hydrochloric acid and diluted with water to about 750 cc. This was boiled and stirred as before, and a dilute solution of sodium cacodylate added until a fair sized precipitate was formed. The fractionation was then carried on as shown in the following diagram:

Precipitate 1 — Filtrate 1
Addition of more sodium cacodylate

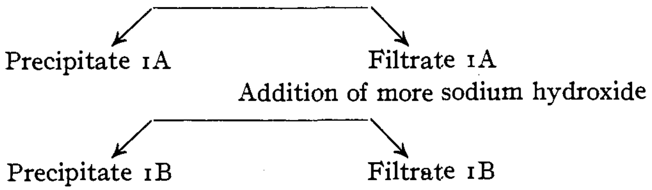
Precipitate 2 — Filtrate 2
Addition of sodium hydroxide

Precipitate 3 — Filtrate 3

Precipitate 3: Dissolved in hydrochloric acid, precipitated as oxalate, ignited, dissolved in hydrochloric acid, precipitated as oxalate, ignited, a portion taken, ignited to constant weight and the equivalent determined.

Filtrate 3: Discarded

Precipitate 1 was dissolved in hydrochloric acid, boiled, and a 4% solution of sodium hydroxide added.



Precipitate 1A

Filtrate 1A
Addition of more sodium hydroxide

Precipitate 1B

Filtrate 1B

Precipitates 1A and 1B were then treated in the same manner as precipitate 3.

Precipitate 2 was then subjected to the same treatment as precipitate 1, 2A and 2B being obtained. These were treated as precipitate 3.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1A	96.80	2.16
1B	93.70	1.90
2A	93.70	2.70
2B	92.20	0.90
3	91.80	0.59

(*D*) *Fractional Precipitation by Means of the Phosphates.*—A small amount of the mixed oxides was dissolved in nitric acid and diluted to about 750 cc. with water, which made the solution about 1:9 concentration of nitric acid. A solution of ammonium phosphate was then prepared by nearly neutralizing a 10% solution of phosphoric acid with ammonium hydroxide. The solution of the mixed oxides was boiled and stirred as before and about 100 cc. of the ammonium phosphate added. The precipitate thus obtained was filtered, washed, dissolved in concentrated hydrochloric acid, diluted, and precipitated as the oxalate. This was then ignited, redissolved in hydrochloric acid, filtered, precipitated as the oxalate and ignited. A small amount of this oxide was taken and the equivalent determined. In a like manner, with the filtrate of the first precipitate, another fraction was obtained, purified and the equivalent determined. Fraction 3 was obtained by the same method.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	97.20	2.85
2	94.3	2.87
3	91.4	1.22

(*E*) *Fractional Precipitation by Means of the Monomethyl Phosphates.*—About 7 or 8 g. of the mixed oxides were dissolved in hydrochloric acid and water added to make the solution about 1:10 concentration of hydrochloric acid. The solution was then boiled and stirred as before and the solution of sodium monomethyl phosphate added until a fair sized precipitate appeared. This was taken as fraction 1 and from the filtrate fraction 2 was obtained in a similar manner. In this way four fractions were procured. Each fraction was then dissolved in hydrochloric acid, precipitated as the oxalate, ignited, redissolved, filtered, precipitated as the oxalate, and ignited. The equivalents were then determined, by using a small portion of each.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	96.10	2.07
2	94.9	1.83
3	93.8	0.72
4	91.7	1.44

(*F*) *Fractional Precipitation by Means of the Arsenates.*—A small amount of the mixed oxides was dissolved in nitric acid and diluted to about 750 cc. This was boiled and stirred as before and a dilute solution of sodium arsenate added until a fair sized precipitate resulted. This first precipitate was somewhat gelatinous, but the succeeding fractions grew more crystalline. Four fractions were obtained by the addition of more sodium arsenate. These were purified by dissolving in hydrochloric acid, precipitating as oxalate, and igniting, after which the equivalents were determined.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	97.4	1.56
2	95.9	0.80
3	95.8	0.84
4	91.8	2.64

(*G*) *Fractional Precipitation by Means of the Phosphites.*—A dilute solution of sodium phosphite was run into a dilute solution of the chlorides of the rare earths. The rare earth material and the method of obtaining the various fractions was similar to the method employed in the previous fractionation. The five fractions thus obtained were somewhat gelatinous, but seemed to filter very readily. They were dissolved in hydrochloric acid and precipitated as the oxalate, ignited, redissolved in hydrochloric acid, filtered, precipitated as the oxalate, and ignited. A portion of each was then taken and the equivalent determined.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	97.60	0.22
2	96.85	0.72
3	95.50	1.75
4	94.00	2.00
5	91.70	1.05

(*H*) *Fractional Precipitation by Means of the Chromates.*—A small quantity of the mixed oxides was dissolved in a solution of chromic acid and water. This was made neutral by the addition of a slight amount of oxide and then diluted with water to about 750 cc. A 10% solution of potassium chromate was added to this solution, while it was being stirred by means of steam and heated with a bunsen burner. After the addition of about 250 cc. of the potassium chromate solution, the first fraction was obtained. Three more fractions were obtained in a like manner and the filtrate from fraction 4 treated with ammonium hydroxide to obtain fraction 5. The various fractions thus obtained were dissolved in hydrochloric acid by using a slight excess, reduced by means of ethyl alcohol, boiled, and the rare earths precipitated by means of oxalic acid. These oxalates were ignited, dissolved in hydrochloric acid, filtered, oxalic acid added, the resulting oxalates ignited, and the equivalents determined.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	103.40	0.26
2	98.00	1.60
3	96.15	0.45
4	94.20	0.90
5	89.70	1.93

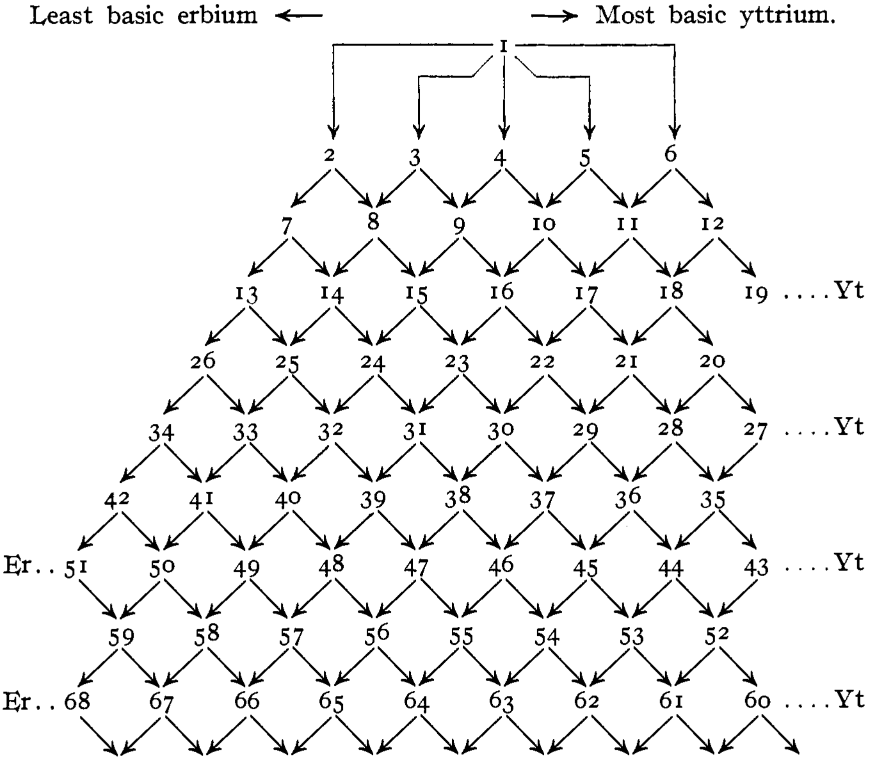
(*I*) *Fractional Precipitation by Means of the Iodates.*—In this fractionation a dilute solution of potassium iodate was added slowly to a nitric acid solution of the rare earth oxides. The rare earth material and the procedure were the same as in the previous method. The five fractions thus obtained were dissolved in hydrochloric acid and oxalic acid added, which set free the iodine and also precipitated the oxalates. These were ignited, dissolved in hydrochloric acid, filtered, precipitated as oxalates, ignited, and the equivalents determined.

SUMMARY.

No. of fraction.	Atomic weight.	Weight of fraction.
1	98.50	0.59
2	96.70	0.32
3	96.60	2.09
4	95.50	0.93
5	93.20	2.65

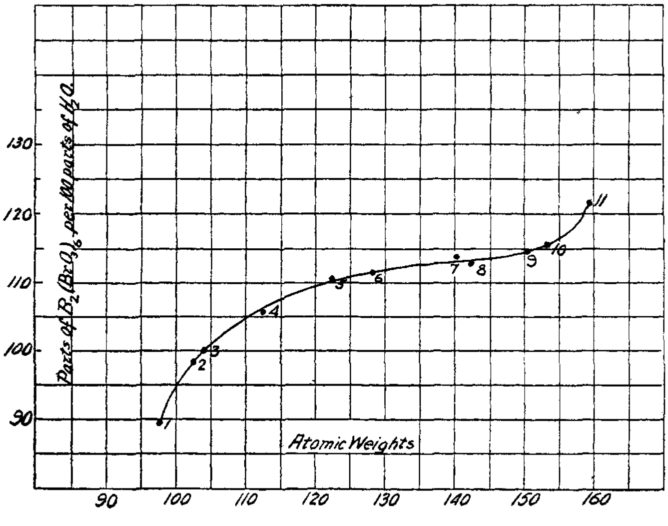
(*J*) *Separation by Means of the Fractional Crystallization of the Bromates of Erbium Containing Yttrium.*—The material used in conducting this work was ytterspar, euxinite, gadolinite, xenotine and fergusonite and from these, several kilograms of crude erbium bromate were obtained. This erbium bromate, containing some yttrium, was boiled with sodium hydroxide, the precipitate being filtered off and well washed with boiling water. The hydroxide was then dissolved in hydrochloric acid and the solution precipitated by means of oxalic acid. The resulting oxalate possessed an exceedingly beautiful rose tint. For separating yttrium from erbium, the method of fusing the nitrates is said to be the best. The next step was to dissolve the oxides, obtained by igniting the oxalates, in nitric acid. The solution was evaporated and the nitrates heated until brown fumes were evolved. This decomposition was allowed to proceed for a little time. When the desired period had elapsed, the "melt" was poured into an enamel iron vessel and the latter cooled by placing in cold water. The glassy nitrates were thus obtained in thin cakes which cracked into small portions and were readily removed. On boiling this product with water—the correct amount is soon judged by experience—a precipitate remained. On cooling, the solid portion increased owing to the less soluble basic nitrates crystallizing out. As erbium nitrate decomposes more readily than the corresponding salt of yttrium, the solid obtained by filtering the above is much richer in erbium than the mother liquor. The original portion was split into five fractions. The fractionation from the second series onward, was treated similarly to a fractional crystallization, *i. e.*, the mother liquor of the richest yttrium fraction was poured off, forming a new fraction while the mother liquor from the next was added to the solid remaining from the first fraction of that series and so on. After a series had been poured, nitric acid was added to each to dissolve the basic salts, after which they were evaporated to dryness and again submitted to careful fusional decomposition. These operations can be better understood from the following diagram:

FUSION OF NITRATES.



All the fractions richest in erbium were then united. This least basic portion showed the presence of scandium and ytterbium when tested in the spectrograph, and was placed on one side. The resultant fractions consisting of erbium with some yttrium were converted into the bromates and fractionated for a time. Samples were then obtained from the various fractions, placed in bottles and sufficient water added to dissolve about one half the crystals. The bottles were then carefully sealed, placed in the thermostat and rotated at 25° until equilibrium was reached. They were then allowed to stand at this temperature until the solid had settled. Samples of the supernatant liquid were withdrawn for analysis. The analysis was carried on as follows: The samples of liquid were weighed, diluted with water and oxalic acid added to free the bromine and also precipitate the oxalates of the rare earths. These were ignited and weighed. About 0.1500 g. was then taken and the equivalent determined by the method used in the previous cases. With these data the parts of $R_2(BrO_3)_6$ per 100 parts of water were determined and the following results obtained:

Bottle No.	Fraction No.	Atomic weight.	Parts of $R_2(BrO_3)_6$ per 100 parts of H_2O.
1	7	159.50	123.03
2	8	153.40	115.24
3	9	150.40	114.56
4	12	142.50	112.65
5	15	140.50	113.98
6	17	128.20	111.52
7	19	122.70	110.45
8	20	112.70	105.37
9	22	104.05	99.90
10	23	102.40	98.10
11	25	97.60	89.35



These results were then plotted as can be seen by the accompanying figure.

Conclusions.

Of all the fractional precipitational methods studied up to the present time, the chromate and phosphate show the greatest efficiency.

Fractional crystallization methods are being carried on in order to investigate the curves obtained by plotting solubilities against atomic weights.

DURHAM, N. H.

NEGATIVE OSMOSE.

BY F. E. BARTELL.

Received February 5, 1914.

In the usual osmotic experiments, a solution is separated from the solvent by means of a semipermeable membrane and there is produced, as a result, a flow of liquid through the membrane. The flow of the liquid, as a whole, is toward the more concentrated solution tending, thereby, to increase the volume of the more concentrated solution. This phenomenon is commonly known as osmosis; however, when referred to in this paper, it will be designated as *positive osmose.* In some of the experiments described in this paper the direction of flow of the liquid, as a whole, through the membrane is not in the direction usual in the process of osmosis but is, on the contrary, from the concentrated to the more dilute solution. This latter mentioned phenomenon will be referred to as *negative osmose.*[1]

Numerous experiments have been carried out in this laboratory in an attempt to determine the maximum size of the capillary pores in membranes with which small but definite osmotic effects can be obtained. Plain unglazed porcelain membranes and membranes of porcelain clogged with various insoluble precipitates have been investigated.[2] The main object of these experiments has been to determine the relation of pore diameter to osmotic effects produced when these different membranes are used with one and the same solute (sugar).

An attempt has been made in the present investigation to determine the relation of pore diameter to osmotic effect, when different solutes are used with one and the same grade of unglazed porcelain membranes. The value of the pore diameter of the porcelain selected was near the border line between osmotic effect and no osmotic effect for sugar solutions.

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[1] The terms positive osmose and negative osmose were used by Graham to describe similar phenomena in connection with his work on "Osmotic Force." *Phil. Trans.*, **144**, 177 (1854).

[2] Bigelow and Bartell, THIS JOURNAL, **31**, 1194 (1909). Bartell, *J. phys. Chem.*, **16**, 318 (1912).