Summary.

Previous work by the authors has shown that Fe_2O_3 dissociates to form a solid solution of Fe_3O_4 in Fe_2O_3, and that the curve of dissociation pressure against composition at a given temperature rises rapidly as the composition approaches pure Fe_2O_3. The present experiments show that there is a measurable dissociation of Fe_2O_3 in air at all temperatures between 1100° and 1300°, and that the amount of dissociation increases with the temperature. This is shown by the increasing difference in weight between ignitions in air and in oxygen as the temperature is increased. The dissociation-pressure-composition curve thus takes the form of a curve asymptotic to the axis of ordinates, when the ordinates are pressures.

The best container for the Fe_2O_3 at 1100° and 1200° is alundum (bonded fused alumina) which is almost absolutely constant in weight at these temperatures, although it loses weight steadily at higher temperatures. The loss in weight of pure platinum at 1000–1200° is very small, but is considerably increased if the platinum is in contact with ferric oxide.

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THE SEPARATION OF ERBIUM FROM YTTRIUM.

[PART I.]

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The element erbium, or neoerbium as it is sometimes termed, is very much rarer than was formerly supposed. Very small amounts, when mixed with yttrium, cause the precipitates and solutions to show a pink or rose color. Also, concentrated solutions of yttrium nitrate, containing very small quantities of erbium, show a strong absorption spectrum due to the latter element. During the last few years, practically no work has been done upon this substance apart from the researches of Hoffmann and Burger.[1] These investigators obtained erbium salts which, if not absolutely pure, are the purest yet known. They also claim that erbium is a simple definite element and not complex, as stated by Auer von Welsbach. This is entirely in agreement with the later work of one of the authors who has submitted erbium bromate to a very long series of fractionation without causing any change in the absorption spectrum. All differences observed were proved to be due to varying conditions of concentration, acids or acidity.

Fractional crystallization, so far, has failed to separate erbium from yttrium rapidly. This type of operation, when bromates or ethylsulfates are employed, quickly removes terbium, dysprosium and holmium in the

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[1] *Ber.*, 41, 308 (1908).

least soluble, while thulium, ytterbium and lutecium collect in the mother liquor.

In order to study the separation of erbium from yttrium systematically, it seemed necessary to start with two types of yttrium erbium oxide material, one in which yttrium was in excess, while the other consisted mainly of erbium. The results obtained should show whether selected methods will work with the same rapidity at both ends of the series, or whether it would be advisable to use two different ones.

The results obtained by using oxides containing an excess of yttrium are given in this paper which forms part one. Part two will appear at a later date.

Fractional Precipitation by Means of Sodium Phosphate.—Twelve grams of the oxides of yttrium and erbium were dissolved in dilute nitric acid, diluted to one liter, boiled and stirred with steam. A 10% solution of sodium phosphate was then added drop by drop from a separatory funnel. When sufficient of the precipitate had formed it was filtered off, and the process was repeated until four fractions had been taken. A concentrated solution of oxalic acid was then added to throw out what rare earths remained. The first four fractions were dissolved in a mixture of equal volumes of concentrated nitric acid and water, precipitated as oxalates and ignited to oxides. The fifth fraction was ignited, boiled with water to remove the sodium, filtered and well washed. The oxide was then dissolved in nitric acid and precipitated as the oxalate, and again ignited. The equivalents were then determined.

At. wt. of fraction.....	(1)109.2	(2)106.9	(3)104.1	(4)106.8	(5)98.9
Grams..............	1.01	0.34	0.56	0.67	8.77

Fractional Precipitation by Means of Potassium Ferrocyanide.—Ten grams of oxides were dissolved in about 140 cc. of formic acid, and diluted to about one liter. The liquid was boiled and stirred and a 10% solution of potassium ferrocyanide added drop by drop. The precipitate, which was somewhat colloidal, was easily separated by filtering through a paper matte. Three fractions were taken. The precipitates, which gradually turned blue, were dissolved in concentrated hydrochloric acid, and thrown down as oxalates. These oxalates upon ignition gave brownish oxides, which were dissolved in nitric acid and reprecipitated and ignited.

At. wt. of fraction.....................	(1)102.0	(2)102.4	(3)97.7
Grams............................	1.25	3.94	3.66

Fractional Precipitation by Means of Sodium Nitrite.—Ten grams of oxides were dissolved in hydrochloric acid, diluted to one liter, boiled and stirred with steam. Sodium nitrite was gradually added until enough precipitate had formed. The precipitate was removed and the process repeated until five fractions were obtained. The sixth one was obtained by adding concentrated oxalic acid to the acidified liquid. In this last case the oxide formed by igniting the oxalates was boiled with water to remove any sodium which might have been present. All the fractions were purified and the equivalents determined.

At. wt. of fraction	(1)115.9	(2)115.5	(3)109.1	(4)103.3	(5)101.8	(6)89.9
Grams	1.17	0.64	1.84	1.05	1.01	3.60

Fractional Precipitation by Means of Potassium Cobalticyanide.—Ten grams of oxides were dissolved in hydrochloric acid and diluted to one liter. A 10% solution of the cobalticyanide was slowly added to the boiling and well-stirred solution. Four fractions were taken in this manner, while the last fraction was formed by adding oxalic acid. The rare earth cobalticyanides were decomposed by boiling with sodium hydroxide. The resulting hydroxides were poured upon a filter, well washed with water, dissolved in hydrochloric acid and precipitated as oxalates. These oxalates were purified by several precipitations.

At. wt. of fraction	(1)112.2	(2)107.1	(3) ...	(4)100.3	(5)87.8
Grams	2.07	2.06	...	0.72	2.70

Fraction three was too small to work with. During the purification of the oxides a certain amount of the material was lost.

The potassium cobalticyanide was prepared in the following way: Potassium cyanide was added to a hot solution of cobalt chloride until no more cobalt cyanide was precipitated. The cyanide was filtered off, washed, dissolved in potassium cyanide, boiled and acetic acid gradually added. The crude cobalticyanide solution was then added to a strongly acid and boiling solution of copper chloride. The precipitated copper compound was removed by filtration, washed and boiled with potassium hydroxide. The copper oxide was separated and the yellow solution evaporated until crystals of the potassium salt were obtained upon cooling.

Fractional Crystallization of the Ammonium Double Sulfates.—About 10 g. of oxides were dissolved in hydrochloric acid, diluted, and an excess of ammonium sulfate crystals added. The solution was then evaporated upon the water bath, and three fractions taken. The fourth was obtained by the addition of oxalic acid.

The equivalents of the first and last fractions only were determined, since the method showed no fractionation.

At. wt. of fraction	(1)101.1	(4)101.3
Grams	1.95	1.12

Fractional Crystallization of the Diphenylmonosulfonates.—Three grams of oxides were dissolved in dilute hydrochloric acid and slightly diluted. The solution was heated to boiling and a solution of sodium diphenylmonosulfonate added. Upon cooling, scales of the diphenylsulfonates separated out. The process was repeated until four fractions had been taken. These were dissolved in large quantities of hot water and precipitated in the form of the oxalates, and ignited.

At. wt. of fraction	(1)98.5	(2)98.9	(3)100.3	(4)100.8
Grams	0.46	0.15	0.61	1.34

Crystallization of the Picrates.—Twenty grams of the oxides were dissolved in a slight excess of picric acid solution at 100°. The oxides dissolved very slowly. When the solution was complete, the liquid was allowed to cool and crystallize. The usual scheme for fractional crystallization was then followed for about ten series, keeping a maximum of five fractions. The picrates were then changed to oxalates and ignited to oxides.

At. wt. of fraction	(1)99.85	(2)100.00	(3)102.00	(4)102.15	(5)102.70
Grams	0.39	3.95	9.66	2.72	0.85

This work indicates that the erbium accumulates in the most soluble portion, which is the usual circumstance in fractional crystallization. This method of fractionation does not compare favorably with several of the well-known methods, since the separation of yttrium and erbium is so slow and the solution so dilute.

Fractional Precipitation by Means of Sodium Carbonate in the Presence of Ammonium Acetate.—About 10 g. of oxides were dissolved in dilute hydrochloric acid, the liquid diluted to about a liter, and 30 g. of ammonium acetate added. The solution was boiled, well stirred with steam, and precipitated with a 5% sodium carbonate solution. Four fractions were taken.

At. wt. of fraction	(1)106.9	(2)106.2	(3)104.95	(4)96.80
Grams	0.30	1.07	3.33	4.29

Fractional Precipitation by Means of Ammonium Oxalate in the Presence of Ammonium Acetate.—The method outlined above was followed in this case with the exception that ammonium oxalate was used in place of sodium carbonate.

At. wt. of fraction	(1)104.25	(2)103.35	(3)100.8	(4)97.65
Grams	2.12	2.07	2.99	2.29

Fractional Precipitation by Means of Ammonium Succinate in Presence of Ammonium Acetate.—This method was similar to the above with the exception that a 10% solution of ammonium succinate was used in place of a 5% ammonium oxalate. Five fractions were obtained.

The equivalents of the first and last fractions only were determined, since the method showed scarcely any separation.

At. wt. of fraction	(1)101.05	(2) ...	(3) ...	(4) ...	(5)98.65
Grams	2.05	1.50	2.22	1.61	2.08

Fractional Precipitation by Means of Sodium Phosphate in the Presence of Ammonium Acetate.—The procedure in this case was similar to the foregoing with the exception that sodium phosphate was substituted for ammonium succinate. This time, however, four fractions were obtained. The equivalents of the first and last were determined.

At. wt. of fraction..........	(1)101.7	(2) ...	(3) ...	(4)98.2
Grams....................	0.96	2.56	2.66	3.18

Fractional Precipitation by Means of Sodium Hydroxide in the Presence of an Excess of Tartaric Acid.—Ten grams of oxide were dissolved in hydrochloric acid, diluted to a liter, and 40 g. of sodium potassium tartrate added. Sufficient acid was then added to dissolve the precipitate formed, and the whole boiled and stirred with steam. A 20% solution of sodium hydroxide was added drop by drop. The precipitate formed very rapidly until the liquid became alkaline. The liquid was filtered, and, because it gave no further precipitate with sodium hydroxide, acidified with hydrochloric acid, and the remaining rare earths thrown out as oxalates.

At. wt. of fraction..................	(1)101.75	(2)98.30
Grams............................	6.28	2.19

Fractional Precipitation by Means of Tartaric Acid from Acetone.—Ten grams of oxides were dissolved in nitric acid and evaporated to crystallization so as to remove the excess of nitric acid. The nitrates were then dissolved in acetone and diluted to 300 cc. Acetone saturated with tartaric acid, by shaking with the finely ground material, was added by means of a buret. Five fractions were obtained in this manner, the sixth being obtained by means of oxalic acid.

Acetone added (cc.)...	(1)13	(2)16	(3)17	(4)20	(5)45	(6)..
At. wt. of fraction.....	100.15	99.7	101.15	100.65	101.10	101.8
Grams..............	0.45	0.65	0.98	0.90	1.71	4.71

This method which was published by O. J. Barnebey[1] appears not to be adapted for the separation of yttrium and erbium.

Fractional Precipitation by Means of Malonic Acid from Acetone Solution.—The acetone solution of the rare earth nitrates was prepared as described above. Four fractions were obtained by adding an acetone solution of malonic acid. The first two fractions were obtained by allowing the malonates to separate from the cold solution, while the last were precipitated from a boiling solution. A fifth fraction was taken by the use of oxalic acid.

At. wt. of fraction......	(1)98.8	(2)99.4	(3)102.4	(4)102.5	(5)100.2
Grams................	0.86	1.15	0.69	0.96	4.36

Conclusion.

It is evident from the preceding results that three methods stand out as being best adapted for the separation of erbium from yttrium. These include the nitrite, cobalticyanide and phosphate processes. The sodium nitrite is probably the best for large scale work owing to its cheapness, and ease of manipulation.

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[1] This Journal, 34, 1174 (1912).