until the 37.5% mixture is reached. No data are available for comparison with rubidium salts in alcohol-water mixtures, but it has been shown that potassium iodide increases the viscosity of these mixtures to that concentration containing 40% alcohol. In this instance, however, caesium nitrate decreases the viscosity of the 50% mixture, positive viscosity manifesting itself only in the 75% mixture.

This shifting of the transition point from negative to positive viscosity towards the more concentrated solvents (regarding water as the diluent) with increase in the molecular volume of the salt, brings out clearly the gradual breaking down of the associated molecules into smaller particles with greater fractional surfaces, the difference in the sizes of the particles at different points on the dilution curve, being clearly brought out by the effect produced by salts of differing molecular volumes.

The apparent transition from negative to positive viscosity with rise in temperature, noted in certain instances, would seem to indicate either a polymerization of the salt or else a solvent envelope which is broken down with rise in temperature. Since these salts are the least solvated, the first assumption is apparently the more plausible.

Measurements are now in progress of the effect of these salts on the viscosity of glycerol and of glycerol-water mixtures.

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

THE SEPARATION OF YTTRIUM FROM THE YTTRIUM EARTHS. PART III.

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This article describes the continued search for a rapid, efficient and economical method for the separation of yttrium from the yttrium earths. All the methods which are herein given are of a fractional precipitation type.

Precipitation by Means of Ammonium Sebacate.—About 12 g. of the mixed oxides were dissolved in dilute nitric acid, diluted to 1200 cc. and made neutral by the addition of ammonium hydroxide. The solution was then boiled and stirred with steam. In order to keep the volume of the liquid in the flask constant, a bunsen burner was always kept going underneath. When the liquid boiled, a 10% solution of ammonium sebacate was added until a fair-sized precipitate had formed. The precipitated sebacates were granular and filtered readily. The filtrate from Fraction I was similarly treated and this was carried out until five fractions were obtained. The various fractions were dissolved in dilute nitric acid, boiled and precipitated with a hot solution of oxalic acid.

The granular oxalates were washed, ignited to constant weight and the equivalent determined as mentioned in Part I.

	1.	2.	3.	4.	5.
Atomic weight..........	97.60	98.00	96.30	94.45	91.70
Weight of fraction.......	7 g.	1.7 g.	2.13 g.	5.23 g.	2.23 g.

A noticeable change of color could be observed in going from Fraction I, which was light pink, to Fraction 5, which was very pale pink, almost white.

Precipitation by Means of Azobenzene Sulfonic Acid.—A little more than 15 g. of the oxides was dissolved in hydrochloric acid and diluted to 500 cc. The solution was heated to boiling in a beaker, and a hot solution of azobenzene sulfonic acid was slowly added. The azobenzene sulfonates were precipitated from acid solution, and when sufficient had formed it was filtered off and the filtrate treated with more of the reagent. Five fractions were obtained in this way, while a sixth was obtained by the addition of oxalic acid. Since the azobenzene sulfonates are very difficultly soluble even in concentrated acids, the precipitates were decomposed by boiling with sodium hydroxide solution. The resulting hydroxides were dissolved in hydrochloric acid, and the oxalates thrown down by oxalic acid. The colors of the fractions showed practically no change, and the atomic weights given below show that no fractionation took place.

	1.	2.	3.	4.	5.	6.
Atomic weight............	95.3	95.0	95.0	94.8	94.0	95.2
Weight of fraction.........	0.3 g.	0.6 g.	0.9 g.	1.6 g.	0.5 g.	11.9 g.

Precipitation by Means of Potassium Sulfite.—In this trial, 13 g. of oxide were dissolved in hydrochloric acid, evaporated to dryness, taken up with water, four drops of HCl added, and the whole diluted to 1200 cc. This was brought to boiling and stirred with steam and a 10% solution of potassium sulfite was added drop by drop from a separatory funnel. Four fractions were taken. They were dissolved in dilute HCl, precipitated by oxalic acid, ignited, treated with boiling water to remove any potassium salts, redissolved and converted into the oxalates. The color of the oxides from these fractions varied from pink to very pale pink. The operations were easily carried out, and no difficulty was experienced in filtering.

	1.	2.	3.	4.
Atomic weight..............	97.8	95.8	93.1	92.2
Weight of fraction...........	2.3 g.	5.6 g.	4.3 g.	0 3 g.

Precipitation by Means of Sodium Citrate.—About 15 g. of oxides were dissolved in HCl and made neutral. This was diluted to 1200 cc. and precipitated in a similar manner to the last, with the exception that sodium citrate was used in place of potassium sulfite, and a current of air was used to stir the solution. Four fractions were obtained, and the filtrate from Fraction 4 was precipitated with oxalic acid. The citrates were ignited to oxide, the latter boiled with water and the oxides reconverted to oxalates. This operation was always carried out whenever sodium or potassium was considered to be present. The color change of the oxide agreed with that of the sulfite method.

	1.	2.	3.	4.	5.
Atomic weight	99.8	97.6	95.6	93.4	92.1
Weight of fraction	1.1 g.	4.4 g.	3.9 g.	2.8 g.	3.1 g.

Precipitation by Means of Sodium Tungstate.—A dilute solution of the nitrates containing about 12 g. of oxide in 1200 cc. was boiled, stirred and precipitated with a 20% solution of sodium tungstate. The tungstates that were thrown down were very colloidal, and could not be easily filtered. They were allowed to stand overnight to settle and were then decomposed by sodium hydroxide and converted into oxalates.

	1.	2.	3.	4.	5.	6.
Atomic weight	96.9	97.7	97.0	96.9	94.4	91.1
Weight of fraction	0.12 g.	1.30 g.	1.20 g.	2.20 g.	1.40 g.	3.70 g.

Precipitation by Means of Sodium Tartrate.—Seven grams of the oxides were dissolved in nitric acid and made neutral. The liquid was precipitated at the boiling point with a 20% sodium tartrate.

	1.	2.	3.
Atomic weight	98.4	96.1	94.4
Weight of fraction	2.1 g.	2.5 g.	2.0 g.

Precipitation by Means of Sodium *m*-Nitrobenzoate.—A solution of 12 g. of the oxides, made similarly to the last test, was diluted to 1200 cc. and fractionally precipitated at the boiling point with sodium *m*-nitrobenzoate. The five fractions obtained showed by color and equivalent determinations that no fractionation had taken place.

Precipitation by Means of Ammonium Camphorate.—Seven grams of oxide were dissolved in nitric acid and made neutral by ammonium hydroxide. The boiling liquid was then precipitated by a solution of ammonium camphorate. The precipitate was very gelatinous and the mass filtered badly.

	1.	2.	3.	4.
Atomic weight	95.1	94.8	93.3	93.3
Weight of fraction	1.9 g.	1.9 g.	1.3 g.	4.3 g.

Precipitation by Means of Sodium Phenoxyacetate.—Eight grams of oxides were used in this case. The precipitation was carried out in beakers at the boiling point of the solution. The equivalent determination showed that in this case, like the last two, almost no fractionation had taken place.

	1.	2.	3.
Atomic weight	95.1	95.1	93.9
Weight of fraction	1.4 g.	2.0 g.	5.0 g.

Precipitation by Means of Potassium Cobalticyanide.—About 15 g. of the oxides were dissolved in hydrochloric acid, the solution evaporated to dryness and taken up with water. The solution was boiled and stirred with steam, while a solution of potassium cobalticyanide was run in slowly by means of a separatory funnel. The cobalticyanides were thrown down in the form of a white, granular precipitate. The liquid filtered easily, and the filtrate was precipitated by oxalic acid. The rare earth cobalticyanide was found to be insoluble in concentrated HCl or HNO_3. However, they were found to be easily attacked by sodium hydroxide. The oxalates that were finally obtained varied very considerably in their color. Fraction 1 was quite pink while Fraction 2 was nearly white. The latter showed only traces of erbium when examined by the spectroscope.

	1.	2.
Atomic weight	97.2	91.3
Weight of fraction	9.4 g.	4.9 g.

This great difference between two fractions appeared to be very promising and Fraction 1 was run again, and the new first fraction examined with regard to the equivalent. The result showed an atomic weight of about 107, and the oxide itself was of a pale rose color. Since the result was so very good, it was thought best to check it by running a larger quantity of oxide. This time four fractions were obtained by adding potassium cobalticyanide, while the fifth was formed by adding oxalic acid to the filtrate from Fraction 4.

	1.	2.	3.	4.	5.
Atomic weight	98.7	95.1	90.8	88.2	90.5
Weight of fraction	11.9 g.	11.3 g.	10.4 g.	4.1 g.	0.7 g.

Fraction 5 was interesting because of the high atomic weight. However, the spectroscope showed the presence of neodymium. This fraction, and also Fraction 4, showed an entire absence of erbium bands. The color of the oxides was white, while that of Fraction 1 had a decided pink tint.

This method for the preparation of pure yttrium is without doubt one of the most rapid that the writers have come across. The greatest difficulty consists in controlling the quantity of precipitate.

Further investigations are to be carried on, in the near future, with this very interesting reagent.

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THE DERIVATIVES OF PERCERIC OXIDE.

[SECOND PAPER.][1]

BY C. C. MELOCHE.

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In a previous paper[2] the author discussed the preparation and properties of perceric potassium carbonate. Special attention was given to the

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[1] This paper is based upon part of a thesis submitted to the Graduate Faculty of the University of Wisconsin for the degree of Doctor of Philosophy.

[2] THIS JOURNAL, 37, 2338 (1915).