[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# Observations on the Rare Earths. XXXIX. The Transference Numbers of the Chlorides of Neodymium, Samarium and Gadolinium. Part I. The Purification of Materials

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The rare earths neodymium, samarium and gadolinium used in the following determinations were obtained from the rare earth residues from a gas mantle factory. The crude material contained high percentages of lanthanum, cerium, neodymium and smaller amounts of praseodymium, samarium, gadolinium and traces of the other rare earths. The cerium was removed as completely as possible as ceric phosphate.[1] The remaining rare earths were fractionally crystallized as the magnesium rare earth nitrate. The separation of the various individual earths was followed by means of the absorption spectrum as observed with the direct vision spectroscope. During the course of the fractionation the head fractions were set aside as soon as they were found to contain mainly lanthanum and praseodymium with only a trace of neodymium. The dishes at the other end of the series which contained gadolinium and the rare earths of higher atomic numbers were set aside when difficulty was encountered in crystallization. The difficulty in crystallization in these fractions was due to the high concentration of the heavier rare earths which do not readily crystallize as the double rare earth magnesium nitrate. These dishes were designated as series Gd.

The intermediate fractions of the original series were fractionally crystallized as a single series until a sharp separation was noted between the neodymium and samarium. It was then split into two series, a soluble samarium series, S, and an insoluble neodymium series, I. After two years of daily treatment the middle fractions of series I were considered as pure neodymium. The samarium series S was given the same treatment as series I except that 6 normal nitric acid was substituted for water as the solvent during the latter part of the fractionation. This change of solvent permits a more rapid purification of the samarium but can be used only when the bulk of the neodymium has been removed. The pure samarium used for this study was from the middle fractions of this series.

To the fractions designated as Gd, bismuth magnesium nitrate was added and the fractionation continued using nitric acid of a density of 1.42 as the solvent. The addition of bismuth and the use of nitric acid instead of water overcomes the difficulty in crystallization noted above. In a fractionation series of this type the bismuth double salt is found to concentrate between europium and gadolinium. Consequently when, after

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(1) Neckers and Kremers, THIS JOURNAL, 50, 955 (1928).

continued fractionation, the center fractions were practically pure bismuth magnesium nitrate the fractionation was stopped. The fractions more soluble than bismuth, that is, those containing gadolinium and the rare earths of higher atomic numbers, were each converted to the simple nitrate and again fractionated. Bismuth nitrate in a series of this type[2] concentrates between gadolinium and terbium. This fractionation was therefore stopped when the center fractions were again pure bismuth. The head fractions were gadolinium free from the other rare earths but mixed with bismuth. The bismuth was removed by converting the nitrate to the chloride and precipitating the bismuth with hydrogen sulfide from the slightly acid solution.

The samples of the supposedly pure rare earths were each examined spectroscopically by means of their arc spectra. The arc was struck between pure graphite electrodes, drilled to contain a small sample of the particular rare earth oxide and the spectrum photographed with a Hilger E 1 spectrograph.

The purity of the neodymium with respect to samarium was shown by the absence of the persistent arc lines of this element,[3] which are visible down to 0.1%.[4] The absorption spectrum of this material contained only the bands due to neodymium. The praseodymium absorption band at 4450 Å. may be observed in concentrated neodymium solutions when this element is present in concentrations as low as 0.1%. The rich blue color of the neodymium oxide was taken as further evidence of its purity. It is known that over 0.2% of praseodymium in neodymium changes this blue color to grey.

The samarium sample exhibited none of the absorption bands of neodymium and neither of the persistent lines of europium. It was therefore considered as free from the other rare earths.

The sample of gadolinium was found to be free of samarium but gave several of the arc lines of europium. The maximum amount of europium present was estimated as 0.1%.

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(2) Urbain and Lacombe, *Compt. rend.*, **137**, 792 (1903).

(3) Meggers, "International Critical Tables," Vol. 5, McGraw Hill Book Co., 1930.

(4) Selwood, *Ind. Eng. Chem.*, *Anal. Ed.*, **2**, 93 (1930).