[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF NORTH CAROLINA.]

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.

STUDY OF NEODYMIUM: PREPARATION OF PURE MATERIAL[1]—EFFORTS TO DECOMPOSE IT INTO ITS CONSTITUENTS.

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Synopsis.—This paper presents a new and rapid method of freeing neodymium from lanthanum, *viz.*, fractional precipitation of the chloride solution by saturation with gaseous hydrochloric acid. A number of fractionations of the purified material were made to prove the complexity of neodymium, but without success. The methods used were, fractional precipitation by gaseous hydrochloric acid (over 100); partial decomposition by fusion of the double alkaline nitrates (23); precipitation by primary ammonium oxalate (31); solution in ammonium carbonate and precipitation with acetic acid (3); fractional precipitation by such organic bases as aniline (4), benzylamine (29), piperidine (19) and phenylhydrazine (8).

Naturally investigations were to be carried along with the foregoing, looking toward the preparation of pure neodymium compounds. It was noted that the preparation of pure neodymium salts, according to Auer's method, presented numerous difficulties and required much time and many repetitions of the process. Boudouard[2] has shown that neodymium gives a double sulphate with potassium more soluble in water than that of praseodymium and presents a more rapid separation than is perhaps possible by fractional crystallization. Muthmann and Rölig,[3] working with didymium, had from yttria, extracted from monazite sand, found weeks, after making sixty crystallizations, to obtain a neodymium sulphate containing only 0.3 per cent. of praseodymium. The oxide, Nd_2O_3, obtained by them was described as "fast weiss"—(see below).

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[1] Presented in abstract at the Cleveland meeting of the American Chemical Society.

[2] *Compt. Rend.*, **126**, No. 12; *Chem. News*, **77**, 193.

[3] *Ber. d. chem. Ges.*, **31**, 1718–1731 (1898).

Reference has been made to the tentative acceptance of neodymium as an element. The agreement of the figures given for the atomic weight of neodymium by Jones,[1] Brauner,[2] and von Scheele[3] point clearly to a constant material obtained from different sources. The same was also true of didymium before the classical work of Auer von Welsbach.[4] Urbain,[5] in studying didymium had from yttria extracted from monazite sand, found not only neodymium, but such other earths as erbium and Soret's X, (holmium) members of the terbic group and a little cerium. While absorption band 469 was distinctly visible, 482 and 444 were doubtful (see papers following). Demarcay[6] and Krüss and Nilson[7] had previously made analogous observations with variations of the relative intensities of these bands. Later Demarcay[8] showed that some absorption bands have been found in didymium which appear to belong neither to neodymium nor praseodymium. Further, the presence of a certain amount of samarium causes the blue bands to disappear in a vague, hardly visible nebulosity. He concluded, as a result of a number of fractionations by different methods and examinations of the absorption bands, spark spectra (including the ultra-violet region), fluorescent spectrum in calcium sulphate and by spectral colorimeter, "in spite of statements of several chemists, neodymium is a simple body and not a mixture." Yet the work by Brauner[9] on variations in the oxides gives evidence of the complexity of that element.

Our investigation was begun with the intention of testing the nature of neodymium. Many have difficulty in assigning neodymium a satisfactory location in the periodic system. Therefore, in the event we learned that neodymium was simple, it was highly desirable to determine positively its place in the natural system.

Obviously the first step was to prepare neodymium as pure as possible. The constant associates of neodymium are lanthanum and praeseodymium, which are separated by methods which, at best, are long, slow and difficult of execution. It is very de-

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[1] *Am. Chem. J.*, **20**, 345.
[2] *Proc. Chem. Soc.* (1898), No. 191, p. 70.
[3] *Ztschr. anorg. Chem.*, **17**, 310.
[4] *Loc. cit.*
[5] *Bull. Soc. Chim.* [3], **20**, 9; *Chem. News*, **78**, 74.
[6] *Compt. Rend.*, **104**, 580.
[7] *Ber. d. chem. Ges.*, **20**, 2124.
[8] *Compt. Rend.*, **126**, 14; *Chem. News*, **77**, 219.
[9] *Proc. London Chem. Soc.*, March 31, 1901.

sirable, therefore, to secure a method thorough and quick for the absolute elimination of these accompanying substances.

Five hundred (500) grams of crystalline, double ammonium neodymium nitrate were used during the preliminary trials of different methods.[1]

PARTIAL DECOMPOSITION OF DOUBLE NITRATES BY FUSION.

The classic method of Berlin[2] was applied to 200 grams of the ruby-colored crystals which had lanthanum as the main impurity and some praseodymium. The numerous variations of the directions given by Berlin, offered by subsequent workers, looking toward uniform heating and decomposition, failed to improve the process. At best, such methods of fractionation require a great amount of time and patience. The material was carried through twenty-three fractionations and, while much of the lanthanum was removed, the neodymium still contained praseodymium.

Hood,[3] discussing principles of fractioning, observed: It is evident then that fractional precipitation is a method for separating two oxides differing but slightly in basic properties. It may be the work of a lifetime, even when working on a large amount of material." Having the latter and not being assured of the temporal allotment of a chemist (thirty years), we looked for more encouraging methods.

SATURATION OF NEODYMIUM CHLORIDE SOLUTION WITH HYDROCHLORIC ACID.

The neodymium ammonium nitrate containing lanthanum as chief impurity with some praseodymium was converted into the chloride by the precipitation as hydroxide with ammonia, and washing free of the precipitant. It is inadmissible to convert the double salt to the oxide by direct ignition in platinum, as the metal is attacked. To be sure, it would appear that this contamination could be readily removed by subsequent solution of the oxide in hydrochloric acid. In practice, however, the platinum is found in the solution. The explanation of this is easily had. In the first place, Brauner[4] has shown the formation of a dioxide

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[1] Obtained through the generosity of Dr. H. S. Miner, chemist of the Welsbach Lighting Co.

[2] *Scand. Naturf. 8 Möde Kjöpenhavn*, p. 448 (1860).

[3] *Chem. News*, **52**, 271.

[4] *Proc. London Chem. Soc.*, March, 1901; *Chem. News*, **83**, 197.

when the nitrate is ignited. This oxide causes the evolution of chlorine on dissolving it in hydrochloric acid with the consequent solution of the platinum. In the second place, the metal is finely divided and W. L. Dudley[1] and Mallet[2] have shown that platinum in this condition and exposed to the air *is* soluble in hydrochloric acid. In later work, where large quantities were used, large earthenware tubs of 100-liter capacity with a spiral row of decantation openings on one side were used. The hydroxide was allowed to settle and supernatant liquid drawn off, and the hydroxide washed twice with water by decantation. The decantations were filtered free of any suspended hydroxide and the filtrate discarded.

It may be well here to call the attention of those beginning work on the rare earths to the advisability of pursuing the very safe plan of saving all filtrates until they are thoroughly tested. These filtrates were not thrown away unless 10 to 20 liters had been evaporated and ignited and showed only a trace of residue. In many cases the clear water became turbid on standing exposed to the air. This was no doubt due to the absorption of carbon dioxide, which caused the precipitation of the neodymium compound or solution of the hydroxide in the wash-water and subsequent precipitation on neutralization by the excess of ammonium hydroxide in the filtrate. The hydroxide was thrown upon a filter, dried and ignited. The unglazed porcelain filter was eventually utilized in this work, as with the praseodymium, giving most satisfactory results.

The dried hydroxide was ignited in platinum over powerful Bunsen burners until no more fumes arose. The ignited product was pulverized in an agate mortar and added to the concentrated hydrochloric acid in large porcelain casseroles. The solution, which was facilitated by heat, exhibited dichroism, presenting the color of juniper swamp water (yellowish brown) with transmitted light and purple with reflected light (especially noticeable upon pouring), and faintly purple on dilution.

The neodymium chloride was filtered to remove a small gray residue of platinum obtained from the vessels and concentrated until a crust of crystals formed on top of the solution. On cooling, yellow-brown crystals appeared abundantly. They were

[1] This Journal, **15**, 272 (1893).

[2] *Am. Chem. J.*, **25**, 430 (1901).

separated, dissolved in water and the mother-liquor of neodymium chloride separately fractioned by saturation with hydrochloric acid gas.

This method of treatment possesses nothing essentially new, having been fully described previously by Dennis.[1] The gas was generated by allowing concentrated hydrochloric acid to fall dropwise upon concentrated sulphuric acid. The generator was provided with a safety-flask and the gas let into the solution by means of an inverted funnel or thistle tube which just dipped underneath the surface of the liquid.

During the early work and with the small quantities of material, only pure acids were used. When, however, later, large quantities of material (several carboys of acids) were employed, on account of the expense, commercial reagents were had recourse to. A satisfactory generator of gaseous hydrochloric acid from commercial acids was devised by one of us (Stevenson), and W. M. Marriott (of this laboratory), and is described elsewhere.

The solution was saturated with the gas until crystals appeared. The supernatant liquid was carefully decanted, the crystals washed with concentrated chemically pure hydrochloric acid, and the liquid again decanted from any crystals which subsequently formed in the mother-liquor. It was later learned that by allowing the solution to cool, the two crops of crystals could be collected in the one beaker, and washed several times with hydrochloric acid; the mother-liquor was subjected to another fractionation, crystals redissolved in the least amount of water, and fractioned again. Whenever solutions became too weak to be further fractioned, they were concentrated and subjected to the action of the gas.

During the earlier part of the work, forty-five fractionations were made and the resulting fractions classified according to the absorption spectra into four large solutions; the extreme crystals, medium crystals, medium solutions and extreme solutions, and into two small solutions—the pene-extreme crystals and the pene-extreme solutions. These solutions were fractioned as before, except that the application of the gas was continued until no more crystals appeared and the "crisscrossing" preceded each fractionation.

After twenty-two more of such fractionations, there resulted

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[1] This Journal, **24**, 431 (1902), and previously.

four fractions: Extreme crystals, a very large fraction; medium crystals, about two-thirds as large; medium solutions, a moderate-sized fraction; and extreme solutions, small fraction. The extreme crystals in neutral nitrate solution showed an absorption spectrum identical with the spectrum of the extreme solution, except that in the latter the band λ 460-466 had disappeared. This band belongs to samarium. The arc spectrum of the oxide from the extreme crystals showed only vanishing traces of lanthanum.[1] The oxide of the extreme solution was brown and violet. The brown portion was largely lanthanum and neodymium with some praseodymium. The method, therefore, was promising, as almost pure neodymium was obtained in the heads.

It may be well to state the result of some of our observations here for the guidance of others in the application of this method. The method was improved as follows: The concentrated neodymium chloride solution was saturated with hydrochloric acid gas until no more crystals appeared. These crystals were then dissolved to a saturated aqueous solution and refractioned. After seven such complete precipitations, the last crystals were absolutely free from lanthanum, according to the arc spectrum. This method was used on a large scale subsequently, working with as much as 8 kilograms of neodymium ammonium nitrate, using the hydrochloric acid generator of Stevenson and Marriott. Within a week, a kilogram of neodymium oxide absolutely free from lanthanum was obtained. This serves to illustrate the value of the method.

REMARKS.

During all our investigations with the rare earths, on account of their value, the fragile containers are always placed in a second large vessel in case of accidental breakage.

The precipitation with the hydrochloric acid gas sometimes began immediately, generally in about twenty minutes. In a few cases, where the solution was dilute, only after two hours and in a few very dilute solutions, not at all. The mother-liquor decanted from crystals frequently yielded another crop on standing. Oftentimes, apparently, a supersaturated solution would be had which, when poured from one vessel to another, gave rise to spontaneous crystallization.

[1] These determinations were made by Dr. W. J. Humphreys, of the University of Virginia, with the same instrument as mentioned in the praseodymium paper.

The precipitates were always crystalline. Rapid precipitation from saturated solutions gave trellised translucent crystals which appeared white in the mother-liquor. Vitreous needles resulted from the concentrated solutions; fine irridescent crystals from dilute solutions. The spontaneous crystals, especially when formed after days of standing, were handsome pyramids from 4 to 7 millimeters in length. The crystals were always more or less colored; the extreme crystals were redder and the crystals from the extreme solutions were yellowish. Sometimes the crystals appeared in alternate layers of rose and white, very likely due to a different manner of precipitation, because no difference was observed in the absorption spectra of solutions made from the two. This is no proof, however, that different substances did not separate out more or less contaminated with each other, for, as is well known, the absorption spectrum is not a final test of a fractionation. These observations were made near the time when it would become necessary for one of the authors (S.) to leave this laboratory, so that checks could not be made by means of atomic weight determinations. This work will be taken up later.

The colors of the solutions obtained in the fractionations were striking. The characteristic dichroism of the original chloride solution has been adverted to. The extreme solutions were a bright yellow in transmitted light and bright green in reflected light. The criss-crossing was determined by the color of the solutions; and the classification by color, location in the chart of the fractionations, but mainly by the absorption spectra. All these methods agreed.

The absorption spectra at first were taken of fractions as obtained without any attempt at uniform concentration. As a result, the spectra were deceptive and not comparable. Subsequently a basis was assumed for all comparisons, 1 gram of oxide being converted into neutral chloride and diluted to 10 cc. An interesting observation was made in the examination of the fractions by means of the absorption spectrum, for band λ 460-466, the strong band belonging to samarium according to Thalèn, disappeared coincident with the loss of the yellow purple dichroism.

The bands λ 569, 482, 469 and 443, characteristic of praseodymium, persisted throughout; yet, according to the arc spectrum, the praseodymium was present in a very small amount—less than

1 per cent., as shown by Jones.[1] We were so fortunate as to have in our possession some of the material used by Dr. H. C. Jones in his careful atomic weight determination of neodymium and praseodymium. The arc spectrum of the purest preparation showed traces of gadolinium and samarium in both samples, but by a comparative examination of a solution of samarium, the absorption lines of this element were not found as impurities in our purest neodymium.

The color of the oxides obtained from the different fractions presented an interesting study. Demarçay[2] states that pure neodymium is a violet-colored oxide. A pale violet oxide was given by the extreme crystals, but a lump of it had a brown core, which easily became violet upon ignition.[3] This same oxide upon recovery after use for precipitation by organic bases (see below) was a mixture of brown cinders, rose-colored scales, mole-skin dust and black specks; yet each of these, carefully picked out and separately examined, gave the same absorption bands—the true spectrum of our purest neodymium. The oxides of the extreme solutions was a mixture of lavender and brown. It sometimes became almost white upon vigorous ignition, indicating the predominence of lanthanum. Certain blue oxides were also obtained and when sufficient shall have accumulated, will be examined.[2] Perhaps this may prove to be Chroustschoff's glaukodymium. The dark oxides go into solution in nitric acid more energetically than the lavender-colored oxides, a temporary rose-colored residue being obtained.

FURTHER EXPERIMENTS LOOKING TO PROOF OF COMPLEXITY OF NEODYMIUM.

Having secured pure neodymium containing only a trace of praseodymium, we applied a few methods looking toward a determination of the nature of that element. Below are given the methods used.

PRECIPITATION BY PRIMARY AMMONIUM OXALATE.

A neutral neodymium chloride solution prepared from the pure oxide obtained according to the method given above was used. A saturated aqueous solution of ammonium oxalate was added

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[1] *Am. Chem. J.*, **20**, 345.

[2] *Compt. rend.*, **126**, 14; *Chem. News*, **77**, 219.

[3] Compare Muthmann and Rölig above.

[4] *See J. Russ Phys. Chem. Soc.*, **29**, 206.

until a permanent cloudiness was obtained. About 5 cc. of saturated primary ammonium oxalate were then added, giving local turbidity, which became a mealy precipitate upon stirring. This was essentially the method used by Dennis and Dales in their work upon the purification of yttrium.[1] After twelve hours, the precipitate settled as a rose-colored powder, leaving the supernatant liquid clear. Thirty-one such fractionations were made. The last two fractions were obtained as follows: To the boiling mother-liquor 10 cc. of the primary oxalate were added and no precipitate formed, but on cooling, crystals gradually appeared. The plan of adding praseodymium oxalate crystals to induce a separation of that constituent of didymium was tried, but the solution was exhausted. The final mother-liquor was evaporated to dryness, ignited, converted into neutral chloride solution, and examined with the spectroscope. All of the mother-liquors obtained throughout the fractioning were similarly treated, as well as the precipitates. The same absorption spectrum was obtained in every case; therefore, the process was not tried more elaborately.

SOLUTION IN AMMONIUM CARBONATE AND PRECIPITATION BY ACETIC ACID.

Pure neodymium hydroxide obtained from the chloride above by precipitation with ammonia, was washed twice by decantation. Four hundred cc. of water saturated with pure ammonium carbonate were added. No perceptible solution of the hydroxide was observed. The liquid was poured off and the hydroxide washed three times by decantation. The liquid gave no precipitate with acetic acid, but on evaporation and ignition a very small residue was obtained. Converted into a neutral chloride solution, the liquid showed only the stronger absorption bands of neodymium. It was too small in amount to be made up to the standard strength adopted. The neodymium hydroxide was treated once more with 300 cc. of saturated ammonium carbonate for several days with a similar result, consequently it was abandoned.

FRACTIONAL PRECIPITATION BY ORGANIC BASES.

G. Krüss[2] fractioned certain of the rare earths with such substituted ammonias as aniline. Smith and Jefferson[3] published

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[1] This Journal, **24**, 425 (1902).

[2] *Ztschr. anorg. Chem.*, III, 108 (1893).

[3] This Journal, **24**, 540 (1902).

the effect of precipitating the rare earths with aromatic bases. We endeavored to utilize their observations in making fractional precipitations similar to the work of Schutzenberger and Boudouard, and other workers in fractioning the rare earths with ammonia. E. T. Allen[1] later used certain weak organic bases for separating thorium and zirconium from iron and beryllium.

Aniline.—To a moderately concentrated, slightly acid solution of neodymium chloride, aniline was added in excess, with stirring. No precipitate appeared at once. The solution was concentrated and more aniline added. After three days, a slight white precipitate formed, adhering to the beaker. It was filtered and the filtrate treated with aniline and boiled. More aniline was added and another meager white precipitate formed. Further attempts to get a larger precipitate even after allowing the solution to stand for three months, failed. These three precipitates showed similar absorption bands and were identical with the spectrum of the diluted mother-liquor. The process was unpromising and, therefore, discontinued.

Benzylamine.—Benzylamine upon addition to a neutral neodymium chloride solution immediately gave a rose-colored, flocculent precipitate, the liquid becoming somewhat cloudy upon stirring. The precipitate settled after twelve hours and was very difficult to filter. Only eight drops of the organic base were used to get a fractional precipitation because, as stated by Smith and Jefferson,[2] the precipitation is quantitative. After twenty-nine fractionations, the solution was exhausted. Spectroscopic examination of the precipitates, the mother-liquors and the final residue, according to the methods already cited, showed nothing noteworthy and the process was not further elaborated.

Piperidine.—Piperidine acted similarly to benzylamine, nineteen fractions being carried out. The mother-liquor soon assumed a bright yellowish green color. Some of the hydroxides were rose color and some were almost pale yellow.

Phenyl Hydrazine.—The phenyl hydrazine was added in an excess to a neutral chloride solution. Gradually, in the course of twenty-four hours, there formed a dark red precipitate which adhered to the beaker and was difficult to filter. The precipitate was dissolved in concentrated nitric acid and gave a dark red

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[1] *Ibid.*, **25**, 421 (1903).

[2] *Loc. cit.*

solution due to the action of the acid upon the organic base, or a decomposition product of the base. Seven fractionations, each one requiring a week, were carried out. The precipitates showed no divergence from the original, when in the form of neutral chloride solutions they were examined with the spectroscope. After the third precipitation, the filtrate became so turbid, either from decomposition products of the phenyl hydrazine. or through hydrolysis of such double compounds as are mentioned by Delafontaine, that the process was given up.

SUMMARY.

In endeavoring to prove the complexity of neodymium by fractional precipitation, in our hands the following methods failed: Fusion of the double nitrate (according to Berlin[1]) ; precipitation by primary ammonium oxalate; solution in ammonium carbonate and precipitation by acetic ocid; fractional precipitation by gaseous hydrochloric acid; precipitation by the organic bases—aniline, benzylamine, piperidine, and phenyl hydrazine.

The following methods are among those which will be tried in this laboratory: The use of sodium acetate and hydrogen peroxide, electrolysis, reduction by metallic magnesium, magnesium usta, treatment with mercury oxide and nitrate, copper oxide (method applied by Schutzenberger and Boudouard to cerium), dialysis and ammonium persulphate.

UNIVERSITY OF NORTH CAROLINA,
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[CONTRIBUTED FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.

A GENERATOR FOR THE CONTINUOUS PREPARATION OF GASES ON A LARGE SCALE IN THE LABORATORY.

BY RESTON STEVENSON AND W. MCKIM MARRIOTTE.

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A continuous stream of hydrochloric acid gas was required by one of us (S) in an investigation of the rare earths.[2] As the

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[1] See preceding paper.

[2] Also modified by Dennis and Magee: This Journal, 16, 653.