

other considerations, the theory advanced by F. Sommer in explanation of the formation of hydronitric acid and of ammonia by oxidation of hydrazine by means of oxidizing agents that contain no nitrogen is, in all probability, to be regarded as untenable.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

## A REVISION OF THE ATOMIC WEIGHT OF NEODYMIUM.

[SECOND PAPER.]

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Received November 11, 1915.

In an earlier investigation on the atomic weight of neodymium by Baxter and Chapin,<sup>1</sup> the material examined was purified first by crystallization of the double ammonium nitrate and then by crystallization of the nitrate from concentrated nitric acid. The first process was found particularly successful in eliminating samarium, the second in freeing the neodymium from praseodymium. The fractions in the final series were converted to chloride, which, after very careful dehydration, was analyzed by comparison with silver, with the result that the atomic weight of neodymium was found to be 144.27 (Ag = 107.880).

During the purification of the neodymium material as described above, attempts were made to free the neodymium from its companions by other methods. One of these was the fractional crystallization of the chloride. This crystallization proceeds less readily than that of either the double nitrate or nitrate, and after the process had been carried on for ten series of crystallizations little evidence of separation could be observed. At the same time another portion of the original material was converted to nitrate and fractionally crystallized from concentrated nitric acid. As the chief impurity, praseodymium, seemed to accumulate rapidly in the more soluble fractions, the portion which had been crystallized as chloride also was converted to nitrate and fractionally crystallized from nitric acid. Fractional crystallization of these two portions was carried on separately for some time, for 75 series with one portion, for 76 with the other, then the two portions were combined and further crystallized in the same way. Both the least soluble and the most soluble fractions frequently were rejected, the least soluble fraction to eliminate samarium, gadolinium, etc., the most soluble to remove praseodymium, cerium and lanthanum, for Demarçay<sup>2</sup> has shown that the separation occurs in this order. The least soluble fraction was thus forty times dis-

<sup>1</sup> *Proc. Amer. Acad.*, **46**, 213 (1911); *THIS JOURNAL*, **33**, 1; *Z. anorg. Chem.*, **70**, 1.

<sup>2</sup> *Compt. rend.*, **122**, 728 (1896); **130**, 1021 (1900).

carded, the most soluble eighty-four times. After 158 series of crystallization in all had been carried out, the purity of the fractions of the last series, 17 in number, was investigated spectroscopically. As all of the fractions seemed to be fairly pure and the intermediate fractions very pure, it was decided, for the purpose of comparison with the material purified for the earlier investigation, to examine quantitatively the new material. Since at the outset only one and one-half kilograms of fairly pure double ammonium nitrate was used, the final fractions were not large, and, therefore, instead of analyzing each fraction separately, they were combined in pairs except that the three least soluble fractions, 2590, 2591 and 2592, were combined. The combinations actually analyzed were: 2590 + 2591 + 2592, 2593 + 2594, 2595 + 2596, 2597 + 2598, 2599 + 2600, 2601 + 2602, 2603 + 2604.

The purity of each of these combinations was carefully determined by photography of the visible and ultraviolet regions of the absorption spectrum with a Féry quartz spectrograph. The solutions were prepared by dissolving 2 g. portions of the ignited oxides in a slight excess of nitric acid and diluting the solution to a volume of about 10 cc. The absorbing layer was 10 cm. long. The less soluble fractions contained small amounts of samarium, and the more soluble ones praseodymium. In order to determine the proportions of these impurities, to a solution of a 2 g. portion of the oxide of Fraction 2605-6, which was free from samarium although it contained praseodymium, were added known amounts of a standard solution of pure samarium nitrate, the absorption spectrum of the solution being photographed after each addition of samarium.<sup>1</sup> By comparing photographs of the different fractions with those of the material containing known amounts of samarium, it was possible to estimate with considerable exactness the proportion of samarium<sup>2</sup> in the former. The percentage of praseodymium<sup>3</sup> in the more soluble fractions was estimated in a similar fashion by comparing the photographs of the fractions analyzed with those of a solution of Fraction 2590-1-2, to which known amounts of praseodymium were added. The results of these comparisons are given below.

Fraction.	Samarium. %.	Fraction.	Praseodymium. %.
2590-2591-2592	0.6	2599-2600	0.00
2593-2594	0.4	2601-2602	0.05
2595-2596	0.2	2603-2604	0.1
2597-2598	0.1	2605-2606	0.2
2599-2600	0.0		

Since cerium and lanthanum nitrates are both more soluble in con-

<sup>1</sup> The samarium material was very kindly furnished by Professor C. James of New Hampshire College.

<sup>2</sup> Through the band  $\lambda$  401.

<sup>3</sup> Through the band  $\lambda$  444.

concentrated nitric acid than praseodymium nitrate, the quantities of these impurities remaining must have been very small indeed.

Although the proportions of impurity are small, yet because the atomic weights of both samarium and praseodymium are considerably different from that of neodymium it is not surprising that the extreme crystal fraction yielded a result somewhat higher than the average, and that the more soluble fractions apparently possessed an atomic weight slightly lower than the average. However, since the amounts of impurity were determined with some accuracy, corrections could be applied to the final result.

#### Preparation of Materials.

**The Preparation of Neodymium Chloride.**—In order to change the nitrate to chloride, essentially the same processes were employed as in the previous investigation. Neodymium oxalate was first precipitated by adding to the dilute solution of the nitrate a considerable excess of oxalic acid. The oxalate was collected upon a disk of filter paper in a porcelain Gooch crucible and after being dried was ignited to oxide in a platinum boat in an electrically heated porcelain tube, pains being taken to avoid heating the boat to a temperature at which platinum might vaporize into the contents.<sup>1</sup> The resulting oxide was dissolved in redistilled nitric acid in a quartz dish, and after the solution had been diluted, the oxalate was reprecipitated by means of a dilute solution of either recrystallized oxalic acid or recrystallized ammonium oxalate. The oxalate was washed, dried and ignited as before. Then it was dissolved in a quartz dish in hydrochloric acid which had been distilled through a quartz condenser, and the chloride was at least three times crystallized in quartz dishes by saturating the aqueous solution with hydrochloric acid gas at a low temperature. Centrifugal drainage of the crystals was always employed. The product was preserved in quartz in a desiccator containing fused sodium hydroxide.

**Reagents.**—Pure silver, water and reagents were prepared exactly as recently described in the account of similar work by Baxter and Stewart on praseodymium chloride.<sup>2</sup>

**The Drying of Neodymium Chloride.**—In the earlier work by Baxter and Chapin the attempt was made to prepare the salt for analysis by drying it carefully in a current of hydrochloric acid gas, and eventually fusing the salt. In the first experiments, the salt dried in this way invariably yielded a considerable amount of insoluble material, the exact nature of which was not discovered until later. Hence, the expedient was adopted of drying the salt for analysis as carefully as possible below the fusing temperature, and then determining the proportion of water

<sup>1</sup> See Baxter and Chapin, *THIS JOURNAL*, 33, 16 (1911).

<sup>2</sup> *THIS JOURNAL*, 37, 524 (1915).

retained. Ultimately it was found possible to obtain fused salt which would yield a perfectly clear solution, but the necessary information as to the proper treatment was obtained too late to be of service. It was partly because of the slight uncertainty involved in applying a correction for the residual water that the present investigation was undertaken. In the recent research by Baxter and Stewart upon praseodymium chloride a similar difficulty was met,<sup>1</sup> and in the latter research it was shown that the insoluble material is the oxychloride, and that its formation can be wholly or almost completely avoided by drying the salt as completely as possible previous to fusion, and then fusing the salt as rapidly as possible. No matter how carefully the preliminary drying is carried out, and no matter what precautions are taken in the drying of the hydrochloric acid gas in which the salt is fused, prolonged fusion invariably yields a very considerable proportion of insoluble matter, probably owing to a small amount of air contained in the hydrochloric acid gas. In these respects the neodymium chloride resembles the praseodymium salt exactly. A considerable amount of the insoluble neodymium compound was prepared by fusing some of the carefully dried chloride for an hour. The insoluble residue was collected and weighed, and its content of neodymium and chloride was determined. The results of these experiments indicate conclusively that the insoluble matter is the oxychloride. The following table contains the results of these experiments:

Weight of insoluble material.....	0.00775 g.
Weight of AgCl found.....	0.00602 g.
Weight of AgCl calculated from NdOCl.....	0.00568 g.
Weight of Nd <sub>2</sub> O <sub>3</sub> found.....	0.00685 g.
Weight of Nd <sub>2</sub> O <sub>3</sub> calculated from NdOCl.....	0.00666 g.

By following the same procedure in the drying of the neodymium chloride that was used in the drying of the praseodymium chloride, we were able to prepare salt which yielded immediately a clear solution. The details of this procedure are as follows: A platinum boat containing the powdered crystals of the hydrated salt was placed in a quartz tube forming part of a Richards "bottling apparatus." The bottling apparatus, which contained the weighing bottle in which the boat had initially been weighed, was connected with an apparatus for delivering dry hydrochloric acid gas, nitrogen and air. This apparatus is described in the paper on praseodymium chloride.<sup>2</sup> The boat was then gradually heated to a temperature slightly above 100°, but considerably lower than the transition temperature of the salt, 124°, until nearly all of the first five molecules of water of crystallization had been expelled by efflorescence. The temperature was then raised to 180° or thereabouts, where the sixth molecule

<sup>1</sup> THIS JOURNAL, 37, 527 (1915).

<sup>2</sup> *Ibid.*, 37, 526 (1915).

of water evaporates, and finally the salt was heated to about  $350^{\circ}$  for several hours. The aluminum block oven which had been used for producing uniform temperature up to this point was now replaced by an electrically heated sleeve, and the salt was brought to the fusing point,  $785^{\circ}$ ,<sup>1</sup> as quickly as possible. Then it was allowed to cool rapidly, and after the acid gas had been displaced by nitrogen and finally by air, the boat and contents were transferred to the weighing bottle without exposure to moisture and weighed. In a few cases a trace of insoluble salt was visible when the chloride was dissolved in water, but the proportions in these cases, judging from earlier experience, were less than 0.1 mg. By allowing the solution to stand for a day or two the basic salt dissolved completely. In Analyses 1, 2, 3, 5, 11, 13, 15, 16, 17, 18, 19, 21, 27, 29, 31 and 32 the solution of the chloride was clear at the outset.

Since the basic salt seems to form through the action of the air in the hydrochloric acid upon the fused salt more readily at higher than at lower temperatures, in three experiments the salt, after the usual careful preliminary drying, was heated almost, but not quite, to the fusing point for some time. In this way all but negligible amounts of water must have been expelled. In fact these analyses (Nos. 4, 7, 9, 20, 23 and 25) show a slightly greater percentage of chlorine, rather than smaller, than the specimens which were actually fused. In these cases also the salt yielded a perfectly clear solution.

#### The Method of Analysis.

The method of analysis was like that previously used with neodymium and praseodymium and other chlorides. The salt was dissolved in water and the solution was diluted to a volume of 1000–1500 cc. in a glass-stoppered precipitating flask. Pure metallic silver<sup>2</sup> equivalent to the chloride within a very few tenths of a milligram, was weighed out, dissolved in nitric acid and diluted to about the same volume. The silver solution was then added to the chloride solution in small portions with frequent agitation. After standing at room temperature for some time, the analysis was cooled to  $0^{\circ}$ , in order to reduce the solubility of silver chloride,<sup>3</sup> and the clear solution was tested in a nephelometer for excess of chloride or silver. The estimated deficiency of either was added in the form of hundredth normal solution, and the solution was again thoroughly shaken, allowed to clarify and tested as before, and the process was repeated until exactly equivalent quantities of silver and chloride had been used.

In the analyses by Mr. Whitcomb, after the end point of the comparison had been reached, an excess of 0.05 g. of silver nitrate was added for each liter of solution and the analyses were allowed to stand some time longer

<sup>1</sup> Matignon, *Compt. rend.*, 133, 289 (1901); 140, 1340 (1905).

<sup>2</sup> The silver used had already been tested in the praseodymium work.

<sup>3</sup> Richards and Willard, *THIS JOURNAL*, 32, 32 (1910).

at 0°. Then the silver chloride was washed several times with ice-cold silver nitrate solution containing 0.05 g. per liter and many times with ice-cold water, before being collected on a weighed platinum-sponge Gooch crucible. The chloride was dried in an electrically heated air bath at 190° for at least 18 hours and weighed. Residual moisture was determined by the loss in weight when the main bulk of the precipitate was fused in a porcelain crucible. The weight of silver chloride dissolved in one liter of the filtrate and silver nitrate washings was assumed to be 0.000004 g. per liter.<sup>1</sup> Chloride dissolved in the aqueous washings together with that obtained from the precipitating flask was estimated by nephelometric comparison with standards.

TABLE I.  
The Atomic Weight of Neodymium.

NdCl<sub>3</sub> : 3Ag.

Ag = 107.880. Cl = 35.457.

Number of analysis.	Analyst.	Fraction.	Weight of NdCl <sub>3</sub> in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio NdCl <sub>3</sub> :3Ag.	Atomic weight of Nd.
1	Whitcomb	2590-1-2	3.34038	4.31322	-0.00035	4.31287	0.774514	144.293
2	Stewart	2590-1-2	4.03869	5.21540	-0.00095	5.21445	0.774519	144.294
						Average,	0.774517	144.294
3	Whitcomb	2593-4	4.48251	5.78795	-0.00035	5.78760	0.774503	144.289
4 <sup>2</sup>	Whitcomb	2593-4	3.75204	4.84483	-0.00025	4.84458	0.774482	144.282
5	Stewart	2593-4	6.00909	7.75942	-0.00050	7.75892	0.774475	144.280
						Average,	0.774487	144.284
6	Whitcomb	2595-6	4.96466	6.41065	-0.00020	6.41045	0.774464	144.276
7 <sup>2</sup>	Whitcomb	2595-6	4.15431	5.36422	-0.00030	5.36392	0.774492	144.285
8	Stewart	2595-6	5.53210	7.14341	-0.00003	7.14338	0.774437	144.268
						Average,	0.774464	144.276
9 <sup>2</sup>	Whitcomb	2597-8	4.73995	6.12054	0.00000	6.12054	0.774433	144.267
10	Whitcomb	2597-8	4.22430	5.45464	-0.00020	5.45444	0.774470	144.278
11	Stewart	2597-8	5.93271	7.66037	+0.00051	7.66088	0.774416	144.261
						Average,	0.774440	144.269
12	Whitcomb	2599-2600	5.60324	7.23524	0.00000	7.23524	0.774439	144.268
13	Stewart	2599-2600	7.22817	9.33324	+0.00035	9.33359	0.774426	144.264
						Average,	0.774433	144.266
14	Whitcomb	2601-2	5.16230	6.66582	+0.00020	6.66603	0.774419	144.262
15	Stewart	2601-2	4.50348	5.81508	+0.00050	5.81558	0.774382	144.250
						Average,	0.774401	144.256
16	Whitcomb	2603-4	6.42333	8.29438	0.00000	8.29438	0.774419	144.262
17	Stewart	2603-4	7.59534	9.80745	+0.00077	9.80822	0.774385	144.251
						Average,	0.774402	144.256

<sup>1</sup> Calculated from the solubility product of silver chloride at 0° as found by Kohlrausch,  $9 \times 10^{-12}$ . *Z. physik. Chem.*, **64**, 167 (1908).

<sup>2</sup> The neodymium chloride used in this experiment was heated almost but not quite to the fusing point.

TABLE II.  
The Atomic Weight of Neodymium.

		NdCl <sub>3</sub> : 3AgCl.							
		Ag = 107.880.							
No. of analysis.	Analyst.	Fraction.	Weight of NdCl <sub>3</sub> in vacuum. Grams.	Weight of AgCl in vacuum. Grams.	Loss on fusion. Gram.	Total dissolved AgCl. Gram.	Corrected weight of AgCl in vacuum. Grams.	Ratio NdCl <sub>3</sub> : 3AgCl.	Atomic weight of Nd.
18	Stewart	2590-1-2	4.03869	6.92658	0.00048	0.00176	6.92786	0.582963	144.310
19	Whitcomb	2593-4	4.48251	7.68865	0.00016	0.00156	7.69005	0.582897	144.281
20 <sup>1</sup>	Whitcomb	2593-4	3.75204	6.43617	0.00041	0.00162	6.43738	0.582852	144.262
21	Stewart	2593-4	6.00909	10.30826	0.00056	0.00106	10.30876	0.582911	144.287
						Average,		0.582887	144.277
22	Whitcomb	2595-6	4.96466	8.51602	0.00033	0.00065	8.51634	0.582957	144.307
23 <sup>1</sup>	Whitcomb	2595-6	4.15431	7.12648	0.00056	0.00151	7.12743	0.582862	144.266
24	Stewart	2595-6	5.53210	9.49047	0.00031	0.00118	9.49134	0.582858	144.264
						Average,		0.582892	144.279
25 <sup>1</sup>	Whitcomb	2597-8	4.73995	8.13139	0.00014	0.00107	8.13232	0.582853	144.262
26	Whitcomb	2597-8	4.22430	7.24613	0.00018	0.00119	7.24714	0.582892	144.279
27	Stewart	2597-8	5.93271	10.17821	0.00025	0.00095	10.17891	0.582844	144.258
						Average,		0.582863	144.266
28	Whitcomb	2599-2600	5.60325	9.61209	0.00019	0.00109	9.61299	0.582883	144.275
29	Stewart	2599-2600	7.22817	12.40020	0.00024	0.00102	12.40098	0.582871	144.270
						Average,		0.582877	144.273
30	Whitcomb	2601-2	5.16230	8.86100	0.00090	0.00137	8.86147	0.582556	(144.134) <sup>2</sup>
31	Stewart	2601-2	4.50348	7.72660	0.00025	0.00083	7.72718	0.582810	144.244
32	Whitcomb	2603-4	6.42333	11.02125	0.00078	0.00237	11.02284	0.582729	(144.209) <sup>2</sup>

In the analyses by Mr. Stewart, after a similar excess of silver nitrate had been added, the system was allowed to stand at room temperature for several days before filtration. In computing the correction for silver chloride dissolved in the filtrate and silver nitrate washings, which were not chilled, the assumption is made that the solutions were saturated at 25°, since the experiments were carried out during the summer months. Using Kohlrausch's determination of the solubility product of silver chloride at 25°,  $1.7 \times 10^{-10}$ , the solubility in 0.0003 normal silver nitrate is 0.00008 g. The aqueous washings were chilled to diminish the solubility of the precipitate and were analyzed nephelometrically.

The main mass of silver chloride was dried at 150° and the moisture retained was found from the loss on fusion.

<sup>1</sup> The neodymium chloride used in these experiments was heated almost but not quite to the fusing point.

<sup>2</sup> The results of Analyses 30 and 32 are inexplicably low. As they were the first two experiments carried out by Mr. Whitcomb, we feel that it is justifiable to omit them in the final treatment of the results.

In Mr. Whitcomb's experiments the portions of the original solution removed for nephelometric comparisons were returned and a correction applied for the silver chloride thus introduced. In Mr. Stewart's experiments the test portions were rejected and a correction of 0.00005 g. was added for each 100 cc. of solution removed.

All objects were weighed by substitution for similar counterpoises, a No. 10 Troemner balance being used for the purpose. Weights were standardized to hundredths of a milligram by the Richards' substitution method. The following vacuum corrections were applied:

	Specific gravity.	Vacuum correction per g.
Weights.....	8.3	
NdCl <sub>3</sub> .....	4.134	+0.000145
AgCl.....	5.56	+0.000071
Ag.....	10.49	-0.000031

TABLE III.

Fraction.	NdCl <sub>3</sub> : 3Ag.	NdCl <sub>3</sub> : 3AgCl.	Average of all analyses.	Corrected average of all analyses.
2590-1-2	144.294	144.310	144.299	144.263
2593-4	144.284	144.277	144.280	144.256
2595-6	144.276	144.279	144.278	144.266
2597-8	144.269	144.266	144.268	144.262
2599-2600	144.266	144.273	144.269	144.269
2601-2	144.256	144.244	144.252	144.254
2603-4	144.256	...	144.256	144.259
			Av.,	144.261

The results with the different fractions are summarized in Table III, in the last column of which corrections also are made for praseodymium and samarium impurity, on the basis of the atomic weights 140.9 and 150.4, respectively.

Analyses.	Ag : AgCl.
2 and 18	0.752678
3 and 19	0.752609
4 and 20	0.752570
5 and 21	0.752653
5 and 22	0.752723
7 and 23	0.752574
8 and 24	0.752621
9 and 25	0.752619
10 and 26	0.752633
11 and 27	0.752623
12 and 28	0.752652
13 and 29	0.752649
14 and 30	(0.752249) <sup>2</sup>
15 and 31	0.752613
16 and 32	(0.752472) <sup>2</sup>

Av., 0.752632

<sup>1</sup> THIS JOURNAL, 22, 144 (1900).

<sup>2</sup> See note on page 308.

The concordance of the results with each fraction is satisfactory. It is interesting to note that with the uncorrected results a perceptible difference exists between the head and tail of the series and that this difference largely disappears when corrections are applied for rare earth impurity. The uncorrected results with the purest fractions and the corrected result with all the fractions differ very little from Baxter and Chapin's earlier result, 144.275 ( $Ag = 107.880$ ).

In the preceding table the ratio of silver used to silver chloride obtained in the same experiment is given for all complete pairs of analyses. Since the average ratio is essentially identical with that found by Richards and Wells,<sup>1</sup> 0.752634, it can reasonably be concluded that errors from occlusion by the silver chloride, or from loss of silver chloride, are absent. This is in accord with earlier experience of the same kind.

#### Summary.

Neodymium nitrate was purified by fractional crystallization of the nitrate from concentrated nitric acid. Chloride, prepared from the final fractions of nitrate, was analyzed by comparison with silver. The atomic weight of neodymium was thus found to be 144.261. The average of this result and that found earlier by Baxter and Chapin, 144.275, is 144.268. The rounded-off figure 144.27 ( $Ag = 107.88$ ) seems to represent fairly the final outcome of both researches.

We are very greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance, as well as to Dr. H. S. Miner, of the Welsbach Light Company, for the neodymium material.

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## THE SOLUBILITIES OF THE SULFATES OF BARIUM, STRONTIUM, CALCIUM AND LEAD IN AMMONIUM ACETATE SOLUTIONS AT 25° AND A CRITICISM OF THE PRESENT METHODS FOR THE SEPARATION OF THESE SUBSTANCES BY MEANS OF AMMONIUM ACETATE SOLUTIONS.

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Received November 18, 1915.

In the last few years several attempts have been made to separate lead sulfate from the other sulfates which are relatively insoluble in water by the use of ammonium acetate solution. Such a method, where lead sulfate could be completely separated from the sulfates of barium, strontium and calcium, would be of value both in qualitative and quantitative analysis.

Qualitative statements of the solubilities of the four sulfates occur frequently in chemical literature. In the case of lead sulfate it is the general

<sup>1</sup> *Publ. Carnegie Inst.*, No. 28, 1905; *THIS JOURNAL*, 28, 456 (1908).