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

Observations on the Rare Earths. XLVI. The Atomic Weight of Gadolinium[1]

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The object of the work described in this paper was to determine the atomic weight of gadolinium by the gadolinium chloride-to-silver ratio. Several previous determinations have been made, but none by this method. Marignac,[2] the discoverer of the element, assigned the "equivalent" of 120.5 to it. This was equal to an atomic weight of 156.75. It is probable that this equivalent was referred to sulfur trioxide, which was assumed to have a molecular weight of 80. Bettendorf[3] was the first to publish the determinations with their individual data. He effected the synthesis of the sulfate from the oxide, and obtained 156.75 for the atomic weight. Benedick[4] and Marc,[5] also using the sulfate-to-oxide ratio, obtained 156.52 and 156.39, respectively. Brauner's[6] single determination, made with material contaminated with samarium, may be disregarded. The material used by Urbain[7] in 1905 was probably the purest of all. He calcined the octahydrated sulfate to the oxide and obtained 157.24 as the average of two series of determinations. Feit and Przibylla,[8] using a volumetric method of sulfuric acid against gadolinia, obtained 157.377 and 157.398. The value adopted by the International Union of Chemistry[9] is 157.3. This value, of course, is based on the oxide-to-sulfate ratio. The disadvantages of the oxide-to-sulfate ratio have been discussed critically by Hopkins and Balke[10] and Brauner and Svăgr.[11] Because of these disadvantages and the large difference between the atomic weight of europium and that of gadolinium, it was thought advisable to redetermine the atomic weight of gadolinium, and to use the chloride-to-silver ratio.

Purification of Gadolinium Material

The original source of the gadolinium material was Brazilian monazite and Norwegian gadolinite. The gadolinite ore was broken up and taken into solution at this Laboratory, and the Brazilian monazite was obtained as the crude rare earth oxides from the Welsbach Company. The cerium was removed by the permanganate–phosphate method.[12] The cerium-free material was then converted to the double magnesium nitrates and fractionated as such. The samarium–europium–gadolinium fractions at the more soluble ends of the series were set aside and then put into a new series.[13]

The major part of the fractionation was carried out as described by Meyers and Hopkins[14] in their recent paper on the atomic weight of europium. The resulting fractions which were gadolinium rich and europium poor were run for a time as the double magnesium nitrates with bismuth[15] magnesium nitrate as the separating agent. After 150 fractionations in this fashion the gadolinium material was converted to the simple nitrates and again run with bismuth nitrate present.

At the conclusion of the fractionation, eight fractions were obtained, six of which were used for the atomic weight work. A portion of the bismuth was removed by hydrolysis, and the remainder was precipitated as the sulfide with hydrogen sulfide gas. This procedure was carried out six times to ensure complete removal of the bismuth. The gadolinium material was purified further by five alternate precipitations of the hydroxide and the oxalate. All of these precipitations were carried out in conductivity water. The final oxalate obtained from each fraction was ignited to the oxide in a platinum crucible at 800°.

A spectroscopic analysis of each sample was made, using an E_1 Hilger spectrograph and pure graphite electrodes. The first six fractions, GD-7 to GD-12, showed only gadolinium lines. Fractions GD-13 and GD-14 showed very faintly the most persistent lines of europium. No evidence of either bismuth or magnesium was found in any of the fractions. Similarly, no evidence of platinum was found.

Purification of Reagents

The purification of the reagents was carried out in a manner similar to that described in earlier publications from this Laboratory.[16] The purified gadolinium oxide was dissolved in redistilled hydrochloric acid and twice recrystallized.

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[1] Summary of part of a thesis presented to the Graduate School of the University of Illinois by C. R. Naeser in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

[2] Marignac, "Oeuvres Complètes," Vol. II, p. 704.

[3] Bettendorf, *Ann. Chem. Pharm.*, **270**, 376 (1892).

[4] Benedick, *Z. anorg. Chem.*, **22**, 393 (1899).

[5] Marc, *ibid.*, **38**, 121 (1904).

[6] Brauner in Abegg, "Handbuch der anorg. Chem.," Leipzig, 1906, 3i, p. 304.

[7] Urbain, *Compt. rend.*, **140**, 583 (1905).

[8] Feit and Przibylla, *Z. anorg. Chem.*, **50**, 260 (1906).

[9] Report on Atomic Weights of the International Union of Chemistry, THIS JOURNAL, **57**, 793 (1935).

[10] Hopkins and Balke, *ibid.*, **38**, 2334 (1916).

[11] Brauner and Svăgr, *Coll. Czech. Chem. Commun.*, **4**, 51 (1932).

[12] Neckers and Kremers, THIS JOURNAL, **50**, 955 (1928).

[13] All fractionation of the samarium–europium–gadolinium material was carried out in this Laboratory by Drs. Quill and Selwood and the junior author.

[14] Meyers and Hopkins, THIS JOURNAL, **57**, 241 (1935).

[15] Urbain was probably the first to use a separator element to split in between two elements. For a summary of his work, see *Chem. Rev.*, **1**, 155 (1924).

[16] Kremers, Hopkins and Engle, THIS JOURNAL, **40**, 598 (1918).

Formation of Anhydrous Gadolinium Chloride[17]

The purified gadolinium chloride was transferred to a quartz reaction flask and dissolved in redistilled hydrochloric acid and conductivity water. A mixture of nitrogen and hydrogen chloride was then passed in from a purifying train while the flask was maintained at a temperature of 95°. When the gadolinium chloride began to crystallize, the stream of nitrogen was stopped, and only hydrogen chloride was allowed to pass into the flask. The temperature of the flask was slowly raised to 110° and kept there until the first five molecules of water of crystallization were removed. The temperature was then gradually raised to 180°, at which point the last molecule of water of crystallization began to be evolved. The dehydration was complete when a temperature of 225° was reached. To ensure complete dehydration, however, the temperature was raised to 350° and maintained there for one hour. Then, with hydrogen chloride still passing through the flask, the gadolinium chloride was fused by means of a Bunsen burner. After the flask had cooled, the stream of hydrogen chloride was stopped, and nitrogen was passed through until the exit gas gave no test for a chloride. The nitrogen was then displaced by dry air and the stoppered flask was placed in the balance case, where it was allowed to hang for three hours before being weighed.

The Ratio of Gadolinium Chloride to Silver

After it had been weighed, the gadolinium chloride was dissolved in conductivity water and transferred to a 1.5-liter glass-stoppered bottle. An approximately equivalent amount of silver was weighed out and etched with nitric acid. The silver was then washed, dried and carefully weighed again. After weighing, it was dissolved in redistilled nitric acid, diluted with conductivity water, and added slowly, with constant shaking, to the gadolinium chloride solution. The glass-stoppered flask was placed in a shaking machine for six hours and was then allowed to remain undisturbed for twenty-four hours. After this period of standing, a portion of the clear liquid was removed and tested in the nephelometer for excess of silver or chloride. Weighed portions of 0.01 *N* silver nitrate or sodium chloride solution were added until the nephelometer indicated equivalence. After each addition of the standard solution, the bottle was shaken for an additional six hours and allowed to stand for twenty-four before testing for equivalence again.

In the following table the fraction number in the series, the determination number, and the weight of the anhydrous chloride and silver, ratio of weights, and the atomic weights are given.

Detn.	Fraction number	$GdCl_3$, g.	Ag. g.	Ratio $GdCl_3/3Ag$	Atomic weight of gadolinium
I	GD-7	0.38265	0.47047	0.813333	156.86
II	GD-7	.82483	1.01416	.813311	156.85
III	GD-8	1.56656	1.92608	.813344	156.86
IV	GD-8	0.63482	0.78060	.813247	156.82
V	GD-9	.68899	.84716	.813304	156.85
VI	GD-9	2.27153	2.79249	.813442	156.89
VII	GD-10	1.89197	2.32637	.813289	156.84
VIII	GD-10	1.41902	1.74486	.813262	156.83
IX	GD-11	1.23485	1.51829	.813317	156.85
X	GD-11	1.61684	1.98796	.813315	156.85
XI	GD-12	1.72986	2.12689	.813329	156.86
XII	GD-12	2.48952	3.06091	.813326	156.85
				Average	156.85

All weighings were made by the method of substitution. The tare flask was made of quartz and differed from the reaction flask by only a few milligrams. The balance used was sensitive to 0.01 mg. and the weights were carefully standardized against a set recently checked by the Bureau of Standards. All weighings were corrected to vacuum standard. A sample of thorium oxide was kept in the balance case to eliminate all electrostatic charges.

The density of gadolinium chloride was determined by displacement of xylene and carbon tetrachloride, and checked the value given by Bourion,[18] namely, 4.52. The atomic weight of silver was taken as 107.88, and that of chlorine as 35.457. Other density values used were: silver, 10.49; platinum weights, 21.5; platinum-plated brass weights, 8.4. Since both platinum and platinum-plated brass weights were used, the two densities were used in reducing the weighings to vacuum standard. Both densities were also used in standardizing the weights.

Discussion of Results

The value of 156.85 ± 0.011 is lower than the accepted value for the atomic weight of gadolinium by 0.45 units, but is in good agreement with Aston's[19] latest determination with the mass spectrograph, namely, 156.9 ± 0.2.

Summary

1. The ratio of gadolinium chloride to silver is found to be 156.85, with a mean deviation of 0.011. This is lower by 0.45 than the present accepted value, but is in good agreement with the latest determination made with the mass spectrograph.

2. The density of anhydrous gadolinium chloride is found to check with the value given in the literature, 4.52.

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[17] In the preparation of anhydrous rare earth chlorides in this Laboratory we have been following the methods developed by such careful studies as those of Matignon, *Compt. rend.*, **133**, 289 (1901), and Baxter and Chapin, THIS JOURNAL, **33**, 15–19 (1911).

[18] Bourion, *Ann. chim.*, [8] **21**, 29–131 (1907).

[19] Aston, *Proc. Roy. Soc.* (London), **A146**, 46 (1934).