

effect increases with, but less than in proportion to, the alkali concentration.

4. Varying proportions of calcium and magnesium have no effect upon the equilibrium concentration of sulfur dioxide as sulfurous acid.

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

OBSERVATIONS ON THE RARE EARTHS. XII. THE ATOMIC WEIGHT OF LANTHANUM

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During the progress of the work upon the rare-earth group, there was received at this laboratory a shipment of 182 kg. of sodium rare earth sulfates, which was generously supplied by the Welsbach Company of Gloucester, New Jersey, and its chief chemist, Dr. H. S. Miner. The early treatment of this material¹ consisted in the removal of cerium by the method proposed by James and Pratt,² and fractional crystallization as the double magnesium nitrate. This work was done by Dr. Edward Wichers. Later the fractions from the insoluble end of the series which contained lanthanum and praseodymium were subjected to a long series of fractional crystallizations as the ammonium-rare earth nitrates under the care of Dr. E. W. Engle. The fractionation was continued until the first 20 fractions failed to show the slightest trace of praseodymium in their absorption spectra, when viewed through a 10cm. layer of concentrated solution.

Purification of Material

Portions of Fractions 7 and 8 of the double ammonium nitrate series were diluted and treated with a hot dil. solution of oxalic acid. The precipitate was washed, dried and ignited to the oxide in an electric muffle. The oxide was redissolved in nitric acid, diluted to 2000 cc. and lanthanum hydroxide precipitated by distilling ammonia vapors into the solution. This precipitate was washed thrice by decantation and redissolved in nitric acid. The alternate precipitation of hydroxide and oxalate was repeated four times, the last two precipitations being carried out in conductivity water. The ignited oxide was then suspended in conductivity water and dissolved by passing over it the vapor obtained by distillation of c. p. hydrochloric acid from a quartz flask.

A portion of Fraction 8 of this series was sent to the Bureau of Standards where it was examined spectroscopically by the use of 4 gratings, 1 of 7,500 lines per inch for the infra-red region, 1 of 10,000 lines per inch and

¹ See Hopkins and Kremers, *Bur. Standards Sci. Papers*, **421**, Part II (1921).

² James and Pratt, *THIS JOURNAL*, **33**, 1326 (1911).

2 of 20,000 lines per inch for other portions of the spectrum. Photographs were made in the region between 5500 Å. and 9000 Å., and these "have been compared with similar results derived by Eder from Auer von Welsbach's preparation." The material was found to be "of a high degree of purity, no lines being found thus far which can be attributed to any of the related elements."³

All the reagents used in this investigation were carefully purified by the identical methods that have been used and described in earlier publications from this laboratory.⁴

Preparation of Anhydrous Lanthanum Chloride

Two methods were used in the preparation of the anhydrous chloride. The first consisted in placing a portion of the chloride solution in a quartz reaction flask and drying in a current of air and hydrogen chloride until the salt began to crystallize. The air was then stopped and only hydrogen chloride was passed through. The temperature was maintained below 85° by means of an electric oven until the first 5 molecules of water had been driven off. The temperature was then gradually raised to 125° when the last molecule began to come off. As soon as this evolution was complete the temperature was raised to 325° and kept at this point for 1 hour after which the salt was rapidly fused in the Bunsen flame.

Due to the slow removal of water from the chloride solution by this method, the last 5 determinations were made by first evaporating the lanthanum chloride solution to a small volume and separating the salt by saturating the solution with hydrogen chloride. The hydrated salt was filtered, dried and crushed in an agate mortar and kept in a desiccator over fused potassium hydroxide. A portion of this was introduced into the reaction flask for each determination and the dehydration carried out as described in the preceding paragraph. This method enabled us to prepare the anhydrous chloride much more quickly and satisfactorily than when the chloride solution was introduced into the reaction flask.

Determination of Atomic Weight

After fusion of the anhydrous salt in the reaction flask the hydrogen chloride was displaced by passing air through the apparatus until the escaping air gave no test for chloride when bubbled through a silver nitrate solution. The caps on the outlet and inlet tubes were then adjusted and the flask was hung in the balance case for several hours and weighed.

The fused lanthanum chloride was then dissolved in conductivity water, transferred to an Erlenmeyer flask and diluted to about 1000 cc.

³ "Report on Progress of the Study of the Spectra of the Rare Earth Elements" *Bureau of Standards*, Sept., 1920.

⁴ Kremers, Hopkins, and Engle, *THIS JOURNAL*, **40**, 601 (1918).

Silver was etched and weighed to within 1 mg. of the calculated amount, dissolved in redistilled nitric acid and diluted to about the same volume. The silver solution was then added to the chloride solution with constant shaking and placed in a shaking machine overnight. The clear solution was tested in a nephelometer for excess of silver or chloride and the calculated deficiency was added from a standard solution of silver nitrate or sodium chloride until the nephelometer indicated equivalence.

The weighings were made by the method of substitution, the tare flask used being of quartz and differing in weight from the reaction flask by only a few milligrams. The weights were standardized to 0.01 mg. and weighings were corrected to the vacuum standard.

The following densities were used: lanthanum trichloride, 3.947;⁵ silver, 10.5; weights, 8.4. The atomic weight of silver was taken as 107.88 and that of chlorine as 35.457.

TABLE I

No.	Wt. of LaCl ₃ G.	Wt. of Ag. G.	Ratio	At. Wt. of La
1	0.60680	0.80078	0.75776	138.87
2	0.73504	0.96987	0.75787	138.91
3	1.02450	1.35189	0.75783	138.89
4	0.92965	1.22654	0.75794	138.93
5	1.84436	2.43317	0.75807	138.97
6	0.72863	0.96164	0.75769	138.85
7	0.59234	0.78180	0.75766	138.84
8	0.98017	1.29330	0.75788	138.91
9	1.02852	1.35729	0.75778	138.88
10	0.85193	1.12428	0.75775	138.87
			Av. At. Wt.	138.89

Summary

On the basis of 10 determinations of the atomic weight of lanthanum by the precipitations of the chloride, the average value of 138.89 was obtained, in excellent agreement with the value 138.91 found by Baxter, Tani and Chapin.⁶ The close agreement of these two results indicates that the value selected by the International Committee, 139.0, is slightly too high.

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⁵ *Compt. rend.*, **140**, 1339 (1905).

⁶ Baxter, Tani and Chapin, *THIS JOURNAL*, **43**, 1080 (1921).