

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE REVISION OF THE ATOMIC WEIGHT OF LANTHANUM. Preliminary Paper—The Analysis of Lanthanum Chloride.

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In line with the recent determinations of the atomic weights of neodymium¹ and praseodymium,² the atomic weight of the closely related element, lanthanum, has been subjected to investigation by a method essentially identical with that used for the other two elements. This investigation was begun independently by Chapin, who purified by fractional crystallization a considerable quantity of lanthanum material and began the analysis of the chloride. A second sample of impure lanthanum salt was fractionated in a similar way by Tani. Although it has not been possible to complete the analysis of a sufficient number of fractions of material to fix the atomic weight of lanthanum beyond question, yet since the work has been interrupted for an indefinite period, the preliminary results are presented in a brief fashion.

The Purification of Lanthanum Salt.

The purification of the lanthanum material was effected by fractional crystallization of the double ammonium nitrate. The original material used by Chapin was very kindly furnished by Dr. H. C. Miner, of the Welsbach Light Company. The material fractionated by Tani consisted of the less soluble portions resulting from the fractionation of crude praseodymium ammonium nitrate,³ which also had been furnished by Dr. Miner for the previous investigation on praseodymium.

According to Auer von Welsbach, in the crystallization of the double ammonium nitrates, the bases separate in the order, lanthanum, cerium, praseodymium, neodymium, samarium, terbium and ytterbium earths.⁴ Because the lanthanum separates at the head of a series of fractions the purification of lanthanum is simpler than that of any other rare earth. It is also economical of material because rejection of fractions containing impurities is necessary at only one end of the series. The fractionation was carried out by dissolving the double nitrate in a very dilute solution of nitric acid and allowing the salt to crystallize. The crystals were then dissolved and recrystallized; the mother liquor was evaporated to crystallization. The mother liquor of the less soluble fraction was now combined with the crystals of the more soluble and the process continued

¹ Baxter and Chapin. *THIS JOURNAL*, **33**, 16 (1911); Baxter, Whitcomb. Stewart and Chapin, *ibid.*, **38**, 302 (1916).

² Baxter and Stewart, *ibid.*, **37**, 516 (1915).

³ Baxter and Stewart, *loc. cit.*

⁴ A. von Welsbach, *Sitzungsb. Acad. Wiss. Wien.* **112**, 1043 (1903).

until the number of fractions was 12 or more. The mother liquor of the most soluble fraction was frequently rejected. The crystals from the least soluble fraction, as soon as it became small, were, in the case of Chapin's fractionation, separated and preserved to be united later with similar fractions, but the mixture was never returned to the fractionation series. In Tani's fractionation, as soon as the least soluble fraction became very small, it was set aside and later added to the extreme fraction of a later series of crystals so that no material was removed from the less soluble end of the fractionation series.

In Chapin's fractionation, 96 series of crystallizations were made, involving over 2300 fractions. In Tani's fractionation, although the number of series of crystallizations was the same, the total number of fractions was only somewhat over 1100, owing to more frequent rejection of the most soluble fraction. The final series contained 39 fractions in Chapin's, 12 in Tani's fractionation.

The crystallization was continued in both cases until the most soluble fraction, when its absorption spectrum was examined, seemed to be free from praseodymium. Furthermore, the most soluble fraction in the last series of Tani's material, No. 12, was tested for cerium by passing chlorine into a suspension of its hydroxide in dil. aqueous sodium hydroxide. The cerium dioxide remaining was found to represent about 1% of the whole fraction. Fraction No. 8, in the last series of crystallizations, when examined in the same way, gave no indication whatever of cerium. Since the atomic weights of cerium and lanthanum are separated by only a single unit, even 1% of cerium would affect the average atomic weight of the mixture by only one one-hundredth of a unit, hence the first 8 fractions must have been amply pure for the purpose. The absence of cerium, since it falls between lanthanum and praseodymium in the order of separation, insures the absence of praseodymium as well.

The arc spectra also of the different fractions were examined by photographing the ultra-violet region, $\lambda 5000-2200$, with a Féry quartz spectrograph. Pure graphite electrodes were used. In the spectrogram of Tani's Fraction No. 11, which must have contained less than one per cent. of cerium, the lines of this element were plainly visible, but in the case of Fractions 1 and 5 even the presence of the stronger cerium lines was doubtful. This was also the case with Chapin's fractions 3 and 4.

The Preparation of Lanthanum Chloride.—Selected fractions of material were converted to chloride in a fashion identical with that used in the case of neodymium and praseodymium, as follows. Lanthanum oxalate was precipitated with an excess of oxalic acid and the precipitate was washed, dried, and ignited in an electrically-heated muffle to a mixture of oxide and carbonate. Then the oxide was dissolved in nitric acid and the process repeated twice. The ignited oxide was now dissolved in a quartz dish in hydrochloric acid which had been distilled through a quartz condenser. After the solution had been evaporated to small bulk, the salt was separated

by saturating the solution at zero degrees with hydrogen chloride conducted to the solution through a quartz tube. Centrifugal drainage followed, and then the salt was recrystallized 4 times in the same way. In order to remove superficial water as far as possible, it was left in a vacuum desiccator over fused potassium hydroxide for some time, with occasional crushing in an agate mortar.

All of the reagents were carefully purified by processes that have been described in some detail in the papers on the atomic weights of neodymium and praseodymium.

The Drying of Lanthanum Chloride.—In order to prepare the lanthanum chloride in as nearly as possible an anhydrous condition, the crystal water was first removed by a series of processes of efflorescence, and the salt was finally fused as rapidly as possible in a current of dry hydrogen chloride. As has been pointed out previously,¹ it is of vital importance that the moisture be removed as far as possible at a low temperature before the final fusion, otherwise basic lanthanum chloride forms in appreciable quantities. The transition temperature of the heptahydrate we found to be about 91°. Therefore, until the greater part of the crystal water had been expelled, the temperature was maintained below 85°. Then the temperature was raised to about 130°, where the last molecule of crystal water evaporates. As soon as this process apparently was complete the temperature was raised to about 360° and kept at this point for some time. Finally, the salt was fused as rapidly as possible by means of an electrically-heated sleeve. The salt was probably heated to nearly 1000° in this operation for Bourion² found the melting point to be 890°. During the drying the salt was contained in a platinum boat placed in a transparent quartz tube connected with a glass bottling-apparatus, which is essential for the subsequent handling of hygroscopic salts.³

After the fusion of the lanthanum chloride it was allowed to cool rapidly and the hydrogen chloride was displaced by nitrogen and this in turn by air. Then the boat was transferred from the quartz tube to the weighing bottle without exposure to moisture, and weighed.

In some instances the salt gave a perfectly clear solution in water; in others, owing apparently to difficulty and delay in attaining the rather high fusing point of the chloride, traces of insoluble material were visible. Although not analyzed, there is little question that this was the basic chloride, for both neodymium and praseodymium chlorides, under similar circumstances, become slightly basic.⁴ The quantity of insoluble material apparently never exceeded a few tenths of a milligram, and on allowing the solution to stand for a day or two the basic salt dissolved completely in most cases.

¹ THIS JOURNAL, 37, 527 (1915).

² Bourion, *Ann. chim. phys.*, [8] 20, 547 (1910).

³ Richards and Parker, *Proc. Am. Acad.*, 32, 59 (1896).

⁴ THIS JOURNAL, 37, 527 (1915); 38, 305 (1916).

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 to 1500 cc. in a glass-stoppered precipitating flask. Pure metallic silver equivalent to the chloride within a 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 clear solution was tested in a nephelometer for excess of chloride or silver. The estimated deficiency of either was added in the form of 0.01 *N* 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 computing the quantity of silver equivalent to the chloride allowance was made for solution removed and not returned in the nephelometric tests. In all but one of the analyses several months intervened between the precipitation and the final adjustment of equilibrium so that occluded material had abundant opportunity to be leached out.

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. Then the silver chloride was washed several times with silver nitrate solution containing 0.05 g. per liter and many times with cold water, before being collected on a weighed platinum-sponge Gooch crucible. The chloride was dried in an electrically-heated air-bath at 290° 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 0.00005 g. per liter.¹ Chloride dissolved in the aqueous washings, together with that obtained from the precipitating flask by rinsing with ammonia, was estimated by nephelometric comparison with standards.

In most of the experiments the portions of the original solution removed for nephelometric comparisons were rejected, and a correction of 0.00015 g. was added for each 100 cc. of solution removed. In a few experiments the test portions were returned and a correction applied for the silver chloride thus introduced.

All objects were weighed by substitution for similar counterpoises, a No. 10 Troemner balance being used for the purpose. Weights were

¹ Calculated from the solubility product of silver chloride at 20° as found by Kohlrausch, 1×10^{-10} , *Z. physik. Chem.*, **64**, 167 (1908).

standardized to hundredths of a milligram by the Richards¹ substitution method. The following vacuum corrections were applied.

Weights.....	Specific gravity.	Vacuum correction per G.
.....	8.3
LaCl ₃	3.947 ^a	+0.000159
AgCl.....	5.56	+0.000071
Ag.....	10.49	-0.000031

^a Matignon, *Compt. rend.*, **140**, 1339 (1905).

THE ATOMIC WEIGHT OF LANTHANUM

Series I.

LaCl₃ : 3 Ag.

Ag = 107.880. Cl = 35.457.

No. of Analysis.	Analyst.	Fraction of LaCl ₃ .	Wt. of LaCl ₃ in vacuum. G.	Wt. of Ag in vacuum. G.	Wt. of Ag added or subtracted. G.	Corrected Wt. of Ag in vacuum. G.	Ratio LaCl ₃ 3 Ag.	Atomic Wt. of lanthanum.	
1	Chapin	C 27	3.45559	4.55597	+0.00353	4.55950	0.757888	138.910	
2	Tani	C 3 + 4	5.75303	7.59221	-0.00087	7.59134	0.757841	138.897	
3	Tani	C 3 + 4	8.18782	10.80358	+0.00003	10.80361	0.757878	138.909	
4	Tani	T 1	6.80122	8.97404	-0.00045	8.97359	0.757915	138.921	
5	Tani	T 1	6.73670	8.88887	-0.00058	8.88829	0.757930	138.925	
6	Tani	T 5	5.43254	7.16816	-0.00044	7.16772	0.757919	138.922	
Average,								0.757895	138.914

Series II.

LaCl₃ : 3 AgCl.

No. of Analysis.	Analyst.	Fraction of LaCl ₃ .	Wt. of LaCl ₃ in vacuum. G.	Wt. of AgCl in vacuum. G.	Loss in wt. on fusion. G.	Dissolved AgCl. G.	Corrected wt. of AgCl in vacuum. G.	Ratio LaCl ₃ 3AgCl.	Atomic wt. of lanthanum.	
7	Chapin	C 27	3.67748	6.44443	0.00014	0.00129	6.44558	0.570543	138.969	
8	Tani	C 3 + 4	5.33464	9.35196	0.00042	0.00101 ^a	9.35255	0.570394	138.905	
9	Tani	C 3 + 4	5.75303	10.08459	0.00029	0.00181	10.08611	0.570391	138.904	
10	Tani	C 3 + 4	8.18782	14.35541	0.00041	0.00125	14.35625	0.570331	138.880	
11	Tani	T 1	6.80122	11.92149	0.00017	0.00200	11.92332	0.570405	138.909	
12	Tani	T 1	6.73670	11.80828	0.00021	0.00145	11.80952	0.570438	138.924	
13	Tani	T 5	5.43254	9.52361	0.00022	0.00124	9.52463	0.570368	138.893	
Average,									0.570410	138.912

^a The concentration of AgCl in the aqueous washings was assumed to be the average of that found in the other experiments, 0.00120 g. per liter.

The foregoing table includes all the experiments made by Chapin and Tani. Two analyses made by W. A. Turner with another fraction are not included because the fused salt and its solution were not satisfactory in appearance.

The average atomic weight of lanthanum found by us, 138.91, is nearly one-tenth of a unit lower than the value selected by the International Committee on Atomic Weights, 139.0, but just as much higher than the

¹ Richards, *THIS JOURNAL*, **22**, 144 (1900).

value 138.8 calculated by Clarke.¹ Nearly all the earlier determinations depend upon the results of methods in which lanthanum oxide plays an important rôle. The recognized difficulty of preparing rare-earth oxides free from traces of the compounds from which they are made by ignition is probably a chief cause of the wide variation among earlier determinations.

It is to be noted that the presence of the usual companions of lanthanum, namely, cerium, praseodymium and neodymium would raise the apparent atomic weight of lanthanum so that the value obtained in this investigation unquestionably represents a maximum.

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ATOMIC WEIGHT OF GERMANIUM.

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It is recognized that the atomic weight of germanium is not accurately known, the accepted value being entirely dependent upon the investigations of its discoverer.² Aside from the lack of confirmation of this constant on the part of other workers it should be noted that Winkler's determinations were made very shortly after his discovery of the element, so that the time interval between the announcement of the existence of the new element and the determination of its atomic weight could not have permitted the determination of special means of purification to which germanium compounds may now be subjected.

The purpose of this investigation was to develop a more thorough means of purification of germanium compounds, especially in connection with the elimination of tin, arsenic and silica with which germanium is always associated, and to use the purified product for a redetermination of this much neglected constant.

Winkler decomposed the tetrachloride by sodium carbonate, added an excess of standardized silver solution and titrated back the excess of the latter with ammonium thiocyanate solution. Four determinations were recorded. Winkler's reasons for the use of the Volhard method are interesting, namely, that the silver chloride which he precipitated after decomposition of the tetrachloride could not be determined gravimetrically on account of occlusion of germanic acid in the precipitated silver chloride. His effort to oxidize the disulfide with nitric acid and to precipitate the equivalent of sulfuric acid as barium sulfate also met with failure for the same reason.

¹ Smithsonian Misc. Coll., "Constants of Nature," Part V. *A Recalculation of the Atomic Weights*, 493, 1910.

² *J. prakt. Chem.*, [2] 34, 177 (1886).