If the values of column one are plotted against the logarithms of the vapor pressures, all points except the first and the third fall within two straight lines whose distance apart is within experimental error. In the original article Dolezalek expresses the concentration in mols per liter of solution. In order therefore to obtain from the curve the values for the vapor pressures for the corresponding concentrations of HCl given in Table I (16.0, 10.0 and 6.75 mols per 1000 g. of water) a liter of each of these solutions was weighed, and the concentration computed to mols per liter of solution. The vapor pressures corresponding to these concentrations are indicated by ⊕ on the curve. By means of these values and the heats of solution of HCl for the corresponding concentrations, the vapor pressures for 25°, were calculated by means of the equation

$$\ln \frac{[\mathrm{HCl}]_2}{[\mathrm{HCl}]_1} = \frac{\Delta \mathrm{H}(\mathrm{T}_2 - \mathrm{T}_1)}{\mathrm{RT}_2\mathrm{T}_1},$$

where Δ H denotes the partial molal heat of vaporization of HCl at the given concentration n (mols HCl per 1000 g. H_2O). Δ H is numerically equal to the slope obtained by plotting against n the heat change Q,[1] when n mols of HCl gas are dissolved in 1000 g. H_2O. The results of these calculations are given in Table V.

TABLE V.

Mols HCl per 1000 g. H_2O.	$[HCl]_{30°}$ mm.	$[HCl]_{25°}$ mm.	ΔH cal.
6.75	(0.404)	(0.270)	14630
10.00	5.24	3.66	12930
16.0	210.0	156.6	10580

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF SAMARIUM.

THE ANALYSIS OF SAMARIUM CHLORIDE.

BY O. J. STEWART AND C. JAMES.

Received August 11, 1917.

Soon after the discovery of samarium by Boisbaudran, in 1878, Marignac[2] announced its atomic weight to be 149.4. This work was followed by that of Brauner,[3] who claimed to have prepared a purer material, giving the number 150.7. No details, however, were given.

Cleve's[4] systematic work, involving the synthesis of the sulfate from

---

[1] The values for Q were taken from a paper by G. N. Lewis, THIS JOURNAL, **35**, 11 (1913).

When the change in Q with n is so large as to necessitate a scale of about 1000 cal. to 1 mm. on the plotting paper, as in the present case, then dQ/dn may be resolved in such a manner as to render plotting more convenient. Thus, let $Q = nQ'$. Then $dQ/dn = d(nQ')/dn = dQ'/d \ln n + Q'$. The change in Q' is only 3940 cal. for the chosen range of concentration of the HCl (0.185 to 18.5 molal) while the change in Q for the same range is 244000 cal.

It will be noted also that if the values for log n are plotted as abscissae and those for Q' as ordinates, the values for Q' fall below the horizontal axis, so that the slopes $dQ'/d \ln n$, will be of opposite sign with respect to Q'.

[2] *Arch. Sci. Phys. Nat.*, [3] **3**, 435 (1880).

[3] *J. Chem. Soc.*, **43**, 287 (1883).

[4] *Ibid.*, **43**, 362 (1883).

oxide, brought forth 150.17 as the average value and Bettendorff,[1] following the same method, found the atomic weight to be 150.46.

In a single analysis of the hydrous sulfate, Brauner[2] obtained the value 150.71, while Käppel,[3] by the same process found 151.59.

Urbain and Lacombe,[4] working with material which was in a high state of purity, converted weighed portions of the octohydrated sulfate to the anhydrous salt and this in turn to oxide. The average value obtained by them was 150.46.

Matignon,[5] using the ratio $Sa_2(SO_4)_3$: Sa_2SO_6, the latter basic salt being obtained by heating the normal salt between 500 and 1000°, found the atomic weight to be 150.67.

Finally, Feit and Przibylla[6] found volumetrically four values, the average of which is 150.47.

Clark, in his "Constants of Nature" calculates the probable value for the atomic weight of samarium to be 150.39 with an actual uncertainty of 0.1.

The Extraction of Samarium.

The material from which the samarium salts were extracted came from various sources: a considerable quantity of commercial didymium hydroxide; cerium earths from gadolinite, euxenite and ytterspar; a large amount of the oxides derived from the more soluble double potassium sulfates obtained from monazite. This latter product was supplied by the Welsbach Light Co. through the courtesy of Dr. H. S. Miner to whom the authors offer their most sincere thanks.

Minerals such as gadolinite were decomposed by means of hydrochloric or sulfuric acids. The residue, after heating to render the silica insoluble, was stirred in large tanks with water, and the resulting solution precipitated by means of oxalic acid.

The oxalates were ignited to oxides, dissolved in hydrochloric acid, diluted and stirred with sodium sulfate. The precipitated double sulfates were separated by filtration and washed with a solution of sodium sulfate. The double sulfates were thrown into a boiling solution of sodium hydroxide and thoroughly stirred. After the mass had boiled for about thirty minutes it was poured upon a Buchner funnel and the hydroxides well washed. Very large funnels and filter flasks were obtained for the purpose.

These crude hydroxides, the commercial didymium hydroxide, and the oxides from the more soluble double potassium sulfates derived from monazite were treated in exactly the same manner from now on. The

---

[1] *Am. Chem. Pharm.*, 263, 164 (1891).

[2] *Abegg's Handbuch*, Bd. 3, Abth. I, p. 284.

[3] *Ann.*, 331, 16 (1904).

[4] *Compt. rend.*, 138, 1166 (1904).

[5] *Ibid.*, 141, 1230 (1905).

[6] *Z. anorg. allgem. Chem.*, 50, 259 (1906).

hydroxide or oxide was dissolved in nitric acid. Any ceric nitrate which formed was reduced by the addition of either oxalic acid or rare earth oxalate of a composition similar to the material being worked up. A quantity of nitric acid, slightly less than that required by the oxides and hydroxides, was neutralized by means of magnesium oxide. The rare earth nitrates were then mixed with the magnesium nitrate and the whole submitted to fractional crystallization.

It was taken for granted that the raw material contained certain amounts of every one of the rare earth metals. During the first stages the major portions of the lanthanum, cerium, praseodymium and neodymium were removed.

The rare earth group contains the elements lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium, lutecium and celtium. As we proceed up the series the stability of the double magnesium nitrates ($2R'''(NO_3)_3.3Mg(NO_3)_2.24H_2O$) becomes less. The elements up to holmium give double nitrates while those beyond do not. Moreover the elements just preceding holmium form the double magnesium nitrates with the greatest difficulty.

The solubilities of the double magnesium nitrates are also in the order of the list given above. The solubility increases with increase in the atomic weight.

Since the magnesium double salts of lanthanum, cerium, praseodymium and neodymium are much less soluble than the corresponding compound of samarium, they will separate in the least soluble crystals. The similar double nitrates of europium and gadolinium, etc., are much more soluble than the above-mentioned samarium salt. These will be removed in the most soluble portions along with those elements remaining in the form of the simple nitrates.

After a few fractional crystallizations, the least soluble crystals rapidly became pale in color, while the intermediate crystals showed a very strong amethyst tint. As soon as it was evident that most of the neodymium had been removed from the least soluble crystals they were taken from the series.

Whenever the mother liquor showed samarium, erbium or holmium bands, it was diluted and precipitated by means of oxalic acid. This procedure was followed for the purpose of removing the impurities, such as iron, aluminium, etc., which had accumulated and would hinder further crystallization.

After the fractionation had been carried on for a considerable time, there were found to be three products: (*a*) Pale-colored crystals consisting of the double nitrates of magnesium with lanthanum, cerium, praseodymium and neodymium; (*b*) fairly pure neodymium magnesium nitrate;

(*c*) the oxalates from the mother liquors containing samarium, gadolinium, yttrium, and small amounts of every other earth in all probability.

Products (*a*) and (*b*) which contained no samarium were discarded.

The oxalates (*c*) were ignited to oxides and dissolved in nitric acid. An amount of nitric acid corresponding to about two-thirds of that required by the rare earth oxides was neutralized by pure magnesium oxide. This solution was added to that of the rare earth nitrates, and the whole again submitted to fractional crystallization from 1 : 2 nitric acid.

The mother liquors soon failed to show any samarium bands when a thick layer was examined by means of a spectroscope. However, bands of dysprosium, holmium and erbium were very strong. As the fractionation proceeded, the least soluble began to show a pink tint due to neodymium, while the samarium free mother liquors showed an increase in holmium and dysprosium over erbium. Since these mother liquors were placed aside as soon as the samarium absorption disappeared, the erbium was rapidly removed. When the absorption bands of erbium began to fade those of europium began to appear. The most soluble portions of the series consisted mainly of gadolinium at this stage. They were practically colorless when removed. Whenever it was possible, neodymium magnesium nitrate was taken away from the least soluble end.

Finally there remained samarium magnesium nitrate containing only mere traces of neodymium and europium together with a little gadolinium. This material consisted of about twelve kilograms spread over fifteen fractions. The fractionation was continued daily for six months further, after which the three least soluble fractions were selected. These were selected for the continuation of the purification since they were the farthest away from any fraction which might possibly contain europium. The only impurity which this samarium might contain was neodymium, an element easily detected by its strong absorption spectrum. The material after considerable fractionation from 1 : 2 nitric acid gave a least soluble portion which when dissolved in water gave a faint indication of the strongest of the neodymium absorption bands. The middle portion of the fractions was selected for the final purification.

The final purification was carried out in a similar manner. The series was allowed to expand to ten fractions and kept at that number by occasionally removing end fractions for thirty-five series. Absolutely no change in color could be detected, the first and last fractions possessing exactly the same tint. The least soluble fraction showed no signs of the presence of neodymium when the absorption spectrum was observed through a thick and concentrated layer of solution. An examination of the arc spectrum of the most soluble fraction failed to show the presence of europium.

Since the absence of neodymium and europium was proved, it was concluded that all the other rare earth elements were absent.

Fractions 1 to 5 and beyond 15 were discarded.

The Preparation of Samarium Chloride.

On account of the small quantity of material in each fraction of the final series of the double magnesium samarium nitrate fractionation, adjacent fractions were combined before preparing the chloride; the numbers of the fractions so combined are set off in brackets: [6–7], [8–9–10], [11–12–13], [14–15], fraction 6 being the least soluble.

Each of the above groups of fractions was then treated as follows: The double salt was dissolved in pure water and diluted to a large volume in a five-liter Jena flask and acidified with pure nitric acid. When its temperature had been raised to the boiling point, an equally dilute boiling solution of pure oxalic acid was added slowly. After washing the precipitate five times by decantation with two-liter portions of pure water, it was collected upon a porcelain Gooch crucible which was provided with an ashless filter-paper mat and dried at 105°. The Samarium oxalate was then ingited to oxide in a platinum dish at a dull red heat produced in an electrically heated quartz muffle furnace.

The oxide was then dissolved in hydrochloric acid in a quartz dish, and, after evaporation to a small volume, transferred to a platinum dish and evaporated to dryness and baked at 115° in an electrically heated glass oven. The dry chloride was then acidified with pure hydrochloric acid and diluted and filtered through ashless filter paper to remove the silica. The entire process mentioned above was repeated with each group of fractions at least three times to remove the silica.

The samarium chloride was then converted to oxide by the method already described. This oxide, after being transferred to a quartz dish, was dissolved in pure nitric acid, transferred to a large Jena flask, diluted to three liters, and precipitated hot with a hot solution of pure ammonium oxalate. The samarium oxalate, after being washed five times by decantation with large portions of pure water, was collected as before, dried and ignited to oxide in a platinum dish.

This oxide was then dissolved in a quartz dish with pure hydrochloric acid, followed by crystallization twice as chloride, the crystal yield being brought to the maximum by saturating the ice-cold solution with hydrogen chloride gas led in through a quartz tube from a heated solution of fuming hydrochloric acid; the mother liquor was effectively removed by centrifugal drainage in platinum vessels. After the salt had been dried over fused potassium hydroxide in a vacuum desiccator and ground in an agate mortar, it was ready for final dehydration and analysis.

The Preparation of Pure Silver.—In purifying silver for this work an attempt was made to follow, as closely as facilities would permit, one of the methods used at Harvard.

Fifteen hundred grams of C. P. silver nitrate were dissolved in pure water and filtered through ashless filter paper and diluted to eight liters in large Jena flasks. Redistilled C. P. hydrochloric acid was then added in excess and the silver chloride was washed by decantation five times with large portions of pure water. The silver salt was then covered with pure water and ammonia gas was led in through a glass tube until the salt had dissolved. The solution was then filtered through a large Buchner funnel which was provided with an ashless filter paper mat and the silver chloride was reprecipitated by the addition of redistilled hydrochloric acid. After the silver chloride had been washed as before, it was reduced to metal by a solution of granulated sugar made alkaline with C. P. sodium hydroxide. Careful washing of the silver was followed by drying and sintering in a porcelain dish and finally fusing before the blast on charcoal blocks. The silver buttons were scrubbed with beach-sand, etched with nitric acid, washed with pure water and finally re-dissolved in pure nitric acid.

The above silver nitrate solution was then diluted and heated to boiling and treated with a dilute solution of pure ammonium formate. The ammonium formate was prepared by passing ammonia gas into re-distilled formic acid. When the metallic silver had been carefully washed and dried, it was fused to large buttons in a porcelain dish which was lined with pure lime.

These buttons, after being thoroughly cleansed, next served as a dissolving anode in an electrolyte of pure silver nitrate and the resulting electrolytic crystals were fused in a current of pure electrolytic hydrogen on a boat of the purest lime. After the buttons thus obtained had been sawed to a convenient size, and had been cleansed with nitric acid, ammonia, and pure water, they were heated to about 400° in a vacuum. The silver was preserved over fused potassium hydroxide in a desiccator.

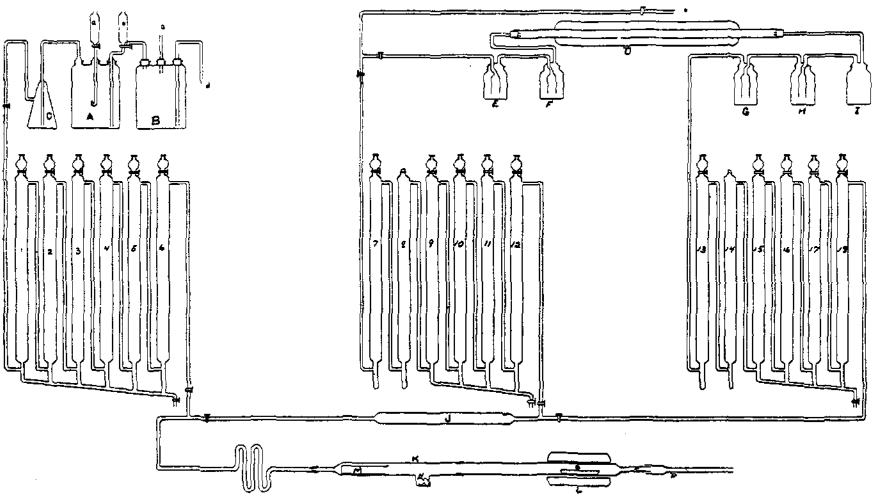
The Preparation of Other Reagents.

The ordinary distilled water of the laboratory was twice distilled, once from alkaline permanganate and once from dilute sulfuric acid, through block tin condensers and received in Jena flasks. Hydrochloric acid and nitric acid were once distilled through quartz condensers, the first and last thirds being rejected. Electric ovens, muffles and stoves were used whenever the products of combustion of gas would have caused harm and quartz and platinum were used in place of glass or porcelain whenever the latter two materials would have introduced objectionable impurities.

The Drying of Samarium Chloride for Analysis.

The dehydration of the salt was carried out in the light of knowledge gained by Matignon and by Baxter and his students. The process was essentially that used by Baxter and one of the present authors[1] in their work on praseodymium, the apparatus being only slightly changed as shown in the drawing, Plate 1.

PLATE 1



The weighing bottle, the stopper, and the boat containing the salt having been placed in positions M, N and O, respectively, the "bottling apparatus" was freed from air by sweeping with nitrogen which was generated by passing air from *e* through the strong ammonia solutions E and F and through the electrically heated tube D containing copper gauze, the nitrogen then being purified by passing through dilute sulfuric acid in G and H and then through the tower 13 containing beads wet with silver nitrate solution, then through tower 14 containing small pieces of fused potassium hydroxide and through the towers 15, 16 17, and 18 containing beads drenched with boiled, concentrated, C. P. sulfuric acid and finally through the tube J which was filled with resublimed phosphorus pentoxide.

After the air had been removed, pure, dry hydrogen chloride was also admitted in a continuous stream to the "bottling apparatus" and the temperature of the salt was slowly increased by means of the nichrome wound mica sleeve L.

The hydrogen chloride gas was generated by admitting concentrated sulfuric acid from *a* to a fuming solution of hydrochloric acid contained in A. The gas bubbled through a hydrochloric acid solution in C and was dried in its passage through the six towers 1, 2, 3, 4, 5, 6, which were filled with glass beads drenched with concentrated and boiled sulfuric acid. The glass stoppered separatory funnels at the top of each tower

---

[1] THIS JOURNAL, 37, 516 (1915).

permitted the addition of fresh reagent without the entrance of air. Spent liquid in A could be removed to B by applying suction at *c* and closing *d* and by generating a small quantity of hydrogen chloride gas in A. Fresh hydrochloric acid could then be admitted to A from *b* without the entrance of air. Air pressure then being applied at C would force the spent liquid from B through the tube *d*.

According to Matignon,[1] hydrated samarium chloride $SaCl_3.6H_2O$, when heated to 100° in a current of hydrogen chloride gas, loses five mols. of water and the sixth mol. is driven off after prolonged heating at 180°. The anhydrous salt fuses below 1000°.

Accordingly, the temperature of the salt was kept below 100° until most of the crystal water was driven off, when the temperature was raised slowly to 180° where it remained for some time. The temperature was then raised to 300° and hydrogen chloride alone allowed to pass for some time. After the heating element had been removed and the salt had cooled somewhat, the hydrogen chloride gas was displaced by nitrogen and the salt was removed and ground in an agate mortar. The boat and salt were then returned to the bottling apparatus which was first swept out with nitrogen after which a mixture of nitrogen and hydrogen chloride was allowed to pass while the temperature was raised to 300°. Hydrogen chloride gas alone was now allowed to pass while the temperature rose to the melting point of the salt. Quick fusion of the salt was followed by cooling and displacement of the hydrogen chloride gas by nitrogen and this in turn by pure air which was purified in its passage through the tower 7 containing glass beads drenched with silver nitrate and the tower 8 containing stick potassium hydroxide and the towers 9, 10, 11 and 12 which were filled with glass beads drenched with concentrated sulfuric acid and the tube J which was filled with resublimed phosphorus pentoxide.

The boat containing the fused salt was then pushed along the tube into its bottle, the stopper inserted and the bottle then transferred to a desiccator before weighing.

The Method of Analysis.

After the salt had been weighed, it was carefully transferred to a glass-stoppered Erlenmeyer flask and treated with about half a liter of pure water. All samples analyzed dissolved perfectly and quickly. The solution was then transferred quantitatively to a ten-liter glass-stoppered bottle and diluted to about three liters.

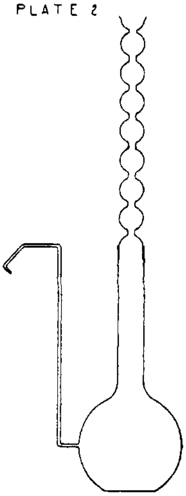
A quantity of pure silver, equivalent to within a few tenths mg. to the samarium chloride was dissolved in pure dilute nitric acid in a flask provided with a delivery tube and a column of bulbs as shown in Plate 2. After the oxides of nitrogen had been expelled, and the solution had been diluted to 2500 cc., the delivery tube of the silver flask was introduced

---

[1] *Compt. rend.*, 134, 1308 (1902).

into the neck of the bottle containing the samarium chloride solution in such a way that the stream of silver nitrate solution would strike the walls of the bottle near the top while the bottle was rotated on a motor driven revolving table, the speed of which could be controlled by the operator's foot. The silver nitrate solution having been quantitatively transferred, the analysis bottle was stoppered and was frequently shaken for several days after which the solution was tested nephelometrically for deficiencies in silver or chlorine, these deficiencies then being supplied from a solution of silver nitrate containing 1 g. of silver per liter or from an equivalent solution of potassium chloride, both solutions having been carefully made up determinately. When equilibrium had been established, mathematical deduction of added chlorine could be made and the ratio $SaCl_3 : 3Ag$ could be calculated. Needless to say, all work involving the handling of materials affected by light was carried out in a room illuminated by a ruby lamp. All weighings were made on a slightly used Staudinger balance which was sensitive to 0.02 mg. with platinum-plated weights which were carefully standardized by the method described by Richards.[1] The balance case contained radioactive material for dissipating electrical charges and fused potassium hydroxide for drying the air. The vessels containing the salts were weighed by substitution for a counterpoise as nearly as possible like the vessels themselves in weight, and volume. Vacuum corrections were applied as follows:

PLATE 2



Weights.	Specific gravity.	Vacuum correction per g.
$SaCl_3$	4.465[2]	+0.000124
Ag	10.49	0.000031

THE ATOMIC WEIGHT OF SAMARIUM.

Ratio $SaCl_3$: 3Ag.

Ag = 107.880. Cl = 35.457.

No. of analysis.	Fraction.	$SaCl_3$ in vacuum, g.	Ag. in vacuum, g.	Ag. added. g.	Corrected weight of Ag. in vacuum, g.	Ratio $SaCl_3$: 3Ag.	Atomic weight of samarium.
Preliminary Series.							
1	6:7	4.05609	5.11222	0.00362	5.10860	0.793973	150.59
2	6:7	3.00065	3.78244	0.00200	3.78044	0.793730	150.51
3	6:7	5.28891	6.66367	0.00057	6.66424	0.793625	150.48
4	8:9:10	3.75782	4.73457	0.00291	4.73748	0.793211	150.34
5	8:9:10	4.76695	6.00618	0.00255	6.00873	0.793337	150.39
6	11:12:13	2.97764	3.75132	0.00102	3.75234	0.793542	150.45
7	11:12:13	3.82407	4.81861	0.00100	4.81761	0.793769	150.53

---

[1] THIS JOURNAL, **22**, 144 (1900).

[2] Matignon, *Compt. rend.*, **140**, 1339 (1905).

Atomic Weight of Samarium (*continued*).

No. of analysis.	Fraction.	$SaCl_3$ in vacuum. g.	Ag. in vacuum. g.	Ag. added. g.	Corrected weight of Ag. in vacuum. g.	Ratio $SaCl_3$: 3Ag.	Atomic weight of samarium.
8.......	14:15	4.47775	5.64295	0.00070	5.64365	0.793414	150.41
9.......	14:15	3.33781	4.20662	0.00050	4.20712	0.793374	150.40
	Average of series						150.45
	Final Series.						
10.......	6:7	4.65174	5.86126	0.00002	5.86128	0.793639	150.48
11.......	6:7	5.13023	6.46373	0.00204	6.46577	0.793445	150.42
12.......	8:9:10	4.52826	5.70641	0.00086	5.70727	0.793420	150.41
13.......	8:9:10	6.65425	8.38568	0.00060	8.38628	0.793469	150.43
14.......	11:12:13	6.02908	7.59642	0.00027	7.59669	0.793628	150.49
15.......	11:12:13	5.09858	6.42431	0.00089	6.42520	0.793528	150.45
16.......	14:15	4.68220	5.90040	0.00071	5.90111	0.793444	150.42
17.......	14:15	4.32763	5.45310	0.00241	5.45551	0.793258	150.36
	Average of series						150.43
	Average of both series						150.44

Summary and Conclusions.

The preparation of a very pure samarium material has been described, and its purity proven by spectroscope and analysis.

The possibility of the occlusion of samarium chloride, samarium nitrate or silver nitrate by silver chloride is thought to have been extremely remote because of the special mixing method employed and because of the great dilution of the reacting materials, since the concentration was far less than that used by Baxter and his students. These investigators used a similar method in analyzing similar materials (neodymium chloride and praseodymium chloride) and they found no trace of occlusion.

A considerable disagreement of results in the Preliminary Series is thought to have been due to the diameter of the quartz fusion tube. This was entirely too great when compared with the volume of the sweeping gas. In order to prevent backward diffusion in the final series, a smaller tube was employed. The discordant result of analysis 17 is not explained.

The average value 150.43 of the final series is almost identical with the general average 150.44 of both series.

Durham, N. H.

[Contribution from the Chemical Laboratory of the University of Illinois.]

OBSERVATIONS ON THE RARE EARTHS. IV.

THE PURIFICATION OF GADOLINIUM.

By Louis Jordan and B. Smith Hopkins.

Received July 15, 1917.

The object of this work was to study some methods for the separation of gadolinium from rare earth mixtures and for the purification of gado-