

The compound was therefore a double cesium neodymium sulphate containing 3 molecules of water of crystallization, $\text{Nd}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.

Attempts were also made to prepare the potassium neodymium alum by electrolysis. The same method employed in preparing the praseodymium body was used. The crystals which separated out at the cathode gave, on analysis:

Neodymium sulphate.....	60.92
Cesium sulphate	33.08
Water of crystallization by difference ..	6.00

This body was also a double sulphate containing 3 molecules of water of crystallization.

Aluminum salts possess weak basicity, while the praseodymium and neodymium are, comparatively, basic.¹ This may account in part for our failure to prepare these alums. It is particularly interesting to note in considering these two so-called elements that the one gives a series of double salts with 2 and 4 molecules of water of crystallization, while the other gives one with 3.

UNIVERSITY OF NORTH CAROLINA.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF NORTH CAROLINA.]

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.

LANTHANATES.

BY CHARLES BASKERVILLE AND GEORGE F. CATLETT.

Received November 9, 1903.

Synopsis.—The resemblance of lanthanum to aluminum was taken advantage of and the preparation of such bodies as the lanthanates and meta-lanthanates, hitherto not reported, described. The new substances are sodium tetra-lanthanate ($\text{Na}_2\text{La}_4\text{O}_7$) and meta-lanthanates of sodium, potassium, lithium and barium ($\text{MH}_9\text{La}_5\text{O}_{15}$). Two methods were used: Fusion of lanthanum oxide with alkaline carbonates, and prolonged digestion in a concentrated solution of the alkaline hydroxides at 100°C . These bodies do not serve as a means for the separation and purification of lanthanum.

Aluminum, which belongs to the third group in the periodic

¹ *Am. Chem. J.*, 26, 166.

classification, may be separated from many elements by the solubility of its hydroxide in the non-volatile alkalis. This is due to the formation of soluble aluminates or meta-aluminates. It, therefore, appeared reasonable that lanthanum, which is classed with the same group, would deport itself similarly and perhaps offer a desirable new mode of separation from other or the rarer elements.

In their work on zirconates, Venable and T. Clarke¹ proposed the following methods for the preparation of this class of bodies.

- I. Fusing with boron trioxide (Ebelmen).
- II. Fusing with alkaline carbonates (Hjortdahl).
- III. Fusing with alkaline hydroxides.
- IV. Fusing with alkaline or earthy chlorides (Hjortdahl).
- V. Precipitation of solutions of salts with alkaline hydroxides (Watts).
- VI. Dissolving the hydroxide in strong solutions of sodium or potassium hydroxide and precipitation by dilution or by neutralization with an acid.

The process used by Ebelmen was not applicable with zirconia because that oxide does not dissolve in boron trioxide. The second and third processes given above, gave the most successful results. Water and dilute acetic acid were used to dissolve the alkali from the zirconate.

In the work on the lanthanates, those two methods, which were most successfully used by Venable and Clarke, were applied with some alterations, as will be noted in the detailed account which follows. Water was found useless as a washing medium, as, with the exception of the sodium tetra-lanthanate, the other bodies appeared to be decomposed. Acetic acid dissolved the lanthania and supposed lanthanate with equal ease, but it was used effectively in the preparation of the lithium lanthanate. Alcohol was used in most of the experiments, and, as far as could be seen, had little action on the product. In the case of the fusion of lanthania and barium hydroxide, a solution of ammonium chloride in water was used to dissolve out the remaining barium hydroxide.

The lanthanum compounds used were prepared from a quite pure lanthanum ammonium nitrate, generously loaned by H. S. Miner, of the Welsbach Lighting Company. The hydroxide was prepared from this compound by precipitation

¹ This Journal, 18, 5; *Chem. News*, 74, 42 and 54 (1896).

with ammonia and washing until free from that volatile alkali. As is well known, lanthanum hydroxide readily absorbs carbon dioxide from the air; hence it was kept covered with water most of the time, filtered and used fresh in each experiment. The oxide used was obtained by igniting the hydroxide obtained in platinum. Very concentrated solutions (nitrates and chlorides, neutral and acid) of varying thicknesses gave no absorption bands, showing the absence of certain of the rare earths that are likely to be present.

The analyses of the preparations were made by dissolving a definite quantity of the dried body in hydrochloric acid, precipitating the lanthanum hydroxide with ammonium hydroxide. The precipitate was thoroughly washed, burned and weighed as lanthanum oxide. The filtrate was evaporated to dryness and the alkalies or alkaline earths converted into sulphates and weighed as such. When water was determined, the material was ignited in combustion tubing and the moisture collected in a tared calcium chloride tube, dry air being drawn through. In several cases, either the washing medium failed to remove all of the carbonate used in the fusion, or some carbonate was formed when the material was exposed to the air. The carbon dioxide was determined in the ordinary alkalimeter by evolution and absorption.

EXPERIMENT I.—DI-SODIUM TETRA-LANTHANATE, $\text{Na}_2\text{La}_4\text{O}_7$.

Two grams of lanthanum oxide and eight grams of sodium carbonate were kept in a state of fusion for three hours. The reaction was carried out in a platinum crucible at the temperature of a blast lamp. At the end of the fusion, it was specked with small yellowish particles and white crystals were formed. The mass was treated with water until the wash-water was no longer alkaline, corallin being used as indicator. The white crystalline undissolved body remaining was dried at 100° and, on analysis, gave the following results: .

Lanthanum oxide	88.00
Sodium oxide	8.00
Carbon dioxide.....	2.50
Water (by difference)	1.50
	100.00

The carbon dioxide was very probably in combination as lanthanum carbonate, $\text{La}_2(\text{CO}_3)_3$, as sodium carbonate would have

been removed by the wash-water. Accounting for the carbon dioxide as being present in this form, we have 8.64 per cent. of this carbonate or 91.46 per cent. of lanthanum and sodium oxides and water. Disregarding the water and revising the calculations, we have

Lanthanum oxide	90.99
Sodium oxide.....	9.00

or the ratio 2 : 1, *i. e.*, $\text{Na}_2\text{La}_4\text{O}_7$, di-sodium tetra-lanthanate, similar to the boron compound.

EXPERIMENT II.—HYDRATED MONO-SODIUM POLY-META-LANTHANATE.

Two grams of lanthanum oxide and 8 grams of sodium hydroxide were digested in a silver dish on a water-bath for thirty hours. A white mass, almost insoluble in water but decomposed by it, was obtained. Alcohol was used and the unchanged sodium hydroxide washed out; but not all of the sodium carbonate produced by the absorption of carbon dioxide from the air. The body gave, on analysis:

Lanthanum oxide	79.60
Sodium oxide.....	2.80
Carbon dioxide.....	3.00
Water (by difference)	14.6

Providing for the carbon dioxide as in the first experiment, we have $\text{NaH}_9\text{La}_5\text{O}_{15}\cdot 4\text{H}_2\text{O}$, comparable to the poly-meta-stannates in which one of the hydrogen atoms appears to have been replaced by the metal sodium.

EXPERIMENT III.—HYDRATED MONO-LITHIUM POLY-META-LANTHANATE.

Two grams of lanthanum oxide and eight grams of lithium carbonate were fused in a platinum crucible for five hours. Much difficulty was experienced in washing out the alkali, which was eventually removed by careful treatment with 5 per cent. acetic acid. The acid was subsequently removed by means of alcohol. A small amount of material insoluble in hydrochloric acid was found when it was examined. The analysis of the white body gave the following results:

Lanthanum oxide	82.9
Lithium oxide.....	1.2
Carbon dioxide	4.3
Water	9.8
Body insoluble in hydrochloric acid.	1.3

99.5

Allowing carbon dioxide to be combined in the form of lanthanum carbonate, as all of the lithium carbonate was washed out with the acetic acid, we have $\text{LiH}_9\text{La}_5\text{O}_{15}\cdot 2\text{H}_2\text{O}$ similar to the above, with the exception of having 2 molecules of water instead of 4.

EXPERIMENT IV.—HYDRATED MONO-POTASSIUM POLY-META-LANTHANATE.

Two grams of lanthanum oxide and 16 grams of potassium hydroxide were digested in a covered silver crucible on a water-bath for thirty hours. It was leached with alcohol, as it was found that water decomposed the material as in the case of the sodium hydroxide digestion. The white body gave, on analysis, the following results:

Lanthanum oxide	79.50
Potassium oxide.....	2.53
Carbon dioxide.....	0.40
Water	18.69
	101.12

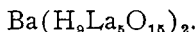
which approximates the formula $\text{KH}_9\text{La}_{10}\text{O}_{15}\cdot 1.5\text{H}_2\text{O}$.

The body without doubt was decomposed during the washing; hence no value can be attached to the results obtained by analysis.

EXPERIMENT V.—CALCIUM COMPOUND.

An attempt was made to fuse calcium carbonate with lanthanum oxide, but such great difficulty was experienced in making the fusion and removing the unchanged calcium salts that the experiments were discontinued.

EXPERIMENT VI.—BARIUM POLY-META-LANTHANATE,



Barium hydroxide was substituted for the sodium hydroxide and the digestion carried out as in the first experiment. A concentrated water solution of ammonium chloride was used for leaching. The body obtained gave, on analysis,

Lanthanum oxide	75.97
Barium oxide.....	6.05
Carbon dioxide	1.8
Water	14.9
	99.72

or, disregarding the carbon dioxide, we have $\text{Ba}(\text{H}_9\text{La}_5\text{O}_{15})_2$.

As a result of these experiments, it appears that a number of bodies, quite complex in character, may be had, which seems to show the existence of a series of compounds of lanthanum which may be termed meta-lanthanates or poly-meta-lanthanates. At the same time it is quite evident from this and other work which immediately follows, that the methods are not suitable as a means of separation of these rare earths, and really little value can be attached to the above.

A per-lanthanate, or hydrated peroxide, $\text{La}_2\text{O}_5 \cdot x\text{H}_2\text{O}$, was obtained by fusion with sodium peroxide. Such a body has already been reported by Melikoff and Pissarjewsky.¹

UNIVERSITY OF NORTH CAROLINA.

THE THERMAL EFFICIENCY OF A ROTARY CEMENT KILN.²

BY JOSEPH W. RICHARDS.

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THE following tests and results were obtained on a rotary cement burner, 60 feet long by 6 feet external diameter, fired by pulverized bituminous slack coal, at the plant of the Dexter Cement Company, at Nazareth, Pa.³

The ground cement mixture has the following composition:

	Per cent.
Silica.....	13.3 ^S
Aluminum oxide }	6.04
Ferric oxide }	
Calcium oxide.....	41.96
Magnesium oxide.....	1.53
Carbon dioxide.....	34.65
Moisture.....	0.43

The burnt cement clinker contains:

	Per cent.
Silica.....	21.27
Aluminum oxide.....	6.42
Ferric oxide.....	3.18
Calcium oxide.....	66.70
Magnesium oxide.....	2.43

¹ *Ztschr. anorg. Chem.*, **21**, 70.

² Read before the Lehigh Valley Section of the American Chemical Society, in Gayley Hall, Lafayette College, Easton, Pa., November 18, 1903.

³ The writer wishes to thank Mr. Brobst, manager, and Mr. Meade, chemist of the Company, for their coöperation, and Mr. W. S. Landis, instructor in metallurgy at Lehigh University, for his assistance in making the measurements and analysis of the gases.