VOL. XXXVII. SEPTEMBER, 1915. NO. 9.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

THE ELECTROLYSIS OF SOLUTIONS OF THE RARE EARTHS. II.

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Received July 2, 1915.

In a recent number of THIS JOURNAL[1] there was described a method for the fractional separation of the rare earths by means of the electrolysis of neutral solutions of their nitrates. The present article describes results that were obtained in a further study of that method.

Dennis and Lemon electrolyzed a solution of the nitrates of various rare earths, using a cathode of mercury and an anode of platinum. They did not employ a diaphragm, and consequently it was possible that the separation of the rare earths they obtained might be ascribed to the fractional precipitation of the hydroxides of the earths by the ammonia formed by cathodic reduction of the nitric acid. To ascertain whether the rare earths could fractionally be separated by the electrolysis of solutions of their salts under such conditions as would preclude the formation of ammonia, a solution of the chlorides of the earths was subjected to electrolysis.

I. Electrolysis of a Neutral Solution of the Chlorides of the Rare Earths.

Material.—The material that was employed for this electrolysis consisted of about 1200 g. of the oxides of the yttrium group from which the

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[1] Dennis and Lemon, THIS JOURNAL, 37, 131 (1915).

cerium had been separated by chlorination, and almost all of the didymium earths had been removed by precipitation with sodium sulfate. The purified material contained neither iron nor other common elements, and its solution showed no absorption bands of neodymium.

A neutral solution of the chlorides of these earths was prepared by slowly adding the oxides to warm dilute hydrochloric acid until the oxides were in slight excess. The liquid was then heated to boiling in the presence of the excess of oxides until a test with Congo-red paper showed that all of the acid had been neutralized. The undissolved oxides were then removed by filtration, and the filtrate was diluted with distilled water until it contained an amount of the chlorides equivalent to 10% by weight of the solution in oxides of the rare earths.

Apparatus.—The cell that was used for the electrolysis was a thick-walled glass cylinder with an internal diameter of 32.5 cm. and a depth of 35 cm. A layer of mercury 1.5 cm. deep was placed in the bottom of this cylinder, a glass cup filled with mercury was set in the middle of the bottom of the cylinder, and a porous cup 5 cm. in diameter and 12 cm. high was placed upon this glass cup base. Electrical connection with the layer of mercury was made by fusing a short platinum rod through the end of a glass tube, filling the tube with mercury, and then fastening this tube in such position in a clamp that the projecting end of the platinum dipped into the mercury in the cylinder. A cylindrical carbon rod, 2 cm. in diameter and 30 cm. long, inserted in the porous cup served as anode. The chlorine gas that was liberated at the anode was carried off to the flue by fitting the top of the porous cup with a perforated rubber stopper, and blowing a current of air through the cup. The neutral solution of the chlorides of the rare earths was poured into the cell upon the layer of mercury, and this solution and the mercury were vigorously stirred throughout the electrolysis by air that was blown through three glass tubes that dipped below the surface of the mercury. Current for the electrolysis was taken from a 110 volt direct circuit through a lamp bank. An ammeter was connected in series with a cell and a voltmeter was connected across the terminals.

Procedure.—After the cell had been charged in the manner above described, the porous cup was placed upon its support in the middle of the cell, and was filled with dilute hydrochloric acid (0.1 *N*) until the level of the acid inside the cup was slightly below the surface of the solution in the cell. The carbon anode was then set in position within the cup, connections with the source of current were made, the air for stirring the mercury cathode was turned on, and the electrolysis was continued until the equivalent of about 40 g. of oxides of the earths had been precipitated at the cathode in the form of hydroxides.

The character of the hydroxides obtained in this manner is entirely different from that which results from the precipitation of a solution of the earths with an alkali hydroxide. The electrolytic precipitate is granular, and appears to possess a crystalline character, although a microscopic examination failed to show crystalline characteristics.

When the desired amount of the rare earths had been precipitated, the current was turned off, the agitation of the mercury cathode by air was discontinued, the precipitated hydroxides were allowed to settle, and the supernatant liquid was siphoned off. The precipitate and the mercury at the bottom of the cell were transferred to a separatory funnel, and the mercury was drawn off. The hydroxides were then thrown upon a Büchner funnel and were thoroughly washed with water. They were next warmed with dilute hydrochloric acid, which dissolves the hydroxides readily, but left most of the finely divided mercury undissolved. The undissolved mercury was separated by filtration, and the small amount of mercury that had passed into solution was removed by precipitation with hydrogen sulfide. The filtrate was freed from hydrogen sulfide by boiling, and the rare earths were then precipitated by oxalic acid. The oxalates were washed with hot water until free from chlorides, and were then dried. A small portion of this precipitate of the oxalates was set aside for the determination of the average atomic weight of the earths, and the remainder of the oxalates was converted to the oxides by heating in a platinum dish.

The supernatant liquid that was siphoned off from the hydroxides precipitated during the electrolysis, and the wash water from the washing of these hydroxides were united, placed in the cell, and the electrolysis was repeated until the second fractional precipitate of hydroxides of the earths was obtained. This precipitate was purified as before, and the procedure was repeated until nearly twenty fractions resulted. As the end of the fractional precipitation was approached, the voltage across the terminals of the cell rose because of the decreasing concentration of the electrolyte.

The atomic weight of each fraction was determined by the oxalate-oxide method. The absorption spectrum of each fraction was observed with a Krüss spectroscope in the manner described by Dennis and Bennett.[1] The solution employed for this purpose was prepared by dissolving 5 g. of the oxide in a slight excess of hydrochloric acid, removing the excess of acid by evaporation and diluting the solution to 25 cc. with distilled water. Whenever Congo-red paper showed there was still an excess of acid, the evaporation was repeated until the free acid was removed.

The details of this series of electrolyses are given in Table I. The atomic weights of the various fractions and the relative intensities of dis-

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[1] THIS JOURNAL, 34, 7 (1912).

tinctive absorption bands of the different colored earths in the fractions are plotted in Plate I. The spacing of the fractions along the axis of abscissas is based upon the actual weights of the several fractions.

TABLE I.—ORIGINAL ATOMIC WEIGHT, 106.6.

Fraction No.	Atomic weights.	Weight oxides (g.).	Volts.	Ampere-hours.	Remarks.
1	121.98	26	8.4	100	Oxalates pink, color deepened through No. 4, after which it faded. The oxalates of fractions 19 and 20 were almost white. The oxides were of a brownish yellow color which deepened to fraction 4 and then gradually became lighter.
2	123.79	57	8.5	154	
3	122.12	42	8.4	114	
4	121.16	54	8.0	121	
5	115.55	36	8.0	87	
6	113.37	55	8.2	150	
7	110.71	56	7.5	155	
8	108.69	46	9.2	143	
9	106.74	40	8.0	141	
10	104.28	44	8.5	129	
11	103.11	40	7.5	109	
12	97.09	30	8.0	97	
13	98.87	40	10.1	164	
14	99.03	38	9.0	132	
15	98.63	36	8.5	110	
16	98.27	25	10.0	170	
17	96.53	40	10.5	137	
18	96.12	55	10.9	152	
19	94.28	50	11.0	153	
20	93.16	41	13.0	179	

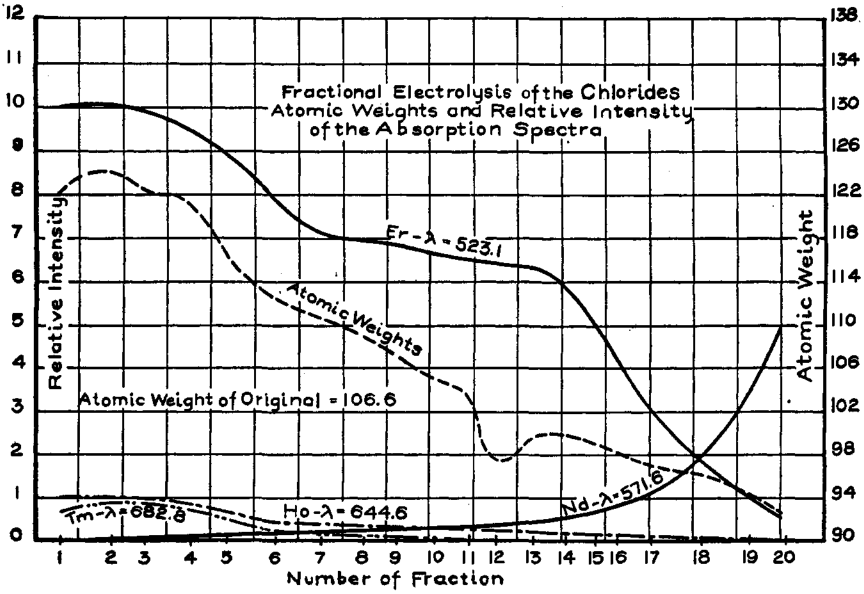

Plate I.

The results obtained in the above fractional electrolysis of a neutral solution of the chlorides of the rare earths demonstrate that the earths of the yttrium group can fractionally be separated under conditions that preclude the formation of ammonia or other basic precipitant. The absorption spectra of the fractions show that the colored earths, erbium, holmium and thulium, are concentrated in the early fractions. Neodymium, which was present in the original solution in such slight amount that its absorption bands were not discernible, was concentrated in the later fractions. The low atomic weights of the last four fractions show that yttrium is precipitated chiefly in the later fractions.

The voltage that was employed in the electrolysis of the chlorides was undoubtedly considerably higher than the decomposition voltage of the salts of the various rare earths that were present. The question naturally arose as to whether the decomposition voltages of the salts of the rare earths might be utilized in obtaining a sharper separation of the different earths than seemed to be possible with higher voltage. To obtain information upon this point, the following experiments were made.

II. Decomposition Voltages of Solutions of Salts of the Rare Earths.[1]

The solution of the rare earth under examination was placed in a small U-tube of 9 cc. capacity, and 8 mm. internal diameter. Dipping into the solution in the two arms of this tube were two terminals of platinum wire. These were cleaned with care, and heated to redness before each determination. These terminals were connected through a galvanometer and switch to a slide wire-resistance, by means of which a gradual change of potential from zero to three volts could be obtained. This potential difference was accurately measured by means of a standard voltmeter that was sensitive to 0.002 volt. The current flowing through the cell was measured by the deflection of a galvanometer which was observed through a telescope. The resistance of the galvanometer was so small that the error caused by placing it in series with the cell was negligible. That such was the case is shown by the fact that when a potential difference so slight that it could not be read on the voltmeter was established between the terminals, with the cell cut out, the deflection of the galvanometer was beyond its highest scale reading.

The solutions of the rare earths that were employed in these measurements were prepared by precipitating the hydroxides of the earths with ammonium hydroxide, washing the precipitate on a Büchner funnel with hot water until it was free from ammonium salts, and then bringing the precipitated hydroxide into contact with an amount of the acid that was just insufficient to dissolve all of the precipitate. The solution was boiled for several minutes with the excess of the hydroxide to ensure

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[1] Mr. A. B. Ray, who also is carrying on investigation in this field, collaborated in the determination of these decomposition voltages.

complete neutralization of the acid. The residual precipitate was then removed by filtration. The concentration of the solution was determined by analysis, and it was then diluted with water until it was of exactly normal strength.

In this manner normal solutions of the nitrates of thorium, lanthanum, cerium and neodymium and of the chlorides of thorium and cerium were prepared.

The decomposition voltage of one of these solutions was determined by placing the solution in a U-tube, making connections in the manner above described, and then gradually raising the potential difference across

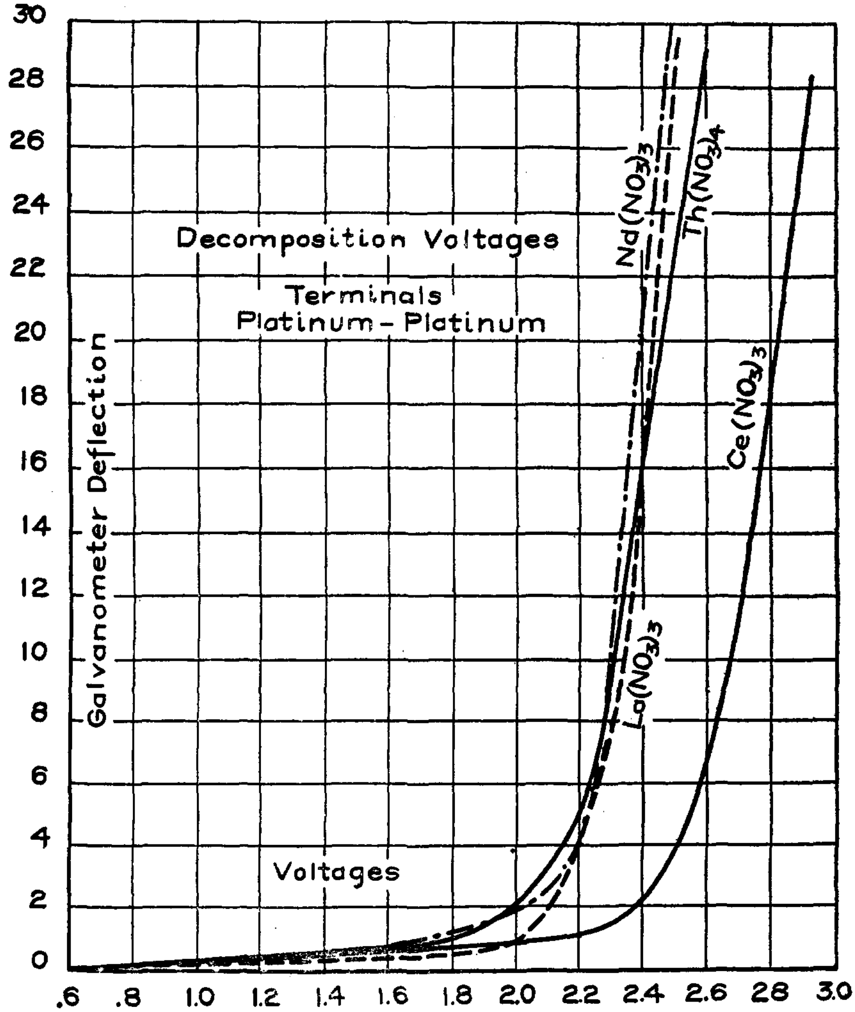

Plate II.

the cell by increasing the external resistance. With each change of potential, connection with the galvanometer was made by throwing in the switch, and the reading of the instrument was taken after the initial momentary deflection had subsided. As the decomposition value, which had to be located approximately beforehand, was approached, very small increments in potential were taken, which gave a large number of points in this region. From the readings thus obtained curves were plotted, using potential differences as abscissas and the galvanometer deflections as ordinates. The point at which the curve shows a decided break is the decomposition value. Sometimes the curve, after passing this point,

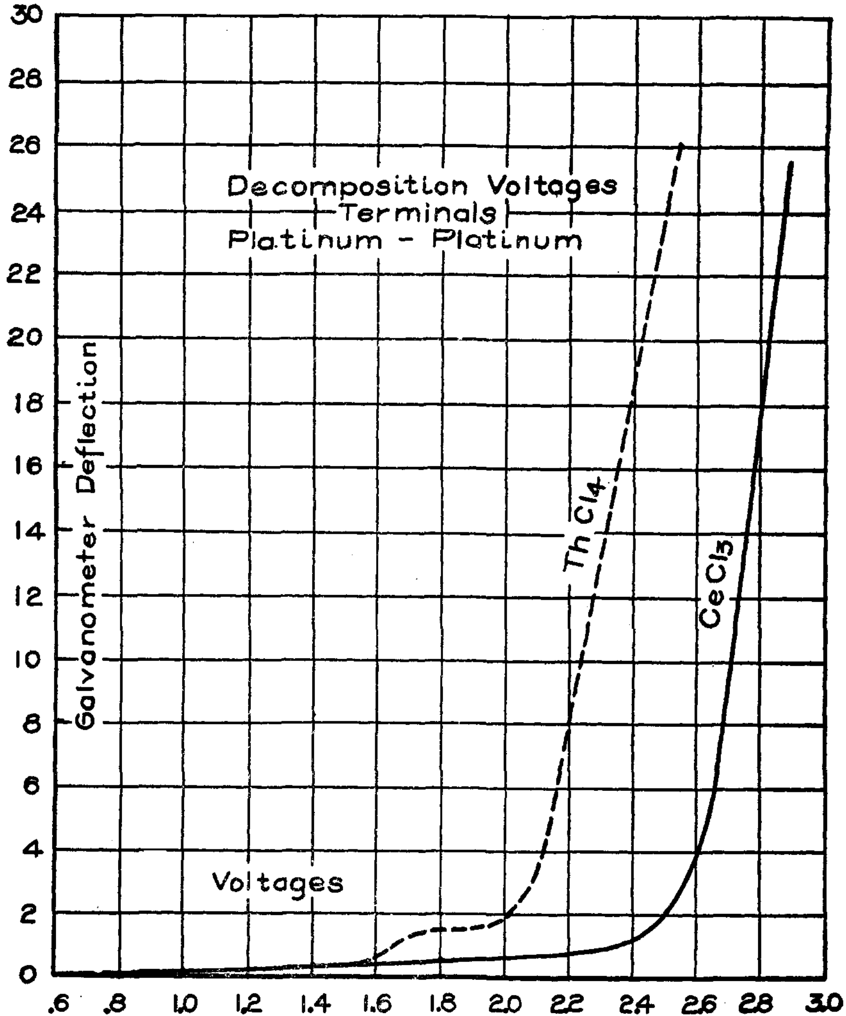

Plate III.

showed peculiar behavior in that it did not rise in a straight line. This was probably due to slight electrolytic decomposition and deposition at one or the other of the terminals. In every case, however, the break came at the same point.

The results that were obtained in the measurement of the decomposition voltages of neutral solutions of the nitrates of thorium, neodymium, lanthanum and cerium, using terminals of platinum, which are plotted in Plate II, were as follows:

TABLE II.

	Volts.		Volts.
Thorium nitrate	1.87	Lanthanum nitrate	2.05
Neodymium nitrate	2.03	Cerous nitrate	2.18

The decomposition voltages of neutral solutions of the chlorides of thorium and cerium with terminals of platinum are shown in Plate III, and were:

TABLE III.

	Volts.
Thorium chloride	1.94
Cerous chloride	2.36

It was further thought desirable to ascertain the decomposition values of some of these salts under conditions that simulated as closely as possible those pertaining in the fractional electrolysis with an agitated mercury cathode.

The container that was here employed consisted of a glass tube with a platinum wire sealed through the closed lower end and a side arm sealed to the tube a short distance above the lower end and bent upward. Mercury was poured into the larger tube until the level of the metal reached nearly to the opening of the side tube, and the main tube and side arm were then filled nearly to the top with the solution under examination. The mercury was kept in agitation by bubbling air through it, the air being passed in through a small tube inserted from above. A platinum wire extending down a short distance into the solution in the side arm served as anode. The results that were obtained with this apparatus are plotted in Plate IV, and were as follows:

TABLE IV.

	Volts.
Thorium nitrate	1.06
Cerous nitrate	1.10
Neodymium nitrate	1.24

These measurements show that the decomposition voltages of solutions of such salts of the rare earths as were here employed lie quite close together, and usually increase with the increase of the basicity of the earth. The decomposition voltages of the nitrates of thorium, neodymium and cerium, when a mercury cathode and platinum anode are employed, are considerably lower than the values obtained between platinum terminals, but the differences are no more pronounced. From these results it is apparent that a sharp separation of the different earths one from another cannot easily be effected by adjustment of the voltage.

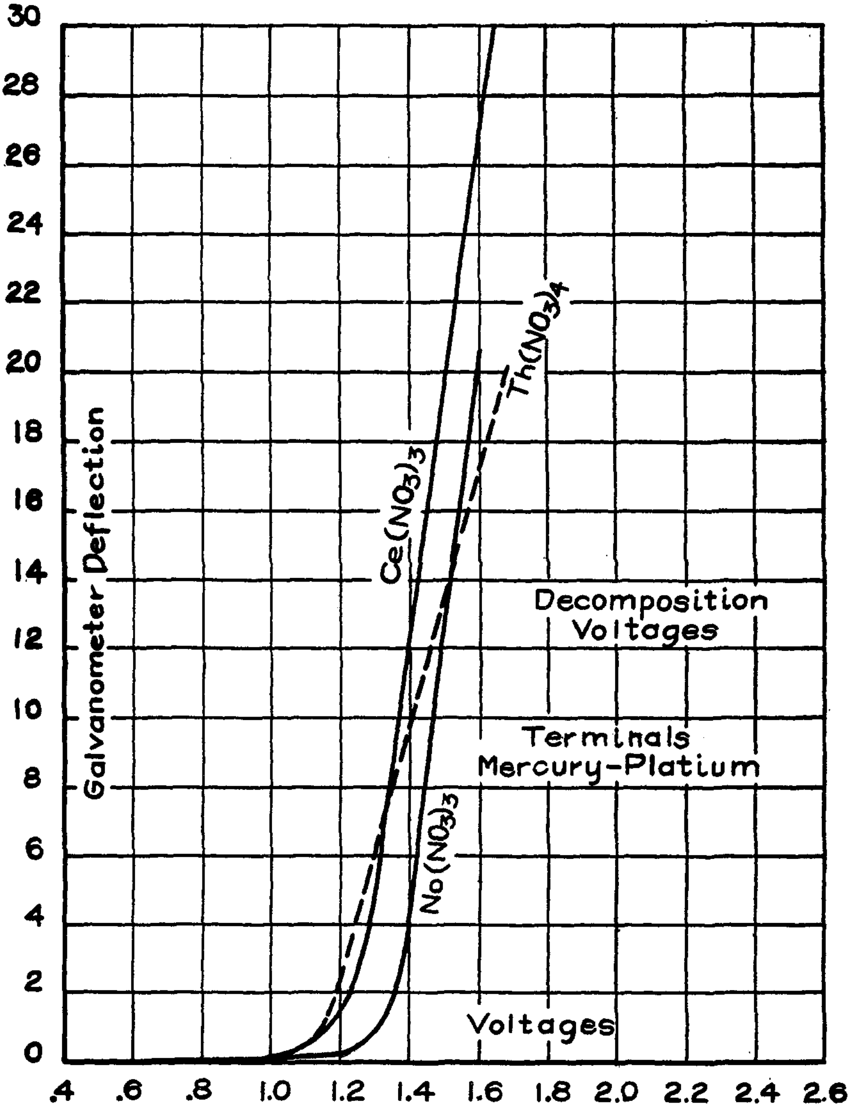

Plate IV.

Moreover, the precipitation of the hydroxides of the earths at these low voltages is so slow as to, of itself, preclude the utilization of these decomposition values in the rapid fractionation of comparatively large amounts of the rare earths. For these reasons recourse was again had to the fractional electrolysis of solutions at voltages considerably above the decomposition values. Preliminary experiments having shown that no ammonia is formed when a solution of the nitrates of the earths is electrolyzed with a mercury cathode, and with a platinum anode that is placed in a porous cup, this modification of the procedure was next subjected to examination.

III. Electrolysis of a Neutral Solution of the Nitrates of the Rare Earths, Using a Diaphragm.

The oxides of the rare earths that were obtained in the twenty fractions of the electrolysis of the chlorides were united and were boiled with an amount of nitric acid that was not quite sufficient to dissolve them completely. The excess of oxides was removed by filtration and the neutral nitrate solution, which contained about 700 g. of the oxides, was diluted to 10 liters. This volume of the solution was maintained throughout the electrolysis. A sheet of platinum 5 cm. square was used as anode. In other respects the cell was exactly the same as that used in the electrolysis of the chlorides. The nitric acid that accumulated in the anode cup was removed by allowing distilled water to drop into the cup from a separatory funnel, and keeping the height of liquid in the cup constant by means of a siphon. A current of 5 amperes was used. The voltage varied from 7.5 to 18. The conduct of the electrolysis, the treatment of the fractions and the determination of the atomic weights of the fractions were performed in exactly the same manner as in the fractionation of the chlorides.

The fractional electrolysis of this solution of the nitrates, using a diaphragm, was found to precipitate the hydroxides of the earths about four times as rapidly as in the chloride electrolysis. It was possible that the hydrogen set free at the cathode might reduce some of the nitric acid to ammonia, as was found to be the case when no diaphragm was employed. Careful qualitative tests of the solution after the ninth fraction had been removed failed, however, to show the presence of a trace of ammonia. The results of this fractional electrolysis of the nitrates are shown in Plate V and Table V.

TABLE V.—ORIGINAL ATOMIC WEIGHT, 106.6.

Fraction No.	Atomic weights.	Weight oxides (g.).	Volts.	Ampere hours.	Remarks.
1	123.84	67	7.45	83.68	Color of oxalates was pink in first fraction, becoming gradually lighter; last three fractions were pure white.
2	120.85	75	6.90	83.9	
3	114.14	80	7.33	107.9	
4	108.08	85	7.25	100.7	
5	104.75	77	7.37	88.43	
6	101.65	92	8.00	99.9	
7	94.95	72	10.00	101.7	Contained no cerium.
8	98.94	60	12.75	75.68	Contained cerium.
9	91.63	40	18.00	62.27	Very slight trace of cerium.
10	94.43	16	Precipitated by oxalic acid		

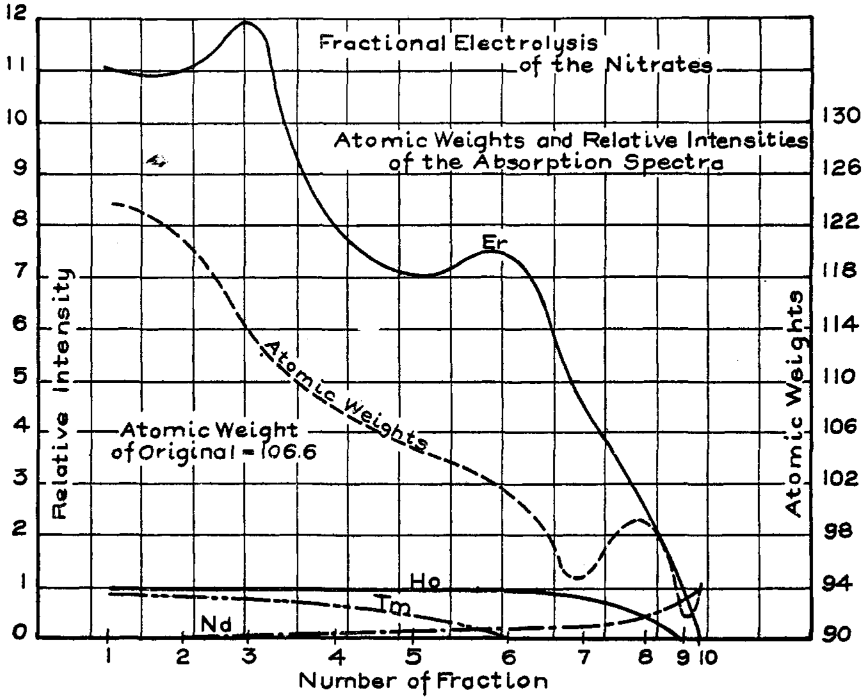

Plate V.

It will be noted that in this series of electrolyses the colored earths erbium, holmium, and thulium were present in preponderating amount in the first four fractions, and were probably accompanied by considerable amounts of yttrium, as is indicated by the relatively low average atomic weight of the earths in these fractions. The last fractions, however, consist chiefly of yttrium, mixed with small amounts of cerium and neodymium that also were concentrated at this point. The method yields, therefore, in the first fractions a rapid concentration of erbium that is nearly entirely free from the didymium group; and, in the later fractions, yttrium that is quite free from the colored earths of the erbium group, but is accompanied by any of the didymium group that may have been present in the original solution. It is interesting to note that the later fractions contained detectable amounts of cerium, although qualitative tests of the original solution failed there to disclose the presence of this element. To obtain further indication as to the efficiency of the method in the separation of the earths of the erbium and yttrium groups, the first four fractions given in Table V were combined, and were converted into a neutral solution of the nitrates. The weight of the oxides in the solution was about 220 g., the volume of the solution was 2300 cc., and the average atomic weight of the earths was 116.54. A cell measuring 21 cm. in diameter and 20 cm. in height was used for the electrolysis. In other respects the same apparatus was employed as before. Six fractions were obtained by electrolytic precipitation. The liquid remaining after the last fraction had been removed possessed high resistance and gave no precipitate with oxalic acid. The results of this fractional electrolysis are shown in Plate VI and Table VI. These results again demonstrate the efficiency of the method in speedily concentrating erbium and yttrium at opposite ends of the electrolytic fractionation, and in the concentration of the erbium earths practically free from the didymium group.

TABLE VI.—ORIGINAL ATOMIC WEIGHT, 116.54.

Fraction No.	Atomic weights.	Weight oxides (g.).	Volts.	Ampere-hours.	Remarks.
1	137.2	30	6.7	37	Oxalates of first three fractions were a deep pink, fading gradually.
2	129.04	48	6.2	45	
3	119.76	45	6.0	45	
4	111.61	38	6.9	47	Fraction 6 was nearly white.
5	99.58	35	11.0	42	
6	95.08	15	29.0	25	

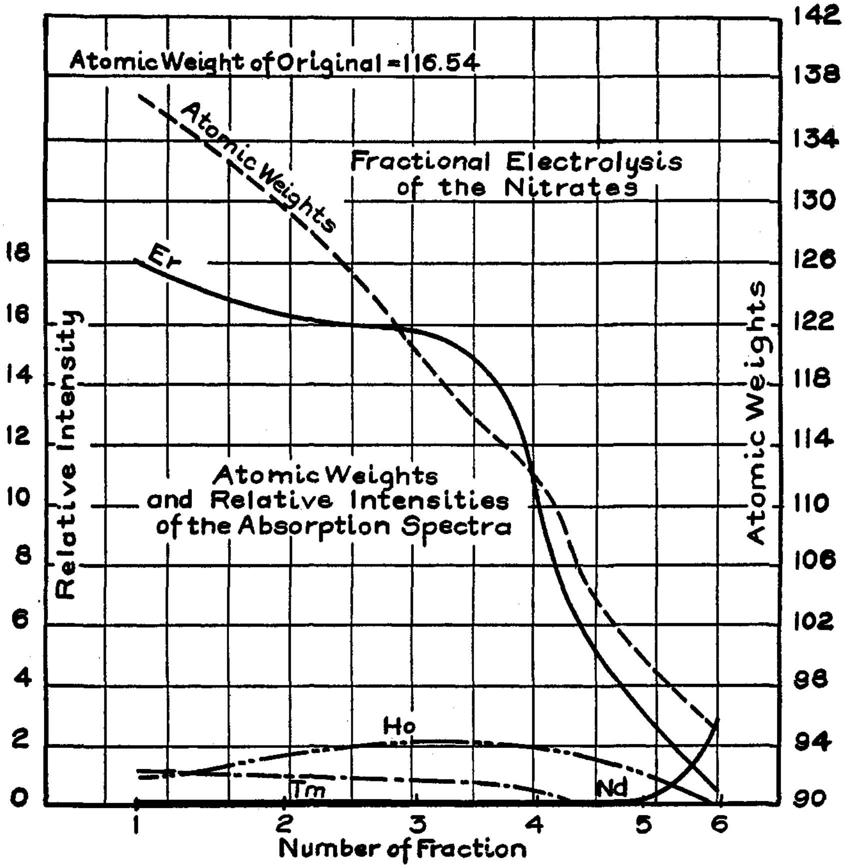

Plate VI.

The eighth fraction, Table V, Plate V, showed a sudden rise in atomic weight, which was probably due to the concentration of neodymium in the later fractions of that run. With a view to ascertaining whether the method of fractional electrolysis might profitably be utilized in separating neodymium (and its group elements) from the erbium group, even when the amount of material is comparatively small, the oxides constituting the eighth fraction were converted to a neutral nitrate solution that contained about 45 g. of rare earth oxides in 600 cc. of solution and this was fractionally electrolyzed in the same manner as before. Six fractions were obtained. The results given in Table VII and Plate VII again demonstrate the ease and rapidity of the separation of neodymium from yttrium and erbium.

TABLE VII.—ORIGINAL ATOMIC WEIGHT, 98.94.

Fraction No.	Atomic weight.	Weight oxides (g.).	Volts.	Ampere-hours.	Remarks.
1	97.67	8.0	6.8	9.6	The oxalates were pink,
2	97.11	9.5	8.2	9.6	fading rather rapidly.
3	94.36	8.5	8.0	9.6	The oxides were light
4	94.04	9.0	11.6	10.5	yellowish brown, and
5	93.24	6.0	19.0	8.4	about the same color.
6	104.27	3.0	Precipitated by oxalic acid		Very dark brown oxide.

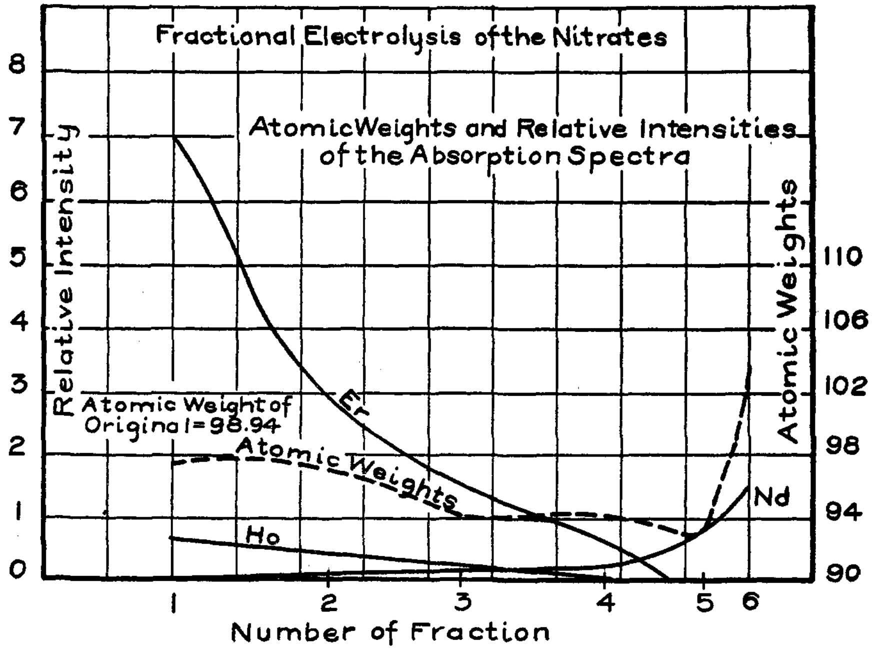

Plate VII.

The separation of the rare earths by the fractional precipitation of their hydroxides upon electrolysis of solutions of their salts at voltages considerably higher than the decomposition values of the salts is probably due to the action of the hydroxyl ions, concentrated near the cathode, upon earths of different basicities. The hydroxide of the weakest base will first tend to form, and if the deposition of this insoluble hydroxide upon the surface of the cathode be prevented, and if the electrolyte be rapidly stirred throughout the electrolysis, a progressive precipitation of the hydroxides of the earths, in the order of their basicities, will result.

Summary.

1. The decomposition voltages of several neutral, normal solutions of salts of the rare earths were determined. The values were found to lie close together and to be in the neighborhood of two volts.

2. Fractional electrolysis of a solution of the chlorides of the yttrium earths yielded rapid concentration of the colored earths in the earlier fractions, and of yttrium in the later fractions. A small amount of neodymium that was present appeared in the last fractions.

3. Fractional electrolysis, with a diaphragm, of a solution of the nitrates of these earths showed concentration of the earths similar to that obtained in the electrolysis of the chlorides. The rate of precipitation of the hydroxides of the rare earths from the nitrate solution was, however, four times as rapid as from the chloride solutions. No ammonium salts were present in the electrolyte at the close of the run.

4. Fractional electrolysis of a solution high in erbium, holmium, thulium and yttrium gave, in a series of six fractions, no appreciable separation of the first three earths one from another, but rapidly separated the three from yttrium.

5. In the fractional electrolysis of solutions of certain salts of the rare earths, the hydroxides of the earths are precipitated, under the conditions here described, in the order of the basicities of the earths. Rapid concentration of certain groups of earths is attained in short series of fractions.

The method is being further studied in this laboratory.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE EQUILIBRIUM BETWEEN CARBON OXYSULFIDE, CARBON MONOXIDE AND SULFUR.

BY GILBERT N. LEWIS AND WILLIAM N. LACEY.

Received May 31, 1915.

The reduction of sulfur dioxide to sulfur by carbon monoxide is a reaction of great technical, as well as scientific, importance. From the free energy of this reaction the free energy of formation of sulfur dioxide could be obtained immediately. Any attempt, however, to determine