(*d*) The solubility is easily determined with accuracy.

Preliminary determinations of the solubility of the dekahydrate of sodium sulfate have been made at about 15°, 17.5°, 20° and 25°, referred to the Paris hydrogen scale through standard Baudin thermometers.

Adequate constants for a usual empirical equation have been derived connecting temperature and solubility over this range, and the values at degree intervals have been computed.

The Baudin scale as given by these two thermometers does not exactly correspond with the platinum scale in this region. For the present we cannot explain the divergence, which diminishes the certainty of the results, but does not entirely destroy their usefulness.

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

THE ELECTROLYSIS OF SOLUTIONS OF THE RARE EARTHS. III.[1]

BY L. M. DENNIS AND A. B. RAY.

Received November 12, 1917.

I. Electrolysis of Neutral Solutions of the Nitrates of the Rare Earths.

In a previous article upon this subject,[1] the fractional precipitation and separation of the rare earths by the electrolysis of aqueous solutions of their salts at voltages considerably higher than the decomposition values of these compounds were explained as probably due to the action of the hydroxyl ions, concentrated near the cathode, upon earths of different basicities, the hydroxide of the weakest base being precipitated first. If this explanation is correct, it follows that the selective precipitation of the hydroxides in the order of the basicities of the earths should proceed more evenly, and the separation of the earths be more complete, as the vigor with which the electrolyte is stirred is increased, because this would bring the hydroxyl ions more frequently into contact with the weakest bases and would thus tend to lessen the simultaneous precipitation of hydroxides of earths of different basicity.

With a view to gaining experimental evidence upon this point, two portions of a solution of certain rare earths were electrolyzed under identical conditions except that one solution was vigorously stirred, whereas the other was agitated just rapidly enough to keep the surface of the mercury cathode free from adherent deposit of the precipitated hydroxides.[3]

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[1] This article is a summary of a portion of the thesis presented to the Faculty of the Graduate School of Cornell University by A. B. Ray in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Dennis and van der Meulen, THIS JOURNAL, 37, 1963 (1915).

[3] For detailed description of the apparatus that was used for the electrolysis see Dennis and van der Meulen, *Loc. cit.*

The mixture of rare earths that was employed contained the yttrium and erbium groups and a trace of neodymium, but was free from thorium, cerium and the more common elements. The average atomic weight of the earths in the mixture was 106.95. A neutral solution of the nitrates of these earths was prepared and was diluted with water until it contained 34 g. of oxides to the liter. Two portions of this solution, of five liters each, were used for the electrolyses. The containers for the solutions were glass cylinders about 20 cm. in diameter. A layer of mercury about 1.5 cm. deep, which served as cathode, was placed in each cylinder, and this was covered with five liters of the solution of the earths. A porous cup 6 cm. in diameter and 15 cm. deep was suspended in the electrolyte and was filled to within one cm. of the height of the outer solution with a 10% solution of nitric acid. The concentration of the acid in the cup was kept approximately constant during the electrolysis by fitting the cup with a constant-level siphon, and slowly dropping distilled water into the cup during the run. Agitation of the mercury cathode and of the solution was effected by air blown through glass tubes that dipped below the surface of the mercury. One cell was provided with two such air jets, the other with twelve. A sheet of platinum, inserted in the porous cup, served as anode.

The electrolysis was begun immediately after the porous cups were put in place and the anodes inserted. A current of three amperes was used and the electrolysis was continued until the amount of the hydroxides desired for the fraction had been precipitated.

The hydroxides precipitated in the two cells were distinctly different in character. Where the stirring had been slight, the hydroxides were granular and were easily collected on a filter. The precipitate in the cell in which the stirring had been vigorous was very finely divided and could rapidly be separated from the liquid only by filtration through a pad of macerated filter paper with the aid of suction. Moreover, the precipitated hydroxides from this second cell were dark in color because of the presence of finely divided mercury. We observed no indication of the formation of an amalgam of the rare earths, thus confirming the statement of Kettembeil.[1]

When an amount of the rare earth hydroxides desired for one fraction had been precipitated, the current and air blast were turned off, and the porous cups were removed from the cells. The solution in each cell was siphoned off and was then filtered on a Büchner funnel to remove the suspended hydroxides. The mercury and the hydroxides still remaining in the cell were transferred to a separatory funnel, the mercury was drawn off, and the hydroxides were then brought upon the filter. The precipitate was thoroughly washed with water and was then treated with

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[1] *Z. anorg. Chem.*, **38**, 213 (1904).

warm 2 *N* hydrochloric acid which quickly dissolved the hydroxides but left most of the finely divided mercury undissolved. Hydrogen sulfide was passed through the filtrate to remove the slight amount of mercury that had been dissolved, the solution was again filtered, the hydrogen sulfide was removed by boiling, and the rare earths were precipitated by oxalic acid. The oxalates were washed with hot water until free from chlorides and were then dried at 100°.

The residual solution from which the precipitated hydroxide has thus been removed, together with the wash water which had been evaporated to small bulk, were returned to the cell and the electrolysis was continued until a second fraction of the rare earth hydroxides had been precipitated. This precipitate was removed and purified as before, and electrolysis was repeated until nine fractions had been obtained. The rare earths still remaining in solution were then precipitated by oxalic acid.

The atomic weight of each fraction was determined by the oxalate-oxide method. The absorption spectrum of each fraction was studied with the aid of a Krüss spectroscope, and the relative intensities of distinctive bands were approximated by the method of Dennis and Bennett.[1] A neutral solution of the chlorides of the earths, containing 5 g. of the oxides in 25 cc., was employed in each spectroscopic examination.

The data obtained in these two series of electrolyses are given in Tables I and II.

TABLE I.

Cathode area—452.4 sq. cm.

Atomic weight of original mixture—106.95.

Catholyte stirred vigorously by means of 12 air jets.

Number of fraction.	Atomic weight.	Weight of oxides (g.).	Ampere hours.	Volts.
1	121.84	19	34.5	7
2	114.80	18.68	27	7
3	112.24	22.16	27	7
4	108.77	17.12	22	7.4
5	105.85	14.42	22	7.6
6	103.15	10.06	18.5	8
7	100.82	12.32	19	9
8	97.58	11.80	22	11
9	94.68	14.50	22	15
10	95.58	2.02	Pptd. by oxalic acid	

The atomic weights of the various fractions and the relative intensities of the distinctive absorption bands of the "colored" earths in the fractions are plotted in Plates I and II. The spacing of the fractions along the axis of abscissas is based upon the actual weights of the several fractions.

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

TABLE II.

Cathode area—452.4 sq. cm.
Atomic weight of original mixture—106.95.
Catholyte slightly stirred by means of two air jets.

Number of fraction.	Atomic weight.	Weight of oxides (g.).	Ampere hours.	Volts.
1	119.61	25.56	34.5	7
2	112.27	25.20	27	7
3	111.42	19.44	27	7
4	105.85	23.30	22	7.4
5	105.22	17.94	22	7.8
6	101.21	13.56	18.5	8.2
7	100.20	13.26	19	9
8	97.10	13.98	22	11
9	96.00	10.36	22	15
10	98.20	1.54	Pptd. by oxalic acid	

Comparing the results of the two series of electrolyses it will be noted that as the vigor of stirring of the catholyte is increased there results a somewhat more rapid segregation of the earths of higher atomic weights in the first fractions and a better concentration of the earths of lowest atomic weight (chiefly yttrium) in the last fractions. Vigorous stirring also accelerates the precipitation of erbium, holmium and thulium, which results in a higher concentration of neodymium (and yttrium) in the last fractions. A third series of electrolyses in which the stirring was still more rapid showed further accentuation of the differences.

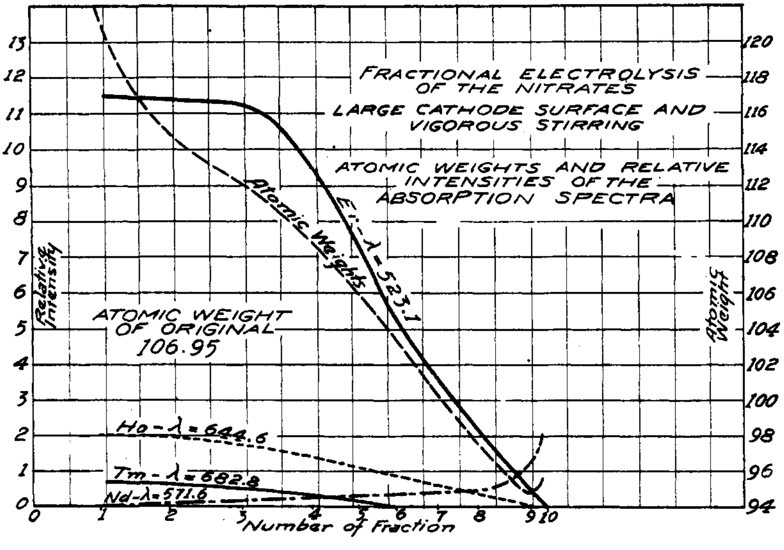

Plate I.

These results show, therefore, that when a neutral nitrate solution of the rare earths here indicated is fractionally electrolyzed with a diaphragm in the manner described, the hydroxides of the earths are precipitated in the order of their basicities,[1] and their separation is the more complete the more vigorously the mercury cathode and the catholyte are stirred.

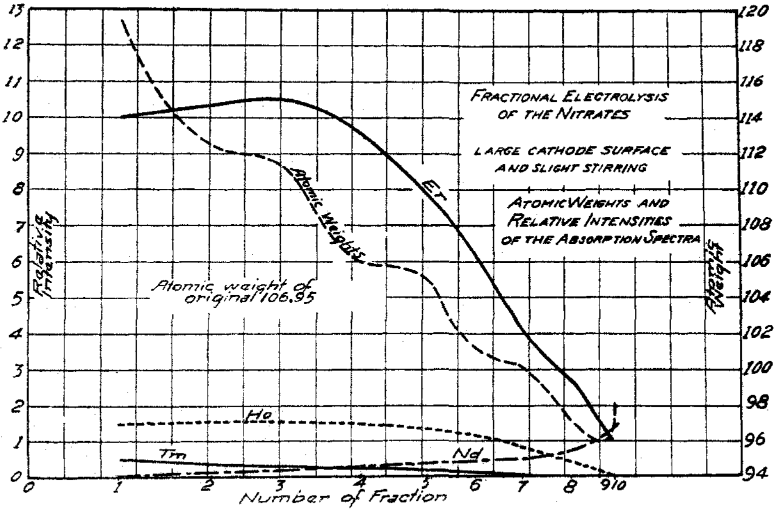

Plate II.

II. Electrolysis of Neutral Solutions of the Nitrates of the Rare Earths and Thorium Nitrate.

The weakly basic character of thorium seemed to render it probable that electrolysis of a solution containing thorium nitrate and nitrates of the rare earths might result in the rapid concentration of thorium in the early fractions. Thorium for commercial uses is now extracted on a large scale (about 300,000 kg. of thorium nitrate per annum) from monazite. For this reason the electrolytic separation of thorium from the earths with which it is associated in monazite, possessing as it does a practical interest, was investigated. The mixture of the rare earths was prepared from the by-product of the technical separation of thorium from monazite. This material was carefully purified and was freed from cerium and thorium. The earths were converted to the oxides, and from this mixture of the oxides a neutral solution of the nitrates was prepared. The concentration of the solution was then determined by precipitation with oxalic acid and ignition of the oxalate to oxide.

A clear, neutral solution of thorium nitrate was prepared by adding pure, moist thorium hydroxide to cold, dilute nitric acid until the hydroxide was in excess, and then allowing the material to stand until a test with Congo-red paper showed the absence of free acid. The solution

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[1] R. J. Meyer, Abegg's "Handbuch der anorganischen Chemie," 3, 147.

was then separated from the undissolved hydroxide, and its concentration was determined.

The electrolysis was conducted in the manner already described, very vigorous stirring of the catholyte and mercury cathode being employed.

(*a*) **Electrolysis of Solutions of Thorium Nitrate.**—Electrolyses of solutions of thorium nitrate alone were first made to ascertain whether the precipitation of the hydroxide may most satisfactorily be made from cool or from hot solution. The electrolyses were made in two cells, connected in series. The solution in one cell was kept at 22° during the run; that in the second cell at about 90°. A dilute solution of thorium nitrate (1.3 g. ThO_2 in 100 cc.) was placed in each cell. The electrolysis was conducted as before described, a current of two amperes being employed. The voltage across the cold cell rose from 6 volts at the beginning to 40 volts at the end of the run; that across the warm cell, from 5 volts to 30 volts. The current required for practically complete precipitation in the cold cell was 5 ampere hours; in the warm cell, 4.75 ampere hours. The current required by theory for complete precipitation was 4 ampere hours. This showed a current efficiency in the cold cell of 80%; in the warm cell, of 84.2%. The precipitate of thorium hydroxide in the cool cell was granular, was easily filtered and washed, and contained almost no finely divided mercury. The thorium hydroxide thrown down in the warm cell was flocculent, contained much finely divided mercury, and was filtered and washed with difficulty.

From these results it was apparent that the electrolysis of a solution of thorium nitrate operates most satisfactorily when conducted at about room temperature.

To determine the influence of the concentration of the electrolyte upon the character of the precipitate, three solutions of thorium nitrate containing 0.5%, 5%, and 20% of thorium dioxide, respectively, were electrolyzed in small cells of about 300 cc. capacity. The thorium hydroxide precipitated from the 20% solution in very finely divided form resembling a colloidal solution. The character of the precipitates in the other two cells showed that as the concentration of the solution is lowered (down to 0.5%) the granular form of the hydroxide becomes more pronounced. Because of these results, the later electrolyses of mixtures of thorium nitrate and the nitrates of the rare earths were made with solutions that contained about 0.5 g. thorium dioxide per 100 cc.

(*b*) **Electrolysis of Solutions Containing Thorium Nitrate and Nitrates of the Rare Earths.**—A solution containing, in 3.5 liters, 14.72 g. of thorium oxide and 85 g. of the oxides of the rare earths (av. at. wt. 140.5) was electrolyzed with a current of one ampere. The mercury cathode was vigorously stirred during the electrolysis, and the concentration of the acid in the porous cup was kept practically constant. At the end of six hours, the electrolysis was interrupted and the precipitated hydroxides were collected and purified in the manner already described. The hydroxides were then dissolved in 2 *N* nitric acid, an excess of acid being avoided. To this solution there was added one-fifth of its volume of a concentrated solution of ammonium nitrate,[1] the solution was then heated to from 60–80°, and an excess of 10% hydrogen peroxide was added. Thorium is thus quantitatively precipitated as the hydrated peroxide, the rare earths remaining in solution.[2] The precipitate was collected on a filter, thoroughly washed, and then dissolved in 2 *N* hydrochloric acid. The solution was diluted to one liter and 25 cc. portions were precipitated by ammonium hydroxide, and the thorium hydroxide ignited to the oxide, and weighed.

The filtrate from the first thorium precipitation by hydrogen peroxide was diluted to 500 cc., 25 cc. portions were precipitated by oxalic acid, and the oxalates of the rare earths were ignited to oxides and weighed.

The filtrate from the first fractional precipitate of the hydroxide, together with the wash water, were returned to the cell and electrolyzed as before. The procedure was again repeated, three fractional precipitations in all being made. The results are set forth in the following table:

TABLE III.

Volume of electrolyte, 3.5 liters. Total amount ThO_2 and R_2O_3 present in the solution = 99.72 g., of which ThO_2 = 14.72 g. (14.76%), R_2O_3 = 85.00 g. (85.24%). Average atomic weight of rare earths = 140.5. Current = one ampere.

Fraction number.	Ampere hours.	Wt. in g.		Per cent.	
		ThO_2.	R_2O_3.	ThO_2.	R_2O_3.
1	4	5.048	1.372	78.63	21.37
2	6	3.94	7.40	34.75	65.25
3	7	2.22	8.88	20.0	80.0

The results show that fractional electrolysis effects a marked concentration of thorium in the early fractions, from about 15% in the original mixture to over 78% in the first fraction, and nearly 35% in the second fraction.

Another electrolysis was run to determine to what degree thorium would be concentrated in the first fraction when it was associated with the monazite earths in approximately the ratio in which it occurs in that mineral. A neutral solution of the nitrates containing 5.95 g. of thorium oxide and 112.85 g. of the rare earth oxides (av. at. wt. = 140.5) was diluted to 6.25 liters and electrolyzed as before with a current of one ampere.

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[1] Benz, *Z. angew. Chem.*, **15**, 303 (1902).

[2] Meyer and Hauser, "Die Analyse der seltenen Erden und der Erdsäuren," pp. 250–251.

TABLE IV.

Fraction number.	Ampere hours.	Wt. in g.		Per cent.	
		ThO_2.	R_2O_3.	ThO_2.	R_2O_3.
1.............	3	1.53	1.44	52	48

From these results it is seen that a single fractional electrolysis of three hours' duration precipitates nearly 26% of the thorium present and that the precipitated hydroxides contain 52% of ThO_2 as against 5% in the original mixture.

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[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE PRECIPITATION OF COLLOIDAL GOLD AND PLATINUM ON METALLIC SURFACES.

BY ELLWOOD B. SPEAR AND KENNETH D. KAHN.

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In this article we submit experimental evidence to show that when colloidal gold or platinum is precipitated by metallic surfaces the most active metals are the most effective, that is, the more electropositive the metal is toward the hydrogen electrode the shorter will be the time required for the complete precipitation of the colloid. The evidence also shows that some of the metal, of which the surface is composed dissolves, is adsorbed by the colloidal particles, and is consequently carried down with the colloid. The precipitation of the colloid by metallic plates is therefore quite analogous to that produced by the addition of an electrolyte.

Our attention was directed to this work through an article by M. Phillippson[1] in which he stated that colloidal silver is precipitated by zinc plates but not by plates of gold or platinum. Phillippson was unable to form any definite conclusions relative to the mechanism of the precipitation, although he surmised that the position of the precipitating agent in the electrode potential series was a vital factor. This we have shown to be correct. Phillippson also suggested that the relation of the activity of the precipitating metal to that of the colloidal metal might have a deciding influence. For example, because copper is more active than silver a plate of copper could precipitate colloidal silver, but a silver plate could not precipitate colloidal copper. From the results of our investigations there would seem to be no necessity for making such an assumption in order to explain the precipitation.

Preparation of the Colloidal Solutions.

The water used in the preparation of the colloidal solutions was that employed for conductivity purposes in the Research Laboratory of

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[1] *Kolloid Z.*, **11**, 49 (1912).