VOL. XXXVI. MAY, 1914 NO. 5.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

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

HYDROLYSIS OF RARE EARTH SULFATES.

BY S. H. KATZ AND C. JAMES.

Received March 5, 1914.

Stock[1] determined aluminum by precipitating the hydroxide with potassium iodide and potassium iodate according to the equation, $Al(SO_4)_3 + 5KI + KIO_3 + 3H_2O = Al(OH)_3 + 3K_2SO_4 + 3I_2$. The hydroxide was then ignited and weighed. He found it was advantageous to have sodium thiosulfate, or excess potassium iodide, present during reaction to prevent precipitation of solid iodine, which, he said, interfered with subsequent working with the aluminum hydroxide.

Moody[2] found that the quantity of iodine, liberated by Stock's reaction with aluminum sulfate, was only about two-thirds of the theoretical amount. When this iodine was removed with sodium thiosulfate, more was liberated. When the solution of potassium iodide, potassium iodate and aluminum sulfate was heated in a current of hydrogen, or steam, for fifteen to twenty minutes and the volatilized iodine collected in potassium iodide solution, titration of the iodine in the receiver and that left in the distilling flask furnished a means of estimating aluminum. Later Moody[3] found that stannic salts and those of nickel, cobalt and chromium reacted quantitatively, and, as in the case of aluminum, the liberated iodine, when

---

[1] *Compt. rend.*, **130**, 175 (1914).

[2] *Am. J. Sci.*, **20**, 181 (1905).

[3] *Ibid.*, **22**, 176 (1906).

collected and titrated, afforded a means of estimating the quantity of metal. Though zinc gave only 80.1% of the theoretical amount of iodine, this percentage was constant. Thus Moody was enabled to estimate zinc too by this method.

That the bases of the different rare earths differ greatly in strength, is well recognized. Meyer[1] states that there are probably two series of earths when arranged in order of their decreasing positive character:

+ La, Ce, Pr, Nd, Sa,—
+ Y, – – –Gd, Tb, Er, Yb, – – –Sc—.

Boisbaudran[2] states that, on purifying gadolinium by fractional precipitation of the hydroxides with dilute ammonium hydroxide, he found samarium concentrated in the head fractions and didymium in the tail. Assuming that the un-ionized hydroxides have the same order of solubility, which is very small in comparison with the solubility of the ionized hydroxides, Boisbaudran's results would indicate that gadolinium hydroxide is a stronger base than samarium hydroxide. Its ions maintain equilibrium with a greater concentration of hydroxyl ions than the samarium ions. Benedicks[3] also found that, in the purification of gadolinium by fractional precipitation with dilute ammonium hydroxide, samarium was concentrated in the first fractions.

Experimental.

Apparatus.—The apparatus used in carrying out the experiments herein described is a modified form of that used by Moody[4]. The steam generator consisted of a globular flask provided with a thistle tube and an exit tube for the steam. The exit tube was connected to a three-way tube, of which one arm was closed by a cork stopper. Distillation could be interrupted by removing the cork and allowing the steam to escape into the air. The third arm was connected to a tube which led to the bottom of a 500 cc., side-tubed distilling flask. The exit tube of the distilling flask was joined to a glass condenser, and another condenser of the same kind was attached to the first condenser. At the end of the second condenser was an adapter for leading the distillates into two hundred and fifty cubic centimeter, graduated flasks in which they were collected and measured. The necks of the graduated flasks were so flanged that, between the flask and the adapter, solid, moistened potassium iodide could be placed for extracting the iodine from the atmosphere displaced from the flasks. All joints in the apparatus were made of cork.

Solutions.—According to Stock's equation, $M_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2M(OH)_3 + 3K_2SO_4 + 3I_2$, one molecule of $M_2(SO_4)_3$ will

---

[1] Die Analyse der Seltenen Erden und die Erdsäuren, p. 32.

[2] *Compt. rend.*, **111**, 393 (1890).

[3] *Z. anorg. Chem.*, **22**, 398 (1900).

[4] *Loc. cit.*

react with five molecules of KI and one molecule of KIO_3. One gram atom of iodine is then equivalent to one-sixth of a gram molecule of $M_2(SO_4)_3$, five-sixths of a gram molecule of KI and one-sixth of a gram molecule of KIO_3.

Solutions were in most cases prepared in small quantities at a time. In making them the proportions expressed by the following figures were used:

Eight-tenths normal solution of potassium iodide was made by accurately weighing $^8/_{10} \times {}^5/_6 = {}^2/_3$ of the gram molecular weight of chemically pure potassium iodide, dissolving and diluting to one liter.

Eight-tenths normal solution of potassium iodate was made by accurately weighing one-sixth of the gram molecular weight of chemically pure potassium iodate, dissolving and diluting to one liter.

Eight-hundredths normal solutions of the various rare earth sulfates were prepared and standardized as follows: Solutions of the purest rare earths available were treated with oxalic acid in excess and the resulting oxalates ignited to oxides. The oxides were dissolved in a slight excess of dilute hydrochloric acid and the solution filtered. Sulfuric acid, in small excess of that required to combine with the oxides used, was then added and this solution poured into a large excess of alcohol. As the hydrated sulfates dissolve very slowly, those obtained were dehydrated by heating in an oven to temperatures not in excess of 250°. The dehydrated salts were dissolved in water and diluted so that the concentration did not become lower than 0.08 normal. Two portions of 25 cc. were measured with pipet, the earth precipitated as oxalate and weighed as oxide. From the results the volume of solution required to furnish salt for 250 cc. of 0.08 normal solution was calculated. This was accurately measured and diluted to 250 cc.

A 0.1 normal solution of sodium thiosulfate was prepared and standardized by the usual methods.

In making all solutions the water used was boiled to expel carbon dioxide and other dissolved gases.

Procedure and Results.—50 cc. of the 0.08 N rare earth sulfate solution, 50 cc. of boiled water, 10 cc. of 0.8 N potassium iodide and 10 cc. of 0.8 N potassium iodate solution were mixed in the distilling flask of the apparatus. If the rare earths contained were completely hydrolyzed to hydroxide, with liberation of the equivalent quantity of iodine, 40 cc. of $1/N$ sodium thiosulfate solution would be required to titrate the iodine produced. The 10 cc. of the iodine solution and the 10 cc. of the iodate solution furnished twice the theoretical quantities of these reagents required for the complete reaction with the rare earth sulfates.

In carrying out the experiments, it was found that equilibrium of the reaction had practically been reached by the time 1250 cc. of distillate had collected. Also, that increasing the volume of solution, in which hydrolysis was taking place, decreased the quantity of iodine liberated in a given volume of distillate. On the other hand, decreasing the volume increased the quantity of iodine, and the slower the distillation proceeded, the more iodine was delivered per unit of distillate.

To overcome these variations, the distilling flask was marked at the height at which it contained 120 cc. A burner with a small flame, which could be regulated, was placed under the flask to compensate for condensation. Although the solution was agitated by passing steam, it was possible after some trials to maintain the volume constant within limits of 10–20 cc. Small increases and decreases in volume, which alternately occurred, served to compensate each other during the distillation of the entire 1250 cc. The rate of distillation was regulated so that each portion of 250 cc. was obtained in as nearly thirty minutes as possible. The time required for obtaining the entire distillate was recorded.

During the first part of the distillation of the solutions of earths of higher molecular weight, much solid iodine was collected in the condenser. While the first portion was being distilled, cooling water was run through the second condenser only. When 250 cc. of distillate were obtained, water was run through the first condenser, the two condensers were disconnected, an adapter was attached to the first, and the process carried on as before with the use of one condenser only.

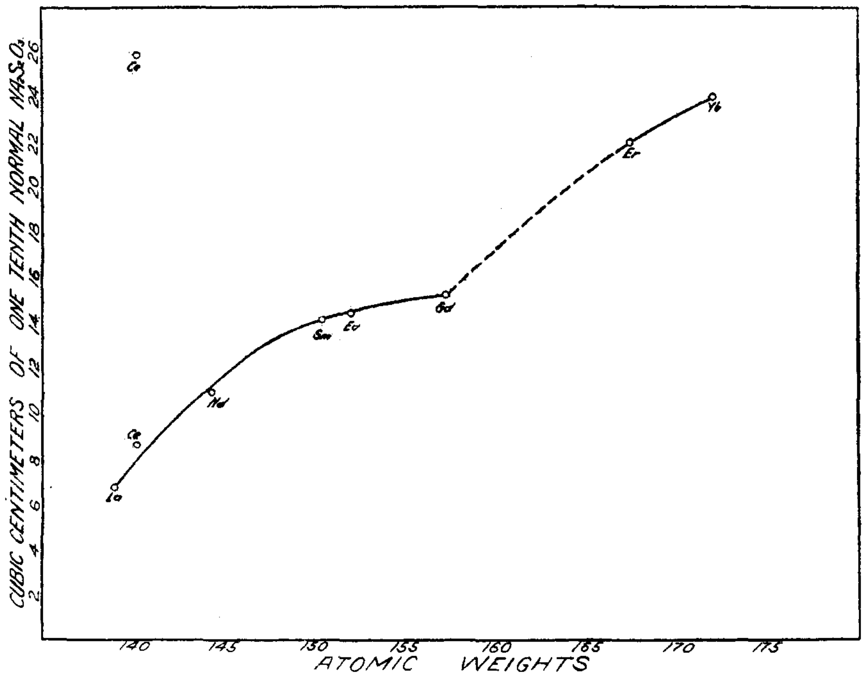
Cerium acted in the same manner as the other earths during the distillation of the first 750 cc. But while the fourth and fifth portions were being obtained, cerous compounds were oxidized to ceric. The ceric compounds readily hydrolyzed with liberation of much iodine. A sixth portion of 250 cc. of distillate, collected from the experiment with cerium, showed that reaction had almost ceased after the distillation of 1250 cc. Using the values obtained from the first, second and third portions of distillate from cerium, and for the fourth and fifth, averaging the values obtained from the corresponding portions from lanthanum and neodymium, a summation in accordance with those of the other elements was obtained.

In securing the first results by the process of distillation, conditions were not standardized. However, the same general relations in results were obtained from the different elements, as are given in the figures following, these figures being secured under regulated conditions. This table shows the atomic weight of each rare earth used, the time required for the complete distillation process, the volume of solution in the distilling flask at the conclusion of the experiment with each earth, the volume of 0.1N sodium thiosulfate solution required to titrate each 250 cc. portion of distillate and the total thiosulfate required for the experiment with each earth.

DATA FROM EXPERIMENTS.

$M_2(SO_4)_3$.	Time.		Final volume in distilling flask in cc.	Cc. of 0.1 *N* thiosulfate used to titrate each portion of distillate.						Total thiosulfate solution.
	Hr.	Min.		No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	
$La_2(SO_4)_3$......	2	34	130	2.98	1.85	1.22	0.44	0.32	..	6.81
$Ce_2(SO_4)_3$......	2	42	100	4.80	1.89	1.23	6.53	11.23	0.17	25.90
$Nd_2(SO_4)_3$.....	2	34	130	7.99	1.68	0.55	0.37	0.48	..	11.07
$Sa_2(SO_4)_3$......	2	36	120	8.58	4.24	0.51	0.38	0.27	..	14.04
$Sa_2(SO_4)_3$......	2	34	115	10.97	1.86	0.71	0.47	0.35	..	14.36
$Sa_2(SO_4)_3$......	2	34	135	11.57	1.25	0.60	0.56	0.37	..	14.35
$Eu_2(SO_4)_3$......	2	33	130	10.84	1.40	0.89	0.71	0.66	..	14.50
$Eu_2(SO_4)_3$......	2	32	130	11.49	1.77	0.74	0.66	0.46	..	15.12
$Eu_2(SO_4)_3$......	2	33	130	9.52	1.80	1.00	0.90	0.83	..	14.05
$Gd_2(SO_4)_3$.....	2	33	135	11.84	1.71	0.71	0.42	0.42	..	15.
$Gd_2(SO_4)_3$.....	2	35	130	11.55	2.28	0.61	0.53	0.58	..	15.5510
$Er_2(SO_4)_3$......	2	33	110	17.92	2.17	0.81	0.64	0.51	..	22.05
$Yb_2(SO_4)_3$.....	2	33	130	21.20	1.57	0.58	0.40	0.26	..	24.01

In the accompanying diagram the atomic weights of the rare earths are the abscissae and the total number of cc. of 0.1 *N* sodium thiosulfate solution used in titrating the distillates from each earth are the ordinates. When more than one experiment was made with an element, the average of the results is plotted on the diagram.



As no elements with atomic weights between those of gadolinium and erbium were available for this work, a dotted line is used in this portion of the curve.

Conclusions.

It will be noticed that, although sulfates of samarium, europium and gadolinium gave approximately the same results, the tendency to hydrolyze throughout the series increased with increase in atomic weight.

Meyer[1] includes yttrium in his series. This element has an atomic weight of 89 and can not fit the curve formed by the rare earths, so it has not been used in this work. Considering actual rare earths, no sharp division of the elements into two series, when comparing basicity with atomic weights, has been found.

The results of this investigation indicate that, in the purification of gadolinium from samarium by fractional precipitation with ammonium hydroxide, the samarium would be concentrated in the tail fractions and not, as found by Boisbaudran[2] and Benedicks,[2] in the head. Concerning this difference the authors have at present nothing further to offer.

Durham, N. H.

ELECTROSTENOLYSIS.[3]

By Harry N. Holmes.

Received March. 4. 1914.

Historical.

Braun and Coehn, who have done most of the work in this subject, made their capillaries by heating thick glass tubes, closed at one end, and plunging them into cold water. The tubes were shivered into a number of fine cracks which were really capillary spaces. A platinum anode with a water solution of some salt was placed in this tube, which rested in a beaker containing more of the same solution and the platinum cathode. On passing through a direct current at 40 v. or more, preferably 110 v., a spongy deposit of metal or oxide was found in the cracks.

Coehn[4] explained this phenomenon on the assumption that, when two substances are brought into contact with each other, the one possessing the higher dielectric constant will become positively charged. Since water has a very high dielectric constant it must be positive to most insoluble substances. The layer of water in contact with the walls of a glass capillary is positive and, under the influence of an electric current of sufficient voltage, must be attracted to the cathode leaving the glass

---

[1] *Loc. cit.*

[2] *Ibid.*

[3] By electrostenolysis is meant the deposition of a metal or its oxide in very fine capillaries when the solution filling these capillaries is electrolyzed. Frequently there is an evolution of gas from the deposit.

[4] *Z. Elektrochem.*, 4, 501 (1898); *Z. physik. Chem.*, 25, 651 (1898).