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THE RATES OF HYDROLYSIS OF THE RARE EARTH CARBONATES AND THE SERIAL ORDER OF THE RARE EARTH ELEMENTS.

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Introduction.

If the elements of the rare earth group are arranged in the order of increasing atomic weights, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, (Y), Er, Tm, Yb, Lu, Ct, it is found that in general this series represents the order of progressive variation in a number of other properties of the compounds of these elements. This *Serial Order*, as it is called, represents the order of solubilities of many series of rare earth salts, and therefore, usually, the order in which the compounds of the elements separate from solution in the operations of fractional crystallization. The order of decomposition of the nitrates on heating, and the order of precipitation by gradual addition of hydroxyl ion are also in general harmony (inversely) with this series, so that the series seems to represent the order of decreasing basicity of the elements.

A number of inconsistencies exist, however. Thus yttrium, with an atomic weight far below that of lanthanum, is placed, by general considerations of the solubilities of its compounds, between holmium and erbium; while the order of precipitation by ammonium hydroxide shows that its relative basic strength places it about with neodymium. Measurements of the dissociations of the anhydrous sulfates¹ indicate a degree of basicity for yttrium second only to that of lanthanum, admittedly the most strongly basic of the rare earths. By this same method samarium is given a place between gadolinium and terbium, and by fractional precipitation with ammonium hydroxide² samarium falls in the same position. Solubility considerations, on the other hand, place samarium between neodymium and europium in the serial order; and this same position has been accorded samarium by a study of the hydrolysis of sulfates.³

With a view to securing further data on the relative basicities and the serial order of the rare earth elements we have studied the rates of hydrolysis of the carbonates of 12 of these elements. In briefest outline,

¹ Wöhler and Gründzweig, *Ber.*, **46**, 1726 (1913).

² de Boisbaudran, *Compt. rend.*, **111**, 393 (1890); Benedicks, *Z. anorg. Chem.*, **22**, 398 (1900).

³ Katz and James, *THIS JOURNAL*, **36**, 779 (1914).

the method was to prepare accurately standardized solutions of the rare earth sulfates, to add equivalent amounts⁴ of each sulfate solution to separate portions of 0.5328 g. of purest sodium carbonate, and to heat for given lengths of time, under carefully controlled temperature conditions. The carbon dioxide resulting from the hydrolysis was weighed. Volume, and other conditions were maintained as uniform as possible in all experiments.

Preparation of Materials.

The methods of separation and purification of the compounds of the various elements considered in this paper have been described elsewhere,⁵ and need not be repeated here.

The method of preparing the sulfate solutions was the same for all the solutions. The oxide finally obtained from ignition of the purest oxalate was dissolved in the smallest possible amount of hydrochloric acid. Slightly more than the theoretical amount of sulfuric acid was then added to the somewhat diluted solution, and this was then poured into a large excess of 95% ethyl alcohol. The precipitated sulfate was thoroughly washed with alcohol, and dehydrated by heating to 280–300°. The anhydrous sulfate thus obtained was dissolved in ice-cooled water. By evaporating to small volume in a bath of boiling water the hydrated sulfate was deposited in crystalline form. The crystals were filtered, and washed repeatedly with small amounts of boiling water until no trace of acid reaction could be detected in the washings. The crystals were allowed to stand over sulfuric acid in a desiccator for a day, and then dissolved in carbon dioxide free water to make a 0.1 *N* solution. The solution was standardized by precipitating pipetted samples as the oxalate, and igniting to the oxide, R_2O_3 .

The only deviations from the above methods of standardization were the following: ytterbium was precipitated by ammonium hydroxide, owing to the considerable solubility of the oxalate; praseodymium was weighed as the oxide Pr_2O_3 , after ignition in a current of hydrogen; terbium was weighed as Tb_4O_7 , after ignition in the air.

Figures showing the concordance of these determinations may be replaced by the statement that the most discordant pair of the duplicates was in the case of ytterbium, which gave 0.3308 g. and 0.3301 g. of ytterbium oxide.

Sodium carbonate was prepared by saturating water at 60° with the purest sodium hydrogen carbonate of commerce. Carbon dioxide was passed into the filtered solution until cold, and the deposited sodium hydrogen carbonate was heated in platinum at 270 to 300° for several hours. 102.218 g. lost only 4. mg. on heating for 2 hours more at the same temperature; so it was heated for 1 hour after the last weighing, cooled in a desiccator over sulfuric acid, and quickly transferred to small stoppered bottles. 1.9796 g. of the sodium carbonate yielded on evaporation with sulfuric acid and gentle ignition with ammonium carbonate, 2.6547 g. of sodium sulfate. This agreed with the theoretical amount to within 4 parts in 10,000, so the sodium carbonate was considered pure enough for our purposes.

Experimental.

The reaction chamber was a 500-cc. round-bottom flask with a neck

⁴ Equivalent amounts of rare earth sulfate and sodium carbonate were used in order to avoid the formation of double carbonates or double acid salts. Such compounds as these are very characteristic of the rare earth metals.

⁵ Vid. James and co-workers, *ibid.*, 1907 to date.

15 cm. long. Through one hole of the stopper a glass tube passed almost to the bottom of the flask, and the outer end of this tube could be connected with a funnel for the introduction of liquid, or with a large soda-lime tower for the purification of incoming air. Through the other hole of the stopper a 24-cm. bulb condenser was vertically set. Following the condenser was a train consisting of a large U-tube filled with sulfuric acid, a long horizontal calcium chloride tube, a Geissler potash bulb with a calcium chloride guard tube, and then another sulfuric acid tube, beyond which was the aspirator bottle.

The heating was accomplished by a gas flame 7.5 cm. high, with an inner cone 2.5 cm. high. The bottom of the flask was 4 cm. above the top of the burner. All draughts were excluded, and a pressure-equalizing tank between the burner and the main gas supply insured uniformity of flame.

In making a run, exactly 0.5328 g. of sodium carbonate was rinsed into the flask with 25 cc. of water. (All water used in these experiments was previously freed from carbon dioxide by boiling, and then cooled with the usual precautions.) The flask and train were then freed from carbon dioxide by aspirating several liters of pure air through. Next, the weighed potash bulb was placed in the train, and an amount of rare earth sulfate solution chemically equivalent to the sodium carbonate was introduced through a funnel attached to the tube leading to the bottom of the reaction flask, and this was rinsed with enough water to give a volume of 229.12 cc. This volume, and the weight of sodium carbonate were empirical, resulting from the experimental conditions of the first run, and maintained as standard throughout the series. The funnel was disconnected, the large soda-lime tower connected in its place, and aspiration was then started at the rate of 2.5 liters per half-hour. The flame was next placed under the flask, and the heating continued for exactly 30 minutes after incipient ebullition. The flame was then turned out and the "sweeping" with pure air continued for exactly 20 minutes. The potash bulb was weighed with the usual precautions, placed back in the train, the boiling and "sweeping" being repeated exactly as before. This operation was usually repeated 6 to 8 times with each sample, and the percentage hydrolysis calculated for each half-hour boiling period. Duplicates were run on all the elements considered in this paper with the exception of europium, terbium, and thulium, of which we had amounts sufficient for one run only.

Below are given the results of the experiments, giving the percentage hydrolysis, (*i. e.*, the amount of carbon dioxide given off, divided by the total carbon dioxide originally present in the system), at the end of each half-hour period.

Hours of Boiling.	0.5.	1.0.	1.5.	2.0.	2.5.	3.0.	3.5.	4.9.
$\text{La}_2(\text{CO}_3)_3$								
%Hydrolysis, 1st sample	27.9	27.9	28.0					
2nd "	27.5	27.5	27.6					
3rd "	28.1	28.3	28.3					
Average	27.9	27.9	28.0					
$\text{Ce}_2(\text{CO}_3)_3$								
	28.5	28.5	28.7					
	29.3	29.4	29.4					
	28.9	28.9	29.0					
$\text{Pr}_2(\text{CO}_3)_3$								
	22.4	26.7	28.8	29.9	31.2	32.1	33.2	
	24.0	28.0	30.1	31.8	32.6	33.1	33.5	
	23.2	27.4	29.5	30.9	31.9	32.6	33.3	
$\text{Nd}_2(\text{CO}_3)_3$								
	26.8	30.2	32.7	34.3	35.4	36.4	36.9	
	26.3	30.4	32.6	34.4	35.5	36.4	37.2	
	26.6	30.3	32.7	34.4	35.5	36.4	37.1	
$\text{Sm}_2(\text{CO}_3)_3$								
	30.8	34.7	37.2	39.2	40.8	42.2	43.4	44.2
	32.0							
	32.6	36.0	38.4	39.8				
	31.8	35.4	37.8	39.5	40.8	42.2	43.4	44.2
$\text{Eu}_2(\text{CO}_3)_3$								
	33.4	37.4	39.9	41.9	43.6	45.1	46.3	47.0
$\text{Gd}_2(\text{CO}_3)_3$								
	35.0	39.4	41.9	43.7	45.3	46.3	47.4	48.3
	34.6	38.4	40.7	42.5	43.5	45.0	46.1	46.9
	34.8	38.9	41.3	43.1	44.4	45.6	46.7	47.6
$\text{Tb}_2(\text{CO}_3)_3$								
	37.6	42.5	45.7	48.1				
$\text{Dy}_2(\text{CO}_3)_3$								
	39.4	43.6	46.8					
	40.6	45.3	48.5	50.7	52.2	53.4		
	40.0	44.4	47.6	49.9	51.4	52.8		
$\text{Y}_2(\text{CO}_3)_3$								
	46.8	50.6	53.4	55.3	56.0	57.0		
	43.0	46.5	48.5	50.3	51.9	53.1		
	44.9	48.5	51.0	52.8	54.0	55.1		
$\text{Tm}_2(\text{CO}_3)_3$								
	49.0	53.1	55.5	57.5	59.3			
$\text{Yb}_2(\text{CO}_3)_3$								
	52.6	57.3	60.4	62.4	64.4	66.1	67.3	68.5

The degree of accuracy of the individual determinations may be judged by the concordance in the results of analyses of the duplicate samples. While the concordance is not as close as might be desired in certain classes of measurements, yet it seems fair to assume that the position of an element in this series is not rendered doubtful by the limitations of the experimental methods used. Thus it will be seen that in the first (which

is the most important) stage of each run the highest figure for one element is lower than the lowest figure of the next higher element.

The results are graphically shown in Fig. 1, in which the percentages hydrolyzed are plotted against the time of boiling.

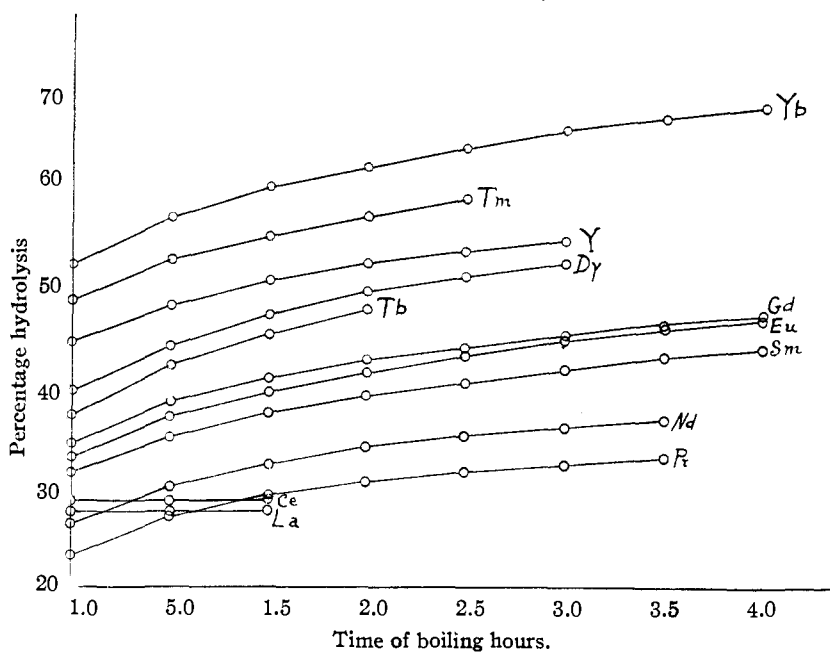


Fig. 1.

Discussion of Results.

The behavior of lanthanum and cerium^{III} is abnormal in comparison with the others. Hydrolysis seems to reach its limit in the first half-hour with these elements, while with the others there is a continuous, gradually decreasing amount for each additional period of boiling. That cerium should show a different behavior is not surprising, since cerium is really a fourth group element, and is not to be regarded as a "rare earth" element. Lanthanum also shows certain variations from the strict rare earth group.⁶ It gives no absorption spectra, it finds a place in the old periodic table, and in general shows greater characteristic individuality than do the other members of the rare earth group.

The position of yttrium is interesting. General considerations of the solubilities of its compounds places yttrium between holmium and erbium, but the order of precipitation by ammonia places it about with neodymium. Our results on the hydrolysis of yttrium carbonate place the element between dysprosium and thulium, and while holmium and erbium were

⁶ Hauser and Wirth, *Z. anal. Chem.*, **47**, 395 (1908).

not available for our tests, these two also come between dysprosium and thulium in the generally accepted serial order, and it is not improbable that had we been able to investigate holmium and erbium they would have found a place on each side of yttrium. From our results the position accorded to yttrium (just below lanthanum in basicity) by Wöhler and Grünzweig⁷ from their study of the dissociation of the anhydrous sulfates seems to be erroneous.

Hydrolysis of the carbonates places europium between samarium and gadolinium, and lends additional support to the serial order established by solubility relations. This is at variance with the order of precipitation by ammonia, as well as that indicated by the sulfate tensions investigated by Wöhler and Grünzweig.

It is worthy of note that a large space occurs in our Fig. 1 between neodymium and samarium. This is in harmony with the idea derived from study of the atomic numbers⁸ that there is an undiscovered rare earth element with a position between those of neodymium and samarium.

Summary.

The relative rates of hydrolysis of 12 rare earth carbonates have been determined.

Lanthanum and cerium^{III} showed an abnormal behavior, for which no explanation can now be offered.

Yttrium has been assigned a position in the order of basicity which agrees with the solubilities of its compounds. Previous determinations of its basicity have not done this.

Additional evidence on the serial order of samarium, europium and gadolinium has been offered.

Omitting lanthanum and cerium^{III} for the present, the other ten elements investigated are placed in the following order: Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Tm, Yb.

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⁷ Wöhler and Grünzweig, *Ber.*, **46**, 1726 (1913).

⁸ Moseley, *Phil. Mag.*, **26**, 210 (1913); **27**, 703 (1914).