

FRACTIONATION OF THE RARE EARTHS BY ELECTROLYSIS OF AQUEOUS SOLUTIONS

H. C. KREMERS and L. L. QUILL

University of Illinois, Urbana.

The various methods used for the separation and isolation of the individual rare earth elements may be divided into three classes: 1, fractional crystallization, which depends on differences in solubility; 2, fractional precipitation, which depends on differences in basicity; and 3, physical processes. The first two methods are undoubtedly the most important.

For the isolation of certain members of the rare earth group, basicity separations, as the second classification is called by the rare earth chemist, are the most efficient. In actual practice the property of basicity is usually interpreted as meaning the relative solubilities of the rare earth hydroxides, the least basic being the least soluble, and *vice versa*. In other words, the least basic rare earths are the first to be precipitated when a basicity method is employed. The order of decreasing basicity of the rare earths generally accepted at the present is as follows: lanthanum, cerium (ous), praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium, and scandium. This order, it will be observed, is the reverse of the order of their atomic numbers. Yttrium, which is ordinarily classified with the rare earth elements, has a basicity somewhere between neodymium and dysprosium, somewhere near gadolinium.

Various methods have been used to bring about a partial precipitation of the hydroxides or basic salts. The addition of small amounts of ammonia or caustic alkalies to effect a separation was used early in rare earth chemistry. This method has only been partially successful, perhaps because the precipitated hydroxides are very gelatinous in nature.

The most popular basicity methods are the old basic nitrate fusion method and the fractional precipitation by means of sodium nitrite. In the nitrate fusion method the nitrates are fractionally decomposed by fusion, the basic portion being insoluble in water. The sodium nitrite method was first suggested by Holden and

James¹. This is carried out by boiling a slightly acid or neutral solution of the rare earth chlorides or nitrates with sodium nitrite. An insoluble basic nitrite of the rare earth is gradually formed.

The hydroxides may also be precipitated when a neutral salt solution of the rare earth chlorides or nitrates is electrolyzed. The hydroxides thus precipitated are formed at the cathode. Here again a fractionation may be effected through differences in the basicities of the earths. Dennis² and co-workers electrolyzed solutions of the rare earths, using platinum anodes and mercury cathodes. Kremers and Neckers³ carried out electrolytic separations on the Ce group earths in this laboratory. They found nitrates and chlorides to be equally satisfactory.

MATERIALS AND METHODS

In the present investigation, the authors were interested in making a rather comprehensive study of the electrolytic method, having in mind the feasibility of the process in regard to the large scale separation of those rare earths which lend themselves to separation by basicity methods.

The anode was made of platinum, a satisfactory substitute not being found. The anode was isolated by means of a porous porcelain cup. In the larger electrolytic cells, a simple open porous cup was used. In the smaller units, a closed cup as shown in Figure 1 was used, thus making it possible to completely immerse the anode compartment in the solution.

The cathode as finally developed was made of molybdenum. All previous investigators used mercury. Various metals were used during the present investigation. Mercury is satisfactory, yet is obviously inconvenient. Platinum is satisfactory, but expensive. Copper, nickel, and iron were partially successful.

When these materials were used reactions sometimes took place which could not be wholly explained. If the electrolyte was a nitrate solution, and the rare earth concentration became too dilute, ammonia was formed at the cathode, thus causing a partial solution of these metals. It was also observed that when the electrolyte contained an appreciable quantity of iron, nickel, or copper, the alternate oxidation and reduction of these metals apparently utilized most of the current input and prevented the for-

¹ Holden and James. *J. Am. Chem. Soc.* 36, 2332 (1914).

² Dennis. *J. Am. Chem. Soc.* 37, 131, 1963 (1915); 40, 174 (1918).

³ Kremers and Neckers. *J. Am. Chem. Soc.* 50, 950 (1928).

mation of the rare earth hydroxide at the cathode. Molybdenum was found to be quite inert when used as a cathode and was by far the most satisfactory metal tried.

The current densities used were varied. A series of experiments were performed in which the amount of cathode surface exposed was varied to give current densities from 0.01 amperes to 0.5 amperes per square centimeter. Apparently there was no variation in the efficiency of separation due to this.

The electrolyte in this research was made up on nitrate solutions. The best results were obtained with concentrations of approximately 10 per cent of total rare earth oxides. Vigorous mechanical stirring was, of course, always necessary during the electrolysis. The electrolytic cells varied in size from two liter beakers to 80 liter stoneware jars. The units as used are shown in Figures 2, 3, and 4.

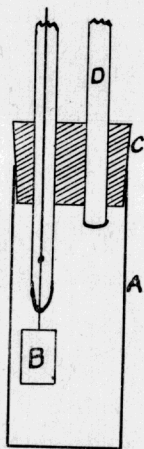


FIG. 1. Diagram of closed cup.
(A) porous cup, 30 mm. diameter.
(B) platinum foil with platinum wire seal through glass and platinum to copper seal.
(C) two-hole rubber stopper.
(D) gas vent.

The current efficiency varied from about 25 to 50 per cent. This low effect may be attributed to a number of factors, such as the reduction of the nitrate to the nitrite or ammonia, the resistance of the solution to the current causing a heating of the solution, the alternate oxidation and reduction of such groups as Fe, Ni, Cu, and Ce, and the diffusion of the nitric acid formed in the anode cup back into the solution.

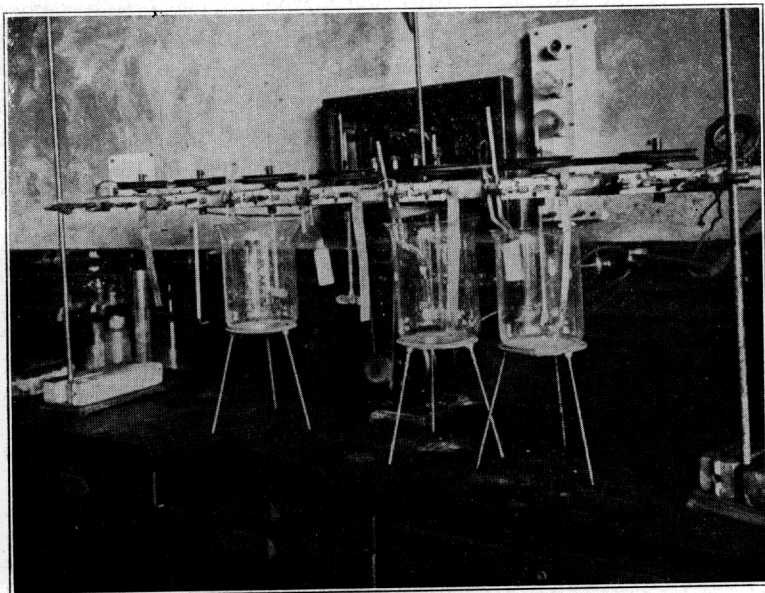


FIG. 2.

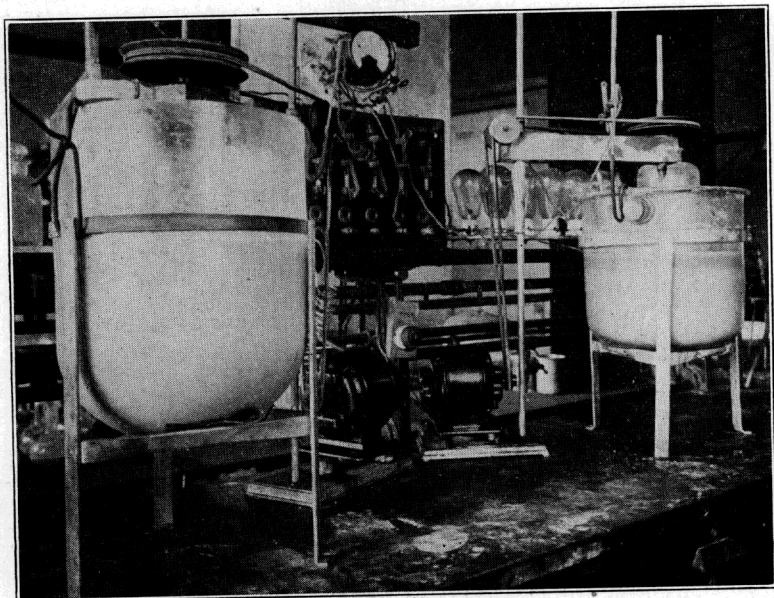


FIG. 3.

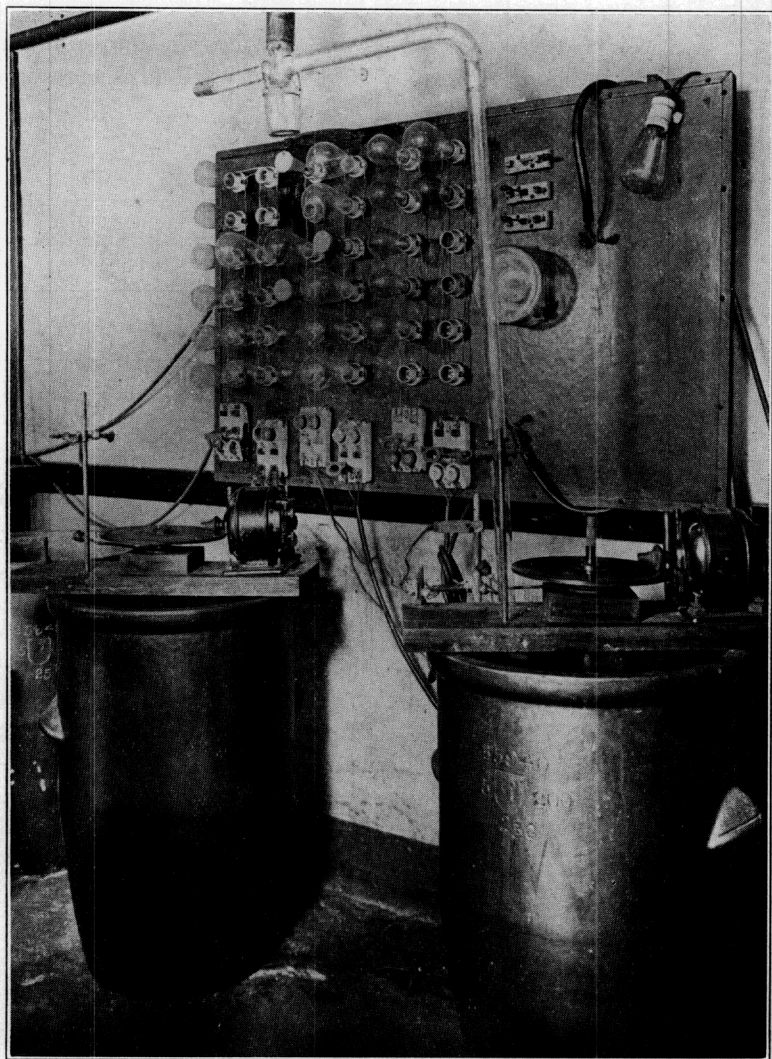


FIG. 4.

TYPICAL RUNS

This method has been used for a period of two years and has thus been given a very thorough trial. It will be necessary to describe only a few typical runs.

Run No. 1 was composed of an yttrium, erbium-holmium mixture containing approximately 93 per cent yttrium. The results are shown in Table I.

TABLE I.

Fraction number	Wt. in gms.	Amps.	Composition of fractions in % of oxide		
			Er ₂ O ₃	Ho ₂ O ₃	Y ₂ O ₃
1.....	2565	10	8.0	0.5	90+
Residue (Filtrate).....	1100	1.0	0.05	98+

Run No. II. The material in this run was composed of 3,510 grams of oxides of the following composition: Er₂O₃, 2.0%; Ho₂O₃, 0.5%; Nd₂O₃, 0.2%; Ce₂O₃ trace; Pr₂O₃ trace; La₂O₃ trace; Y₂O₃, 95% approx. Results are given in Table II.

Run No. III. Some doubt existed in the minds of the authors as to the relative basicities of yttrium and neodymium. Accordingly a mixture, 143 grams in weight, of the following composition was made up: Er₂O₃, 0.2%; Ho₂O₃, trace; Nd₂O₃, 40.0%; Pr₂O₃, 1.0%; Y₂O₃, 58+%. Results of the fractions of this mixture are shown in Table III.

Results seem to indicate very definitely that neodymium and praseodymium are more basic than yttrium.

DISCUSSION OF RESULTS

The order of decreasing basicity of the rare earth elements as given at the beginning of this paper was found to hold in the case of all earths studied. Britton's determinations⁴ of the pH of solutions of several of the rare earths at the point at which the hydroxides began to precipitate, partially verify the generally accepted order. Britton's values show yttrium to be less basic than samarium.

TABLE II.

Fraction number	Wt. in gms.	Amps.	Composition of oxides in % of oxide				Remarks
			Er ₂ O ₃	Ho ₂ O ₃	Nd ₂ O ₃	Pr ₂ O ₃	C ₂ O ₂
1.....	760	20	4.0	0.5	0.1
2.....	325	20	3.0	0.5	0.15
3.....	375	20	0.9	0.6	0.15
4.....	475	20	0.6	0.45	0.15
5.....	560	20	0.5	0.3	0.2	trace	trace
6.....	500	20	0.2	0.1	0.4	trace	trace
7.....	405	20	0.2	0.1	0.5	1.0	0.5
Residue.....	110	trace	trace	2.0	1.5	2.0

Highest per cent of yttrium concentrated here.

Practically all of the lanthanum concentrated here.

TABLE III.

Fraction number	Wt. in gms.	Composition of fractions in % of oxide				
		Er ₂ O ₃	Ho ₂ O ₃	Nd ₂ O ₃	Pr ₂ O ₃	Y ₂ O ₃
1.....	66	0.2	trace	40.0	-----	59+
2.....	29	-----	-----	60.0	1.0	39
3.....	25	-----	-----	70.0	1+	28+
Mother liquor.....	23	-----	-----	80.0	3.0	17

Rapid separations were noted in several cases. The concentration of certain earths was found to be ten-fold in many cases between the fraction and mother liquor. From the standpoint of convenience, the electrolytic method of fractionation is better than other basicity methods. Yttrium can be separated from holmium and erbium very readily by basicity methods. The electrolytic method is very convenient for large quantities of material.

Molybdenum was found to be a very satisfactory cathode material, although copper, platinum, and mercury can be used.

⁴ Britton. J. Chem. Soc. 2142 (1925).