

STUDIES IN COMPARATIVE EFFICIENCIES OF RARE EARTH SEPARATIONS

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Numerous methods available for the separation of the rare earths have frequently been suggested by different investigators who made little or no comparison of the efficiencies of the various procedures. The purpose of this paper is, therefore, to attempt a critical study of the comparative efficiencies of the better-known separations where two or more exist for the same purpose and where the required data are available. It is desired to outline the practical applications of the methods which have actually been used by the authors and to discuss two new physical methods of separation which have recently been suggested.

Methods for the separation of the rare earths may be divided into three classes: 1, fractional crystallization, which depends upon differences in solubility; 2, fractional precipitation and decomposition, which depend upon differences in basicity; and 3, physical methods.

SOLUBILITY METHODS

A very large number of salts of the rare earths have been prepared for the purpose of fractional crystallization, but only a few of these are in common use in rare earth laboratories. Of the simple salts the nitrates and the bromates are the most important. At present complete quantitative solubility measurements are available only in the case of the latter¹. In these as in other instances the maximum possible efficiency of separation during fractional crystallization is based on the *ratio of solubilities* of the salts being treated. It is sometimes erroneously concluded that the arithmetical difference in solubility is the criterion of efficiency. A little consideration will show that this is not the case. For instance, if two salts, say AX and BX, have solubilities of 25 and 20 parts per 100, respectively, and two other combinations, AY and BY, have solubilities of 50 and 40 parts per 100, respectively, then although the difference in solubilities has been doubled yet the distribution of the two salts in solution in contact with the

¹James, Fogg, McIntire, Evans and Donovan, J. Am. Chem. Soc. 49, 132 (1927).

crystals will remain in the ratio 5 to 4 in the absence of complicating factors. When the solubility data are available the efficiency of the various salts for the separation of two given rare earths may readily be calculated. In an article of this length it would be impossible to treat all the possible combinations. The figures are given, however, in Table I for the separation of neodymium and samarium which has received intensive study in connection with the concentration of illinium.

The simple rare earth nitrates may be conveniently fractionated from concentrated nitric acid, which represses the solubilities sufficiently to render the ratio large enough to produce a separation. The fractionation is, nevertheless, exceedingly slow, several months of daily treatment being required to obtain even a small proportion of samarium completely free from neodymium. The salts readily

TABLE I—RATIOS OF SOLUBILITIES OF CERTAIN NEODYMIUM AND SAMARIUM SALTS.*

Formula	Ratio	Investigator
2R(NO ₃) ₃ ·3Mg(NO ₃) ₂ ·24H ₂ O at 16° C. in HNO ₃ d ₄ ¹⁶ = 1.325..	$\frac{\text{Sm}}{\text{Nd}} = 2.49\dagger$	Jantsch, Z. anorg. Chem. 76, 303 (1912).
2R(NO ₃) ₃ ·3Ni(NO ₃) ₂ ·24H ₂ O.....	$\frac{\text{Sm}}{\text{Nd}} = 2.48$	Jantsch, Z. anorg. Chem. 76, 303 (1912).
2R(NO ₃) ₃ ·3Co(NO ₃) ₂ ·24H ₂ O.....	$\frac{\text{Sm}}{\text{Nd}} = 2.25$	Jantsch, Z. anorg. Chem. 76, 303 (1912).
R(C ₃ H ₅ O ₂) ₃ ·xH ₂ O (lactate) 20° C.	$\frac{\text{Nd}}{\text{Sm}} = 2.10$	Jantsch, ibid 153, 9 (1926).
2R(NO ₃) ₃ ·3Zn(NO ₃) ₂ ·24H ₂ O at 16° C. in HNO ₃ d ₄ ¹⁶ = 1.325	$\frac{\text{Sm}}{\text{Nd}} = 2.07$	Jantsch, ibid 76, 303 (1912).
2R(NO ₃) ₃ ·3Mn(NO ₃) ₂ ·24H ₂ O.....	$\frac{\text{Sm}}{\text{Nd}} = 1.68$	Jantsch, ibid 76, 303 (1912).
R [(CH ₃) ₂ PO ₄] ₃ 25° C. dimethyl phosphate.....	$\frac{\text{Nd}}{\text{Sm}} = 1.59$	Morgan and James, J. Am. Chem. Soc. 36, 10 (1914).
R(BrO ₃) ₃ ·9H ₂ O 20° C.....	$\frac{\text{Nd}}{\text{Sm}} = 1.28$	James and co-workers, ibid 49, 132 (1927).

* Further solubility data on the double nitrates are given by Prandtl and Ducreux, Z. anorg. allgem. Chem. 150, 105 (1926).

† There appears to be a typographical error in the solubility of samarium double magnesium nitrate as given by Jantsch.

form super-saturated solutions and must, therefore, be seeded or else incompletely dissolved. From work at present being carried on in this laboratory it appears that both terbium and holmium nitrates have solubilities intermediate between those of neodymium and samarium in concentrated nitric acid (sp. gr. 1.4). In the experience of the authors the simple nitrates effect a more rapid separation of neodymium and samarium than do the bromates².

The rare earth bromates find their principal application in the yttrium group. They have, nevertheless, been used efficiently in the separation of praseodymium and neodymium, and it was through their use that illinium was discovered. Their use for the yttrium earths is rendered less convenient because of slow hydrolytic decomposition. The efficiency of the separation of neodymium and samarium by the bromate method is aided by the intermediate solubility of terbium and in the neighborhood of 0°C. probably by that of gadolinium. Unfortunately, terbium is not sufficiently abundant to be of much use in this connection. The efficiency of the neodymium-samarium separation decreases with increase in temperature, while the samarium-gadolinium separation is slightly more efficient at higher temperatures.

The simple sulfates and a rather large number of organic salts have been fractionated with varying success. The value of any simple salt in the neodymium-samarium separation is, of course, due to the practical reversal of the solubility order. Some quantitative measurements are available for the sulfates, nitrates, oxalates, glycolates, and lactates, but in several of these it is difficult to distinguish between the effects of solubility and basicity.

The rare earth double salts are probably the most important in the resolution of the cerium and yttrium groups and in the separation of the individual members of the cerium group. For the first purpose the alkali double sulfate separation has the distinction of being one of the nearest approaches to a quantitative procedure in all the rare earth separations. The more important double nitrates are those with magnesium, manganese, ammonium, thallium, and nickel, of which the double magnesium nitrate is the best for most purposes. The extremely tedious processes, involving literally tens of thousands of operations which are used in these separations, render extremely desirable the use of salts which will give as little trouble to the worker as possible. In this respect

² There is some evidence in the literature that rare earth salts do not always crystallize in the order of their respective solubilities. See, for instance, Jantsch, *Z. anorg. Chem.* 76, 303 (1912).

the double magnesium nitrates are nearly ideal, as they do not supersaturate readily and may easily be recovered if accidentally evaporated to dryness. In addition, their comparatively slight solubility in nitric acid requires the use of a fairly large volume of mother-liquor. This is desirable, as it has been observed that equilibrium and hence maximum efficiency is not reached for several hours and perhaps days after partial crystallization has taken place. It is, therefore, advantageous to have the mother-liquor remain in contact with as large a surface of crystals as possible during the crystallization period, provided that too large a proportion of the salt is not thereby taken into solution.

Other double salts which have been successfully applied are the ammonium double oxalates, used by von Welsbach for the resolution of ytterbium and cassiopeium or lutecium, and the alkali double sulfates already mentioned. In addition to these there are numerous complex salts of which the dimethyl phosphates³ and the ethyl sulfates are examples. The former especially have great differences in solubility from element to element, but unfortunately their hydrolytic decomposition renders them most unsatisfactory for use.

BASICITY METHODS

Of almost equal utility with fractional crystallization are the methods of fractional precipitation and decomposition which are founded on the differences in basicity of the rare earth metals. As pointed out by Mellor⁴ the efficiency of such methods does not depend directly on the affinity (or basicity) of the earths for the acid but rather on the excess of affinity of the precipitant. In the ammonium hydroxide precipitation "if the affinities of the two earths are represented by 100 and 101 and that of ammonium hydroxide by 150, the affinities on which the precipitation depends would be represented by $150-100=50$, and $150-101=49$." Obviously, the efficiency is to be increased by decreasing the affinity of the precipitant.

The only quantitative measurements available on the basicity of the rare earths are those of Hildebrand⁵ and of Britton⁶, on the pH at which precipitation of the hydroxides takes place, and it is questionable whether such information constitutes an accurate

³ Morgan and James, *J. Am. Chem. Soc.* **36**, 10 (1914).

⁴ Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 5, p. 540.

⁵ Hildebrand, *J. Am. Chem. Soc.* **35**, 847 (1913).

⁶ Britton, *J. Chem. Soc.* **127**, 2142 (1925).

measure of basic strength. According to Britton, the hydrogen ion concentrations which govern the precipitation of the hydroxides of samarium, yttrium, neodymium, and praseodymium—all about 10^{-7} —are so close together that separation of these elements by fractional precipitation of the hydroxides is impossible. No quantitative information is available on the basicity of the remaining yttrium earths, and it is in the separation of these from yttrium itself that basicity methods are most efficient.

Of the precipitation methods the oldest is by the addition of ammonium hydroxide to a nitrate or chloride solution. This procedure has the disadvantage of permitting local action between the base and the rare earth ions and of the production of a gelatinous precipitate difficult to filter. Various modifications have been suggested by Prandtl⁷ and others with a view to eliminating the first of these defects, and such is the purpose of the electrolytic and sodium nitrite precipitations which have been very successful. Magnesium oxide is used on a large scale by at least one commercial firm and organic bases such as aniline have received some application in the separation of the erbium earths. Two of the most satisfactory methods, namely, electrolytic and sodium nitrite basic precipitations, have been extensively described in the literature, the former by Dennis⁸ and by Kremers⁹ and their respective co-workers, and the latter by James¹⁰ and by Hopkins¹¹ and others. Other suggested precipitants are potassium chromate, oxalic acid, and potassium ferrocyanide, together with a large number of organic acids such as cacodylic, valeric, stearic, nitrobenzoic, acetic, salicylic, and lactic. For details of such separations reference should be made to one of the comprehensive texts on the subject.¹²

In addition to the precipitation methods, fractional decomposition of the nitrates by heating is at once one of the oldest and most satisfactory methods of treating the yttrium earths. Under suitable conditions this method yields a rapid separation of yttrium from erbium or holmium¹³.

⁷ Prandtl and Lösch, *Z. anorg. Chem.* **122**, 159 (1922); Prandtl and Rauchenberger, *ibid* **122**, 311 (1922); **120**, 120 (1921).

⁸ Dennis and Lemon, *J. Am. Chem. Soc.* **37**, 131 (1915).

Dennis and van der Meulen, *ibid* **37**, 1963 (1915).

Dennis and Ray, *ibid* **40**, 174 (1918).

⁹ Neckers and Kremers, *J. Am. Chem. Soc.* **50**, 950 (1928).

¹⁰ Holden and James, *J. Am. Chem. Soc.* **36**, 1419 (1914).

¹¹ Hopkins and Balke, *J. Am. Chem. Soc.* **38**, 2332 (1916).

¹² Little, "A Text-Book of Inorganic Chemistry" (Friend). Vol. 4.

¹³ Kremers and Balke, *J. Am. Chem. Soc.* **40**, 593 (1918); Driggs and Hopkins, *ibid* **47**, 363 (1925).

PHYSICAL METHODS

Two physical methods, namely distillation and ionic migration, have met with some success in the separation of the rare earths. A third method which attempts to utilize the magnetic properties of these elements has not as yet yielded positive results. Extensive use of distillation and sublimation is discouraged by the very high and relatively slight differences in the boiling points of the stable rare earth compounds. Scandium and thorium have been concentrated by fractional sublimation of the anhydrous chlorides¹⁴, and pure scandium has been obtained by sublimation of the scandium-thorium acetylacetonates¹⁵.

The ionic migration method devised by Kendall and co-workers¹⁶ suggests a relief from the slow process of fractional crystallization. A study has therefore been made in this laboratory of the application of the method to the problem of the concentration of illinium. "In this method an agar gel containing the mixture is placed in a long glass tube behind a gel containing a faster ion of the same sign as those to be separated, and in front of a gel containing a slower ion. On electrolysis the two boundaries of the middle section remain sharp, and if the constituents of the mixture possess appreciably different mobilities, the faster ion gradually concentrates in the front of the section, and the slower in the rear. Recovery of the separated mixture can then be effected by slicing up the gel at the conclusion of the run"¹⁷.

Following the procedure of Kendall and Clarke, three migration tubes were started using a natural mixture of neodymium and samarium chlorides. The 10 cm. rare earth section was preceded by potassium ions and followed by chromic ions. A potential difference of 220 volts produced a current of about 0.3 amperes. After 16 meters of migration the rare earth section was examined spectroscopically, but every portion was found to be identical in composition with the original material.

It was reported by Kendall that "substantially complete separation" of praseodymium and neodymium had been accomplished by this method within ten days. An attempt was made, therefore, to duplicate this separation. After a run of 10 meters during 30 days, absolutely no concentration could be detected.

¹⁴ Meyer and Winter, *Z. anorg. Chem.* **67**, 398 (1910).

¹⁵ Morgan and Moss, *J. Chem. Soc.* **105**, 196 (1914).

¹⁶ Kendall and Clarke, *Proc. Nat. acad. Sci.* **11**, 393 (1925);

Kendall, *Science*, **LXVII**, 163 (1928).

¹⁷ Kendall and West, *J. Am. Chem. Soc.* **48**, 2619 (1926).

Further runs were made with a natural mixture of samarium and gadolinium and with an artificial mixture of yttrium and erbium. In both of these cases a partial separation was obtained. Measurements of the magnetic susceptibility of the fractions indicated in the first case a concentration of samarium from 53 to 76%, and in the second case a concentration of yttrium from 76 to 89%.

In the opinion of the authors the ionic migration method cannot compete successfully with the established methods of separating the rare earths such as have already been described. One of the most striking disadvantages of the migration method is that it becomes less efficient as the quantity of material is increased while the older methods, especially fractional crystallization, gain in efficiency as the quantity is increased.

The magnetic susceptibility of the rare earths is almost unique in being a property exhibiting very wide variations from element to element. Any fractional method using this property gives promise of being much more efficient than the methods founded on solubility and basicity. A study, therefore, has been made in this laboratory of the conditions under which a magnetic separation might be realized.

In a non-homogeneous magnetic field, that is, one in which the intensity changes from point to point, a magnetic atom will not only be oriented but will be deflected by a force proportional to the magnetic moment of the atom and to the degree of non-homogeneity of the field. Such a field has been obtained by the use of special pole-pieces attached to a large electromagnet. The shape of the pole-pieces and the diminution in intensity of the field are shown in the accompanying figure, which was obtained by sprinkling fine iron filings on photographic paper over the ends of the pole-pieces.

Dilute solutions both aqueous and alcoholic were prepared of the chlorides of samarium and erbium, whose magnetic susceptibilities are in the ratio of about 1 to 40. These were passed very slowly through the magnetic field, and means were provided for the collection of the supposedly more and less magnetic fractions as they emerged. All the results were unsatisfactory inasmuch as no positive separation was obtained. The method appears theoretically sound, but apparently a very much larger magnet must be obtained before a practical separation may be achieved.

Such magnets are available but require tremendous quantities of liquid air for cooling purposes, and their use introduces extraordinary difficulties in the design of the apparatus¹⁸.

¹⁸ A complete description of the experiments on ionic migration and magnetism will be found in a forth-coming publication by the authors in the Transactions of the American Electrochemical Society. (1929).