

527. *The Separation and Purification of Lanthanum. Part II. Nitrate Fusion: Solubility of Rare-earth Hydroxides in Fused Ammonium Nitrate.*

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Studies of the solubility of rare-earth hydroxides in fused ammonia nitrate show that solubility is in the same relationship as basicity, although yttrium appears to find a place higher in the series than hitherto recorded. By applying ammonium nitrate fusion to the separation of hydroxide mixtures it is found that a very good and fairly clean separation is obtained of lanthanum from its congeners. The influence of cerium in the fusion is studied, and its separational effect confirmed. Ammonium nitrate fusion also appears to be a method for the removal of erbium from yttrium.

FUSION of rare-earth nitrates, alone or with sodium and potassium nitrates, has long been a classic method for their separation. Marsh (*J.*, 1946, 17 *et seq.*) has added to our knowledge

of the mechanisms involved, and correlated the separational effect with the crystal structure of the rare-earth oxides. In rare-earth nitrate melts with sodium and potassium nitrates at 300–500°, Marsh by the addition of cerous nitrate obtained good separation of lanthanum and praseodymium, and eventually obtained a certain concentration of praseodymium.

The inhibitory effect of ammonium nitrate on precipitation of lanthanum hydroxide was studied by Prandtl (*Ber.*, 1920, **53**, 843; *Z. anorg. Chem.*, 1922, **120**, 120, etc.), and the solubility of rare-earth hydroxides in aqueous solutions of ammonium salts has long been recognised (Berzelius, *Pogg. Ann.*, 1839, **46**, 648; **47**, 207); and there have been several applications of this effect to separational techniques (see Moeller and Kremers, *Chem. Reviews*, 1945, **37**, 140). It is known (see also preceding paper) that an increase in ammonium nitrate concentration in solutions more effectively enables separation of lanthanum during hydroxide separation, and it appeared likely that this inhibitory, or solution, effect would be more pronounced in melts of ammonium nitrate and rare-earth hydroxides. With ammonium nitrate melting at 120–140°, it is doubtful whether the crystal transition effects considered by Marsh could largely be brought into play; nor does the formation of basic nitrates appear to occur (see below, however) and any separation must therefore be dependent almost solely upon basicity characteristics.

According to Brønsted's definition (*Proc. Nat. Acad. Sci.*, 1934, **20**, 221) "onium" salts in the fused state should be considered as acids, and it is known that in liquid ammonia ammonium salts behave as acids (Franklin, *J. Amer. Chem. Soc.*, 1913, **35**, 1459; Franklin and Krause, *Amer. Chem. J.*, 1900, **23**, 205; *J. Amer. Chem. Soc.*, 1905, **27**, 822). The most probable theory for the dissolution in fused ammonium nitrate of rare-earth hydroxides would therefore appear to be based upon its acid properties. This is further indicated by the evolution of ammonia which occurs during the fusion reaction; no nitrogen oxide fumes are produced, so extensive formation of basic salts is improbable.

As pointed out by Marsh, cerium and "didymium" oxides form solid solutions of cubic structure, whereas lanthanum oxide is hexagonal. At the temperatures here employed, decomposition of the hydroxides to oxides cannot be at all advanced, but there appears no reason to assume that the oxide structures do not hold for the hydroxide, particularly as Weiser and Milligan (*J. Physical Chem.*, 1938, **42**, 473) and Seitz (*Z. Naturforsch.*, 1946, **1**, 321) have indicated that the rare-earth hydroxides are hydrated oxides rather than pure hydroxides and that these trihydrates crystallise in the hexagonal system; it would appear therefore that the introduction of cerous hydroxide into the melt would effect a similar "scavenging" effect to that of cerous nitrate in Marsh's nitrate fusion. That it did so is indicated below.

Hopkins *et al.* (*J. Amer. Chem. Soc.*, 1931, **53**, 1805) dissolved lanthanum oxide in fused ammonium nitrate at 170°, and found that lanthanum and neodymium oxides dissolved quite readily but that the less basic elements dissolved only incompletely. They also found that the anhydrous neodymium nitrate finally obtained always contained ammonium nitrate and apparently formed a basic nitrate. In application to separation of the rare earths (below), although no direct evidence has been obtained for the formation of basic neodymium nitrates during the fusion, yet on prolongation of the fractionation the head, insoluble, fractions became gummy and thixotropic and on drying formed hard cakes—they were nevertheless quite soluble in water. Formation of this gummy mass of crystals persisted even when cerium was added to the melt of cerium-free hydroxides. With cerium originally present in the hydroxide it is immediately and completely eliminated from the lanthanum-containing fractions.

No attempt was here made to achieve optimum conditions of working (*i.e.*, temperature, ratio of hydroxide to nitrate, time of fusion, etc.), but solubility ratios for some rare-earth hydroxides were obtained. It is shown that the order of solubilities is similar to the basicity sequence although not in precise comparison.

In his studies on basic ammonia precipitation, Prandtl (*loc. cit.*) introduced cadmium ions to aid separation. Although it was shown (preceding paper) that the presence of these ions is not necessary for efficient separation in presence of a sufficiently high concentration of ammonium ions, the inclusion of this element was examined and found not to influence separation. Cadmium is known to form basic compounds fairly readily, but in the melts examined there appeared no evidence of such a decomposition—rather there occurred the formation of the crystal mass previously noted.

EXPERIMENTAL.

Hydroxide Solubilities.—An approximate ratio of solubilities of individual rare-earth hydroxides was determined by mixing 5 g. of the appropriate hydroxide with 10 g. of ammonium nitrate, fusing at 130° for 10 minutes, cooling, digesting the melt with a minimum of water, and removing the soluble

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portion by filtration; the hydroxide remaining undissolved was ignited to oxide and weighed. The aqueous filtrate was acidified and precipitated with oxalic acid, and the oxalate filtered off, ignited, and weighed. Complete summation was not obtained owing to the solubility of the oxalates in the ammonium salt solution—in fact, from the data obtained it was possible to obtain not only figures for the solubility of hydroxides in fused ammonium nitrate, but also for the solubilities of oxalate in ammonium nitrate solution (see table).

Solubility of rare-earth hydroxides in ammonium nitrate.

[5 G. of $R(OH)_3$ fused in 10 g. of NH_4NO_3 at 130° .]

	R(OH) ₃ , g. :		G. of oxalate [as R(OH) ₃ sol. in NH ₄ NO ₃ soln. (see text).]		R(OH) ₃ , g. :		G. of oxalate [as R(OH) ₃ sol. in NH ₄ NO ₃ soln. (see text).]
	insol.	sol.			insol.	sol.	
La	2.60	2.39	1.55	Sm	3.58	1.42	0.25
Pr	3.35	1.65	0.45	Yt	3.36	1.62	0.55
Nd	3.40	1.58	0.37	Ce ^{IV}	4.52	0.50	0.09

The hydroxides employed for this part of this study were all of *ca.* 99.5% purity, except for the yttrium compound (kindly supplied by Dr. J. K. Marsh) which initially contained *ca.* 2% of erbia. It was found, however, on initial fusion of this hydroxide with ammonium nitrate that fractional removal of the erbium was obtained (see below); a final yttrium hydroxide was obtained which, from the absence of erbium absorption lines in the spectrum and from average atomic-weight determination, appeared to be also of *ca.* 99.5% purity.

Separation of Lanthanum.—The oxide mixture employed was from monazite sources (see preceding paper for analysis) and contained 36.5% of La_2O_3 ; after conversion into the hydroxides and drying, fractionation was carried out employing a hydroxide : NH_4NO_3 ratio of 1 : 7 and a temperature of 130° for 5 minutes. A silica vessel was used for the fusion and the mix was stirred with a thermometer. By pre-mixing the hydroxides and nitrate a lower m. p. was obtained than by first fusing the nitrate and then adding the hydroxide.

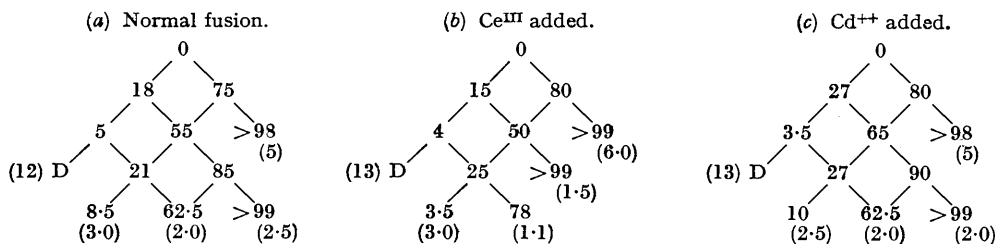
Pyramidal fractionation was carried out and, as indicated above, as it progressed, the hydroxides of the head fraction became gummy and hard and required grinding before re-fusion. For comparison with Marsh's results on potassium nitrate fusion, a ceroso-ceric hydroxide was prepared and kept under alcohol until required, whereupon, after rapid drying, it was added to the fusion in small portions. The "scavenging" effect of this addition, demonstrated in the attached scheme, must be attributed to its oxidation and hence rapid passage through the fractions to the head. In one fusion of 30 g. of a lanthanum hydroxide containing 15% of cerium, 25 g. of $La(OH)_3$ were recovered completely free from cerium which was found quantitatively in the head fraction; in this instance the influence of cerium is dubious owing to its preliminary oxidation to the ceric state by drying. These experiments confirmed the separational effect of cerium noted by Marsh.

As indicated above, the solubility of the tail fractions in ammonium nitrate solution of the oxalates prevented complete recovery of these fractions at each step. The filtrates from the oxalate precipitations were, however, retained and evaporated nearly to dryness with a little sodium hydroxide; the hydroxides thus obtained showed in all cases an apparently slightly enhanced purity when compared with their parent fractions. A secondary fractionation is therefore apparent.

After the introduction of cerium into the fusions, a further fractionation was carried out in which cadmium nitrate was added to each fusion. As the data in the scheme show, no enhanced separation was obtained.

Fractionation of mixed oxides by ammonium nitrate.

(Figures in parentheses are oxide weights, in g. Other figures are La_2O_3 purity, %. D = discarded as free from lanthanum.)



Determination of the composition of internal fractions was made, first, by visual spectroscopic examination through 5-cm. layers of 10% solutions and comparison with standard solutions of neodymium and praseodymium in the presence of lanthanum, and secondly, by the absorptiometric methods employed by Marsh (*loc. cit.*). Such results could only be considered to approximate to $\pm 5\%$ accuracy but were sufficient for following the progress of the separation. Outside lanthanum fractions were checked by arc spectrography.

Purification of Yttrium.—20 G. of yttrium hydroxide containing *ca.* 2% of erbia (see above) were fractionated by ammonium nitrate fusion, a total of 15 operations being carried out. It was not possible to obtain quantitative spectrographic data, but the series was followed by visual observations of the erbium absorption band at 5250 Å. Average atomic-weight determinations of the final six fractions gave

95·8, 93·2, 90·3, 89·5, 89·3, 89·3, successively; these figures can, however, be considered to give indications of purity only slightly better than those obtained by visual observation of absorption bands, but as in the final two fractions no lines were observed through 5 cm. of 10% nitrate solution and in the fourth fraction only very faint diffuse lines could be seen, a good separation was considered to have been achieved with recoveries of 4·9, 5·0, 4·6, 3·8, 1·0, and 0·5 g., respectively.

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