6. *Rare-earth Metal Oxides. Part II. A New Study of Oxide Precipitation by Nitrate Fusion.*

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At 450—500° praseodymium oxide forms solid solutions either with hexagonal lanthanum oxide or with cubic ceric and neodymium oxides. In nitrate fusions as previously conducted cerium dioxide was precipitated at low temperatures and was thus rendered unavailable to partner praseodymium dioxide in the latter's precipitation at higher temperatures. More effective separation of lanthanum and praseodymium by nitrate fusion is brought about by putting the mixed earth nitrates into an already fused alkali nitrate mixture. The resulting nascent cerium dioxide then carries down a large proportion of praseodymium dioxide. Still better results are obtained if anhydrous cerous nitrate is added to a cerium-free melt of earth and alkali nitrates. Methods of estimating neodymium and praseodymium by means of the Hilger "Spekker" absorptiometer are described.

When a mixture of cerium-group nitrates is fused with sodium and potassium nitrates at 300—350° cerium dioxide is precipitated almost pure, though not quite quantitatively. When the temperature is raised to 360—400° the rest of the cerium is precipitated accompanied by small amounts of neodymium and praseodymium, but practically without lanthanum. At 410—460° didymium oxide is precipitated, and several days' fusion at 460° will precipitate nearly all the didymium and much of the lanthanum (Debray, *Compt. rend.*, 1883, **96**, 823; Dennis and Magee, *J. Amer. Chem. Soc.*, 1894, **16**, 649; Esposito, *Proc.*, 1906, **22**, 20; Schutzenberger, *Compt. rend.*, 1895, **120**, 663, 1143). The earths are thus precipitated in the order of their basicity, and previous work has demonstrated the possibility of (1) separating cerium from the other earths, (2) separating lanthanum from praseodymium rapidly, provided initially the lanthanum does not constitute more than 33% of the mixture (Brauner, *Proc.*, 1898, **14**, 71; 1901, **17**, 66; *Coll. Czech. Chem. Trav.*, 1933, **5**, 279); (3) rapidly obtaining lanthanum almost pure but only in small yield (Urbain, *Ann. Chim. Phys.*, 1900, **19**, 225).

The present study is undertaken with a knowledge of the crystal structure of the various oxides not possessed by previous investigators, and already referred to in Part I (preceding paper). Cerium and didymium oxides, despite the ease with which they are separable by nitrate fusion, form solid solutions with a cubic structure, whereas lanthanum oxide has a hexagonal structure. The low temperature at which cerous nitrate decomposes to ceric oxide points to the probability of a basic ceric nitrate being formed as an intermediate. If no ceric salt was formed the stability of cerous nitrate would be comparable with other cerium-group nitrates. Cerium oxide, however, is formed from nitrate at a temperature so low that the other nitrates are quite stable, and so it separates pure, and its influence on the subsequent nitrate–oxide system is largely eliminated. Now praseodymium, and to a lesser extent, neodymium oxide in the presence of lanthanum may take the lanthanum oxide hexagonal structure. This was discussed in Part I. Lanthanum oxide, on the other hand, does not appear to have much capacity for assuming the cubic structure of CeO_2 or Sm_2O_3, etc. The removal of cerium at the first stage of the nitrate fusion is therefore disadvantageous to the separation of lanthanum and praseodymium as it removes a cubic crystal-forming influence which can be used to promote formation of praseodymium oxide in its cubic form, and so assist its separation from hexagonal lanthanum oxide.

Two new methods of carrying out the nitrate fusion have therefore been investigated. (1) The rare-earth nitrates, mixed with alkali nitrates, are added to already fused alkali nitrates a little at a time so that a nearly constant temperature is maintained; finally pure cerous–alkali nitrate may also be added. (2) Cerium is completely eliminated from the other nitrates, which are then fused with alkali nitrates. In this condition a basic nitrate of the rare earths is formed, and the melt becomes very thick and pearly in appearance. Oxide is formed only at a high temperature (500°), but when cerous and alkali nitrates are added to the thick paste there is immediate reaction and fluidity is restored: basic nitrate $\rightarrow$ normal lanthanum nitrate + $Nd_2O_3 + PrO_2 + CeO_2$. The quantity of cerium required to effect the separation of didymium and lanthanum is moderate, and the separation achieved is most satisfactory. Initially, the cerium reacts with the full concentration of other earths in place of a low concentration by the first method. By either of these methods cerium and didymium oxides are co-precipitated and a better extraction of didymium from lanthanum is achieved than by Debray's original method in which cerium oxide is removed from the system early in the fusion. In suspension it can still influence the system, however, as seen by its effect in preventing the formation and separation of the basic nitrate formed in its absence, but it cannot readily enter into solid solution and thus influence the type of oxide formed at high temperatures. No attempt is here made to achieve the most economic conditions of working (*e.g.*, time of heating, temperature at various stages, or proportions of sodium and potassium nitrates), but it is demonstrated that the basicities of neodymium, and even more of praseodymium oxides may vary according to the oxides with which each is associated, *i.e.*, with the crystal structure which they assume. The fusion of nitrates will consequently rapidly separate the rare earths into cubic and hexagonal oxide forms, but solid solution effects and labile states prevent a sharp separation of the elements being thereby achieved.

In carrying out nitrate fusions on mixed cerium earths it has been found that praseodymium behaves as an intermediate between neodymium and lanthanum. This indicates that there is no appreciable ionic quadrivalency of praseodymium called into play. If there was, praseodymium would behave more like cerium and act as a weaker base than neodymium. It must therefore be supposed that the reactions respectively take the courses $Ce^{\cdot\cdot\cdot} \longrightarrow Ce^{\cdot\cdot\cdot\cdot} \longrightarrow CeO_2$ and $Pr^{\cdot\cdot\cdot} \longrightarrow Pr_2O_3 \longrightarrow PrO_2$. The presence of CeO_2, however, has been shown to produce a marked influence on the balance $Pr_2O_3 + O \rightleftharpoons PrO_2$, stabilising PrO_2 formation and thus enabling a separation of praseodymium from lanthanum to be effected.

$$\begin{tikzcd}
 & \mathrm{CeO_2} + \mathrm{Pr_2O_3}\ (\text{cubic}) + \mathrm{O} \arrow[r] \arrow[dd, shift left] & \mathrm{PrO_2} \\
\mathrm{Ce(NO_3)_3} \arrow[ur] \arrow[dr] & & \\
 & \mathrm{NO_3'} + \mathrm{Pr_2O_3}\ (\text{hexagonal}) + \mathrm{La(NO_3)_3} \arrow[r] \arrow[uu, shift left] & \mathrm{Pr(NO_3)_3}
\end{tikzcd}$$

Pr_2O_3 appears to be very labile between cubic and hexagonal forms at 450—500°. If in a lanthanum–praseodymium nitrate mixture there is a good preponderance of praseodymium, on fusion with alkali nitrates nearly pure PrO_2 will precipitate, but if lanthanum exceeds about 33% no separation has heretofore been brought about (Brauner, *loc. cit.*). The lanthanum content in a praseodymium preparation has now been found to be reduced from 12% to about 2% in one fusion; also by throwing cerous nitrate into a lanthanum-rich (87%) mixture, it is now possible without using an undue amount of cerium to obtain 96% lanthanum from the melt, and a high concentration of praseodymium in the CeO_2 residue obtained on lixiviation. A good proportion of PrO_2, but little lanthanum, was coprecipitated with the CeO_2, and the praseodymium could of course be separated subsequently from the cerium by any of the well-known methods. Pure praseodymium nitrate yields on fusion PrO_2, and the cubic form results whenever dioxide formation is possible, but in the absence of cerium only a little lanthanum is required to hold praseodymium oxide in the hexagonal form at the temperatures of nitrate fusions.

EXPERIMENTAL.

Nitrate fusions were conducted in a 300-watt electric furnace built to fit a 100-ml. beaker. Temperatures recorded are uncorrected readings of a glass thermometer (a reading 17° low was found at 420°, the m. p. of zinc).

Estimation of Neodymium and Praseodymium with the Hilger "Spekker" Absorptiometer.—Nitrate solutions and 1-cm. cells were used, and for neodymium the Ilford green light filter 604. No interference by other cerium earths was encountered, and estimations between 0 and 100 g./l. were possible with an accuracy of 1 g./l. Praseodymium was estimated with both Ilford yellow and orange filters 606 and 607 used together, and a water setting of 0·50. Light transmission was rather low, but estimates between 0 and 100 g./l. with an accuracy of 2 g./l. were possible. Some slight overestimate of praseodymium seemed likely when neodymium was also present, and the following method was later adopted. Filters of neodymium nitrate solution (400 g./l. of Nd_2O_3) free from all praseodymium were used. On the left side of the instrument it was found possible to accommodate two cells 0·9 and 1·1 cm. thick, and on the right one cell 3·3 cm. thick. The Ilford violet filter 601 was also used. Only a sharply cut band of light $\lambda\lambda$ 4540—4340 was transmitted, the intensity being fair. In the middle of this spectral region falls the broadest and strongest of the visible praseodymium absorption bands, having its head at λ 4440. A correction for the amount of neodymium present was required, the effect of neodymium being about 3% of that of praseodymium. The calibration curve for praseodymium was far from a straight line. Sensitivity fell off rapidly above 30 g./l. of Pr_2O_3, but from 0 to 30 g./l. Pr_2O_3 could be estimated to ±1 g./l., the optimum concentration being about 20 g./l., giving an accuracy of ±5% on the praseodymium estimate. In order to ensure that no ceric cerium was present, solutions were treated with one drop of saturated oxalic acid solution before use. The absorptiometer affords a quick and easy means of estimating neodymium and praseodymium in admixture with a degree of accuracy and delicacy suitable for most purposes.

Purification of Praseodymium.—The starting material was a praseodymium oxide containing Nd_2O_3, 0·5; CeO_2, 1·5; La_2O_3, 11%. Praseodymium oxide (1 part) was converted into nitrate, and potassium and sodium nitrates (5 parts each) were added and fused at 300—350°. Ceric oxide was removed after lixiviation of the cooled melt. Re-fusion at 440° caused production of pearly green scales, presumably of a basic nitrate, and brown fumes and much thickening. After 80 mins. the temperature was raised to 460°, and darkening started after thickening had reached a maximum. After 2·5 hours and heating to 480°, a clear green melt could be decanted fairly well from the black precipitate. A further 45 mins. heating at 500° gave better decantation and a nearly colourless melt. The whole was treated on cooling with water and filtered. The filtrate was precipitated with alkali and yielded 1·45 g. of La_2O_3 (pale brown). The precipitate was well stirred with dilute acetic acid. From the resulting acetate solution 1·6 g. of oxide were recovered. This was pale brown and contained about 16% of La_2O_3 (by arc spectrum). The residue (6·1 g.) contained 1—2% of La_2O_3 (arc estimation). It was very dense and black.

Other mixtures of lanthanum and praseodymium were also separated. One containing about 70% of praseodymium gave three fractions: 2·9 g. of 97·5%, 1·1 g. of 72%, and 2·1 g. of 27·5% Pr_2O_3 (absorptiometer estimates). A sample of nearly pure praseodymium oxide gave 7·5 g. of Pr_6O_{11} with feeble lanthanum arc lines, 1·6 g. of acetic acid extract with less than 1% of lanthanum, and 1·4 g. of oxide not precipitated from the melt with a lanthanum content of 1%. A second treatment of the main precipitate, however, still gave a product in which lanthanum arc lines were detected.

Attempted Separation of Praseodymium from Lanthanum by Simple Nitrate Fusion.—Lanthanum oxide (80%) with praseodymium oxide (14%) and ceria (6%) was converted into nitrate and fused with mixed nitrates as before. The ceria precipitate was removed by lixiviation and filtration after fusion at 350°; a second fusion was given in which a final temperature of 580° was reached. There was darkening to a chocolate-brown towards the end, and the pasty melt regained fluidity. On lixiviation, a brown scaly precipitate was separated (6·8 g.) which dissolved in acetic acid leaving a small brown residue (0·4 g.). This mostly dissolved in concentrated nitric acid, leaving 75 mg. of cerium oxide. The whole of the rare earth was found to have been precipitated from the melt. Nearly all the precipitate being soluble in acetic acid, no separation of lanthanum and praseodymium was here effected. The small fraction insoluble in acetic acid but soluble in nitric acid was found to contain 34·5% of Pr_2O_3, but the experiment confirms previous observers' reports of the impossibility of separating praseodymium from lanthanum when it is a minor constituent by this form of nitrate fusion proceedure.

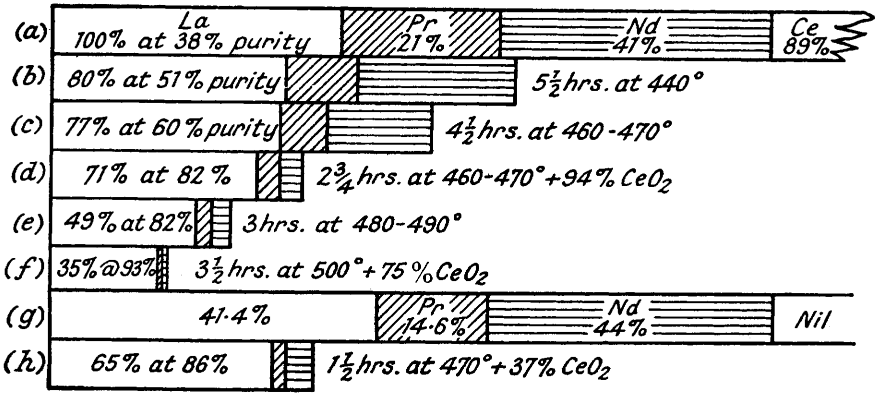
Separation of Praseodymium from Lanthanum with the Aid of Cerium.—17 G. of oxide (Pr_2O_3, 18; La_2O_3, 82%) were made into nitrate, potassium and sodium nitrates (50 g. of each) added, and the whole fused at 440—450° for 3 hours during which a cold powdered cake, containing the equivalent of 7 g. of CeO_2, of fused cerous, potassium and sodium nitrates was added, causing a precipitate in the melt. On lixiviation this was separated. The solution was evaporated, and the fusion, with the addition of cerous and alkali nitrates, twice repeated, the final heating being at 470°. The precipitate obtained by the first lixiviation was partly dissolved in dilute acetic acid. The remainder was brought into solution with nitric acid and hydrogen peroxide, and the cerium removed from the neutral solution by means of potassium permanganate and sodium carbonate ($KMnO_4 + 4Na_2CO_3$). The rare earth, mainly praseodymium, was recovered. The precipitates from the second and the third fusion were not extracted with acetic acid, but were at once treated to remove cerium. There were thus obtained the following products which were examined and estimated by the "Spekker" absorptiometer:

		Oxide, g.	Pr_2O_3, %.	Pr_2O_3, g.
First fusion precipitate:	Soluble in HOAc	0·44	65	0·29
	Insoluble in HOAc	1·50	70	1·05
Second fusion precipitate		1·20	55	0·66
Third fusion precipitate		1·80	29	0·52
Remainder held in melt		11·4	4	0·45
Total		16·34	—	2·97
Input		17·0	—	3·0

Hence, addition of cerous nitrate equivalent to 21 g. of CeO_2 to 14 g. of lanthanum oxide mixed with 3 g. of praseodymium oxide yielded 11 g. of lanthanum oxide mixed with 0·45 g. of praseodymium oxide; or with the addition of 14 g. of CeO_2 and two fusions only, the recovery of praseodymium was 66% at a concentration raised from 18% to 64%.

Separation of Lanthanum and Didymium in Crude Cerium Earths.—Some crude earths from cerite (approx. La_2O_3, 20; Pr_2O_3, 11; Nd_2O_3, 22; CeO_2, 47%, or reckoned as cerium-free oxides, La_2O_3, 38; Pr_2O_3, 21; Nd_2O_3, 41%) were converted into nitrates and fused with mixed nitrates (2 parts each). Portions of the resulting melt were added portion-wise to a melt of $KNO_3 + NaNO_3$, the temperature being held steady. A series of trials were made, the same crude nitrate but different fusion temperatures being used. On each addition to the melt there was a rapid decomposition with liberation of brown fumes, and a fine precipitate was formed. Each cooled melt was finally lixiviated with a minimum of water, for otherwise the precipitate tended to become colloidal. The crude lanthanum remaining in solution was collected as double potassium sulphate, converted into nitrate, and estimated absorptiometrically. In this series of experiments praseodymium was estimated by means of its absorption in the orange-yellow region, and results may be slightly high. They are shown graphically: (*a*) represents the composition and quantity of the starting material, and (*b*)—(*f*) that of the unprecipitated earth recovered as double sulphate in the series of experiments at the temperatures indicated; (*g*) represents the starting material for the experiment (*h*) when no cerium was originally present in the rare earth. As experimental temperatures were raised, fuller precipitation occurred and purer lanthanum was left, but at 480—490° the yield of lanthanum was down to 50% of input at a purity a little over 80%. Best results were obtained at a temperature of 460—470° with addition of some pure cerous nitrate at the end. The yield of lanthanum was thus raised to 70% at a purity of over 80% starting from 38%. In experiment (*h*) the equivalent of 10·7 g. of oxide was fused with 70 g. of alkali nitrates. Decomposition occurred rapidly above 420° and the melt thickened. It was heated to 500° but remained pasty and darkened only slightly. 16 G. of mixed cerous and alkali nitrates were added (=4 g. of CeO_2), and finally the temperature was held at 470° for 15 mins. The whole reaction occupied 90 mins. A detailed analysis is given below:

		Nd_2O_3,		Pr_2O_3,		La_2O_3 (by diff.),	
	Total, g.	g.	%.	g.	%.	g.	%.
Input	10·7	4·72	44 ± 1	1·56	14·6 ± 1	4·42	41·4
Output, precipitate	6·9	4·00	58 ± 1	1·38	20·1 ± 1	1·52	22
,, retained in melt	3·44	0·30	9 ± 0·25	0·16	4·75 ± 0·25	2·88	86·25



Hence, 65% of the lanthanum was recovered with a purity raised from 41% to 86%. This is a rather better separation than was obtained in experiment (*d*) despite the fact that the cerium used represents only 0·37 part of the cerium-free weight of earths in place of 1·83 parts in (*d*), where much of the cerium was originally in admixture with the other earths.

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