7. *Rare-earth Metal Oxides. Part III. Their Precipitation from Potassium Hydroxide Melts.*

By Joseph K. Marsh.

Rare-earth hydroxides are peptised in KOH,H_2O, and on desiccation at high temperatures and with oxidising conditions PrO_2 and TbO_2 are the first oxides to be precipitated. The cerium earths may be precipitated crystalline, but not always anhydrous. Thus the good separation obtainable of praseodymium from neodymium is attributed in part to isomorphism of PrO_2 and NdO(OH) and solid solution with *C*-form Nd_2O_3. These three are precipitated before *A*-Nd_2O_3. TbO_2 forms solid solutions with Gd_2O_3 or Dy_2O_3, and the Tb^{IV} ion, being small and highly charged, is concentrated in early precipitates, and the elimination of terbium from dysprosium is efficient.

Beck (*Angew. Chem.*, 1939, **52**, 536) has found that the rare-earth oxides are soluble in fused potassium hydroxide and that in oxidising conditions the higher oxides of praseodymium and terbium may be precipitated from the melts, and a concentration of the two elements thus brought about. PrO_2 collected at the anode on electrolysis of a melt containing a commercial didymium preparation with a 10% praseodymium content. The higher oxide of terbium was precipitated from a melt to which potassium chlorate was added. Praseodymium could also be concentrated by this method. He claims that one fusion raised the terbium content from an initial 1% to 35%, but this conclusion will be criticised later. Complete purification of neodymium he claimed to be possible, but elimination of all neodymium from praseodymium was not accomplished because, he supposed, both praseodymates $Pr(PrO_4)$ and $Nd(PrO_4)$ were formed. Formations of potassium praseodymate and potassium neodymite were also postulated, but no evidence for any of these compounds was advanced.

The author has found that the rare-earth oxides are insoluble in fused anhydrous potassium hydroxide, but the hydroxides possess a solubility of the order found by Beck in fused potassium hydroxide stick of ordinary laboratory type which contains 15—17% of water, and melts about 140° instead of 360° for the anhydrous material. It now appears that when fractionation of mixed earths occurs it is due to their different affinities for water. Weiser and Milligan (*J. Physical Chem.*, 1938, **42**, 669, 673) have studied the dehydration of hydrous neodymium and praseodymium oxides. They find inflexions in the isobars of each, indicating definite $Nd_2O_3,3H_2O$ or $Nd(OH)_3$ and $Pr(OH)_3$ formation at temperatures of 150—200°, but thereafter praseodymium oxide loses water much more readily than neodymium oxide, so that dehydration of the former at 400° is equal to that of the latter at 600°. Since the dehydrations were done in air, the possibility arises in the case of praseodymium that oxidation took place and PrO_2 was removed from the system, and that the difference between the two isobars is in part due to this side reaction. If this is so under strong oxidising conditions due to potassium chlorate or anodic oxygen in a melt, the differentiation between neodymium and praseodymium behaviour is likely to be still more marked.

The author has studied the precipitation of lanthanum, praseodymium and neodymium oxides from potassium–sodium hydroxide melts and obtained a number of crystalline precipitates. In the case of lanthanum at 290° the precipitate consisted of microcrystalline octahedra with two well-developed square faces. These crystals are clear and colourless. From an impure lanthanum melt they separated side by side with dark PrO_2 octahedra. They lost weight on ignition corresponding to over one molecule of water per La_2O_3, but retained their outward form, and in air they were not carbonated rapidly. At 320—350° the precipitate consisted of prismatic crystals, and at 370—420° of large hexagonal plates easily distinguished with a hand lens. These lost a little weight on ignition but are believed to be *A*-type La_2O_3, which has a hexagonal layer lattice.

Melts of praseodymium at all precipitation temperatures gave only black octahedra of PrO_2. Praseodymium and the other dioxides could not be dissolved in "stick" potassium hydroxide under any conditions. As hydrated praseodymium sesquioxide is dehydrated much more readily than its neodymium analogue and probably also its lanthanum analogue, if dehydrating and oxidising conditions are provided Pr_2O_3 must form first, pass at once into PrO_2 and be precipitated, while the others remain in the melt.

Neodymium melts containing some praseodymium in presence of potassium chlorate gave at low temperatures (320°) large numbers of small brown grains which were only identifiable as octahedra if praseodymium was not too scarce. These are probably solid solutions of PrO_2, NdO(OH) and *C*-Nd_2O_3. The existence of the hydrous oxide NdO(OH) is known (Joye and Garnier, *Compt. rend.*, 1912, **154**, 510; Weiser and Milligan, *loc. cit.*). The latter authors find it to be the only stable hydrous oxide between 300° and 500°. No other rare earth has been reported as giving an analogous compound, and the probability that this oxide hydrate has been mistaken in the past for NdO_2 is referred to later. It is probably isomorphous with PrO_2, and capable of solid solution with *C*-Nd_2O_3. In being precipitated it will thus help to carry down PrO_2. A didymium melt as it loses water appears to precipitate (1) PrO_2, (2) NdO(OH), (3) *C*-Nd_2O_3, (4) one or two forms of *B*-Nd_2O_3, or hydrated forms of *A*-Nd_2O_3, (5) *A*-Nd_2O_3. As (1), (2), and (3) can form solid solutions, the black octahedra of PrO_2 are succeeded by brown amorphous grains, since *C*-oxides are always amorphous; *C*-Nd_2O_3, however, is not the stable oxide form for neodymium at the temperatures of the melts, but requires the stabilisation afforded by solid solution. Thus the brown grains are found mixed with pale blue crystals which obviously contain no PrO_2. These appear to be of two prismatic forms, one having a very limited range of stability and twinning at 90°, the other twinning at 60° often in 6-pointed stars and resembling the 320—350° lanthanum precipitate. Their identity has not been established. Two possibilities seem open: they may be hydrated forms of *A*-Nd_2O_3 or the *B*-forms of Nd_2O_3 of which little is known.

Finally, at high temperatures these forms redissolve and the last fraction of oxide is recovered as large hexagonal plates as in the case also of lanthanum, but here tinted blue. These hexagonal plates have not been observed in the case of elements not known to give *A*-oxides.

In nitrate fusions (Part II, preceding paper) anhydrous melts are encountered and a rapid separation of lanthanum from praseodymium and neodymium takes place on the basis of different oxide crystal forms, but there is little separation of the last two. In potash melts use is made of the differential stability of the oxide hydrates, and the didymium pair separate well. From the work of Weiser and Milligan by analogy with samarium and yttrium oxides it is unlikely that gadolinium and dysprosium oxides form any monohydrate isomorphous with TbO_2 and NdO(OH). All attempts to prepare recognisably crystalline precipitates of these earths from potassium hydroxide melts were failures. The lesser affinity of terbium for a fourth equivalent of oxygen, and the more ready dehydration of gadolinium and dysprosium hydrous oxides, combine to make the separation of terbium less efficient than that of praseodymium. The separation which does occur must take place mainly on account of the insolubility of TbO_2. When through loss of water anhydrous oxide begins to form in the melt, oxidation of Tb_2O_3 takes place and TbO_2 is precipitated. Since with the neighbours of terbium the *C*-oxide is the normal form, and this gives a solid solution with TbO_2, the separation is not sharp, but depends upon the relative solubilities and concentrations of terbium and the other oxides in solution in the melt. It is a case of Goldschmidt's generalisation (J., 1937, 655) that a small highly charged ion separates early in magmatic crystallisations. As a method of separating terbium and gadolinium except on a very small scale, potash fusion compares unfavourably with fractionation of the double magnesium nitrates in presence of bismuth magnesium nitrate; but for the separation of small quantities of terbium which remain obstinately in dysprosium during a dimethyl phosphate fractionation (Marsh, J., 1939, 554) the method proved satisfactory, and it was found possible to prepare a white dysprosium oxide. Four oxide fractions from a melt varied from deep brown to a pale straw colour, showing a remarkable degree of fractionation.

Beck's finding that praseodymium-free neodymium was readily obtained has not been confirmed. One fractionation failed to give any appreciable removal of an initial 8% of praseodymium, and with an initial 15% the purest neodymium retained 5% after one fusion. Whereas, in the case of terbium, fractionation proceeds during the whole course of the operation, since a single solid solution forms the precipitate throughout, yet in the case of didymium as soon as blue hexagonal types of precipitate begin to be formed appreciable further fractionation probably stops. Theoretically it should be possible to help the elimination of praseodymium by adding a naturally *C*-type earth, but the experiment of adding some samaria did not result in any noticeable improvement. Alkali fusion is better adapted to give a very rapid rough separation of praseodymium and neodymium than to prepare the pure products.

The stability of NdO(OH) appears to account for much of the common attribution of a quadrivalency to neodymium, which is often accepted in modern text-books. Brauner (*Coll. Czech. Chem. Comm.*, 1935, **5**, 279), for instance, gently ignited some oxalate and subsequently heated the product in hydrogen and collected $1H_2O$. He therefore claimed that the oxalate yielded Nd_2O_4, whereas it would appear almost certain that it yielded NdO(OH). He admits (Proc., 1901, **17**, 66) that the supposed Nd_2O_4 had no oxidising properties like the other higher oxides in the rare-earth group. Marc (*Ber.*, 1902, **35**, 2370), on the other hand, contended that it had: on addition of CeO_2 to a lanthanum and didymium oxide (15% Pr_2O_3), the available oxygen, measured iodometrically, at first below expectation for quantitative CeO_2 formation, at 2% outstripped theory, and between 5% and 10% outstripped theory for $CeO + PrO_2$; thus with Ce, 15; Pr, 15%, the dioxide amounted not to

30% but to 45%, and some neodymium dioxide formation was therefore postulated. Marc, however, appears to have used no delicate test for cerium, and there is room for doubt as to whether his didymium mixture was entirely free from cerium. The author made an oxide mixture with neodymium and the above proportions of cerium and praseodymium, all pure oxides, dissolved it in nitric acid, and precipitated it as oxalate; after ignition the oxide contained rather less oxygen than theoretical for full $CeO_2 + PrO_2$ formation. Marc's result was thus not confirmed.

The rare-earth sesquioxides are all soluble in fused " stick " potash, but appear first to become hydrated and less dense. The absorption of water from the potash may even raise the m. p. of the latter so that hard solid lumps of KOH incrusting the rare earth form in a cool melt. For maximum solubility of oxide, water up to a total of about 30% should be present in the alkali, and the oxides are with advantage mixed to a paste with saturated potassium hydroxide before use. If hydroxides are dissolved, additional water is not required. Probably solubilities of oxides increase a little with atomic number. Ytterbium oxide was more soluble than the early members of the series. On lixiviating the cool melt it was obtained in a colloidal state. In general, losses of material were encountered with all the rare earths. These were probably due to non-recovery of unprecipitated hydroxides on lixiviation of melts owing to their passage to a sol condition. These losses at times amounted to 10% and detract from the advantages of the process as applied to valuable materials. Fused sodium hydroxide has little power of dissolving rare earths, probably on account of its weaker affinity for water. Their solubility in potassium hydroxide is low under 250°, but rises rapidly to a maximum roughly at 320°. At this temperature sodium hydroxide is anhydrous, but boiling potassium hydroxide solution contains 16% of water. At slightly higher temperatures, when the KOH,H_2O phase becomes unstable, precipitation of rare earth begins. The m. p. of potassium hydroxide then rises rapidly, but may be kept low conveniently by addition of 10—20% of sodium hydroxide. This assists decantation, and the precipitates are formed at lower temperatures and appear to be more crystalline.

It has been shown in Part I (this vol., p. 16) that terbium in admixture with gadolinium oxide may be oxidised in oxygen to a higher degree than is represented by Tb_4O_7, but not fully to TbO_2. Precipitation of terbium from potash melt is likely to yield an oxide not less oxygenated than by heating in 1 atm. of oxygen. Beck's claim to have produced in one fusion a terbium oxide with 0·25% of active oxygen cannot be said to indicate for certain a terbium content over 6% instead of the 35% suggested (TbO_2 contains 4·2%). Nothing can be assumed as to the state of oxidation which terbium may attain on precipitation from a potash melt. No reliance can be placed upon iodometric estimates of terbium peroxide unless it is known that the terbium is (1) nickel-free, (2) oxidised to a definite state. The first condition is not attained in the original precipitates from potash. For the second condition it is necessary to heat the oxide carefully at 330°, and to know the nature of the diluent earths. Even then there is an ambiguity, for oxygenation probably passes through a maximum value at a particular dilution.

Nickel crucibles become deeply oxidised in contact with moist potash melts, and considerable rare earth is taken up in the oxide coat. This may be dissolved upon the next occasion when the crucible is used, and may cause serious contamination of the new charge. In separating traces of terbium from dysprosium by fractional precipitation, it is therefore essential that a set of crucibles be used in the same sequence: a clean empty crucible from the head must not be used to receive a tail fraction. When ytterbium oxide was dissolved in a potash melt in an oxidised nickel crucible, the nickel oxide was dissolved and the crucible showed bright metal. Iron was rapidly attacked in a potash–ytterbium melt and a green deposit believed to have been $Yb(OH)_2$ was formed. Ytterbium thus appears to be very easily reducible in potash.

The rare-earth hydroxides in moist potassium hydroxide are best regarded as being peptised. Their case is similar to that of the alkaline earths though the solubility is rather less. Salt formation does not appear to play a part. In fact, the quadrivalent oxides which might most conceivably be salt forming are the first to be precipitated from the melts. Further investigation is required to establish firmly all the facts concerning the reactions taking place, and the natures of the interesting products formed in potash melts.

EXPERIMENTAL.

The melts were made in a 300-watt electric furnace built to fit a 100-ml. nickel crucible. Temperatures recorded are readings of a glass thermometer shod with nickel. Electrolysis was carried out with a thick platinum wire cathode dipping slightly into the surface of the melt, the crucible acting as anode, and 4 volts were applied.

Treatment of Crude Dysprosium Material.—The dysprosium gave a dark rust-coloured oxide and contained perhaps 10% of gadolinium in addition to terbium, which, however, by arc spectrum appeared a quite minor constituent. 17·5 G. of dysprosium oxide were dissolved in 75 g. of "stick" potassium hydroxide and 3 g. of potassium chlorate added. Gassing began at 345°, and frothing at 370°. The first precipitate (2·5 g.) was of a deep rust colour, the second (4·5 g.) at temperatures up to 400° was deep red brown, the third (2·9 g.) up to 420° was pale ochre, the fourth (3·0 g.) up to 450° was biscuit-coloured. The final residue amounted to 50% of the alkali and was almost free from rare earth. The oxides as precipitated from alkali were very dense, and darker than after solution and reprecipitation as oxalate. 42 G. of dysprosium oxide were worked up, and the fractions united according to colour. After three fractionations some very dark head fractions were obtained, and small tail fractions of which the last was much paler than Sm_2O_3, indeed practically white. The terbium content could not exceed 0·01%.

Lanthanum.—A clear melt was obtained at 300° by heating a mixture of 50 g. KOH (stick) + 20 g. NaOH + 8 g. H_2O + 10 g. La_2O_3. After 5 mins. and at 310° precipitation started. As it appeared to be exothermic, heating was stopped and the temperature reduced to 290°. After 20 mins. the melt was decanted and a crop of crystals obtained. The melt was reheated at 260—280° for 2½ hours, and good crystals were formed. These were collected and washed with dilute acetic acid. Under magnification they were seen to be octahedral with two strongly-developed square faces.

When less lanthanum was in solution and the temperature of precipitation was higher (310—340°) the crystals were smaller and of indeterminate form. On reheating to 350° acicular crystals showing twinning at an angle of 60° with occasional perfect six-pointed stars were obtained. There were also a few hexagonal plates and roundish specks (dissolving octahedra ?). A final heating to 410° gave a crop of good hexagonal plates.

Praseodymium.—The oxide PrO_2 was unattacked by fused "stick" potassium hydroxide but Pr_2O_3 (89%) was dissolved. It gave a colourless melt, which however became greenish on cooling. A mixture of 25 g. KOH + 10 g. NaOH + 2·5 g. H_2O + 4 g. Pr_2O_3 + 2 g. $KClO_3$ at 320—335° gave a clear melt which later formed a skin of shining black crusts, from which it was decanted. Second and third heatings at 350° and 380° gave further crops. There was some frothing at 380°. All the precipitates were seen under magnification to be octahedra. The arc spectra showed a concentration of lanthanum in the later fractions, but it was not striking.

Neodymium.—Oxide containing 8% of praseodymium was dissolved in "stick" potassium hydroxide to give a sky-blue melt. Electrolysis at 340° for ½ hour gave a small dark precipitate. Further electrolysis at 350—380° gave a coarser precipitate, which was collected. Under magnification only brown grains of indefinite form were seen. A third heating without electrolysis gave a crop of good crystals, bluer, and mostly hexagonal plates. The first precipitate lost 1% by weight on ignition, the last only 0·3%. No definite enrichment in praseodymium was found in the first precipitate when examined absorptiometrically.

Didymium.—70 G. of potassium hydroxide ("stick") + 11 g. of earths (Nd_2O_3, 83·5; Pr_2O_3, 15·5; La_2O_3, 1·0%; CeO_2, trace) gave a clear melt at 320°. After 45 mins. of electrolysis, during which the temperature rose to 360°, a brown precipitate appeared suddenly and subsequently darkened to maroon. Electrolysis was stopped after 10 mins. (380°), and after short standing the melt was decanted and the precipitate (1) recovered (1·1 g.). The melt was reheated and 10 g. of sodium hydroxide added. A second crop of precipitate (2) was recovered (3·8 g.). The third heating gave a precipitate (3) brown at first but later blue-grey (1·4 g.). Under magnification crops (1) and (2) were mainly brown grains of indeterminate form, but (2) contained some pale needles. Crop (3) was mainly blue hexagonal plates. After removal of nickel the praseodymium contents were estimated absorptiometrically and were found to be (1) 25, (2) 13, (3) 5%. Only a very little earth remained unprecipitated.

In another similar experiment 1 g. of samarium oxide was added and three precipitates obtained and estimated: (1) 2·7 g., 80% Nd_2O_3, 19% Pr_2O_3; (2) 2·0 g., 79% Nd_2O_3, 19% Pr_2O_3; (3) 1·1 g., 84% Nd_2O_3, 4·5% Pr_2O_3 (11·5% Sm_2O_3 by diff.). The effect of the samarium was to increase the proportion of brown grains, but this was not helpful in concentrating the praseodymium. The recovery of earths is shown much below 100% owing to difficulty in decanting, any hydroxide appearing on lixiviation of residues being lost on washing the precipitate with acetic acid. The effect of a little cerium in the earths is to cause the precipitate to be fine and therefore more easily held in suspension.

Electrolysis of the melts resulted in liberation of hydrogen at the cathode until most of the oxides had been precipitated and the water lost, but finally there was often an indication of metal formation.

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