

279. The Preparation of Ytterbous Sulphate and its Elimination from Lutecium Sulphate.

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Amalgamated lead may replace mercury as cathode for reduction of ytterbium sulphate, and a 95% yield of ytterbous sulphate is obtained. Four precipitations raise the purity from 30% to 100%. Freedom of electrolyte from heavy metals, and purity of cathode materials are essential. Similarly 95% lutecium oxide has been prepared from ytterbium-lutecium mixtures.

HITHERTO, ytterbous sulphate has been prepared at a mercury cathode and only in small quantities (Ball and Yntema, *J. Amer. Chem. Soc.*, 1930, **52**, 4264; Prandtl, *Z. anorg. Chem.*, 1932, **209**, 13; Pearce, Quirke, and Hopkins, *Amer. J. Sci.*, 1935, **30**, 116; Pearce, Naesen, and Hopkins, Preprints Electrochem. Soc., 1936). It is now found that electrodes of amalgamated lead are more convenient, and may be employed successfully in cells of low resistance, but the purity of the lead is a matter of prime importance, and the freedom of the electrolyte from heavy metals a factor upon which the stability of the reduced salt is largely dependent. The presence of heavy metals is indicated if, when reduction starts, a darkening of the solution takes place. This darkening has been observed by previous workers, and the great instability of the ytterbous sulphate which has been noted is due in large measure to the catalytic oxidising action of the impurity. An ytterbous sulphate solution, free from solid and not unduly exposed to air, remains green for several hours, and if some undissolved salt is also present the evolution of hydrogen is very slow. If, however, the crop of ytterbous sulphate is contaminated with reduced lead or mercury, the evolution of gas is extremely rapid and the salt will decompose in a few minutes, so that a large part of the yield is lost before it is possible to collect it on a Buchner funnel. The objectionable matter is held on the precipitate, however, so that one or two filtrations remove it, and thereafter the reduction proceeds with greater rapidity.

Further reduction is very slow when the ytterbium oxide content of the solution falls to 10–15 g./l. This represents about 95% efficiency, with a concentrated sulphate solution initially, and marks the usual limit to which it is worth working.

Ytterbium acetate undergoes ready reduction in presence of acetic acid when treated with sodium amalgam. Addition of sulphate ion then gives a precipitate. Owing to difficulties in recovering the rare earth in presence of much sodium, it is doubtful if this method of reduction can compete in utility with the electrolytic.

A lutecium preparation was purified as far as possible by the removal of ytterbous sulphate. The crude oxide contained 70% Lu_2O_3 , and this was raised to 95%. The final solution contained 250 g./l. Lu_2O_3 , but the same limit for removal of ytterbium was obtained (10–15 g./l. Yb_2O_3) as when ytterbium was present alone in solution. Fractionation methods for the purification of lutecium have hitherto not been very successful, so an easy method of obtaining preparations of 95% purity is of value.

EXPERIMENTAL.

8.6 Kg. of rare earths from Norwegian gadolinite were made into chloride solution. 50 Kg. of sodium sulphate were added gradually during a month, and the precipitate removed from time to time. The cerium earths, nearly all the gadolinium and dysprosium, and much of the yttrium were thus removed, but erbium, ytterbium, and lutecium remained almost wholly in solution. They were, however, precipitated almost quantitatively on boiling. These earths were then transformed into nitrates, and basic nitrates cropped systematically, at first by the addition of sodium hydroxide, but later, when the bulk had been reduced, by the nitrate fusion process. Very quickly, much nearly colourless material collected in the most weakly basic fractions, and formed the starting material for the preparation of pure ytterbium oxide.

The crude oxide was made into a concentrated sulphate solution, either by treating a suspension with sulphuric acid and mechanically stirring it, any great rise of temperature being avoided, or by precipitating the sulphate from a concentrated chloride solution with excess of sulphuric acid and subsequent addition of alcohol. Reduction to ytterbous sulphate was

effected in a 400-ml. tall-form beaker containing a porous pot (106 × 37 mm.). The anode in the pot was a 15-cm. length of stout lead pipe, of 13-mm. bore, closed at the lower end and with a side tube near the top. The cathode in the beaker was a flag (100 × 45 mm.) of pure lead sheet (99.995%) which had been repeatedly amalgamated with pure mercury. A cathode which contained a small amount of tin was found to be quite useless.

The cell rested in 4 or 5 turns of 13-mm. lead pipe suspended in water in a 1.5-l. beaker. During the electrolysis, cooling water was passed through the lead coil and the interior of the anode. Dilute sulphuric acid filled the anode chamber, and up to 200 ml. of sulphate solution were placed in the cathode compartment. No reduction occurred if the electrolyte was not sufficiently acid. The exact degree of acidity was not critical, but from 2*N* to *N*/2 was found suitable. Up to six cells were used in series supplied by a 100-volt main and a cathode current density of 0.3 amp./cm.². At first, reduction was conducted intermittently, the electrolyte being entirely withdrawn for filtration from the accumulated ytterbous sulphate. The current efficiency with concentrated solutions was high, little hydrogen being evolved. When the solution became dilute the electrolysis was made continuous, the reduced salt being withdrawn with a part of the electrolyte by means of a probe, but the cathode was left covered to avoid possibility of corrosion. A heavy crop of ytterbous sulphate was produced in the first 10 minutes, and the reaction brought to completion in 2—3 hours. Starting with material showing strong erbium absorption bands, four reductions were necessary to eliminate all trace of them. A yield of 200 g. of ytterbium oxide was obtained.

Lutecium Preparation.—The material which had not suffered reduction was converted into bromate and recrystallised about 3000 times. The bulk, however, consisting of an yttrium-erbium mixture, was eliminated during the course of this fractionation, and there finally remained at the head crude thulium, in the middle ytterbium which had escaped reduction, and at the tail a mixture of lutecium and ytterbium. The separation of lutecium from ytterbium is not so satisfactory as the separation of thulium, but although the solubility of these bromates is high, they crystallise well, and if the mass of crystals is broken up and allowed to settle, the mother-liquor may be decanted.

The tail fractions (36 g.) which contained only traces of thulium were converted into sulphate (Tm absorption band λ 6830, visible but only weak in 6.5 cm. of 1000 g./l. solution of oxide). A modified reduction cell suitable for handling smaller quantities of precious material was used. The porous pot was replaced by a parchment bag (70 × 20 mm.) attached to a short piece of glass tube. A stout lead wire acted as anode. The glass tube passed tightly through a beaker cover of vulcanite. The outer vessel was a 200-ml. tall-form beaker, cooled by melting ice. The cathode size remained unchanged. When, as here, only one or two cells were in use, a 10-volt supply sometimes replaced the mains. On electrolysis, 9 g. of ytterbium oxide were removed, and a measurement of the magnetic susceptibility of the resultant lutecium oxide showed a purity of 95%.

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