434. *Notes on the Preparation of Pure Europium, Gadolinium, and Terbium Compounds.*

By Joseph K. Marsh.

1. *Europium.*—Since the discovery by Yntema (*J. Amer. Chem. Soc.*, 1930, **52**, 2782) that europium sulphate could be reduced to a highly insoluble europous sulphate at a mercury cathode, an easy method of preparing pure europia has been available, but the form of apparatus he employed was not designed for more than small quantities of material. By reaction at an amalgamated lead cathode, however, it is now shown that europia can be separated quantitatively in one operation from a 3% mixture with gadolinia. The apparatus is in the form of a simple battery cell with large cathode and low resistance, and would appear to be capable of being adapted to handle large amounts of material.

35 G. of the mixed oxides were converted into chlorides and mixed with 1 l. of $N/2$-sulphuric acid. A clean lead sheet was amalgamated and bent to slip inside a 1500 ml. beaker on the bottom of which was a layer of mercury, giving with the lead a cathode area of 500 cm.^{2}. The anode of platinum was placed in N-sulphuric acid in a central porous pot. The rare-earth solution was electrolysed with a current of 5 amps. at 4—5 volts. A deposit of europous sulphate began to form after ½ hour. After 3 hours, the temperature had risen to 40°, and the cell was placed in cold water. After 6 hours the europous sulphate was collected. A further 4 hours gave a slight additional yield.

Owing to corrosion, it is important that the cathode should not remain in the bath when current is not passing. It must be kept bright and clean, but even so, steps should be taken to separate the europium from lead.

The separation from gadolinium appeared to be quantitative, and the europium was of good quality. A second reduction afforded material of the highest purity.

2. *Gadolinium.*—The separation of gadolinium from terbium has always been more troublesome than that from europium. The solubility of the double magnesium nitrate is very great, and conversion into double nickel nitrate or into simple nitrate is commonly recommended. The latter gives a purer product but only after a laborious fractionation.

Terbium shows less tendency than gadolinium to form a double magnesium nitrate. Terbium is the link between the cerium earths down to gadolinium, which give double magnesium nitrates, and the yttrium earths from dysprosium onwards, which do not; it therefore quickly concentrates in the mother-liquors, leaving a double magnesium nitrate yielding a pure white gadolinia. The objection to the fractionation of gadolinium magnesium nitrate is its high solubility, which exceeds that of magnesium nitrate, but this may be countered by the liberal admixture of bismuth magnesium nitrate.

The double magnesium nitrates of gadolinium are crystallised from nitric acid (*d* 1·3), and bismuth magnesium nitrate is continually added to the tail fractions. If simple salts separate, they may be redissolved in the course of a day by seeding with bismuth double salt, and double salts then crystallise; this seeding of the cooling solution was adopted as a matter of routine, and fractionation then proceeded rapidly. On no account must the mother-liquor be poured from a fraction in which the simple salts have separated, for the amount of magnesium in the remaining solid will thereby be rendered excessive. The volume of mother-liquor in each fraction should be small, and a cool place for crystallisation is desirable.

The final removal of bismuth is best effected by heating the material to 130°. The consistency will then be creamy, the water of crystallisation will be lost, and much of the bismuth will have separated as basic nitrate. On treatment with water near the boiling point, nearly all the bismuth will be precipitated as a dense deposit (violent bumping is liable to occur); the amount of water required for this hydrolysis is not excessive if the first heating has been carried to the right point. The remainder of the bismuth is easily removed by hydrogen sulphide. It is not desirable to omit the hydrolysis and rely on removal by hydrogen sulphide alone.

3. *Terbium.*—James (*J. Amer. Chem. Soc.*, 1914, **36**, 10) studied the possibility of utilising the dimethylphosphates, where the rate of change of solubility from one earth to another is almost the highest known; he noted as a disadvantage that there was a tendency to the formation of a troublesome colloidal precipitate, but the author has now minimised this difficulty and thereby achieved a highly efficient purification.

The starting material consisted of the bromates of gadolinium, dysprosium, and terbium, which had already been fractionated from a crude mixture about 170 times till much of the first two metals had been almost freed from terbium and eliminated. Traces of neodymium were also present in the series. The bromate fractions were united in pairs and converted into oxides. Most gave dark oxides, the lightest being of a pale ochre colour. The oxides were mixed with water to a thin cream in mortars and the dimethylphosphoric acid added. On standing, union took place and the mixtures hardened. To effect attack on the richer terbium fractions (darkest oxides) it was necessary to add hydrogen peroxide. The products were ground, and lixivated with ice water, any residue of oxide being again treated with the acid.

Solutions should be nearly saturated when cooled with ice, and crystallisation effected by warming them slowly in a water-bath to 40—50°, the troublesome hydrolysis being minimised if the latter temperature is not appreciably exceeded. Since crystallisation occurred as a cotton-wool-like deposit on all the sides of the beaker, occasional stirring was required to facilitate heat transference, and filtration was then necessary for the separation of the crystals; for this purpose a coarse, sintered, Jena-glass funnel was effective. A large amount of material was quickly eliminated at the head, giving a buff-coloured oxide, and neodymium was very soon found at the tail. Only about six fractions separated a nearly pure dysprosium at the head from approximately pure terbium. Gadolinium was even more quickly concentrated at the tail. The series consisted of 15—20 fractions. When most of the dysprosium had been removed, the crystals were coarser, and if the solution was undisturbed on warming, decantation was possible without filtration; 30—50% of the mother-liquor, however, then remained with the crystals. Nevertheless, efficiency was unimpaired, as re-solution of the crystals was much facilitated, the tightly felted wad from filtration having presented some difficulty.

Final control of the fractionation was secured by observation of the arc lines of gadolinium in the tail fractions and observations of the absorption bands of dysprosium in the head, in particular the strong band λ 3871. At first, observation of the colour of the oxide was sufficient. About 15 g. of material in which neither neighbour could be detected were finally prepared, and a larger quantity of material only a little less satisfactory.

Soluble terbium salts, usually described as colourless, possess a very faint pink tint when seen in sufficient quantity. The tint is much weaker than for europium, but is in conformity with the possession of a weak blue-green absorption band; further, it completes the symmetry in sequence of the colours of the rare earths centred round gadolinium (No. 64), *viz.*, 63 and 65, faint pink; 62 and 66, yellow; 61 (?) and 67, orange; 60 and 68, red; 59 and 69, green; 57, 58, 70, 71, colourless.

Freed (*J. Amer. Chem. Soc.*, **1931**, **53**, 3906) has drawn attention to the probability that unsolvated salts of the rare earths should prove suitable for fractionation, on account of known differences in ionic radii. The dimethylphosphates are an example of such salts, but whether this is the real cause of their suitability is doubtful. It is noteworthy that the salts which in several instances show an unusually great range of solubility among the rare earths are those which may be described as mixed aliphatic–inorganic, *viz.*, cacodylates, dimethylphosphates, ethylsulphates. These monobasic derivatives show an increased solubility over the arsenates, phosphates, and sulphates respectively. In general, the rare-earth salts of polybasic acids are of low solubility, but in such salts the ionic radii of the earths should play a more important part. The influence of the size of crystal unit may probably be traced in the common behaviour of a remnant of a less soluble salt in failing to concentrate with the bulk at the head, even on prolonged fractionation. Solubility is the chief factor in the separation, but it must be supposed that when the tail crystals pass a certain point in composition their lattice is no longer of a size which will accommodate the deposition of a unit of the head material, and in effect the latter acquires a greater solubility. If, now, change is made to a salt with a reverse order of solubility, rapid expulsion of the impurity is effected, for solubility and lattice dimensions will no longer be opposed. The 4% change in length of unit face of the rare-earth oxides between samarium and ytterbium would appear to be a very unfavourable property on which to base a method of separation when compared with the 3000% change between the solubilities of samarium and ytterbium dimethylphosphates.

SUMMARY.

Pure europous sulphate may be separated electrolytically in one or two steps from material with a low (3%) europium content.

Conditions are described for the efficient purification of gadolinium by fractionation of double magnesium nitrates.

Fractional crystallisation of the dimethylphosphates has proved efficient in yielding very pure terbium.

The probably real, but small, influence of changes of lattice dimension during the process of fractionation is discussed.

THE QUEEN'S UNIVERSITY OF BELFAST. [*Received, October 23rd,* 1934.]