

THE SEPARATION OF THE LANTHANONS (RARE-EARTH ELEMENTS)

By J. K. MARSH, D.Sc., F.R.I.C.

Terminology.—The rare-earth group has at no time been a well-defined body of elements. Some present-day physicists confine the term to the elements Nos. 58—71 (Ce, Pr, Nd, 61, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), for here the 4f electron shell comes into being and fills up while the rest of the electron structure remains unchanged. Some chemists would include also the elements of Group IIIa, viz., scandium, yttrium, lanthanum, and actinium, but it is better to include only lanthanum (No. 57). Chemically, yttrium certainly falls within the group though its chemical position varies, so that the term “yttrium group” is unfortunate, since yttrium may on occasion associate with elements outside the “yttrium group”. The term “heavy” earths is to be preferred, and for the cerium and terbium groups the terms “light” and “middle” earths, but without defining exact boundaries. The appellation “rare” is also now known to be inappropriate. According to V. M. Goldschmidt¹ yttrium and three members of the group are more abundant in the crust of the earth than lead, while thulium, the rarest member, is estimated to equal iodine in abundance, and to be three times more plentiful than silver. They are normal constituents of igneous rocks, but they show very poor power of segregation. Only where large pegmatite formation has occurred is there any high degree of concentration. Thus they are ordinarily concealed, and the term “lanthanon” (Ln) is proposed to denote any element of the group from lanthanum to lutecium inclusive, and to replace such objectionable terms as “lanthanate” or “lanthanide” which have recently had some currency, and to bring them into conformity with their new analogues the “actinons”.

Scope.—Previous accounts of the separation of the lanthanons have been written by L. M. Dennis,² G. Urbain,³ C. James,⁴ and W. Prandtl,⁵ who during the present century have each added substantially to our knowledge of the group, and whose accounts are based upon personal work. The author likewise during the past eighteen years has added to knowledge affecting the separation of each of the fourteen members of the group with the exception of cerium.^{6a-6l} The reviews of D. W. Pearce⁷ on bi- and

¹ *J.*, 1937, 655.

² L. M. Dennis and B. Dales, *J. Amer. Chem. Soc.*, 1902, **24**, 401.

³ *J. Chim. physique*, 1906, **4**, 31, 105, 232, 321.

⁴ *J. Amer. Chem. Soc.*, 1908, **30**, 979; 1912, **34**, 757; ref. 37.

⁵ *Z. anorg. Chem.*, 1933, **238**, 321.

^{6a} *J.*, 1929, 2387 (II); ^{6b} *J.*, 1934, 1972 (Eu, Gd, Tb); ^{6c} *J.*, 1937, 1367 (Yb, Lu);

^{6d} *J.*, 1939, 554 (Tb, Dy, Ho); ^{6e} *J.*, 1942, 398 (Sm, Eu, Gd); ^{6f} *J.*, 1942, 523 (Nd, Sm, Gd); ^{6g} *J.*, 1943, 8 (Tm, Yb, Lu); ^{6h} *J.*, 1943, 531 (Eu, Sm); ⁶ⁱ *J.*, 1946, 15 (Pr, Tb); ^{6j} *J.*, 1946, 17 (La, Pr); ^{6k} *J.*, 1946, 20 (Pr, Tb); ^{6l} *J.*, 1947, 118 (Er, Y).

⁷ *Chem. Reviews*, 1935, **16**, 121.

quadri-valency and of T. Moeller and H. E. Kremers⁸ on basicity in the group will also be found useful. No attempt has been made to catalogue recent work, but it is hoped that no important recent method applicable on a moderate scale as distinct from analytical procedure has been overlooked. Any complete account must take into consideration methods of testing purity. These, however, must now be left with the passing remark that modern spectrophotometric methods make possible rapid complete analyses of the light and heavy groups respectively in regard to the coloured constituents of each.⁹

Historical.—In 1794–97 yttria was recognised in gadolinite, and in 1804 ceria was recognised in cerite, but not until the work of C. G. Mosander (1839–43) were these two earths shown to be complex. Ceria was split by the action of chlorine on the suspended hydroxide whereby a part, lanthanum hydroxide, dissolved. Lanthana in turn by extraction with 1% nitric acid left a residue of didymia. Mosander also split yttria into three fractions, true (colourless) yttria, and the weaker bases erbia and terbia. Fractional precipitation by ammonia or oxalic acid was used. Thus there came to be recognised six elements. No true new member was added to the group till 1878, when J. C. G. de Marignac, using N. J. Berlin's nitrate fusion process (1860), separated ytterbia from erbia. Between 1878 and 1880 holmia and thulia (P. T. Cleve), samaria (Lecoq de Boisbaudran), gadolinia (Marignac), and scandia (L. F. Nilson) were recognised, though most of them were not prepared pure till the twentieth century.

In 1885 C. A. von Welsbach introduced the use of double ammonium nitrates for fractional crystallisation of the light group, and split didymia into neo- and praseo-didymia. E. Demarçay in 1900 introduced the use of the double magnesium nitrate method of fractionation. This marks the next and almost final step forward in the separation of the first half of the lanthanon group. Possible replacement of magnesium by other bivalent metals followed quickly, but magnesium is the most generally useful. All the members of the light group (freed from cerium) can be purified by double magnesium nitrate fractionation. Addition of the isomorphous bismuth magnesium nitrate assists the separations at the more soluble (gadolinium) end of the series. Demarçay prepared pure europia by this method in 1900. In 1898 G. Urbain introduced the use of ethyl sulphates for the fractional crystallisation of the heavy group. His important work on this group was presented in a completed form in 1906.³ The most notable achievement was the isolation of dysprosium. Since the ethyl sulphates have the disadvantage of being prone to hydrolysis, the introduction of bromates by C. James in 1908 gave a more stable salt and one which is capable of separating each of the heavy earths from gadolinium to lutecium in a state of purity, except that the overwhelming abundance of yttrium, which interpolates in the series between holmium and erbium, prevents the purification of these two by bromates alone.

Since 1908 the most notable developments have been in use of the bivalent

⁸ *Ibid.*, 1945, **37**, 97.

⁹ C. J. Rodden, *J. Res. Nat. Bur. Stand.*, 1941, **26**, 557; 1942, **28**, 265.

state for the separation of the three elements samarium, europium, and ytterbium, which alone have any significant bivalent stability, and the use of the quadrivalent oxides of praseodymium and terbium for the isolation of these two elements. Holmium and erbium are thus now the only lanthanons, together with yttrium, which have not at least one neighbour which can be separated in one or two operations. Lanthanum, neodymium, gadolinium, and lutecium have no neighbours not thus separable.

Sub-atomic Structure.—The lanthanon series of elements arise from the growth of an inner electron shell, $4f$, while the outer valence shells remain fixed. A tendency appears for this shell to contain 0, 7 or 14 electrons, the normal trivalent quotas of lanthanum, gadolinium, and lutecium respectively. Multivalence is due to this tendency. Thus quadrivalent cerium arises from the single electron present on the $4f$ level in trivalent cerium migrating to an outer or valence level. The stability of two electrons in the $4f$ level is not complete though much greater than one: thus arises the formation of praseodymium dioxide. Seven electrons in the $4f$ shell appear to constitute some sort of sub-group, for in many respects gadolinium represents a turning-point in the series. Thus several series of salts have a maximum or minimum solubility at or near this point, and in general the differences in chemistry become less when the electrons exceed seven. The elements of the heavy group are much more difficult to purify than those of the light group. The average frequency of the absorption bands is at a maximum with gadolinium, all the bands of which lie in the ultra-violet, and shift on either side of gadolinium (No. 64) towards the red, so that the salts of the whole series in number sequence pair off in visual colour— 64 ± 1 , 64 ± 2 , etc. The strong attraction to complete the $4b$ septet is seen in the tendency of europium (No. 63) to lose an outer valence electron to this level. Samarium (No. 62) has a lesser tendency of the same sort. Terbium (No. 65) on the other hand tends to lose the eighth electron by migration to the valence level as exemplified by the formation of a higher oxide. Ytterbium, with thirteen $4f$ electrons, tends to complete the shell by migration inwards of a valence electron. The building up of electrons at the $4f$ level does not entirely compensate for the growing nuclear charges, so that there is a progressive fall in ionic radius with increasing atomic number. The fall is particularly large from lanthanum to cerium, and large between cerium and praseodymium, and is accompanied by chemical differences of more than the usual magnitude. Frequently the early lanthanon salts carry more water of crystallisation than the later members. The ionic radius of yttrium is reached about the position of holmium in the series and gives rise to the extraordinarily close chemical likeness of these two elements. However, the writer⁶¹ has shown that when the non-ionised states are compared, though there is still a contraction with increasing atomic number, yttrium now appears to interpolate between neodymium and samarium.

Illinium.—Something like seventy false reports of new members of the lanthanon series have been made, but with the advent of Moseley's demonstration of the regular decrement of X -ray wave-lengths with rising atomic number it became apparent that at that time (1913) the complement of the

series was correctly made up, except for the long suspected missing member between neodymium and samarium. Confirmation of a place here for a possible element was welcome, and three claims to have found it were staked in 1926,¹⁰ but they do not appear to be well established. According to J. Mattauch's¹¹ empirical rule, two isobars differing by one unit in nuclear charge are never both stable. Now the isotopic constitutions of Nos. 60 and 62 are known to include the following mass numbers :¹²

Neodymium	142	143	144	145	146		148		150			
Samarium			144				147	148	149	150	152	154

Unless therefore No. 61 is to prove to be an exception to the Mattauch rule its mass number must be below 142 or above 150. These possibilities both seem unlikely. If it existed in Nature as a radioactive element it would almost certainly have been detected. S. Takvorian has discussed the evidence for the existence of illinium.¹³ Several artificial radioactive isotopes of No. 61 have been made of which ¹⁴⁷61 with a half-life of 3.7 years is the most stable. It should be producible in tangible quantities.^{13a}

We may note here¹² that the even numbered lanthanons average more than 6 stable isotopes each and the odd numbered only 1.1. The approximately six-fold greater abundance of the even numbered elements is thus seen to coincide largely with a corresponding abundance of isotopes. All mass numbers from 139 to 176 are represented by stable lanthanon bodies.

Sources of the Lanthanons.—The Travancore monazite deposits are of unparalleled richness and constitute the only important source in the British Empire of the light lanthanons. The composition of the lanthanon oxide from monazite approximates to : CeO₂, 50% ; La₂O₃, 16% ; Pr₂O₃, 8% ; Nd₂O₃, 18% ; Sm₂O₃-Gd₂O₃, 7% ; Tb₂O₃-Lu₂O₃ + Y₂O₃, 1%. In view of the industrial utilisation of monazite considerable amounts of the middle earths (samarium to holmium) and yttrium may be obtained as by-products, but the heaviest earths (erbium to lutecium) are scarce in Travancore sand. Monazite is usually a very poor source of europium, and the Travancore deposits are no exception. Indeed, lanthanon minerals are generally poor in europium, and on account of its strong bivalence it is often relatively abundant in alkaline earth minerals and minerals of secondary origin like pitchblende¹⁴ and scheelite.¹⁵

Heavy earth minerals are scarce by comparison with monazite, but deposits in pegmatite formations in North America and Scandinavia are well known. The commonest mineral with a high content is probably gadolinite, a basic silicate containing beryllium and iron. The lanthanon

¹⁰ J. A. Harris, L. F. Yntema, and B. S. Hopkins, *J. Amer. Chem. Soc.*, 1926, **48**, 1585, 1594 ; J. M. Cork, C. James, and H. C. Fogg, *Proc. Nat. Acad. Sci.*, 1926, **12**, 696 ; L. Rolla and L. Fernandes, *Gazzetta*, 1926, **4**, 498 ; *Z. anorg. Chem.*, 1926, **157**, 371.

¹¹ *Z. Physik*, 1938, **91**, 361.

¹² *Physikal. Z.*, 1940, **41**, 1.

¹³ *Ann. Chim.*, 1945, **20**, 113.

^{13a} "The Plutonium Project", *J. Amer. Chem. Soc.*, 1946, **68**, 2411

¹⁴ J. K. Marsh, *Phil. Mag.*, 1929, **7**, 1005.

¹⁵ *Idem, J.*, 1943, 577.

content and composition both vary widely,¹⁶ but gadolinite, and the phosphate xenotime, and the tantalum-niobate fergusonite may be expected to yield more than 40% of lanthanon oxide. The average atomic weight of the heavy earth group from Scandinavian gadolinite varies between 96.5 and 109:¹⁷ about 106—107 has been the author's experience. Thus yttrium is usually about four times more abundant than the combined heavy earth elements. No minerals rich in lanthanons are known in which the middle earths normally predominate.

The Treatment of Monazite.—Formerly the lanthanons were of little economic value, and thorium oxide for gas mantles was the commercial objective in working monazite; but ceramic, metallurgical, and pyrotechnical uses are now important. The sand, a phosphate, is always heated with sulphuric acid, but thereafter various processes have been applied. The anhydrous sulphates if treated with cold water are readily soluble, but hydrate and precipitate on warming. If half the lanthanons are precipitated as oxalates all the thorium comes down simultaneously; when thorium was the objective the remainder could be rejected, but at the present time this rejection is uneconomic. The oxalate precipitate is contaminated with phosphate, and in presence of sufficient sulphuric acid to hold all the lanthanon phosphate in solution the oxalate precipitation is not quantitative.

A modern monazite process¹⁸ treats the paste of sulphates, sulphuric acid, and phosphoric acid with a little water and removes a liquor by filtration or centrifuging consisting approximately of 12% phosphoric acid, 55% sulphuric acid, and 33% water. This liquor is valuable for preparing fertilisers. The anhydrous sulphates are then dissolved in cold water, and the solution is neutralised with previously prepared lanthanon oxide. By this means thorium, zirconium, titanium, and the like are precipitated. The filtered solution is next treated with alkali sulphate, and the light-earth double sulphates are thereby thrown down while yttrium and the heavy earths alone remain in solution. Alternatively nearly all the lanthanon sulphate may be precipitated simply by boiling. Hot alkali transforms either precipitate to hydrous oxide or hydroxide, the alkali sulphate being recoverable. The hydroxide is dried in air at a temperature in the neighbourhood of 100°. Thereby over 97% of the cerium is oxidised and remains insoluble when the product is treated cautiously with dilute nitric acid. The leached product, now almost free from trivalent earths, is treated with nitric acid (d 1.375) to give a solution which is next added slowly to about five times its volume of water containing some sulphuric acid. There is thus formed the well-known basic nitrate-sulphate precipitate of pure cerium. The mother liquor is used again for leaching more dried hydroxides. The dilute lanthanon solution from the leaching of the hydroxides is treated with sulphuric acid and sodium sulphate. The precipitate of almost

¹⁶ I. and W. Noddack, "Das Rhenium", Verlag v. Voss, Leipzig, 1933.

¹⁷ Dana, "System of Mineralogy", 6th edition, K. Paul, Trench, Trubner & Co. Ltd., London, 1892.

¹⁸ A. R. Powell and Johnson, Matthey & Co. Ltd., B.P. 510,198, 1938; J. Blumenfeld, U.S.P. 2,327,992, 1943.

cerium-free lanthanons is recovered, and the liquor is distilled for recovery of nitric acid. The recovery and utilisation of all products is thus complete. Further separation of the light earths will be dealt with later. This process is applicable to other minerals which are attacked by sulphuric acid, such as xenotime and some tantaloniobates and silicates.

The Separation of Cerium from other Lanthanons.—Use is made of the fact that cerium alone of the lanthanons gives a quadrivalent ion in solution. The quadrivalent solutions, however, are very weakly basic and readily undergo hydrolysis.

It is usually best to eliminate cerium as a first step from all earths which are to be purified, since cerous salts undergo slow oxidation, and unless concentrating at the tail cerium will spread all down a fractionation series, e.g., a double magnesium nitrate series. In the monazite earths ceria will amount to nearly 50% of the total. The basic nitrate-sulphate process as used above is very satisfactory. The basic nitrate-bromate process in which a 20% neutral nitrate solution is boiled with potassium bromate and near-neutrality maintained by addition of marble is a convenient laboratory process.¹⁹ Mosander's original chlorine or bromine treatment of the hydroxides whereby $\text{Ce}(\text{OH})_4$ alone remains insoluble is now obsolete. Formation of ceric ammonium nitrate, $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$, and its crystallisation from the mixed nitrate solution has been used industrially but does not give a sharp separation. The basic bromate process is said to leave a cerium-free solution if carried to a point at which a little trivalent earth is precipitated. The process should be interrupted in order to remove pure cerium before the last contaminated precipitate forms. No process will give a perfectly clean separation of cerium and the other lanthanons. A cerous-ceric equilibrium always exists in acid solutions, and only if the solution is sufficiently alkaline to precipitate some trivalent earth can all the cerium be oxidised. For removing completely small amounts of cerium from other earths addition of $\text{KMnO}_4 + 4\text{Na}_2\text{CO}_3$ to the boiling, faintly acid, and finally neutral nitrate solution until the permanganate colour persists is excellent. Ammonia and hydrogen peroxide give a yellowish precipitate so long as cerium is present, but bluish white in its absence. Anodic oxidation of an acid phosphatic solution results in the precipitation of ceric phosphate from a solution too acid to permit trivalent phosphate to precipitate, such as is obtained after "breaking" monazite with sulphuric acid.²⁰

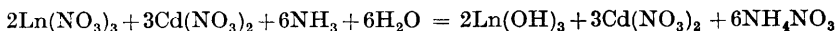
Separation of the Light Earths (freed from Cerium).—C. James⁴ recommended starting by fractionation of the double magnesium nitrates, $2\text{Ln}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$, but the strong basicity of lanthanum allows of its ready separation by preferential precipitation of the weaker bases. The ratio of the solubility products for yttrium, praseodymium, and lanthanum hydroxides have been determined as being 1 : 80 : 1300²¹ and

¹⁹ C. James *et al.*, *J. Amer. Chem. Soc.*, 1911, **33**, 1326 ; 1912, **34**, 757 ; 1916, **38**, 41.

²⁰ J. W. Neckers and H. C. Kremers, *ibid.*, 1928, **50**, 955 ; I. A. Atanasiu and M. Babor, *Bull. Acad. Sci. Roumaine*, 1939, **20**, 27, 32.

²¹ G. Endres, *Z. anorg. Chem.*, 1932, **205**, 321.

1 : 333 : 1235.²² W. Prandtl and his collaborators^{23a-23g} have carefully examined the basic precipitation of the light earths. The solubility of the hydroxides is increased by the addition of ammonium chloride or nitrate when ammonia is used as precipitant. The presence of cations like Cd⁺⁺ or Zn⁺⁺ capable of binding a part of the ammonia is favourable. The optimum conditions for lanthanum are represented by the reaction



conducted at 100° in 3N-ammonium nitrate solution, the ammonia being added slowly at 1% strength. The solubility of lanthanum oxide is 1.65 g./100 ml. and of praseodymium oxide 0.75 g./100 ml. under these conditions.^{23d} The method has been reported upon by J. Wierda and H. C. Kremers²⁴ who say it is more effective but less convenient than the magnesium oxide precipitation procedure. It does not appear to be sufficiently effective with other pairs of earths to be of practical value.

When magnesium oxide is added gradually to a boiling nitrate solution of lanthanons there is a preferential precipitation of didymium and weaker bases leaving lanthanum in solution. The separation is easy, judged by standards applicable in lanthanon chemistry. Probably, however, the magnesium process is best used only to prepare a crude lanthanum which is subsequently purified by fractional crystallisation of the double ammonium nitrate, $\text{La}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$. Lanthanum tungstate of good quality is now in demand as an optical glass.

Praseodymium.—The best crystallisation methods for praseodymium are the double magnesium or manganese nitrates for elimination of neodymium, and the double ammonium nitrate for the elimination of lanthanum. The manganese salt is said to surpass the magnesium salt in speed, but magnesium is cheaper and more easily eliminated when no longer wanted. Praseodymium and neodymium are the most difficult pair of the light earths to separate by crystallisation, but the anhydrous nitrates have been found to differ widely in solubility in ethyl ether at low temperatures.²⁵ Praseodymium nitrate is insoluble at 22° at which temperature 6 g./l. of neodymium nitrate dissolve. Two low-pressure extractions with ether boiling at 10° raised 55% neodymium to 85%; while 94% praseodymium was rendered substantially pure when treated in a modified Soxhlet apparatus. One shaking of nitrate in ether at 10° raised 83% neodymium to 97%. A large plant would appear capable of making a rapid separation by this means.

G. Beck²⁶ has found a very successful method of separating praseodymium by solution of the hydroxides in fused KOH, H₂O. With potassium chlorate or anodic oxygen present, after a time a precipitate forms which can be largely left on decantation, and which is mainly praseodymium dioxide. The residue is extracted with acetic acid and only the neodymium

²² T. Moeller and H. E. Kremers, *J. Physical Chem.*, 1944, **48**, 395.

^{23a} *Ber.*, 1920, **53**, 843; ^{23b} *Z. anorg. Chem.*, 1922, **120**, 120; ^{23c} *ibid.*, **122**, 159; ^{23d} *ibid.*, p. 311; ^{23e} *ibid.*, 1923, **127**, 209; ^{23f} *ibid.*, **129**, 176; ^{23g} *ibid.*, 1924, **136**, 289.

²⁴ *Trans. Amer. Electrochem. Soc.*, 1925, **48**, 159.

²⁵ B. S. Hopkins and L. Quill, *Proc. Nat. Acad. Sci.*, 1933, **19**, 64.

²⁶ *Angew. Chem.*, 1939, **52**, 536.

is dissolved. Starting with materials containing 10% of praseodymium there was obtained a product with over 50% of praseodymium, and also pure neodymium. Further comments on the process will be found later.

W. Prandtl and K. Huttner²³⁰ have separated lanthanum from praseodymium by a process similar to that used for the purification of lanthanum. No details of any commercial process for preparing pure praseodymium based on higher oxide formation have been published, but such a process would appear feasible and may perhaps have been used, for praseodymium dioxide was marketed at a very low price in 1939.

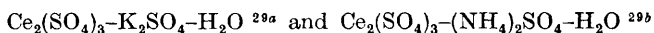
Neodymium.—It is doubtful if Demarçay's double magnesium nitrate fractionation can be surpassed on an economic basis, but this again must depend upon the applicability of a process for the separation of praseodymium by means of higher oxide formation. The magnesium nitrate process quickly expels earths of higher atomic weight than neodymium at the soluble end. The solubility of samarium magnesium nitrate is 2.5 times as great as that of the neodymium salt in nitric acid (d 1.325), but neodymium is only 26% greater in solubility than praseodymium. Perfectly pure neodymium should begin to collect after 500—1000 crystallisations. As soon as neodymium is free from praseodymium it may be removed and any samarium present extracted by amalgam formation.^{6f} G. Beck's potash-fusion method is excellent for separating praseodymium and neodymium, and will save much fractionation, but the writer feels some doubt as to whether it can be relied upon to give a really clean removal of praseodymium.

Samarium and Europium.—These are best purified by amalgam formation.^{6f, 6h} The process will be dealt with later. The amount of europium in Travancore monazite is only about 1/80th of the amount of samarium. The double magnesium nitrate fractionation will very rapidly give a samarium salt of 95% purity using nitric acid (d 1.3) as solvent. Care must be taken that magnesium nitrate does not crystallise out, but in presence of a seed of double salt it will redissolve and the double salt appear. Addition of bismuth magnesium nitrate in liberal quantities aids the separation of samarium and gadolinium and also of gadolinium and terbium.^{6b}

Gadolinium.—This element is easily purified from a little samarium or europium by causing them to form amalgam.^{6f} Purification from terbium is satisfactory by double magnesium nitrate fractionation aided by bismuth magnesium nitrate.^{6b} Bismuth is easily removed by fusing the salt at the conclusion at 220° whereby the bismuth is converted almost entirely into oxynitrate, and recovered on lixiviation. The solution of gadolinium and magnesium nitrates will then give only a slight precipitate with hydrogen sulphide.^{6b} Gadolinium magnesium nitrate is much more soluble than magnesium nitrate, and in order to obtain satisfactory crystallisation nitric acid is used as solvent and bismuth magnesium nitrate continuously added at the tail of the series. The separation of terbium is followed by observing the tint of the oxide. This may be done by direct ignition of the double salt except in the most critical cases. Gadolinium oxide with 0.01% of terbium oxide will not be pure white. The tinting is more delicate as a test

than arc spectroscopy, but white gadolinium oxide is readily obtainable. Alternatively a dimethyl phosphate fractionation gives a rapid method of purification.^{6d, 27}

The Use of Double Alkali Sulphates.—Potassium or sodium sulphate has been in use since 1803 as a reagent to separate the light and heavy earths, yet little is known of how best to conduct the separation. The sulphates and double sulphates are much given to forming supersaturated metastable solutions, so that phase studies are difficult and have afforded little practical guidance towards effecting separations. C. James and H. C. Holden,²⁸ for instance, found that nine months of continuous shaking was insufficient to establish complete equilibrium in a study of the system $Y_2(SO_4)_3-Na_2SO_4-H_2O$ at 25°. The work of W. Schröder on



systems covers a complete range of temperatures, but F. Zambonini and his collaborators³⁰ have studied many of the phases of the sulphates of La, Ce, Pr, and Nd, with NH_4 , Na, K, Rb, Cs, and Tl(I) at 25°. As many as six phases are reported for the Nd-K- H_2O sulphate system alone, at this temperature. The data on middle and heavy earth double sulphates are very scanty, and some were obtained before materials of sufficient purity were available. It may be said that for $xLn_2(SO_4)_3, yM_2SO_4, zH_2O$, the precipitate formed from solutions low in y is very often $x, y, z = 1, 1, 2$; that $y/x = 1-6$; that as temperatures rise solubilities fall, and also often the value of z in the solid phase; and that high y values are associated with precipitates which are produced by addition of much alkali sulphate to hot solutions. In other words the lanthanon double sulphates are most fully precipitated by abundant alkali sulphate and high temperature. So far little evidence in favour of one or the other of these variables has been produced, but it may be surmised that slow precipitation will be the most selective. Where the double sulphates have a moderate solubility this is likely to be attained with moderate alkali sulphate in solution by slow warming. However, a reported experience is that the temperature influence is not large.³¹

The earths probably separate by double sulphate precipitation in serial order with yttrium interpolating between holmium and erbium. Cerium is best removed or reduced to the tervalent form before applying the process. Only mixtures with more than 20—30% of heavy earths are suitable for treatment. For others a double magnesium nitrate fractionation may prove more effective till the simple heavy earth nitrates collect at the soluble end. The separation of the light and heavy earths by double

²⁷ C. James and J. C. Morgan, *J. Amer. Chem. Soc.*, 1914, **36**, 10; L. Jordan and B. S. Hopkins, *ibid.*, 1917, **39**, 2614.

²⁸ *Ibid.*, 1913, **35**, 559.

^{28a} *Z. anorg. Chem.*, 1934, **220**, 389; ^{29b} *ibid.*, 1938, **238**, 209, 305.

³⁰ *Atti R. Accad. Lincei*, 1924, [v], **33**, 301, 308; 1925, [vi], **1**, 278; **2**, 153, 300, 374; 1926, [vi], **3**, 178; **4**, 5, 86, 175, 424; 1927, [vi], **5**, 630, 828, 832; 1928, [vi], **7**, 449; 1929, [vi], **9**, 131; 1930, [vi], **11**, 774.

³¹ T. Moeller and H. E. Kremers, *Ind. Eng. Chem. Anal.*, 1945, **17**, 44.

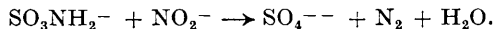
sulphate formation is remarkably sharp, but it is of course only fractional. Some heavy earths precipitate before all neodymium is removed, but in the initial precipitation of crude heavy lanthanons, *e.g.*, from gadolinite, a yield of two-thirds of the heavy earths may be expected perfectly free from neodymium. It has been found recently that, carried out fractionally, the double sodium sulphate process rapidly separates the middle lanthanons from yttrium and the heavy earths in monazite residues.³¹ The author believes that the process is capable of even further development and that the heavy group may be separated advantageously into pre-yttrium, crude yttrium, and post-yttrium fractions. He found that a single precipitation of gadolinite earths occupying one month gave a good concentration of ytterbium in the last precipitate and mother liquors.³² He has since treated some crude gadolinite earths with sodium sulphate, splitting them into eleven fractions in ten days, the final being a hydroxide precipitate. These (a) had weights (b) of sulphate precipitate (unwashed) of average atomic weight (c) as shown,³²

(a)	.	.	1	2	3	4	5	6	7	8	9	10	11
(b)	.	.	30	32	18	38	32	120	32	81	118	66	(18)
(c)	.	.	135	138	128	122	114	106	102	97	102	107	127

Lanthanum and praseodymium were maximum in 1, neodymium in 2, and yttrium in 8. Nos. 1 and 2 were practically free from heavy earths, 7 was free from neodymium, 10 from terbium, and 11 from holmium.

It is usual to start with a nitrate or chloride solution containing about 100 g./l. of oxide, but a solution of anhydrous sulphates may be used if convenient. It is essential to successful use of bromate fractionation later that the double sulphate precipitation be carried at least to the point of complete precipitation of neodymium. Lanthanum and praseodymium will then also have been eliminated. Otherwise these three earths spread among the heavy earth bromates. Omission to remove praseodymium caused it to be the last impurity which H. C. Fogg and C. James had to remove in preparing yttrium for an atomic weight determination after a bromate fractionation.³³

J. Kleinberg, W. A. Taebel, and L. F. Audrieth^{33a} propose the addition of sodium nitrite to a lanthanon sulphamate solution (67 g./l. of oxide). A controlled rate of precipitation by sulphate is obtained :



A slight advantage is observed over the classical double sulphate method, but the value of the process would appear to depend chiefly upon cost and convenience.

The Elimination of Yttrium.—The crude heavy earths from an yttrium mineral like gadolinite, after elimination of the light earths, will generally be found to consist of about 75 molecular % of yttria. The first aim must therefore be to eliminate as much of this as possible in order to reduce bulk,

³² J. K. Marsh, unpublished.

³³ *J. Amer. Chem. Soc.*, 1922, **44**, 307.

^{33a} *Ind. Eng. Chem. Anal.*, 1939, **11**, 368.

labour, and cost of operations generally. Use is made of the fact that yttria has a greater apparent basic strength than the heavy earths. The separation of yttrium from the earths holmium to lutecium by basic processes is satisfactory, but the parting from terbium and dysprosium is less easy. The further concentration of these two earths, which probably occur chiefly in fractions 4—7 of the above double sodium sulphate fractionation, would therefore appear desirable. For this purpose a further short double sulphate fractionation is applicable.³¹ When dysprosium and terbium have been reduced to small amounts in the crude yttrium a choice must be made from several good processes for parting the heavy earths and yttrium.³⁴ The so-called basic nitrite and the ferricyanide^{6l, 35} precipitations are capable of placing yttrium right up the series between neodymium and samarium, and may therefore be expected to give a good separation from terbium and dysprosium. Some other processes also give rapid separation of yttrium, but it is less certainly known how suitable they are when applied to terbium-containing earths. These include the use of urea decomposition as a source of ammonia,³⁶ and basic nitrate precipitation by addition of sodium hydroxide to boiling nitrate solution till a small precipitate persists.³⁷ On cooling, a crystalline crop of basic nitrate, $\text{Ln}_6\text{O}_5(\text{NO}_3)_8 \cdot 20\text{H}_2\text{O}$ ^{37a} (or $18\text{H}_2\text{O}$)³⁸, forms which is rich in the weakly-basic heavy earths. After a few crops taken thus recourse must be made to the basic nitrite process. This precipitates $\text{Ln}_8\text{O}_{10}(\text{NO}_3)_4 \cdot 17\text{H}_2\text{O}$.³³ Chromate,^{2, 34} phosphate,^{4, 34} or cobalticyanide³⁴ precipitations may be equally good, but are less practicable. The subject has indeed been little studied from the point of view of quick elimination of yttrium. James did not practise this but converted the total earth into bromate. W. Prandtl^{5, 35} recommends the ferricyanide process, and this is indeed excellent,^{6l} but the nitrite method employs a cheaper reagent; it has the disadvantage, however, that with accumulating sodium nitrate the precipitate tends to become colloidal and progress stops, but by this time the crude yttrium should be sufficiently extracted to make further recovery of the heavy earths from it uneconomic. The ferricyanide method may be reserved for dealing with fairly rich heavy earth concentrates. Prandtl prefers to start with a ferricyanide treatment and to apply the double sulphate separation subsequently.

The Separation of the Heavy Earths.—These having undergone a double sodium sulphate treatment for the removal of the light earths, and having been concentrated by the elimination of as much yttrium as possible, are converted into bromates. C. James (1908) used double decomposition between barium bromate and lanthanon sulphate. More recently lanthanon perchlorates and potassium bromate have been recommended,³⁹ while

³⁴ C. James *et al.*, *J. Amer. Chem. Soc.*, 1914, **36**, 638, 1418; 1915, **37**, 1198, 2643; 1917, **39**, 933.

³⁵ W. Prandtl and S. Mohr, *Z. anorg. Chem.*, 1938, **236**, 243; **237**, 160.

³⁶ H. C. Fogg and L. Hess, *J. Amer. Chem. Soc.*, 1936, **58**, 1751.

³⁷ C. James and A. J. Grant, *ibid.*, 1916, **38**, 41.

^{37a} C. James and L. A. Pratt, *ibid.*, 1910, **32**, 873.

³⁸ W. Feit, *Z. anorg. Chem.*, 1940, **243**, 276.

³⁹ H. E. Kremers and T. Moeller, *J. Amer. Chem. Soc.*, 1944, **66**, 1795.

Prandtl⁵ recommends preparing bromic acid from barium bromate and sulphuric acid. On conclusion of the fractionation most of the bromate can be recovered as barium bromate by treatment with concentrated barium chloride solution.

On fractional crystallisation of the bromates, samarium, europium, and gadolinium soon collect at the head. Solubility⁴⁰ increases steadily from samarium or europium down to lutecium, with yttrium falling between holmium and erbium. These last three cannot conveniently be prepared pure by bromate fractionation alone, though W. Feit³⁸ prepared good holmium after daily crystallisations of a bromate series for four years followed by a basic nitrate fractionation. The other heavy earths—terbium, dysprosium, thulium, ytterbium, and lutecium—can probably all be obtained pure by prolonged bromate fractionation alone, but more convenient methods are available. They all either can undergo a valence change or have one neighbour which does. It is likely that some of the late double sodium sulphate fractions after yttrium elimination will consist largely of ytterbium, in which case they are treated with sodium amalgam and the ytterbium⁶⁰ removed before the remainder is converted into bromate. The middle fractions of the whole bromate series which may spread to 70—80 fractions will soon become rich in yttrium. At the tail thulium, more ytterbium, and lutecium will collect. As soon as tail fractions are free from any absorption spectrum they consist only of lutecium, ytterbium, and impurities. They are then removed and these two separated by sodium amalgam. Further up the series erbium and thulium will be separating. Thulium-containing fractions are ready for withdrawal as soon as they are free from erbium absorption bands and are found to show no lutecium arc spectrum lines. The thulium and ytterbium are then separated by sodium amalgam. The erbium-thulium separation is, however, very slow. Gradually holmium will have been collecting above the yttrium present and erbium below it. The fractionation must proceed till the absorption spectra show that each is free from the other. This is likely to require daily bromate fractionation for a year. The separation of erbium and thulium will require even longer. C. James (1911) crystallised thulium fractions 15,000 times, but the modern method of removing ytterbium should enable this number to be reduced. When erbium fractions are free from both thulium and holmium they are converted into chloride and treated with potassium ferricyanide. This is a most effective method for obtaining pure erbium.⁶¹ Unlike the basic nitrate process it does not slow up when the amount of yttrium gets small. Starting with an oxide which we may represent as $Y_{60}Er_{40}O_{150}$ and splitting it into six fractions these had respectively the compositions (1) $Y_{33}Er_{67}O_{150}$, (2) $Y_{41}Er_{59}O_{150}$, (3) $Y_{49}Er_{51}O_{150}$, (4) $Y_{56}Er_{44}O_{150}$, (5) $Y_{69}Er_{31}O_{150}$, and (6) $Y_{90}Er_{10}O_{150}$.

As soon as the main bulk of holmium is free from absorption bands of erbium the bromate fractionation may stop. There will then be a quantity of yttrium containing small amounts of both holmium and erbium which may serve as a source of very pure yttrium when these two are removed

⁴⁰ C. James *et al.*, *ibid.*, 1927, **49**, 873.

and set aside for further treatment with any future batch of earths. The holmium-yttrium fractions now require to have nearly all the yttrium removed by the ferricyanide process, since the next step is conversion into the dimethyl phosphate, and yttrium dimethyl phosphate has an inconveniently small solubility (about the equivalent of 7 g./l. of oxide at 25°). The ferricyanide process for holmium⁶¹ is only a little less satisfactory than for erbium, but probably a purer product can be obtained by final application of dimethyl phosphate fractionation.

The *dimethyl phosphates*⁶² are interesting salts with several peculiarities. They are the only simple salts of the lanthanons to crystallise from water anhydrous. (Some double alkali sulphates do the same.) They are practically insoluble at the lutecium end of the series and increase by a factor of about 1.6 for each unit decrease in atomic number till gadolinium dimethyl phosphate is reached with a solubility at 25° of 24 g./100 g. water, after which the increase is less rapid. This means that the rate of change of solubility is very much greater than is ordinarily encountered among the lanthanons. Further, it is most unusual, if not unique, for the rate of change to be greater for the heavy earths than for the light earths. Solubility also usually rises from gadolinium to lutecium whereas in the dimethyl phosphates it falls steeply, but this is paralleled in the ferricyanides, ferrocyanides, tartrates, and perhaps other series. The solubilities like those of the sulphates and double sulphates decrease with rising temperature.

The solubility is too small and the degree of hydrolysis too great for yttrium together with the earths nearer the lutecium end of the series than holmium to allow of dimethyl phosphate fractionation for their purification; but the separation of holmium, dysprosium, terbium, and gadolinium is good and very rapid. Since slight hydrolysis passes back basic products to the head of the series counter to the main separation, the removal of the last of dysprosium from holmium, or of terbium from dysprosium, is not quite complete, but with the less hydrolysed gadolinium the separation from terbium is very good. So too is the separation of the last traces of yttrium from holmium, for long considered the most difficult separation in inorganic chemistry, also of holmium from dysprosium and of dysprosium from terbium. Thus terbium of the highest purity is obtainable. Dysprosium oxide prepared by this process always had a light buff colour, but this tint due to terbium can be eliminated quickly by a potash fusion,^{63, 26} which concentrates terbium in the first oxide to precipitate. If solutions are refrigerated and crystallisations conducted below 50° hydrolysis is kept to a minimum. It is possible that some double sulphate fractions may be suitable for direct conversion into dimethyl phosphate without passing through a bromate fractionation.

W. Prandtl⁵ recommends changing from bromate to double ammonium oxalate for the last stage of the holmium-erbium separation. The opportunity may probably be taken with advantage to eliminate yttrium once again by ferricyanide precipitation of the richer yttrium fractions. The double ammonium oxalates are less soluble, and so better suited for handling small quantities of material, and give a more rapid separation than bromates.

Prandtl recommends them for the final stage in the purification of terbium, holmium, erbium, thulium, and lutecium. The writer has no experience of the salts, and no experimental particulars with regard to their use have been published.

Separation Processes based on Reduction to Bivalent States.—It is remarkable how slow chemists have been to exploit bivalence in the lanthanon group. The field of “anomalous” valence has been reviewed by D. W. Pearce⁷ up to 1935. The then current use of the term “anomalous” illustrates the hypnotic effect that a chorus of fourteen trivalent elements had upon chemists for a number of years. Samarium, although the least stable in the bivalent state, was in 1906 the first to be so prepared. Europium chloride was reduced in 1911, and ytterbium chloride in 1929.^{40a} L. F. Yntema⁴¹ in 1930 was the first to use reduction to a bivalent state as a means of purifying a lanthanon. He reduced EuCl_3 at a mercury cathode in presence of sulphate ions and obtained insoluble EuSO_4 . The next decade saw rapid developments. It was found that the trivalent europium chloride solution could be reduced by metals.⁴² Electro-reduction of ytterbium solutions was also found to be an effective means of separating ytterbium and of obtaining approximately pure thulium and lutecium, but the solubility of YbSO_4 is higher than that of EuSO_4 .^{43, 67} H. N. McCoy⁴⁴ has done much successful work in this field. He treated a chloride solution of monazite residues (386 kg. of oxalates) containing about 0.5% of europium with zinc dust (5 kg.) and acetic acid, and, after reduction had taken place, with magnesium sulphate (30 kg.) and barium chloride (8 kg.). The formation of barium sulphate helped to carry down the isomorphous but slightly soluble europous sulphate. Treatment of the precipitate with sodium carbonate and hydroxide yielded 7.2 kg. of 20% europous hydroxide. Two more treatments yielded a 70% product, and this in concentrated chloride solution (d 1.35), treated with concentrated hydrochloric acid, precipitated $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$, giving a very perfect separation from trivalent chlorides. McCoy⁴⁵ also studied the electrolytic preparation of amalgams of europium and ytterbium using acetate solutions in presence of potassium citrate. Yields were not unsatisfactory, but for samarium his maximum yield was 13.6%. Some interesting observations were also made by German chemists. It was found by using strontium amalgam on sulphate solutions of the light lanthanons that these in addition to europium, ytterbium, and samarium were to some extent reduced and found stabilised as bivalent sulphates mixed with strontium sulphate.⁴⁶ In purifying samarium by reduction, 1% calcium

^{40a} W. Klemm and W. Schüth, *Z. anorg. Chem.*, 1929, **184**, 352.

⁴¹ *J. Amer. Chem. Soc.*, 1930, **52**, 2782.

⁴² W. E. Pearce, Thesis, University of Illinois, 1934.

⁴³ R. W. Ball and L. F. Yntema, *J. Amer. Chem. Soc.*, 1930, **52**, 4264; W. Prandtl, *Z. anorg. Chem.*, 1932, **209**, 13.

⁴⁴ *J. Amer. Chem. Soc.*, 1935, **57**, 1756; 1936, **58**, 1577; 1937, **59**, 1131; 1939, **61**, 2455.

⁴⁵ *Ibid.*, 1941, **63**, 1622, 3432; 1942, **64**, 1009.

⁴⁶ L. Holleck and W. Noddack, *Angew. Chem.*, 1937, **50**, 819; L. Holleck, *Attì X Cong. Intern. Chim.*, 1938, **2**, 671.

amalgam was prepared in a special steel bomb and used to treat anhydrous chlorides in dry ethanol containing some hydrochloric acid. 55% Eu-Sm was raised to 92% in one precipitation, and to 99.8% on a second treatment and recovered as red samarous chloride by centrifuging. 1—1.5% of samarium was left with the trivalent earths. SmSO_4 is red, but the bivalent carbonate and hydroxide are reported to be green.⁴⁷

It was early evident that bivalent lanthanons resembled alkaline earth elements. The sulphates are isomorphous.⁴⁴ EuSO_4 is more soluble than BaSO_4 and possibly than SrSO_4 . YbSO_4 dissolves to the extent of 4 g./l. in 0.2N-sulphuric acid. The addition of freshly precipitated SrSO_4 has been used as a means of more fully precipitating YbSO_4 .⁴⁷ Now the alkali and alkaline earth metals in amalgam if treated with a different alkali or alkaline earth solution all undergo reciprocal replacement following the law of mass action, though the equilibrium may be greatly in favour of certain metals remaining in amalgam and others in solution. The displacement order beginning with the most positive amalgam is Mg, Li, Ca, K, Na, Sr, Ba.⁴⁸ Since lanthanon(II) is virtually an alkaline-earth metal these considerations lead the Reviewer to argue that treatment of a lanthanon solution with a suitable amalgam should bring about reduction at the amalgam face followed by replacement giving rise to a lanthanon(II) amalgam, when the relative positions in the amalgam series were favourable. It should be noted that the amalgam series is not the same as the electropositive series on account of compound formation. McCoy's use of acetate solutions for electro-reductions suggested their use here, but the presence of an alkali in solution was considered to be contra-indicated. It was found at once that very full and perfect exchange between sodium amalgam and europium, samarium, or ytterbium acetate solutions took place.^{6c} Samarium reduces and passes into amalgam with an ease comparable to europium and probably more readily than ytterbium. Heretofore it had proved much less tractable to reduction, and was never successfully obtained as SmSO_4 on account of the great instability of the Sm^{2+} ion. The removal of the last traces or down to 0.01% of the reducible lanthanon in a preponderating quantity of a trivalent earth is possible provided that the solution is rendered free from sodium and that fresh amalgam free from lanthanon is finally used. Only dilute sodium amalgam can be employed. With over 0.3% sodium on exchange, partially solid lanthanon amalgam may result, particularly with europium, and cause trouble in the mechanical separation of amalgam and solution, the ease and perfection of which is one of the advantages of the method. Furthermore, strong sodium amalgams tend to react with water liberating hydrogen and causing accumulation of sodium in the lanthanon solution. The efficiency of the reaction, which should amount to 80%, is lowered. In order to prevent hydroxide formation the solution

⁴⁷ A. Brukl, *Angew. Chem.*, 1937, **50**, 25; 1938, **51**, 192; 1939, **52**, 151.

⁴⁸ E. F. Smith, *J. Amer. Chem. Soc.*, 1905, **27**, 540; *J. Physical Chem.*, 1905, **9**, 13; *Amer. Chem. J.*, 1907, **37**, 506; E. F. Smith and J. R. Withrow, *J. Amer. Chem. Soc.*, 1907, **29**, 321; S. B. Frank and J. R. Withrow, *ibid.*, 1920, **42**, 671.

is kept weakly acidic with acetic acid during the course of the reaction which may take 1—2 minutes.

In preparing samarium amalgam, some of the trivalent earths (chiefly neodymium) may also enter the amalgam, but they appear to be held in the amalgam in a different combination, and much more firmly. Thus from 70% neodymium the 30% of samarium was extracted as amalgam and the greater part of this was obtained with 0.01% of neodymium by decomposing the amalgam with weak acid, but the last small acid extract contained 50% of neodymium.^{6f} Samarium and europium being neighbours are extracted together as amalgam, but they can be separated by acid attack on the amalgam. From the atomic volumes of the metals we know that neodymium is trivalent, samarium apparently partially trivalent, and europium largely bivalent.⁴⁹ This probably also holds in amalgams, for europium is more readily attacked by acid than samarium. Dilute acetic acid mixed with a little dilute sulphuric acid yields with the mixed amalgam samarium(III) acetate and a mixed (SmEu)SO₄ precipitate containing perhaps 20% of EuSO₄. Since europium accumulates in early fractions of the sulphate precipitate europium amalgam must be more readily attacked than samarium amalgam. The mixed sulphate is then selectively oxidised by dilute nitric acid, giving a 90% europous sulphate. This is converted *via* acetate into amalgam once more and is then subjected to attack by concentrated hydrochloric acid. There results a precipitate of pure EuCl₂·2H₂O, which is filtered off and washed with concentrated acid. The filtrate contains all the samarium with a little europium.

In order to obtain samarium free from europium, samarium acetate solution is treated with a little dilute sulphuric acid and dilute sodium amalgam. A lanthanon(II) sulphate precipitate is formed in which europium rapidly concentrates. Thus the precipitate may be pale at first, but later yields are red and mainly SmSO₄. These are examined spectroscopically and further crops taken till the arc lines of europium are no longer found. The samarium acetate solution is then absolutely free from europium. Eight precipitates amounting in all to 8% of the samarium were required to prepare samarium of a purity never before obtained (absence of Eu line, λ 3819.66, intensity 500).^{6h}

It is interesting to note that high concentrations of europium(II) solutions may stabilise other very weakly bivalent lanthanons. Thus a little neodymium in concentrated Eu²⁺ solution may not be detectable by its absorption spectrum. This is predictable from the law of mass action. Similarly, it is difficult to extract the last of a potentially bivalent earth from a predominantly trivalent solution. This difficulty is, however, lessened in the case of samarium and europium since their neighbours are capable of some bivalent ion formation. Nevertheless in the case of ytterbium–lutecium mixtures, lutecium having no bivalent stability, it was found possible to reduce ytterbium in lutecium to a concentration believed to be below 1 in 10,000.

⁴⁹ W. Klemm and H. Bommer, *Z. anorg. Chem.*, 1937, **231**, 138; H. Bommer and E. Hohmann, *ibid.*, 1939, **241**, 268.

The amalgam methods just described give fuller separation and purer products than the older methods based on bivalent sulphate formation. Where sulphate formation is used as in the separation of samarium and europium the solubility is lower in the acetate solutions employed than in chloride solutions. A more theoretical investigation of the formation of ytterbium amalgam has confirmed the use of acetates as the salts of greatest practical value yet found.⁵⁰ These sodium amalgam methods supersede all previous methods for separating the lanthanons by means of bivalency.

Separations based on Oxidation to Quadrivalent State.^{6i, 6j, 6k}—Cerium has already been dealt with. It is the only lanthanon which gives rise to a quadrivalent ion. Praseodymium and terbium, however, give oxides in which quadrivalence is shown. Unlike CeO_2 the oxides are dark or black, and it is difficult to maintain that there is full valence bonding of the extra oxygen. The structure of the lanthanon oxides from samarium to lutecium is cubic of a peculiar type, the unit cell of which may be regarded as comprised of eight modified fluorite type cells. Cerium dioxide has a true fluorite type structure, but in these others, Ln_2O_3 , 1/4th of the fluorine positions are unfilled by oxygen. It is thus seen that very little structural change is required to fit in the oxygen required to give PrO_2 or TbO_2 . The amount of dioxide formation is much affected by oxygen gas pressure.^{51, 6k} The extra oxygen appears to be not fully valence bound, but on the other hand not entirely in solid solution. It was pointed out earlier how quadrivalence was related to atomic structure.

Praseodymium sesquioxide usually has a hexagonal form similar to La_2O_3 . In this form it is incapable of dioxide formation, but the transition to cubic Pr_2O_3 is ready, and by oxidation this passes to a stable cubic structure. When light lanthanon nitrates are fused with mixed alkali nitrates cerium dioxide is precipitated at temperature from 200° upwards, and is largely removed from effective participation in the system. Neodymium and praseodymium oxides tend to separate only at temperatures above 300°. If a cerous salt is thrown into the melt at these temperatures it gives of necessity at once a cubic oxide which tends to stabilise cubic neodymium and praseodymium oxides, and thus to promote the clean separation of these elements from lanthanum, the oxide of which has little cubic stability and which therefore stays in the melt as nitrate, since also it is the strongest base.

The lanthanon hydroxides have considerable solubility in fused potash, $\text{KOH}, \text{H}_2\text{O}$, at temperatures of 300—320°, but, as G. Beck²⁶ has found, after a time with oxidising conditions, produced either by the presence of potassium chlorate or anodic oxygen, a precipitation of praseodymium or terbium dioxide takes place. Beck believed this to be due to these elements giving a quadrivalent anion, but the author, who has pointed out that water is necessary for the solution in potash to take place, believes that loss of water is the primary cause of precipitate formation. If a trivalent

⁵⁰ T. Moeller and H. E. Kremers, *Ind. Eng. Chem. Anal.*, 1945, **17**, 798.

⁵¹ W. Prandtl and G. Rieder, *Z. anorg. Chem.*, 1938, **238**, 225.

hydroxide can pass to a quadrivalent oxide it ceases to be a competitor in the system for the limited amount of water, and therefore given available oxygen the quadrivalent oxide will be the first to precipitate as the temperature is raised too high for water to be retained. The higher oxide of praseodymium or terbium, thus heavily concentrated in the early precipitate, settles, so that much of the melt can be decanted. The higher oxides are not easily attacked by acetic acid, and use is made of this fact to separate them from hydroxides. The process in its present form unfortunately appears too costly for commercial application, but the exploitation of valence changes is not yet complete.

Other Modes of Fractionation : Extraction Processes.—Fractional partition of lanthanum and neodymium thiocyanates occurs between water and *n*-butyl alcohol, the Nd/La ratio in the alcohol being 1.06 of the water value.⁵² Though the separation is small it is proposed by the use of a suitable counter-current extraction apparatus to exploit it rapidly. The extraction by ether of scandium thiocyanate⁵³ from aqueous solutions has been found to be very rapid, and to give better separation from Ln, Al, Fe, Th, and Zr than older methods.

Zeolite and chromatographic methods have been tried. A variety of zeolitic materials and methods were used by R. G. Russell and D. W. Pearce⁵⁴ and aluminium oxide by O. Erämetsä *et al.*⁵⁵ The small lanthanon ions were found to be preferentially held, and pH has an influence. The addition of citric acid reverses the absorption series in the light earths. The results so far give little promise of successful application on a practical scale, but the methods may prove useful in analytical operations.

This review should serve to show that the arduous task which the chemist once undertook in starting to separate the rare earths has now been much lightened. Yet it is still formidable, particularly for the scarce heavy-group coloured earths found mixed with much yttrium. With their persistent tervalency only laborious crystallisation will separate holmium, erbium, and thulium. Knowledge of the close resemblance in physical properties like ionic radii gives no ground for optimism that easy methods of separation will ever be found. Yet, given the incentive, nothing stands in the way of large-scale production of any member of the group.

⁵² D. B. Appleton and P. W. Selwood, *J. Amer. Chem. Soc.*, 1941, **63**, 2029.

⁵³ W. Fischer and R. Bock, *Z. anorg. Chem.*, 1942, **249**, 146.

⁵⁴ *J. Amer. Chem. Soc.*, 1943, **65**, 595.

⁵⁵ *Bull. comm. geol. Finlande*, 1941, **14**, 36; *Ann. Acad. Sci. Fennicæ*, 1943, *A*, **57**, Nos. 3, 5.