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# THE METALS OF THE RARE EARTHS

BY

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# PREFACE.

For a number of years, after the study of the rare earths commenced, these substances were only known to occur in a small number of minerals which were found in but few places, and even there not in very large quantities. This relative scarceness of material caused the investigation of these substances to remain in the hands of a very few chemists, who, fortunately for the progress of knowledge, were in many cases the most eminent and efficient of their generation. But notwithstanding this, the term rare earths grew to have a meaning among the chemists, who had not had experience with these elements, which implied that there was something mysterious connected with this group of metals. With the discovery of large tracts of monazite in various parts of the world, the amount of the rare earths available for investigation has been enormously increased, so that now it is quite open to anyone who desires and has sufficient training to join the workers in this branch of chemistry. A further cause which has accelerated the rate of progress of our knowledge of these substances is the introduction of the incandescent gas mantle industry. Here compounds of two metals, thorium and cerium, are required, but in order to extract these elements from monazite the remaining rare earths have also to be separated from the mineral, and since there is at present no commercial use for these substances a large amount of material is available for the use of those who wish to investigate it. This commercial supply has enor-

mously reduced the labour which was formerly necessary in preparing compounds of the rare earths, and has consequently accelerated the rate at which knowledge has been accumulated.

Since the rare earths have attained a commercial and economic importance, and since their scientific importance is so very great, and will probably become greater, it would seem essential that a student, before leaving his college career behind him, should possess some knowledge of these substances. Consequently it has been deemed advisable to add this work to the series of monographs on Inorganic and Physical Chemistry.

In dealing with the subject the history of the metals, both from the standpoint of discovery and of general progress, has been considered from the time of Gadolin up to the present day.

The literature of the subject has been considered up to June 30, 1918, and it is hoped that the list of references given at the end of the book contains all the important papers published on the subject and the majority of the less important papers. A certain amount of difficulty has been experienced with continental literature over the period 1914-18, and it is not at all unlikely that some papers published during that period may not have come to my notice. In the last chapter, a short review of the industrial applications of the rare earths has been given. This does not make any claim to completeness, the object being merely to indicate some of the possibilities which lie before the rare earths from the commercial point of view.

In preparing the material for this monograph considerable use has been made of the following works of reference :—

(i) *Die Darstellung der seltenen Erden* (Richard Böhm).
(ii) *Traité de Chimie minérale* (H. Moissan).
(iii) *Handbuch der anorganischen Chemie* (R. Abegg).

Thanks are due to Messrs. Edward Arnold, Masson et Cie (*Annales de Physique et de Chimie*), and Amedée Guillet (*Journal de Physique*), for permission to reproduce diagrams from their publications.

I would like, in conclusion, to express to my colleague, Mr. Holland Crompton, Head of the Department of Chemistry, Bedford College, my gratitude for the advice which he has willingly given me in arranging the material and for reading the whole work in manuscript, and also to Mr. F. W. Clifford, Librarian of the Chemical Society, who has kindly verified the references.

J. F. SPENCER.

BEDFORD COLLEGE,
REGENT'S PARK, N.W. 1,
*March* 21, 1919.

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# CHAPTER I.

## INTRODUCTION.

THE term "rare earths" is applied to the oxides of a number of metals, which are mainly characterised by a remarkable similarity of the physical and chemical properties of their compounds. They are fairly widely distributed over the surface of the earth, but the minerals from which they are extracted, and in which they are found in workable quantities, occur only in a few places. In nature these elements are always associated in more or less complex mixtures, which, on account of the similarity in properties of the constituents, are very difficult to separate. The separation and preparation of pure derivatives of these elements is a most laborious and difficult process which can never be effected quantitatively, since up to the present it has been found impossible to devise quantitative processes even for their estimation in minerals. All the elements of the rare earths with the exception of cerium are tervalent and give rise to oxides of the type $M_2O_3$ which are basic. The basicity varies between that of the alkaline earths on the one hand and that of aluminium oxide on the other. Cerium, although very similar to these elements, is, however, quadrivalent and in addition to an oxide $Ce_2O_3$ forms also an oxide $CeO_2$. It is usually regarded as coming under the general title of rare earths since it invariably occurs in nature associated with the other members of the group, and is very similar to the other elements in its properties. Notwithstanding the great similarity of these elements it has been found possible to divide them into two sub-groups, namely, those of the cerium earths, including cerium, lanthanum, neodymium, praseodymium, and samarium, and the yttrium earths consisting of yttrium, erbium, holmium, terbium, thulium, dysprosium, neoytterbium, scandium, lutecium, europium, gadolinium, and celtium. It must not, however, be supposed that this separation into two groups means any great difference in properties between the two series, for such is not the

case; the members of one group are exceedingly like the members of the other in most of their properties. In addition to the elements already mentioned there is one other, thorium, which is closely associated with the rare earths, and although it is not usual to include it in the group of rare earths, still it has much in common with them, and in consequence will be considered along with them here. The history of thorium is bound up with that of cerium, its occurrence in nature is associated with that of the rare earths, and it is associated with cerium in the manufacture of incandescent gas mantles. These points and others seem to show the advisability of the course adopted here.

## History of the Discovery of the Rare Earths.

The history of the rare earths may be said to commence in the year 1794, with the discovery of an oxide of an hitherto unknown element in a mineral found at Ytterby. This discovery was made by Gadolin,[1] who found that the oxide occurred to the extent of 38 per cent. in the mineral, and resembled in its properties the oxides of calcium and aluminium. The name Gadolinite was later applied to this mineral, and a further examination of it in 1797 by Ekeberg[2] resulted in his finding 47·5 per cent. of Gadolin's new oxide; he thus confirmed the discovery and designated the new oxide by the name yttria. Further confirmation was provided independently by Klaproth[3] and Vauquelin[4] in 1801, who analysed gadolinite and gave an account of the properties of yttria. A second new earth, termed ceria, was simultaneously discovered by Klaproth,[5] and Berzelius and Hisinger[6] in 1803. This earth they discovered in the minerals cerite and tungstein or ochroite; it resembled yttria generally but differed from it in being insoluble in ammonium carbonate, and in becoming light brown in colour on ignition. The colour change on ignition led Klaproth to suggest the name ochroite for the element. The two earths ceria and yttria were, however, soon shown to be complex mixtures of the oxides of a number of unknown elements, for in 1802, Ekeberg,[7] by boiling yttria with caustic alkali, was able to separate from it the earth beryllia which had been discovered four years earlier by Vauquelin; and in 1814, Berzelius[8] showed that yttria obtained from orthite contained considerable quantities of ceria. Berzelius,[9] in 1817, isolated a substance which he regarded as a new earth to which

he assigned the name thorine; this substance, however, proved not to be new, for in 1824[10] he was able to recognise it as a basic phosphate of impure yttria. The earth thoria was definitely isolated by Berzelius[11] in 1828 from the mineral thorite, a silicate of thorium. In 1851, Bergemann,[12] during the isolation of thoria from the mineral orangeite, obtained a fraction which he stated contained an unknown element to which he applied the name donarium. This substance, however, was shown successively by Damour[13] (1852), Berlin[14] (1852), and Delafontaine[15] (1863) to be composed of thorium rendered impure by lead and uranium. Bergemann,[16] in 1852, was himself convinced that the "element" donarium had no real existence. The complexity of ceria was proved in 1839 by Mosander,[17] who found that on heating cerium nitrate until a portion of it had been decomposed, and then treating with very dilute nitric acid, he was able to extract from the ignited mass an earth which differed in properties from ceria whilst the undissolved portion gave all the reactions of cerium. He therefore gave the name lanthana to the earth which had dissolved in the acid and retained the name ceria for the insoluble oxide. Later,[18] in 1841, he found that on treating lanthana with dilute nitric acid he was able to extract a rose-coloured earth from it, to which he gave the name didymia. Mosander[19] was also responsible for the proof that yttria was highly complex, for in 1843 he was able to show that yttria from which ceria, lanthana, and didymia had been completely removed was still complex and was made up of at least three earths, a colourless substance for which the name yttria was retained, a yellow earth, named erbia, and a rose-coloured earth named terbia. The separation of these three earths depended on the difference in their basicity, and was achieved by fractional precipitation by ammonia when erbia, the least basic, was precipitated in the first fractions and yttria the most basic in the last fractions. The existence of terbia was placed in doubt by Berlin[20] (1860), Popp[21] (1864), Bahr and Bunsen[22] (1866), and Cleve and Höglund[23] (1873), who generally regarded it as a mixture of yttria and erbia. The earth which they were able to isolate from yttria was rose coloured, and this was named erbia by Bahr and Bunsen. Later work of Delafontaine[24] (1865), Marignac[25] (1878), Smith[26] (1878), Cleve[27] (1879), and finally Lecoq de Boisbaudran[28] (1886) showed that both erbia and terbia

existed in crude yttria, thus confirming the original contention of Mosander.[19] The name erbia was, however, retained for the rose-coloured earth and that of terbia was given to the yellow earth, thus the original names assigned to these earths were interchanged. The means employed in the investigation of the rare earths up to about 1860 consisted almost entirely of strictly chemical operations, such as fractional precipitation and crystallisation together with the determination of the equivalent weight of the oxide of the various fractions as the test for uniformity of the substance. But about this time the introduction of spectrum analysis brought a new and more refined and at the same time more delicate instrument of investigation into use, and the work became relatively less laborious and more fruitful.

Before passing on to the further discoveries, a word must be said with regard to the valency of the rare earths. Until the year 1870 the metals of the rare earths, on account of the basicity of their stable oxides, were uniformly regarded as bivalent, and the general formula MO was applied to their oxides, but in 1873, Mendeléeff,[29] from considerations of their probable positions in the periodic system and from the specific heat of cerium, came to the conclusion that they were tervalent and that the stable oxides must consequently have the formula $M_2O_3$, and the accepted atomic weights must be increased proportionately. Delafontaine[30] objected to the change, urging the strongly basic character of the oxides and the isomorphism of some of the salts with those of magnesium as evidence of their bivalent character. This objection was successfully answered when the specific heats of metallic lanthanum and didymium were obtained, and when Cleve[31] and his pupils showed that certain of the salts of the rare earth metals were isomorphous with the corresponding salts of elements whose tervalent character was definitely proved. Consequently, with this, the tervalent character of the metals was finally established.

During an examination of the mixed rare earths from orthite and gadolinite, in 1862, Bahr[32] found that after the removal of calcium, cerium, yttrium, and didymium, an earth was precipitated by potassium oxalate. This earth had properties like those of thorium, and was regarded by its discoverer as the derivative of an unknown element which he termed wasium. The existence of this element was doubted by Delafontaine,[33] who regarded it as impure cerium, and by Nickles,[34] who regarded the oxide as an

impure mixture of the yttrium earths containing terbia and didymia. The question was finally settled in 1864 by Bahr [35] himself, who succeeded in identifying wasium with thorium. From the results of a detailed study of the earths obtained from samarskite, Delafontaine [36] came to the conclusion that he had discovered an element, termed phillipium, which held a position intermediate between terbium and yttrium in its properties. Roscoe [37] and Urbain [38] proved, however, that phillipia was a mixture of yttria and terbia. About the same time (1877) Smith [39] announced the discovery of an element mosandrium in North Carolina samarskite. This mineral was reputed to contain cerium, which Smith was unable to confirm, and it was found that what had previously been regarded as cerium was an earth which was more difficult to precipitate with potassium sulphate than cerium, and which was more easily soluble in dilute nitric acid than ceric oxide. This supposed element was also proved by Marignac [40] and Delafontaine [41] to be a mixture of known earths, whilst Lecoq de Boisbaudran [114] (1886) proved it to be a mixture of gadolinium and terbium. During an examination of erbia from gadolinite, Marignac [42] (1878) was able, by heating the nitrate until it decomposed to form a pasty mass and then extracting with water, to separate it into two oxides of different basicity, one red for which he retained the name erbia, and the other colourless to which the name ytterbia was allotted. In the following year, Nilson [43] isolated the predicted ekaboron from ytterbia. The separation was effected by the partial decomposition of the nitrate which yielded two fractions of very different equivalent weights. The fraction of lower equivalent weight was examined spectroscopically by Thalen,[43] and shown to possess a spectrum quite distinct from that of ytterbium, and to be a new element which Nilson named scandium. After the removal of ytterbium and scandium from the crude erbia earth, Cleve [44] was able to resolve the residue into three earths, erbia (neo-erbia), holmia, and thulia. The absorption spectra of salts of these earths were then studied by Soret,[45] who was able to show that the element *X* which he had discovered in 1878 [46] in crude erbia earths was identical with holmium.

In 1853 Marignac [47] had doubted the purity of Mosander's didymia, and in 1878 Delafontaine [48] found that specimens of didymia from different sources had different spectra, and he was

able to isolate an earth which he named decipia. Lecoq de Boisbaudran [49] was able, in 1879, to confirm Delafontaine's observation on the spectrum of didymium from various sources, and further was able to separate didymium into two fractions of different basicity. He showed that if a solution of a didymium salt was treated with either potassium sulphate or oxalic acid there was no separation, but if the precipitation was carried out with ammonia, a new earth was thrown out of solution before the didymia. This new earth had a different spectrum from decipia, and received the name samaria. Two new elements $\gamma_\alpha$ and $\gamma_\beta$ were isolated from samarskite in 1880 by Marignac.[50] The mixed earths were fractionated by partial decomposition of the nitrates by heat and then by precipitation with a saturated solution of potassium sulphate. In this way three fractions were obtained (*a*) that soluble in less than 100 volumes of potassium sulphate solution, (*b*) that soluble in 100-200 volumes of potassium sulphate solution, and (*c*) that still less soluble. The fraction (*b*) was termed $\gamma_\alpha$ and (*c*) $\gamma_\beta$. From the absorption spectrum, Soret [51] was able to show that samarium and $\gamma_\beta$ were identical, and that decipium differed from both $\gamma_\alpha$ and $\gamma_\beta$. Decipium was shown in 1881 by Delafontaine [52] to be a mixture of samarium and a new earth which has not been further investigated, but which doubtless was a mixture of $\gamma_\alpha$ and samarium. The element $\gamma_\alpha$ was obtained in 1886 by Lecoq de Boisbaudran [113] and named gadolinium. Brauner [53] expressed the view, in 1882, that didymia, from which all the known earths had been removed, was still a mixture, and this was proved to be correct by Auer von Welsbach,[55] in 1885, who, by a prolonged and careful series of fractional crystallisations of the double nitrates of ammonium and didymium, separated the mixture into two elements, neodymium and praseodymium. Krüss and Nilson [56] made a spectroscopic examination of solutions of the salts of the two didymiums, and stated that they had obtained evidence to show that these two substances contained at least eight elements. No confirmation of this statement has been published, and the elements of Auer von Welsbach have resisted all attempts to subdivide them, although Chroustschoff [149] states that he has isolated a third constituent, with bluish-coloured salts, which he terms glaucodidymium. At this stage (1887) in the history of the rare earths, Crookes [57] examined spectroscopically the phosphorescent light emitted by the rare earths when they

were submitted to cathode rays in an exhausted tube, and from his results he was led to put forward a theory [58] of the formation of the elements. He carried out a fractional precipitation of yttrium by means of diluted ammonia, and obtained seven fractions of different basicity which he showed had different absorption spectra. Similar results were obtained with samarium and $\gamma_a$. Crookes did not favour the view that these different fractions were due to different materials, i.e. to different elements, but rather that they were due to differences in size and structure of the different molecular types (meta-elements). The study of phosphorescent spectra was taken up by Lecoq de Boisbaudran [59] in 1888, and he was able to show that pure yttrium compounds exhibit no phosphorescent spectrum, and that the spectra obtained by Crookes were due to the presence of two new earths,[60] $Z_\alpha$ and $Z_\beta$, and in the other cases he was of the opinion that Crookes' results were due to traces of foreign material. Marignac [61] made a similar investigation, and demonstrated the large effect which small traces of foreign substances have on phosphorescence spectra. In 1900 Muthmann and Baur [62] examined the phosphorescence spectra of lanthanum and yttrium earths, and showed that although the colourless earths give phosphorescence spectra which are excessively sensitive to traces of foreign materials, still the phosphorescence spectrum is of great utility in the identification of the rare earths. Baur and Marc [63] showed that pure yttrium, gadolinium, and lanthanum do not give discontinuous phosphorescence spectra, but if traces of coloured earths, or even gypsum or chalk be present, complicated spectra are obtained which differ as the amount and nature of the impurity is varied. Later, Urbain [91] showed that the phosphorescence spectra of varying mixtures of gadolinium and terbium sulphates contain the bands which Crookes [92] attributed to the meta-elements $G_\alpha$, $G_\beta$, ionium and incognitum. Conclusions very similar to those of Crookes were reached by Krüss and Nilson [50, 64] in 1887 from a study of the absorption spectra of the salts of the coloured earths. They observed that different preparations of the earths gave absorption bands of different intensities, and estimated that the elements erbium, holmium, didymium, samarium, and thulium were composed of more than twenty different elements. Bailey [65] and Schottländer,[66] among others, showed, however, that the intensity of an absorption band can be varied by

the addition of traces of foreign substances, and consequently the spectra obtained by Krüss and Nilson must have been due to impurities in the substances they examined.

It was shown in 1886 by Lecoq de Boisbaudran [67] that holmium could be separated into two elements which he named respectively holmium and dysprosium. The separation was achieved by fractional precipitation of solutions of the original holmium salts, first with ammonia and then with a saturated solution of potassium sulphate. The fractions obtained in this way by several repetitions of the process were found to have different absorption spectra. Further, it was shown that by treating somewhat impure holmium solutions with potassium sulphate and alcohol, that the constituents were precipitated in the order—terbium, dysprosium, holmium, and erbium. About this time, Lecoq de Boisbaudran was also able to prepare gadolinium, the $\gamma_\alpha$ of Marignac,[50] in an almost pure state.

The uniformity of terbia, the existence of which had finally been established in 1886 by Lecoq de Boisbaudran,[28] was still open to doubt; in the same year he was able to show that after it had been freed from gadolinium and dysprosium, which always occur with it, it was still to be regarded as a mixture. This conclusion was reached after prolonged fractionation and subsequent spectrographic examination of the salts. Hofmann and Krüss,[68] in 1893, carried out a series of fractional precipitations of terbium salts by means of aniline, and apparently separated it into two parts of different basicity. They adopted the same method also with erbium and holmium,[69] and showed that these elements were also to be regarded as complex. Welsbach [150] has also expressed the view that terbium consists of three different elements, but James and Bissel,[151] after careful fractionation of the bromates, are able to deny this, and to state that terbium is an homogeneous substance.

Samarium, in 1883, had been regarded by Cleve [70] as a uniform substance, but in 1886, Demarçay [71] separated a new element from it which was shown by its absorption spectrum to be a constituent of the original samarium. This earth he designated by the symbol $S_1$. Bettendorf [72] was unable to confirm Damarçay's results in 1891, but in 1892-3 Lecoq de Boisbaudran,[73] by the fractional precipitation of samarium salts by ammonia and oxalic acid, separated Cleve's samarium into at least

two fractions $Z_\epsilon$ and $Z_\xi$, and perhaps others. Demarçay[74] was able, in 1896, to obtain considerable quantities of an unknown constituent from samarium which he provisionally termed $\Sigma$, the separation being effected by the fractional crystallisation of the nitrate from nitric acid solution of specific gravity 1·45. He found that three fractions were obtained, gadolinium, samarium, and a third substance, which was characterised by its greater solubility in nitric acid, by the ready solubility of its double potassium sulphate, and by its feeble basicity. Further work by Demarçay[75, 76] in 1901 enabled him, by means of fractional crystallisation of the double magnesium nitrate, to get the earth pure, and to identify it with $Z_\epsilon$ and $Z_\xi$ of Lecoq de Boisbaudran, and $S_\delta$ of Crookes. There being now no doubt as to the existence of this substance as a new element, he named it europium. The substance $S_\delta$ was one of the meta-elements of Crookes, supposed to be obtained from the fractionation of samarium salts. Very recently,[986] as the result of a spectrographic examination of the fractions of a samarium earth, Eder has stated that an element, which he terms eurosamarium, exists in samarium.

Until about the middle of the eighth decade of the nineteenth century, the only source of the rare earths lay in the minerals found in the Scandinavian peninsula; these minerals were not at all plentiful, so that of necessity the number of workers in this field was somewhat restricted. But with the discovery of large beds of monazite sand in Brazil and Carolina, new possibilities were opened. But even though the mineral supply was ample, it is not very likely that the work on the rare earths would have increased much in bulk, for every investigator would still have had to isolate his own material from the minerals. Happily, however, just at this time, the incandescent gas mantle industry sprang into existence, and at once solved the problem of isolating large quantities of the rare earths from the minerals. In the manufacture of gas mantles, the two earths thoria and ceria are essential. These earths are obtained from monazite sand; the residue, containing practically all the other earths, was therefore available in large quantities for further investigation. Naturally, therefore, a tremendous impetus was given to further work on these fascinating substances. New processes of purification and extraction of the various elements were introduced by

Demarçay,[76] Urbain and Lacombe,[77] Brauner,[78] Wyrouboff and Verneuil,[79] and Drossbach.[80] The atomic weights of cerium, praseodymium, neodymium, and lanthanum were determined by Wyrouboff and Verneuil,[79] Jones,[81] Auer von Welsbach,[82] Brauner,[83] and von Scheele.[84] The metals were isolated from the cerite earths, and their chief physical and chemical properties were investigated by Muthmann[85] and his pupils.

As a result of all this work, Brauner[86] stated that cerium, as at present recognised, is not a uniform substance, but is mixed with another element which he termed metacerium. Brauner obtained metacerium by the addition of alcohol to the mother liquors from the crystallisation of cerous sulphate, and by other methods. He states that pure cerium oxide is nearly white, and metacerium gives a rose-brown oxide. These results have never been definitely proved or disproved, but the writer is in possession of a series of unpublished results which show that cerium has been separated, by methods differing from those of Brauner, into a substance giving a pure white oxide, and a substance with a pale brown oxide. Many other investigators have doubted the uniformity of cerium, among whom may be mentioned Schützenberger and Boudouard,[87] but their conclusions were proved to be faulty by Wyrouboff and Verneuil,[88] who showed that the cerium compounds employed by them were impure, containing both yttrium and thorium.

By this time (1900) the elements of the cerium group have come to be regarded as probably uniform and unmixed with unknown elements. The same cannot, however, be said of the members of the yttrium group. Ytterbium was the first to be subdivided. This was achieved in 1907 by Urbain,[89] who, by a series of fractional crystallisations of ytterbium nitrate from nitric acid solution, was able to obtain two fractions of different properties. To the elements in these fractions, he applied the names neoytterbium and lutecium. Auer von Welsbach[90] was also able to obtain two earths from ytterbium in 1908, by fractional precipitation of the oxalate. He chose the names aldebaranium and cassiopëium for his elements, which have, however, been shown to be identical with neoytterbium and lutecium respectively. Von Welsbach[90] is further of the opinion that a third element is present, because the spectrum of the old ytterbium contains certain lines which do not appear in either neo-

ytterbium or lutecium. It is quite probable that von Welsbach is correct in his opinion, for whilst isolating lutecium from gadolinite earths by crystallisation of the nitrates from nitric acid, Urbain [93] separated in 1911 a small quantity of an earth, from the uncrystallisable mother liquor, which was characterised by a low magnetic susceptibility and by its arc spectrum. The name celtium was given to the element of this earth.

Thulium, which had been isolated from ytterbium by Cleve [44] in 1879, was submitted to spectroscopic examination by Auer von Welsbach [94] in 1911, and he came to the conclusion that it contained three elements, thulium I, II, and III respectively. The substances thulium I and III, he states, are not separable by the methods at present in use, but thulium II he has succeeded in isolating, although James [95] states that "the element, giving the characteristic absorption spectrum of thulium, cannot be separated into any simpler constituents even after 15,000 fractional crystallisations of the bromates".

Spectrographic [987, 988] examination of aldebaranium-thulium fractions of von Welsbach by Eder has led the latter to assert that these elements, and also erbium, are complex; he identifies lines in the fraction aldebaranium-thulium I as due to an element denebium, those in the fraction aldebaranium-thulium II as due to an element dubhium.

Before completing this chapter, it will probably be well to give some short account of work which has resulted in the announcement of new elements that have either been shown not to exist or have not been substantiated by investigators other than the original discoverer.

The earliest of these announcements was made in 1811 by Thomas Thomson,[96] who asserted the existence of an element junonium in allanite. Scheerer [97] and Thomson himself (1818) showed, however, that an error in the analytical work was responsible for the belief in the existence of this element. An element vestium was announced in the same year by Gilbert,[98] but nothing further has been heard of this substance. In 1879 Tellef Dahll announced the discovery of norwegium, which was stated in 1880 by Prochazka [100] to be present in American lead, and which, according to Blomstrand [101] and Rammelsberg, consisted of impure bismuth. Linnemann [102] announced the discovery of austrium in orthite, which Lecoq de Boisbaudran [103]

proved to be gallium. Chroustschoff[104] announced the discovery of russium in monazite. Damarium[105] was announced by Lauer and Antsch in 1890, and masrium by Richmond and Off,[106] the latter being an element with properties resembling glucinum and calcium. In 1896 Barriere[107] found lucium in monazite; this was stated by Chroustschoff to be very like russium, and was shown by Crookes to be yttrium mixed with didymium, erbium and ytterbium. Monium, afterwards re-named victorium, was announced in 1900 by Crookes.[108] This was obtained by partial decomposition of the nitrates of yttrium earths by heat, followed by fractional crystallisation of the oxalates. Baur and Marc,[63] however, in 1901, characterised victorium as a mixture of known earths from an examination of its phosphorescence spectrum. Baskerville[110] separated two radio-active elements from thorium, in 1901, which he termed carolinium and berzelium. Hofmann and Prandtl[115] isolated from Norwegian euxenite an earth which they named euxenium. They determined its atomic weight and obtained a value 177·75. Whether such an element exists or not is an open question. In addition to the foregoing, there have been announced all too prematurely and on insufficient evidence the following substances, kosmium and neokosmium by Kosmann[111] in 1896, and dämonium by Rowland[112] in 1894. The mere fact that so many unconfirmed or disproved statements of discoveries have been made in this field of work is perhaps the best evidence that can be offered of the extreme difficulty of the investigation of the rare earths.

To sum up the results as far as the discoveries take us, we can state that the existence of the elements thorium, cerium, lanthanum, neodymium, praseodymium, samarium, scandium, yttrium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, lutecium, neoytterbium, and celtium is regarded as having been satisfactorily proved, although it is doubtful if the elements erbium, terbium, dysprosium, holmium, thulium, celtium, and probably cerium, are in reality simple substances.

## CHAPTER II.

### OCCURRENCE OF THE RARE EARTHS IN NATURE.

UNTIL comparatively recently, the minerals, in which the rare earths occur, were found in very few places, among which may be noted, Bastnäs and Ytterby in Sweden, Brewig, Hitterö, and Arendal in Norway, and Miask in the Urals. Consequently, when incandescent gas lighting was introduced, it appeared highly probable that the scarcity of material would so raise the cost of production of the mantles that the project could scarcely become a commercial success. However, soon after the introduction of the mantles, a diligent search for rare earth minerals resulted in the discovery of large tracts of sand (monazite sand) which contained these substances in Brazil, Australia, Carolina, Virginia, and in the Urals. Other minerals were also found at the same time to be widely distributed over the surface of the earth, chiefly in the United States of America, Canada, Brazil, England, Sweden, Norway, Finland, Russia, France, Belgium, Switzerland, Germany, Austria, and Australia,[116] so that at the present moment there is no scarcity of supplies for the various industries connected with the rare earths. The minerals always contain a number of rare earths in varying proportions. Generally speaking, the two groups of the earths are both present, although the members of one of these groups are present in much larger quantities than those of the other group, thus characterising the mineral as a cerium earth mineral or an yttrium earth mineral. It does not follow by any means that all the members of either group are present in a given mineral. Furthermore, as will be seen from the analyses given below, a given mineral has a composition which varies widely, depending only on its place of origin. The minerals are mainly silicates, zirconates, titanates, niobates, tantalates, or phosphates, and practically all contain calcium, iron, aluminium, thorium, and helium, and often uranium. It is quite probable that many of these minerals, in which thorium has not been as yet found, do in reality contain it in small quantities. The constant presence of radio-active material with the rare earths is a most significant fact, and it may fairly be concluded that the two things are closely connected in some way;

perhaps the rare earths may be regarded as the ultimate disintegration products of thorium.

## I. Thorium Minerals.

(*a*) **Monazite** is chiefly an orthophosphate of the metals of the cerium group, containing also thorium oxide and silica. The general formula $CeYtPO_4,ThO_2,SiO_2$ is given to the mineral. On account of the great abundance of this mineral it is the commercial source of thorium and the cerium earths. The mineral is found in Norway, in the Urals, in North and South Carolina, and in Canada.

In addition to the mineral monazite, there is also its disintegration product, monazite sand.[141] This consists of a fine gravel or sand found on river banks, and on the seashore in Brazil, North and South Carolina, and Australia; it also occurs in large tracts in the Urals and in very rich and extensive beds in the state of Travancore. Monazite sand beds are very extensive, and vary in thickness from four inches to as many feet. The sand, as found naturally, consists of particles of monazite, rutile, thorite, cassiterite, topaz, magnetite, quartz and other heavy minerals, and contains amounts of monazite which vary from the merest trace up to 2 per cent. The crude material is concentrated by washing and by magnetic separation before it is transported from its place of origin, and then contains 65-75 per cent. of monazite. The minerals edwarsite, eremite, kryptolith, monazitoid, mengite, phosphocerite and turnerite are identical with monazite.

ANALYSES OF MONAZITE.

| Name. | Source. | Cerium Earths. | Yttrium Earths. | Thoria. |
|---|---|---|---|---|
| Edwarsite[117] | Connecticut | 49·6-67·5 | — | — |
| ,, [118] | Urals | 64·7-67·5 | — | 0-17·95 |
| Kryptolith[119] | Arendal | 73·7-70·2 | — | — |
| Turnerite[120] | Virginia | 51·0 | 1·10 | 18·6 |
| ,, [121] | Arendal | 55·46 | 3·82 | 9·57 |
| Monazite[122] | Ceylon | 42·28-57·6 | 0·94-39·3 | 9·4-28·2 |
| ,, [122] | Travancore | 59·9 | 0·46 | 8·65-10·22 |
| ,, [122] | Malay | 58·2-66·4 | 0·91-2·8 | 3·40-9·41 |
| ,, [122] | Nigeria | 59·18-66·55 | 0·39-2·74 | 2·30-8·00 |
| Monazite sand[123] | Quebec | 50·2 | 4·5 | 1·1 |
| ,, ,, [124] | N. Carolina | 63·8 | — | 2·32 |
| ,, ,, [125] | Bahia | 53·0 | 1·2 | 1·2 |
| ,, ,, [126] | Minas Geraes | 51·00 | 2·2 | 2·4 |
| ,, ,, [126] | Madagascar | 47·6 | 0·8 | 5·5 |

Monazite and monazite sand will obviously be suitable minerals for the preparation of most of the rare earths.

(*b*) **Thorianite** is a thorium uranium oxide, $ThO_2,U_3O_8$, found associated with thorite and allanite in alluvial sands in Ceylon. Until the discovery of monazite, this mineral was the chief source of thorium, but unfortunately it does not occur in large quantities. The average composition is given by the figures $ThO_2$ 70-80 per cent., cerium earths 12-25 per cent., $UO_3$ 12-25 per cent., although many specimens contain much smaller quantities of the cerium earths; for example, a specimen from Ceylon [126] was found to contain 1·02-8·04 per cent. cerium earths, and 72·24-78·86 per cent. of thoria. Thorianite serves as a source of the cerium earths and thorium.

(*c*) **Thorite** is mainly composed of thorium ortho-silicate, $ThSiO_4$, and occurs at Lowö, Brewig, Arendal, and Hitterö in Norway, and in various places in the United States of America. The mineral is a commercially important source of thorium, and contains small quantities of the cerium and yttrium earths. The average percentage composition can be seen from the following table of analyses.

ANALYSES OF THORITE.

| Source. | Cerium Earths. | Yttrium Earths. | Thoria. |
|---|---|---|---|
| Brewig [127] | 0-1·39 | | 57·91-73·80 |
| Låven and Arö [128] | — | — | 59·35 |
| Arendal [129] | — | — | 69·92 |
| Texas [130] | 6·69 | | 41·44 |

A large number of other minerals can be regarded as thorium minerals; these are of no great importance as sources of the rare earths, and will only be enumerated here in tabular form.

ANALYSES OF THORIUM MINERALS.

| Name. | Source. | Cerium Earths. | Yttrium Earths. | Thoria. |
|---|---|---|---|---|
| Calciothorite [138] | Låven | — | — | 59·35 |
| Auerlith [131] | N. Carolina | — | — | 69·23-70·13 |
| Freyalith [132] | Barkevikscheeren | 31·27 | — | 28·39 |
| Eucrasite [133] | Brewig | 14·03 | 5·95 | 35·96 |
| Aeschynite [134] | Miask | 14·36 | 4·30 | 22·57 |
| Bröggerite [135] | Anneröd, nr. Moos | 0·38 | 2·42 | 5·64 |
| Cyrtolith [136] | Ytterby | trace | 22·01 | 15·13 |
| Erdmannite [137] | Brewig | 17·66 | 2·14 | 9·93 |
| Karyocerite [138] | Stockö | 41·81 | 2·21 | 13·64 |
| | | 1·86 | | |
| Mackintoshite [139] | Texas | | | 45·30 |
| Loranskite [140] | Finland | 3·00 | 10·00 | 20·00 |

## II. Cerium Minerals.

(*a*) **Cerite,** a polysilicate of iron, calcium, and the cerium metals, to which the formula $H_3(CaFe)Ce_3Si_3O_{13}$ is applied. Before the discovery of monazite, this mineral was the chief source of the cerium metals. It is found at Riddarhyttan, and Bastnäs in Sweden, and is of variable composition. It is a suitable starting-point for the isolation of the elements cerium, lanthanum, praseodymium, neodymium, and samarium.

ANALYSES OF CERITE.

| $Ce_2O_3$. | $(LaPrNd)_2O_3$. | $Fe_2O_3$. | CaO. | $SiO_2$. |
|---|---|---|---|---|
| 60·99 [142] | 7·41 | 1·46 | 1·65 | 21·35 |
| 24·06 [143] | 35·37 | 3·92 | 4·35 | 22·79 |
| 33·25 [144] | 34·6 | 3·18 | 1·69 | 18·18 |

(*b*) **Orthite (allanite),** $H(CaFe)_2(AlCe)_3Si_3O_{13}$, a calcium iron aluminium polysilicate containing cerium metals. The mineral is known under several other names such as, xantho-orthite, bodenite, pyro-orthite, cerin, wasite, and muromontite. It is fairly widely distributed, being found at Riddarhyttan, Ytterby, and Tunaberg in Sweden, at Fahlun, Miask, Mauresberg, and on the island of Rönsholm near Stockholm, in Canada, and in Colorado, Virginia and Carolina, United States of America. It is a suitable mineral for the isolation of the cerium earths, and some specimens contain quantities of the yttrium and erbium earths.

ANALYSES OF ORTHITE.

| Source. | Cerium Earths. | Yttrium Earths. | Thoria. |
|---|---|---|---|
| Tunaberg [145] . . | 9·77 | — | 3·48 |
| Hitterö [146] . . | 19·75 | 1·39 | 0·87 |
| Ytterby [146] . . | 17·63 | 4·74 | trace |
| Boden [147] . . | 18·03 | 17·43 | — |
| Finbö [148] . . | 17·39 | 3·80 | — |

An idea of the relative amounts of the individual rare earths present can be gained from the following analyses:—

ANALYSES OF ORTHITE.

| Source. | $Ce_2O_3$. | $Di_2O_3$. | $La_2O_3$. | $Yt_2O_3$. | $Er_2O_3$. | $ThO_2$. |
|---|---|---|---|---|---|---|
| Ytterby [146] . | 5·90 | 7·57 | 5·16 | 2·74 | 2·00 | trace |
| Hitterö [146] . | 8·69 | 5·60 | 5·46 | 0·87 | 0·52 | 0·87 |

The cerium earths are found very largely in monazite and monazite sand (see thorium minerals), and in a large number of much rarer minerals, such as tysonite ($CeF_3$), aeschynite, a niobate and titanate of the cerium earths, fluocerite ($Ce_2OF_4,4CeF_3$), yttrocerite ($CaF_2(CeYt)F_3$), lanthanite ($La_2(CO_3)_3,9H_2O$), beckelite, a silicate of the cerium earths containing yttrium earths, and many others. The percentage of the various groups of rare earths is indicated in the following table:—

ANALYSES OF CERIUM MINERALS.

| Name. | Source. | Cerium Earths. | Yttrium Earths. | Thoria. |
|---|---|---|---|---|
| Tysonite [152] . | Pike's Peak | 70·56 | — | — |
| Fluocerite [153] . | Brodbö | 82·64 | 1·12 | — |
| Yttrocerite [154] . | Finbö | 16·4-18·2 | 8·1-9·1 | — |
| Lanthanite [155] . | Pennsylvania | 54·90 | — | — |
| Ancylite [156] . | S. Greenland | 46·26 | — | — |
| Bastnäsite [157] . | Riddarhyttan | 74·26 | — | — |
| Churchite [158] . | Cornwall | 51·97 | — | — |
| Melanocerite [159] | Langesund-fiord | 45·05 | 9·17 | 1·66 |
| Parisite [160] . | Urals. | 64·37 | — | — |

An idea of the relative amounts of the various individual earths may be gained from the subjoined analyses:—

ANALYSES OF CERIUM MINERALS.

| Name. | $Ce_2O_3$. | $La_2O_3$. | $Di_2O_3$. | $Yt_2O_3$. | $Er_2O_3$. |
|---|---|---|---|---|---|
| Lanthanite [161] | 25·52 | 28·34 | | 0·79 | — |
| Beckelite [162] . | 28·10 | 13·6 | 18·0 | 2·8 | |

## III. Yttrium Minerals.

(*a*) **Gadolinite (Ytterbite)**, $Fe_2Gl_2Yt_2Si_2O_5$, an iron yttrium glucinum silicate found in Scandinavia, at Ytterby, Fahlun, and Hitterö; in the counties of Galway and Down, Ireland; in

Silesia, the Harz mountains, and in Colorado and Texas, United States of America. This mineral is one of the most important sources of yttrium earths, and serves as a suitable source of most of them.

ANALYSES OF GADOLINITE.

| Name. | Source. | Cerium Earths. | Yttrium Earths. | Thoria. |
|---|---|---|---|---|
| Ytterbite [163] | Ytterby | 7·90 | 50·00 | — |
| ,, [164] | Fahlun | 14·31 | 36·54 | — |
| ,, [165] | Colorado | 32·33 | 22·24 | 0·89 |
| ,, [165] | ,, | 25·97 | 27·71 | 0·81 |
| Gadolinite [166] | Hitterö | 5·47 | 46·51 | 0·39 |
| ,, [166] | Ytterby | 4·71 | 45·96 | 0·30 |
| ,, [167] | Batum | 14·77 | 39·39 | — |

An idea of the amounts of the individual earths contained in gadolinite will be seen from the following analyses:—

ANALYSES OF GADOLINITE.

| Source. | $Yt_2O_3$. | $Ce_2O_3$. | $Er_2O_3$. | $(LaDi)_2O_3$. | $ThO_2$. | GlO. |
|---|---|---|---|---|---|---|
| Colorado [168] | 9·50 | 11·10 | 12·74 | 21·23 | 0·89 | 7·19 |
| Silesia [169] | 43·0 | 5·00 | — | — | — | 8·0 |
| Ytterby [170] | 38·13 | 13·55 | — | — | — | 10·05 |
| Colorado [168] | 12·63 | 6·87 | 15·80 | 19·10 | 0·81 | 5·46 |

(*b*) **Xenotime,** an yttrium phosphate, $YtPO_4$, which contains a large number of the elements of the cerium and yttrium groups, is also known by the names castelnaudite, ytterspar, wiserin, and hussakite. This mineral is chiefly found at Ytterby and Hitterö, on the St. Gothard, along with monazite in Brazil, at Arendal, and in Colorado and N. Carolina. It is a suitable source of yttrium, gadolinium, terbium, europium, dysprosium, holmium, thulium, and ytterbium.

ANALYSES OF XENOTIME.

| Name. | Source. | Cerium Earths. | Yttrium Earths. | Thoria. |
|---|---|---|---|---|
| Ytterspar [171] | Lindesnäs | — | 62·58 | — |
| Castelnaudite [172] | Bahia | — | 60·40 | — |
| Wiserin [173] | St. Gothard | 62·49 | | — |
| Xenotime [174] | Minas Geraes | — | 64·10 | — |
| ,, [175] | Hvalö | 1·22 | 56·38 | 3·33 |
| ,, [175] | Arendal | 0·96 | 54·57 | 2·43 |
| ,, [176] | Colorado | — | 67·78 | — |
| ,, [177] | Hitterö | 1·50 | 58·00 | — |

(*c*) **Samarskite,** also known as yttroilmenite and uranotantalite, is a niobate and tantalate of uranium, and the cerium and yttrium metals. It corresponds with the general formula $R_4(NbTa)_2O_7$, in which R represents $\frac{1}{3}$(YtCe) or $\frac{1}{2}$UO, ThO, Fe, Ca. It is found in the Urals; the Ilmen mountains, in Sweden; in Canada; and in N. Carolina, and many other localities in the United States of America. This mineral serves as an excellent source of yttrium earths.

ANALYSES OF SAMARSKITE.

| Name. | Source. | Cerium Earths. | Yttrium Earths. | Thoria. |
|---|---|---|---|---|
| Yttroilmenite [178] . | Ilmensee | 2·48 | 21·03 | 2·83 |
| Uranotantalite [179] . | Miask | 2·83 | 13·29 | |
| Samarskite [180] . . | N. Carolina | 3·95 | 11·11 | — |
| ,, [181] . . | Colorado | 2·34 | 17·12 | 3·64 |
| ,, [182] . . | Urals | 1·18 | 21·20 | 1·73 |

(*d*) **Euxenite** is of somewhat the same composition as samarskite, but corresponds with the general formula

$$R_2(NbO_3)_3, R_2(TiO_3)_3, \tfrac{3}{2}H_2O,$$

in which R has the same meaning as in the case of samarskite. It serves as a source of the yttrium earths, and is found at Arendal and Hitterö, in Greenland, and Henderson, Carolina. This mineral is more important as a source of niobium and tantalum. A specimen found at Arendal [183] was found to contain 3·31 per cent. cerium earths, 29·35 per cent. yttrium earths, and 2·5 per cent. thoria.

(*e*) **Fergusonite,** also termed bragite, brown yttrotantalite, and tyrite, is mainly a niobate and tantalate of the yttrium earths, containing cerium earths, uranium, thorium, and zirconium. It is found at Arendal, at Ytterby, in Greenland, Japan, Australia,

ANALYSES OF FERGUSONITE.

| Name. | Source. | Cerium Earths. | Yttrium Earths. | Thoria. |
|---|---|---|---|---|
| Fergusonite [184] . . | Greenland | 4·68 | 41·91 | — |
| ,, [185] . . | Ytterby | — | 39·80 | — |
| ,, [186] . . | Hampemyr | 0·77 | 37·15 | 3·44 |
| Tyrite [187] . . . | Arendal | 6·10 | 27·83 | — |
| Bragite [188] . . | ,, | 7·43 | 32·71 | — |
| Yttrotantalite [189] . | Ytterby | 7·80 | 30·45 | — |
| Sipylite [190] . . | Virginia | 9·35 | 27·49 | — |

and the United States of America. The mineral sipylite is very like fergusonite, and is peculiar since it contains more praseodymium than neodymium, whereas the reverse is generally found to be the case.

In addition to the minerals considered, mention may be made of the following less common yttrium minerals: rowlandite, ($2Yt_2O_3 3SiO_2$); yttrialite ($(YtCe)_2O_3, 2SiO_2$); yttrocrasite, a hydrated yttrium thorium cerium titanate; polycrase,

$$R_2(NbO_3)_3, 2R_2(TiO_3)_3, 3H_2O,$$

a titanate and niobate of yttrium and cerium earths, along with uranium and sometimes scandium; hellandite, an hydrated orthosilicate of calcium and the rare earths; and yttrocerite,

$$Ce_2F_6, 2Yt_2F_6, 9CaF_2, 2H_2O.$$[191]

ANALYSES OF YTTRIUM MINERALS.

| Name. | Source. | Cerium Earths. | Yttrium Earths. | Thoria. |
|---|---|---|---|---|
| Rowlandite[192] . | Texas | 14·40 | 47·70 | 0·59 |
| Yttrialite[193] . | ,, | 6·56 | 46·50 | 12·83 |
| Polycrase[194] . | Hitterö | 2·72 | 32·14 | — |
| Hellandite[195] . | Kragerö | 1·01 | 34·72 | 0·62 |
| Ytterocerite[154] . | Finbö | 16·4-18·2 | 8·1-9·1 | — |
| Thalenite[196] . | Dalekarien | — | 63·35 | — |

Before concluding this chapter, a word must be said concerning the occurrence of scandium in nature. This element occurs in practically all yttrium minerals, but with the exception of one mineral, thortveitite,[197] it is rarely found in quantities amounting to 1 per cent. of the mineral. Eberhard[198] and Crookes[199] have examined a large number of minerals, and obtained evidence that scandium occurs in small quantities in a large number of them. The mineral thortveitite $(ScYt)_2Si_2O_7$[197] contains 40 per cent. $Sc_2O_3$ and 17 per cent of yttrium earths; wiikite[199] contains 1·17 per cent. $Sc_2O_3$, 7·5 per cent. $Yt_2O_3$, and 2·5 per cent. $Ce_2O_3$. Scandium also occurs in wolframite from the Zinnwald to the extent of 0·1 per cent., and Böhm[200] has shown that the residue, after the tungsten has been removed from wolframite in the manufacture of sodium tungstate, is a profitable source of scandium. Although scandium is only present to the extent of 0·1 per cent. in the wolframite, its separation is relatively easy, since it constitutes 56·4 per cent.[201] of the total rare earths present.

## CHAPTER III.

### SEPARATION OF THE RARE EARTHS.

THE analytical processes generally employed for the separation of metals, fail entirely when applied to the rare earths, although they are usually effective in separating the rare earths from the commoner and better-known metals. The reason for this is to be found in the fact that the rare earths are so very similar in their properties that they all behave in an identical manner with the reagents employed in the ordinary separations. One is therefore compelled to rely, for their separation, on two properties (*a*) their basicity, and (*b*) the solubility of their salts in water and other solvents.

(*a*) The basicity of the rare earths varies from element to element, and consequently a number of reactions which depend on the relative basicity can be employed. Among these reactions may be noted the fractional precipitation of the hydroxides by means of ammonia, caustic alkalis, magnesia, and other basic oxides, aniline and other organic bases. Since the basicity of the elements is different, it is to be expected that the temperature at which their decomposable salts are destroyed will vary, and it is found that this is the case; so that a partial decomposition, by heat of a mixture of rare earth nitrates, effects a separation.

(*b*) The solubility of the corresponding salts of the various elements varies to a slight extent, so that a careful fractional crystallisation will often effect a separation of a mixture of these substances. This method of separation has been the subject of a large amount of research, with the result that very many salts have been found suitable for this purpose, among which may be mentioned the sulphates, nitrates, oxalates, formates, acetates, ethyl sulphates, bromates, double nitrates with ammonium, magnesium, bismuth, manganese or nickel, double sulphates with the alkali metals, acetylacetonates, dimethyl phosphates, and picrates. It is to be

observed that a single operation, either precipitation or crystallisation, is insufficient to effect a separation of the rare earths; in many cases it has been found necessary to repeat the process thousands of times. The effect of a single treatment is merely to furnish a series of fractions, each of which is a complex mixture, little, if any, less complex than the original mixture. But by a repetition of the process with each fraction it will be found that a single element tends to concentrate at either end of a series of fractions, so that by many repetitions of the process it is possible to obtain a pure salt of at least two of the elements in the mixture. The extreme difficulty of the separation has led to the introduction of a great many methods of separation which depend almost entirely on the two properties mentioned above. In practice it is found advantageous in many cases to combine two or more methods, that is to use one up to a given point, and to complete the separation by other methods. Before proceeding to a discussion of the actual methods of separation, a few words on the means employed in obtaining a solution of the minerals may not be out of place.

The mineral which must be very finely powdered is digested either with hot hydrochloric acid or with hot concentrated sulphuric acid. This treatment will give a solution in many cases, but there are some minerals which require fusion with sodium hydrogen sulphate or digestion with hydrofluoric acid. The minerals cerite, orthite, gadolinite, thorite, and yttrialith yield readily to treatment with hydrochloric acid. Xenotime, yttrotitanite, thorianite, and monazite require sulphuric acid for their decomposition, whilst fergusonite, euxenite, polycrase, samarskite, and yttrotantalite can only be got into solution by fusion with sodium bisulphate or treatment with hydrofluoric acid. It is always wiser when a mineral has to be fused to use sodium bisulphate in preference to potassium bisulphate, because many of the rare earth sulphates form sparingly soluble double sulphates with potassium sulphate, whereas those that they form with sodium sulphate are much more soluble. When a mineral is digested with hydrofluoric acid, the rare earths are left as insoluble fluorides which must be decomposed by boiling with sulphuric acid in order to obtain a solution. Before a method of separation can be chosen it is necessary to make a preliminary examination of the solution to ascertain which group of elements is present

in the larger quantity. A spectroscopic examination usually is sufficient for this purpose, and additional evidence as to the composition of the mixture can be gained from the nature of the mineral from which the earths have been derived. Thus it would at once be known whether the cerium earths or the yttrium earths represented the bulk of the material, and the method of separation could be chosen accordingly. The yttrium group of earths has been divided into three sub-groups, the erbium earths, consisting of erbium, dysprosium, thulium, and holmium ; the terbium earths, consisting of terbium, gadolinium, and europium ; and the ytterbium earths, consisting of ytterbium, lutecium, and celtium. It is of value to know which of these sub-groups represents the yttrium earths in a mixture, when a method of separation has to be chosen.

The constant occurrence of certain of the rare earths together with one another, and their absence from minerals which contain certain other elements, has led many investigators to ask if there is any regularity in the nature and quantity of the members of the rare earth group present in any of the minerals. Generally speaking, no such regularity has been observed except in the case of minerals containing titanic and tantalic acids. Hauser and Wirth,[109] from the examination of a large number of specimens of euxenite, samarskite, and polycrase, have shown that yttrium earths containing the erbium earths always occur in these minerals in amounts which vary from one-third to three-sevenths of the total rare earths present, and that with an increasing titanic acid content the proportion of holmium and dysprosium increases at the expense of the erbium, although these earths are generally only present in small quantities. On the other hand, the quantities of scandium and ytterbium are relatively greater with increasing titanic acid content. In the case of the cerium earths the relationships are more noticeable. Those euxenites which are relatively poor in tantalic acid and rich in titanic acid are quite free from samarium and praseodymium. A specimen of euxenite from South Carolina, which was rich in tantalic acid and poor in titanic acid, contained 2 per cent. of samarium oxide, whilst the gadolinium was less than the usual amount. From this it follows that with an increase in the amount of tantalic acid and a decrease in the amount of titanic acid the otherwise missing samarium makes its appearance. The presence of thorium in

niobates also appears to depend on the presence of titanic acid. If titanic acid is absent or only present in small quantities then thorium is also absent.

The methods used for the separation of the rare earths can be considered under four heads: (1) fractional crystallisation; (2) fractional precipitation; (3) oxidation methods; and (4) physical methods.

**I. Separation by Fractional Crystallisation of Salts.**[202]

(*a*) *Sulphates.*—This method depends on the fact that the sulphates of the rare earths are less soluble in hot water than in cold, but to varying extents in the different cases. Consequently, when a saturated solution of the anhydrous sulphates is made in ice-cold water and the temperature raised, one or more of the constituents will separate as crystalline hydrates. This mass of crystals is separated, washed and dehydrated, and the process repeated until finally the sulphate of a single element is obtained. This process was introduced by Mosander,[203] who used it to separate lanthanum from cerium, and didymium from lanthanum. Marignac,[204] Brauner,[205] and Wyrouboff and Verneuil [206] have employed the method for the purification of cerium compounds, although it has been shown that if thorium or lanthanum are present, the method fails to remove the last traces. By means of this method, Böhm [207] was able to separate a 96-97 per cent. neodymium preparation from didymium, and Schützenberger and Boudouart [208] separated the cerium earths from the yttrium earths of monazite by the same means. Thorium is easily freed from all other rare earths by this method.

(*b*) *Alkali Double Sulphates.*—This method, which has been used by practically all the investigators of the rare earths, is based on the difference of solubility of the double potassium and sodium sulphates of the rare earths in saturated solutions of potassium and sodium sulphates respectively. The rare earths can be divided into three groups with respect to the solubility of their double potassium sulphates in a saturated solution of potassium sulphate,[209] namely:—

I. Soluble. Yttrium, ytterbium, erbium, thulium, holmium, and dysprosium.

II. Slightly soluble. Gadolinium, terbium, and europium.

III. Practically insoluble. Thorium, cerium, lanthanum, neodymium, praseodymium, samarium, and scandium.

The separation is effected by adding, little by little, powdered potassium sulphate to a solution of the rare earth sulphates, the concentration of which varies with the nature and relative quantities of the earths present. For the separation of the cerium earths from the yttrium earths, Meyer and Marckwald [342] place the solution of the earths in a large porcelain dish and raise to the boiling-point, then, after the flame has been removed, powdered potassium sulphate is added little by little whilst the liquid is stirred by means of a jet of steam. The addition of potassium sulphate is continued until a test portion of the solution shows only the faintest trace of the didymium absorption spectrum. When this point is reached, the crystals, which consist almost entirely of the double potassium sulphates of the cerium earths, are allowed to settle, and the solution, containing the yttrium earths, is poured off. If potassium sulphate is added until the didymium absorption spectrum has entirely disappeared some of the yttrium earths will be found along with the cerium earths which have crystallised out. This method has been largely used either in the form described above or with modifications. Hofmann [210] uses a saturated solution of potassium sulphate in place of the powdered crystals. Good results have been obtained by the use of this method in the separation of ytterbium and scandium,[211] and also in the purification of gadolinium.[211] Potassium sulphate may be replaced by sodium sulphate as was shown by Erk,[213] who separated the cerium earths from the yttrium earths by adding a not too concentrated solution of sodium sulphate to a solution of the nitrates of the earths when the double sulphates of the cerium earths crystallised out leaving the corresponding yttrium salts in solution. The use of sodium sulphate enabled Lecoq de Boisbaudran to separate an yttrium erbium mixture more rapidly than was possible by ammonia precipitation (see II. (*g*), p. 39). Other sulphates have been used in place of sodium and potassium with more or less success, amongst the most successful are those of the luteo- and roseo-cobaltammines [214] which behave much in the same way as the sulphates of sodium and potassium.

(*c*) *Nitrates.*—This method is due to Demarçay,[74] and consists in the fractional crystallisation of the mixed nitrates from nitric acid of specific gravity 1·3-1·54. The efficiency of this method is particularly good when the mixture of earths contains no element

of atomic weight less than that of dysprosium (162·5). The reason for this is found in the fact that the solubility of the nitrates in nitric acid decreases with increasing atomic weight to a minimum, which is reached with gadolinium nitrate, after which it increases steadily with increasing atomic weight and reaches a maximum with ytterbium nitrate. Baur and Marc [215] have shown that the method is very efficient for separating gadolinium from yttrium; in this case on repeated crystallisation the gadolinium concentrates in the crystals and the yttrium in the mother liquor. By recrystallisation of a mixture of the nitrates of ytterbium, erbium and thulium, Urbain [89] obtained ytterbium free from the other elements, and by repeating the fractionation 15,000 times with the pure ytterbium nitrate, using nitric acid of 1·3 specific gravity, he was able to divide the ytterbium into two fractions which contained respectively the new elements lutecium and neo-ytterbium (ytterbium). Further, from the final mother liquor of this prolonged series of crystallisations, he was able to show the presence of the unknown element celtium.[93] Pure ytterbium [989] was also obtained by 4000 crystallisations of the nitrate.

The nitrates of the rare earths can be separated by a judicious use of solvents other than water. Thus Bröcklemann [216] obtained a didymium preparation which could not be further purified by any of the usual crystallisation methods, but on treating a concentrated aqueous solution of the neutral nitrate of this substance with alcohol, a colourless earth consisting of yttrium and scandium separated out. The basic nitrates of the cerium group are readily separated in acetone solution; [217] cerium being quickly obtained in the first fraction, and didymium concentrating in the last fraction.

(*d*) *Double Nitrates.*—Amongst the double nitrates which have been used for the separation of the rare earths those of ammonium, magnesium, bismuth, nickel, and manganese are the most important.

(i) *Double Ammonium Nitrates.*—This method, although it is generally known as the Welsbach method, was in reality first used by Mendeléeff [29] for the separation of lanthanum from didymium. Auer von Welsbach modified it [218] by crystallising from nitric acid solutions instead of from aqueous solutions as had been usual. The double ammonium nitrates are used in the first place for the preparation of pure cerium compounds,[219, 220] and the method

depends in this case on the formation of a double ceric ammonium nitrate; cerium, with the exception of thorium, being the only member of the rare earth group to form such a higher double ammonium nitrate. To effect this separation the mixture of oxides is dissolved in nitric acid (sp. gr. 1·4) at the boiling-point and allowed to stand for some time, so that impurities, such as lead and copper, may separate out. Then the solution is diluted with one-half its volume of water, and a quantity of ammonium nitrate, equal to one-third the weight of the rare earth oxides, is added. The solution is then concentrated on the water-bath until, on the surface of an almost black liquid, crystals begin to separate when it is allowed to cool. Thereupon, ceric ammonium nitrate, $Ce(NO_3)_4,2NH_4NO_3$, separates out as a mass of crystals of the colour of potassium bichromate. The mother liquor is poured from the crystals and concentrated, whereupon lanthanum, cerous, and didymium double ammonium nitrates crystallise out. These are reconverted into the oxides and the above process repeated to free the compounds from cerium.

The chief application of the double ammonium nitrates of the rare earths is not for the separation of cerium but for the separation of lanthanum from didymium and for the separation of didymium into its constituents neodymium and praseodymium. These separations were carried out by Auer von Welsbach in a research which may be truly termed classic.[218] The oxides from which the cerium had been removed, although the presence of a little cerium does not affect the separation disadvantageously, were dissolved in nitric acid and the requisite quantity of ammonium nitrate added. The mixture was then heated until crystals appeared on the surface, when it was cooled and allowed to stand for six to twelve hours. A quantity of crystals was thus obtained from which the mother liquor was removed and concentrated so that a second crop of crystals was produced. This process was repeated until 6-8 fractions had been separated and the final mother liquor, containing excess of ammonium nitrate, nitrates of samarium, terbium, and any other of the yttrium earths which were present in the original mixture, had become uncrystallisable. The first fraction contains most of the lanthanum and the last practically the whole of the didymium. These eight fractions have now to be systematically recrystallised, and this is done by dissolving the first fraction in water and crystallising; the

second fraction is then dissolved in the mother liquor from the first fraction, and so on through the series. In this way after a few recrystallisations pure lanthanum compounds are obtained.[209, 221, 222, 223] On repeating the crystallisation of the fractions containing didymium in a systematic manner, von Welsbach[218] finally separated didymium into neodymium and praseodymium, the praseodymium crystallising out before the neodymium. Despite the large amount of material used by von Welsbach, and the large number of crystallisations carried out, it is extremely doubtful whether he got praseodymium free from lanthanum, and neodymium free from praseodymium by this method. Sodium nitrate[223] may be substituted for ammonium nitrate in this separation, when salts of the type

$$M^{III}(NO_3)_3,2NaNO_3,H_2O$$

are obtained, by means of which the major portion of the lanthanum and praseodymium can be removed from the neodymium. This modification is not economical or efficient, for the individual salts cannot be obtained pure by its means, and such results as are obtained are the product of some thousands of recrystallisations. Von Scheele[223] introduced a modification of the original process, such that, instead of removing the cerium before fractionating the double ammonium nitrates as had been customary, he purposely left it in; and in cases where cerium was not already present he added it. The reason for this is that the cerous ammonium nitrate has a solubility which is between that of the corresponding salts of lanthanum and praseodymium. Consequently when the pure neodymium fractions begin to form, the praseodymium is associated, not with lanthanum which is difficult to remove, but with cerium which is easily removed. The Scheele modification, therefore, in one series of crystallisations, yields pure lanthanum compounds and separates a large amount of didymium into its constituents.[224] James[225] employs this method for the completion of the separation of lanthanum and praseodymium, and Esposito,[226] by the same method, effected a practically complete separation of lanthanum, praseodymium, and neodymium.

(ii) *Double Magnesium Nitrates.*—The crystallisation of the double magnesium nitrates of the rare earths was introduced by Drossbach[227] for the separation of neodymium and praseodymium. The cerium earths form double nitrates with magnesium nitrate

of the general formula $2M^{III}(NO_3)_3, 3Mg(NO_3)_2, 24H_2O$. The material used by him for this separation was a didymium lanthanum fraction obtained by the oxychloride method (II. (*p*), p. 44). The mixture was converted into oxides which were then dissolved in nitric acid; the same quantity of nitric acid was treated with as much magnesia as it would dissolve, and the two solutions were mixed. This ensures the addition of exactly the correct amount of magnesium nitrate for the formation of the double salts. The mixed solution was then heated and small quantities of magnesia added until the solution was alkaline to congo paper. On diluting the solution, impurities such as iron, manganese, aluminium, silica, and phosphoric acid were precipitated by the excess of magnesia. The solution was then filtered and concentrated until practically the whole of the double nitrates had separated out. The crystals were removed from the mother liquor, placed in a dish and treated with boiling water until only a small portion remained undissolved. Cooling was then brought about by floating the dish in water at 30°-40°, and a small quantity of cold water was sprayed on to the surface of the solution. A quantity of large crystals separated on the bottom of the dish, and as soon as about one-tenth of the total earths had crystallised out, the liquor was poured from the crystals into a second dish which was floated on water at 10°-15° and cooled on the surface as before when a second crop of crystals was obtained. The mother liquor from the second crop of crystals was then treated at 0° in the same way, and a third crop of crystals obtained. The mother liquor from the third crop of crystals was concentrated and the process repeated. The final mother liquor being rejected for this purpose was used for the isolation of erbium, samarium, yttrium, and gadolinium which it contained. The various crops of crystals were then recrystallised systematically when the following materials were obtained: neodymium containing traces of praseodymium, a little pure neodymium, and much lanthanum containing praseodymium. The double magnesium nitrates of the rare earths crystallise from water in the order[228, 229] lanthanum, praseodymium, neodymium, excess magnesium nitrate, samarium, europium, erbium, gadolinium, and yttrium, and the remaining yttrium earths. By using this method, Feit[230] was able to concentrate terbium from a mixture of monazite earths in the least soluble

fraction, and James [225] uses it for the initial separation of the cerium earths.

(iii) *Double Bismuth Nitrates.*—The principle underlying this method is the same as that of the addition of cerium [223] to the double ammonium nitrates (I. (*d*) (i), p. 26), namely, the addition of a salt which crystallises isomorphously with the salts to be separated and which has a solubility lying between those of the salts constituting the mixture. This method of separation is applied to the non-crystallisable mother liquor from the magnesium double nitrate separation. On adding a quantity of bismuth nitrate, equal in quantity to that of the magnesium nitrate already present, the gadolinium immediately separates out as a double gadolinium bismuth nitrate,[77] so that pure gadolinium is at once obtained. In the same way, gadolinium can be separated from the mixed yttrium earths,[77] and the method can also be used for the separation of the yttrium earths from the cerium earths. Urbain,[231] by other methods, had obtained a mixture of ytterbium, lanthanum, lutecium, and cerium. This mixture he converted into the nitrates and added a quantity of bismuth and magnesium nitrates. The solution was concentrated and allowed to cool when all the lanthanum and cerium separated out as double bismuth nitrates. Many other separations have been carried out by this process among which may be noted, the preparation of pure europium compounds from a mixture of europium, samarium, and gadolinium by Urbain and Lacombe,[232] and Eberhard;[233] the separation of terbium and gadolinium by Urbain,[234] and a general separation by James,[235] with the object of obtaining europium from the earths of Brazilian monazite.

(iv) *Double Nickel Nitrates.*—The double nickel nitrates have been used by Urbain [236] for separating traces of europium and the element $Z\delta$ (terbium) from gadolinium. From an aqueous solution of the double nickel nitrates of the elements mentioned, the compound $2Gd(NO_3)_3,3Ni(NO_3)_2,24H_2O$ crystallises out perfectly pure. Further, by a continuation of the fractionation the compounds of terbium have been obtained quite pure, and are shown to differ slightly in their spectrum from the substances hitherto regarded as pure terbium compounds, but which, according to Urbain, contained a small quantity of gadolinium.[341]

(v) *Double Manganese Nitrates.*—The double manganese nitrates have only been used by James for the separation of neodymium and praseodymium. This method appears to give a rapid and good separation of these elements.

(*e*) *Bromates.*—The fractional crystallisation of the bromates was introduced by James [225, 238, 239, 237] for the separation of the members of the yttrium group of earths. The process is carried out as follows: The mixture of earths is converted into the anhydrous sulphates, dissolved in ice-cold water and poured into an excess of barium bromate. It is then heated to 100° on a water-bath and stirred vigorously by means of a mechanical stirrer. When the double decomposition is complete, the mixture is filtered and the filtrate evaporated to such an extent that about one-half of the material in solution crystallises out. This is separated and recrystallised, and after about twenty recrystallisations the least soluble fraction is colourless and consists of yttrium bromate with traces of dysprosium, samarium, holmium, and terbium; the next fractions are yellow and show in their spectra the lines of dysprosium and holmium, while following these come pink fractions which show only the erbium lines, a fraction consisting mainly of thulium, and finally the most soluble fraction which is chiefly ytterbium. The solubility of the bromates in water is given in increasing order by James [238] as samarium, europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, and ytterbium. By the above method, James has obtained large quantities of pure thulium [95, 240] and yttrium [241] compounds. Jordan and Hopkins [998] have shown that terbium can be readily removed from samarium and europium by the bromate method, and Kremers [999] and Balke have effected a rapid concentration of dysprosium and holmium in a mixture of the yttrium earths by the same method.

(*f*) *Ethylsulphates.*—The ethylsulphates of the yttrium earths crystallise well, and have solubilities which allow of a fairly easy separation of the individual elements being accomplished.[209, 242] They separate from aqueous solution in the order terbium, yttrium, holmium, dysprosium, erbium, and ytterbium. In the preparation of the ethylsulphates, care must be taken that the ethylsulphuric acid, from which they are prepared, contains no free sulphuric acid. By means of the ethylsulphates, Urbain [243] has prepared pure dysprosium compounds from a mixture of

yttrium, terbium, and dysprosium, and Hofmann and Burger [244] have obtained pure erbium from a mixture of thulium, holmium, dysprosium, and erbium. The ethyl sulphates can also be used to fractionate a lanthanum didymium mixture, when neodymium concentrates in the first fraction and lanthanum in the last fraction. Kremers, Hopkins, and Engle [995] find that the ethylsulphates are very efficient for separating dysprosium from neodymium, praseodymium, and terbium, but do not separate holmium and dysprosium.

(*g*) *Acetyl Acetonates.*—The rare earth derivatives of acetyl acetone crystallise well, and in some cases serve as a method for the purification of these substances. The method was first applied to the separation of pure thorium [245] from the crude product in the following manner: The mixed hydroxides were dissolved in nitric acid and the solution evaporated to dryness on a water-bath; the residue was dissolved in water and treated with the sodium derivative of acetyl acetone,

$$(CH_3COCH = C(ONa)CH_3),$$

and again evaporated to dryness. The residue was then crystallised from chloroform, when the practically pure thorium compound was obtained. Urbain [209, 242] showed that this method could be used in the case of yttrium earths. He converted the yttrium earths from monazite into the acetyl acetonates, and fractionally crystallised these first from absolute alcohol and then from light petroleum, and found that the compounds of the elements of smallest atomic weight concentrated in the first fraction. Making use of the same process, Hofmann [246] separated erbium from holmium and dysprosium by crystallising from absolute alcohol, and Meyer [201] obtained pure scandium from the mixture of earths which accompany this element in wolframite.

(*h*) *Formates.*—The fractional crystallisation of the formates of the rare earths offers a means of separating the cerium earths from the yttrium earths, since the formates of the latter group are much more soluble than those of the former group. This method of separating the two groups has been used successfully by Brauner.[247] Urbain [209, 242] has used the formates for the separation of neodymium and praseodymium. He dissolved the crude didymium hydroxide in formic acid and boiled the solution, whereupon neodymium formate crystallised out whilst the praseodymium with a little neodymium remained in solution. The

fractional crystallisation of the formates of the yttrium earths furnishes a good preliminary method of separation. Thus Bettendorf[248] found that the mixture could be divided into three fractions, the equivalents of whose oxides were 120·0, 91·7, and 80·5 respectively. This method is particularly good for isolating the terbium earths from the remaining yttrium earths. In this case the solution of the formates is concentrated until a microcrystalline mass separates out which contains terbium and gadolinium, whilst the remaining earths remain in solution. Sterba-Böhm[249] also finds the method good for removing the last traces of ytterbium from scandium.

(*i*) *Acetates.*—By the fractional crystallisation of the acetates of an yttrium erbium earth mixture, Postius[250] has shown that the erbium concentrates in the crystals, whilst didymium, samarium, and the other earths remain in the mother liquor. This obviously offers a means of separating erbium and samarium. The method consists in dissolving the mixed oxides in fairly strong acetic acid, evaporating until crystallisation commences, cooling and filtering under pressure. The success of the process depends on there being only a small quantity of mother liquor after each crystallisation.

(*j*) *Picrates.*—For the successful use of the picrates[251, 378] it is necessary that neither cerium nor thorium be present. These earths are, therefore, first removed by a suitable process and the residual earths converted into hydroxides. The hydroxides are then dissolved in a hot solution of picric acid and fractionally crystallised. The first six fractions contain all the neodymium and praseodymium, and are entirely free from erbium and holmium, so that the method serves as a ready means of separating erbium and holmium from the didymium earths and yttrium.

(*k*) Many other salts have been used for the purposes of separation by fractional crystallisation. Of these, two may be mentioned. The *m*-nitrobenzene sulphonates of the cerium earths crystallise particularly well, and have been used in the isolation of neodymium[252, 253] from the mixed cerium earths. Garnier[1000] finds this a very speedy method of obtaining pure neodymium from mixtures with samarium and praseodymium. A frequent crystallisation of the didymium salts of sulphanilic acid[254] has been shown to effect a partial separation of neodymium from praseodymium. The method has little to recommend its use

in preference to the other methods, particularly as it loses its efficiency in the presence of other earths.

## II. Separation by Fractional Precipitation.

(*a*) *Partial Decomposition of the Nitrates.*—This method depends upon the precipitation of the basic nitrates of the rare earths in the order of their basicity. The order of basicity of the rare earths, commencing with the least basic, may be taken as that of the oxide of thorium, cerium,[IV] scandium, ytterbium, thulium, erbium, holmium, terbium, yttrium, samarium, gadolinium, neodymium, praseodymium, and lanthanum.

This method consists in melting a mixture of the nitrates at as low a temperature as possible, and then raising the temperature until decomposition begins, as evidenced by the expulsion of red vapours. The temperature is maintained constant until the vapours cease to be evolved. The mass is cooled and treated with just so much water that it dissolves to a clear solution on boiling. It is then allowed to cool when a basic nitrate separates out; this is filtered off and the filtrate evaporated to dryness and the process repeated. In this manner a series of fractions of different basicity is obtained. The first nitrate to decompose will obviously be that of the least basic element, and the last that of the most basic element. After the fractions have been obtained it is usually advisable to treat them by some other method to obtain pure compounds. The method is not practicable when the terbium earths are present in large quantity. The method was employed by Marignac[255] in the work which led to the discovery of ytterbium, and by Nilson[43] in the discovery of scandium. Kremers[999] and Balke have found that holmium and yttrium cannot be separated by this method, but if a little samarium is mixed with them an exceedingly rapid separation of yttrium is obtained.

(*b*) *By Means of Magnesium Oxide.*—This method also depends on the relative basicity of the rare earths. A neutral solution of a salt of the mixed earths is raised to the boiling-point and magnesia added in small quantities either in the form of a thin paste or as a fine powder. When a small quantity of precipitate is permanently formed, it is filtered off and the process repeated with the filtrate. In this way a series of fractions is obtained, the first of which will contain the least basic element,

whilst the most basic element will remain in the filtrate if the precipitation is not carried to completion. By means of magnesia precipitation, Drossbach[256] was able to separate the major portion of the yttrium from a mixture of yttrium earths which contained yttrium, erbium, and other weaker bases, and Muthmann and Roelig[257] by a single treatment effected the separation of didymium and lanthanum.

(*c*) *By Means of Cuprous Oxide.*—Cuprous oxide was used by Lecoq de Boisbaudran[258] for the separation of thorium from the other rare earths. A solution of the sulphates or chlorides was acidified by means of a few drops of hydrochloric acid, and then boiled for several minutes with copper turnings. This treatment has the effect of reducing the weakly basic ceric compounds to the strongly basic cerous compounds, and it also renders the solution free from oxygen. A slight excess of finely powdered cuprous oxide is added, and the solution boiled for about an hour, when all the thorium is precipitated as hydroxide along with a little cerium. The precipitate is filtered off, washed with air-free water, and freed from copper by means of hydrogen sulphide, and again subjected to the same process. After two or three repetitions the pure thorium compound is obtained.

(*d*) *By Means of the Rare Earth Oxides Themselves.*—This method was shown to be of the greatest importance by Auer von Welsbach,[259] since it gives a complete and rapid separation of the yttrium earths from the cerium earths, and also separates erbium from ytterbium, lanthanum from didymium, and cerium from all the other rare earth metals. The process of separation differs slightly in details with the various mixtures, but for the yttrium earths is as follows: The mixture of oxides is ground with water into a thin paste. About one-half of this is then treated with nitric acid, and when all action has ceased, small quantities of the paste of the oxides and nitric acid are successively added to the solution with constant stirring. Care must be taken that at no point in the process is all the oxide dissolved. When all the oxide has been added, the solution, which has become heated by the reaction, should be of a syrupy consistency and should contain a moderate quantity of undissolved oxide. The mixture will then commence to thicken, and its colour will change from yellow to greyish-red. It is then allowed to cool when the

greater part of the yttrium and erbium will be found in the crystalline precipitate as basic nitrate. Then just so much nitric acid is added, with continuous stirring, as will change the colour of the solution to red, and dissolve all the residual oxide and carbonate, and the mixture is left to stand for some hours. A rose-coloured precipitate is formed which sets to a hard mass. The mother liquor is poured off and the residue extracted with alcohol to remove the normal nitrates from the basic nitrates which are insoluble. The basic nitrates consist of those of the erbium group with some scandium and ytterbium, whilst the nitrates of yttrium and of the cerium earths remain in the mother liquor. At this stage it is advisable to remove the cerium by the partial decomposition of the nitrates. When this has been done the further separation of the yttrium earths may be proceeded with, by adding the mixed oxides to a boiling solution of the nitrates. In this way a series of fractions is obtained, the first of which contains erbium, ytterbium, and scandium, and the last, yttrium, terbium, europium, and gadolinium, whilst the mother liquor contains the cerium earths which may be present. Further separation is then effected by treating the various fractions systematically by the same process. The object of the addition of the oxides in this method is the same as that of the addition of magnesia in the previously described method, namely, to bring about the formation of sparingly soluble basic salts of the elements of weakest basicity.

(*e*) *By Means of Oxalic Acid or Oxalates.*—This method depends on the varying solubility of the oxalates of the different earths in acids of varying concentration. The process was introduced by Mosander,[260] and has undergone many modifications. The best method of procedure[223, 261] consists in making a solution of the nitrates slightly acid with nitric acid, raising to the boiling-point, and then adding oxalic acid solution drop by drop until a slight permanent precipitate is formed. The solution is then allowed to cool when a precipitate of an oxalonitrate is produced. This is filtered off and the filtrate subjected to the same treatment as the original solution. If the original mixture contained only cerium earths and thorium, they will be precipitated in the order: thorium, samarium, neodymium, praseodymium, cerium, and lanthanum. Working in this way, lanthanum has been separated from didymium,[204, 262, 263] and neodymium has been

separated from samarium and the yttrium earths. In the case of the yttrium earths, using the method of precipitation as described above, the order of separation is:[264, 265] terbium earths (terbium, europium, and gadolinium), erbium earths (dysprosium, holmium, thulium, and erbium), scandium, ytterbium, and finally yttrium. In this way pure yttrium can be obtained, and ytterbium can be separated from erbium. This method is often modified by completely precipitating the oxalates from a solution, and then effecting a partial solution of the precipitate in oxalic acid, mineral acid of varying concentration, or ammonium oxalate. Wirth[266] states, for example, that thorium may be obtained free from the other earths if the solution is treated with oxalic acid in the presence of 5-N sulphuric acid. A precipitate of pure thorium oxalate is obtained, although a small amount of thorium remains in solution with the other earths. The partial solution of the oxalates in ammonium oxalate finds a wide application in the separation of the rare earths. The relative solubility[261] in ammonium oxalate solution is indicated by the figures in brackets: thorium (2663), ytterbium (104), yttrium (10·99), cerium (1·8), neodymium (1·44), praseodymium (1·13), and lanthanum (1·0). Pure thorium oxalate can be obtained from a mixture of earths by precipitating as oxalates in the manner described above. The first precipitate is collected, washed with hot water, and then digested at 100° with a strong solution of ammonium oxalate. Then after some time a quantity of water of about forty times the weight of the ammonium oxalate is added and the solution left to stand. The clear liquid is then decanted, evaporated considerably, and treated with nitric acid when pure thorium oxalate[261] separates as a crystalline powder. Auer von Welsbach,[267] using ammonium oxalate, was able to separate a mixture of the oxalates of dysprosium, holmium, erbium, and ytterbium, and his results pointed to the possible existence of unknown elements in the mixture, and also to the probable complexity of ytterbium. Orloff,[268] taking advantage of the solubility of cerium and thorium oxalates in ammonium oxalate solution, was able to separate these elements from the remaining cerium earths. A solution of the mixed oxides in sulphuric acid was added to an excess of ammonium oxalate solution when the oxalates of lanthanum, praseodymium, neodymium, and the yttrium earths were precipitated. The filtrate contained cerium and thorium,

and from it, on standing, the cerium slowly separated out as cerous oxalate, leaving the thorium in solution. The precipitation of the cerium can be hastened by the addition of a reducing agent, such as sodium sulphite, to the solution. James[269] has used, as a means of separation, the solubility in ammonium carbonate solution of the oxalates of the earths which give no precipitate with sodium sulphate. The oxalates are treated with a saturated solution of ammonium carbonate in dilute ammonium hydroxide (1 : 5). When gently warmed the oxalates dissolve, but on boiling separate out again and are filtered off. The filtrate is concentrated and a second fraction obtained, and so on. In this way erbium can be quickly freed from dysprosium, holmium, and terbium. Esposito[226] has shown that a fractional crystallisation of the oxalates from nitric acid solution effects a separation of lanthanum from didymium, but the method is not economical. Potassium oxalate[203] and acid oxalate are also used for the separation of the cerium earths from the yttrium earths. An acid solution of the earths is treated with a solution of acid potassium oxalate, drop by drop, until a permanent precipitate is formed. The mixture is allowed to stand for some hours and filtered. The filtrate is treated with the acid oxalate as long as a precipitate is produced, and again filtered. The filtrate now contains the yttrium earths whereas the cerium earths are to be found in the precipitate. By this method, Mosander[203] states that yttrium earths can be obtained free from cerium earths. The method was also employed by Delafontaine[270] for the fractionation of cerium-free gadolinite earths. Grant[1001] and James have attempted the separation of the oxalates by crystallisation from 20 per cent. solutions of amine oxalates. They show that this method is unsuccessful because the solubilities of the various oxalates are too close together.

(*f*) *By Means of Chromic Acid and Chromates.*—This method was introduced by Krüss and Loose,[271] and systematically studied by Muthmann and Böhm.[272, 273] The method, as applied to the cerium earths, consists in grinding up a mixture of the oxides with sufficient chromium trioxide to convert them into dichromates. The mixture is then treated with water, when all dissolves except the cerium which remains behind as a basic dichromate. The solution is filtered off and largely diluted, raised to the boiling-point, and a solution of potassium chromate

added whilst the liquid is vigorously agitated by leading a current of steam into it. This causes a separation of the earths as neutral chromates in the order: lanthanum, praseodymium, neodymium, and samarium. The various fractions are filtered off as they are formed, and the process repeated with each one. In the cerium group the individual members cannot be obtained pure by this method, but a very good fractional separation of a mixture is achieved which is easily completed by other methods. When the yttrium earths are treated in the same way the separation occurs in the order: terbium, ytterbium, erbium, yttrium, and gadolinium. Yttrium is readily separated from terbium and gadolinium[275] by this method, and when used in conjunction with the bromate[274] method (see p. 31), small quantities of pure yttrium can be rapidly obtained.[311] Hopkins[1002] and Balke find that erbium and holmium cannot be completely separated from yttrium by the chromate method, but the other yttrium earths are separable.

(*g*) *By Means of Ammonia.*—Fractional precipitation by ammonia is one of the most used methods of isolating the rare earths. It has been very largely employed by Crookes,[276] Lecoq de Boisbaudran,[28, 67] Brauner,[53, 277] and others. This method has the advantage over other methods which depend on the basicity of the elements, in that it effects a separation in the strict order of the basicity, which, starting with the weakest base, that is the first to be precipitated, is as follows: thorium, cerium,[IV] scandium, ytterbium, thulium, erbium, holmium, terbium, yttrium, samarium, gadolinium, neodymium, praseodymium, cerium,[III] and lanthanum. A different sequence is, however, given by many investigators, among whom may be mentioned Krüss and Loose,[278] Urbain,[209] Marc,[265] and Muthmann and Weiss.[279] The method consists in preparing a faintly acid solution of the mixed nitrates, containing about 15 per cent. of the earths, if a complicated mixture is to be fractionated, and about 1 per cent. of the earths when a final purification is being effected. Then ammonia is added to the solution with constant stirring until a test portion shows that a given constituent has been entirely precipitated. The precipitated hydroxide is filtered off, and the process repeated with the filtrate. In this way a number of fractions are obtained which are redissolved separately and again submitted to the same process. The ammonia used in the process consists of a

solution of 30 c.c. of 10 per cent. ammonia in a litre of water for the rough separation of a complex mixture, and this is diluted about fifty times for the final purification of individual elements. Hofmann and Burger[244] have found this method to be the most efficient in removing traces of thulium, holmium, and dysprosium from erbium.

(*h*) *By Means of Caustic Alkalis.*—This process is identical with the process last described except that a dilute solution of caustic alkali is used instead of ammonia. It has been used for the removal of didymium from lanthanum, and for the fractionation of an erbium mixture which had previously had the yttrium extracted by the magnesia process, both with satisfactory results.[256, 280, 281]

(*i*) *By Means of Organic Bases.*—The most important of the organic bases for this purpose is aniline. Using this substance the separation can be carried out in two ways :—

(i) A neutral solution of the chlorides in 50 per cent. alcohol is raised to 90° and treated with a 2 per cent. solution of aniline in 50 per cent. alcohol. In this way one-third of the earths may be precipitated from solution, but the remaining two-thirds cannot be precipitated owing to the fact that the hydroxides of the rare earths are soluble in a solution of aniline hydrochloride. The precipitate is filtered off, reconverted into the chloride and the process repeated. The original filtrate is freed from aniline hydrochloride and again treated with aniline as before. This yields a number of fractions which may be further treated by the same method or by an entirely different method. This treatment is not suitable for working up large quantities of material but is very useful for small separations, although here it occasionally fails entirely, notably in the separation of holmium, thulium, and dysprosium from erbium.[244]

(ii) The solution of chlorides is partially precipitated with dilute ammonia and the mixture raised to 60°, then a quantity of aniline hydrochloride is added and the mixture maintained at 60° and vigorously stirred for two to three hours. In this way separation is effected, the weak bases being precipitated and the strong bases remaining in solution. Krüss[282] employed this modification to fractionate a holmium mixture, and as a result of his work came to the conclusion that terbium was a mixture of unknown earths. Thorium[283] can be entirely separated from

the other earths by this method. In this case it is necessary first to reduce the cerium to the cerous condition and exactly to neutralise with ammonia, and then to add aniline drop by drop as long as a turbidity is produced. Thorium being a weak base is precipitated.

A large number of other organic bases have been used for the separation of the rare earths. The manner of their application is much the same as that employed in the case of aniline. Amongst those which have been investigated are: *o*-toluidine, xylidine, dimethylaniline, diethylaniline, benzylamine, pyridine, quinoline, piperidine, phenylhydrazine, dimethylamine, triethylamine, diphenylamine, naphthylamine, *m*-chloraniline, benzidine, and picoline. These various bases are not used for general separations, but in special cases, and with small quantities of material they yield good results.

(*j*) *By Means of Sodium Sulphite.*—When a saturated solution of sodium sulphite is added to a neutral solution of the mixed earths, the cerium and yttrium earths are precipitated but the thorium remains in solution; on the other hand, sodium bisulphite precipitates thorium from a cold solution but not the cerium earths. This separation has therefore been used for the preparation of pure thorium compounds,[284, 285] and is also of the greatest use in the removal of small quantities of the other elements from the rare earths. Batěk[286] uses this method to separate the cerium earths. These are converted into basic sulphates, which are then suspended in water and treated for two hours with a rapid stream of sulphur dioxide. The solution is then filtered and the filtrate converted again into the basic sulphates and the process repeated; after four operations a sulphate is obtained which is practically free from didymium, the didymium basic sulphates being more easily converted into the soluble normal sulphate than the less basic cerium sulphate.

(*k*) *By Means of Sodium Thiosulphate.*—When a solution of sodium thiosulphate is added to a solution of the mixed earths and the solution boiled, a yellowish precipitate of thorium thiosulphate is thrown down, whilst the other earths remain for the most part in solution. The precipitate of thorium thiosulphate is not free from the other earths, but if it is converted into oxalate and this extracted with ammonium oxalate solution, in which lanthanum and thorium oxalates are soluble, and then largely

diluted with water to precipitate the lanthanum, a pure thorium oxalate can be obtained [209, 287] from the solution. Scandium can be separated from all the rare earths by means of sodium thiosulphate, but a difficulty arises with thorium which cannot be completely removed from scandium by this method.

(*l*) *By Means of Fluorides and Double Fluorides.*—When hydrofluoric acid or a solution of potassium fluoride is added to a mixture of the rare earths containing, as they often do, zirconium and titanium, a mixture of the fluorides is produced. This is filtered off, dried and fused with acid potassium fluoride, and the cooled melt extracted with water. The zirconium and titanium pass into solution as double fluorides leaving the earths completely free from these elements. The precipitate of solid fluorides is then converted into sulphates and worked up by other methods. Scandium can be readily isolated from the earths contained in wolframite,[289] tinstone, and tinslag by means of fluorides. These substances generally contain about 0·2-0·3 per cent. of the rare earths of which 90-95 per cent. consists of scandia. To effect the separation the mineral or residue, after the commercial separation of the main constituents, tin and tungsten, is dissolved in hydrochloric acid, and a neutral solution of the chlorides prepared. This is treated with an excess of aqueous hydrofluoric acid, so that the whole of the iron is converted into a soluble complex and the rare earths precipitated as fluorides. A repetition of this portion of the process with the precipitated fluorides is often necessary to free the rare earths from other metals, and this part of the separation may be equally well carried out with oxalic acid or a mixture of hydrofluosilicic acid and potassium silicofluoride.[290] The purified fluorides are then converted into oxides by digesting with concentrated sulphuric acid, and igniting. The oxides are dissolved in hydrochloric acid and solid sodium silicofluoride [288] is added and the solution boiled for half an hour when a precipitate is formed which contains practically the whole of the scandium and none of the other earths. The precipitate is thereafter separated from traces of iron and copper by the usual methods, and yields a very pure scandium oxide. Sterba-Böhm [249] used ammonium fluoride to separate scandium from hydrochloric acid solutions of wolframite residues, and in this way obtained two kilograms of a slightly impure scandium oxide from 700 kilograms of the residues.

(*m*) *By Means of Carbonates of Ammonium and the Alkali Metals.*—If a dilute solution of an alkali carbonate is added to a solution of the rare earths a simple carbonate is precipitated, but if a concentrated solution is used a precipitate of the double carbonates is produced which has the composition,

$$K_2CO_3,R_2^{III}(CO_3)_3 12H_2O\,;\ 3Na_2CO_3,R_2^{III}(CO_3)_3(20\text{-}24)H_2O\,;$$
$$\text{and } (NH_4)_2,CO_3,R_2^{III}(CO_3)_3(4\text{-}6)H_2O$$

in the various cases. Of these three series of double carbonates the most suitable for the present purpose is the potassium series because they are the most soluble in water. The double carbonates of the cerium group are the least soluble, then follow those of the yttrium group, and finally comes the thorium double carbonate which is most soluble. If a solution of the double carbonates is prepared and diluted with water, the double carbonates of the cerium group are decomposed and precipitated as simple carbonates in the order lanthanum, praseodymium, cerium, and neodymium, whilst the compounds of thorium and the yttrium group remain in solution undecomposed. This method has been made use of in the separation of lanthanum and praseodymium by Meyer,[291] who was able by means of it to obtain both elements in the pure condition. A method depending on the use of carbonates was introduced by Damour[292] for the separation of thorium from the cerium earths. It consists in treating the crude thorium oxalate with a solution of ammonium carbonate, whereby calcium carbonate, magnesia, and the cerium earths remain undissolved, whilst the yttrium earths and thorium oxalates pass into solution and can be separated by other methods.

Barium carbonate,[47] when added to a solution of the earths, precipitates thorium and the cerium earths but not the yttrium earths. One of the best methods[201] of separating scandium and thorium consists in boiling a mixture of the carbonates with a solution of sodium carbonate when a sparingly soluble double carbonate of scandium, $Sc_2(CO_3)_3,4Na_2CO_3,6H_2O$, separates at concentrations at which the thorium remains completely in solution.

(*n*) *As Basic Sulphates.*—This method serves only for the preparation of pure cerium compounds. The mixed oxides are dissolved as far as possible in concentrated nitric acid and the insoluble portion in concentrated sulphuric acid, taking care to avoid an excess of the acid. The two solutions are mixed,

diluted largely with water and boiled when a basic sulphate of cerium is precipitated. The precipitate is washed, redissolved in sulphuric acid and reprecipitated, when pure cerium basic sulphate is obtained. Brauner[293] prefers to redissolve the precipitate in nitric acid, since an excess of nitric acid is not so harmful as one of sulphuric acid, and ceric nitrate is more easly converted into the basic salt than is ceric sulphate.

(*o*) *As Basic Nitrates.*—This method also applies only to the cerium separation. The mixture of nitrates[294] is evaporated until a syrupy solution is obtained. This is poured into a large volume of water which has been slightly acidified with nitric acid when basic ceric nitrate is precipitated. This is filtered off, washed with water containing a little nitric acid, and dried. According to Brauner[205] a practically pure cerium compound is in this way obtained, whereas Behrens[295] states that it contains both neodymium and samarium.

(*p*) *As Chlorides and Oxychlorides.*—Drossbach[227] uses a method similar to (II. (*d*), p. 35) for the separation of a crude erbium yttrium mixture. The mixed oxides are dissolved in hydrochloric acid, and then a quantity of a paste of the mixed oxides is added, little by little, until the solution ceases to show the erbium spectrum bands. The mixture is heated for several hours on a water-bath, and then a large quantity of boiling water added and the whole allowed to settle. The solution which is now free from erbium is poured off, and the precipitate which contains all the erbium is repeatedly boiled out with ammonium chloride to remove any traces of yttrium which it may contain. The same method has been applied to the cerium earths, particularly for the separation of neodymium and praseodymium.[227] The oxychlorides can also be used in the same way as the nitrates (II. (*a*), p. 34). On heating a mixture of the crystallised chlorides, some of the chlorides, chiefly lanthanum and didymium, pass into the oxychlorides whilst the others do not, so that on treating with water a separation is effected. This method of separation was used by Marignac[296] for the preparation of didymium compounds, and it has been used for the initial separation of the monazite earths.[297] The oxides from monazite were dissolved in hydrochloric acid, and the solution evaporated to dryness. The dry mixture of chlorides was heated on an asbestos plate until it became white. It was then cooled

and treated with water when the cerium earths passed into solution and a 50 per cent. thoria remained insoluble.

(*q*) *By Means of Alkali Azoimides.*—This method has been stated by Dennis [298, 299] to yield, after several repetitions, pure thoria, and ceria free from thoria, although Wyrouboff and Verneuil [300] have not been able to obtain the same results. The method consists in adding a 0·3 per cent. solution of sodium or potassium azoimide to a cold solution of the earths containing thorium. On boiling, the thorium is precipitated as hydroxide according to the equation

$$Th(NO_3)_4 + 4NaN_3 + 4H_2O = Th(OH)_4 + 4NaNO_3 + 4N_3H.$$

(*r*) *By Means of Potassium Ferrocyanide.*—This method is particularly useful in the case of the yttrium earths. If a neutral solution of the mixed earths is fractionally precipitated by means of a saturated solution of potassium ferrocyanide the erbium can all be concentrated in the first fraction and eventually obtained almost pure.[112, 301]

(*s*) *By Means of Iodic Acid.*[201]—Precipitation by means of iodic acid constitutes a good method of separating scandium from thorium. If a concentrated solution of iodic acid is added to a solution containing a mixture of scandium and thorium salts the major portion of the thorium is precipitated whilst the scandium remains entirely in solution.

(*t*) *By Means of Sodium Nitrite.*—Fractional precipitation by sodium nitrite is an effective and rapid method of separating yttrium from the yttrium earths.[302, 997] The method consists in dissolving the oxides in nitric acid, diluting, boiling, and adding to the boiling solution sodium nitrite to precipitate the desired fraction. The yttrium concentrates in the later fractions. A large yield of yttrium can be obtained by this method more rapidly and at a smaller cost than by the dimethyl-phosphate or the chromate methods, but it is not effective in the case of yttrium terbium mixtures. Hopkins [1002] and Balke find this the most rapid and effective method of separating yttrium from holmium and erbium. Hofmann and Burger [244] have modified the process for the isolation of erbium from mixtures containing thulium, holmium, and dysprosium. A solution of the nitrates is mixed with excess of sodium nitrite and evaporated to dryness. The dry residue is then extracted with water when most of the erbium remains insoluble as the oxide.

(*u*) *By Means of Hypophosphates.*[303]—Hypophosphoric acid and sodium hypophosphate effect a very complete separation of thorium from the rare earths which occur in monazite. Consequently this method is largely used for this purpose, and consists in adding hypophosphoric acid or sodium hypophosphate to a solution of the earths in hydrochloric acid when the thorium alone is precipitated as hypophosphate.[990] A difficulty arises in this method if sodium hypophosphate is used with a solution of the earths in sulphuric acid, for in such a case the insoluble double sodium cerium earth sulphates separate out with the thorium hypophosphate. The difficulty is overcome by preparing hypophosphoric acid in the solution by the oxidation of yellow phosphorus or by the anodic oxidation of copper phosphide.

(*v*) A solution[1004] of sodium pyrophosphate precipitates both cerium and thorium, but cerium pyrophosphate will dissolve completely in hydrochloric acid, and is therefore easily separated from thorium which forms an insoluble pyrophosphate.

(*w*) *By Means of Salts of Organic Acids.*—The salts of a very large number of organic acids have been used in the separation of the rare earths with more or less success. Amongst these may be noted :—

(i) *m-Nitrobenzoic Acid.*—Kolb and Ahrle[304] have shown that this acid effects a complete precipitation of thorium, whilst lanthanum, didymium, and cerous salts are not precipitated, although ceric salts give a pale yellow precipitate. If, therefore, *m*-nitrobenzoic acid is added to a solution of the cerium earths containing thorium, the thorium is precipitated in the pure condition if no ceric compounds are present. The precipitation is more complete in the presence of a little aniline.

(ii) *Stearic Acid.*—Stoddart and Hill[305] have shown that an effective fractionation of a neutral solution of the rare earths can readily be brought about by slowly adding an alcoholic solution of potassium stearate to a cold, well agitated solution of these substances. The method has been successfully applied to the separation of the yttrium earths from gadolinite and samarskite, practically pure yttrium being obtained in a few operations. The members of the cerium group can also be separated by the same process.

(iii) *Sebacic Acid.*—James and Smith[306, 307, 996] have shown that thorium can be completely separated from the rare earths

by adding a boiling solution of sebacic acid to a hot neutral solution of the earths. Thorium sebacate is precipitated as a white easily filtered precipitate, whilst the other earths are not precipitated even on boiling for a long time.

(iv) *Cacodylic Acid.*[307]—On fractionally precipitating a solution of the chlorides of yttrium, holmium, and dysprosium with sodium cacodylate, the yttrium was concentrated in the earlier fractions whilst the holmium and dysprosium accumulated in the later fractions. With respect to the cerium group, it was found that a mixture of the hydroxides of neodymium, gadolinium, and samarium, when dissolved in cacodylic acid and fractionally crystallised, could be readily separated. The neodymium collected in the more soluble fractions, and the gadolinium and samarium in the less soluble fractions.

(v) *Valeric Acid.*[308]—When this acid is added to a solution of cerium and didymium nitrates, pure cerium valerate is precipitated whilst the didymium with a little cerium remains in solution.

(vi) *Succinic Acid.*—The precipitation of a hot solution of the normal nitrates of the yttrium earths by means of sodium succinate effects a speedy partial fractionation.[309] The succinate should be added drop by drop, and the solution of nitrates should not be stronger than 1-2 per cent. The result of such a treatment is two fractions, (i) a more soluble fraction consisting mainly of yttrium with small quantities of holmium, europium, and samarium (apparent atomic weight 93), and (ii) a less soluble fraction of apparent atomic weight 139 and consisting of terbium, holmium, and europium, with some yttrium.

Among the many other organic acids which have been used or suggested for the separation of the rare earths are malic acid, which precipitates thorium but not the cerium earths, whilst alkali malates precipitate the yttrium earths if an excess of the reagent is not used; dimethyl phosphoric acid, [998, 311, 312] which effects a fractionation of the yttrium earths; tartaric acid,[217] which is found to be effective in fractionating an acetone solution of the yttrium earths; lactic acid, salicylic acid, and many others.[313, 996, 997, 998]

## III. Separation by Means of Processes of Oxidation.

(*a*) *Ignition of Carbonates, Nitrates, and Oxalates.*—This method is of the greatest importance in the separation of cerium

from the other elements of the rare earths. When any of the salts mentioned are ignited they are converted into oxides, cerium and thorium into dioxides, the other elements into sesquioxides. On treating the ignited oxides with dilute nitric acid, cerium dioxide alone is insoluble, or at most dissolves only to a slight extent, depending on the amount of lanthanum and didymium oxides present.[17, 314] Using this method and treating the mixed oxides with nitric acid (1 part in 200 parts of water), Mosander[17, 203] separated lanthanum and didymium from the substance originally regarded as ceria.

(*b*) *Ignition of the Nitrates with Potassium Nitrate.*—This method in the first instance is due to Debray, who mixed the nitrates of the cerium earths with eight to ten times their weight of potassium nitrate, and melted the mixture. The molten mass was maintained at a temperature of 300°-350° for several hours, whereby a decomposition of the cerium nitrate is effected; lanthanum and didymium nitrates being undecomposed. On cooling the mass and extracting with water the two latter elements can therefore be dissolved leaving cerium dioxide insoluble. The method, as carried out by Debray, is, however, open to objection, as was shown by Dennis and Magee.[298] Cerium nitrate decomposes at 200°, didymium nitrate at 300°, and as the melting-point of a mixture of nitrates, as used by Debray, lies in the region of 325°, it is clear that the cerium dioxide must contain some didymium oxide. To obviate this difficulty they therefore made use of an equimolecular mixture of sodium and potassium nitrates instead of potassium nitrate. The equimolecular mixture of alkali nitrates melts at 231° (Carnelley and Thompson[316]) so that it becomes possible to effect the fusion at a much lower temperature. The method finally adopted consists in evaporating a solution of the mixed cerium earths nitrates with the requisite quantity of an equimolecular mixture of the sodium and potassium nitrates until it has reached a syrupy consistency. It is then poured into a crucible which is half full of a mixture of the alkali nitrates. The crucible is heated to a stated temperature until the evolution of red fumes ceases, which indicates that the maximum decomposition at that temperature has been attained. At 320° and above, didymium oxide is found in the insoluble portion, although all the cerium nitrate has not been decomposed. By heating to 300° cerium dioxide is obtained

which is quite free from lanthanum and didymium oxides, but if thorium or the yttrium earths are present in the original mixture these substances will be found present in the cerium oxide after fusion.

(*c*) *Treatment with Chlorine.*—Treatment with chlorine in alkaline solution is an effective method of completely separating cerium from the remainder of the rare earths. The process is carried out by suspending the mixed hydroxides in a solution of sodium hydroxide, and passing a rapid stream of chlorine into the mixture for some hours. This has the effect of converting the hydroxides of all the earths except cerium into soluble chlorides, whilst the cerium remains undissolved as a light yellow powder of hydrated ceric oxide. If this process [298, 317, 318, 319] is repeated several times a perfectly pure cerium preparation is obtained, and the solution of the other earths is entirely free from cerium.[317, 318, 319, 320, 321, 322, 323] Bromine has been substituted for chlorine by Browning and Roberts [326] with marked advantages. The main points of superiority of bromine over chlorine lie in the facts that bromine can be more easily added and manipulated than chlorine, and that the hydrobromic acid formed towards the end of the operation does not dissolve the ceric hydroxide produced by the oxidation. A single treatment removes 50 per cent. of the other earths from cerium, whilst by repeating the process three times with the precipitate practically pure cerium is obtained. In a later piece of work Browning [991] shows that the lanthanum hydroxide dissolves more readily than neodymium and praseodymium hydroxides.

(*d*) *Treatment with Potassium Permanganate.*—This method is used for the removal of cerium from the other earths, and depends on the oxidation of cerium in alkaline or neutral solution to the ceric condition as expressed by the equation

$$6Ce(NO_3)_3 + 2KMnO_4 + 8H_2O = 6CeO_2 + 2MnO_2 + 2KNO_3 + 16HNO_3.$$

The oxidation was originally carried out in the presence of mercuric oxide by Winkler,[324] but later zinc oxide was substituted by Stolba,[325] and the method as adopted was worked with marked success by several investigators.[239, 257, 326, 327] The removal of zinc compounds from the cerium, however, proved a long and troublesome process, and consequently the carbonates and hydroxide of the alkaline earths were substituted for zinc oxide by

Böhm.[328] The modern method is to use sodium carbonate to remove the nitric acid formed in the process, and when this is used the separation is carried out in the following manner:[329] a neutral solution of the mixed nitrates is placed in a stout vessel fitted with a mechanical stirrer, and a solution containing potassium permanganate and sodium carbonate in the ratio of one gram molecule to four gram molecules is slowly added until the solution becomes permanently red. The mixture is then boiled for ten minutes, when a precipitate of hydrated ceric oxide and manganese dioxide settles out. This is filtered off and the manganese removed in the usual way. A single repetition of the process gives pure cerium compounds. This process has the additional advantage that the whole of the cerium is removed, and in consequence it is used for the quantitative estimation of cerium.[330]

(*e*) *Treatment with Lead Dioxide or Bismuth Tetroxide.*—This method of separation was introduced by Gibbs [331] and consists in oxidising cerous salts by boiling with nitric acid and lead dioxide. Zschiesche [314] used red lead instead of lead dioxide, and later Gibbs [332] substituted bismuth tetroxide in place of lead dioxide. The separation is effected in the following manner: a solution of the mixed sulphates is treated with concentrated nitric acid and lead dioxide and boiled until a test portion gives no precipitate with lead acetate. Small quantities of lead dioxide and nitric acid are added from time to time as the reaction proceeds. When all the sulphuric acid has been removed from the solution it is boiled for about one-and-a-half hours longer and nitric acid added from time to time to replace the liquid which has evaporated. The solution is then allowed to cool and decanted from the heavy precipitate of lead sulphate. The precipitate is digested several times on the water-bath with nitric acid, to remove any rare earths which it may contain. The solutions are mixed and concentrated to a syrupy consistency on the water-bath. The syrup is then poured into ten times its volume of boiling water, when the cerium is precipitated as basic nitrate. This is well washed with water, treated with concentrated sulphuric acid, heated to remove excess of sulphuric acid, and dissolved in ice-cold water. This solution contains pure cerous sulphate.

(*f*) *Treatment with Hydrogen Peroxide.*—Until 1886 hydrogen peroxide had been used for the precipitation and separation of

zirconium as hydrated pentoxide.[333, 334] It was found, however, that if the oxidation was effected in ammoniacal solution,[335, 336] thorium was also precipitated as $Th_4O_7,SO_3$ from a solution of sulphates whilst the other rare earths remained in solution. Consequently the oxidation by hydrogen peroxide constitutes a method of separating thorium from the rare earths. The separation is best carried out in a neutral solution of the nitrates, to which an excess of hydrogen peroxide is added and the mixture warmed to 60°, when all the thorium is precipitated. It is essential that the hydrogen peroxide used should be free from phosphoric acid. The separation of thorium takes place in the presence of cerium and yttrium earths, but if large quantities are present the thorium precipitate will always contain small quantities of these earths. It is therefore advisable, when using this method for the separation of thorium, that the bulk of the cerium and yttrium earths should be previously removed. It is then comparatively easy to obtain pure thorium compounds.[79, 300] Urbain [209, 242] has made use of this method to separate thorium from ytterbium. Oxidation by hydrogen peroxide in boiling solution in the presence of sodium acetate gives a voluminous precipitate of didymium as an oxidised acetate which dissolves again on cooling. Consequently a rapid concentration of didymium can be effected in this way since lanthanum is not precipitated, and the cerium basic acetate is less easily soluble than the didymium acetate under these conditions.

(*g*) *Treatment with Sodium Peroxide.*—The addition of an ice-cold solution of sodium peroxide to a solution of the rare earths effects an oxidation and complete precipitation of the cerium as hydrated ceric oxide. The precipitate is well washed with cold water, dried at 120°-130°, redissolved, and the process repeated, whereby pure ceric oxide is obtained.[323]

(*h*) *Treatment with Persulphates.*—This method is due to Knorre [337] and consists in the oxidation of cerous compounds to ceric compounds, which are precipitated as basic salts by the addition of potassium or ammonium persulphate to a neutral boiling solution of the rare earths.

$$K_2S_2O_8 + H_2O = K_2SO_4 + H_2SO_4 + O.$$

It is essential that the solution be kept neutral, and this is best achieved by effecting the reaction in the presence of barium or

calcium carbonate. Wyrouboff and Verneuil [79] used this method to remove the last traces of cerium from the cerium earths, but instead of using an alkali earth carbonate to keep the solution neutral, they boiled with a mixture of sodium acetate and ammonium persulphate. Should there be much thorium present it is advisable to dilute the solution to such an extent that little or no thorium sulphate or basic sulphate is present in the cerium precipitate.

(*i*) *Treatment with Potassium Bromate.*—This method was introduced by James [237, 338] and has been used by him for the removal of cerium from the other rare earths. A neutral solution of the nitrates is boiled with potassium bromate in the presence of small lumps of marble, when the cerium is entirely precipitated as a mixture of basic ceric nitrate and bromate. If the operation is carefully carried out the cerium is obtained free from the other earths. When this method is employed on the large scale it is advisable to interrupt the oxidation when all the cerium, except about 1 per cent., has been precipitated.

(*j*) *Electrolytic Oxidation.*—Cerium can be separated from the other earths by the electrolytic oxidation in acid solution. To obtain good results by this process it is essential that a very high cathode current density and a low anode current density should be maintained.[337, 339]

## IV. Separation by Physical Methods.

(*a*) *Adsorption.*—This method, although as yet unused for actual separations, appears, from the results of its investigation, to be suitable for use in the complete fractionation of the rare earths. The method consists in shaking a solution of the earths with "phosphate-free" charcoal. Hofmann and Krüss [340] placed a solution of the earths, of equivalent weight $R^{III} = 116{\cdot}8$, in a bottle, together with charcoal, and shook for some time. The solution was then filtered and the equivalent weight of the earths contained in the charcoal determined, and found to be $R^{III} = 134{\cdot}4$. Obviously therefore a decided separation had been effected. It must, however, be noted that the amount of material adsorbed by the charcoal is small; in the case mentioned 0·5 gram was adsorbed by 8 grams of charcoal from 2 grams of the mixture. The weaker bases are adsorbed first by the charcoal. In the case of a mixture of yttrium earths ($R^{III} = 93{\cdot}03$)

a mixture of earths was adsorbed by the charcoal in a single operation, which gave $R^{III} = 96{\cdot}0$. This is a far more efficient separation than is possible in one operation by means of the aniline fractionation.

(*b*) *Distillation.*—On account of the tremendous labour involved in the separation of the rare earths by chemical methods, Pettersson [321] attempted fractionally to distil the mixture of anhydrous chlorides, with negative results. Neodymium chloride and yttrium chloride are the most volatile of the cerium and yttrium earths respectively, but these only volatilise at a red heat. Despite this failure, however, Meyer and Winter [201] have shown that scandium can be got quite free from thorium by the fractional sublimation of the anhydrous chlorides. Morgan and Moss [348] have shown that a distillation of the mixed acetylacetonates of scandium and thorium can be used as a method of separation. At low pressure (8-10 mm.) thorium acetylacetonate begins to sublime at 160°, whilst scandium acetylacetonate sublimes at a lower temperature. At atmospheric pressure scandium acetylacetonate sublimes undecomposed between 210°-260°, whereas thorium acetylacetonate decomposes at 260° and leaves a brown charred residue. Urbain [231] has shown that fractional sublimation of ytterbium chloride is a possible means of separating it into lutecium and neo-ytterbium chlorides.

(*c*) *Electrolysis.*—In 1893 Krüss showed that on electrolysing an aqueous solution of yttrium earths, hydroxides of varying composition separated at the cathode and thereby furnished a means of separating the yttrium earths. Dennis and Lemon [379] have applied this method to the separation of cerium earths. A neutral solution of the mixed nitrates is poured into a beaker containing a mercury cathode and a platinum anode and electrolysed for six hours, using an E.M.F. of nine volts. A current of air is blown continuously through the mercury to prevent the formation of a non-conducting layer of hydroxide on its surface. After six hours the current is stopped, and when the precipitate has settled the clear liquid is syphoned off and treated in the same way as the original solution. The hydroxide precipitate is reconverted into nitrate and again submitted to electrolysis. In this way ten operations completely separate lanthanum from neodymium and praseodymium. Dennis [380] states that two operations are sufficient to separate erbium from yttrium.

It has been suggested that the separation is effected by the ammonia produced by cathodic reduction of the nitric acid. To settle this point electrolyses were carried out with solutions of chlorides of the yttrium earths,[992] using the same method as before. It is shown that the coloured earths separate in the earlier fractions, yttrium in the middle fractions, and neodymium in the last fractions. The rate of precipitation is about four times as great in the case of the nitrates as with the chlorides. It has also been shown[993] that if the solution is stirred rapidly during electrolysis there is a more rapid concentration of the earths of high atomic weight in the earlier fractions and of those of low atomic weight in the final fractions. If thorium is present it is concentrated in the earlier fractions.

A typical separation of the constituents of a single mineral will perhaps give a clearer view of the way in which the various processes are combined and applied in the isolation of the individual elements. As a type the complete separation of the cerium and yttrium earths, as carried out by James,[237] may be considered. A solution of the earths in either hydrochloric acid or sulphuric acid is treated with solid sodium sulphate until the absorption spectra of neodymium and praseodymium disappear from the solution. This is determined by withdrawing small portions of the solution from time to time and examining them spectroscopically; the absorption spectra are very characteristic so that the test is done in a very few minutes. The solution is now filtered, the precipitate consisting chiefly of the double sodium sulphates of the cerium earths and the filtrate containing the yttrium group of earths. The precipitate of double sulphates is washed with sodium sulphate solution and the washings added to the original filtrate. The filtrate is then treated with oxalic acid to precipitate the earths as oxalates. The double sulphates constituting the original precipitate are converted into oxides, dissolved in nitric acid, and the boiling solution treated with potassium bromate. If bromine is evolved, marble is added to keep the solution neutral, and the boiling is continued until all the cerium is precipitated as basic nitrate; this is ascertained by testing a small portion of the solution with hydrogen peroxide. The precipitate of basic ceric nitrate is filtered off, washed, dissolved in nitric acid and precipitated by alcohol, and by a few repetitions can be got quite pure.

*Separation of the Lanthanum Group.*—The filtrate from the cerium precipitate is precipitated by oxalic acid, and the oxalates are ignited to oxides, which are dissolved in nitric acid and separated by the fractional crystallisation of the double magnesium nitrates, $2R^{III}(NO_3)_3,3Mg(NO_3)_2,24H_2O$. The material in this way is separated into four fractions of different solubility. The least soluble fraction contains lanthanum and praseodymium magnesium double nitrates, the second fraction contains similar double compounds of praseodymium and neodymium, the third fraction crude neodymium double nitrate, and the fourth fraction contains samarium, europium and gadolinium double nitrates and simple nitrates of terbium, dysprosium, holmium, and yttrium, and other elements of the yttrium group which have not been removed by the sodium sulphate treatment. Lanthanum is separated from praseodymium by the fractional crystallisation of the double ammonium nitrates,

$$M^{III}(NO_3)_3,2NH_4NO_3,4H_2O,$$

and purified by means of the oxalates. Praseodymium and neodymium are separated by crystallisation of the double manganese nitrates $2M^{III}(NO_3)_3,3Mn(NO_3)_2,24H_2O$. Pure neodymium is readily obtained from the crude neodymium magnesium nitrate (fraction 3) of the lanthanum separation. Samarium and europium are separated from gadolinium, yttrium, dysprosium, and erbium by crystallisation of the double magnesium nitrates from 30 per cent. nitric acid. The whole of the europium can be got free from yttrium by means of the double bismuth nitrate. Gadolinium and terbium of the nitrates crystallise out easiest, then follow dysprosium, holmium, and yttrium, whilst erbium and part of the yttrium remain behind in the mother liquor. Gadolinium and terbium are separated by crystallisation of the double nickel nitrates.

*Separation of the Yttrium Group.*—This group contains dysprosium, holmium, erbium, thulium, ytterbium, lutecium, celtium, and traces of gadolinium and terbium. The sulphates are first obtained from the oxalates and converted into bromates, which are fractionally crystallised. Samarium, gadolinium, and terbium separate first, then follows yttrium, which contains traces of holmium, erbium and dysprosium. The main quantity of erbium comes in the next fraction, then follow thulium,

ytterbium, lutecium, and celtium. Terbium is separated from dysprosium and gadolinium either by fractional crystallisation of the nitrates or ethylsulphates or by fractional precipitation with dilute ammonia. Dysprosium is separated from the other related elements by fractional crystallisation of the ethylsulphates. Holmium has not yet been got quite pure. Yttrium is got pure by the method of partial decomposition of the nitrates by heat. Erbium is separated from the other earths by partial decomposition of the nitrates. Ytterbium, lutecium, and celtium can be obtained by a careful fractionation of the bromates. The whole scheme will be seen more clearly from the diagram. It must, however, be emphasised that generally each fractionation, and indeed each process, from the beginning of the separation to the end, must be repeated many times to obtain the individual elements in the pure condition.

James and Grant [994] have recently published a scheme for the separation of the rare earths which have the more soluble double sodium sulphates.

# CHAPTER IV.

## METHODS OF CONTROLLING FRACTIONATION OF THE RARE EARTHS.

IN all fractional operations it is necessary to employ some method of indicating the extent to which the separation has proceeded. It is usual, when a direct chemical test is not available, to employ a method which depends on the physical properties of the substances under investigation. Thus, for example, in the purification of an organic substance by fractional crystallisation, the melting-point of the different crops of crystals serves to indicate their purity. In the case of the rare earths, except in a very few cases, particularly in proving the absence of a given constituent, definite chemical tests cannot be made use of to indicate the progress or efficiency of a fractionation. Physical methods have therefore to be adopted, and of these six are at present in use, namely, (*a*) determination of the mean equivalent weight, (*b*) measurement of the absorption spectrum, (*c*) measurement of the spark spectrum; (*d*) measurement of the arc spectrum; (*e*) measurement of the phosphorescence spectrum, and (*f*) measurement of the magnetic susceptibility.

### Determination of the Mean Equivalent Weight.

Until the year 1860, when the spectroscope was discovered and applied to chemical analysis, the determination of the mean equivalent weight was the only method available for controlling a fractionation of the rare earths. Although it is by no means necessary that the mean equivalent weight should be determined with the same degree of accuracy as an atomic weight, yet in the separation of earths where the atomic weights lie near to one another, and in the final stages of a fractionation where a given constituent is slowly passing from a slightly impure to an absolutely pure state, a very high degree of accuracy is essential in this determination. The mean equivalent weight can be obtained by four methods, namely, (i) conversion

of the oxide into sulphate, (ii) conversion of the sulphate into oxide, (iii) conversion of the oxalate into oxide, and (iv) by volumetric methods. Other methods are possible under special conditions, but those mentioned above are generally applicable and are the methods most frequently employed.

(i) This method of controlling the progress of a fractionation was first introduced by Bahr and Bunsen.[345] A quantity of the ignited oxide (0·3-0·5 gram) is placed in a platinum crucible, dissolved in dilute hydrochloric acid by heating on a water-bath and evaporated almost to dryness. Dilute sulphuric acid is added and the mixture again evaporated on the water-bath. The excess of sulphuric acid is removed by cautiously heating the crucible on an iron plate. When the mixture is dry the crucible is removed and placed either in an electric furnace or in an air oven, and heated to 400°-500° for 4-5 hours, whereby the free sulphuric acid is expelled and all acid sulphate decomposed. The crucible is cooled in a desiccator and weighed, heating being repeated until a constant weight is obtained. In this way the ratio $E_2O_3 : E_2(SO_4)_3$ is obtained, whence if $w_1$ represent the weight of oxide taken, $w_2$ the weight of sulphate obtained, and E the mean equivalent—

$$w_1 : w_2 :: 2E + 48 : 2E + 288.$$

Some difference of opinion exists as to the temperature to which the product should be heated. Too high a temperature has the effect, particularly in the case of the weaker bases, of producing basic sulphates, whilst too low a temperature fails to decompose the acid sulphates. Krüss,[344] to whom the method of procedure described above, is due, considers that a temperature of 360° is sufficient, whilst Wild [346] maintains that 400°-450° is necessary to decompose completely the acid sulphates. It is doubtful whether a lower temperature than 450° will give a neutral sulphate in every case since Brauner and Pavlicêk [281, 347] have shown that traces of acid sulphates remain even when the heating has been carried up to 500°; on the other hand, H. C. Jones,[348] in a series of atomic weight determinations of lanthanum by this method, finds that the acid sulphate is entirely decomposed at this temperature. Brill,[349] using small quantities of material and weighing with a Nernst [350] microbalance, has shown that at 480° the whole of the acid sulphate is decomposed, whilst the normal sulphate is not in the least decomposed. Conse-

quently it would seem that 500° is a sufficiently high temperature to employ. Indeed the quantity of acid sulphate undecomposed at 440° is so small that both Brauner[78] and Urbain[209] consider this method is the best for determining the mean equivalent, and recommend the final heating of the sulphate to 440° either in a sulphur-bath or in an electric furnace. Urbain[209] carries out the operation by dissolving the oxide in nitric acid in a weighed platinum capsule P (fig. 1). The solution is then treated with a slight excess of sulphuric acid and gently heated to drive off water and nitric acid. The temperature is then raised to 440° to expel sulphuric acid and decompose acid sulphates. The final heating at 440° is carried out in sulphur vapour in a furnace

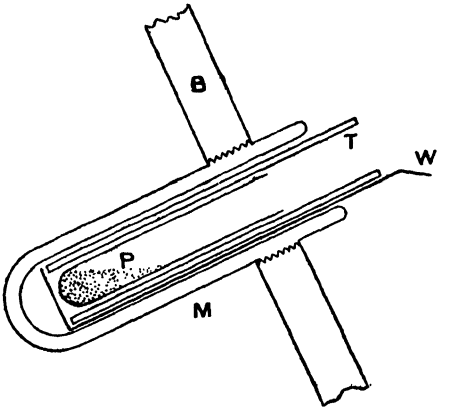



FIG. 1.

*From Annales de Physique et de Chimie (Masson et Cie).*

(fig. 1) consisting of an iron mercury bottle B, fitted with small iron muffles M, which are screwed almost horizontally into the side. The platinum capsule is placed in a hard glass tube T open at both ends. The glass tube and capsule are fitted with a platinum wire W which is used for withdrawing them from the muffle.

(ii) When a mixture of the rare earths contains only yttrium earths, the conversion of the sulphates into oxides may be employed for the determination of the equivalent weight. In the case of these earths the anhydrous sulphates can easily be obtained, and they are comparatively easily decomposed, whereas the sulphates of the strongly basic elements require a very high temperature, up to 1200°, for complete decomposition. The sulphates are weighed in a platinum crucible and converted

directly into oxides by heating to a bright red heat in a blowpipe flame until of constant weight.[309] The actual temperature required for the production of the oxides will be obvious from the figures obtained by Brill,[349] who showed that between 850°-950° basic sulphates are formed, and between 950°-1150° the last trace of basic sulphate is decomposed into oxide.

(iii) Brauner[83] has made use of the oxalate in the determination of the atomic weight of cerium, and consequently the oxalates may serve for the determination of the mean equivalent of a product of a fractionation. The method consists in carefully igniting a weighed specimen of the oxalate in a platinum crucible, when it is decomposed with the formation of oxide. If $w_1$ be the weight of oxalate taken, $w_2$ that of the oxide produced, and E the mean equivalent, then

$$w_1 : w_2 :: 2E + 264 : 2E + 48.$$

(iv) The volumetric method of determining the mean equivalent weight has been carried out in several ways. Krüss and Loose[351] dissolve a known weight (0·5-1·0 gram) of the oxide in an excess of 12 per cent. sulphuric acid. The solution is then exactly neutralised and the earths precipitated by a measured excess of standard oxalic acid solution. The excess oxalic acid is titrated with standard potassium permanganate solution. The weight of oxalic acid equivalent to a known weight of the oxide is therefore known. If $w_1$ be the weight of the oxide, $w_2$ that of the oxalic acid used in the precipitation, and E the mean equivalent, then

$$w_1 : w_2 :: 2E + 48 : 3 \times 90.$$

This method is unreliable, since the oxalate formed in the process dissolves to some extent in the acid set free in the reaction, and this is, of course, titrated along with the free oxalic acid. A modification due to Brauner[78] consists in dissolving a known weight of the oxalate in dilute sulphuric acid and titrating the solution with standard potassium permanganate solution. In this case if $w_1$ be the weight of oxalate taken, $w_2$ the weight of oxalic acid set free by the sulphuric acid, and E the mean equivalent

$$\text{then } w_1 : w_2 :: 2E + 264 : 90 \times 3.$$

Wild[346] employs a rather different method, he dissolves 0·1-

0·2 gram of the oxides in a measured excess of $\frac{N}{10}$-sulphuric acid. The solution is treated with an excess of normal potassium oxalate and the excess sulphuric acid titrated with $\frac{N}{10}$-sodium hydroxide using phenol phthalein as indicator. If $w_1$ be the weight of oxide taken, $w_2$ the weight of sulphuric acid which exactly combines with the oxide, and E the mean equivalent, then

$$w_1 : w_2 :: 2E + 48 : 3 \times 98.$$

The most suitable volumetric method, however, is that due to Feit and Przibylla,[229, 352] which consists in dissolving a convenient quantity of the oxide in a measured excess of $\frac{N}{2}$ sulphuric acid and titrating the excess with $\frac{N}{10}$ sodium hydroxide solution using methyl orange as indicator. This method gives uncertain results with the weakly basic elements but is very reliable with the strongly basic elements.

In the case of all the methods considered in this section it has been tacitly assumed that the oxide, produced or used in the determinations, has a composition represented by the general formula $E_2O_3$; this, however, would not be the case if cerium or thorium were present since the oxide of these elements produced by ignition has the general formula $EO_2$; and, again, if considerable quantities of praseodymium or the terbium earths are present, the mixture will probably not have a uniform composition corresponding with $E_2O_3$ since terbium yields a peroxide $Tb_4O_7$ on ignition of its salts, and praseodymium by the same treatment yields $PrO_2$ and $Pr_4O_7$. In these cases those methods which involve the use of weighed quantities of oxides are useless for the determination of the mean equivalent and consequently cannot be employed in controlling a fractionation.

## Measurement of Absorption Spectra.

Those members of the group of rare earths which give coloured compounds yield, when in solution, absorption spectra that differ from the absorption spectra of the coloured salts of the other elements, inasmuch as they are made up of a few well-defined and highly characteristic bands in the visible region of the spectrum.

Hence an examination of the absorption spectrum of a mixture of the rare earths serves to show at once whether one or other of these elements is or is not present in a given fraction. Of the cerium earths, the elements neodymium, praseodymium, and samarium give characteristic absorption spectra, whilst erbium, thulium, holmium, dysprosium, and europium of the yttrium earths also give absorption spectra. Of these elements only neodymium, praseodymium, and erbium are readily identified in mixtures by the absorption spectra. Hence the presence or absence of these elements alone, in a fraction, can be definitely settled by this means, although the presence of the others may be indicated. The examination is usually effected by interposing a 10 per cent. solution in a rectangular glass vessel, 1 cm. wide, directly between the slit of a spectroscope and an incandescent burner. The various absorption bands can then be seen and roughly measured if the instrument is calibrated, or the whole spectrum may be photographed and the bands measured from the photograph by means of a comparison photograph of a known spectrum, e.g. iron, on the same plate. The latter method has the advantage that the ultra-violet bands are included. Should the mixture under examination be one in which all but the last trace of coloured earths has been removed, it may be necessary to use a much thicker layer of the solution before the absorption band becomes visible. In such a case a Baly absorption tube,[353] which allows the thickness of the layer being rapidly changed, should be used.

The wave lengths of the maxima of the stronger absorption bands of the elements mentioned above are given for reference:—

Praseodymium:[354] 5964, 5882 (weak), 4813 (very intense), 4863 and 4442.

Neodymium:[355] 6775, 6217, (5785, 5754, 5735, 5716) in concentrated solutions these appear as a single band, (5323, 5216, 5204, 5124, 5087) a single band in concentrated solutions, 4745, 4687, 4610, and 4271.

Samarium:[356] 4760, 4630, 4170, 4020, 3750, and 3620. All of these bands are visible only in moderately concentrated solutions.

Europium:[357] 5250, 4650 (a broad band).

Dysprosium:[358, 359] 7530, 4750, 4515, 4275, 3865, 3795, 3650, 3510, 3380, 3225.

Holmium: [360] (6446-6418), (6414-6384), (5385-5349), (4860-4846), (4554-4459), (4223-4216), and (4199-4152).

Erbium: [361] 6665, (6530-6515), 5231, 4870, (4500-4494), and 4427.

Thulium: [361] 7015, (6845-6825), (6593-6585), (4643-4638), and (3604-3595).

The determination of the absorption spectrum is, however, not quite so simple as the foregoing description would make it appear, for the intensity of the bands and in some cases their actual positions are changed by changing conditions. The temperature of measurement sometimes causes a slight shift of the bands, but this change is of little importance in the present measurements, and no difficulty is to be expected if the measurements are carried out at atmospheric temperature. The concentration of the solution, or perhaps more exactly the "optical density" causes a change in the intensity of the bands which is expressed by Beers' Law, $I = I_0 a^{dc}$, where I is the intensity of the light after absorption, $I_0$ the intensity of the light entering the solution, $d$ the thickness of the layer, $c$ the concentration, and $a$ the absorption constant. So that in comparing two solutions they should have the same concentration, and layers of the same thickness should be measured, or, if they have different concentrations the thickness of the solution should be so adjusted that the two solutions have the same optical density. The nature of the solvent, due probably to varying ionisation, causes changes in the positions of the bands, but this is a condition not likely to be of any importance here, since aqueous solutions are practically the only ones employed. The nature of the negative radical of the salt measured is, however, of considerable importance, since it often occasions a shift of the bands, in the sense that they move toward the red with increase of molecular weight of the compound. In a given series of experiments this also can be overcome by always using the same acid in the preparation of solutions of the oxides from the fractions. Finally the presence of colourless earths, i.e. earths which give no absorption spectrum, often bring about changes in the position of the bands, and as all too little is known about this difficulty, errors may easily creep in. It is extremely probable that the many unsubstantiated announcements of the existence of new earths, based on absorption spectrum measurements, have their origin in some change in the position

of known bands by a colourless earth. Above all things, in determining the absorption spectrum, for the purpose of controlling a fractionation, a high dispersion must not be used; that produced by a 60° flint glass prism is ample, and in many cases all that is required can be obtained by means of a pocket spectroscope. Absorption spectra, therefore, serve only to detect the presence or absence of a few elements in mixtures, and conclusions as to the relative amounts of these elements in such mixtures can, at the best, only be very rough approximations and should be treated as such.

A further type of absorption spectrum can be used for detecting the presence or absence of the elements mentioned above; this is generally known as the reflection spectrum. The minerals and oxides of the coloured earths reflect light which when examined spectroscopically exhibits the characteristic absorption spectra of the elements contained in the mixture, and often more sharply than in the case of solutions. Reflection spectra have been studied chiefly by Hofmann and Bugge[362] in the case of erbium oxide, by Waegner[363] in the case of neodymium oxide, and by Urbain[209] with a glass-like mass of mixed oxychlorides and also with mixed nitrates obtained by evaporating solutions to dryness. The method of examination consists in concentrating the light from the positive carbon of an electric arc on to the substance by means of a quartz lens and receiving the reflected light into the slit of a spectroscope. The measurement of the bands is then carried out as in the case of an ordinary absorption spectrum.

## Measurement of Spark Spectra.

Since the whole of the rare earth compounds may be volatilised in an electric spark, the investigation of the spark spectrum offers a ready and suitable means of identifying the constituents of a mixture and consequently of controlling the progress made in a fractionation. The measurement may be carried out by embedding a platinum wire, connected to the negative terminal of an induction coil, in a mixture of the earths and examining the light produced when a discharge is passed. It is best to photograph the spectrum and compare the photograph with the spectra of the individual rare elements.

Another method consists in placing the negative electrode,

which is made of either gold or platinum, in a solution of the earths in such a way that the end of the electrode projects from the solution. The other electrode is placed immediately above and at a short distance from the negative electrode. The discharge is then passed in the usual way and the spectrum photographed. A particularly convenient form of apparatus for the latter type of determination has been described and used by Crookes.[364] A very simple form of apparatus for the same type of determinations is due to Pollok.[365] This consists of a U tube which has limbs of unequal length as shown in fig. 2. The tube is made of thick walled glass tubing 2-3 mm. bore, the longer limb being 10 cms. long, and the shorter 5 cms. long. Both limbs are terminated by small cups. The electrodes consist of stout platinum wire terminated by about 1 cm. of gold wire of 1 mm. diameter. One wire is forced down the tube so that the gold end just projects above the level of C, and the other is placed above it as indicated in the drawing so that there is a spark gap of about 5-10 mm. The solution to be examined is poured in at A until the cup C is just filled. The gold electrode protruding from C is thus kept moist with the solution by capillary attraction, and consequently the spark passing between the two electrodes is continually fed with the solution. The light from the spark is allowed to fall on the slit of the spectroscope and examined in the usual way.

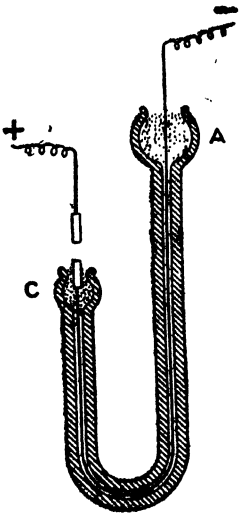


FIG. 2.

Spark spectra often vary very much in the intensity and number of lines. This is due to several circumstances, among which may be noted, the size of the coil, voltage applied, length and resistance of the leads, and the presence or absence of Leyden jars in the circuit. A reversal of the current brings about a phosphorescent appearance which yields a spectrum very like the phosphorescent spectra of Crookes (*vide infra*). On the whole, however, the spark spectra are very reliable and pre-eminently suited for controlling fractionation.

## Measurement of Arc Spectra.

The arc spectrum is, of all methods of detection of the rare earths, the most reliable, since the spectrum obtained is constant under all experimental conditions. The method consists in making a hollow in the lower carbon of a carbon arc and filling it with the substance under investigation. This may be either the oxide or a salt, preferably in the latter case the sulphate. The arc is then struck and the light allowed to enter the slit of a spectroscope where the spectrum is photographed. Instead of using a solid substance for the determination, the lower carbon may be soaked in a solution of the material, dried, and then used for producing the arc. In measuring arc spectra it is immaterial which pole contains the material; and for purposes of comparison it is advisable to photograph on the same plate the spectrum of some well investigated substance, usually the spectrum of the iron arc is employed for this purpose. If a comparison spectrum is not used, as above described, the spectra may be compared with the known spectra of the individual elements.

## Measurement of Phosphorescence Spectra.

When certain of the rare earths are subjected to a stream of cathode rays a brilliant phosphorescence is induced, which, when examined spectroscopically, is seen to possess a definite spectrum. The nature of the spectrum changes as a mixture is fractionated, and consequently fractionation may be controlled by means of such a spectrum. The phosphorescence spectrum was first studied by Crookes,[57, 108] who found that fractions of apparently the same chemical composition and of the same physical properties yielded different phosphorescence spectra, and as a result of this, he was led to enunciate the hypothesis of meta-elements. Lecoq de Boisbaudran,[59] and Baur and Marc,[63] however, showed that the colourless earths, such as lanthana, do not yield discontinuous spectra under the influence of cathode rays, and that the phosphorescence spectra, previously observed for these substances, were due to the presence of a small quantity of a coloured earth which acted as a phosphorogen. Hence it follows that for the production of a phosphorescence spectrum of a colourless earth, it is necessary that a small quantity of a coloured earth should be present. The maximum intensity of the phosphorescence is observed when about 1 per cent. of the

coloured earth is present. Consequently it will be seen that the use of this method is of limited value in following the course of a fractionation, but it furnishes the sharpest means of deciding whether a product is absolutely pure or not. Indeed so sharp is it that only seldom can the rare earths be got so pure as to stand the test for purity by this method. Urbain[366, 367] has shown that the presence of 0·0001 per cent. of a phosphorogen is sufficient to bring about a considerable phosphorescence. The phosphorescence spectrum is obtained by placing the oxide or a dry salt of the earths in a glass capsule D (fig. 3), which by means of a ground glass joint fits a cathode ray bulb B. The bulb is connected to a mercury pump by the side tube S and is fitted with a concave cathode C and an annular anode A. The anode is so placed that the cathode rays can pass freely through it and so strike the substance in D. This arrangement has the advantage that the phosphorescence produced by the earth is not in any way affected by the luminescence of the glass which only occurs between A and C.

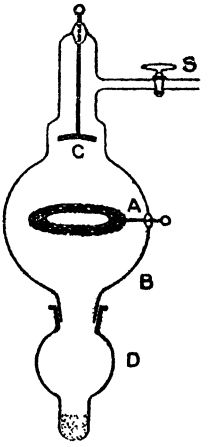



FIG. 3.

*From Annales de Physique et de Chimie (Masson et Cie).*

## Measurement of the Magnetic Susceptibility.

The measurement of the magnetic susceptibility of a mixture of rare earths is probably the best and most rapid method of controlling the progress of a fractionation. It is particularly useful in those cases where the mixtures concerned consist of elements of so nearly the same atomic weight that a determination of the mean equivalent weight when carried out in the ordinary way ceases to give a very clear idea of the relative composition of the mixture. The magnetic susceptibility of the rare earths varies considerably from element to element,[368, 369, 370, 371] and since Urbain[371] in the course of a careful investigation of this property has shown that it is strictly additive, it follows that from the susceptibility of a binary mixture and the known susceptibilities of the constituents the relative composition can be calculated with a high degree of accuracy. The

order of the magnetic susceptibilities, expressed as coefficients of magnetisation, for the oxides of several of the elements is given in the adjoining table:—

| | Atomic Weight. | Coeff. of Magnetisation × $10^{-6}$. |
|---|---|---|
| Scandium . . . | 44·1 | − 0·05 |
| Yttrium [372] . . | 89·0 | − 0·14 |
| Lanthanum [372] . . | 139·0 | − 0·18 |
| Neodymium [371] . . | 144·3 | + 33·5 |
| Samarium [371] . . | 150·4 | 6·5 |
| Europium [371] . . | 152·0 | 33·5 |
| Gadolinium [371] . . | 157·3 | 161·0 |
| Terbium [371] . . | 159·2 | 237·0 |
| Dysprosium [373] . . | 162·5 | 290·0 |
| Celtium [93] . . . | ? | ca. 4·1 |

In addition to the above-mentioned figures, S. Meyer [374] gives the values of coefficient of magnetisation × $10^{-6}$ for ytterbium and lutecium as 18·3 and 3·78 respectively, whilst Urbain [89] finds that ytterbium is more strongly paramagnetic than lutecium and the ratio of the coefficients of the oxides is 53 : 13. From these figures it will be seen that the two results are not in agreement, and consequently neither result can be unreservedly accepted without confirmation. It will be seen from the figures above that the values of the coefficient of magnetisation differ far more than the atomic weights, and in consequence the determination of the magnetic susceptibility is much more sensitive than the determination of the mean equivalent in following the progress of a fractionation. Urbain and Jantsch [371] determine the magnetic susceptibility by means of the Curie and Cheveneau [375] magnetic balance, and since this instrument appears not to be well known, it has been deemed well to describe it shortly in this place, along with the method of making a determination.

The magnetic balance is in reality a torsion balance by means of which it is possible to measure the attraction or repulsion of a permanent magnet on a weighed quantity of a comparatively feebly magnetic substance. The balance consists of a light aluminium arm T.T. (fig. 4) which is supported at O by a thin platinum wire. The swing of the arm is damped by a light metallic vane B which dips into a vessel of oil D. To one end of the arm a test tube *t* is hung by means of two metallic bands which form a receptacle for it. The test tube contains the sub-

stance under investigation. At the other end of the arm is a glass scale *m* which can be read by means of a microscope M which is fixed into the top of the balance case and is illuminated by the mirror A. Parallel with the experimental tube is a permanent magnet NS of annular form and cut as in the figure. The magnet is supported on a carriage C which can be moved between two guides by means of a screw. One of the guides is graduated so that the amount of movement may be easily known. Two sliding weights P and *p* sit on the longer arm of the balance to counterpoise the test-tube and contents. A screw

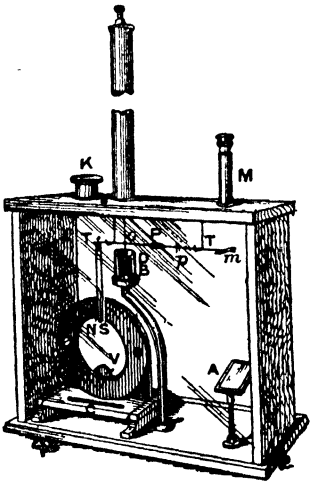



FIG. 4.

*From Journal de Physique (Amedée Guillet).*

opening K serves for the removal of the tube without opening the case of the balance.

In making a measurement the empty tube is suspended on the balance arm and the weights P and *p* adjusted so that the whole swings horizontally. The tube will be either attracted or repelled by the magnet according as it is paramagnetic or diamagnetic. The magnet is then moved until the scale shows that the deflection is a maximum, say $x'$ divisions, as shown in position 1 (fig. 5), then the magnet is moved back again and over to the other side of the tube so that a maximum deflection on the other side of the scale is obtained, say $x''$ (position 2). The difference of the two readings $x' - x'' = \Delta''$ is proportional to the maximum

force in the two directions, which if the apparatus is symmetrical, are equal. A known weight of a substance of known coefficient of magnetisation, e.g. cobalt sulphate, is placed in the tube and two values again obtained, say $x'''$ and $x^{IV}$, then $x''' - x^{IV} = \Delta'$. Finally a known weight of the substance under investigation is placed in the tube and the values $x^{V}$, $x^{VI}$, and $x^{V} - x^{VI} = \Delta$ obtained. If now $m$ is the mass of the substance under investigation, $m'$ that of the comparison substance, $k$ the specific coefficient

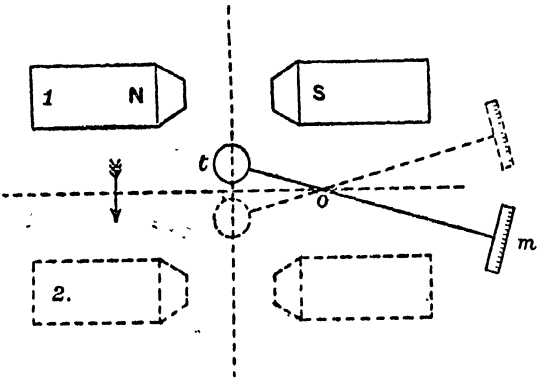



FIG. 5.
*From Journal de Physique (Amedée Guillet).*

of magnetisation of the substance under investigation, and $k'$ that of the comparison substance, then

$$\frac{\Delta - \Delta''}{\Delta' - \Delta''} = \frac{km}{k'm'} \text{ or } k = \frac{k'm'}{m} \cdot \frac{\Delta - \Delta''}{\Delta' - \Delta''}.$$

Due attention, of course, must be paid to the nature of the magnetisation of the substances under investigation. A determination of this kind can be carried out in a very few minutes, and has been used in controlling fractionations by Urbain[376] in showing the accumulation of holmium in a dysprosium yttrium mixture; and from his results he shows that in a mixture the composition can be deduced to within 2-3 per cent. Meyer and Goldenberg,[377] in the separation of thorium and scandium, show that this is the most convenient method of detecting traces of thorium in scandium, and at the same time they show that spectroscopic methods fail to detect 0·5 per cent. of thoria in scandia.

# CHAPTER V.

## THE CERIUM GROUP OF RARE EARTHS.

IT is usual to include in the cerium group the elements cerium, lanthanum, neodymium, praseodymium, and samarium. These elements are strongly electropositive, and give rise to oxides of the type $M_2O_3$ which are powerful bases and form well-defined salts with acids. Cerium, in addition, forms an oxide $CeO_2$ which is also basic, but much weaker than the oxides $M_2O_3$, and samarium forms salts of the type $SaX_2$ corresponding to an unknown oxide SaO. The elements of this group are amongst the most basic of all elements as is shown by the very large heats of dissociation of their sulphates; these values have been calculated according to the Nernst heat theorem from their dissociation pressures at 900°.[381] The values of $Q$, the heat of dissociation of the sulphates $M_2(SO_4)_3$ of this group, are La 59·8 $K$, Pr 57·4 $K$, Nd 57·2 $K$, Sa 56·6 $K$, and Ce 52·4 $K$. Strictly speaking, this ought to be the order of decreasing basicity of the elements, but it is not the same as that deduced from the order in which the hydroxides are precipitated from solution by a strong base, or from the order in which the nitrates $M(NO_3)_3$ are decomposed by heat, or from consideration of the electro-conductivity of solutions of the chlorides. All of these methods place the order of decreasing basicity as La, $Ce'''$, Pr, Nd, Sa, and $Ce^{IV}$. The elements of this group are most notably distinguished from the other rare earths by the fact that they form sparingly soluble double sulphates with sodium and potassium sulphates.

## CERIUM, Ce. At. Wt. 140·25.

Cerium compounds occur in a large number of widely distributed minerals, which include orthite, cerite, monazite, aeschynite, yttrocerite, fluocerite, bastnäsite, tysonite, parisite, lanthanite, and melanocerite. Of these, monazite is almost exclusively used in the preparation of cerium compounds, on the commercial scale; for

this purpose use is made of the residues obtained after the extraction of thorium. Orthite and cerite, which contain notable quantities of cerium, also find some small use on the large scale. Many of the other minerals contain far larger quantities of cerium than those used on the large scale, but their relative scarcity renders them unsuitable for the extraction of large quantities of cerium.

Pure cerium compounds can be more readily obtained than can compounds of any of the other rare earths. This is mainly due to the fact that cerium compounds can be readily converted into the ceric condition and that ceric salts undergo hydrolysis with great ease, whereas the remaining elements form no such more highly oxidised salts. The most profitable and efficient methods for the preparation of pure cerium compounds are :—

(i) The basic nitrate method (p. 34).

(ii) The bromate method (p. 31).

(iii) The Drossbach permanganate method (p. 49).

(iv) A method, due to Koppel,[382] which consists in dissolving a mixture of the oxides in hydrochloric acid in methyl alcohol solution and treating the solution with pyridine when a double ceric pyridinium chloride $(C_5H_5NH)_2CeCl_6$ separates which can be purified by recrystallisation from a mixture of alcohol and ether.

Pure cerium compounds show no absorption spectrum when examined in thick concentrated layers, and this behaviour can be regarded as a final test of purity when any of the above methods is used for their preparation.

Metallic cerium can be obtained in the form of a powder by the reduction of anhydrous cerous chloride by means of sodium, potassium,[383, 384] magnesium, or aluminium, but in no case is a pure product obtained. Hillebrand and Norton[385] obtained metallic cerium in coherent form by the electrolysis of the fused chloride. For this purpose the molten cerous chloride, covered by a layer of ammonium chloride, was contained in a porous cell which was surrounded by a mixture of molten sodium and potassium chlorides contained in a porcelain crucible; the electrolysis was carried out between an anode of thin iron sheet and a cathode of iron wire. A method, by which large quantities of the coherent metal were obtained, due to Muthmann, Hofer, and Weiss,[386] consists in the electrolysis of a fused mixture of 90 per cent.

cerous chloride and 10 per cent. potassium and sodium chlorides in a water-cooled copper vessel by a current of 30-40 ampères at 12-15 volts. The electrodes were of carbon, the anode being much thicker than the cathode. The cathode entered the electrolysis cell through the bottom, whilst the anode dipped into the electrolyte from above. This method has been further modified [228] by enlarging the anode, whereby a very high temperature is maintained, and by using pure cerous chloride. In this way, 750 grams of the metal were obtained in 6 hours with a current of 120 ampères. Muthmann, Weiss, and Scheidelmandel [387] prepare cerium by the electrolysis of a solution of a dioxide in molten cerous fluoride, using a current density of 8-10 ampères per square centimeter at the cathode and 3 ampères per square centimeter at the anode. Hirsch [388] obtained cerium containing 2 per cent. of impurities (Fe, $Ce_2O_3$, and $Ce_4C_3$) by electrolysing the fused anhydrous chloride in an iron crucible. The crucible serves as cathode, a graphite rod being used as anode. Small quantities of sodium chloride, potassium fluoride, and barium chloride are added from time to time as the electrolysis proceeds to increase the resistance of the bath and to check decomposition. The metal, thus obtained, is purified by amalgamating with boiling mercury, skimming off the undissolved impurities and distilling in a vacuous quartz tube lined with magnesia.

Metallic cerium has a colour and lustre similar to that of iron, it is moderately stable in dry air, but after a while becomes coated with a yellow deposit which slowly changes to bluish green and in all probability consists of dioxide. It is soft and ductile and can be cut with a knife; the hardness is near to that of lead.[388] The specific gravity is recorded as 6·628,[345] 6·920,[388] and 7·0424;[228] melting-point 623°;[228] specific heat at ordinary temperatures, 0·04479;[389] at temperatures between the boiling-points of hydrogen and nitrogen, 0·0330;[390] heat of formation of the oxide $\frac{1}{4}CeO_2$ = 56·1 kilogram calories.[388] Cerium is paramagnetic, susceptibility [368] $\mu = 12 \times 10^{-6}$; specific resistance, 78 ohms. Cold water slowly attacks cerium, whilst hot water is very rapid in its action on the metal; cerium is therefore usually preserved in glycerol or benzene. Cerium is readily dissolved by dilute mineral acids but in concentrated nitric acid it becomes coated with a brown deposit consisting mainly of cerium dioxide. When cerium is scratched with a steel needle or when filed or struck

with a piece of flint, it emits brilliant showers of sparks. When in the form of wire, it burns in the bunsen flame with a more intense light than magnesium ribbon. It burns brilliantly in chlorine, and also in the vapours of bromine and iodine but not so brightly as in chlorine. Heated cerium reduces the oxides of carbon to carbon, the dioxide of the metal being formed. Methyl chloride, passed over cerium at 500°-600°, is decomposed with the formation of cerous chloride and hydride and carbon,

$$3CH_3Cl + 4Ce = CeCl_3 + 3CeH_3 + 3C.$$

Cerium has a great affinity for oxygen as is evidenced by the large heat of formation of the oxide and by the fact that the metallic alloy (mixed metal), obtained by the electrolysis of a mixture of the chlorides of the cerium earths, is capable of reducing the oxides of manganese, iron, and chromium, in the same way that aluminium does in the thermite process, with the evolution of large quantities of heat. When cerium is heated to 200°-300° in hydrogen the hydride $CeH_3$ is formed. A nitride is formed by heating cerium in nitrogen, although Dafert and Miklauz [391] dispute the fact. Cerium combines with boron and silicon and alloys with many metals. The alloys are generally brittle substances which easily powder, but in the case of antimony they are soft. Amongst the alloys a number of intermetallic compounds have been observed, amongst which the following may be noted:—

1. *Magnesium.*—Cerium and magnesium, when heated under a layer of sodium and potassium chlorides, combine with absorption of heat. Alloys containing 50 per cent. of cerium are brittle and silver white in colour. They burn with a dazzling white light and are entirely soluble in acetic acid and dilute mineral acids. Dilute solutions of ammonium chloride decompose them with the formation of ceric hydroxide. Definite compounds $Ce_4Mg$, $CeMg$, $CeMg_3$, and $CeMg_9$ have been isolated.[392]

2. *Zinc.*—The two metals combine explosively when heated together; the alloy, consisting of 1 part of Ce and 2 parts of Zn, is bluish in colour and is rapidly oxidised in the air.

3. *Aluminium.*—When the product obtained by heating aluminium and cerium is treated with potassium hydroxide solution, the compound $CeAl_4$ remains insoluble as a shining powder composed of needle-shaped crystals. Density, 4·193. Large

amounts of heat are evolved during the combination. The compounds $Ce_3Al$, $Ce_2Al$, CeAl, and $CeAl_2$ have also been isolated.[393]

4. *Mercury.*—When cerium is plunged into boiling mercury it dissolves to form a liquid amalgam if not more than 3 per cent. of cerium is added. The amalgams containing 3-8 per cent. cerium are soft, but become hard when more than 8 per cent. of cerium is present. Amalgams cannot be obtained by the electrolysis of cerium salts with a mercury cathode, the same being true for the whole of the rare earth metals.[394]

5. *Tin.*—In the case of this element the compounds $Sn_2Ce$, $Sn_3Ce_2$, and $SnCe_2$ have been isolated.[395]

6. *Bismuth.*—Four intermetallic compounds with cerium are known in the case of this element, $Bi_2Ce$, $Bi_3Ce_4$, BiCe, and $BiCe_3$. These are all superficially oxidised in the air and decomposed by water. $Bi_3Ce_4$ melts at 1630°; $BiCe_3$ decomposes at 1400° to form $Bi_3Ce_4$; BiCe decomposes at 1525° to form $Bi_3Ce_4$; and $Bi_2Ce$ decomposes at 882° to form BiCe.[396]

7. *Copper* forms compounds[1007] $CeCu_6$, $CeCu_4$, and $CeCu_2$ when the metals are melted together.

Brittle alloys with iron, nickel, tungsten, manganese, and cadmium have been prepared, and these all possess the same properties as cerium of emitting sparks when struck.

## Compounds of Cerium.

### Cerium and Oxygen.

Cerium forms two oxides of ascertained composition, cerous oxide $Ce_2O_3$ and cerium dioxide $CeO_2$; and in all probability other oxides also exist. When ammonia and hydrogen peroxide are added to a solution of a cerous salt a slimy brown precipitate, of the formula $CeO_2\ H(OH)_3$,[336, 397, 398, 399] is produced, which can be regarded as a hydrated perceric oxide $CeO_3$. Wyrouboff and Verneuil, however, consider that the precipitate is to be regarded as $CeO_2,CeO_3,H_2O_2$. An oxide corresponding to the formula $Ce_4O_7$ also probably exists.

*Cerous Oxide*, $Ce_2O_3$.—This compound cannot be prepared by the more obvious methods, such as heating the corresponding oxalate, nitrate, carbonate, or hydroxide, which in every case yield the dioxide. If these substances are heated in absence of air or in hydrogen an oxide is obtained which is dark blue in colour and has a formula which approximates to $Ce_4O_7$.[400, 401] It

is prepared, however, by reducing the dioxide with metallic calcium,[402] and in this way a yellowish-green powder is obtained. If the oxide is prepared by heating cerous hydroxide in an inert atmosphere it is perfectly white in colour.[403] On standing in the air it slowly absorbs oxygen and is converted into the dioxide. It burns when heated to 200° in the air, again forming the higher oxide.

*Cerous Hydroxide*, $Ce(OH)_3$, is formed by treating solutions of cerous salts with ammonia or caustic alkali, or by the action of water on cerous carbide in the absence of air. It is a slimy white precipitate with strongly reducing properties, and on standing in the air absorbs oxygen forming a reddish-violet mass which finally passes into a yellow mass of ceric hydroxide. If cerous hydroxide is precipitated and desiccated in the absence of air it may be obtained as a white powder.[402, 404] The oxidation of cerous hydroxide to ceric hydroxide takes place with greater rapidity in the presence of caustic alkali, but in the presence of alkali carbonate the dark brown hydrated peroxide is produced. It is to be noted that the oxidation to the peroxide in the presence of air does not occur with ceric hydroxide but only with cerous hydroxide.

*Cerium Dioxide*, $CeO_2$, is produced by the ignition of cerium salts, both cerous and ceric, of volatile acids. It is also produced by the ignition of both hydroxides and by burning the metal in air or oxygen.

When pure, cerium dioxide is a white or pale yellow powder, the exact colour depending on the method of preparation. The product obtained by heating ceric sulphate is lightest in colour and that from the hydroxides darkest. All specimens take on a lemon-yellow colour when heated to dull redness. The colour is lost again on cooling and the oxide regains its original colour if the heating has not been too prolonged or intense.[405] The difference in colour is generally regarded as due to the existence of polymeric[406, 407] varieties of the compound. Several observers, including Wyrouboff and Verneuil[406, 407] and Sterba,[401, 408] consider that pure cerium dioxide is white, whilst Brauner[409] attributes the white colour to the presence of silica as an impurity. The present writer has obtained cerium dioxide pure white in colour, and this specimen did not contain silica.[405] The presence of other elements of the cerium group, neodymium and praseody-

mium, impart a reddish tint to the oxide, which becomes deeper the larger the amount of these substances present. The colour in this case is regarded as being due to the formation of salts in which the cerium dioxide plays the part of an acidic oxide. Pure cerium dioxide is absolutely insoluble in hydrochloric acid and nitric acid, but dissolves in the presence of reducing agents such as hydriodic acid, hydrogen peroxide, stannous chloride, and hydroquinone.[410] In all cases cerous salts are produced. Concentrated sulphuric acid on warming on the water-bath converts cerium dioxide into ceric sulphate without solution occurring. Sulphuric acid containing a little water dissolves cerium dioxide producing both cerous and ceric sulphates with the liberation of oxygen which contains considerable quantities of ozone. Cerium dioxide can act as an oxygen carrier, and is used for this purpose in the Dennstedt combustion furnace instead of platinum.[411] Specific gravity, 6·405 at 17°, specific heat, 0·0877; cerium dioxide does not melt[412] but volatilises at 1875°. Cerium dioxide can be obtained crystallised in cubes and octahedra by melting the amorphous oxide with borax,[401] sodium chloride, or potassium hydrogen sulphate, or by fusing the anhydrous chloride with borax, the fused product, in all cases, being extracted with hydrochloric acid. The crystalline oxide is unattacked by acids, and alkalis; it has a density 6·94 (Nordenskiöld), 7·314-7·905 (Sterba). Cerium dioxide is reduced to the metal by heating with aluminium or magnesium powder. When heated in vacuo in complete absence of air a dark blue oxide of the approximate composition $Ce_4O_7$ is produced, which is probably identical with the product obtained by drying the blue hydroxide in vacuo. This compound on warming in the air glows and is reconverted into cerium dioxide. Wyrouboff and Verneuil differentiate different polymeric forms of cerium dioxide; these include the paraoxide $(CeO_2)_{40}$, the metaoxide $(CeO_2)_{56}$, and a third oxide $(CeO_2)_8$.[406, 413, 414] In this connection, see also Wyrouboff and Verneuil.[415]

*Ceric Hydroxide*, $Ce(OH)_4$, is obtained by precipitating ceric salts with ammonia or caustic alkalis or by the oxidation of cerous hydroxide. The oxidation takes place slowly when cerous hydroxide is allowed to stand in the air, or by the addition of hydrogen peroxide when the hydrate of the peroxide is first produced which on boiling yields ceric hydroxide. Ceric hydroxide

is a yellowish gelatinous precipitate when prepared as above; when freshly prepared or when dried at 120° it is completely soluble in nitric acid with the production of a reddish solution of the nitrate. It dissolves in hydrochloric acid with the evolution of chlorine and the production of cerous chloride; sulphuric acid converts it into a mixture of cerous and ceric sulphates with the evolution of oxygen. In the presence of platinum, sulphuric acid dissolves ceric hydroxide with the production of cerous sulphate only.[409] Ceric hydroxide can be obtained in colloidal solution by dialysing a 10 per cent. solution of ceric ammonium sulphate in water. The solution produced is very sensitive to electrolytes, a few drops of a solution of an electrolyte being sufficient to coagulate it. On evaporating the solution to dryness, a gum-like mass remains which dissolves in hot water to form a clear solution.

## Cerous Compounds.

*Cerous Hydride*, $CeH_3$.—When cerium is heated in hydrogen to 250°-270° combination takes place with incandescence and the formation of the hydride.[391, 416, 417] It is somewhat doubtful whether this compound is cerous hydride or ceric hydride since the percentage of hydrogen contained in it is found to vary between the amounts required for the two compounds.

It is a non-crystalline dark blue or black powder[391] which takes fire spontaneously in the air. It is rapidly decomposed by moist air, water, and alkalis, with the evolution of hydrogen: acids decompose it with the evolution of hydrogen and the formation of cerous salts. When heated in the air it decomposes with slight explosion and forms a mixture of oxide and nitride, ammonia also being produced.[391] When heated to 800°-900° in nitrogen it is converted into nitride. When cerous hydride is shaken in a closed glass tube it emits light. Specific heat 0·0889.[418]

*Cerous Fluoride*, $CeF_3,\frac{1}{2}H_2O$.—This compound is prepared as a white slimy precipitate by the addition of an aqueous solution of hydrofluoric acid to a solution of a cerous salt. On warming or standing the precipitate becomes crystalline.[419] Anhydrous cerous fluoride is obtained by heating ceric fluoride to dull redness.[420, 421] When fused with calcium fluoride, mixed crystals of the composition $xCaF_2,yCeF_3$ are obtained up to a composition

55·8 per cent. $CeF_3$. These crystals correspond to the naturally occurring mineral cerofluorite.[422]

*Cerous Chloride*, $CeCl_3$.—The anhydrous salt may be prepared by heating the metal, the sulphide, the carbide, or a mixture of the dioxide and carbon in chlorine; by heating the oxalate, carbide or dioxide in a stream of hydrochloric acid gas; by heating the dioxide in carbon tetrachloride vapour, a mixture of carbon monoxide and chlorine, or in a mixture of sulphur monochloride and chlorine; and by evaporating a solution of cerous chloride to dryness with ammonium chloride and gently igniting the residue to remove the ammonium chloride.

Cerous chloride is a white deliquescent crystalline substance, which is readily soluble in water, dissolving with a hissing noise; it is also soluble in alcohol. It has specific gravity 3·92 and melts[423] at 848°. It forms two crystalline hydrates,

$$2CeCl_3,15H_2O^{419,424,425} \text{ and } CeCl_3,7H_2O,^{403}$$

the former of which separates when a solution of cerous chloride is evaporated to a syrupy consistency and the latter by evaporating solutions of cerous chloride over sulphuric acid at low temperatures when rhombic crystals are formed. Both hydrates on heating lose water and hydrochloric acid, and form the oxychloride CeOCl. Cerous chloride in solution is slightly hydrolysed. Denham[426] has shown that a $\frac{N}{32}$ solution is hydrolysed to the extent of 0·14 per cent. Anhydrous cerous chloride absorbs ammonia at low temperatures with evolution of heat and formation of compounds with 20, 12, 8, 4, and 2 molecules of ammonia.[427] Solutions of cerous chloride unite with metallic chlorides to form double salts. A large number of these compounds have been characterised, among which may be mentioned:—

$CeCl_3,4HgCl_2,10H_2O$; $2CeCl_3,3SbCl_3,20H_2O$;
$CeCl_3,2SbCl_3,10H_2O$; $CeCl_3,BiCl_3,13{\cdot}5H_2O$;
$CeCl_3,SnCl_2,8H_2O$; $CeCl_3,SnCl_4,10H_2O$;
$CeCl_3,2PtCl_2,10H_2O$; $CeCl_3,PtCl_4,13H_2O$;
and $CeCl_3,AuCl_3,13H_2O$.

Organic bases combine with cerous chloride; the compound $CeCl_3,C_5H_5N,2C_2H_6O$ is formed when hydrochloric acid gas is led into a suspension of cerous carbonate in alcohol containing

pyridine.[425] The compound crystallises from the solution thus formed with two molecules of alcohol of crystallisation. A compound $CeCl_3,2C_6H_{12}N_4,14H_2O$ is formed in silky needles by the action of a concentrated solution of cerous chloride on a saturated solution of hexamethylene tetramine.[428]

*Cerous Oxychloride*, CeOCl.—This compound is formed in shining micaceous leaflets by heating hydrated cerous chloride. When amorphous it has a violet tinge, is readily soluble in dilute acids, and when ignited is converted into the dioxide.

*Cerous Bromide*, $CeBr_3$, is obtained as a snow-white crystalline powder by leading hydrogen bromide at 400°-600° over cerium sulphide;[429] by heating the oxalate in hydrogen bromide;[430] and by passing a mixture of sulphur monochloride and hydrogen bromide over the heated dioxide.[431]

It is an excessively deliquescent substance which dissolves in water, forming slightly acid solutions. No hydrates of definite composition have been isolated. A number of double bromides with metallic bromides are known, among which may be noted:

$CeBr_3,SbBr_3,12H_2O$; $CeBr_3,BiBr_3,12H_2O$; $CeBr_3,6BiBr_3,20H_2O$; $CeBr_3,SnBr_4,10H_2O$ and $CeBr_3,AuBr_3,8H_2O$.

*Cerous Iodide*, $CeI_3,9H_2O$, is formed by the action of a solution of hydriodic acid on cerium dioxide; the solution thus obtained is evaporated in the presence of sulphuretted hydrogen and crystallised in vacuo over sulphuric acid.[424] It forms colourless crystals which readily lose iodine.

*Cerous Sulphide*, $Ce_2S_3$, is formed by heating the metal in sulphur vapour; by heating a mixture of one part of cerium dioxide and four parts of sulphur in sulphuretted hydrogen;[432] by heating the anhydrous sulphate in sulphuretted hydrogen;[401, 429, 433] and by heating the disulphide, $Ce_2S_4$, to 720°.[433]

Cerous sulphide is a brown or blackish-purple powder, although Biltz[433] states that it is red, having density 5·1; it is moderately stable in the air and is slowly decomposed by boiling water. When finely divided it is pyrophoric and takes fire when heated in the air, forming a mixture of dioxide and sulphate. It is readily soluble in dilute acids with the evolution of sulphuretted hydrogen. Fuming nitric acid attacks it violently with liberation of sulphur.

*Cerous Sulphate*, $Ce_2(SO_4)_3$.—The anhydrous salt is obtained

by heating any of the hydrates to 400°-450°.[78, 407, 434] It is a white hygroscopic powder which is stable up to 500°. At this temperature it begins to lose sulphuric anhydride, and at a white heat it is completely converted into the dioxide. Cerous sulphate is generally prepared by the action of sulphuric acid on the carbonate or by the action of sulphuric acid on the dioxide in the presence of hydroquinone.

The anhydrous salt is very soluble in ice-cold water; 100 parts of water dissolve 60 parts of the salt (Brauner),[435] 40 parts of the salt (Muthmann and Rolig)[436] at 0°. Five definite hydrates, with 12, 9, 8, 5, and 4 molecules of water respectively, are known, and possibly a sixth hydrate $Ce_2(SO_4)_3,6H_2O$ also exists.

The dodecahydrate is obtained in asbestos-like needles by evaporating a saturated solution of the anhydrous salt at 0° over sulphuric acid[436, 437, 438] or in the air,[419] or by stirring the octo- or ennea-hydrates with ice-cold water. A saturated solution of the dodecahydrate contains the following weights of anhydrous sulphate per 100 grams of water:[437] 16·56 grams at 0°, 17·52 grams at 18·8°, and 17·70 grams at 19·2°. At 16° the dodecahydrate passes slowly into the octohydrate,[437] although, as the accompanying solubility curves[437] (fig. 6, see next page) show, it is stable in contact with the solution only between 0° and 3°.

The enneahydrate is obtained by the slow evaporation of a saturated, but not supersaturated, solution of the sulphate at 40° to 45°, and sowing with a crystal of the enneahydrate. If the solution is not sown a mixture of octo- and enneahydrate will be obtained.[437, 438] It forms hexagonal crystals isomorphous with the corresponding hydrate of lanthanum sulphate, density 2·841. 100 grams of water contain the following weights of anhydrous sulphate when saturated with the enneahydrate:—[437]

| Temperature | 0° | 15° | 30° | 45° | 50° | 60° | 65° |
|---|---|---|---|---|---|---|---|
| Grams | 20·98 | 11·87 | 7·353 | 5·13 | 4·673 | 3·88 | 3·595 |

It is stable in contact with solution between 33° and 41°.

The octohydrate is obtained by crystallising solutions between 30° and 70°. It crystallises rhombic or triclinic and is not isomorphous with the octohydrates of the other rare earth sulphates, which crystallise monoclinic; 100 grams of water, when saturated with this hydrate, contain the following weights of the anhydrous salt:—[437]

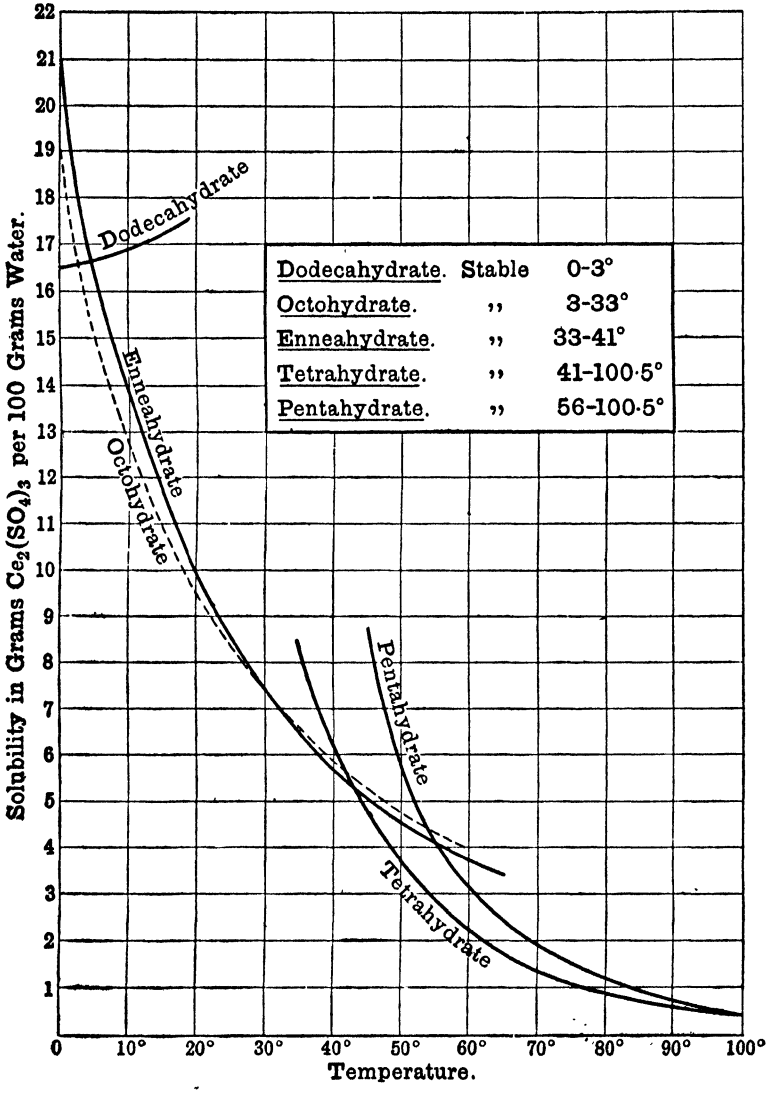



FIG. 6.

*From Cowley and Levy's Rare Earths (Edward Arnold).*

| Temperature | 0° | 15° | 20·5° | 30° | 40° | 50° | 60° |
|---|---|---|---|---|---|---|---|
| Grams . | 19·09 | 11·06 | 9·525 | 7·388 | 5·947 | 4·785 | 4·064 |

It is stable in contact with the solution between 3° and 33° and at 70° passes spontaneously into the pentahydrate.

A hexahydrate is stated to exist by Hermann[397] and Jolin,[419]

but Wyrouboff[438] and Koppel[437] have been unable to obtain this compound.

The pentahydrate is formed in monoclinic crystals by evaporating the solution between 70° and 100°.[436, 437, 438] It has specific gravity 3·220, specific heat 0·1999, and 100 grams of water contain, when saturated with this hydrate, the following weights of anhydrous salt:—[437]

| Temperature | 45° | 60° | 70° | 80° | 90° | 100·5° |
|---|---|---|---|---|---|---|
| Grams | 8·833 | 3·247 | 1·929 | 1·207 | 0·8355 | 0·469 |

It is stable in contact with solution between 56° and 100·5°.

The tetrahydrate is formed by heating the octohydrate to 100°, or by shaking the enneahydrate with a little water at 70°, or by evaporating a 1 per cent. solution of the sulphate on the water-bath, and sowing with the tetrahydrate.[437] A saturated solution of this hydrate contains the following weights of anhydrous salt per 100 grams of water:—[437]

| Temperature | 35° | 40° | 50° | 57° | 65° | 70° | 82° | 100·5° |
|---|---|---|---|---|---|---|---|---|
| Grams | 8·5 | 6·04 | 3·43 | 2·34 | 1·883 | 1·38 | 1·01 | 0·43 |

It is stable in contact with solution between 41° and 100·5°.

Cerous sulphate forms double sulphates with alkali sulphates and with the sulphates of certain other metals. The most important of these are the compounds with the alkali sulphates. When a concentrated solution of potassium sulphate is added to one of cerous sulphate, sparingly soluble double sulphates separate, which are still less soluble in solutions of potassium sulphate. At ordinary temperatures the salt $Ce_2(SO_4)_3,3K_2SO_4$ is formed whilst at 50° $Ce_2(SO_4)_3,2K_2SO_4,2H_2O$ separates. A solution containing one part of potassium sulphate to two or more of cerous sulphate yields the compound $2Ce_2(SO_4)_3,3K_2SO_4$. When a solution of sodium sulphate is added to one of cerous sulphate the compound $Ce_2(SO_4)_3,Na_2SO_4,2H_2O$ separates as a crystalline precipitate. From a solution of ammonium sulphate and cerous sulphate the compound $Ce_2(SO_4)_3,(NH_4)_2SO_4,8H_2O$ separates out on boiling. This compound loses $6H_2O$ at 100° and the remainder at 150°, but in contact with its saturated solution the whole of the water is lost at 45°, and the salt becomes anhydrous.[439, 440] The hydrated salt dissolves to the following amount in 100 grams of water:—

| Temperature | 22·3° | 35·1° | 45·2° |
|---|---|---|---|
| Grams, Anhydrous salt | 5·331 | 5·184 | 4·993 |

The anhydrous salt dissolves in water to the following extent per 100 grams of water:—[439, 440]

| Temperature | 45° | 55·3° | 75·4° | 82·2° |
|---|---|---|---|---|
| Grams | 2·994 | 2·240 | 1·482 | 1·184 |

In addition to the above-mentioned alkali double sulphates, Barre has isolated the following:—

$$Ce_2(SO_4)_3,K_2SO_4,2H_2O\,;\ 2Ce_2(SO_4)_3,3K_2SO_4,8H_2O\,;$$
$$Ce_2SO_4,5(NH_4)_2SO_4.$$

On mixing the corresponding solutions of sulphates, the double sulphates

$$Ce_2(SO_4)_3,3Tl_2SO_4,H_2O\,;\ Ce_2(SO_4)_3,Tl_2SO_4,4H_2O$$ [442]
and $Ce_2(SO_4)_3,CdSO_4,6H_2O$ [439]

are obtained. The last-named salt is best obtained from a slightly acid solution. A double sulphate

$$CeHSn(SO_4)_4 = Ce_2(SO_4)_3,2Sn(SO_4)_2,H_2SO_4$$

is formed as a microcrystalline powder by treating stannic sulphate with cerous sulphate.[443] Cerous sulphate forms double sulphates with the sulphates of pyridine and quinoline.[444] These salts, which are well crystallised, are formed by mixing solutions of the two sulphates. They have respectively the formulæ

$$Ce_2(SO_4)_3,3(C_5H_5N)_2H_2SO_4,3H_2O$$
and $Ce_2(SO_4)_3,6C_9H_7N,4H_2SO_4,17H_2O.$

*Cerium Acid Sulphate,* $Ce_2(SO_4)_3,3H_2SO_4 = CeH_3(SO_4)_3$.—This compound is obtained by dissolving the normal sulphate in concentrated sulphuric acid and crystallising.[445] It forms brilliant needles. It can also be formed by saturating ice-cold water with the anhydrous normal sulphate and precipitating with concentrated sulphuric acid.[446] The excess of free acid is removed by evaporating at 130° in a vacuum. It commences to decompose at 180°, and the decomposition is almost complete at 280.°

*Cerous Sulphite,* $Ce_2(SO_3)_3$, is formed by dissolving cerous carbonate in sulphurous acid; on warming the solution, the salt separates in small white prisms which have been obtained with 3 and 9 molecules of water of crystallisation.

*Cerous Nitrate,* $Ce(NO_3)_3,6H_2O$, is obtained by treating a solution of cerous sulphate with barium nitrate and by treating cerous oxide or oxalate with nitric acid in the presence of hydrogen peroxide.[419, 424] On evaporating the solution to a

syrupy consistency, the nitrate separates as a crystalline mass which is readily soluble in water and alcohol. At 100° it loses three molecules of water, and begins to decompose at 200°. It forms crystalline double nitrates with many metallic nitrates. When a solution of potassium nitrate is mixed with one of cerous nitrate and the mixed solution concentrated, small shining crystals of $Ce(NO_3)_3,2KNO_3,2H_2O$ separate. These crystals are completely dehydrated at 180°.[424] When sodium nitrate is substituted for potassium nitrate the double salt

$$Ce(NO_3)_3,2NaNO_3,H_2O$$

is formed in slender hygroscopic needles which are not completely dehydrated at 150°. The compounds

$$Ce(NO_3)_3,2Rb(NO_3),4H_2O \text{ and } Ce(NO_3)_3,2TlNO_3,4H_2O$$

are formed similarly in hygroscopic needles.[447] With ammonium nitrate under similar conditions the double salt

$$Ce(NO_3)_3,2NH_4NO_3,4H_2O$$

is formed.[439, 440] This substance is very soluble in water and may be recrystallised unchanged. It is stable between 9° and 65°; at 74° it melts in its water of crystallisation. At 25°, 100 parts of water saturated with this compound contain 296·8 grams of the anhydrous salt, and at 65°, 817·4 grams. The solubility between 25° and 65° is given by the expression $P = 68{\cdot}7 + 0{\cdot}172t + 0{\cdot}002t^2$ where P is the percentage of the anhydrous salt contained in the saturated aqueous solution. A second compound, $2Ce(NO_3)_3,3NH_4NO_3,12H_2O$, separates if the mixture of the two sulphates is crystallised at 0°. This substance on recrystallisation passes into the first-mentioned salt.[448] A second series of double nitrates is formed with the nitrates of sodium, rubidium, caesium, and thallium.[447, 449] This series has the general formula $3Ce(NO_3)_3,4M'NO_3,nH_2O$ where $n = 8$ in the case of rubidium and 5 in the case of caesium. A series of isomorphous double nitrates of the general formula $2Ce(NO_3)_3,3M''(NO_3)_2,24H_2O$ is formed with the metals magnesium, manganese, cobalt, nickel, and zinc. These salts are hexagonal, easily soluble in alcohol and water, and are formed by crystallising a mixture of the concentrated solutions of the two salts, when they form large six-sided tablets or prisms which possess a definite melting-point. They are soluble with

difficulty in concentrated nitric acid.[424, 448, 314, 450, 451] A number of double nitrates are formed with the nitrates of pyridine, quinoline and piperidine, and in the case of the two former compounds are

$$Ce(NO_3)_3,5C_5H_5N,HNO_3 \text{ (m.p. } 82{\cdot}5^\circ)$$
$$\text{and } Ce(NO_3)_3,3C_9H_7N,HNO_3,H_2O \text{ (m.p. } 165^\circ).^{444}$$

*Cerous Nitride*, CeN, is formed, according to Muthmann and Kraft,[452] by passing pure nitrogen over heated cerium. At a red heat the reaction occurs slowly, but at higher temperatures it occurs suddenly with incandescence and evolution of heat. Dafert and Miklauz[391] state that the nitride cannot be obtained by the above method, but may be prepared by passing nitrogen over the hydride at 800°-900°. It is also prepared by passing ammonia over the heated carbide[453] and by heating metallic cerium with molten potassium cyanide[454]

$$KCN + Ce = CeN + C + K.$$

Cerous nitride is variously described as a lustrous bronze, yellow, or white substance;[454] it is stable in dry air, but gives off ammonia and hydrogen in moist air. When moistened with water it becomes red hot, evolving ammonia and hydrogen,

$$2CeN + 4H_2O = 2CeO_2 + 2NH_3 + H_2$$

When treated with dilute mineral acids, cerous and ammonium salts are formed,

$$2CeN + 4H_2SO_4 = Ce_2(SO_4)_3 + (NH_4)_2SO_4.$$

*Cerous Phosphates.* — (*a*) *Cerous Orthophosphate*, $CePO_4$.— This compound constitutes the major part of monazite. It is obtained by fusing cerium dioxide with sodium metaphosphate.[432] When prepared artificially its colour varies from yellow to greenish-grey; it forms rhombic prisms and has a density of 5·22.

(*b*) *Cerous Hydrogen Pyrophosphate*, $CeH(P_2O_7)$, is formed by saturating a solution of pyrophosphoric acid with cerous carbonate.[419] It forms microscopic needles. The normal pyrophosphate[1004] $Ce_4(P_2O_7)_3,12H_2O$ is obtained by adding a cerous salt to an excess of a solution of sodium pyrophosphate.

(*c*) *Cerous Metaphosphate*, $Ce(PO_3)_3$, is formed by evaporating the hypophosphite with nitric acid and igniting the residue,[455] and also by treating the anhydrous sulphate with metaphosphoric acid.[456] It forms microscopic crystals which are insoluble in acids. It has a density 3·723.

*Cerous Carbonate*, $Ce_2(CO_3)_3,5H_2O$, is formed in microcrystalline prisms by adding ammonium carbonate to a solution of a cerous salt. It is sparingly soluble in water, but less so in dilute ammonium carbonate solution. It loses its water of crystallisation at 100°, and in contact with alkali carbonate solutions forms double carbonates. Small quantities of cerous carbonate stimulate the growth of plants.[457] Of the double carbonates the following are important: Cerous potassium carbonate

$$Ce_2(CO_3)_3,K_2CO_3,3H_2O \text{ and } Ce_2(CO_3)_3,K_2CO_3,12H_2O.$$

This is formed by dissolving cerous carbonate in a boiling solution of potassium hydrogen carbonate, and by adding a solution of cerous chloride to a 50 per cent. solution of potassium carbonate and diluting the mixture until the double salt just begins to separate. The precipitate, which is at first amorphous, slowly changes into silky leaflets, and these are readily soluble in 30 per cent. potassium carbonate. It is decomposed by water, and when allowed to stand in the air it becomes yellow owing to the formation of perceric potassium carbonate, $Ce(CO_3)_3,O_3,4K_2CO_3,12H_2O$, by autoxidation. Cerous sodium carbonate

$$2Ce_2(CO_3)_3,3Na_2CO_3,24H_2O$$

is formed as a gelatinous precipitate by adding sodium carbonate solution to a concentrated solution of cerous chloride. It slowly crystallises on standing and is quite insoluble in sodium carbonate solution. Cerous ammonium carbonate

$$Ce_2(CO_3)_3,(NH_4)_2CO_3,6H_2O$$

is formed as a voluminous precipitate by adding excess of ammonium carbonate to cerous chloride solution. The precipitate becomes crystalline on standing and acquires a yellow colour when left in contact with the air.

*Cerous Carbide*, $CeC_2$, is formed by heating 4 parts of cerium dioxide with 1 part of sugar charcoal in an electric furnace until the mixture melts. It forms microscopic crystals,[458,459] specific gravity 5·23. Water decomposes it, giving a mixture of hydrocarbons consisting approximately of 75 per cent. acetylene, 4 per cent. ethylene, and 21 per cent. methane. It is easily decomposed by mineral acids giving cerous salts. Sterba states that if in the preparation less carbon is used than indicated

above, a mixture of compounds is obtained, which, when treated with ice-cold water to decompose the cerous carbide, leaves behind brown crystals consisting of an oxycarbide, $Ce_3O_4C_2$. These crystals are comparatively stable towards water, and are decomposed by acids with the formation of unsaturated hydrocarbons.[401, 460] Damiens[461] considers that the above does not represent the facts accurately. He is of the opinion that the reduction of cerium dioxide by carbon takes place in three stages: $2CeO_2 + C = Ce_2O_3 + CO$: $Ce_2O_3 + 9C = 2CeC_3 + 3CO$: $CeC_3 = CeC_2 + C$. He describes the compound $CeC_3$ as a red crystalline substance which is very slowly attacked by water, with the formation of acetylenic hydrocarbons.

*Cerous Acetate*, $Ce(C_2H_3O_2)_3,1\frac{1}{2}H_2O$, is formed by treating cerous sulphate with barium acetate, and by dissolving cerous carbonate in acetic acid. It is a white crystalline salt which is less soluble in hot water than in cold water; 100 grams of saturated solution contain 19·61 grams of the anhydrous salt at 15° and 12·97 grams at 76·2°

*Cerous Oxalate*, $Ce_2(C_2O_4)_3,10H_2O$, is formed by precipitating cerous salts with oxalic acid or alkali oxalates in neutral or acid solutions. It crystallises in small rhombic crystals which are somewhat soluble in sulphuric acid and in ammonium oxalate solution. It dissolves readily in hydrochloric acid and separates from solution as a crystalline oxalo-chloride,

$$2CeCl_3,Ce_2(C_2O_4)_3.$$

The oxalate dissolves[517] in water to the extent 0·41 mgrms. per litre at 25°.

*Cerous Acetylacetonate*, $Ce(CH_3COCHCOCH_3)_3,3H_2O$, is obtained by digesting ceric hydroxide with acetylacetone,[461] and also by adding a mixture of ammonia and acetylacetone to cerous ammonium nitrate solution when a light yellow crystalline precipitate is formed. It is readily soluble in alcohol, forming a brownish-red solution and is hydrolysed by water. Melting-point 131°-132°. When treated with alcoholic ammonia it forms a crystalline addition compound,

$$Ce(CH_3COCHCOCH_3)_3NH_3.^{462}$$

A very large number of other cerous salts have been prepared, for description of which the reader is referred to the original memoirs. The most important of these are enumerated

below: The double *platinocyanide*, $2Ce(CN)_3,3Pt(CN)_2,18H_2O$, which forms yellow prisms with a blue metallic lustre;[424,463] the *azide*, $CeN_3$;[464] *perchlorate*, $Ce(ClO_4)_3,H_2O$;[419] *bromate*, $Ce(BrO_3)_3,9H_2O$;[465,510] *iodate*, $Ce(IO_3)_3,2H_2O$;[419,466] *selenates*,[419,472] $Ce_2(SeO_4)_3,6H_2O$; $9H_2O$ and $12H_2O$; *selenite*, $Ce_2(SO_3)_3,12H_2O$;[419,467] *silicate*, $Ce_2(SiO_3)_3$;[468] *tungstate*,[469,470,471] $Ce_2(WO_4)_3$; *cobalticyanide*,[1008] $Ce_2(Co(CN)_6)_2,9H_2O$, and a large number[312,253,440,511,512,514,515,516,202] of organic salts. The *cyanide* and *chlorate* have not been prepared, and apparently are not capable of existence.

## Ceric Compounds.

*Ceric Fluoride*, $CeF_4,H_2O$, is formed by dissolving ceric hydroxide in aqueous hydrofluoric acid. It forms a brown mass which on being heated evolves water, hydrofluoric acid, and probably fluorine. When ceric hydroxide is dissolved in a solution of potassium hydrogen fluoride a double fluoride $2CeF_4,3KF,2H_2O$ is produced as a microcrystalline powder which is insoluble in water.[420,421,473] A series of double fluorides[474] of the general formula $CeF_4,M''F_2,7H_2O$ are formed with the fluorides of the metals cadmium, copper, cobalt, nickel, and zinc by dissolving a mixture of the two hydroxides in hydrofluoric acid. These substances are slightly decomposed by water.

*Ceric Chloride* does not exist in the free condition, but if a ceric compound is dissolved in hydrochloric acid without warming, a dark red solution is obtained which in all probability contains the hypothetical acid $H_2CeCl_6$. This solution is slowly reduced on standing in the cold and rapidly on warming, in both cases with evolution of chlorine. A number of double chlorides, with the hydrochlorides of organic bases, corresponding with this acid are known, among which are ceric pyridinium chloride, $(C_5H_5NH)_2CeCl_6$, formed as a yellow crystalline precipitate by adding pyridine to a solution of ceric hydroxide in hydrochloric acid. This compound is decomposed by water but may be recrystallised from a mixture of ether and alcohol. Ceric quinolinium chloride, $(C_9H_7NH)_2CeCl_6$, is obtained similarly.[382] An oxychloride, $CeOCl_2,10H_2O$, is produced by the electrolysis of slightly hydrated molten cerous chloride.[947]

*Ceric Sulphate*, $Ce(SO_4)_2$.—The anhydrous compound is formed by warming cerium dioxide on the water-bath with concentrated sulphuric acid. No solution takes place but the change

is quantitative. The powder is washed with ice-cold water or with glacial acetic acid and dried over caustic alkali. Ceric sulphate can also be formed by fusing the dioxide with acid potassium sulphate.

Ceric sulphate is a deep yellow crystalline substance readily soluble in water, producing a reddish-yellow solution which becomes deep red on the addition of sulphuric acid. It is hydrolysed in solution and on dilution a lemon-yellow basic sulphate, $CeO_2,SO_3,2H_2O$, is deposited.[475, 405] A basic sulphate is also precipitated when the solution is boiled.[475] Ceric sulphate forms a crystalline hydrate, $Ce(SO_4)_2,4H_2O$. This may be prepared by dissolving the dioxide in moderately concentrated sulphuric acid, an orange-red solution being produced with the evolution of ozonised oxygen. On evaporating, ceric cerous acid sulphate is first deposited and then the crystalline hydrate. It may also be obtained by dissolving ceric sulphate in water and concentrating over sulphuric acid. It crystallises in sulphur-yellow rhombic crystals which are very soluble in water. Ceric cerous acid sulphate, $2Ce(SO_4)_2,Ce_2(SO_4)_3,H_2SO_4,24H_2O$, the preparation of which is given above, is an orange-red to dark-red coloured crystalline substance forming hexagonal prisms. The composition of the salt has been variously described, but in all probability that given above, which is due to Brauner, is correct.[476] Ceric sulphate and ceric compounds generally oxidise nitrites without evolution of gas in the cold. Hence this reaction may be used for the volumetric estimation of nitrites,

$$2Ce(SO_4)_2 + KNO_2 + H_2O = Ce_2(SO_4)_3 + KNO_3 + H_2SO_4.$$

The end of the reaction is known by the solution becoming yellow when the first drop of ceric sulphate in excess is added.[477] In addition to the basic sulphate mentioned above three others have been isolated. A dilute ice-cold solution of ceric sulphate, on standing twenty-four hours, deposits pale-yellow crystals of $4CeO_2,3SO_3,12H_2O$, whilst a saturated solution under the same circumstances deposits crystals of the composition

$$2CeO_2,3SO_3,4H_2O;$$

the latter compound is readily soluble in water.[478] When ceric sulphate is heated to 195° sulphur trioxide is lost and a pure white basic sulphate, $3CeO_2,4SO_3$, is formed.[405]

Ceric sulphate forms many double sulphates, among which the following may be noted. Ceric potassium sulphate,

$$Ce(SO_4)_2,2K_2SO_4,2H_2O,$$

is obtained by adding potassium sulphate to a sulphuric acid solution of ceric sulphate. It forms small sparingly soluble orange-yellow monoclinic prisms. On evaporating an acid solution of ceric sulphate and ammonium sulphate two ceric ammonium sulphates are formed, the solution depositing first small yellow crystals of $Ce(SO_4)_2,2(NH_4)_2SO_4,2H_2O$ and then orange-red monoclinic prisms of $Ce(SO_4)_2,3(NH_4)_2SO_4,2H_2O$. A compound,[479] $10Ce(SO_4)_2,6Ag_2SO_4$, is formed as a bright orange-yellow precipitate when silver nitrate is added to a solution of ceric sulphate in concentrated sulphuric acid. It dissolves slowly in cold water but is rapidly decomposed on boiling.

*Ceric Nitrate.*—Normal ceric nitrate has not yet been isolated, but a basic nitrate, $Ce(NO_3)_3,OH,3H_2O$, can be obtained by dissolving ceric hydroxide in concentrated nitric acid and evaporating in the presence of calcium carbonate. It forms long red needles and dissolves in water, forming a yellow solution which has an acid reaction; the colour slowly diminishing owing to hydrolysis. A freshly prepared solution immediately becomes dark red on the addition of nitric acid, but a solution which has lost its yellow colour only slowly becomes dark red on the addition of nitric acid. A freshly prepared solution is at once reduced to the cerous condition by the addition of hydrogen peroxide, but a solution which has lost its yellow colour is oxidised by hydrogen peroxide to the peroxide condition, and then after some time reduced to the cerous condition.[480] Double nitrates of the type $Ce(NO_3)_4,2M'NO_3$ are known with the metals of the alkalis. These double salts are formed by adding a solution of the alkali nitrate to a solution of ceric hydroxide in nitric acid. They are well-crystallised hygroscopic substances, readily soluble in water and alcohol but sparingly soluble in nitric acid.[436, 439, 480] One of the most important of the double nitrates is $Ce(NO_3)_4,2NH_4NO_3$, which is most economically prepared by the electrolytic oxidation of cerous ammonium nitrate. This is effected by placing a solution of 50 grams of cerous nitrate and 25 grams of ammonium nitrate in 200 c.c. of water in a beaker inside of which stands a porous cell containing nitric acid. The

anode consists of a platinum strip which is wrapped round the porous cell, and the cathode consists of a platinum wire which dips into the nitric acid. A current of 0·1-0·2 amps. per sq. dcm. is used for the electrolysis.[481]

Ceric ammonium nitrate has a colour similar to that of potassium bichromate; the solubility in water between 25° and 85° is given by the expression $P = 52{\cdot}07 + 0{\cdot}314t - 0{\cdot}0013t^2$ where $P$ is the percentage of the salt in the saturated aqueous solution. At temperatures above 60° it is partially decomposed to cerous nitrate, and at 122° the solution, after boiling for three hours, contains 9·8 per cent. of cerous nitrate.[440] A further series of double nitrates is formed with the nitrates of certain divalent metals; these have the formula $Ce(NO_3)_4,M''(NO_3)_2,8H_2O$, and are formed by the addition of the nitrate of the divalent metal to a solution of ceric hydroxide in nitric acid. The best known are those of magnesium, manganese, zinc, cobalt, and nickel; they are well-crystallised salts, soluble in water and nitric acid. They are characterised by their intense colour, the salts of zinc, magnesium, and manganese being dark red, that of nickel olive-brown, and the cobalt salt dark reddish-violet.

*Cerium Disulphide*, $Ce_2S_4$, is obtained by heating anhydrous ceric sulphate in sulphuretted hydrogen.[433] It is a dark yellowish-brown crystalline substance which dissolves in 17·7 per cent. hydrochloric acid, forming hydrogen disulphide with subsequent deposition of sulphur. Biltz [433] is of the opinion that this behaviour proves that the disulphide is not the analogue of the dioxide, but a polysulphide $Ce_2S_3,S$. It decomposes at 720° into cerous sulphide and sulphur. Among other ceric salts which have been prepared are the *selenite* $Ce(SeO_3)_2$,[482] *acid arsenates* $Ce(H_2AsO_4)_4,H_2O$, and $Ce(HAsO_4)_2,6H_2O$,[482] and many organic compounds.

## Perceric Compounds.

*Potassium Perceric Carbonate*[1009] is prepared by treating a saturated solution of potassium carbonate with hydrogen peroxide, adding a solution of cerous ammonium nitrate and heating to 60° as long as the colour deepens. The solution is cooled to 0° and carbon dioxide is bubbled into the solution as long as potassium hydrogen carbonate separates. The bicarbonate is

removed by filtration and the filtrate kept at 5° for forty-eight hours, when the double perceric carbonate

$$Ce_2O_4(CO_3)_2,4K_2CO_3,12H_2O$$

crystallises out. The corresponding sodium compound cannot be obtained by the same method, but a solution of the ammonium compound is obtained in this way. The sodium compound [1010] $Ce_2O_4(CO_3)_2,4Na_2CO_3,30H_2O$ may be obtained by adding an excess of sodium carbonate to the solution of the ammonium salt. This compound separates in well-formed crystals which are sparingly soluble in cold water and are hydrolysed in warm water with the formation of an orange-yellow precipitate. A similar rubidium compound has been prepared.

**Estimation of Cerium.**—Pure cerous or ceric compounds when in solution are estimated by precipitation as oxalate in the presence of free mineral acid. The precipitate is collected, washed, dried, and ignited to dioxide, in which form it is weighed.

Ceric compounds are estimated by heating with potassium iodide and a slight excess of hydrochloric acid. Iodine is liberated in accordance with the equation

$$2CeO_2 + 8HCl + 2KI = 2CeCl_3 + 4H_2O + I_2,$$

and is estimated by titration, after dilution, with standard sodium thiosulphate [265, 317, 489, 425, 490] solution. This method may not be used in the analysis of mixtures of cerium earths, for praseodymium and neodymium are capable of liberating iodine in the same way. The estimation of cerium in mixtures of the earths may be effected volumetrically in several ways.

(*a*) A solution containing all the cerium in the ceric condition can be estimated by von Knorre's [337, 491] method. The solution is made acid with sulphuric acid and then treated with a measured excess of a very dilute solution of standard hydrogen peroxide; the solution is thereby reduced and becomes colourless. The excess of hydrogen peroxide is then determined by titration with standard permanganate solution. Should the cerium be present in the cerous condition the solution is acidified with sulphuric acid and raised to the boiling-point; ammonium persulphate or bismuth tetroxide is then added in small quantities at a time until 3 grams have been added for every quarter of a gram of cerium present. The solution is then boiled until the whole of the persulphate is decomposed. The

solution now contains the cerium in the ceric condition, and this is estimated as above,[337, 491, 492, 493, 494]

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2.$$

(*b*) Cerous compounds can be estimated by adding the cerous solution from a burette to a measured quantity of standard permanganate to which a quantity of magnesia, zinc oxide, calcium carbonate, or magnesium carbonate, has been added. The disappearance of the red colour denotes the end of the reaction which proceeds according to the equation :[80, 227, 495, 509]

$$3Ce_2O_3 + 2KMnO_4 + H_2O = 6CeO_2 + 2KOH + 2MnO_2.$$

The reaction is best carried out as described above, for if the permanganate is added to the cerous salt and base, a portion of the cerium is oxidised by the air. Potassium permanganate in acid or neutral solution oxidises cerous compounds very slowly, and is therefore not suitable for estimations. If magnesia is used as the base then the results are good, the other bases invariably give a result which is too low. In the presence of the other cerite earths the results are always too high.

(*c*) Cerium when in the cerous condition can be volumetrically estimated in the presence of the other rare earths by the reduction of potassium ferricyanide in the following way :—[496]

A measured volume of a solution containing about 0·1 gram of cerium is treated with a measured excess of standard potassium ferricyanide solution of about 2 per cent. concentration and a slight excess of a solution of potassium hydroxide. The precipitate is filtered off and the filtrate and washings, amounting to about 200 c.c., are made slightly acid with sulphuric acid and the ferrocyanide titrated with standard permanganate. The reactions take place according to the equations :—

(i) $2K_3Fe(CN)_6 + Ce_2O_3 + 2KOH = 2K_4Fe(CN)_6 + 2CeO_2 + H_2O$

(ii) $5K_4Fe(CN)_6 + KMnO_4 + 4H_2SO_4 = 5K_3Fe(CN)_6 + 3K_2SO_4 + MnSO_4 + 4H_2O.$

(*d*) A solution containing cerium as sulphate is mixed with 1 gram of sodium bismuthate and 2 grams of ammonium sulphate, and boiled to oxidise the cerium to the ceric condition. 50 c.c. of 2 per cent. sulphuric acid and a measured excess of standard ferrous ammonium sulphate solution are added to the filtered solution and the excess of ferrous iron is then titrated with standard permanganate.[497, 498]

**Catalytic Action of Cerium Compounds.**—Many of the compounds of cerium exhibit strong catalytic properties in connection with many types of chemical reactions. Cerium chloride, and indeed the chlorides of all the rare earths, exhibit an oxydase action and accelerate the rate of absorption of oxygen by hydroquinone. Fouard [499] has shown, that when a quantity of hydroquinone is sealed in a series of tubes, together with equivalent quantities of chlorides of the rare earths and a measured volume of air, larger quantities of oxygen are absorbed than would be the case in the absence of the rare earth chlorides. Thus the following percentages of the oxygen present are absorbed in the different cases: with samarium chloride 75·75 per cent.; thorium chloride 63·1 per cent.; cerous chloride 57·71 per cent.; neodymium chloride 54·23 per cent.; praseodymium chloride 53·35 per cent.; and lanthanum chloride 22·60 per cent. When sodium chloride was used the percentage of oxygen absorbed was only 17·82 per cent. The velocity of oxidation of oxalic acid by nitric acid is greatly accelerated by the presence of cerous sulphate, whereas the sulphates of yttrium, lanthanum, praseodymium and neodymium have no such action. Oxalic acid is rapidly oxidised by potassium permanganate in the cold in the presence of cerous salts, thus showing that cerium is akin to manganese in this respect.[500] A layer of cerium dioxide serves as a catalytic agent in the burning of organic substances in the Dennstedt method [411] of combustion; it is not "poisoned" by arsenious oxide or sulphur dioxide. Ammonia is oxidised at 650° when passed over a layer of cerium dioxide; the oxides of lanthanum, praseodymium, and neodymium have the same action.[501] Nitrogen and hydrogen when passed over cerium nitride at 200° combine to form ammonia to the extent of about 1 per cent.[502]

**Spectra of Cerium.**—Cerous salts being colourless have no visible absorption spectrum; the yellow and red ceric salts give absorption at the blue and violet end of the visible spectrum. The emission spectrum of cerium is one of the richest in lines. The spark spectrum has been measured by Brauner,[263] Cooper,[503] Exner, and Haschek;[504] and the arc spectrum by Cooper,[505] Eder,[612] Bakowski,[506] Eder and Valenta,[507] and Exner and Haschek.[508] The last-named investigators have measured 2894 lines in the arc spectrum in the region 2051-6774.

The following lines of intensity 10 are the most suitable for

the detection of cerium: 4150·11, 4186·78, 4222·78, 4296·88, 4337·96, 4382·32, 4386·95, 4460·40, 4479·52, 4487·06, 4527·51, 4528·64, 4539·90, 4562·52, 4572·45, 4594·11, 4628·33, and 5512·72.

## LANTHANUM, La. At. Wt. 139·0.

Lanthanum was discovered in 1839 by Mosander,[17] who separated it from the original cerium. It is the most strongly electropositive of all the rare earth metals, and forms an oxide $La_2O_3$ which is a strong base. This oxide absorbs carbon dioxide from the air, and slakes in the same way as quicklime when sprinkled with water. When moist it turns litmus blue and liberates ammonia from ammonium salts. The salts of lanthanum are colourless and only slightly hydrolysed by water. In general, lanthanum is nearly related in its properties to the metals calcium and magnesium. The solubility of its salts is such that it is the most easily separated of the rare earths by methods of fractional crystallisation. Lanthanum occurs in all the minerals which contain cerium, and is found to the largest extent in lanthanite and beckelite, and to a fairly large extent in orthite, cerite and samarskite.

Pure lanthanum compounds are most easily obtained:—

1. By the fractional crystallisation of the double magnesium nitrates of the cerium earths after the cerium has been removed[75, 281, 347, 356] (see Chap. III., p. 28).

2. By the double carbonate method after the separation of the cerium[77, 518] (Chap. III., p. 43).

Metallic lanthanum is obtained by the reduction of the chloride by means of potassium; in this way the metal is obtained as a powder and is not pure. It can be obtained in the coherent condition by the electrolysis of the fused anhydrous chloride;[385] the most satisfactory method of preparing metallic lanthanum consists in the electrolysis of a fused mixture of anhydrous lanthanum chloride, potassium chloride, sodium chloride, and barium chloride by the method described for the preparation of metallic cerium. A current of 50 ampères at 10-15 volts is required in this case and the cathode carbon must be very small to ensure a sufficiently high temperature to melt the liberated metal.[228, 416]

Lanthanum is an iron-grey metal capable of taking a high polish, but it tarnishes immediately in dry air, and becomes

coated with a steel-blue film. It is ductile and may be hammered into foil or drawn into wire. It melts at 810°, has a specific gravity 6·1545 and a specific heat 0·04485 at ordinary temperatures. At temperatures between the boiling-points of hydrogen and nitrogen the specific heat is 0·0322.[390] It is paramagnetic, and has a heat of combustion per gram of 1602 cals. The heat of formation of the oxide being $1/6La_2O_3 = 74{\cdot}1$ Cal., a value which is larger than that of aluminium, and shows that metallic lanthanum cannot be reduced from its oxide by means of aluminium. The hardness of lanthanum lies between that of cerium and zinc. In moist air lanthanum is rapidly converted into the hydroxide, and when heated in the air it burns and is converted into a mixture of oxide and nitride. The finely divided metal burns brilliantly when thrown into a Bunsen flame. It takes fire when thrown into chlorine, combines with bromine vapour with evolution of light, and with iodine vapour without the evolution of light. It is slowly converted into the hydroxide by cold water but rapidly by hot water, in both cases with the evolution of hydrogen. When heated in hydrogen it is converted into the hydride, and with nitrogen it forms the nitride. Cold concentrated sulphuric acid has little action on lanthanum, but dilute sulphuric acid and hydrochloric acid attack it violently; nitric acid oxidises it violently. Lanthanum forms alloys with aluminium and iron; in the former case a compound, $LaAl_4$,[519] has been isolated in lustrous rhombic or monoclinic crystals which are stable in the air. They are unattacked by nitric acid, slowly dissolved by hydrochloric acid, and rapidly dissolved by concentrated sulphuric acid. The crystals have a specific gravity 3·923. The iron alloys of lanthanum are pyrophoric and give sparks when struck just as in the case of the cerium alloys. The maximum of the pyrophoric property occurs at 30 per cent. lanthanum.[520]

## Lanthanum Compounds.

*Lanthanum Oxide*, $La_2O_3$, is formed by the ignition of the hydroxide, carbonate, nitrate, or oxalate. It cannot be obtained quite free from sulphuric acid by ignition of the sulphate unless a very high temperature is used.

It is a pure white powder which rapidly absorbs water and carbon dioxide from the air, and slakes, in the same way as quicklime, with the evolution of heat, when sprinkled with water. It

has a specific gravity 5·97 (Hermann),[521] 6·53 (Cleve);[31] specific heat 0·0749.[522] It is diamagnetic[368] and has a susceptibility $\mu = -0{\cdot}18 \times 10^{-6}$. It is easily soluble in acids even after strong ignition, and can be reduced to the metal by heating with magnesium.[523] When fused with borax it is obtained in rhombic prisms of specific gravity 5·296.[524]

*Lanthanum Hydroxide*, $La(OH)_3$, is formed as a white slimy precipitate by the addition of ammonia or alkali hydroxide to a solution of a lanthanum salt. It dries to a white powder which is alkaline to litmus, absorbs carbon dioxide from the air, and liberates ammonia from ammonium salts. It is the strongest base of all the rare earths. It has been stated that lanthanum hydroxide possesses acidic properties and forms lanthanates when fused with alkali carbonates.[525] This statement has not been confirmed and appears to be extremely unlikely when the similarity of lanthanum hydroxide to calcium hydroxide is considered. Vesterberg[1011] considers that the strength of the base is comparable with that of ammonium hydroxide.

*Lanthanum Peroxide.*—When solutions of lanthanum salts are treated with ammonia in the presence of hydrogen peroxide a gelatinous hydrated peroxide is precipitated, to which Cleve[526] attributes the formula $La_4O_9$; Melikoff and Pissarjewski,[222] however, give it the formula $La_2O_5,nH_2O$ or $LaOOH,(OH)_2$. When treated with dilute sulphuric acid or with carbonic acid, this compound liberates hydrogen peroxide; concentrated sulphuric acid liberates ozonised oxygen. On standing over sulphuric acid water and oxygen are lost. Lanthanum oxide does not absorb oxygen[314] when heated in the air unless an "activating" substance such as cerium dioxide is present.[265] Under these circumstances, oxygen is absorbed and an oxide with the nature of a peroxide is produced.

*Lanthanum Hydride*, $LaH_3$, is formed by passing hydrogen over the metal at 240° when combination occurs with incandescence.[416]

It is a black powder which does not take fire in the air, has a specific heat 0·0873,[527, 528, 529] and generally has similar properties to cerium hydride, but is less stable.

*Lanthanum Fluoride*, $LaF_3$.—Anhydrous lanthanum fluoride has been obtained by the action of fluorine on the carbide.[530] When hydrofluoric acid is added to a solution of the acetate a

white gelatinous precipitate of $2LaF_3,H_2O$ is formed,[81] but if a solution of the sulphate is treated similarly, the compound $2LaF_3,3HF$ is obtained.[531]

*Lanthanum Chloride*, $LaCl_3$, is prepared by heating the oxide in a mixture of sulphur monochloride and chlorine ;[532, 533] by heating the sulphide[429] or carbide[534] in hydrochloric acid gas ; by heating the hydrate with ammonium chloride[521] or hydrochloric acid gas ;[535] or by heating the carbide in chlorine.[530]

The anhydrous salt is colourless and crystalline, very soluble in water with a large evolution of heat, and soluble in alcohol. It melts at 907°, and the melt solidifies to form long deliquescent needles, which resemble arragonite and have a specific gravity 3·947.[536] The molecular heat of solution is 31·3 cal. and the heat of formation from oxide and hydrochloric acid gas 80·3 cal.[536] The molecular weight determined by the ebullioscopic method in alcohol solution corresponds with the formula $LaCl_3$. In aqueous solution it is hydrolysed to a very slight extent,[537] and the solution deposits large colourless triclinic crystals of $2LaCl_3,15H_2O$ and $LaCl_3,7H_2O$ which dissolve readily in alcohol. An alcoholic solution deposits crystals of $LaCl_3,2C_2H_6O$.[425] Solutions of lanthanum chloride are physiologically active, a 0·8 per cent. solution coagulates the proteins in serum, and 0·1 gm. injected hypodermically in guinea-pigs causes convulsions followed by death. Small doses of lanthanum chloride have little or no effect on bacteria.[539] Lanthanum chloride forms a large number of double chlorides with chlorides of various metals, among which may be noted :—

$LaCl_3,4HgCl_2,12H_2O$ ;[538] $LaCl_3,2BiCl_3,8H_2O$ ;[540]
$2LaCl_3,3SbCl_3,20H_2O$ ;[540] $2LaCl_3,3PtCl_2,18H_2O$ ;[541]
$LaCl_3,PtCl_4,13H_2O$ ;[31] $2LaCl_3,3PtCl_4,24H_2O$ ;[531]
$LaCl_3,AuCl_3,10H_2O$ ;[31] and $2LaCl_3,3AuCl_3,21H_2O$.[541]

When solutions of lanthanum chloride are evaporated with solutions of organic bases, crystalline double compounds are formed in many cases : with pyridine, the compound

$$2LaCl_3,3C_5H_5N,HCl,2C_2H_6O$$ [425]

separates from alcoholic solution ; the compound

$$LaCl_3,2C_6H_{12}N_4,14H_2O$$ [428]

is formed with hexamethylene tetramine, and

$$LaCl_3,3NH_2CH_2COOH,3H_2O$$

is formed in colourless prismatic needles with glycocoll.[548]

Hydrated lanthanum chloride loses both water and hydrochloric acid when heated and forms the basic chloride

$$2LaCl_3,3La_2O_3.^{521}$$

A second basic chloride is formed when lanthanum oxide is heated in chlorine at 200°. This has the formula

$$LaCl_3,La_2O_3 = LaOCl.^{542}$$

*Lanthanum Bromide*, $LaBr_3$.—The anhydrous bromide is obtained by heating lanthanum oxide in a mixture of sulphur monochloride and hydrogen bromide at temperatures just below a red heat.[431] A white fused mass is thus obtained which dissolves in water, with a hissing noise, producing a solution in which the salt is slightly hydrolysed and which turns litmus a port wine tint but is without action on methyl orange. A crystalline hydrate, $LaBr_3,7H_2O$, is formed in colourless crystals when a solution of lanthanum oxide in hydrobromic acid is evaporated.[31]

The crystalline salt is readily soluble in alcohol and water, and forms a number of double bromides with various metallic bromides, among which the following may be noted:

$2LaBr_3,3ZnBr_2,39H_2O$;[531] $LaBr_3,BiBr_3,12H_2O$;[540]
$LaBr_3,SbBr_3,12H_2O$;[540] $LaBr_3,3SbBr_3,20H_2O$;[540]
$2LaBr_3,3NiBr_3,18H_2O$;[531] and $LaBr_3,AuBr_3,9H_2O$[31].

A basic bromide, LaOBr, is formed when lanthanum oxide is heated in bromine vapour.[531]

*Lanthanum Iodide* is unknown, but a double lanthanum zinc iodide, $2LaI_3,3ZnI_2,27H_2O$, has been described by Frerichs and Smith.[531]

*Lanthanum Sulphide*, $La_2S_3$, is formed by heating the oxide in sulphuretted hydrogen[468] or in carbon disulphide vapour to a fairly high temperature. A more convenient method of preparation is to heat the anhydrous sulphate in sulphuretted hydrogen to 650°.[429] In this reaction a disulphide, $LaS_2$, is first formed, but this substance is completely decomposed at 650°.[544]

It is a yellow powder fairly stable in the air but decomposed by boiling water. On ignition in air it is converted into a mixture of the oxide and sulphate.

*Lanthanum Sulphate*, $La_2(SO_4)_3$.—The anhydrous sulphate is obtained by dehydrating the crystalline hydrate or by heating the oxide with concentrated sulphuric acid. These processes

must be carried out at 600°-650°, otherwise, in the first case, the whole of the water will not be expelled, and, in the latter case, some acid sulphate will remain undecomposed.[281, 348, 347]

It is a white hygroscopic powder, very soluble in water, 1 part of the sulphate dissolving in 6 parts of water at 2°-3°, and 1 part in 115 parts of water at 100°. It readily forms supersaturated solutions and has a specific gravity 3·6, a specific heat 0·1186,[545] and heat of formation 138·2 cal.[547]

It forms crystalline hydrates with 16, 9, and 6 molecules of water; of these the most important is the enneahydrate, $La_2(SO_4)_3,9H_2O$.[257] This substance is stable over the range of temperature 0°-100°, and separates when a solution of the anhydrous salt is warmed to 30°-40°. It forms large hexagonal prisms isomorphous with the corresponding hydrate of cerous sulphate. It is the least soluble of all the tervalent sulphates of the rare earths. A saturated solution contains the following weights of anhydrous sulphate in 100 grams of water.[257]

| Temperature | 0° | 14° | 30° | 50° | 75° | 100° |
|---|---|---|---|---|---|---|
| Grams | 3·0 | 2·6 | 1·9 | 1·6 | 1·0 | 0·7 |

The hydrate, $La_2(SO_4)_3,16H_2O$, is obtained in fine needles by crystallising from an ice-cold saturated solution. It is very unstable and commences to decompose at 0°.[281]

The hexahydrate, $La_2(SO_4)_3,6H_2O$, separates from a strongly acid solution of the sulphate.[531]

Solutions of lanthanum sulphate, like solutions of most lanthanum salts, are physiologically active. When injected into monkeys, it is shown to have a beneficial effect in cases of experimental cholera.[546]

An acid sulphate, $LaH_3(SO_4)_3$, is formed in fine white silky needles when a concentrated solution of lanthanum sulphate in concentrated sulphuric acid is allowed to stand. This substance commences to lose sulphuric acid at 180°, and at 280° 95 per cent. of the free sulphuric acid is rapidly expelled. The remaining sulphuric acid is not lost until a temperature of 600°-650° is reached.[446]

When ammonia is added to solutions of lanthanum sulphate, basic sulphates of variable composition are formed and not the hydroxide.[531] A basic sulphate, $La_2O_3,SO_3$, is formed in white needles by heating the anhydrous sulphate to 700°.[349]

Lanthanum sulphate forms a series of double salts with

metallic sulphates of which the following are the most important: lanthanum potassium sulphate, $La_2(SO_4)_3,3K_2SO_4$, which is formed as a sparingly soluble crystalline precipitate when excess of potassium sulphate is added to a solution of lanthanum sulphate; lanthanum sodium sulphate, $La_2(SO_4)_3,Na_2SO_4,2H_2O$, and lanthanum ammonium sulphate,

$$La_2(SO_4)_3,(NH_4)_2SO_4,8H_2O,$$

both of which are formed in the same way as the potassium compound. Other alkali double sulphates include:—

$3La_2(SO_4)_3,2Rb_2(SO_4)$;[548] $La_2(SO_4)_3,Rb_2SO_4,2H_2O$[548]; $La_2(SO_4)_3,Cs_2SO_4,2H_2O$;[548] $3La_2(SO_4)_3,2Cs_2SO_4$;[548] $La_2(SO_4)_3,5K_2SO_4$;[441] $La_2(SO_4)_3,K_2SO_4,2H_2O$,[441] and $La_2(SO_4)_3,5(NH_4)_2SO_4$.[441]

A double cerium lanthanum acid sulphate, $CeHLa(SO_4)_4,12H_2O$,[476] and lanthanum stannic acid sulphate, $LaHSn(SO_4)_4$,[443] are known. Lanthanum sulphate combines with pyridine sulphate to form $La_2(SO_4)_3,6C_5H_5N,3H_2SO_4,4H_2O$[444] in lustrous columnar crystals. Similar compounds are also formed with the sulphates of quinoline and hydrazine.[444]

*Lanthanum Nitride*, LaN, is formed along with the oxide when lanthanum burns in the air.[416, 528, 529] It is also formed by heating the metal in nitrogen or ammonia.[534] As thus prepared it is described as a black powder which is decomposed in moist air, forming lanthanum hydroxide and liberating ammonia. It can also be prepared by heating the metal with potassium cyanide when it is obtained as a white powder.[454]

*Lanthanum Nitrate*, $La(NO_3)_3,6H_2O$, is formed by dissolving the oxide, hydroxide, or carbonate in nitric acid and evaporating the solution. It forms large colourless triclinic pyramids, which are readily soluble in water and alcohol. On heating, it is converted first into a basic nitrate and finally into oxide. The fermenting power of yeast is destroyed by 5 per cent. solutions of the nitrate.[549] Lanthanum nitrate forms double salts with alkali nitrates. The compound, $La(NO_3)_3,2NH_4NO_3,4H_2O$, is the most important of these; it forms large monoclinic crystals which are isomorphous with the corresponding cerium and didymium compounds. The following double alkali nitrates[447, 449] have been isolated:—

$3La(NO_3)_3,4NaNO_3,3H_2O$; $La(NO_3)_3,2NaNO_3,H_2O$; $La(NO_3)_3,2KNO_3,H_2O$; $La(NO_3)_3,4KNO_3,4{\cdot}5H_2O$; $3La(NO_3)_3,4RbNO_3,8H_2O$; $La(NO_3)_3,2RbNO_3,4H_2O$; $3La(NO_3)_3,4CsNO_3,5H_2O$; and $La(NO_3)_3,2CsNO_3,H_2O$.

All these compounds crystallise well, but if they are deposited from solutions above 70° they all separate anhydrous with exception of the sodium salts.

A series of isomorphous double nitrates is formed with the nitrates of the bivalent metals nickel, cobalt, zinc, manganese, and magnesium. These have the general formula,

$$2La(NO_3)_3,3M''(NO_3)_2,24H_2O,$$

and form hexagonal crystals.[451, 550] Lanthanum [1012] ferrous nitrate, $2La(NO_3)_3,3Fe(NO_3)_2,24H_2O$, has also been prepared in flat green hexagonal crystals.

Double nitrates are formed with pyridine,[444] quinoline,[444] and hexamethylene tetramine.[428] These have, respectively, the formulæ,

$La(NO_3)_3,5C_5H_5N,HNO_3,H_2O$ (m.p. 91·5°);
$La(NO_3)_3,3C_9H_7N,HNO_3,H_2O$ (m.p. 153°),
and $La(NO_3)_3,2C_6H_{12}N_4,8H_2O$.

A double compound is also formed with antipyrine.[551]

*Lanthanum Carbide*, $LaC_2$, is obtained by reducing the oxide with sugar charcoal in an electric furnace.[458, 459, 530, 534] It is a yellow microcrystalline substance and has a specific gravity 4·71 (Pettersson),[534] 5·02 (Moissan).[530] It is decomposed by water, giving a mixture of gases containing 70-71 per cent. acetylene, 27-28 per cent. methane, and 1-2 per cent. ethylene, with traces of solid and liquid hydrocarbons.

*Lanthanum Carbonate*, $La_2(CO_3)_3$, occurs naturally as lanthanite, $La_2(CO_3)_3,8H_2O$. It forms, in addition, hydrates with 3 molecules and with 1 molecule of water. When lanthanum salts are precipitated by alkali carbonate a gelatinous precipitate is formed, which when dried at 100° gives a white powder of $La_2(CO_3)_3,H_2O$. If the precipitate is left in contact with the solution, or if carbon dioxide is passed through water containing the hydroxide in suspension, the carbonate is formed in shining leaflets.[31]

Lanthanum carbonate forms double salts with alkali carbonates. The most important may be mentioned here, lanthanum

potassium carbonate, $La_2(CO_3)_3,K_2CO_3,12H_2O$, is formed in shining needles by adding a solution of the chloride to a 50 per cent. solution of potassium carbonate; a precipitate is first formed which redissolves, and on diluting, the double carbonate crystallises. It is decomposed by water. Lanthanum sodium carbonate, $2La_2CO_3)_3,3Na_2CO_3,20H_2O$, is formed as a heavy gelatinous precipitate by adding a concentrated solution of a lanthanum salt to a cold concentrated solution of sodium carbonate; and lanthanum ammonium carbonate, $La_2(CO_3)_3,(NH_4)_2CO_3,4H_2O$, is formed as a gelatinous precipitate, which slowly becomes crystalline, by adding a solution of lanthanum chloride to a 20 per cent. solution of ammonium carbonate.

*Lanthanum Acetate*, $La(C_2H_3O_2)_3,1\frac{1}{2}H_3O$, is formed by dissolving the carbonate or hydroxide in acetic acid. On concentrating, a syrupy solution is obtained which deposits prisms of the above composition.[31, 552, 553, 1011] When a solution of lanthanum acetate is treated with ammonia a slimy precipitate of basic acetate is produced, which, after washing, absorbs iodine and takes on an intense blue colour.[554] Lanthanum acetate acts as an oxygen carrier in the oxidation of hydroquinone, and this points to the possibility of lanthanum existing in a higher state of oxidation.[555]

*Lanthanum Oxalate*, $La_2(C_2O_4)_3,9H_2O$, is formed by precipitating a solution of a lanthanum salt with oxalic acid or an alkali oxalate in neutral or acid solution. It forms a semi-liquid precipitate which speedily becomes crystalline and is then isomorphous with cerous oxalate. It is sparingly soluble in water, a litre of water[517] dissolving 0·62 milligram of the oxalate at 25°. It is more soluble than the other rare earth oxalates in mineral acids[556] and in ammonium oxalate.[223] It appears that the number of molecules of water of crystallisation depends on the temperature at which the precipitate is washed, for it has been obtained with 3, 5, 7, 8, 10, and 11 molecules of water.[347, 557, 558]

When oxalic acid is added to a solution of lanthanum chloride in strong hydrochloric acid solution an oxalo-chloride is precipitated; in the same way an oxalo-nitrate is formed when the nitrate is used in nitric acid solution. On crystallising lanthanum oxalate from hydrochloric acid an oxalo-chloride, $LaC_2O_4Cl$, is formed which is decomposed by water into oxalate and chloride, and on ignition forms LaOCl.

*Lanthanum Acetylacetonate*, $La(CH_3COCHCOCH_3)_3$, is formed by shaking a warm alcoholic solution of acetyl acetone with lanthanum hydroxide.[559] It forms small white needles which melt at 185°, and can be crystallised from aqueous solution when crystals containing three molecules of water are obtained.[462]

Among other lanthanum compounds, the following have been prepared, for details of which the reader is referred to the original memoirs: *Azide*,[560] *bromate*,[510, 521, 538] *cobalticyanide*,[1008] *iodate*,[31, 466, 521] *ferricyanide*,[1001] *selenate*,[31] *phosphate*,[31, 521, 561] and a large number of organic compounds.[202, 253, 307, 312, 511, 553, 562, 563, 564, 565, 1012]

## Detection of Lanthanum.

1. When lanthanum acetate is precipitated with ammonia a slimy semi-transparent precipitate is produced. This precipitate, when well washed and treated with a little iodine solution, slowly takes on a deep blue colour which slowly permeates the whole mass. The reaction only occurs when the acetate is used and when the precipitate is slimy. If the precipitation is effected from hot solution, the basic acetate is granular, and this does not form the absorption compound with iodine. The reaction is indeterminate and useless in the presence of other cerium earths.

2. The only reliable test for lanthanum is the spectroscopic examination. Detection is very sharp when the arc spectrum, particularly the violet and ultra violet, is examined. The other regions of the spectrum are not so characteristic. The best test for the purity of lanthanum compounds is the absence of absorption and luminescence spectra.

## Estimation of Lanthanum.

Lanthanum is estimated in the pure salts by precipitating as oxalate or hydroxide and igniting to oxide, in which form it is weighed. In the presence of the other rare earths there is as yet no method known for the estimation of lanthanum.

Lanthanum may be estimated volumetrically by means of oxalic acid and potassium permanganate.[566] For this purpose 10-20 c.c. of a neutral 1 per cent. solution of the nitrate is mixed with a measured excess of $\frac{N}{10}$ oxalic acid or $\frac{N}{10}$ ammonium oxalate and a few drops of acetic acid. The precipitated oxalate is collected in a Gooch crucible and thoroughly washed with

water. The crucible and contents are then placed in a beaker containing 100-300 c.c. of water and 10-30 c.c. of 10 per cent. sulphuric acid. The liquid is heated to the boiling-point and at once titrated with $\frac{N}{10}$ permanganate. As a check, the filtrate may also be titrated with $\frac{N}{10}$ permanganate and the excess of oxalic acid, originally taken, estimated.

### Spectra of Lanthanum.

The spark spectrum of lanthanum has been investigated by Bettendorf,[567] Forsling,[568] Crookes,[108] Lohse,[569] and by Exner and Haschek.[504, 508]

The arc spectrum has been investigated by Exner and Haschek,[504, 508] Eder,[612] Kellner,[570] Wolff,[571, 575] and Eder and Valenta.[574] Wolff has also described the band arc spectrum.[575]

Lanthanum has no absorption spectrum, and when absolutely pure no cathode luminescence spectrum. The records which describe a luminescence spectrum are based on experiments with slightly impure material.[62, 63, 572, 573] Spectrum regularities are discussed by Paulson.[1013]

The most characteristic lines in the lanthanum spectrum are 3949·27 and 4238·55 of intensity 20, and 3988·69, 4333·98, 6250·14, 6262·52, and 6394·46 of intensity 15.

## PRASEODYMIUM, Pr. At. Wt. 140·9.

Praseodymium was discovered in 1885 by Auer von Welsbach[55] as a constituent of the old didymium which had been separated from lanthanum in 1841 by Mosander.[18] Praseodymium forms two well-defined oxides, $Pr_2O_3$ and $PrO_2$, a hydrated peroxide of the formula $Pr_2O_5$, and possibly other oxides intermediate between $Pr_2O_3$ and $PrO_2$. The sesquioxide is basic, and gives rise to the praseodymium salts, which are of a greenish colour and analogous to the cerous and lanthanum salts. It is probable that the dioxide is weakly basic, but the existence of salts corresponding to this oxide has not been definitely established. Solutions of praseodymium salts exhibit a characteristic and strong absorption spectrum.

Pure praseodymium compounds are extremely difficult to obtain; the best methods of preparing them are:—

(i) Fractional crystallisation of the double ammonium nitrates of the cerium earths [55] (p. 26).

(ii) Fractional crystallisation of the double magnesium nitrates, followed by that of the double manganese nitrates [227, 237] (pp. 28, 31).

Praseodymium occurs in all the minerals which contain cerium and lanthanum, but to a very small extent. It is a remarkable fact that the ratio of the quantities of praseodymium and neodymium in minerals is practically constant; the amount of neodymium being twice that of the praseodymium.

Metallic praseodymium has been isolated by Muthmann and Weiss [228] by the electrolysis of the fused chloride, using the method which was adopted in the case of cerium and lanthanum. In this case a current strength of 30-40 ampères is employed at the start and raised eventually to 70 ampères. If the current exceeds this value a layer of peroxide is formed which prevents further electrolysis. The metal is remelted under a layer of barium chloride in a magnesia crucible. Praseodymium can also be obtained mixed with magnesium oxide by the reduction of the oxide with magnesium.[528, 529]

Metallic praseodymium has a faint yellow colour and is only very slowly acted on by air. Its specific gravity is 6·4754, its melting-point 940°, heat of combustion per gram 1476·8 cal., the heat of formation of the oxide $\frac{1}{6}$ $Pr_2O_3$ = 68·7 Cal., and its specific resistance [1006] 88 ohms. Its hardness is between that of neodymium and samarium. It burns when heated in the air to form a mixture of oxide and nitride. No alloys of praseodymium have been prepared.

## Compounds of Praseodymium.

*Praseodymium Oxide*, $Pr_2O_3$, is formed by heating the dioxide or any of the intermediate oxides in hydrogen. It is a yellowish-green amorphous powder which is readily oxidised in air to a brown powder consisting of intermediate oxides. This change takes place more rapidly the purer the oxide.[82] It has a specific gravity 6·88 (von Scheele [223]), 7·07 (Brauner).

*Praseodymium Hydroxide*, $Pr(OH)_3$, is formed as a slimy green precipitate when praseodymium salts are treated with ammonia or alkali hydroxide. When dry it is a green amorphous powder which has similar properties to the other members

of the group. If precipitation of the hydroxide is effected in the presence of hydrogen peroxide a hydrated peroxide is produced which, according to Brauner, is hydrated $Pr_2O_5$, and, according to Melikow and Klimento, is $PrOOH,(OH)_2$. Dilute sulphuric acid decomposes this substance with the formation of hydrogen peroxide, and concentrated sulphuric acid with the liberation of ozonised oxygen. Potassium hydroxide is oxidised to potassium peroxide by this substance.

*Praseodymium Dioxide*, $PrO_2$, is formed by heating the nitrate with potassium nitrate at 400°-450°.[291, 580]

As thus prepared it is a brownish-black to deep black powder, which acts as a strong oxidising agent, liberating iodine from hydriodic acid, chlorine from hydrochloric acid, and converting manganous salts to permanganates and cerous salts to ceric salts. It does not completely oxidise ferrous or stannous salts; in these cases a portion of the active oxygen is set free in the gaseous condition. It excites cathodic luminescence in colourless oxides, such as $La_2O_3$ and $Yt_2O_3$, and acts as a catalyst in the oxidation of ammonia.[501]

When praseodymium hydroxide, nitrate or oxalate is heated in the air a black powder is obtained which has a formula approximating to $Pr_4O_7$,[55] although von Scheele [223] has shown that the composition varies and depends on the method of preparation. Thus the product obtained by heating the oxalate at as low a temperature as possible contains the most oxygen, whilst that obtained from the nitrate contains the least. When the product of any of these preparations is strongly heated it loses oxygen but reabsorbs it on cooling. Meyer has shown that the product obtained in this way has the formula [291, 577] $Pr_6O_{11}$, whereas Brauner [578, 579, 580] finds the formula $Pr_5O_9$. It is extremely probable that neither investigator has had a uniform product but a mixture of oxides intermediate between $Pr_2O_3$ and $PrO_2$. The product approaches the composition $PrO_2$ if a small quantity of cerium oxide is present,[265, 421] but the presence of lanthanum or neodymium [425] hinders the formation of the dioxide.

*Praseodymium Hydride* is formed when the metal is heated in hydrogen at 220°, the action taking place with incandescence. It is a green amorphous shining powder which is evidently not uniform, for the quantity of hydrogen combined is between that required for $PrH_3$ and $PrH_2$.

*Praseodymium Fluoride*, $PrF_3$, is obtained as a gelatinous precipitate when hydrofluoric acid is added to a solution of the nitrate. On warming the precipitate in contact with the solution it passes into a yellow crystalline mass.

*Praseodymium Chloride*, $PrCl_3$.—The anhydrous salt is formed by the action of chlorine on the carbide;[582] hydrochloric acid gas on the sulphide;[429] a mixture of chlorine and sulphur monochloride on the oxide;[532, 533] and by heating the crystallised salt in hydrochloric acid gas.[583]

It is a bluish-green hygroscopic substance forming transparent needles. It melts at 818° to form a black liquid[423] and is not volatile at 1000°. It is very soluble in water and alcohol and somewhat soluble in pyridine; 2·14 grams dissolve in 100 grams of pyridine at 15°. Heat of solution in water is 33·9 cals.; heat of formation from the oxide and hydrochloric acid is 73·9 cals.[536, 583, 584]; specific gravity 4·017. The molecular weight in alcohol solution agrees with the simple formula.[580] When treated with hydrobromic or hydriodic acid it is converted into the bromide and iodide respectively.[584] Praseodymium chloride has a similar action on quinol as the chlorides of lanthanum and cerium,[499] and its physiological action is similar to that of lanthanum chloride.[539] It forms two crystalline hydrates with six and seven molecules of water. The heptahydrate $PrCl_3,7H_2O$ separates in large green crystals from a solution of the oxide in hydrochloric acid. These crystals do not lose water when allowed to stand over sulphuric acid (von Scheele),[223, 585] although Matignon[584] states that they effloresce in the air, forming $PrCl_3,6H_2O$. When heated to 115° in the air hydrochloric acid and water are lost and a basic chloride of undetermined composition is formed. Heating in oxygen converts the heptahydrate into the oxychloride PrOCl.[1014, 584] It has a specific gravity 2·251, and melts in its water of crystallisation at 105°. At 13° 100 parts of water dissolve 334·2 parts of the heptahydrate with evolution of heat.[536, 583] It forms double chlorides in the same way as cerium and lanthanum. The best known are

$$PrCl_3,AuCl_3,10H_2O \text{ and } PrCl_3,PtCl_4,12H_2O,^{[283]}$$

both of which form large yellow crystals; a compound, $PrCl_3,2CH_5N$, is formed by evaporating a solution of the anhydrous chloride in pyridine to dryness.[584]

*Praseodymium Bromide*, $PrBr_3$.—The anhydrous salt is obtained by heating the brown oxide in a mixture of sulphur monochloride vapour and hydrobromic acid gas.[431] It is a green crystalline powder which dissolves slowly in water, forming a solution in which the salt is slightly hydrolysed. When the sesquioxide is dissolved in hydrochloric acid, and the solution evaporated, green crystals of $PrBr_3,6H_2O$ separate. It forms with platinic bromide a double bromide $PrBr_3,PtBr_4,10H_2O$ which crystallises in large dark red crystals.

*Praseodymium Sulphide*, $Pr_2S_3$, is obtained by the reduction of the anhydrous sulphate in sulphuretted hydrogen at high temperatures.[429] If, in this preparation, the temperature is not sufficiently high a disulphide, $PrS_2$, is formed which decomposes at higher temperatures into the sesquisulphide and sulphur.[544] Praseodymium sulphide is a brown powder which is easily decomposed by hot water and has a specific gravity 5·042. On heating in oxygen it is converted into an oxysulphide, $Pr_2O_2S$.

*Praseodymium Sulphate*, $Pr_2(SO_4)_3$.—The anhydrous sulphate is obtained as a light green powder by dehydrating the crystalline hydrates. It has a specific gravity 3·726 at 15·8°, and dissolves in water to the extent of 23·64 parts at 0° and 17·7 parts at 20° in 100 parts of water.[233] It forms hydrates with $15\frac{1}{2}$, 12, 8, and 5 molecules of water. The hydrate, $Pr_2(SO_4)_3,15\frac{1}{2}H_2O$, is formed when a dilute solution of the sulphate is allowed to crystallise at ordinary temperatures. The dodecahydrate,[257] $Pr_2(SO_4)_3,12H_2O$, is deposited at temperatures in the region of 0° in fine hard crystals which resemble the corresponding cerium compound. At ordinary temperatures it passes into the octohydrate. The octohydrate, $Pr_2(SO_4)_3,8H_2O$, separates from solution in monoclinic crystals at temperatures between 0° and 75°. It is isomorphous with the corresponding sulphates of yttrium, neodymium, samarium, and erbium.[586, 587] It has a specific gravity 2·827 at 13·3°,[587] and 100 grams of water dissolve the following weights of the crystallised salt:—[257]

| Temperature | 0° | 18° | 35° | 55° | 75° |
|---|---|---|---|---|---|
| Grams | 19·80 | 14·05 | 10·40 | 7·02 | 4·20 |

It changes at 75° to the pentahydrate,[257] the change being very rapid at 85°. The pentahydrate, $Pr_2(SO_4)_3,5H_2O$, is formed in thick monoclinic prisms, isomorphous with the corresponding cerium salt,[587] on crystallising from solution at 90°-100°. It has

a specific gravity 3·176 at 16° and the following weights of the hydrated salt dissolve in 100 grams of water :—

| Temperature . . . . . | 85° | 90° | 95° |
|---|---|---|---|
| Grams . . . . . | 1·60 | 1·35 | 1·00 |

A basic sulphate, $(PrO)_2,SO_4$, is formed by heating the sulphate.[588] An acid sulphate, $PrH_3(SO_4)_3$, is formed by evaporating the oxide with concentrated sulphuric acid or by treating the anhydrous sulphate with boiling sulphuric acid. It crystallises in fine needles.[446]

Praseodymium sulphate forms double salts with alkali sulphates. Of these, the most important are: praseodymium potassium sulphate, $Pr_2(SO_4)_3,3K_2SO_4,H_2O$, which is obtained as a sparingly soluble crystalline precipitate by adding a solution of potassium sulphate to one of praseodymium sulphate;[233] praseodymium ammonium sulphate, $Pr_2(SO_4)_3,(NH_4)_2SO_4,8H_2O$, which is formed similarly to the potassium double salt and loses its water of crystallisation at 170°.[233] The two compounds $Pr_2(SO_4)_3,Cs_2SO_4,2H_2O$ and $Pr_2(SO_4)_3,Cs_2SO_4,4H_2O$ are formed with caesium sulphate.[589]

*Praseodymium Nitride*, PrN, can be prepared by heating the carbide[453, 582] to 1200° in ammonia and by heating the metal in nitrogen at 900°.[417, 590] It is a black powder which is decomposed in moist air forming the hydroxide and liberating ammonia.

*Praseodymium Nitrate*, $Pr(NO_3)_3,6H_2O$, is formed in long efflorescent needles when a solution of the oxide in nitric acid is allowed to stand over sulphuric acid. It forms double salts with alkali nitrates,

$$Pr(NO_3)_3,2NaNO_3,H_2O \text{ and } Pr(NO_3)_3,2NH_4NO_3,4H_2O,$$

as sparingly soluble well-crystallised substances, and

$$Pr(NO_3)_3,2RbNO_3,4H_2O$$

as greenish hygroscopic needles, which melt in their water of crystallisation at 63·5°.[447] A series of isomorphous double nitrates of the general formula $2Pr(NO_3)_3,3M''(NO_3)_2,24H_2O$ is formed in well-defined crystals with the nitrates of the metals magnesium, manganese, zinc, cobalt, and nickel.[451]

*Praseodymium Carbide*, $PrC_2$, is formed by heating a mixture of the oxide and carbon in an electric furnace.[582] It forms a yellow crystalline mass of specific gravity 5·10. It is not reduced

by hydrogen at a red heat, and is decomposed by water [404] yielding a mixture of gases containing 67-68 per cent. of acetylene, 2·5-3·5 per cent. of olefines, and 28-30 per cent. of paraffins.

*Praseodymium Carbonate*, $Pr_2(CO_3)_3,8H_2O$, is formed by passing carbon dioxide into water containing the hydroxide in suspension or by precipitation from a solution of the chloride by ammonium carbonate.[233] It is thus obtained in sparingly soluble silky plates. It forms double carbonates with alkali carbonates, of which the following are the most important: Praseodymium potassium carbonate, $Pr_2(CO_3)_3,K_2CO_3,12H_2O$, formed by adding a solution of the chloride to a concentrated solution of potassium carbonate as a green precipitate composed of fine needles; praseodymium sodium carbonate, $Pr_2(CO_3)_3\ 3Na_2CO_3,22H_2O$, formed as an amorphous green precipitate by adding a solution of the chloride to a saturated solution of sodium carbonate; and praseodymium ammonium carbonate, $Pr_2(CO_3)_3,(NH_4)_2CO_3,4H_2O$, formed as a light green crystalline precipitate by adding a solution of the chloride to a solution of ammonium carbonate.[291]

*Praseodymium Acetate*, $Pr(C_2H_3O_2)_3,3H_2O$, crystallises in fine green needles from a solution of the oxide in acetic acid.[223] It is readily soluble in water and is not hydrolysed to a measurable extent.[591] When a solution is treated with ammonia a basic acetate is formed as a gelatinous precipitate, and this, when washed and treated with a little solid iodine, gives a violet blue adsorption compound as in the case of lanthanum.[592]

*Praseodymium Oxalate*, $Pr_2(C_2O_4)_3,10H_2O$, is formed as a light green crystalline precipitate by the addition of oxalic acid or an alkali oxalate to a solution of a praseodymium salt in acid or neutral solution. It is soluble to a slight extent in sulphuric acid and nitric acid solutions,[223, 261] and a litre of water dissolves 0·74 mg. at 25°.[517]

*Praseodymium Acetylacetonate*, $Pr(CH_3COCHCOCH_3)_3$, is formed as a crystalline precipitate by adding an ammoniacal solution of acetylacetone to a solution of the nitrate. It melts at 146° and is soluble in carbon tetrachloride. The molecular weight determined in carbon disulphide solution corresponds with the bimolecular formula.[462]

For details of other praseodymium compounds the reader is referred to the original memoirs: these include the *selenate*,[233] *selenite*,[233] *molybdate*,[593] *tungstate*,[593, 594] *bromate*,[510] *iodate*,[595] and

*uranate*,[596] and a large number of organic salts.[312, 202, 233, 253, 307, 533, 562, 563, 564, 597, 598]

Many so-called didymium salts have been prepared, but these cannot be regarded as strictly analogous to the praseodymium compounds.

## Detection of Praseodymium.

1. The brown colour of ignited oxide mixtures of the rare earths is very often an indication of the presence of praseodymium.

2. The absorption spectrum of aqueous solutions of praseodymium salts is very characteristic and is made use of to detect very small quantities of praseodymium.

3. Praseodymium acetate solution, when treated with ammonia, gives a gelatinous precipitate of the basic acetate. This precipitate when washed and treated with solid iodine gives a violet-blue absorption compound similar to that of lanthanum.[592] This reaction is unreliable in the presence of other earths.

4. Praseodymium salts form yellowish-green borax beads in the reducing flame and green beads in the oxidising flame.[599]

## Estimation of Praseodymium.

There is no method, as yet, for the quantitative estimation of praseodymium in mixtures of the rare earths.

## Spectra of Praseodymium Salts.

1. *Absorption Spectra.*—The absorption spectrum of praseodymium salts in aqueous solution has been investigated by Forsling,[568, 600] Bettendorf,[601] Schottländer,[577] Brauner,[578] Böhm,[272, 207] Aufrecht,[591] Rech,[602] Stahl,[646] Jones and Guy,[603] and Ball.[604] It consists of five well-defined bands which vary a little in their width and position, with concentration and change in the anion. The maxima of the bands, according to Brauner,[578] lie at 596·8 in the yellow, 589·5 in the yellow, 481·2 and 469·3 in the blue, and 444·7 in the violet. These values differ to a small but unimportant extent from the values found by other investigators. The absorption in the yellow is weak and obvious to the eye only in concentrated solutions; in the blue the absorption is strong, whilst that in the violet is equally strong but more diffused. Measurements of the absorption spectrum in organic solvents have been made by Helen Schaeffer[605] and by Jones and

Anderson.[606] In these solutions the bands change their positions somewhat owing to the formation of complexes between the solvent and dissolved substance.

The spark spectrum of praseodymium has been examined by Forsling [568, 600] and by Exner and Haschek.[607]

The arc spectrum has been investigated by Exner and Haschek,[504, 508] Bertram,[608] and Eder and Valenta.[609]

Measurements of the reflexion spectrum of praseodymium compounds have been made by Muthmann, Weiss and Heramhof,[610] and by Joye.[611]

The most characteristic lines in the emission spectra of praseodymium are 4429·28 of intensity 30, 4100·91, 4118·70, 4143·33, 4179·60, 4189·70, 4206·88, 4223·18, 4225·80, 4305·99, and 4496·60 of intensity 20, and 4241·20 and 4510·32 of intensity 15.

## NEODYMIUM, Nd. At. Wt. 144·3.

Neodymium was discovered, along with praseodymium, by Auer von Welsbach [55] in 1885 as a constituent of the old didymium. The product obtained by von Welsbach was not pure, and in 1898 Demarçay [613] separated from it a further element, samarium. Neodymium occurs along with the other earths of the cerium group in all the minerals which contain cerium. It is, after cerium, the most abundant of the cerium earths. Neodymium forms a characteristic blue sesquioxide, $Nd_2O_3$, and probably an unstable higher oxide. The sesquioxide is basic and gives rise to red or reddish-violet salts, which show, when perfectly pure and finely divided, a bluish-rose to violet-rose coloured fluorescence. Solutions of neodymium salts have a characteristic, although somewhat complex, absorption spectrum.

Pure neodymium compounds are obtained by the same methods as praseodymium. The separation is not, however, so difficult as in the case of praseodymium, and consequently pure neodymium compounds are more readily obtained than those of praseodymium.

Metallic neodymium is prepared by the electrolysis of fused neodymium chloride,[228, 386] using a very thin carbon cathode for the purpose of raising the temperature sufficiently high to melt the metal. A current strength of 90-100 ampères is necessary in this case, otherwise the method is the same as that employed in the preparation of metallic cerium.

Neodymium is a faintly yellow metal which is moderately stable in the air, but after some hours becomes covered with a greyish coating of oxide. It is slowly attacked by cold water but rapidly by hot water. Acids dissolve it rapidly but solutions of alkalis act on it in the same way as pure water. It melts at 840° and has a specific gravity 6·9563. The heat of combustion is 1506 cals. per gram, and the heat of formation of the oxide per equivalent is $1/6Nd_2O_3 = 72{\cdot}5$ Cal. The metal has a specific resistance of 79 ohms.[1006]

## Neodymium Compounds.

*Neodymium Oxide*, $Nd_2O_3$, is obtained by ignition of the nitrate, oxalate, hydroxide, and carbonate. It is a light blue powder showing a faint red fluorescence. The colour of neodymium oxide appears to be dependent to a large extent on the method of preparation, for different [55, 228, 363, 578, 613, 614, 615, 616] investigators describe it very differently. It is quite possible that in some cases the difference in colour is due to the presence of impurities. Pure neodymium is stated [425, 614] to form only the sesquioxide, but in the presence of traces of cerium and praseodymium oxides it forms an oxide approximating to $NdO_2$ in composition.[265, 580, 617] On the other hand, Waegner [363] has found that when the oxalate is heated in oxygen an oxide of the composition $Nd_4O_7$ is produced. This substance when strongly heated in the air yields $Nd_2O_3$. Neodymium oxide excites cathodic luminescence in colourless earths and acts as a catalyst in the oxidation of ammonia.[501] The sesquioxide has a coefficient of magnetisation $33{\cdot}5 \times 10^{-6}$.

*Neodymium Hydroxide*, $Nd(OH)_3$, is formed as a bluish precipitate by the addition of ammonia or alkali hydroxide to solutions of neodymium salts. Under certain conditions of concentration this formation does not occur, e.g. when ammonia is added to neodymium solutions containing glycerine.[618] When the precipitated hydroxide is dried at 310°-325° a greyish-brown substance, $2Nd_2O_3,3H_2O$, is formed; if the temperature is raised to 525° the hydrated oxide $Nd_2O_3,H_2O$ is produced. These two hydrates have different reflexion spectra.[1000, 619]

*Neodymium Hydride*, $NdH_3$, is obtained as an indigo-coloured shining mass by heating the metal [519, 528, 529] in hydrogen at 220°. The analysis of the product does not correspond with the formula

$NdH_3$, but this is probably due to incomplete action of the gas on the metal. Neodymium hydride evolves hydrogen when heated and is only slowly attacked by boiling water. Acids attack it rapidly.

*Neodymium Fluoride*, $NdF_3$, is formed as a gelatinous precipitate when concentrated hydrofluoric acid solution is added to a solution of a neodymium salt. On warming the precipitate in contact with the solution it changes to a lilac crystalline powder.[581]

*Neodymium Chloride*, $NdCl_3$.—The anhydrous salt is formed by dehydrating the crystalline salt in a current of hydrochloric acid gas; by heating the oxide in a mixture of sulphur monochloride vapour and chlorine;[532, 620] and by heating the sulphide in hydrochloric acid gas.[429] It forms a rose-coloured crystalline mass which is very hygroscopic, and melts at 785° to form a clear red liquid, although Matignon states that it becomes green in colour below the melting-point.[423, 536] It has a specific gravity 4·195 at 18°, and a heat of solution 35·4 cals. The heat of formation from the oxide and hydrochloric acid is 71·6 cals.[533, 621] It is soluble in water, alcohol, and pyridine: 100 parts of water dissolve 96·68 parts at 13° and 140 parts at 100°;[623] 100 parts of alcohol dissolve 44·5 parts at 20°, and 100 parts of pyridine dissolve 1·8 parts at 15°.[623] Cold neodymium chloride absorbs ammonia to form compounds with 12, 11, 8, 5, 4, 2, and 1 molecules of ammonia. The compound $NdCl_3,12NH_3$ is best prepared by sealing the anhydrous chloride in a tube with liquid ammonia or by passing the gas over it at low temperatures. This compound dissociates at − 10°, forming $NdCl_3,11NH_3$, which dissociates at 26°. The other compounds, in order, dissociate at 79°, 117°, 157°, 255°, and 360° respectively.[624]

An aqueous solution of the chloride deposits large rose-coloured rhombic prisms of the formula $NdCl_3,6H_2O$.[620] This hydrate has a specific gravity 2·282 at 16·5° and dissolves readily in water: 100 grams of water dissolve 246·2 grams of the hydrate at 13° and 511·6 grams at 100°. The heat of solution of the hydrate is 7·6 cals. When the crystalline hydrate is heated to 115° in a current of hydrochloric acid gas, the hydrate $NdCl_3,H_2O$ is formed, and this substance loses its water at 160° in the presence of hydrochloric acid gas and forms the anhydrous salt. The hexahydrate, when heated in steam or in the air,[622] is converted

into the oxychloride NdOCl, which forms mauve-coloured cubic leaflets. These are infusible at 1000°. Neodymium chloride crystallises from alcoholic solutions as $NdCl_3,3C_2H_5OH$,[623] and from pyridine solutions as $NdCl_3,3C_5H_5N$.[623] It combines with hexamethylene tetramine to form $NdCl_3,2C_6H_{12}N_4,14H_2O$ [428] in silky triclinic needles. Solutions of neodymium chloride exhibit the same oxydase action on quinol as solutions of cerium, lanthanum, and praseodymium,[499] and they have the same physiological action as solutions of praseodymium and lanthanum.[539] Molecular weight determinations in alcohol solution correspond with the formula $NdCl_3$.[620] When acetylene is passed over heated neodymium chloride it is polymerised without changing the neodymium salt, and graphite is deposited.[622]

*Neodymium Bromide*, $NdBr_3$.—The anhydrous salt resembles the chloride; it is prepared by the action of hydrobromic acid gas on the oxide [622] and by the action of sulphur monochloride vapour and hydrobromic acid gas on the oxide.[431] It is a green crystalline substance which melts to form a dark coloured liquid. It dissolves slowly in water and is slightly hydrolysed in solution.[431]

*Neodymium Iodide*, $NdI_3$, is formed as a black crystalline powder by the action of gaseous hydriodic acid on the anhydrous chloride at temperatures just below the melting-point of the chloride.[622] It fuses to a black liquid, which at high temperatures suddenly becomes transparent, due to the formation of an allotropic modification.[622]

*Neodymium Sulphide*, $Nd_2S_3$, is formed by the action of sulphuretted hydrogen on heated anhydrous neodymium sulphate,[429] and by the action of sulphur vapour on the heated oxide. It is an olive-green powder which is readily decomposed by water and has a specific gravity of 5·179 at 11°.

*Neodymium Sulphate*, $Nd_2(SO_4)_3,8H_2O$, is obtained by crystallising a solution of the oxide in sulphuric acid.[257] It forms red monoclinic prisms isomorphous with the corresponding sulphates of erbium, yttrium, and praseodymium.[587] It is moderately soluble in water; 100 grams of water dissolve the following weights of neodymium sulphate, calculated as anhydrous salt:—

| Temperature | 0° | 16° | 30° | 50° | 80° | 100° |
|---|---|---|---|---|---|---|
| Grams | 9·5 | 7·1 | 5·1 | 3·6 | 2·7 | 2·25. |

An acid sulphate, $NdH_3(SO_4)_3$, is formed in light rose-coloured

silky needles in the same way as the corresponding praseodymium compound.[446, 588, 623] A basic sulphate, $(NdO)_2SO_4$, is obtained by heating the normal sulphate.[588, 623]

The double sulphate $Nd_2(SO_4)_3,Cs_2SO_4,3H_2O$ is formed in lavender-coloured crystals by mixing solutions of the two sulphates and crystallising.[589]

*Neodymium Nitride*, NdN, is formed by heating the metal in nitrogen [519, 529, 590] at 900°, and by heating the carbide in nitrogen at 1200°.[453, 582] It is also formed mixed with the oxide when the metal is burnt in the air. The formation in all cases occurs much more slowly than that of the cerium and lanthanum compounds. It is a black powder which is decomposed by moist air with evolution of ammonia.

*Neodymium Nitrate*, $Nd(NO_3)_3,6H_2O$, is formed by crystallisation from a solution of the oxide in nitric acid. It exists also in a labile form with $5H_2O$. Both forms are isomorphous with the corresponding hydrates of bismuth nitrate.[625] With alkali nitrates the double nitrates $Nd(NO_3)_3,2NH_4NO_3,4H_2O$ [55] and $Nd(NO_3)_3,2RbNO_3,4H_2O$ [447] have been prepared. The latter compound crystallises in reddish-violet plates which melt at 47° and lose their water of crystallisation at 60°. A series of isomorphous double nitrates of the general formula

$$2Nd(NO_3)_3,3M''(NO_3)_2,24H_2O$$ [451, 613]

has been prepared with the nitrates of the metals magnesium, manganese, cobalt, nickel, and zinc. A double compound,

$$Nd(NO_3)_3,2C_6H_{12}N_4,8H_2O,$$

is formed in lilac monoclinic needles with hexamethylene tetramine.[428]

*Neodymium Carbide*, $NdC_2$, is formed by heating a mixture of the oxide and sugar charcoal in an electric furnace.[528] It forms hexagonal leaflets of specific gravity 5·15 and is not reduced by hydrogen even at a red heat. It is decomposed by water giving a mixture of gases composed of 65-67 per cent. acetylene, 6-7 per cent. olefines, and 28-30 per cent. paraffins.[404]

*Neodymium Carbonate*, $Nd_2(CO_3)_3$, is formed as a light red precipitate by the addition of an alkali carbonate to a solution of a neodymium salt. When treated with an excess of alkali carbonate double carbonates are formed,[291]

$$Nd_2(CO_3)_3,K_2CO_3,12H_2O;\ 2Nd_2(CO_3)_3,3Na_2CO_3,22H_2O,$$

an amorphous violet precipitate, and $Nd_2(CO_3)_3,(NH_4)_2CO_3,4H_2O$ which crystallises in small prisms.

*Neodymium Oxalate*, $Nd_2(C_2O_4)_3,10H_2O$, is formed by the addition of oxalic acid or an alkali oxalate to an acid or neutral solution of a neodymium salt. It forms a rose-coloured crystalline precipitate. It is the most sparingly soluble of all the rare earth oxalates in acids with the single exception of thorium oxalate.[223, 261] A litre of water dissolves 0·74 mg. at 25°.[517] A hydrate with 11 molecules of water is known which is stable in contact with a solution of the nitrate at 25°. A solution of the oxalate in nitric acid in all probability contains an oxalo-nitrate.[627]

*Neodymium Acetylacetonate*, $Nd(CH_3COCHCOCH_3)_3$, is formed in the same way as the corresponding praseodymium salt. It is a violet crystalline mass which melts at 144°-146° and has a double molecular weight in solution.[462]

Among other neodymium salts the following have been prepared: the *bromate*,[510] *chromate*,[629] *tungstate*,[594] *silico-tungstate*,[628] *molybdate*,[630] *uranate*, *cobalticyanide*,[1008] *ferricyanide*,[1001] and many organic salts.[202, 307, 312, 516, 562, 564, 631, 563 1001]

## Detection of Neodymium Compounds.

Neodymium compounds are detected by means of the spark spectrum, and by the absorption spectrum of solutions of the salts.

Neodymium salts give a violet borax bead in the reducing flame, and a colourless bead in the oxidising flame. This reaction only occurs when a sufficiently large quantity of neodymium is present, and is useless in the presence of other coloured rare earths.[599]

## Estimation of Neodymium.

In mixtures of the rare earths no method has been evolved for the quantitative estimation of neodymium.

## Spectra of Neodymium.

Salts of neodymium yield a characteristic but somewhat complicated absorption spectrum when in aqueous solution. The positions of the maxima differ a little with change in concentration and with a change in the nature of the anion. These small differences are due to differences in the degree of ionisation. One band, namely, that with maximum 469, is found to coincide exactly with one of the praseodymium bands, and this has led to the view that both these elements contain an undiscovered

element.[207, 209, 632, 633, 634] The absorption spectrum in aqueous solution has been measured by Demarçay,[613] Forsling,[600, 635] Welsbach,[55, 82] Brauner,[578] Boudouard,[636] Stahl,[646] Exner,[637] Dimmer,[638] Drossbach,[639] Muthmann and Stutzel,[640] and Rech.[602] Of all these investigators it is probable that Demarçay[613] possessed the purest material. Consequently his values are given here in preference to those of the other investigators. The figures given are the wave lengths of maxima of the bands obtained with a 10 per cent. solution of the chloride 36 mm. thick.

The values are: (673·1), 637·3, 629·2, 578·3, 532·0, 510·9, 476·8, 469·1, 462·4, (435·1), (429·4), 428·1, and (420·0). All the bands are strong with the exception of those indicated in brackets.

The absorption spectrum in non-aqueous solution has been measured by: Helen Schaeffer,[641] Jones and Anderson,[606] Jones and Strong,[626, 642] and by Jones and Guy.[603]

The spark spectrum has been investigated by von Welsbach,[55] and by Exner and Haschek;[507, 508] the arc spectrum by Exner and Haschek,[507, 508] and Bertram,[608] and the reflexion spectrum by Muthmann, Weiss, and Heramhof,[610] and Joye.[643]

Neodymium oxide mixed with alumina gives a discontinuous spectrum when heated in the Bunsen flame.[645] This spectrum is almost identical with a reversed absorption spectrum. It is probable that this spectrum is not obtained with perfectly pure material.

Neodymium oxide when mixed with 1 per cent. of lime gives a luminescence spectrum when subjected to cathode rays.[63] Solutions of neodymium nitrate exhibit an anomalous dispersion.[644]

The most intense lines in the emission spectrum of neodymium are: 4303·70, intensity 20; 4325·87, 6385·32, intensity 15, and 3863·52; 3951·32, 4061·32, 4274·54, 4282·67, 4375·11, 4385·81, 4400·96, 4446·51, 4451·71, 4463·09, 4920·84, 5293·35, 5319·98, 5594·58, 5620·75, 6310·69, and 6314·69 of intensity 10.

## SAMARIUM, Sa. At. Wt. 150·4.

Samarium was discovered in 1879 by Lecoq de Boisbaudran[49] in samarskite. The pure substance was first obtained by Demarçay, and by Urbain and Lacombe,[647] who, in 1904, separated it from gadolinium and europium which often occur along with it. Samarium forms a faintly yellow basic oxide $Sa_2O_3$ which gives rise to topaz-yellow salts. This oxide is

less basic than the corresponding oxides of the other cerium earths, and does not absorb oxygen to form higher oxides. Samarium forms salts of the type $SaX_2$, in addition to those corresponding to the oxide $Sa_2O_3$, a property which is not shared with any of cerium earths and only with europium of all the rare earths. Solutions of tervalent samarium salts possess a weak absorption spectrum, the bands of which lie mainly in the blue and violet regions.

Samarium occurs along with the cerium and terbium earths in all the minerals which contain cerium earths. Samarium compounds are usually obtained from samarskite, cerite, orthite, monazite, and euxenite by crystallisation of the double magnesium nitrates to which a quantity of bismuth nitrate has been added,[77, 647, 648] and by the fractional crystallisation of the magnesium double nitrates alone, in neutral or faintly acid solution.[228, 229]

Metallic samarium is prepared by the electrolysis of a molten mixture of anhydrous samarium chloride and barium chloride containing 33 per cent. of the latter constituent. On account of the high melting-point of samarium, the electrolysis is carried out with a very narrow carbon cathode and a current strength of 100 ampères.[228, 386]

Samarium is a greyish-white metal which is slowly oxidised in the air. It is harder than the other cerium metals and melts at 1300°-1400°. It has a specific gravity of 7·7-7·8. When heated in the air it is converted into a mixture of oxide and nitride.

## Compounds of Samarium.

*Samarium Oxide*, $Sa_2O_3$, is a white powder possessing a faintly yellow tinge,[356 650, 526] obtained by the ignition of the hydroxide, nitrate, and oxalate. It is readily soluble in acids and has a specific gravity 8·347. It does not form higher oxides when heated in the air. When heated in chlorine the oxychloride, SaOCl, is formed in white shining plates.[526, 650] It has a coefficient of magnetisation $6·5 \times 10^{-6}$.

*Samarium Hydroxide*, $Sa(OH)_3$, is formed as a gelatinous precipitate by the addition of ammonia or alkali hydroxide to solutions of samarium salts. It dries to a faintly yellow powder.

If the precipitation is effected in the presence of hydrogen peroxide a hydrated peroxide of the formula $Sa_4O_9,xH_2O$ is produced.[526, 649, 650]

*Samarium Fluoride*, $SaF_3,H_2O$, is formed as a gelatinous precipitate by the addition of hydrofluoric acid to a solution of a samarium salt.[526, 649, 650]

*Samarium Chloride*, $SaCl_3$.—The anhydrous salt is obtained by heating the oxide with a mixture of sulphur monochloride vapour and chlorine;[533] and by dehydrating the crystalline hydrate in a current of hydrochloric acid gas.

Samarium chloride is an almost white crystalline powder with a faintly yellow tinge. It is very hygroscopic, and dissolves in water with a hissing noise; it is soluble in alcohol and in pyridine. The latter solvent dissolves 6·38 grams per 100 grams at 25°.[654] When a solution of samarium chloride in pyridine is heated a gelatinous compound separates out, and redissolves on cooling the mixture. Samarium chloride melts at 686° to form a dark brown liquid; it has a specific gravity 4·465 at 18°, a heat of solution 37·4 cals., and a heat of formation from the oxide and hydrochloric acid of 64·2 cals.[536, 526, 650, 651, 652] When heated in hydrogen it is reduced to samarous chloride, $SaCl_2$, and when heated in oxygen it forms the oxychloride SaOCl.[654] When cold ammonia is passed over the anhydrous chloride absorption occurs, and a large increase in volume, with the formation of addition compounds, which contain 11·5, 9·5, 8, 5, 4, 3, 2, and 1 molecules of ammonia.[653] These compounds have the following dissociation temperatures respectively, 15°, 40°, 76°, 105°, 155°, 200°, 240°, and 375°.

Samarium chloride forms crystalline hydrates with 6 molecules and 1 molecule of water. The hexahydrate is obtained in large yellow plates by crystallising a solution of the oxide in hydrochloric acid. It has a specific gravity 2·383.[526, 650, 652] On heating the hydrate in a current of hydrochloric acid gas at 110°, 5 molecules of water are lost and the hydrate $SaCl_3,H_2O$ is formed. This compound, under the same circumstances, loses its remaining water at 180°, and is converted into the anhydrous salt.

Samarium chloride forms the double compounds

$$SaCl_3,PtCl_4,10\tfrac{1}{2}H_2O \text{ and } SaCl_3,AuCl_3,10H_2O$$

when the two constituent chlorides are brought together in solution. From the resulting solution the double salts can be obtained crystalline. The first-named compound forms orange-coloured prisms.[650, 526] Solutions of samarium chloride accelerate the oxidation of quinol more than any of the other rare earth chlorides.[499]

*Samarous Chloride*, $SaCl_2$, is formed by heating samarium chloride in a current of hydrogen or ammonia in complete absence of moisture.[655] It can also be formed by heating the anhydrous higher chloride with powdered aluminium.[656]

It is a reddish-brown crystalline mass of specific gravity 3·687 at 22°. It is insoluble in alcohol, carbon disulphide, and other organic solvents, but dissolves in water to form a brown solution which immediately evolves hydrogen and becomes colourless with the deposition of oxide and oxychloride.

*Samarium Bromide*, $SaBr_3$. — The anhydrous bromide is prepared by heating the oxide in a mixture of sulphur monochloride vapour and hydrobromic acid gas.[431] It forms a yellow fused mass which dissolves slowly in water and is slightly hydrolysed in solution. Samarium bromide combines with water to form the hydrate $SaBr_3,6H_2O$. This compound is best obtained by crystallising a solution of the oxide in hydrobromic acid.[650, 526] It forms yellow deliquescent crystals of specific gravity 2·971 and forms a double salt,

$$SaBr_3,AuBr_3,10H_2O$$

with auric bromide.

*Samarium Iodide*, $SaI_3$, is formed by heating anhydrous samarium chloride with gaseous hydriodic acid.[654] It is obtained as orange-yellow crystals, which deepen in colour on heating, becoming orange, brick-red, and finally, at 800°, black.

*Samarous Iodide*, $SaI_2$, is formed by reducing anhydrous samarium iodide with gaseous hydriodic acid at high temperatures.[656] It is a yellow compound which dissolves in water to form a brown solution, which, on standing, loses its colour and deposits gelatinous samarium hydroxide.

*Samarium Sulphide*, $Sa_2S_3$, is obtained by the action of sulphur vapour on samarium carbide at high temperatures[657] and also by passing sulphuretted hydrogen over heated anhydrous samarium chloride.[654]

*Samarium Sulphate*, $Sa_2(SO_4)_3,8H_2O$, is produced in topaz-yellow monoclinic[658] crystals by crystallising a solution of the oxide in sulphuric acid. It is isomorphous with the corresponding hydrates of neodymium, praseodymium, erbium, and yttrium sulphates. It has a specific gravity 2·930 at 18·3° and is less soluble in water than the corresponding neodymium and praseodymium sulphates. It is slightly hydrolysed in solution.[659]

An acid sulphate, $SaH_3(SO_4)_3$, is formed in golden-yellow[446, 661] needles by evaporating a solution of the normal sulphate in concentrated sulphuric acid at 200°. A basic sulphate is produced when the anhydrous normal sulphate is heated at 700°. This compound has the formula $Sa_2O_3,SO_3$[349] and is completely converted into the oxide at 1100°. It is a yellow powder which is insoluble in water and in dilute sulphuric acid.[611] On mixing solutions of alkali sulphates and samarium sulphate and crystallising, the compounds

$$Sa_2(SO_4)_3,(NH_4)_2SO_4,8H_2O \text{ and } Sa_2(SO_4)_3,Na_2SO_4,2H_2O$$

are obtained as white crystalline substances, both of which are more soluble in water than the corresponding neodymium and praseodymium compounds.[650, 526] Under special conditions the double sulphates

$$2Sa_2(SO_4)_3,3Na_2SO_4,6H_2O \text{ and } Sa_2(SO_4)_3,(NH_4)_2SO_4,7H_2O$$

have been prepared.[660]

*Samarium Nitride*, SaN, is formed by heating metallic samarium in nitrogen. It is decomposed by moist air and water with the evolution of ammonia and formation of the hydroxide.[590, 664]

*Samarium Nitrate*, $Sa(NO_3)_3,6H_2O$, is formed in very soluble yellow needles by crystallising a solution of the oxide in nitric acid.[650, 526] It melts at 78°-79° and forms a series of isomorphous double nitrates of the general formula

$$2Sa(NO_3)_3,3M''(NO_3)_2,24H_2O$$[451]

with the nitrates of the metals magnesium, manganese, zinc, cobalt, and nickel. The double nitrates form large rhombohedra,[356] which melt at definite temperatures.

*Samarium Carbide*, $SaC_2$, is formed by heating a mixture of the oxide and sugar charcoal in an electric furnace.[657] It forms small yellow crystals of specific gravity 5·86. It is not re-

duced by hydrogen at 1000° but is decomposed with ease by water giving a mixture of gases composed of 70-71 per cent. of acetylene, 7·6-8·1 per cent. olefines, and 20·7-22·3 per cent. of hydrogen and methane.

*Samarium Carbonate*, $Sa_2(CO_3)_3,3H_2O$, is formed by treating a suspension of samarium hydroxide in water with carbon dioxide. It crystallises in yellow microscopic needles. It cannot be prepared by the addition of alkali carbonates to solutions of samarium salts. Under these conditions double carbonates are precipitated as gelatinous masses, which, on standing, slowly become crystalline. In the case of the various alkali carbonates the compounds

$$Sa_2(CO_3)_3,K_2CO_3,12H_2O\ ;\ Sa_2(CO_3)_3,(NH_4)_2CO_3,4H_2O,\text{ and } Sa_2(CO_3)_3,Na_2CO_3,16H_2O$$

are produced respectively.[650, 526]

*Samarium Oxalate*, $Sa_2(C_2O_4)_3,10H_2O$, is obtained by adding a solution of oxalic acid to an acid or neutral solution of a samarium salt. It is precipitated as a semi-liquid mass which, on standing, becomes crystalline.[650, 526] If potassium oxalate is added to a solution of a samarium salt a double oxalate, $Sa_2(C_2O_4)_3,K_2C_2O_4$, is formed as a crystalline precipitate. The oxalate is less soluble in acids and ammonium oxalate solution than the oxalates of the other elements of the cerium group.[662] A litre of water dissolves 0·54 mg. of the oxalate at 25°.[517]

*Samarium Acetylacetonate*, $Sa(CH_3COCHCOCH_3)_3$, is formed by the addition of an ammoniacal solution of acetyl acetone to an aqueous solution of samarium nitrate. It is obtained as a crystalline mass melting at 146°-147°. It is more soluble in water than the corresponding compounds of the other cerium earths and is easily soluble in water. Molecular weight determinations in alcohol solution indicate that it has a molecular weight double that required by the above formula.[462]

Among other compounds of samarium the following have been prepared: the *bromate*,[510] *sulphite*,[526, 650] *thiocyanate*,[526, 650] *selenate*,[526, 650] *selenite*,[526, 650] *phosphate*,[526, 650] *molybdate*,[526, 650] and a large number of organic salts.[253, 307, 312, 516, 562, 563, 564, 650, 631, 526]

Samarium is detected by means of its emission spectrum. The absorption spectrum is too weak for purposes of detection unless large quantities of samarium are present.

## Spectra of Samarium.

Solutions of samarium compounds exhibit an absorption spectrum which, although not very strong, is quite characteristic. The strongest absorption is in the blue and violet regions; the bands with maxima at 476, 463, 417, and 402 being the most intense. The absorption spectrum in aqueous solution has been measured by Demarçay,[71, 356] Böhm,[273] Soret,[666] Lecoq de Boisbaudran,[49, 665] Bettendorf,[72] Forsling,[600, 635] Krüss and Nilson,[682] Thalen,[667] and Muthmann, Weiss, and Heramhof;[610] and Becquerel[663] has studied the influence of a magnetic field and low temperatures on the absorption spectrum. The following figures give the maxima of the bands found by Demarçay,[356] using a 20 per cent. solution of the nitrate: 559, (529), 498, 476, 463, (453), 443, 417, (407), 402, (390), 375, and 362. The bands indicated in brackets are very weak and only visible when thick layers or concentrated solutions are used.

The absorption spectrum in non-aqueous solvents has been examined by Jones and Strong.[642]

Measurements of the spark spectrum have been made by Lecoq de Boisbaudran,[59, 73] Demarçay,[668] Thalen,[667] Exner and Haschek,[607] Eder and Valenta,[673, 988] and Bettendorf.[72] The arc spectrum has been investigated by Eder and Valenta,[674] Exner and Haschek,[504, 508] and Rutten and Mersch.[671]

Pure samarium compounds do not exhibit a luminescence spectrum, but in the presence of traces of other earths characteristic lines are observed. The luminescence spectrum thus produced has been studied by Crookes,[669, 670] Demarçay,[356] and Urbain and Seal.[672]

The most characteristic lines of the emission spectrum of samarium are: 4424·55, intensity 20, and 3739·30, 4152·38, 4203·18, 4225·48, 4229·83, 4236·88, 4256·54, 4319·12, 4329·21, 4334·32, 4347·95, 4391·03, 4420·72, 4421·32, 4434·07, 4434·52, 4452·92, 4454·84, 4458·70, 4467·50, 4519·80, 4524·08, 4544·12, 4566·38, 4577·88, 4642·41, and 4674·79, all of intensity 10.

# CHAPTER VI.

## THE YTTRIUM GROUP OF RARE EARTHS.

THE elements scandium, yttrium, europium, terbium, gadolinium, erbium, dysprosium, holmium, thulium, ytterbium, lutecium, and celtium constitute the yttrium group of rare earths. This group is divided into three sub-groups: (i) the terbium group, consisting of europium, terbium, and gadolinium; (ii) the erbium group, consisting of erbium, dysprosium, holmium, and thulium, and (iii) the ytterbium group, consisting of ytterbium, lutecium, and celtium; the elements scandium and yttrium occupying positions by themselves. The elements of this group are all tervalent and give rise to oxides of the general formula $M_2O_3$; these oxides are basic and yield salts of the type $MX_3$ which are but slightly hydrolysed in solution. Europium, alone of all the elements of this group, gives rise to bivalent salts, $MX_2$, corresponding with an unknown oxide, EuO. The elements of this group decrease in basicity in the order, Yt, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu, Sc, when the basic character is deduced from the order in which they are precipitated from solution by dilute ammonia, but the order becomes somewhat changed if the basicity is deduced from the heat of dissociation of the anhydrous sulphate. As far as the experimental data go the elements have, from this source, the following decreasing order of basicity: Yt (58·9), Lu (58·5), Yb (58·2), Er (57·6), Gd (56·9), and Sc (54·5). The bracketed figures indicate the heats of dissociation of the anhydrous sulphates.[381] The former method of deducing the order of the basicity indicates that the cerium earths, with the exception of samarium, which comes between gadolinium and terbium, are all stronger bases than the yttrium earths.

The elements of the yttrium group form double sulphates with alkali sulphates which are much more soluble in water than the corresponding double alkali sulphates of the cerium elements. This difference in solubility, as has been seen (Chap.

III.), furnishes a method for the rough separation of the two groups.

The properties of the elements scandium and yttrium are somewhat different from those of the other members of the yttrium group, but this is to be expected in view of the small atomic weights of these elements. The terbium sub-group constitutes a group of elements the properties and atomic weights of which are intermediate between those of the elements of the cerium group and those of the remaining elements of the yttrium group. Thus it will be obvious that there is a gradual change in the properties of the rare earths with increasing atomic weight.

## SCANDIUM, Sc. At. Wt. 44·1.

Scandium was discovered in 1879 by Nilson [43, 675] in gadolinite and euxenite, and constitutes the element ekaboron predicted by Mendeléeff [676] in 1871. Scandium forms a white oxide $Sc_2O_3$ which is the weakest base of all the rare earths and gives rise to colourless salts. The salts of scandium are readily hydrolysed and show a decided tendency to complex salt formation. Scandium, alone of the yttrium earths, forms a sparingly soluble double alkali sulphate. This fact would seem to indicate that scandium ought to be included in the cerium group, but the weakly basic properties, on the other hand, place it definitely in the yttrium group. Scandium sulphate crystallises with 6 molecules of water, and is very soluble in water. These properties are closely related to those of glucinum (beryllium), and this similarity is quite in accord with the position of these elements in the periodic system. It will therefore be obvious that the properties of scandium are such as to make it very questionable whether scandium should be included among the rare earths at all. Urbain and Lacombe [677] are of the opinion that scandium should not be included among the rare earths, but against this view must be placed the fact that some scandium compounds, notably the platinocyanide, exist in two forms one of which resembles the platinocyanides of the cerium earths, whilst the other resembles the platinocyanides of the yttrium earths. [678, 679]

Scandium occurs in gadolinite, euxenite, keilhauite, and in most of the rare earth minerals but to a very small extent. It is indeed very widely distributed in nature, and Crookes [682, 683] and Eberhard [198, 684, 685] have shown its presence in some hundreds of

minerals. Amongst the minerals which contain larger quantities of scandium are thortveitite, a very rare mineral containing 37 per cent. of scandia, wiikite containing about 1 per cent. of scandia,[680, 683] and an orthite from Finland[680] which also contains about 1 per cent. of scandium. Wolframite and cassiterite contain appreciable quantities of scandia (0·2-0·3 per cent.),[289, 681] and the residues of these minerals, after the extraction of tin, have been largely used for the preparation of scandium compounds.

The methods by which pure scandium compounds are obtained will be best illustrated by a short description of the extraction of this element from wolframite.[249, 288, 289, 290] The residues from wolframite or tinstone, after the removal of the tin, are fused with soda and the cooled melt extracted with water. The solution thus obtained contains the tungsten as sodium tungstate. The residue is washed and dissolved in hydrochloric acid and the rare earths precipitated by either oxalic acid or hydrofluoric acid, a large excess being used in either case to keep the iron and manganese present in solution. The precipitate of rare earths contains about 90-95 per cent. of scandium. It is converted into oxide and dissolved in hydrochloric acid and the solution boiled with sodium silicofluoride for half an hour, when the scandium is precipitated as fluoride in a very pure form. Traces of the rare earths may be removed from this by a reprecipitation with sodium thiosulphate. In this way scandium, with thorium as its only impurity, is obtained. The thorium is removed either by fractional sublimation of the anhydrous chlorides, precipitation of the thorium as iodate,[377] or by means of the double alkali carbonates.[201]

Metallic scandium has not been isolated.

## Compounds of Scandium.

*Scandium Oxide*, $Sc_2O_3$, is a fine white powder obtained by heating the nitrate, hydroxide, or oxalate. It has a specific gravity 3·864, specific heat 0·1530, and is diamagnetic, having a susceptibility[377] $- 0{\cdot}12 \times 10^{-6}$. It dissolves slowly in cold acids but rapidly in hot acids to form the scandium salts.[686]

*Scandium Hydroxide*, $Sc(OH)_3$, is formed as a gelatinous white precipitate, which dries to a white powder, when a solution of a scandium salt is treated with ammonia. It is readily soluble in acids forming the scandium salts.[686]

*Scandium Fluoride*, $ScF_3$, is formed by the addition of hydrofluoric acid or a soluble fluoride to a solution of a scandium salt. It is also produced when sodium silicofluoride is added to a boiling solution of a scandium salt. In this way the silicofluoride is first produced and then hydrolysed.

$$Sc_2(SiF_6)_3 + 6H_2O = 2ScF_3 + 12HF + 3SiO_2.$$

Scandium fluoride is less soluble in acids than the fluorides of the other rare earths. It is very stable and can only be completely decomposed by fusion with acid potassium sulphate. When freshly precipitated it dissolves in concentrated solutions of alkali fluorides. These solutions when concentrated deposit crystals of double fluorides. The following double fluorides have been prepared: $3NH_4F,ScF_3$, in large transparent crystals, which are very soluble in water; $3KF,ScF_3$, in well-formed crystals, and $3NaF,ScF_3$, which crystallises with difficulty. The double fluorides are evidently very complex, for a boiling solution of the double ammonium fluoride is not precipitated by ammonia.[687] This points to the probability that the double fluorides are alkali salts of the unknown acid $H_3ScF_6$.

*Scandium Chloride*, $ScCl_3$.—The anhydrous salt is prepared by heating the oxide in a mixture of sulphur monochloride vapour and chlorine[423] at 680°. It is a white crystalline substance which dissolves in water with absorption of heat. It forms crystalline hydrates with 12 and 3 molecules of water. The dodecahydrate, $ScCl_3,12H_2O$, is formed in white crystals by concentrating a solution of the oxide in hydrochloric acid. It loses 9 molecules of water at 100° and forms the trihydrate $ScCl_3,3H_2O$. This compound loses hydrochloric acid at a red heat and is converted into the oxide.[682] A double aurichloride,

$$3ScCl_3,2AuCl_3,21H_2O,$$

is formed in yellow needle-shaped deliquescent crystals,[688] which lose 13 molecules of water when allowed to stand over sulphuric acid; when heated to 100°, 19 molecules of water are rapidly lost, the remaining 2 molecules being slowly lost at this temperature. Scandium chloride is hydrolysed[687] to a considerable extent in solution.

*Scandium Sulphate*, $Sc_2(SO_4)_3$.—The anhydrous salt is formed by precipitation from a concentrated solution of the nitrate by means of concentrated sulphuric acid, and removing the excess

of acid by gentle heating. It is a white crystalline substance which dissolves slowly in cold water but rapidly in hot water with the evolution of heat. It has a specific gravity 2·579 and a specific heat 0·1639.[686] It loses sulphur trioxide on heating and is converted into the oxide, and when heated in sulphuretted hydrogen[689] it is converted into the sulphide $Sc_2S_3$. It is highly complex in solution since the metal migrates to the anode on electrolysis.[687] A concentrated solution of scandium sulphate when further evaporated becomes syrupy, and on cooling deposits imperfect crystals of $Sc_2(SO_4)_3,6H_2O$. The hexahydrate is excessively soluble in water, producing a solution with a sweet astringent taste. It loses 4 molecules of water at 100° and becomes anhydrous at 250°. When kept in the air it effloresces and forms the pentahydrate $Sc_2(SO_4)_3,5H_2O$. This substance is the most stable hydrate at ordinary temperatures. It dissolves in water[690] to the extent of 54·61 grams in 100 c.c. at 25°; it dissolves in sulphuric acid (sp. gr. 1·6) and the solution deposits crystals of the acid sulphate $Sc_2(SO_4)_3,3H_2SO_4$.[689] A solution of scandium sulphate, when treated with a concentrated solution of potassium sulphate, deposits well-formed crystals of

$$Sc_2(SO_4)_3,3K_2SO_4,$$

which resemble the corresponding cerium salt and are insoluble in solutions of potassium sulphate.[682] An ammonium double sulphate, $2(NH_4)_2SO_4,Sc_2(SO_4)_3$, is obtained in the same way in sparingly soluble leaflets.[687]

*Scandium Nitrate*, $Sc(NO_3)_3,4H_2O$, is formed in small prisms by concentrating a solution of the oxide in nitric acid until it is of a syrupy consistency, and then allowing it to stand over sulphuric acid. It is very soluble in water, extremely deliquescent and becomes anhydrous when heated on the water-bath.

When carefully and gently heated it forms a glassy mass of basic nitrate which is readily soluble in water; stronger heating produces first less soluble basic nitrates, then insoluble basic nitrates, and finally the oxide.[686] If it is heated in a vacuum at 100° for 17 hours a basic nitrate, $Sc(OH)(NO_3)_2$,[682] is produced, and at 120° for 12 hours the compound $Sc(NO_3)_3,ScO,NO_3$ is formed.[682]

*Scandium Carbonate*, $Sc_2(CO_3)_3,12H_2O$, is formed as a bulky

white precipitate by the addition of ammonium carbonate to a solution of a scandium salt. It is readily soluble in hot solutions of alkali carbonates, and on evaporation these solutions deposit sparingly soluble double carbonates. The addition of water to solutions of the double carbonates causes a precipitation of scandium carbonates. The compounds

$$Sc_2(CO_3)_3,4Na_2CO_3,6H_2O \text{ and } 2Sc_2(CO_3)_3,(NH_4)_2CO_3,6H_2O$$

have been prepared, but no corresponding potassium compound is known.[201]

*Scandium Oxalate*, $Sc_2(C_2O_4)_3,5H_2O$, is formed as a crystalline precipitate by the addition of oxalic acid to a warm solution of scandium sulphate. It is the least soluble of the rare earth oxalates in sulphuric acid; 1 gram dissolves in 1080 grams of 0·2N sulphuric acid.[688] Two molecules of water are lost at ordinary temperatures on standing in the air, 3 molecules at 100°, and 4 molecules at 140°.[682] It forms double oxalates with alkali oxalates. These are very stable, sparingly soluble, and not decomposed by boiling with water.[687] They have the formulæ

$$K_2C_2O_4,Sc_2(C_2O_4)_3;\ Na_2C_2O_4,Sc_2(C_2O_4)_3;$$
$$\text{and } Sc_2(C_2O_4)_3,4(NH_4)_2C_2O_4,7H_2O$$

respectively.[687] A second series of double oxalates of the formulæ

$$Sc_2(C_2O_4)_3,3Na_2C_2O_4,10H_2O;$$
$$Sc_2(C_2O_4)_3,3K_2C_2O_4,10H_2O$$
$$\text{and } Sc_2(C_2O_4)_3,3(NH_4)_2C_2O_4,10H_2O$$

has been prepared.[689] These salts crystallise well and are readily soluble in hot solutions of alkali oxalates. Hydrochloric acid precipitates scandium oxalate from their solutions, and in consequence they are to be regarded as alkali salts of the unknown complex acid, $H_3Sc(C_2O_4)_3$.

*Scandium Acetylacetonate*, $Sc(CH_3COCHCOCH_3)_3$,[343] is obtained by boiling a solution of scandium nitrate with a mixture of acetyl acetone and ammonia. It is soluble in benzene, chloroform, alcohol, and water, and crystallises in colourless plates which melt at 187°-187·5°. It may be sublimed without decomposition at 210°-215°. Molecular weight determinations in benzene and chloroform solutions indicate that it has a normal molecular weight.

Among other scandium salts, the following have been

described: the *borate*,[688] *sulphite*,[687] *selenate*,[682] *iodate*,[688] *platinocyanide*,[688, 678] *thiosulphate*,[687] and many organic salts.[682, 688]

### Detection of Scandium.

Scandium is most easily detected by its emission spectrum. Chemically it can only be detected in the presence of other rare earths when it is present in relatively large quantity. This is best carried out by adding sodium silicofluoride to a boiling hydrochloric acid solution of the rare earths when a white precipitate of scandium and thorium fluorides is thrown down. The precipitate must then be got into solution and the absence of thorium proved by precipitation with potassium iodate. If thorium is present this must be removed by the iodate precipitation and the presence of scandium confirmed by precipitation with sodium thiosulphate.

Scandium oxide is diamagnetic and this property is useful for the detection of small quantities of scandium in other earths.

There is no method for the quantitative estimation of scandium in mixtures of the rare earths.

### Spectra of Scandium.

Scandium salts produce no visible absorption spectrum. The spark spectrum has been measured by Thalen,[691] Nilson,[686] Crookes, Exner and Haschek,[692] and Lockyer and Baxandall.[693] Paulson [694] has shown that the emission spectrum of scandium is composed of 29 series of seven lines. The arc spectrum has been examined by Exner and Haschek,[507, 508] Lockyer [693] and Baxandall, Eder and Valenta,[696] and Fowler.[695]

The strongest lines in the arc spectrum of scandium are: 4247·02, intensity 50; 3572·73, 3614·00, 3907·69, 3912·03, 4023·88, 4314·31, intensity 30; 3353·90, 3372·33, 3558·69, 3567·89, 3576·53, 3630·93, 3642·99, 4020·60, 4320·98, 4325,22, 4374·69, 4400·63, 4415·78, intensity 20; and 6305·94, intensity 10.

## YTTRIUM, Yt. At. Wt. 88·7.

Yttrium was discovered by Gadolin[1] in gadolinite in 1794, and obtained quite pure in 1843 by Mosander.[19] It gives rise to a pure white oxide, $Yt_2O_3$, and this yields colourless salts which have no absorption spectrum when in solution. The oxide is more strongly basic than the other yttrium earths, and

is strong enough to absorb carbon dioxide from the air and to expel ammonia from ammonium compounds.

Yttrium occurs in practically all the rare earth minerals, but more specially in gadolinite, xenotime, euxenite, polycrase, and monazite, all of which are suitable for working up quantities of yttrium salts.

Pure yttrium compounds are best obtained :—[697, 698]

(i) By the fractional hydrolysis of the phthalates, followed by the fractional precipitation of the iodates.

(ii) By fractional crystallisation of the double alkali sulphates, followed successively by the fractional crystallisation of the bromates and nitrates.[237]

(iii) By a rough separation by either the chromate method or by partial decomposition of the nitrates, followed by a combined oxalate and ammonia precipitation.

(iv) By fractional precipitation by potassium ferrocyanide after rough separation by partial decomposition of the nitrates.

(v) In the absence of terbium earths the chromate separation gives good results (Chap. III., p. 38).

Metallic yttrium has never been prepared pure, but it has been obtained in a somewhat impure condition by the action of sodium on the anhydrous chloride;[31] by the electrolysis of a molten mixture of sodium and yttrium chlorides;[21, 699] and by the action of magnesium on the oxide at a high temperature.[523]

As thus prepared it is an iron-grey powder[21] which is readily oxidised in the air and converted into the hydroxide by boiling water.[28]

## Compounds of Yttrium.

*Yttrium Oxide*, $Yt_2O_3$, is obtained as a pure white powder by the ignition of the hydroxide, nitrate, and oxalate. It absorbs carbon dioxide from the air, and is a strong base capable of expelling ammonia from ammonium salts. It is slowly soluble in cold acids, but rapidly soluble in hot acids. The specific gravity is variously given by different investigators, the following values being recorded 5·028 (Cleve),[31] 5·046 (Nilson),[522, 700] and 5·326 (Tanatar and Voljanski).[702] It has a specific heat 0·1026 (Nilson),[522, 700] and 0·11729 (Tanatar and Voljanski).[702] It can be obtained crystalline by fusion with calcium chloride.[701] When yttrium oxide is not quite free from other rare earths it

has a yellow colour. Coefficient of magnetisation of the oxide $-0{\cdot}14 \times 10^{-6}$.

*Yttrium Hydroxide*, $Yt(OH)_3$, is obtained as a white gelatinous precipitate by the addition of ammonia or caustic alkali to a solution of an yttrium salt. It dries to a white powder which readily absorbs carbon dioxide from the air. If the precipitation of an yttrium salt is effected by ammonia in the presence of hydrogen peroxide a hydrated peroxide, $Yt_4O_9,xH_2O$, is produced.[31, 526]

*Yttrium Fluoride*, $YtF_3$.—The anhydrous fluoride is obtained by the action of fluorine on the carbide.[703] When hydrofluoric acid or an alkali fluoride is added to a solution of an yttrium salt, the hydrated fluoride is precipitated as a white gelatinous mass of the formula $YtF_3,\frac{1}{2}H_2O$.[31]

*Yttrium Chloride*, $YtCl_3$.—The anhydrous compound may be obtained by heating an intimate mixture of ammonium chloride and the hexahydrate;[31] by heating the product, obtained by evaporating a solution of the oxide in hydrochloric acid to dryness, in a mixture of chlorine, hydrochloric acid gas, and sulphur monochloride[622, 652] at 170°-180°; by heating the carbide in hydrochloric acid gas;[534, 703] by heating the oxide in a mixture of carbon dioxide and chlorine;[704] and by heating the hexahydrate in hydrochloric acid gas.[705] It melts at 680° and solidifies to form shining white leaflets which volatilise at high temperatures. It is very soluble in water, alcohol, and pyridine; 100 grams of alcohol dissolve 60·1 grams of the chloride at 15° and the solution deposits crystals of $YtCl_3,C_2H_5OH$;[705] 100 grams of pyridine dissolve 60·6 grams of the chloride at 15°[705] and an addition compound is formed. Aqueous solutions deposit crystals of the hexahydrate $YtCl_3,6H_2O$ in large hexagonal prisms. These are soluble in both water and alcohol but not in ether, and have a specific gravity 2·8 at 18°.[705] The crystals, when strongly heated, lose hydrochloric acid, but when heated on the water-bath 5 molecules of water are lost and the last molecule of water passes off at 160° in the presence of hydrochloric acid gas.[652, 705] The double chlorides,

$$2YtCl_3,3PtCl_2,24H_2O,^{[31, 541]}\ 4YtCl_3,5PtCl_4,52H_2O,$$
$$YtCl_3,2AuCl_3,16H_2O, \text{ and } YtCl_3,3HgCl_2,9H_2O\ ^{[21]}$$

have been isolated, and a double compound,

$$YtCl_3,2C_6H_{12}N_4,11H_2O,$$

is formed with hexamethylene tetramine.[428]

*Yttrium Sulphide*, $Yt_2S_3$, is obtained by melting the oxide with sulphur and sodium carbonate,[21] and by heating the anhydrous chloride in sulphuretted hydrogen [31] or the oxide in carbon disulphide.[21] It is a yellow powder which is decomposed by water. A double sulphide, $Yt_2S_3,Na_2S$, is obtained in greenish leaflets by passing a stream of sulphuretted hydrogen over a heated mixture of yttrium oxide and sodium chloride.[704]

*Yttrium Sulphate*, $Yt_2(SO_4)_3$.—The anhydrous sulphate is obtained as a white powder by dehydrating the octohydrate. It has a specific gravity 2·52, a specific heat 0·1319,[522, 700] and is very soluble in cold water.[31, 345] It gives rise to one crystalline hydrate, the octohydrate $Yt_2(SO_4)_3,8H_2O$. This compound is obtained in colourless monoclinic crystals, isomorphous with the corresponding derivatives of neodymium, praseodymium, and erbium,[687] by crystallising from a solution of the oxide in sulphuric acid. This compound has a specific gravity 2·55, and dissolves to the extent of 9·3 grams in 100 grams of cold water and 4·6 grams in 100 of water at 100°. A basic sulphate, $Yt_2O_3,SO_3$, is formed when the anhydrous sulphate is heated to 700°,[349] and a further basic sulphate, $2Yt_2O_3,SO_3,10H_2O$, is produced by the partial precipitation of a solution of the sulphate by dilute ammonia. An acid sulphate, $YtH_3(SO_4)_3$, is formed by crystallising a solution of the anhydrous sulphate in concentrated sulphuric acid.[446] It forms fine prismatic needles. The following alkali double sulphates have been prepared by crystallising mixed solutions of alkali sulphates and yttrium sulphate:

$$4K_2SO_4,Yt_2(SO_4)_3\,;\ Yt_2(SO_4)_3,2(NH_4)_2SO_4,9H_2O\,;$$
$$\text{and } Yt_2(SO_4)_3,Na_2SO_4,2H_2O.^{706}$$

These substances are very soluble in water, the two former being crystalline and the last-named amorphous.[31] A double sulphate is formed with stannic sulphate.[443]

*Yttrium Nitrate*, $Yt(NO_3)_3,6H_2O$, is formed in large deliquescent crystals by concentrating a solution of the oxide in nitric acid. It is very soluble in water, 100 grams of water dissolving 141·6 grams at 25°. On warming the nitrate to 100° 3 molecules of water are lost, but at higher temperatures basic nitrates are formed. A compound, $Yt(NO_3)_3,Yt(OH)_3,3H_2O$, is formed by carefully heating the dry salt until red fumes appear, dissolving the residue in water and crystallising the solution.[345] A

further basic nitrate, $3Yt_2O_3,4N_2O_5,20H_2O$, is formed by shaking the oxide with nitric acid at 25°. This substance is stable in contact with a solution of yttrium nitrate.[241] Hexamethylene tetramine forms a crystalline compound,

$$Yt(NO_3)_3,2C_6H_{12}N_4,10H_2O,$$

with yttrium nitrate.[428]

*Yttrium Carbide*, $YtC_2$, is obtained as a microcrystalline mass by heating the oxide with sugar charcoal in an electric furnace.[534, 703] It is yellow in colour and has a specific gravity 4·13 at 18°. It is decomposed by water, yielding a mixture of gases composed of 72 per cent. acetylene, 18-19 per cent. methane, 4·5-4·8 per cent. ethylene, and 4·5-5·0 per cent. hydrogen.

*Yttrium Carbonate*, $Yt_2(CO_3)_3,3H_2O$, is formed by precipitating a solution of an yttrium salt with alkali carbonate, or by passing carbon dioxide into yttrium hydroxide suspended in water. It is a white powder soluble in excess of alkali carbonate solution to form double carbonates. The following compounds have been prepared in this way as sparingly soluble crystalline substances:

$Yt_2(CO_3)_3,Na_2CO_3,4H_2O$ and $Yt_2(CO_3)_3,(NH_4)_2CO_3,2H_2O$.

Yttrium carbonate acts unfavourably on the growth of plants.[457]

*Yttrium Oxalate*, $Yt_2(C_2O_4)_3,9H_2O$, is formed when oxalic acid is added to a hot acid solution of an yttrium salt. It is a white crystalline powder which dissolves to the extent of 1·0 mg. in a litre of water at 25°,[517] and 1·7258 grams in a litre of normal sulphuric acid. When added to a neutral solution of potassium oxalate it deposits a double oxalate,

$$Yt_2(C_2O_4)_3,3K_2C_2O_4,18H_2O.^{261}$$

Among other salts of yttrium which have been prepared are the *bromate*,[31, 510] *chlorate*,[21, 31] *iodate*,[31] *silicate*,[701] *phosphates*,[31, 456, 707] *silicotungstate*[628] *cobalticyanide*,[1008] *ferricyanide*,[1001] and *platinocyanide*,[710, 711] together with many organic salts,[307, 312, 338, 516, 562, 564, 708 709, 1012]

## Detection of Yttrium.

Yttrium is best detected by means of its spark spectrum. This contains a large number of lines, but two groups of lines near the sodium line toward the red end are especially characteristic.

### Spectra of Yttrium.

Solutions of yttrium salts exhibit no absorption in the visible region of the spectrum.

The spark spectrum has been investigated by Thalen,[712] Bunsen,[262] Auer von Welsbach,[713] Lohse,[669, 719] and Exner and Haschek.[692] The arc spectrum has been measured by Exner and Haschek,[504, 508] Kayser,[716] Eberhard[715] and Eder,[988, 1015] and Valenta.[507] Yttrium compounds, when perfectly pure, do not yield a phosphorescence spectrum. The presence of such a spectrum observed by Crookes[57] was doubtless due to the presence of a small amount of impurity.[62, 63]

The most characteristic lines of the yttrium arc spectrum are:[504, 508] 4375·12, intensity 50; 3710·47, 4077·54, 4128·50, intensity 30; 3216·83, 3242·42, 3328·02, 3600·92, 3611·20, 3621·10, 3633·28, 3664·78, 3774·52, 3788·88, 3950·52, 3982·79, 4102·57, 4143·03, 4309·79, intensity 20; and 4177·74, 4302·45, 4348·93, 4883·89, 6191·91, 6435·27, intensity 15.

## The Terbium Earths.

The elements europium, gadolinium, and terbium constitute the terbium group. These three elements give rise to colourless oxides of the type $M_2O_3$, and in addition terbium forms a higher oxide which probably has the formula $Tb_4O_7$. The sesquioxides are bases of about the same strength, europium being the strongest and terbium the weakest, which give rise to the characteristic salts of these elements. Europium forms a lower chloride, $EuCl_2$, and together with samarium is the only element of the rare earths to form bivalent derivatives. The salts of the elements of this group have been comparatively little investigated, and consequently not much is known about them. The salts of terbium and europium in solution exhibit a weak absorption spectrum in the visible region, whereas those of terbium only exhibit an absorption spectrum in the ultra-violet region. Terbium salts are generally slightly less soluble than the corresponding gadolinium salts.[341] The terbium group of earths is characterised by the fact that the solubility of the double potassium sulphates lies midway between that of the cerium earths and the yttrium earths.

The history of the discovery of the elements of this group is somewhat involved, owing chiefly to changes in nomenclature

of some of the products and to the designation of mixtures of elements as new elements by some investigators. A full account of the discovery will be found in Chapter I. Shortly, however, it can be stated that Marignac[535] discovered gadolinium in 1880, and this was obtained pure by Demarçay[717] in 1901, and by Urbain and Lacombe[236] in 1905; europium was discovered by Demarçay[74,356] in 1900 and obtained free from other elements by Urbain and Lacombe[232] in 1904, and terbium was discovered by Mosander[19] in 1842 and purified by Urbain,[341,718] Potratz,[719] and Delafontaine[720] in 1905.

The terbium earths are found in practically all the cerium and yttrium minerals and are best extracted from gadolinite, xenotime, and samarskite in which they are found to the largest extent, although even in these minerals the amount is very small. Gadolinium is the most abundant of the terbium earths, whilst europium is probably the least plentiful. Monazite, for example, does not contain more than 0·002 per cent. of europium oxide.[232] Europium has been shown to be present in the sun and in certain of the stars.[722]

The terbium earths can be separated as a group from the cerium and yttrium groups by a careful fractionation of the double potassium sulphates under special conditions.[50,212] This method is, however, not to be recommended, since a large part of the terbium earths crystallise with the cerium earths whilst the remainder are in solution with the yttrium earths. The fractionation of the ethyl sulphates, from either alcohol or water solution, effects a satisfactory separation of the terbium earths from the yttrium and cerium earths. In this case the cerium earths separate first and the yttrium earths last. The crystallisation of the mixed formates from an aqueous formic acid solution effects a separation of the terbium earths, although a portion of these elements always remains in solution with the yttrium earths and is not separable by further crystallisation.

The individual earths can be obtained pure from the mixture of earths by the following methods:—

(i) Crystallisation of the double magnesium nitrates in the presence of bismuth magnesium nitrate yields pure europium compounds.

(ii) Crystallisation of the double magnesium nitrates in the

presence of bismuth nitrate, followed by crystallisation of the double nickel nitrates yields pure gadolinium compounds.

(iii) Fractionation of the simple nitrates in the presence of bismuth nitrate from nitric acid solution yields pure terbium compounds.

These methods are extremely lengthy and tedious.

The elements of the terbium group have not been obtained in the metallic condition.

## EUROPIUM, Eu. At. Wt. 152·0.

*Europium Oxide*, $Eu_2O_3$, is obtained as a pale rose-coloured powder by ignition of the nitrate, sulphate, hydroxide, or oxalate. When prepared from the sulphate, a very high temperature (1600°) is required, and under these circumstances the colour is a little more intense.[232, 357] It is magnetic and has a coefficient of magnetisation $33{\cdot}5 \times 10^{-6}$.

*Europium Chloride*, $EuCl_3$, is formed as fine yellow needles by heating the hydrated chloride in a mixture of chlorine and sulphur monochloride.[423] If the oxide is used for the preparation of the anhydrous chloride by the above-mentioned method a mixture of europium chloride and europous chloride is obtained.[723] Europium chloride is soluble in water, and when heated to 600° in air it is converted into the oxychloride EuOCl. This substance is a white powder insoluble in water, but readily soluble in mineral acids.

*Europous Chloride*, $EuCl_2$, is formed as a white amorphous solid by heating europium chloride in hydrogen.[723] It is soluble in water without change, but on boiling the solution, oxidation occurs and europium oxide is precipitated.

$$12EuCl_2 + 3O_2 = 8EuCl_3 + 2Eu_2O_3.$$

Europous chloride is more stable than samarous chloride.

*Europium Sulphate*, $Eu_2(SO_4)_3,8H_2O$, is obtained as a pale rose-coloured crystalline mass from a solution of the oxide in sulphuric acid.[232] It is slightly hydrolysed in solution,[659] and the crystals become anhydrous at 375°.

Several organic salts have been prepared.[564,627]

### Detection of Europium.

Europium is best detected by means of its arc spectrum, the lines of which are very bright,[233] and serve for the detection of the merest traces of europium compounds.

**Spectra of Europium.**

Solutions of europium salts, being rose-coloured, exhibit a visible absorption spectrum. This, however, is weak and not very characteristic. The most important bands have been measured in nitric acid solution by Demarçay,[357] who finds the heads of the bands situated at 590, 570, 535, 525, 465, 395·5, 385·5, and 380. Of these the strongest and most characteristic is the band 465.

The spark spectrum is rich in very bright lines, and has been measured by Demarçay,[357] Eder[1016] and Valenta,[673] Exner and Haschek,[724] and Crookes.[725]

The arc spectrum is very bright and characteristic, and has been measured by Exner and Haschek,[504, 508, 724] Eberhard,[233] and Eder and Valenta.[574] Pure europium exhibits no luminescence spectrum,[729] but when a trace of europium is mixed with calcium sulphide or calcium oxide, or when traces of other earths are present in europium compounds, a very intense luminescence spectrum is obtained. This has been investigated by Crookes,[727] Urbain,[726, 728] and Demarçay.[76]

The following lines are the strongest in the europium emission spectrum, and most suitable for the identification of this element: 4129·90, 4205·20, intensity 100; 3819·80, 3930·66, 3972·16, 4435·75 4594·27, 4627·47, 4662·10, intensity 50; 3725·10, 3907·28, 4522·76, intensity 30; and 3688·57, 6645·44, intensity 20.

## GADOLINIUM, Gd. At. Wt. 157·3.

*Gadolinium Oxide*, $Gd_2O_3$, is obtained by ignition of the oxalate, nitrate, and hydroxide. It is a pure white hygroscopic powder, but a trace of terbium oxide turns it yellow.[233] It absorbs carbon dioxide from the air[730] and dissolves slowly in acids, the rate of solution increasing as the process proceeds. When heated in hydrogen it darkens, although no reduction occurs.[730] It has a specific gravity 7·407 and a magnetic susceptibility $161 \times 10^{-6}$.

*Gadolinium Fluoride*, $GdF_3$, is formed as a white gelatinous precipitate when a solution of the sulphate is treated with hydrofluoric acid.[743] It becomes granular when heated on the water-bath, is insoluble in water but slightly soluble in hot hydrofluoric acid.

*Gadolinium Chloride*, $GdCl_3$.—The anhydrous chloride is

formed when the oxide is heated in a mixture of chlorine and sulphur monochloride.[428] It forms monoclinic prisms of specific gravity 4·52 and melting-point 628°. When heated in air the oxychloride, GdOCl, is produced as a white amorphous non-volatile powder which is insoluble in water but dissolves slowly in hydrochloric and nitric acid. Gadolinium chloride crystallises from aqueous solution in large prismatic crystals as the hexahydrate $GdCl_3,6H_2O$. These are deliquescent and have a specific gravity 2·42. It forms a double chloride,

$$GdCl_3,PtCl_4,10H_2O,$$

with platinic chloride crystallising in golden-yellow prismatic needles, and a double chloride, $GdCl_3,AuCl_3,10H_2O$, with auric chloride, crystallising in yellow tablets.[730]

*Gadolinium Sulphate*, $Gd_2(SO_4)_3$.—Gadolinium sulphate is obtained anhydrous by heating the crystalline hydrate. It is soluble in water (100 grams) to the following extent:—[730]

| Temperature | 0° | 9·3°-10·6° | 14° | 25° | 34·4° |
|---|---|---|---|---|---|
| Grams | 3·98 | 3·33 | 2·80 | 2·40 | 2·26 |

The solubility curve of gadolinium sulphate indicates that the transition point from anhydrous salt to octohydrate lies at 9·3°-10·6°. The anhydrous salt has a specific gravity 4·139 at 14·6°.

In solution, gadolinium sulphate is slightly hydrolysed,[659] and at ordinary temperatures the solutions deposit monoclinic crystals of the octohydrate which are isomorphous with the corresponding sulphates of the metals of both the cerium and yttrium groups. The octohydrate has a specific gravity 3·01 at 14·6°.

A basic sulphate, $Gd_2O_3,SO_3$,[381] is obtained by heating the anhydrous sulphate to 800°-850°.

A double potassium gadolinium sulphate,

$$Gd_2(SO_4)_3,K_2SO_4,2H_2O,$$

is formed by crystallising a solution containing 3 molecules of potassium sulphate to 1 molecule of gadolinium sulphate. It is obtained in well-formed crystals which are sparingly soluble in water. The corresponding sodium double salt,

$$Gd_2(SO_4)_3,Na_2SO_4,2H_2O,$$

is obtained in the same way.[1017]

*Gadolinium Nitrate*, $Gd(NO_3)_3,6H_2O$, crystallises in large, very soluble crystals from a neutral solution of the oxide in nitric acid.[731] Benedicks[730] states that this compound has $6\frac{1}{2}$ molecules of water. It melts at 91° in its water of crystallisation and has a specific gravity 2·33. A second hydrate,

$$Gd(NO_3)_3,5H_2O,$$

is obtained by crystallising the nitrate from nitric acid.[731] This compound melts at 92°. Gadolinium nitrate is the least soluble in nitric acid of all the rare earth nitrates.[730] It is isomorphous with the nitrates of praseodymium and neodymium.[732]

A double gadolinium ammonium nitrate separates from a solution of 2 molecules of ammonium nitrate and 1 molecule of gadolinium nitrate, in long thin needles which are very soluble in water.

A series of isomorphous double nitrates, of the general formula $2Gd(NO_3)_3,3M''(NO_3)_2,24H_2O$, is formed with the nitrates of the metals magnesium, nickel, cobalt, and zinc. A similar compound is formed with manganese nitrate, but this substance is too soluble to be obtained crystalline.[451]

*Gadolinium Carbonate*, $Gd_2(CO_3)_3,13H_2O$, is formed by the prolonged action of carbon dioxide on gadolinium hydroxide suspended in water. If the gas is only passed in for a short time a basic carbonate, $Gd(OH)CO_3,H_2O$, is formed in small white needles.[700]

*Gadolinium Oxalate*, $Gd_2(C_2O_4)_3,10H_2O$, is produced as a crystalline precipitate, composed of fine monoclinic needles, by the addition of oxalic acid to an acid or neutral solution of a salt of gadolinium. It loses 6 molecules of water at 110°, and is sparingly soluble in mineral acids and ammonium oxalate solution.[261]

Among other salts of gadolinium which have been prepared are the *bromide*,[730] *cobalticyanide*,[1008] *selenate*,[730] *selenite*,[730] *sulphide*,[562] and several organic salts.[253, 312, 516, 564, 730]

## Detection of Gadolinium.

Gadolinium is detected by means of its arc spectrum which is very brilliant and characteristic.

## Spectra of Gadolinium.

Solutions of gadolinium salts exhibit no absorption in the visible region,[581 730] but four bands have been detected in the

ultra-violet region. These have been measured by Urbain, and have the values:[733] 3116-3105, 3060-3057, 3056-3055, and 3054-3050.

Gadolinium has a very brilliant spark spectrum which has been measured by Benedicks,[730] Demarçay,[74, 731] Exner and Haschek,[734] Baur and Marc,[63] Urbain,[733] Crookes,[735] and Eder.[1018]

The arc spectrum has been investigated by Exner and Haschek,[504, 508] Eberhard,[233] and Eder and Valenta.[674]

Paulson[1019] has described regularities in the spectrum of gadolinium. Pure gadolinium compounds exhibit no luminescence spectrum, but when slightly impure a brilliant green luminescence is observed.[341, 733, 735]

The following arc lines are the most brilliant and best suited for detection of gadolinium: 3768·60, 4063·62, intensity 20; 3646·36, 4130·59 intensity 15; 3082·15, 3100·66, 3422·62, 3545·94, 3549·52, 3585·12, 3646·36, 3671·39, 3719·63, 3743·68, 3796·62, 3814·18, 3852·65, 3916·70, 4037·49, 4050·05, 4070·51, 4073·99, 4085·73, 4098·80, 4184·48, 4251·90, 4262·24, 4325·83, 4327·29, 4342·35, 6114·26, intensity 10.

## TERBIUM, Tb. At. Wt. 159·2.

*Terbium Oxide*, $Tb_2O_3$,[341] is obtained as a white powder which is strongly magnetic,[371] having a coefficient of magnetisation $237 \times 10^{-6}$. It dissolves in acids to form colourless terbium salts.

*Terbium Peroxide.*—When terbium oxalate is ignited a dark brown oxide is produced, and when the sulphate is ignited at 1600° a black oxide results. This substance is probably $Tb_4O_7$ but may be a mixture of this subtance with $TbO_2$ since the active oxygen content is greater than that required for $Tb_4O_7$. It loses oxygen at high temperatures,[736] and is scarcely acted on by cold hydrochloric and nitric acid. Concentrated acids when hot convert it rapidly into terbium salts.

*Terbium Chloride*, $TbCl_3$.—The anhydrous chloride is prepared by the action of chlorine and sulphur monochloride vapour on the oxide at a high temperature.[423] It is a white crystalline substance, melting at 588° and having a density 4·25. It is soluble in water without hydrolysis. The hexahydrate,

$$TbCl_3,6H_2O,^{234, 341, 718}$$

is formed by crystallising a solution of the oxide in hydrochloric acid. It is very soluble and deliquescent, and has a great tendency to form supersaturated solutions. When the crystals are heated in the air an oxychloride, TbOCl, is formed.[719]

*Terbium Sulphate*, $Tb_2(SO_4)_3,8H_2O$,[234, 341, 718] is formed by the addition of alcohol to a solution of the oxide in sulphuric acid. It crystallises in micaceous lamellæ which are stable in dry air at ordinary temperatures. It is isomorphous with the octohydrates of the other rare earth sulphates. It loses the whole of its water of crystallisation at 360°

*Terbium Nitrate*, $Tb(NO_3)_3,6H_2O$,[234, 341, 718] is formed in monoclinic[736] needles by crystallising from a solution of the oxide in nitric acid. It melts at 89·3°.

*Terbium Carbide*, $TbC_3$, is formed mixed with the oxide by the ignition of organic salts of terbium.[719] The oxide is removed by dilute mineral acids.

Among other terbium compounds that have been prepared are: the *bromate*,[719] *carbonate*,[719] *bromide*,[431] and several organic salts.[719, 1012]

## Detection of Terbium.

Terbium is most easily detected by its arc spectrum, the following lines, according to Eberhard,[737] being the most useful in detecting traces of terbium in rocks and mixtures of oxides: 3523·82, 3676·52, 3704·01, 3703·05, 4005·62, 4278·71.

When terbium is present in fair quantity it may be detected by its absorption band 488.

The colour of the mixed oxides gives a clue to the presence of terbium, for the mixture takes on a yellow to brown colour in the presence of terbium, which is darker the larger the amount of terbium present.

## Spectra of Terbium.

Solutions of terbium salts exhibit a single absorption band in the blue region. This is situated at 488. Nine weak bands occur in the ultra-violet region. The absorption spectrum has been measured by Lecoq de Boisbaudran,[738, 739] and by Urbain.[740]

The spark spectrum is extremely rich in lines, and has been measured by Demarçay[741] and Urbain.[740]

The arc spectrum has been investigated by Eberhard,[737] Eder and Valenta,[742] and Exner and Haschek.[504, 508]

Pure terbium oxide shows no luminescence spectrum, but a trace of terbium oxide in alumina exhibits a pure white luminescence. A beautiful green fluorescence is shown by the chloride when under the influence of cathode rays.[341]

The strongest lines in the arc spectrum of terbium[504, 508] are: 3509·34, 3848·90, 3874·33, 3977·01, intensity 20; 3531·86, 3561·90, 3650·60, 3659·02, 3939·75, 3982·07, 4005·70, intensity 15; 3324·53, 3568·69, 3600·60, 3628·35, 3704·10, 3711·91, 3899·34, 4012·99, 4278·70, 4752·69, intensity 10.

## The Erbium Earths.

The erbium group of rare earths is made up of dysprosium, holmium, erbium, and thulium. These elements have all been separated from the original erbium, i.e. the terbium of Mosander. They are characterised by their highly coloured salts and by the absorption spectra of solutions of their salts. Oxides of the type $M_2O_3$ are formed by these elements, of which dysprosia is the strongest base and is followed in strength by holmia, erbia, and thulia in order.

The earth terbia was discovered in 1843 by Mosander,[19] but at a later date received the name erbia.[22] This material was shown to be complex, in 1879, by Soret[744] and Cleve,[44] and the earth holmia was separated from it. About the same time a further earth, thulia, was separated by Cleve[44] and by Lecoq de Boisbaudran.[745] In 1886, Lecoq de Boisbaudran[67] separated the original holmia into two earths which he named respectively holmia and dysprosia. At the present time the four earths mentioned represent all that have been isolated in this group, although Auer von Welsbach and Krüss have stated that erbia is a mixture; Krüss and Hofmann regard holmia as a mixture, and Marc[265] denies the existence of thulia, whereas Auer von Welsbach regards it as a mixture of three elements. Notwithstanding these statements Urbain has shown that further fractionation does not change the absorption spectrum of erbium, and he has also succeeded in preparing absolutely pure dysprosium[243] compounds. Holmberg[360] and Langlet,[746] have obtained holmium compounds in which only the merest traces of erbium and dysprosium are indicated by spectroscopic analysis. With regard to thulium,

despite the scepticism of Marc, Auer von Welsbach[747] states that he has divided it into three elements which he names thulium I, thulium II, and thulium III. On the other hand, James,[95, 240] by 15,000 crystallisations of the bromate, has failed to effect any separation. The material examined by James was spectroscopically examined by Crookes who found it to be practically pure thulium containing only the slightest trace of ytterbium. Further, the thulium II of von Welsbach is identical with the thulium of James.

It may therefore be taken that pure erbium and dysprosium compounds have been obtained. Holmium and thulium certainly exist, but possibly are not simple substances. Until further work shows that holmium and thulium are in reality mixtures, the products of Holmberg and James respectively may be regarded as representing the pure compounds of these elements. For full details of the discovery of the erbium earths the introductory chapter must be consulted.

The erbium earths occur in practically all of the rare earth minerals, but often only to a very small extent. They are most conveniently extracted from xenotime, fergusonite, euxenite, polycrase, and blomstrandin. Of these elements erbium is the most plentiful, and is, after yttrium, the most abundant of all the yttrium earths.

The individual elements are obtained from the mother-liquors after the precipitation of the cerium earths by means of potassium sulphate. The mixture of earths obtained from this solution is fractionated by one or more of the following methods: (i) precipitation by bases, (ii) by the oxide method, (iii) by decomposition of the nitrates, (iv) by the oxalate, chromate, acetylacetonate or ethylsulphate methods (see Chap. III.). Probably the most successful method is a successive crystallisation of the bromates and ethylsulphates followed by the partial decomposition of the nitrates by fusion (see James[237] and also Chap. III.).

The chemistry of the erbium earths is very incomplete, probably that of erbium is the best investigated. The metallic elements have not been isolated in any case.

## DYSPROSIUM, Dy. At. Wt. 162·5.

The investigation of the dysprosium compounds is mainly due to Urbain[748, 749] who was able to obtain 50 grams of the oxide

free from all known elements by fractionation of the ethylsulphate.

*Dysprosium Oxide*, $Dy_2O_3$, is obtained as a pure white powder by heating the oxalate. It does not absorb oxygen when strongly heated in the gas, and is unaffected by heating in hydrogen. It is strongly magnetic, and has a coefficient of magnetisation $290 \times 10^{-6}$, which is 12·8 times as large as that of ferric oxide.[373] It dissolves in acids to produce green or yellow salts.[750]

*Dysprosium Chloride*, $DyCl_3$.—The anhydrous chloride is prepared by heating the oxide in a mixture of chlorine and sulphur monochloride.[751] As thus prepared it forms yellowish shining crystals which melt at 680° and have a specific gravity 3·67.[423] When heated in oxygen it is converted into greenish-yellow leaflets of the oxychloride DyOCl. This substance dissolves slowly in nitric acid and hydrochloric acid but is insoluble in water.[751] Dysprosium chloride forms the hydrate $DyCl_3,6H_2O$ in bright yellow crystals which resemble the corresponding terbium compound but are less deliquescent.[736] Aqueous solutions are practically neutral.[1005]

*Dysprosium Sulphate*, $Dy_2(SO_4)_3,8H_2O$, is formed in bright yellow crystals which are stable at 110° and are completely dehydrated at 360°. The anhydrous salt is converted into the oxide at a red heat.[752] It dissolves in water, giving a faintly acid solution.

*Dysprosium Nitrate*, $Dy(NO_3)_3,5H_2O$, forms yellow crystals which lose their water in a dry atmosphere. It melts at 88·6° in its water of crystallisation, and resembles bismuth nitrate rather than terbium nitrate.[736]

*Dysprosium Carbonate*, $Dy_2(CO_3)_3,4H_2O$, is formed as an insoluble powder when an aqueous suspension of dysprosium hydroxide is treated with carbon dioxide.[750] It loses 3 molecules of water at 15°, and when added to a concentrated solution of ammonium carbonate it is changed into a white crystalline sparingly soluble double carbonate, $(NH_4)_2CO_3,Dy_2(CO_3)_3,2H_2O$, which loses ammonia at 60°

*Dysprosium Oxalate*, $Dy_2(C_2O_4)_3,10H_2O$, is formed as a microcrystalline powder when a solution of the nitrate is added to a concentrated solution of oxalic acid.[750] It is quite insoluble in water but dissolves in normal sulphuric acid to the extent of 0·1893 gram of the anhydrous salt in 100 c.c. of the solvent at

20°. A double oxalate, $Dy_2(C_2O_4)_3,K_2C_2O_4,2H_2O$,[750] is formed as a white sparingly soluble crystalline powder when a solution of the nitrate is treated with potassium oxalate. It is readily soluble in dilute mineral acids.

Among other salts which are described by Jantsch and Ohl[750] are the *selenate*, $Dy_2(SeO_4)_3,8H_2O$, the *phosphate*, $DyPO_4,5H_2O$, the *chromate*, $Dy_2(CrO_4)_3,10H_2O$, the *platinocyanide*,

$$Dy_2[Pt(CN)_4]_3,21H_2O,$$

the *formate*, $Dy(HCO_2)_3$, and the *acetate*, $Dy(C_2H_3O_2)_3,4H_2O$.

### Spectra of Dysprosium.

Solutions of dysprosium salts exhibit six absorption bands in the ultra-violet and four bands in the visible region; the former have been measured by Urbain[748, 749] and the latter by Lecoq de Boisbaudran.[67] The heads of the bands lie at 3865, 3795, 3650, 3510, 3380, 3225 in the ultra-violet, and 7530, 4750, 4515, 4275 in the visible region.

The spark spectrum contains five lines in the visible region and a large number in the ultra-violet. The spectrum has been measured by Urbain[373] and by Lecoq de Boisbaudran,[67] the former of whom gives the following values for the visible lines: 5835, 5750, 5700, 5269, and 5259.

The arc spectrum has been measured by Eberhard,[753] Eder and Valenta,[754] Urbain,[243] and Exner and Haschek.[504, 508]

The luminescence spectrum has been investigated by Urbain.[243, 755]

The strongest lines of the arc spectrum[504, 508] are 4211·89, 4957·59, intensity 30; 3531·87, 3944·83, 3968·56, 4000·69, 4044·16, 4087·14, 4168·15, 4187·00, intensity 20; 3524·18, 3536·20, 3538·70, 3550·37, 4103·50, 4221·30, 4589·53, intensity 15.

## HOLMIUM, Ho. At. Wt. 163·5.

It is extremely doubtful whether this element has been obtained pure, despite the fact that atomic weight determinations have been carried out. These determinations were carried out with material which contained traces of erbium and dysprosium. The *oxide* $Ho_2O_3$ is pale yellow in colour,[756] and gives rise to yellow salts which have an orange tint.

The absorption spectrum of holmium contains 15 bands which have been measured by Urbain,[748, 749] Forsling,[757] and Holmberg.[360] Using a 100 mm. layer of a 2N solution of an holmium salt the last-named observer finds the following values for the strongest bands: 6446-6418, 6414-6384, 5385-5349, 4860-4846, 4454-4459, 4223-4216, and 4179-4152.

The spark spectrum is very rich in lines and has been measured by Exner and Haschek[758] and Eberhard.[758]

The arc spectrum has been investigated by Exner and Haschek[504, 508] and Eder and Valenta.[674] For purposes of identification and detection of holmium the first-named investigators recommend the following strong arc lines:[504, 508] 3456·15, 3748·32, 3891·17, intensity 30; 3399·12, 3425·49, 3428·27, 3474·40, 3484·98, 3515·73, 3598·92, 3757·41, 3889·10, 4045·58, 4254·59, intensity 20.

## ERBIUM, Er. At. Wt. 167·7.

*Erbium Oxide*, $Er_2O_3$, is a rose-red powder obtained by ignition of the salts of volatile oxy-acids. Its colour is unchanged by strong ignition. It has a specific gravity 8·64 and a specific heat 0·065.[522] It dissolves in acids to form intensely red salts, all of which are shown by the photographic method to be faintly radioactive.[759]

*Erbium Sulphate*, $Er_2(SO_4)_3$.—The anhydrous sulphate is formed by prolonged heating of the hydrated sulphate at 400°. It commences to decompose at 630°, and a basic sulphate, $Er_2O_3,SO_3$, is formed at 845°, in thin white needles.[246, 349] This compound begins to decompose at 950°, and at 1055° is completely converted into the oxide. Hofmann and Burger state that a basic sulphate, $(ErO_2)_2SO_4$, is formed at 850°.[244]

Erbium sulphate forms a crystalline hydrate, $Er_2(SO_4)_3,8H_2O$, in red monoclinic crystals when a solution of the oxide in sulphuric acid is slowly concentrated at 20°-25°. This compound is isomorphous with the corresponding compounds of praseodymium, neodymium, and yttrium.[587, 760] It has a specific gravity[522] 3·18 and is slightly hydrolysed in solution.[659] Readily soluble double sulphates,

$$Er_2(SO_4)_3,K_2SO_4,4H_2O \text{ and } Er_2(SO_4)_3,(NH_4)_2SO_4,4H_2O,$$

are formed by crystallising mixtures of the two simple sulphates.

*Erbium Nitrate*, $Er(NO_3)_3,5H_2O$, forms large red crystals by concentrating a solution of the oxide in nitric acid. The crystals are stable in the air at ordinary temperatures. Erbium nitrate combines with hexamethylene tetramine[428] to form the compound $Er(NO_3)_3,2C_6H_{12}N_4,10H_2O$, which separates in red monoclinic crystals. A further double compound,

$$Er(NO_3)_3,4C_{11}H_{12}N_2O,$$

is formed with antipyrine[511] in pink tablets which melt at 175°-176°.

*Erbium Oxalate*, $Er_2(C_2O_4)_3,10H_2O$, is prepared by the addition of oxalic acid to a hot acid solution of an erbium salt. It separates as a red microcrystalline powder, composed of rosettes of leaflets.[246] When kept over phosphorus pentoxide in a vacuum it loses 7 molecules of water and forms the trihydrate, and at 575° it is decomposed into the oxide.

Among other erbium salts the following have been prepared: the *selenite*,[761] *tungstate*,[762] *platinocyanide*,[761] and a few organic salts.[312, 562, 563, 564, 761]

## Spectra of Erbium.

*Absorption Spectrum.*—Solutions of erbium salts give sharp absorption bands in the red, green, and blue regions. These bands have been measured by Bunsen,[262] Cleve,[44, 763] Soret,[666] Forsling,[764] Hofmann and Bugge,[362] and Exner.[637] The values obtained by the different observers differ considerably from one another, but this is without doubt due to impurities in one or other of the preparations used in the determination. Some 11 bands have been measured which are definitely due to erbium, the maxima of the strongest and most characteristic of which are: 653, 523, 487, 450, and 442. In the infra-red, absorption bands have been found at[769] 0·649$\mu$, 0·687$\mu$, 0·797$\mu$, and 0·980$\mu$. The influence of temperature on the bands of the absorption spectrum has been investigated by Jones,[768] and du Bois has shown that at the temperature of liquid air and under the influence of a magnetic field new erbium absorption bands appear.[767]

*Flame Spectrum.*—When salts of erbium are heated in a Bunsen flame a discontinuous spectrum is emitted, the lines of which lie approximately in the positions of the absorption bands.[22, 765, 766]

*Spark Spectrum.*—The spark spectrum has been measured

by Exner and Haschek,[784] Thalen,[766] and Eberhard.[753] The brightest and most persistent lines are: 3230·72, 3264·91, 3312·56, 3372·92, 3499·28, 3692·85, 3896·40, 3906·47, and 3938·79.

*Arc Spectrum.*—The arc spectrum is very rich in lines and has been measured by Exner and Haschek,[504, 508] Eder [988, 1015, 1020] and Valenta,[674] and by Eberhard.[753]

Erbium oxide gives rise to a reflexion spectrum. The salts, however, are not active in this way.

The most intense lines in the arc spectrum [504, 508] are: 3372·92, 3692·85, 3906·47, intensity 20; 3499·28, 3896·40, 3974·89, 4151·29, intensity 15; 3312·60, 3385·23, 3616·75, 3729·69, 3830·69, 3902·95, 3932·48, 3938·79, 3973·26, 3973·78, 4008·12, 4020·69, 4059·98, 4087·80, 4143·11, 4419·78, 4563·45, 4631·10, 4675·77, 4759·83, 5827·01, 6221·22, intensity 10.

## THULIUM, Tm. At. Wt. 168·5.

It seems probable that the material which has been regarded as thulium is, in reality, complex. Auer von Welsbach [747] claims to have split it into three fractions, thulium I, thulium II, and thulium III; of these, however, he has only been able to get thulium II pure. Thulium II is identical with the thulium obtained by James,[44, 240] who, in all probability, has obtained it purer than anyone else. This material is doubtless uniform and simple, and must be taken to represent the element thulium. It is, however, impossible to assert that the old thulium is complex until the fractions thulium I and thulium III of von Welsbach are definitely identified and characterised.

*Thulium Oxide*, $Tm_2O_3$,[95] is a dense white powder prepared by igniting the oxalate. Under normal conditions it has a greenish tinge, and when cautiously heated it emits a carmine glow. It dissolves in acids to form greenish-tinted salts. The colour of the salts is almost complementary to that of the erbium salts, and consequently traces of erbium salts have a very marked effect on the colour of thulium salts. *Thulium hydroxide* $Tm(OH)_3$ is best prepared by precipitation of solutions of the salts with ammonia.

*Thulium Chloride*, $TmCl_3,7H_2O$,[95] is obtained by crystallising a solution of the oxide in hydrochloric acid. It forms green crystals which are very soluble in water and alcohol.

*Thulium Sulphate*, $Tm_2(SO_4)_3,8H_2O$,[95] is obtained in green crystals by precipitating a solution of the chloride in dilute sulphuric acid with an excess of alcohol. It loses its water of crystallisation at a dull red heat.

*Thulium Nitrate*, $Tm(NO_3)_3,4H_2O$,[95] is formed in green crystals by the usual method.

*Thulium Bromate*, $Tm(BrO_3)_3,9H_2O$,[95] is formed in pale bluish-green hexagonal prisms by the action of barium bromate on thulium sulphate. It is more soluble than erbium bromate, but less soluble than yttrium bromate and is isomorphous with the bromates of the metals of the yttrium group.

*Thulium Oxalate*, $Tm_2(C_2O_4)_3,6H_2O$,[95] is prepared as a greenish-white precipitate by the addition of oxalic acid to the solution of a thulium salt. It is appreciably soluble in solutions of alkali oxalates.

*Thulium Acetylacetonate*, $Tm(CH_3COCHCOCH_3)_3$,[95] is formed by warming thulium hydroxide in a mixture of absolute alcohol and acetylacetone until it dissolves. On cooling, it crystallises with 1 molecule of water.

### Spectra of Thulium.

The absorption spectrum of thulium has been investigated by Cleve,[44, 771] Thalen,[666] and Forsling;[774] the last-named observer found characteristic bands at 7015, 6845-6825, 6593-6585, 4643, 3604, and 3604-3595.

The arc spectrum has been measured by Exner and Haschek,[504, 508] and Eder,[1020] and Valenta.[772] The first-named investigators give the following as the most intense lines:[504, 508] 3848·13, intensity 50; 3131·40, 3462·37, 3718·07, 3744·22, 3761·49, 3762·09, 3795·90, intensity 20; 3700·41, 3701·54, 3734·29, 4094·33, 4105·99, 4187·79, intensity 15; 3134·00, 3362·78, 3425·27, 3441·71, 3453·82, 3608·92, 4481·44, intensity 10.

Regularities in the thulium spectrum have been described by Paulson.[1021]

## The Ytterbium Earths.

The sub-group of earths known as the ytterbium earths is composed of the three elements, ytterbium, lutecium, and celtium, which have been isolated from the old ytterbium in recent years.

The elements of this group give rise to colourless oxides of the general formula, $M_2O_3$, and these dissolve in acids to form colourless salts. These elements are so alike that it is impossible to distinguish between them by chemical tests, and they have so great a resemblance to the old ytterbium that a general description of the properties of the compounds of the old ytterbium could serve as a description of the compounds of each of these elements, provided that the necessary changes were made in the physico-chemical data.

Ytterbium was separated from the erbium earths in 1878 by Marignac,[257,773] and was thoroughly investigated by Nilson.[675,686,774] It was regarded as elementary until 1905, when Auer von Welsbach, from spectroscopic observations, cast doubts on its uniform character. In 1907, Urbain,[89] and in 1908 Auer von Welsbach,[267] published accounts of methods for the separation of ytterbium into two constituents. Auer von Welsbach proposed the names Aldebaranium and Cassiopëium for the two elements, whereas Urbain suggested the names Ytterbium (neo-ytterbium) and Lutecium respectively for these elements. In point of time the isolation of these elements by Urbain preceded [89,777,778,779] that of Auer von Welsbach, and in consequence Urbain is to be regarded as the discoverer of these elements, and the names proposed by him have therefore been generally adopted. The material which Urbain used in the separation of the elements originated from xenotime; when, however, he [93] used ytterbium from gadolinite, he found that a third element, which he named celtium, was present. This element does not appear to be present in xenotime in a detectable amount.

The elements lutecium and ytterbium occur in practically all the rare earth minerals which contain yttrium earths. The quantity of these elements is very small, but they are most conveniently extracted from gadolinite, xenotime, polycrase, and blomstrandin. Celtium has, as yet, been extracted only from gadolinite, but there appears to be no reason to doubt its presence in many of the other minerals.

The isolation of the pure compounds of these elements will, perhaps, be more clearly followed if the separation of the old ytterbium is considered first, and then the separation of this substance into its constituents.

### Isolation of the "Old Ytterbium".

For this purpose, starting from the double potassium sulphates of the yttrium earths, one or more of the following methods may be adopted: (i) precipitation by bases ($NaOH, NH_3$, aniline), (ii) the oxide method, (iii) decomposition of the nitrates, (iv) by the oxalate, chromate, acetylacetonate, ethylsulphate, or bromate methods (see Chap. III.).

### Separation of Lutecium and Ytterbium.

The following three methods have been adopted for this purpose :—

(i) Urbain subjected the nitrates to 15,000 fractional crystallisations from nitric acid solution (specific gravity 1·3).[89]

(ii) Auer von Welsbach fractionated the double ammonium oxalates from ammonium oxalate solution.[267] He states[90] that in this process the separation proceeds slowly until about 200 operations have been carried out, but at this point there is a marked increase in the rate of separation. This behaviour, he considers, could be ascribed to the presence of a third element lying between ytterbium and lutecium; although spectroscopic investigation does not confirm this view.

(iii) Fractionation of the mixed bromates.[237]

## YTTERBIUM (NEOYTTERBIUM, ALDEBARANIUM), Yb. At. Wt. 173·5.

Very little is known of the chemistry of this element. Its oxide, $Yb_2O_3$, is a white powder, which is coloured brown or yellow by traces of thulium. It is more magnetic than lutecium oxide, the ratio of the susceptibilities being

$$Yb_2O_3 : Lu_2O_3 = 53 : 13.^{89}$$

The coefficient of magnetisation of the oxide is given as $18{\cdot}3 \times 10^{-6}$ by St. Meyer[374] and $33{\cdot}6 \times 10^{-6}$ by Blumenfeld and Urbain.[89]

The anhydrous *chloride*, $YbCl_3$, has been prepared by the action of sulphur monochloride and chlorine on the heated oxide. It forms colourless leaflets which melt at 880°.[423]

The *sulphate* crystallises with 8 molecules of water,[89] and has been obtained quite pure for determination of the atomic weight.

### Spectra of Ytterbium.

The arc spectrum of ytterbium has been examined by Eder[1020] and Valenta,[782] Exner and Haschek,[504, 508] and Urbain and Blumenfeld.[781] The lines are exceptionally brilliant, the most intense being: 3289·50, intensity 200; 3988·16, intensity 100; 3464·47, 5556·67, intensity 20; 3031·26, 3107·99, intensity 15. There are about 500 lines[781] in the region 2300-3500.

The spark spectrum has been investigated by Auer von Welsbach,[267] and the phosphorescence spectrum by Urbain.[776] Blumenfeld and Urbain have examined the ultra-violet spectrum.[1022]

## LUTECIUM (CASSIOPËIUM), Lu. At. Wt. 175·0.

The chemistry of lutecium is in the same state as that of ytterbium. The oxide is white, but coloured yellow if the slightest trace of thulium is present. It has a coefficient of magnetisation[89, 374] $3{\cdot}78 \times 10^{-6}$ and gives rise to colourless salts. The anhydrous *chloride*, $LuCl_3$, is obtained in colourless leaflets by the action of chlorine and sulphur monochloride on the heated oxide.[89, 423] The *sulphate* has been obtained quite pure for atomic weight determinations and crystallises with 8 molecules of water.[89]

### Spectra of Lutecium.

The spark spectrum of lutecium has been investigated by Auer von Welsbach,[267] Urbain,[93] and Eder and Valenta,[782] The phosphorescence spectrum has been examined by Urbain[776] and the arc spectrum by Eder[1020] and Valenta,[782] and Exner and Haschek.[504, 508] The last-named investigators give the following lines as the most intense: 6222·10, intensity 100; 3507·57, 4184·40, 5476·88, 6463·40, intensity 50; 3077·75, 3359·74, 3397·21, 3472·65, 3554·58, intensity 30; 2615·50, 2911·53, 3198·27, 3254·45, 3281·89, 3312·30, 3376·69, 3508·55, 3568·00, 3624·10, 3636·41, 3876·80, 4124·87, 4518·74, 5983·92, 5984·32, intensity 20.

The high frequency spectrum has been examined by Friman.[1023]

The lines 5104·6, 5067·4, and 5009·7 do not appear in the spectra of lutecium or ytterbium but are present in the spectrum of the "old ytterbium".[267, 780] This fact points to the presence

of a third element which is evidently not celtium, since these lines are not recorded in the spectrum of this element.

## CELTIUM, Ct.

This element was discovered by Urbain as the result of a fractionation of ytterbium from gadolinite. The process consisted in the fractional crystallisation of the nitrates from nitric acid solution, the progress of the separation being controlled by measurement of the magnetic susceptibility. At the end of a long series of crystallisations, a few drops of a non-crystallisable mother-liquor were obtained which yielded an oxide with a coefficient of magnetisation about $4{\cdot}1 \times 10^{-6}$, i.e. 3-4 times smaller than the value for lutecium oxide. Spectroscopic investigation showed that this residue exhibited a number of lines which did not correspond with the lines of any known element. Hence Urbain decided that a new element was present, and this he named celtium. Pure compounds of this element have not yet been obtained, and in consequence an atomic weight determination has not been possible. From the small amount of knowledge of celtium it would appear that the oxide is a stronger base than scandia but weaker than lutecia. The chloride is more volatile than scandium chloride.

The arc spectrum of celtium has been investigated by Urbain, who finds the following five strong lines: 2685·2, 2765·8, 3080·7, 3118·6, and 3197·9. Other less intense lines are also present: 2481·6, 2536·9, 2729·1, 2834·3, 2837·3, 2845·2, 2888·1, 2903·9, 2949·5, 3171·4, 3326·0, and 3391·5.

### Characteristic Properties of Compounds of "Old Ytterbium".

Since the properties of the compounds of the constituent elements of the "old ytterbium" have not yet been ascertained, a short survey of the properties of the mixed compounds will probably be useful in forming an opinion as to the nature of the compounds of the individual elements. The oxide is a colourless powder which is changed to yellow or brown by traces of thulium. It is very refractory to heat and is slowly soluble in cold dilute acids and rapidly soluble in hot acids to form colourless salts. The anhydrous chloride is formed by the action of chlorine and sulphur monochloride on the heated oxide. It forms colourless leaflets which are readily soluble in water and

crystallise from the solution as the hexahydrate. The sulphate crystallises as the octohydrate, is fairly soluble in water, but less soluble in hot than in cold water, and is slightly hydrolysed in solution. The nitrate crystallises with 3 and 4 molecules of water, and is deliquescent. A normal carbonate which crystallises with 4 molecules of water and a basic carbonate are well known. For a full account of the compounds of the "old ytterbium" reference should be made to the memoir of Astrid Cleve.[783]

## CHAPTER VII.

## THORIUM, Th. At. Wt. 232·4.

THORIUM was discovered in 1828 by Berzelius[10] in a mineral which at a later date received the name thorite. Previous to this discovery Berzelius had isolated a substance to which he gave the name thorine; this substance he recognised in 1824 as a basic phosphate of yttrium. On several occasions doubts[88] have been raised as to the individuality of thorium, particularly by Baskerville,[110] who stated that it is a mixture of two elements, berzelium and carolinium. This statement has, however, not been confirmed,[784, 785] and at present there appears to be no reasonable ground for doubting the elementary character of thorium.

Thorium differs from the rare earth elements in being quadrivalent, whereas the rare earths are all tervalent. The quadrivalent character of thorium is shown by the isomorphism of the crystalline dioxide with stannic oxide (cassiterite), zirconium dioxide (baddeleyite), and titanium dioxide (rutile). The vapour density of the chloride indicates the formula $ThCl_4$ at temperatures from 1050° to 1100°, but above this temperature smaller values are obtained for the vapour density, owing, no doubt, to dissociation.[786, 787] The specific heat of the metal, 0·02787, found by Nilson,[788, 789] is conclusive evidence of the quadrivalency of thorium, for the atomic heat calculated from this figure is 6·47. Finally the molecular weight of thorium acetylacetonate in alcohol solution is found to agree with the formula

$$Th(CH_3COCHCOCH_3)_4.$$

Thorium forms a dioxide, $ThO_2$, which unlike most of the dioxides of the fourth group metals is non-acidic, and in this respect thorium resembles cerium, which also forms a non-acidic dioxide. Thorium dioxide gives rise to colourless salts of

the type $ThX_4$, which are much more stable in solution than the corresponding salts of cerium. The increased stability of thorium salts is most clearly shown by the fact that they are not so easily hydrolysed in solution as are the ceric salts. Thorium, being more basic, has a much smaller tendency to complex formation than the other members of the fourth group. It forms double compounds which are analogous to those formed by cerium, and in this respect it behaves similarly to cerium, and consequently is closely related to the elements of the cerium group. The solubility of many characteristic thorium salts (e.g. the fluoride, phosphate, and oxalate) is very like that of the corresponding salts of the tervalent earths. The most marked difference between thorium and the rare earths is found in its radioactive properties [790] which are not found in the rare earths, with the possible exception of erbium.

Thorium occurs along with the rare earths in practically the whole of the minerals which contain these substances, but in most cases only to a small extent. In only a very few minerals does thorium occur to a fairly large extent, the chief of these being thorite, thorianite, orangeite and monazite. Compounds of thorium may be profitably extracted from all of these minerals, but on account of the relative scarcity of all but monazite, it is only from this source that thorium compounds are obtained on the large scale. Examination of rocks and soil has shown that thorium compounds are very widely distributed in nature, but in amounts which can only be detected by means of radioactivity measurements.

### Extraction of Thorium Compounds from Minerals.

The preparation of pure thorium compounds from minerals, whilst, in general, easier than that of the rare earths, is still not a simple process. It consists, first, in the removal of the rare earths together with the thorium from the other constituents of the mineral. This is generally effected by precipitation as oxalates. The second stage in the process consists in the removal of the rare earths from the thorium. This may be effected by processes which depend on the following principles:—

(i) Hydrolysis of salts, e.g. the acetate or thiosulphate.

(ii) Complex formation, e.g. with alkali oxalates, carbonates, or sulphites.

(iii) Solubility differences, e.g. sulphates.

(iv) Solubility differences in acids, e.g. oxalates, phosphates, or hypophosphates.

The minerals from which thorium is extracted fall into two groups :—

(i) Minerals rich in thorium (50-60 per cent.), $ThO_2$—Thorite and thorianite.

(ii) Minerals poor in thorium (4-5 per cent.), $ThO_2$—Monazite and monazite sand.

The methods employed for the separation of thorium are, of necessity, somewhat different with the two classes of minerals. It will therefore be advisable to consider them separately.

1. *Minerals Rich in Thorium.*—The powdered mineral is digested with either hot hydrochloric acid or hot sulphuric acid for the purpose of decomposing the silicates and rendering the liberated silica insoluble. The acid is removed by evaporation to dryness and the solid residue digested with nitric acid, whereby the whole of the metals present pass into solution. The solution is separated from the silica, suitably diluted and treated with sulphuretted hydrogen to remove heavy metals such as lead and copper. The filtrate from the sulphides is then treated with a solution of oxalic acid, whereby the whole of the rare earths together with the thorium is precipitated. The precipitate is filtered off, washed, and treated by one of the following methods :—

(*a*) *Crystallisation of the Sulphates.*—The mixed oxalates are converted into oxides by ignition and these converted into sulphates by treatment with concentrated sulphuric acid. The excess of acid is removed by heating and the pasty mass of anhydrous sulphates, thus obtained, is dissolved in ice-cold water. The temperature is then slowly raised to 20° when the octohydrate of thorium sulphate crystallises out, since it is much less soluble than the corresponding hydrates of the rare earth sulphates. The crystallised octohydrate is filtered off, converted into the anhydrous salt, and the process repeated until the oxide prepared from the sulphate is pure white.[786, 791] Modifications of the sulphate method as described above have been proposed by Delafontaine [33] and Witt.[792]

(*b*) *Oxalate Method.*—This process was introduced by Bunsen,[287] who found that when the mixed oxalates of the

rare earths are treated with a warm solution of ammonium oxalate the whole of the thorium oxalate dissolves, but only small quantities of the other oxalates pass into solution, and these on dilution of the solution are precipitated. Before using this process it is advisable to treat the mixed oxalates with sulphuric acid and so obtain a solution of sulphates which is precipitated by the addition of a solution of sodium thiosulphate.[127] This precipitate consists mainly of thorium hydroxide and sulphur, but may contain small quantities of zirconium and scandium. The hydroxide is dissolved in acid and treated with an excess of ammonium oxalate when all the metals present, except the thorium, are precipitated. The solution of thorium oxalate is then precipitated by the addition of acid, when pure thorium oxalate is obtained. The efficiency of the ammonium oxalate separation will be evident from the following figures which give the relative amounts of the various oxalates, calculated as oxides, which are soluble in ammonium oxalate solution :—

$ThO_2$, 2663·0 ; $Yb_2O_3$, 105·0 ; $Yt_2O_3$, 11·0 ; $Ce_2O_3$, 1·8 ; $Nd_2O_3$, 1·5 ; $Pr_2O_3$, 1·2 ; and $La_2O_3$, 1·0.

Witt [792] has shown that by this method pure thorium compounds are rapidly obtained and that the process is in use on the large scale. Various modifications have been suggested by Moissan and Etard,[703] Urbain,[209, 245] and Brauner.[83, 261] A somewhat similar process depends upon the solubility of thorium carbonate in ammonium carbonate. When a solution of ammonium carbonate is added in excess to a solution of the rare earths the whole of the thorium carbonate, which is at first precipitated, passes into solution together with small quantities of the carbonates of the other earths.[13] By this method complete separation is not possible, but the method serves well as a means of concentration of the thorium.

2. *Minerals Poor in Thorium.*—In this connection the only mineral of any importance is monazite, chiefly in the form of monazite sand. From this mineral practically the whole of the thorium compounds used commercially are obtained.[793, 794, 795, 796] The exact method by which the extraction of thorium from monazite is effected cannot be stated definitely since it constitutes a "secret process". The following description is based

on published accounts and patent specifications of the commercial methods of extraction.

The finely powdered monazite sand is heated, with about twice its weight of concentrated sulphuric acid, in large cast-iron pans for 4-6 hours, during which time it is stirred continuously: eventually the mixture sets to a pasty mass of sulphates. The semi-solid mass is then treated with cold water whereby the sulphates are dissolved. The solution thus obtained should be strongly acid, and this fact is made use of to guage the success or otherwise of the decomposition of the mineral. If the solution is not strongly acid then it is known that the decomposition of the phosphates has not been complete. The solution is now poured from the undissolved material, which consists of quartz, magnetic iron ore, iron titanate, zirconium silicate, and titanic acid, and partially neutralised with magnesia. This effects the precipitation of most of the thorium as phosphate. The precipitate is removed and the filtrate completely neutralised when the residue of the thorium and all the other rare earths are precipitated as phosphates. By this treatment a considerable concentration of the thorium has been effected. Since thorium phosphate is insoluble in dilute acids the same result can be brought about by largely diluting the solution of sulphates.[300, 797] The phosphate precipitate rich in thorium is dissolved in concentrated hydrochloric acid and the strongly acid solution treated with oxalic acid. This treatment serves two purposes: in the first place, it removes the thorium from the phosphoric acid, and in the second, it effects a partial separation of the other rare earths, for the oxalates of these substances are more soluble in concentrated acid than that of thorium. The precipitate, thus obtained, is filtered off, thoroughly washed with water and digested with warm sodium carbonate solution. This treatment dissolves the thorium and any yttrium earths which may be present, as soluble double carbonates, the cerium earths being converted into insoluble double carbonates. The solution is then treated with either oxalic acid or caustic alkali and the precipitate of oxalates or hydroxides converted into the sulphates and purified by crystallisation of the octohydrate. The final purification may also be carried out by the acetate method.[793] There are several methods of effecting the purification of thorium by means of the acetate. One of the best of these is probably that due to Haber.

The impure hydroxide is dissolved in acid and the thorium precipitated from the neutral solution by means of sodium acetate. The precipitate is redissolved in acid and again precipitated by sodium acetate. This treatment is repeated until the pure product is obtained. The Haber process, despite the good results obtained, is, however, far too costly for commercial purposes.

The complete removal of phosphoric acid from the solution of thorium obtained from monazite is a very troublesome process and involves the use of large quantities of oxalic acid which makes the extraction very costly. Several processes have been suggested for the removal of the phosphoric acid before the thorium extraction is commenced. Muthmann, Hofer, and Weiss[798] fuse the powdered monazite with carbon in an electric furnace; in this way the phosphate is reduced to phosphorus, which is distilled off. The residue obtained is, however, very hard and difficult to powder. A process, described by Baskerville,[799] and in use on the large scale, is not complicated by the difficulty of the last-named process. It consists in heating a mixture of 1 part of monazite with 1·1 parts of petroleum coke, 0·15 parts of fluorspar, and 0·8 parts of lime. The heating is carried out in an electric furnace fed by a current of 125 ampères at 35 volts and is continued until phosphorus ceases to distil over. This requires generally from $1\frac{1}{4}$ to $1\frac{3}{4}$ hours. The fused mass is allowed to cool somewhat, but whilst still hot it is treated with water when acetylene is formed from the calcium carbide formed in the reaction. This has the effect of reducing the mass to a fine powder, which is dissolved in hydrochloric acid and the solution treated as described above for the separation of the thorium. A further method of removing the phosphoric acid consists in fusing the crude phosphate mixture, obtained from the sulphuric acid solution, or even the crushed mineral itself, with sodium carbonate.

The cooled melt is extracted with water when sodium phosphate dissolves and the rare earths are left insoluble.

The foregoing description gives in outline the commercial method of obtaining thorium compounds, which, while regarded as pure from a commercial point of view, are not necessarily pure, although the methods described are capable of producing pure compounds. A number of methods are described below which

have been used for the preparation of chemically pure thorium compounds. Whether any of these are used commercially is unknown, but some of them are obviously unsuitable for this purpose on account of the high cost of the necessary material. Most of these methods are equally applicable for the purification of commercial thorium compounds or for the preparation of pure thorium compounds from very impure mixtures of the rare earths. Rosenheim, Meyer, and Koppel [800] have patented a method which makes use of hydrofluosilicic acid or its sodium salt in the separation of thorium. The process consists in adding a solution of sodium silicofluoride to the boiling sulphuric acid solution of the rare earths, obtained as described above, when thorium silicofluoride is precipitated almost quantitatively. The precipitate is thoroughly washed, preferably by decantation, and converted into sulphate by treatment with sulphuric acid. The sulphate is then purified by crystallisation of the octohydrate.

A further method consists in the precipitation of the thorium by means of a solution of hypophosphoric acid.[801, 802, 803, 804, 990] The precipitate of thorium hypophosphate is boiled with caustic alkali and purified by precipitation as oxalate, or oxidised to phosphate by nitric acid and purified through the oxalate and sulphate. If there is a large quantity of the rare earths present, the precipitation by hypophosphoric acid should be effected in a solution containing 15·2 per cent. of free sulphuric acid, and the precipitate should be boiled before filtration. Formerly, the hypophosphate was precipitated by means of sodium hypophosphate. This procedure has the disadvantage that double sodium sulphates of the cerium earths are precipitated along with the thorium hypophosphate.[303] A drawback to this process for large scale work would appear to be the cost of the hypophosphoric acid, but Rosenheim and Pinkser [805] have shown that it may be prepared cheaply by the anodic oxidation of copper phosphide in an acid electrolyte. Kreidl and Hiller [806] have based a patent for the extraction of thorium on the fact that the difference in solubility of the ethyl sulphate of thorium and the cerium earths is greater than that existing between the sulphates of these elements.

Smith and James [306] have shown that thorium can be completely separated from the cerium and yttrium earths by adding a boiling solution of sebacic acid to a neutral solution of the rare

earths. Thorium sebacate is precipitated as a flocculent precipitate which is easy to filter and wash.

The remaining methods can only be regarded as processes for the preparation of absolutely pure thorium compounds, and are not intended for the preparation of commercial compounds.

Muthmann and Baur[807] have obtained pure thorium compounds by a prolonged series of fractional precipitations of the chromates. In this case a dilute solution of the earths in the presence of a little free acid, when treated with chromic acid or sodium chromate, gives an orange precipitate of thorium chromate, the cerium earths are not precipitated in the presence of free acid, and the yttrium earths are precipitated with difficulty (see Chap. III.).

Wyrouboff[300, 797] has shown that when a warm solution of a thorium salt is treated with hydrogen peroxide a hydrated peroxide of thorium is precipitated. This, in the absence of cerium salts, is pure, but if cerium salts are present a small quantity of this element always accompanies the thorium in the precipitate. A second treatment, however, generally removes the cerium completely. Urbain[209, 245] effects the final purification of thorium by recrystallisation of the acetylacetonate.

Dennis and Kortright[808] obtain pure thorium compounds by treating a boiling neutral solution of impure thorium nitrate with sodium azide. A white precipitate of thorium hydroxide is obtained owing to the hydrolysis of thorium azide,

$$4NaN_3 + Th(NO_3)_4 + 4H_2O = Th(OH)_4 + 4KNO_3 + 4N_3H.$$

Wyrouboff and Verneuil,[797] however, state that thorium compounds obtained in this way invariably contain cerium.

Chavastelon[284] purifies thorium by treating a solution of an impure thorium salt with sodium sulphite when the thorium remains in solution whilst the cerium metals are precipitated. The final purification is then effected by the hydrogen peroxide method. In the presence of large quantities of salts of the cerium earths this method is not applicable.[285]

*Metallic Thorium.*—Chemically pure thorium has not yet been obtained; this is due to a combination of circumstances, among which the high melting-point of the metal and the ease with which it combines with hydrogen, oxygen, nitrogen, and carbon are the most notable.

Berzelius,[11] and Chydenius,[127] prepared an impure metal by the action of sodium or potassium on the double alkali fluoride or chloride of thorium. Nilson [788, 789, 791] heated a mixture of 1 molecule of thorium chloride and 2 molecules of potassium chloride with sodium. The reaction mixture was placed in alternate layers in an iron cylinder and heated to a medium red heat. The product of the reaction was washed successively with water, alcohol, and ether. The metal obtained in this way contained 20 per cent. thorium dioxide. Winkler [809] attempted to reduce thoria by heating it with a 20 per cent. excess of magnesium in an evacuated tube. The product, however, was a mixture of magnesium and thorium together with the oxides of both metals. Attempts to reduce thoria with silicon (Hönigschmidt [810]), carbon and aluminium (Troost,[811] Moissan and Etard [703, 812]), led only to very impure products, containing respectively silicide, carbide, and an aluminium alloy. Moissan and Hönigschmidt [813] prepared the metal by the action of sodium on thorium tetrachloride. The tetrachloride was obtained free from the oxychloride by subliming it in a current of hydrogen. The metal obtained from this material contained only 3 per cent. of oxide. Matignon and Delephine [814] got a similar product by the same method. Electrolysis of a molten mixture of 1 part of thorium tetrachloride and 2 parts of potassium chloride yielded a metal which contained mechanically held oxide, but all attempts to remove the oxide by fusion were unsuccessful. Von Bolton [815] has reduced pure thorium tetrachloride with sodium, and obtained a product which he maintains was free from oxide. This substance, which was a fine powder, he hammered into a thick walled copper tube and then rolled the tube so that its diameter was decreased from 10 mm. to 1 mm. The thin copper layer was dissolved from the metallic thorium by dilute nitric acid and a spongy wire of thorium obtained. This he then rolled into a coherent shining strip. R. J. Meyer,[816 817] however, contests the purity of this metal, whereas Karstens [818] supports von Bolton in asserting its purity. Wartenberg,[819] by the electrolysis of a solution of thorium tetrachloride in a mixture of potassium chloride and sodium chloride, obtained small metallic crystals which, on analysis, were found to be composed of 87·6–88·9 per cent. thorium, 0·06 per cent. iron, 0·04 per cent. sodium, 0·03 per cent. silicon, 0·15 per cent. carbon, and the residue thorium oxide.

Lely and Hamburger [821] have obtained coherent rods of metallic thorium, containing not more than 1 per cent. thoria, by distilling thorium tetrachloride and sodium separately into an exhausted steel cylinder. The two substances were then heated together at 700°, and the metallic product compressed into a rod which was placed in a specially constructed vacuum furnace and sintered by passing a strong alternating current through it. Thorium has also been obtained by distilling sodium and thorium acetylacetonate through a red-hot tube.[820]

As ordinarily obtained thorium is a soft dark grey shining powder, consisting of small six-sided lamellæ.[797,798] The product obtained by von Bolton is microcrystalline [815] before it is rolled, and the rolled coherent metal has a ductility and colour resembling those of platinum. The impure metal has a specific gravity of 11·10, from which Nilson calculates that the pure metal has a specific gravity of 11·0. Von Bolton states that the powder has a specific gravity of 11·32 which becomes 12·16 on rolling. Thorium is magnetic,[868] having a specific susceptibility [823] of $+ 0{\cdot}18 \times 10^{-6}$ which increases rapidly as the temperature rises to 400°. It melts at 1450° according to von Bolton,[815] but Wartenberg [819] gives 1700° as the melting-point, and regards this figure as probably too low owing to the presence of carbon in the material examined. At ordinary temperatures thorium has a specific heat 0·02787 and at temperatures between the boiling-points of nitrogen and hydrogen the value 0·0197 is obtained.[390] When thorium is heated to a temperature just below a red heat it burns with great brilliance forming the oxide and throwing out showers of incandescent sparks, the fine powder ignites when it is rubbed or crushed. At about 450° thorium combines with chlorine, bromine, iodine, and sulphur, with incandescence, and at somewhat higher temperatures (650°) it combines with hydrogen and nitrogen to form hydride and nitride respectively. Dilute hydrochloric acid dissolves it slowly, but the concentrated acid attacks it readily. Nitric acid attacks thorium very rapidly at first, but the action soon ceases owing to the metal becoming passive. Sulphuric acid and hydrofluoric acid act upon thorium very slowly. Aqua regia dissolves it readily, but caustic alkalis are entirely without action on it. Thorium is slightly more electro-positive than magnesium. Metallic thorium is radioactive to a marked extent. It forms alloys with a number

of metals, some of which are made use of for industrial purposes. The most important of these are the alloys formed with aluminium, copper, zirconium, tungsten,[825] and nickel.[824] The alloy formed with the last-named element is regarded as an intermetallic compound of the formula $Th_2Ni$. Salts of thorium exert a considerable bactericidal action.[1024]

## Compounds of Thorium.

*Thorium Dioxide*, $ThO_2$, is formed by igniting the hydroxide or any salt of thorium derived from a volatile oxy-acid.

Thorium dioxide is a pure white amorphous powder, which, depending on its method of formation, may be dense and compact (e.g. by heating the sulphate) or light and voluminous (e.g. by ignition of the nitrate). It may be obtained crystalline by fusion of the amorphous substance with borax[826] or potassium phosphate.[827] The first method yields tetragonal crystals, isomorphous with rutile and cassiterite, whilst the second method gives cubic crystals. Thorium dioxide has a specific gravity 10·22[791] at 17°, a specific heat 0·0548,[522, 828] and melts and volatilises[412] at about 2000°. When pure thoria is strongly heated it emits a pale blue light of very feeble illuminating power, but when mixed with about 1 per cent. of ceria it emits a brilliant light. A mixture of thoria and ceria in the above-mentioned proportions is made use of in the incandescent gas mantles at present in use. The ignited oxide is hygroscopic and readily occludes gases; strongly ignited thorium dioxide is unattacked by all acids except sulphuric acid which slowly converts it into the sulphate on heating. Molten potassium bisulphate has the same action on it, but fusion with alkali carbonates is entirely without action. Thorium dioxide exhibits a type of isomerism of the same kind as that shown by zirconium and stannic oxides. If the oxide, prepared by the gentle ignition of the oxalate or hydroxide, is repeatedly evaporated with small quantities of hydrochloric acid or nitric acid, a syrup is formed, and this dissolves in water to form an opalescent solution (*Thorium metaoxide*). Such solutions contain hydrochloric acid or nitric acid, and may be coagulated by the addition of acids or neutral salts. In the case of the solution prepared by the use of hydrochloric acid the presence of the chloride ion cannot be detected by silver nitrate, consequently it may be concluded that

no chloride ion is present although the solution has an acid reaction. Wyrouboff and Verneuil expressed the opinion that thorium oxide exists in solution as the compound $ThO_2,xHCl$; the present-day view, however, is that the oxide becomes colloidal, and the failure of silver nitrate to precipitate the chloride ions is to be attributed to a protective colloid action. Wyrouboff and Verneuil,[829] however, regard the meta-oxide as a condensed oxide, the preparation of which is favoured by a low temperature. This compound is supposed to be capable of forming soluble addition compounds with acids (see also Chauvenet).[834]

Ignited thoria has been largely employed as a catalyst [830, 831] by Sabatier and Senderens. If a mixture of the vapours of two organic acids is passed over heated thoria, good yields of the corresponding ketones are obtained.[830] If the vapour of a single alcohol [832] is passed over thoria heated to 300°-350° the alcohol is decomposed in the same way that it would be decomposed by sulphuric acid, olefines and water being the products. In certain cases, if the temperature is kept low enough, the separation of water is incomplete and an ether results. The action is supposed to take place according to the following equations:—

$$2C_nH_{2n+1}OH + ThO_2 = H_2O + ThO(OC_nH_{2n+1})_2.$$

Then by an elevation of temperature either an olefine or an ether is formed:—

$$ThO(OC_nH_{2n+1})_2 = ThO_2 + (C_nH_{2n+1})_2O$$
$$ThO(OC_nH_{2n+1})_2 = ThO_2 + H_2O + 2C_nH_{2n}.$$

Vapours of esters, when passed over heated thoria, are decomposed according to the equation below giving ethers, olefines, primary alcohols, and carbon dioxide:—[833]

$$2C_mH_{2m+1}COOC_nH_{2n+1} = (C_mH_{2m+1})_2O + CO_2 + C_nH_{2n} + C_nH_{2n+1}OH.$$

Ammonia and the vapour of alcohols are converted into amines when passed over thoria at 380°. The product is mainly a primary amine,[833] but small amounts of secondary and tertiary amines are also formed. Benzyl alcohol and ammonia yield chiefly benzylamine when treated in the above-mentioned way.

*Thorium Hydroxide*, $Th(OH)_4$, is formed as a gelatinous precipitate by the addition of ammonia or alkali hydroxide to solutions of thorium salts. It is insoluble in excess of the precipitant. Krüss [835] obtained it as a white powder by boiling

solid thorium sulphate with ammonia. It is readily soluble in dilute mineral acids and in solutions of alkali carbonates. It may be obtained in a soluble colloidal form by prolonged washing with water or by boiling the washed hydroxide with small quantities of acids, thorium salts, or other salts such as aluminium chloride or ferric chloride. The salts, which have been used to peptonise thorium hydroxide, cannot generally be detected in the peptonised solution. Thorium hydroxide which has been washed with hot water is more difficult to peptonise than that which has been washed with cold water. Long-continued dialysis of thorium salts also gives rise to similar solutions. Thorium hydroxide forms a positively charged colloid and is easily precipitated by small quantities of electrolytes.

*Thorium Peroxide.*—When ammonia and hydrogen peroxide are added to solutions of thorium salts a white gelatinous precipitate is produced, which is capable of liberating iodine from potassium iodide. This precipitate is a hydrated peroxide derived from the hypothetical oxide $Th_2O_7$.[399, 836] It is very unstable and slowly loses oxygen, passing into $ThO_3$ which is considerably more stable. The hydrated peroxide is also formed by the action of hydrogen peroxide or solutions of sodium hypochlorite on thorium hydroxide, and may be obtained by the anodic oxidation of a suspension of thorium hydroxide in an alkaline solution of sodium chloride.[399]

When it is treated with dilute sulphuric acid, hydrogen peroxide is formed; concentrated sulphuric acid liberates ozonised oxygen. Pissarjewski[399, 836] regards this hydrated peroxide as a thorium salt of hydrogen peroxide, the latter substance being regarded as a monobasic acid. He represents its formation by the equation

$$Th(NO_3)_4 + 4HO_2H = Th(O_2H)_4 + 4HNO_3.$$

The compound $Th(O_2H)_4$ is then supposed to hydrolyse in steps thus:—

$$Th(O_2H)_4 + 2H_2O = Th(O_2H)_2(OH)_2 + 2H_2O_2$$
$$Th(O_2H)_2(OH)_2 + H_2O = Th(O_2H)(OH)_3 + H_2O_2.$$

It is suggested that the precipitate obtained by the action of hydrogen peroxide and ammonia is a mixture of the products of hydrolysis. Wyrouboff and Verneuil,[829] however, do not agree with this view, and are of the opinion that a complex

molecule is obtained containing peroxidised oxygen, hydroxyl groups, and an acid residue. Should hydrogen peroxide alone be added to a solution of thorium acetate,[336] sulphate,[398, 526] or nitrate,[300, 797] a precipitate is obtained which is a peroxidised salt. This substance is also capable of liberating iodine from potassium iodide.

*Thorium Hydride*, $ThH_4$, is formed by heating thorium in hydrogen to a dull red heat. Energetic combination takes place with the evolution of light. It is a greyish-black powder which is stable in the air and not decomposed by water. Dilute acids decompose it with evolution of hydrogen.[528] It evolves hydrogen when heated, and has a dissociation pressure of one atmosphere at 390°.[814, 837]

*Thorium Fluoride*, $ThF_4$.—Anhydrous thorium fluoride is obtained as an amorphous white powder by passing hydrogen fluoride vapour over anhydrous thorium chloride or bromide[838] at 350°-400°. It may also be obtained by fusing the double potassium thorium fluoride, $KF,ThF_4$, with potassium chloride or bromide.[839] The product in this case consists of brilliant cubic crystals which melt at a red heat. They are slowly decomposed by dilute sulphuric acid, but are unattacked by concentrated sulphuric acid. When fused with sodium carbonate it yields crystals of thoria. When aqueous hydrofluoric acid is added to a solution of a thorium salt a gelatinous precipitate is produced, which on drying in the air yields $ThF_4,8H_2O$.[834] This compound loses 4 molecules of water when it is dried in a vacuum, and forms $ThF_4,4H_2O$, which when heated to 110° in a current of hydrogen gives the hydrate $ThF_4,2H_2O$. At 250° all the hydrates are converted into the basic fluoride $Th(OH)F_3,H_2O$. Thorium fluoride is insoluble in hydrofluoric acid, and when the hydrated salt is strongly ignited it is converted into thoria.[11, 127]

An *oxyfluoride*, $ThOF_2$, is produced[838] by heating $ThF_4,4H_2O$ at 800° in a current of hydrogen fluoride, or by heating thorium silicofluoride in a current of hydrogen. It is a white insoluble powder which yields hydrogen fluoride when treated with concentrated sulphuric acid.

Thorium fluoride forms a number of double fluorides with alkali fluorides.[127, 840] The compound, $2KF,ThF_4,4H_2O$, is produced by boiling thorium hydroxide with a mixture of potassium

hydrogen fluoride and hydrofluoric acid. It is an amorphous white powder, insoluble in water. The compound

$$KF,ThF_4,6H_2O$$

is precipitated when an acid solution of a thorium salt is treated similarly, and the compound, $KF,ThF_4,H_2O$, is obtained if the precipitation is effected with potassium fluoride in a neutral solution. Fusion of thorium fluoride with an excess of potassium fluoride and subsequent washing with water yields the anhydrous salt $KF,ThF_4$. Similar compounds have been obtained with sodium fluoride and ammonium fluoride.

When thorium hydroxide is digested with hydrofluosilicic acid a crystalline powder is produced which is probably a basic silicofluoride.[841]

*Thorium Chloride*, $ThCl_4$.—Anhydrous thorium chloride may be obtained by a large number of methods, in all of which it is essential that oxygen and moisture be rigorously excluded, or otherwise the product will contain oxychloride.

The following methods have been described for the preparation of the anhydrous chloride; of these the sixth is probably the most efficient for small preparations whilst the seventh is the best for large preparations.

1. By heating an intimate mixture of carbon and the dioxide in a porcelain tube,[11, 791] through which a stream of chlorine is passing.

2. A mixture of the dioxide and phosphorus pentachloride is heated in an evacuated glass tube. The phosphorus oxychloride formed in the reaction distils away and leaves the pure chloride behind,[842]

$$ThO_2 + 2PCl_5 = 2POCl_3 + ThCl_4.$$

3. Crude metallic thorium is heated in a current of chlorine at a dull red heat. A product is formed which consists of the anhydrous chloride mixed with some dioxide. Purification is effected by sublimation in a current of hydrochloric acid gas.[786, 787]

4. When a mixture of carbon monoxide and chlorine is passed over the oxide, heated to dull redness, thorium tetrachloride is formed, but the product always contains some oxychloride.[814, 837]

5. When the vapour of carbon tetrachloride is passed over

the oxide heated to dull redness, thorium tetrachloride mixed with oxychloride is produced,[814, 837]

$$ThO_2 + 2CCl_4 = 2COCl_2 + ThCl_4.$$

6. Thorium dioxide is converted into the tetrachloride by heating it in a stream of chlorine mixed with sulphur monochloride vapour. If the temperature at which the reaction is carried out is raised to 800°, the thorium tetrachloride sublimes and condenses in the cooler parts of the apparatus. As thus obtained the product is perfectly pure.[532]

7. When crude metallic thorium containing carbide, as obtained by heating thorium dioxide with carbon in an electric furnace, is heated in a porcelain tube with chlorine a very pure tetrachloride is produced. This product can be rendered quite pure by sublimation in hydrogen.[843]

8. Thorium tetrachloride is also formed by passing phosgene gas over thorium dioxide at a red heat,[844]

$$ThO_2 + 2COCl_2 = ThCl_4 + 2CO_2.$$

9. Thorium oxychloride is decomposed at a red heat with the formation of the dioxide and tetrachloride. The tetrachloride may be separated from the dioxide by sublimation,[834]

$$2ThOCl_2 = ThO_2 + ThCl_4.$$

Anhydrous thorium chloride, when sublimed, forms colourless prisms which are fairly stable in the air. The slightly impure substance has a greyish colour. Thorium chloride is readily soluble in water, alcohol, and aqueous ether, with evolution of heat; it is, however, only slightly soluble in absolute ether. It has a specific gravity 4·59 and sublimes at 720°-750° in a vacuum. It melts at 820° and apparently dissociates at 1100°. When the tetrachloride is heated in oxygen to a red heat it is converted into the dioxide; heating in a mixture of sulphur vapour and hydrogen converts it into the sulphide. It is converted into the phosphide by heating in phosphorus vapour and into the selenide by heating in selenium vapour.[786, 787, 843] Calcium reduces it to the metal at 600° with incandescence.[843]

Anhydrous thorium chloride combines readily with ammonia and organic bases to form addition compounds. With ammonia, three series of addition compounds are formed, some of the members of one series being isomeric with members of the other

series. The first series contains compounds with 4, 6, 7, 12, and 18 molecules of ammonia combined with 1 molecule of thorium chloride. These compounds are formed by treating anhydrous thorium chloride with liquid ammonia and allowing the mixture to stand at various temperatures. The whole of these compounds are decomposed by water, and on standing in a vacuum they lose ammonia and are converted into the compound $ThCl_4,4NH_3$.

The second series contains compounds with 4, 6, and 7 molecules of ammonia combined with one molecule of thorium chloride. These compounds are formed by the action of ammonia gas on anhydrous thorium chloride at various temperatures. They are not decomposed by water and are quite stable in a vacuum.

The third series contains compounds with 6, 7, 12, and 18 molecules of ammonia combined with 1 molecule of thorium chloride. These compounds are formed by the action of liquid ammonia on the members of the second series. The compound, $ThCl_4,4NH_3$, of the second series is the only compound of these series which is stable above 120°. This compound, however, loses hydrogen chloride at 250°-300°, forming the tetra-amide $Th(NH_2)_4$, whilst at a red heat the di-imide $Th(NH)_2$,[845, 846] is formed.

A compound, $ThCl_4,8NH_3$, is formed as a white precipitate when gaseous ammonia is passed into an ethereal solution of thorium tetrachloride.[847] Addition compounds have been obtained with the following organic bases: methylamine, ethylamine, propylamine, aniline, toluidine, pyridine, quinoline, and β-naphthylamine.

Thorium chloride forms crystalline addition compounds with alcohol, $ThCl_4,4C_2H_5OH$; with acetaldehyde,

$$ThCl_4,2CH_3CHO;$$

with cinnamic aldehyde, $ThCl_4,2C_6H_5CHCHCHO$; and with acetone, $ThCl_4,2CH_3COCH_3$. When treated with aldehydes or hydroxyesters, anhydrous thorium chloride reacts with the liberation of hydrogen chloride and the formation of organic derivatives. Thus, for example, with benzaldehyde it forms $ThCl_2(C_6H_5CO)_2$, and with salicyl aldehyde it forms

$$ThCl_3OCH_2C_6H_4CHO.$$[840, 848]

Thorium chloride forms crystalline hydrates with 2, 4, 7, 8, and 9 molecules of water. The octohydrate, $ThCl_4,8H_2O$, is obtained by treating a solution of thorium sulphate with barium chloride, and, after filtration, evaporating the solution when it separates in colourless needles.[841] The heptahydrate, $ThCl_4,7H_2O$, is obtained by dissolving the anhydrous salt in water and evaporating at ordinary temperatures in a vacuum over sulphuric acid.[844] Krüss[835] states that this hydrate is also formed by the action of an alcoholic solution of hydrochloric acid on thorium hydroxide, whereas, Rosenheim and Schilling[849] maintain that the compound, $ThCl_4,9H_2O$, is formed in this way. If the octohydrate is dried at ordinary temperatures it loses water and passes into the heptahydrate,[850] and when heated to 50° in a current of hydrogen or hydrogen chloride it passes into the tetrahydrate $ThCl_4,4H_2O$.[850] All the hydrates lose water at 100° and pass into the dihydrate $ThCl_4,2H_2O$.[850] The hydrates of thorium chloride are readily soluble in water and in alcohol. Aqueous solutions of thorium chloride exhibit a strong oxydase action on quinol.[499]

Although thorium chloride does not show so great a tendency as the chlorides of the tervalent earths to form double compounds, a number of these compounds have been prepared, among which the following may be noted:—

$ThCl_4,LiCl,8H_2O$;[851] $ThCl_4,NaCl,10H_2O$;[851]
$ThCl_4,KCl,9H_2O$,[851] $2ThCl_4,KCl,18H_2O$;[11, 841]
$ThCl_4,2RbCl,9H_2O$;[851] $ThCl_4,2CsCl,8H_2O$;[851]
$ThCl_4,3CsCl,12H_2O$; $ThCl_4,2CsCl,11H_2O$;[853, 854]
$ThCl_4,2NH_4Cl,10H_2O$;[851] $ThCl_4,8NH_4Cl,8H_2O$;[127]
$ThCl_4,PtCl_4,12H_2O$; and $2ThCl_4,3PtCl_2,24H_2O$.[541, 855]

All these compounds are prepared by crystallising suitable mixtures of the two salts. The double chlorides with lithium, sodium, and potassium, on heating, yield oxychlorides of the type $ThOCl_3,M'Cl$.[851]

In addition to the hydrated double salts mentioned, a series of anhydrous double chlorides of the type $ThCl_4,2M'Cl$ is formed with the chlorides of sodium, potassium, rubidium, and caesium. These compounds are prepared by fusing together the mixed chlorides in suitable proportions. Anhydrous double chlorides, $ThCl_4,4RbCl$ and $ThCl_4,4CsCl$, are formed in the same way. A double chloride, $ThCl_4,NH_4Cl$, is formed by heating the compound $ThCl_4,2NH_4Cl,10H_2O$ at 150°.[852]

A number of oxychlorides of thorium have been isolated. The compounds, $Th(OH)_2Cl_2,5H_2O$ and $Th(OH)Cl_3,7H_2O$, are obtained by digesting thorium hydroxide, which has been dried by treatment with alcohol, with an alcoholic solution of hydrogen chloride. The former compound is obtained if the alcohol solution is completely saturated, and the latter if the saturation is not complete. Should the thorium hydroxide contain any free water, then the octohydrate of the normal chloride will be the only product.[840] The compound, $Th(OH)Cl_3,H_2O$, is obtained by heating $ThCl_4,7H_2O$ in a current of hydrochloric[844] acid gas at 120°-160°. The above-mentioned compounds are soluble in alcohol and water without decomposition.

The anhydrous compound, $ThOCl_2$, is obtained from the products of the action of carbon tetrachloride on thorium dioxide (see above). When this action is not carried to completion the product contains a considerable quantity of the oxychloride, and on extracting with absolute alcohol it is left behind as a white crystalline powder. Anhydrous thorium oxychloride may also be obtained by heating the heptahydrate of thorium chloride in a current of chlorine at 250°. Thorium oxychloride is very hygroscopic,[814] and on standing in the air it forms $ThOCl_2,6H_2O$.

*Thorium Bromide*, $ThBr_4$.—The anhydrous salt is prepared by heating a mixture of the dioxide and carbon in bromine vapour;[856] by burning metallic thorium in bromine;[791] and by heating the carbide in bromine vapour. In the last method the product is purified by subliming first in hydrogen and then in a vacuum.[843] Probably the most successful method consists in heating thoria in a mixture of hydrobromic acid gas and vapour of sulphur monochloride at 135°, and then in hydrobromic acid gas alone, and finally subliming.[431]

Thorium bromide is stated to form crystalline hydrates with 12, 10, 8, and 7 molecules of water. It is extremely doubtful if all these hydrates really exist.[843, 857, 849] Chauvenet[850] has shown that on evaporating a solution of thorium bromide, formed by dissolving thorium hydroxide in alcoholic hydrobromic acid, crystals with 12 molecules of water are deposited. These when kept at ordinary temperature pass into the decahydrate, and when kept in a vacuum yield the heptahydrate.

Thorium bromide forms an addition compound with am-

monia,[847] $ThBr_4,3NH_3$, and with pyridine hydrobromide,[840, 849] $2C_5H_5N,HBr,ThBr_4$.

*Thorium Oxybromide*, $ThOBr_2$, is formed by boiling an aqueous solution of thorium bromide, evaporating to dryness and heating the residue to 160°.[848] It is also formed when the dioxide is heated in a mixture of hydrobromic acid gas and sulphur monochloride[431] at 125°. It is readily soluble in water, in which it dissolves with a slight hissing noise. The hydrated oxybromides, $Th(OH)_2Br_2,4H_2O$ and $Th(OH)Br_3,10H_2O$, are formed by treating thorium hydroxide with an alcoholic solution of hydrobromic acid in exactly the same way as the corresponding chlorides.

*Thorium Iodide*, $ThI_4$.—The anhydrous compound is formed by burning metallic thorium in iodine vapour. A hydrated salt is formed in large deliquescent crystals, which probably contain 10 molecules of water, by dissolving thorium hydroxide in an aqueous solution of hydriodic acid and crystallising in the dark. These crystals are decomposed on heating or on exposure to light with the evolution of iodine. Double iodides with mercuric iodide, of the formulæ,

$$2ThI_4,HgI_2,18H_2O \text{ and } ThI_4,2HgI_2,12H_2O,$$

are formed in colourless deliquescent crystals by allowing a solution of thorium iodide saturated with mercuric iodide to crystallise.[858, 859] The crystals are decomposed by water, and turn red on exposure to the air owing to the liberation of iodine.

A basic iodide of thorium, $Th(OH)I_3,10H_2O$, is formed by saturating an alcoholic solution of hydriodic acid with thorium hydroxide and allowing the solution to crystallise in the dark. This compound is not stable and is slowly transformed into an unstable substance, $ThOI_2,3\frac{1}{2}H_2O$, when kept in dry air. This compound, under the same conditions, changes to a pure white compound, $ThOI_2$, which rapidly becomes yellow when exposed to light.[834] The mother liquor from the compound, $Th(OH)I_3,10H_2O$, deposits crystals of $ThI_4,10H_2O$.[829, 840]

*Thorium Sulphide*, $ThS_2$, is formed, together with the oxysulphide ThOS, by the action of sulphuretted hydrogen on a mixture of thorium chloride and excess of sodium chloride at a red heat.[860] The product consists of a mixture of large brown crystals of sulphide and small yellow crystals of oxysulphide. The sulphide is obtained from the mixture by shaking

it on sieves of suitable mesh. It forms dark brown leaflets of specific gravity *ca.* 6·7 at 0°. The crystals are violently attacked by nitric acid and have a slight action on polarised light.

The oxysulphide can be obtained pure by treating the product which has been removed from the sulphide with nitric acid at 40°. This dissolves the sulphide and leaves the oxysulphide as an orange-yellow crystalline powder of specific gravity 8·42 at 0°. It may also be obtained by heating anhydrous thorium sulphate in a current of sulphuretted hydrogen at a red heat. Obtained in this way it is a light yellow powder which is spontaneously inflammable in the air.

*Thorium Sulphate*, $Th(SO_4)_2$.—Anhydrous thorium sulphate may be obtained by dehydrating the hydrated salts[784, 786] at 400°. It may also be obtained, mixed with small quantities of basic sulphate, by dissolving the dioxide in sulphuric acid and removing the excess of acid by evaporation.

Thorium sulphate is a pure white crystalline powder of specific gravity[786] 4·225 at 17° and specific heat[522] 0·0972. It is extremely soluble in ice-cold water, and a solution containing about 25 per cent. of the salt may be obtained, but such solutions are labile over the whole temperature range from 0°-100°, and when kept, spontaneously deposit one or other of the hydrates. In solutions, thorium sulphate is hydrolysed considerably, the hydrolysis in an N/64 solution amounting to 46 per cent.[862] Thorium sulphate forms crystalline hydrates with 9, 8, 6, 4, and 2 molecules of water.

The enneahydrate, $Th(SO_4)_2,9H_2O$, forms shining monoclinic prisms which separate from solution at temperatures between 0° and 43°. At 43° these crystals pass into the tetrahydrate. The solubility in water is given below in grams of anhydrous sulphate per 100 grams[863, 864] of water.

| Temperature . . . | 0° | 10° | 20° | 30° | 40° | 44° |
|---|---|---|---|---|---|---|
| Grams . . . . | 0·88 | 1·02 | 1·25 | 1·85 | 2·83 | 3·02 |

See also Roozeboom[865] and Koppel.[866]

The octohydrate, $Th(SO_4)_2,8H_2O$, is best obtained by adding concentrated sulphuric to a concentrated solution of the nitrate or chloride at about 20° when the salt separates in monoclinic crystals which are very similar to those of the enneahydrate. The octohydrate is labile towards the enneahydrate at all temperatures, being more soluble than this salt. It has

a transition temperature a little below 43° when it passes into the tetrahydrate, as will be obvious from the diagram (fig. 7). The octohydrate always crystallises from a solution of the anhydrous salt when it is heated to 20°-47°, but it is often mixed with the enneahydrate. The following values of the

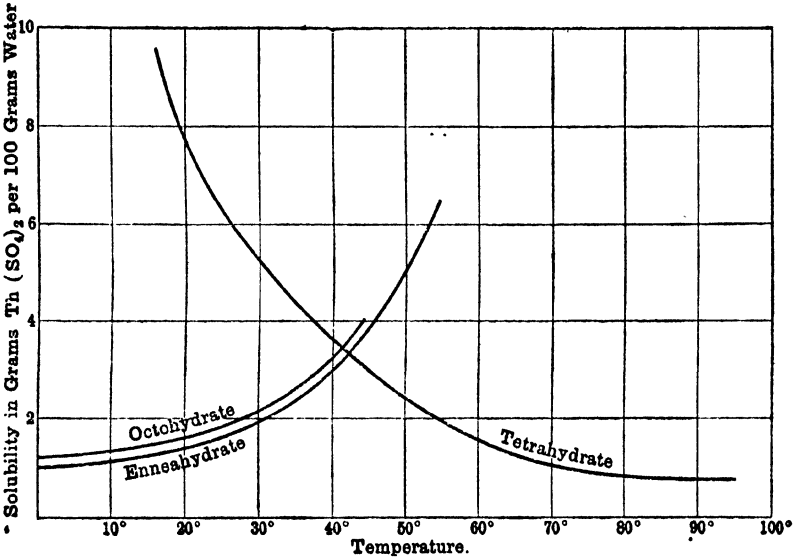



FIG. 7.

*From Cowley and Levy's Rare Earths (Edward Arnold).*

solubility of the octohydrate are given in grams of the anhydrous salt per 100 grams of water:—[864, 865]

| Temperature . . . . . | 0° | 15° | 25° | 44° |
|---|---|---|---|---|
| Grams . . . . . | 1·00 | 1·38 | 1·85 | 3·71 |

The hexahydrate, $Th(SO_4)_2,6H_2O$, is formed occasionally during the crystallisation of thorium sulphate from dilute sulphuric acid. It is labile toward the ennea- and tetra-hydrates.

The tetrahydrate, $Th(SO_4)_2,4H_2O$, is obtained by crystallising solutions of thorium sulphate at temperatures above 47°. It separates in sparingly soluble needles. The solubility in grams of anhydrous sulphate per 100 grams of water is given below:—[863, 865]

| Temperature . . . | 50° | 55° | 60° | 70° | 75° | 95° |
|---|---|---|---|---|---|---|
| Grams . . . . | 2·54 | 1·94 | 1·634 | 1·09 | 1·32 | 0·71 |

The dihydrate, $Th(SO_4)_2,2H_2O$, is formed by heating the other hydrates to 110°. It is stable only above 100°.

Solutions of thorium sulphate have a decided toxic action on the lower organisms and ferments; a solution containing 0·5-1·0 grams per litre being comparable in its action to a solution of corrosive sublimate.[867] Solutions of thorium sulphate have a strong toxic action on *cholera vibris*.[546]

An acid sulphate, $Th(SO_4)_2,H_2SO_4$, is formed by adding concentrated sulphuric acid to a concentrated solution of anhydrous thorium sulphate and heating the precipitate with sulphuric acid. Fine needles are produced which are freed from excess of sulphuric acid by heating at 130° in a vacuum.[446] A compound, $2Th(SO_4)_2,H_2SO_4,2H_2O$, is formed by melting thorium hydroxide with sodium hydrogen sulphate and extracting the product with water.[868]

A basic sulphate, $ThO_2,SO_3$, is known which separates with 1, 2, or 5 molecules of water. The dihydrate, $ThO_2,SO_3,2H_2O$, is obtained by prolonged boiling of a solution of the tetrahydrate of the normal sulphate (Wyrouboff).[863] Hauser and Wirth,[478] however, state that this compound is the monohydrate and not the dihydrate. They obtain it by heating a concentrated solution of thorium sulphate in a sealed tube at 160°-180°. The pentahydrate, $ThO_2,SO_3,5H_2O$, is obtained by boiling a solution of the normal sulphate with magnesium sulphate, or by treating the anhydrous normal sulphate with a small quantity of water in the presence of magnesium carbonate.[869]

The basic sulphate is completely hydrolysed with the formation of the oxide by treatment with a large quantity of water.[870]

Thorium sulphate forms a series of double sulphates of the general formula $Th(SO_4)_2,2M_2'SO_4,2H_2O$, with the sulphates of sodium, ammonium,[840] potassium,[11] rubidium,[868] and cæsium.[868] Of these the salts with potassium, rubidium, and cæsium sulphate are sparingly soluble in water and in solutions of the alkali sulphates, and are formed as crystalline precipitates by the addition of alkali sulphates to a solution of thorium sulphate. The sodium and ammonium salts are soluble in water and in alkali sulphate solution. A number of other double sulphates with alkali sulphates are known, of which the following may be noted:—

$Th(SO_4)_2,K_2SO_4,4H_2O$; $2Th(SO_4)_2,7K_2SO_4$;
$Th(SO_4)_2,Na_2SO_4,6H_2O$; $Th(SO_4)_2,3(NH_4)_2SO_4,3H_2O$;[871]
and $Th(SO_4)_2,(NH_4)_2SO_4,4H_2O$.[840]

Thorium sulphate forms a number of double sulphates with the sulphates of organic bases, of which the following may be noted.[444] With pyridine,

$$Th(SO_4)_2,2C_5H_5N,H_2SO_4,4H_2O;$$

forming colourless leaflets; with quinoline,

$$Th(SO_4)_2,2C_9H_7N,H_2SO_4,4H_2O;$$

with diethyl-amine, $Th(SO_4)_2,2(C_2H_5)_2NH,H_2SO_4,4H_2O$; and with phenylhydrazine, $Th(SO_4)_2,2C_6H_5NHNH_2,2H_2SO_4$.

*Thorium Sulphite*, $Th(SO_3)_2,H_2O$, is produced when thorium sulphate solution is saturated with sulphur dioxide and warmed. It is a white amorphous powder,[841] and is soluble in solutions of alkali sulphites. These solutions deposit, on standing, basic double salts of the formulæ

$$2Na_2SO_3,Th_2(OH)_2(SO_3)_3,xH_2O,$$
and $Th(OH)_2SO_3,2K_2SO_3,10H_2O$.[285]

*Thorium Nitride*, $Th_3N_4$, is formed by heating the metal in nitrogen;[703, 812] or the carbide in ammonia; or by heating the di-imide in nitrogen or ammonia to a bright red heat.[884]

It is a chestnut-brown powder[814, 837] which is rapidly decomposed by water yielding ammonia and thorium dioxide.

*Thorium Nitrate*, $Th(NO_3)_4,12H_2O$, is obtained by crystallising a solution of thorium hydroxide in nitric acid. It forms large white hygroscopic crystals.[11, 841] A hydrate with 6 molecules of water is obtained by crystallising from a hot aqueous solution,[872] and a pentahydrate is obtained when thorium nitrate is crystallised from concentrated nitric acid solution.[261] In addition to the foregoing hydrates a dihydrate is also known. Commercial thorium nitrate is not a definite hydrate or even a single compound of thorium. It contains a quantity of water approximating to $4H_2O$, and generally a small quantity of thorium sulphate. This latter salt is added for the purpose of producing the oxide in the right form when the salt is heated on the incandescent gas mantle. Commercial thorium nitrate of the correct composition when heated swells up, and is converted into a light finely divided variety of the dioxide.

Solutions of thorium nitrate have the power of peptonising albuminous substances.[873] All the hydrates are readily soluble in water and alcohol. Anhydrous thorium nitrate reacts violently with ammonia, forming thorium dioxide and ammonium nitrate

which sublimes.[551] When ammonia is passed over the dihydrate at 50° a white stable compound, $Th(NO_3)_4,3NH_3,2H_2O$, is formed, and when the commercial nitrate is similarly treated a compound, $2Th(NO_3)_4,7NH_3,3H_2O$, is formed. Both these compounds are decomposed by water giving basic nitrates and ammonium nitrate.[551]

Thorium nitrate forms a number of double nitrates with alkali nitrates; of these the following may be mentioned:—

$$3KNO_3,Th(NO_3)_4,3HNO_3,4H_2O;$$
$$NH_4NO_3,Th(NO_3)_4,5H_2O;\ NaNO_3,Th(NO_3)_4,9H_2O;$$
$$KNO_3,Th(NO_3)_4,9H_2O.$$

It also forms a series of anhydrous nitrates of the general formula $2M'NO_3,Th(NO_3)_4$, where M may be ammonium, potassium, rubidium, or cæsium. A series of double nitrates of the formula $M''(NO_3)_2,Th(NO_3)_4,8H_2O$ is formed with the nitrates of magnesium, zinc, nickel, cobalt, and manganese (cp. Cerium Earths).[480]

A number of addition compounds are formed by thorium nitrate with organic bases, of which the following may be noted: with antipyrine,[551]

$$2Th(NO_3)_4,5C_{11}H_{12}ON_2\text{(m.p. 168°)};$$
$$2Th(NO_3)_4,5C_{11}H_{12}ON_2,4H_2O;\text{ and }Th(NO_3)_4,4C_{11}H_{12}ON_2;$$

with diethylamine,

$$Th(NO_3)_4,2(C_2H_5)_2NH,2HNO_3;$$

with pyridine,

$$Th(NO_3)_4,4C_5H_5N,4HNO_3;$$

and with quinoline,

$$Th(NO_3)_4,4C_9H_7N,4HNO_3.$$[444]

## Phosphates of Thorium.

(i) *Normal Thorium Phosphate*, $Th_3(PO_4)_4,4H_2O$, is formed as a bulky white precipitate by the addition of disodium hydrogen phosphate to a solution of thorium nitrate. The precipitate thus obtained generally contains sodium.[456, 841, 874]

(ii) *Acid Thorium Phosphate*, $ThH_2(PO_4)_2,H_2O$, is formed as a white precipitate by the addition of phosphoric acid to a solution of thorium chloride.[456, 841, 874]

(iii) *Thorium Pyrophosphate*, $ThP_2O_7,2H_2O$, is formed as a white precipitate by the addition of a solution of sodium pyrophosphate to a solution of thorium chloride.[456]

(iv) *Thorium Metaphosphate*, $Th(PO_3)_4$, is formed by melting together thorium chloride and metaphosphoric acid. In this way it is obtained in insoluble rhombic crystals.[456]

A large number of double phosphates have been prepared by fusing together mixtures of thorium dioxide or thorium phosphate with alkali phosphates.[827, 856, 875, 876]

Thorium forms a number of mixed halogen phosphates,[876] among which the following may be noted: *Thorium chlorophosphate*, $3ThO_2,ThCl_4,2P_2O_5$, which is prepared by heating thorium chloride with thorium metaphosphate in a current of dry carbon dioxide. It is a heavy white crystalline powder insoluble in water and acids, but is decomposed by boiling with concentrated sulphuric acid or fusion with alkali carbonate. *Thorium bromophosphate*, $ThBr_4(3ThO_2,2P_2O_5)_3$, is prepared similarly to the chlorine compound except that a large excess of thorium bromide is used. It forms a pearly white crystalline powder. It is very stable, and resists the action of fused alkali carbonate, but may be decomposed by boiling sulphuric acid.

The existence of these mixed phosphates is taken to explain the presence of fluorine in monazites.[876]

*Thorium Hypophosphate*, $ThP_2O_6,11H_2O$, is formed as an amorphous white precipitate by the addition of hypophosphoric acid or sodium hypophosphate to a solution of a thorium salt. It is insoluble in water, acids, and alkalis,[877] and is of great importance in the separation of thorium from the rare earths. The precipitation of thorium hypophosphate is quantitative even from a strongly acid solution, consequently this substance is of importance in the quantitative estimation of thorium.

*Thorium Carbide*, $ThC_2$, is obtained by heating an intimate mixture of 12 parts of thorium dioxide and 1 part of carbon in an electric furnace. It is a crystalline mass composed of small yellow crystals of specific gravity 8·96 at 18°. Cold water decomposes it, generating a mixture of hydrocarbons and hydrogen composed of 47-48 per cent. acetylene, 27-31 per cent. methane, *ca.* 5 per cent. ethylene, and 16-18 per cent. hydrogen; other hydrocarbons have been identified in the mixture of gases, including ethane, propane, butane, propylene, and some higher members of

the acetylene series. When thorium carbide is heated in oxygen it is oxidised with a faint incandescence.

*Thorium Carbonate.*—No normal metacarbonate of thorium is known, but the orthocarbonate has been obtained. When solutions of alkali carbonates are added to solutions of thorium salts, precipitates of basic carbonates are obtained. These precipitates are soluble in excess of alkali carbonates, and soluble double alkali carbonates are formed. The solubility of thorium basic carbonate in alkali carbonate is the basis of an important method of separation of thorium from the other rare earths. Crystalline double carbonates with alkali carbonates are well known. The salt $3Na_2CO_3,Th(CO_3)_2,12H_2O$ [841] is formed by adding a solution of sodium carbonate to a thorium salt until the precipitate which first forms has redissolved, and then adding alcohol when the double salt separates as a crystalline powder. An ammonium salt, $(NH_4)_2CO_3,Th(CO_3)_2,6H_2O$, and a potassium salt, $3K_2CO_3,Th(CO_3)_2,11H_2O$, are formed similarly. When dilute solutions of these double carbonates are boiled, decomposition takes place and the hydroxide is precipitated.

A double thallium carbonate, $3Tl_2CO_3,Th(CO_3)_2$, is formed as a crystalline precipitate by adding a solution of a thallium salt to a solution of the double ammonium thorium carbonate,

$$(NH_4)_2CO_3,Th(CO_3)_2,6H_2O.$$ [868]

When thorium hydroxide is treated with carbon dioxide at atmospheric pressure a basic carbonate, $2Th(OH)_4CO_2$, is formed, but if the reaction takes place under a pressure of 30-40 atmospheres much more gas is absorbed and a normal orthocarbonate, $ThCO_4,2H_2O$, is obtained. Under the same conditions the anhydrous oxide, which has been ignited at a temperature not exceeding 430°, yields a basic orthocarbonate, $ThCO_4,6ThO_2$. The hydrate, $ThCO_4,8H_2O$, is formed by the action of sodium carbonate on a thorium salt in aqueous solution; it loses $6H_2O$ in a vacuum, and on heating to 120° it forms the basic orthocarbonate, $ThCO_4,ThO_2,1\frac{1}{2}H_2O$. [879]

*Thorium Acetate*, $Th(CH_3COO)_4$, is formed in fine needles by dissolving thorium hydroxide in acetic acid; by adding ammonium acetate to a solution of the sulphate; [880] and by the action of acetic acid on the chloride. [11, 127, 841] It readily forms basic

salts. When a solution of a thorium salt is boiled with sodium acetate a granular precipitate of $Th(OH)_2(CH_3COO)_2,H_2O$ separates.[319, 881]

*Thorium Oxalate*, $Th(C_2O_4)_2,6H_2O$, is precipitated from solutions of thorium salts by oxalic acid as a white amorphous powder. Precipitation occurs even in the presence of acid, but if the acid is too concentrated the oxalate redissolves, and mixed salts can be obtained from the solution on concentration. Thus an oxalo-chloride, $3Th(C_2O_4)_2,ThCl_4,20H_2O$, is obtained from a solution in hydrochloric acid,[882] and an oxalo-nitrate,[883]

$$6Th(NO_3)_4,Th(C_2O_4)_2,48H_2O,$$

separates from a concentrated solution of thorium nitrate, prepared from the oxalate, on standing for some months.

Thorium oxalate, like other thorium salts, dissolves readily in solutions of ammonium carbonate and ammonium oxalate. Thorium oxalate is less soluble in sulphuric acid than the other rare earth oxalates, and is not attacked by nitric acid.[266, 884] When amorphous thorium oxalate is kept in contact with acids, it becomes crystalline and forms tetragonal prisms. On drying over sulphuric acid, it loses 4 molecules of water and forms the dihydrate $Th(C_2O_4)_2,2H_2O$.

A number of double alkali oxalates have been prepared. When a solution of potassium oxalate is boiled with thorium hydroxide and the solution crystallised, the compound

$$2K_2C_2O_4,Th(C_2O_4)_2,4H_2O$$

is obtained; similarly, $2Na_2C_2O_4,Th(C_2O_4)_2,6H_2O$ has been prepared. Brauner[261] has obtained the salts,

$$2(NH_4)_2C_2O_4,Th(C_2O_4)_2,7H_2O;$$
$$2(NH_4)_2C_2O_4,Th(C_2O_4)_2,4H_2O;$$
$$(NH_4)_2C_2O_4,Th(C_2O_4)_2,7H_2O$$
$$\text{and } (NH_4)_2C_2O_4,Th(C_2O_4)_2,3H_2O$$ [83, 884]

by crystallisation from a solution of thorium oxalate in excess of ammonium oxalate. When hydrochloric acid is added to a similar solution an acid oxalate, $2Th(C_2O_4)_2,H_2C_2O_4,9H_2O$, is obtained.

*Thorium Acetylacetonate*, $Th(CH_3COCHCOCH_3)_4$, may be formed by the action of acetylacetone on thorium hydroxide;[245] by the action of sodium acetylacetone on thorium salts or best of

all methods;[462] by adding a solution of acetylacetone in the minimum quantity of ammonia to an aqueous solution of thorium nitrate. The mixture is treated with a small quantity of ammonia to precipitate it, and the precipitate recrystallised from alcohol. It is a colourless crystalline substance which melts at 171°; it commences to sublime at 160° under a pressure of 8-10 mm., and deposits colourless crystals. At the same pressure it boils at 260°-270° with slight decomposition, but at atmospheric pressure decomposition is complete at 260°.[343] When treated with an alcoholic solution of ammonia it forms the compound $[Th(CH_3COCHCOCH_3)_4]_2NH_3$.

Among other compounds of thorium which have been prepared, reference is made to the *boride*,[887] *silicide*,[810, 885] *chlorate*,[841] *bromate*,[841] *iodate*,[841] *selenite*,[841] *chromate*,[319, 807, 881, 886] *selenate*,[889] *arsenate*,[890] *molybdate*,[891] and many organic salts.[11, 127, 253, 841, 888]

Thorium *cyanide*, *thiocyanate*, and *metacarbonate* are not known.

## Detection of Thorium.

Solutions of thorium salts are precipitated by solutions of alkali hydroxides, ammonium hydroxide, and ammonium sulphide with the formation of thorium hydroxide. Thorium is also precipitated as hydroxide mixed with sulphur by solutions of sodium thiosulphate.

In a mixture of rare earths, thorium is best detected by the following reactions:—

(i) The addition of hydrogen peroxide to a warm acid solution causes the precipitation of a peroxidised salt.

(ii) The addition of sodium azide precipitates thorium hydroxide from boiling neutral, alkaline or faintly acid solutions. If cerium is present it must be reduced to the cerous condition before this reaction is applied.

(iii) The addition of a solution of potassium iodate in concentrated nitric acid solution precipitates thorium iodate. If cerium is present it must be reduced to the cerous condition before applying this reaction. Zirconium, if present, will be precipitated along with the thorium iodate, but since zirconium iodate is soluble in oxalic acid, the presence of thorium is abundantly proved if the precipitate does not dissolve when warmed with oxalic acid.

(iv) The addition of sodium hydrogen hypophosphate in concentrated hydrochloric acid solution precipitates thorium hypophosphate on boiling. Cerium and zirconium also give precipitates, but if hydrogen peroxide is present zirconium is not thrown down.

The precipitation as hydroxide by alkali azides is characteristic of thorium.

**Estimation of Thorium.**

The estimation of thorium in preparations free from the other rare earths is a comparatively simple process. The thorium may be precipitated by any of the reagents mentioned in the following methods, and the precipitate treated according to the directions given below. The estimation of thorium has most generally to be made in specimens of monazite and other minerals which contain the other rare earths. This analysis presents considerable difficulties, so that it will probably be well to consider it at some length here.

The mineral, if monazite, is heated with sulphuric acid until a pasty mass is obtained. This is treated with ice-cold water and the solution filtered from the silica. If, as is the case in many methods of analysis, it is necessary that the solution be neutral, the earths are precipitated as oxalate and washed to free them from phosphoric acid. The oxalates are decomposed by fuming nitric acid, and a neutral solution is obtained in the usual way. The above gives the method of obtaining the necessary neutral solution in the case of monazite; in the case of other minerals, the method of treatment will be obvious from the methods, described at the commencement of this chapter, for the isolation of thorium compounds.

1. *Sodium Thiosulphate Method.*—The neutral solution of the rare earths, which has been made slightly acid with hydrochloric acid, is raised to the boiling-point and treated with an excess of sodium thiosulphate solution. The mixture is boiled for a short time, cooled, and filtered. The precipitate, which consists of a mixture of thorium hydroxide and sulphur, is washed, boiled with hydrochloric acid, and filtered from the sulphur. The solution is almost neutralised with ammonia and the oxalate precipitated by oxalic acid. The precipitate is filtered off, washed, ignited to thoria, and weighed. If large quantities of the other

rare earths are present a small quantity of these substances will be precipitated along with the thorium in the thiosulphate precipitate. A repetition of the thiosulphate precipitation will, however, effectually remove them.[892, 893, 894, 896] Should there, however, be any scandium or zirconium present in the mixture, these elements will be precipitated along with thorium by the thiosulphate. If zirconium is present, the thiosulphate precipitate is dissolved in hydrochloric acid, made almost neutral and treated with a concentrated solution of ammonium oxalate until the precipitate at first formed is just dissolved. The solution is diluted to double its original volume, and treated, drop by drop, with concentrated hydrochloric acid until there is no further precipitation. The thorium, in this way, is precipitated as normal oxalate free from zirconium. This is filtered off and ignited to oxide. Should scandium be present the solution in hydrochloric acid from the thiosulphate precipitate is evaporated to dryness, dissolved in a little water, and poured into 25 c.c. of a 20 per cent. solution of ammonium tartrate with constant stirring. A clear solution is obtained, which is treated with excess of ammonia and boiled until the precipitate of ammonium scandium tartrate has settled. The precipitate is filtered off, washed, and boiled with ammonium tartrate solution, filtered, washed, and ignited to scandia in which form it may be weighed. The filtrates are evaporated to dryness, ignited to oxide, and dissolved in acid. The solution thus obtained is treated with oxalic acid, and the thorium oxalate is converted into oxide and weighed.[895]

2. *Hydrogen Peroxide Method.*—A neutral solution of the earths, preferably as nitrate, is treated with a 10 per cent. solution of hydrogen peroxide when the thorium is precipitated as a very voluminous precipitate of $Th_2O_7,N_2O_5$. This compound, according to Wyrouboff and Verneuil,[79, 300, 897] cannot be directly ignited to dioxide on account of the loss occasioned by decrepitation. Consequently, it is filtered off and dissolved in hydrochloric acid in the presence of a little ammonium iodide. The thorium is then precipitated as hydroxide by ammonia, filtered, washed, ignited, and weighed as dioxide. Benz[896] and Borelli[898] find, however, that by adding either ammonium chloride or nitrate before precipitation, the precipitate settles rapidly and in such a form that it is easily washed and may be directly ignited to dioxide and weighed. If the salts are present originally as

chlorides, a repetition of the process will generally be necessary to remove the whole of the cerium, but if nitrates are used this will not be necessary.

3. *Iodate Method.*[899]—The advantages of this method are due to the fact that it may be carried out in strongly acid solutions. Its adoption, therefore, in the analysis of monazite makes the process much shorter and more rapid since it is unnecessary to remove the phosphoric acid from the solution before precipitating the thorium. The estimation is carried out by adding a quantity of nitric acid to the solution of sulphates obtained from the mineral, and then precipitating with a solution of potassium iodate in nitric acid solution. The thorium iodate is redissolved in nitric acid and reprecipitated, whereby the cerium earths are completely removed. The precipitate is dissolved in hydrochloric acid, reduced by sulphur dioxide, precipitated as hydroxide with ammonia, washed, dried, ignited, and weighed as oxide. The product weighed may contain cerium, zirconium, or scandium. If the cerium present in the original solution is in the ceric condition, it may accompany the thorium in the iodate precipitate since ceric iodate is not very soluble in dilute nitric acid. This, however, can be prevented by reducing the cerium to the cerous condition before adding the iodate solution. If zirconium is present, it will be found in the hydroxide precipitate, but may be completely separated here by dissolving the hydroxides in hydrochloric acid and precipitating the thorium from this solution by oxalic acid when the zirconium remains in solution. For the removal of a possible trace of scandium, the method described above may be employed.

4. *Hypophosphate Method.*[801, 802, 803]—This method may also be employed with acid solutions. A solution of acid sodium hypophosphate, $Na_2H_2P_2O_6,6H_2O$, is added, drop by drop, to a boiling solution of the earths as long as precipitation occurs. This precipitate is thorium hypophosphate, $ThP_2O_6,11H_2O$, together with any zirconium or titanium present in the solution. The last-mentioned element will remain in solution if a little hydrogen peroxide is added before precipitation. The precipitate of hypophosphates is treated with a mixture of concentrated sulphuric acid and fuming nitric acid to oxidise the hypophosphates to phosphates. The excess nitric acid is removed by evaporating to dryness, and the residue is taken up with water and precipitated

with oxalic acid, whereby the zirconium is completely removed. The thorium oxalate is filtered off, washed, dried, ignited, and weighed as oxide.

5. *Pyrophosphate Method.*[900]—The pyrophosphates of the tervalent rare earths are soluble in dilute acids, those of the quadrivalent earths (Th,Ce$^{ic}$,Zr) are insoluble. A method based on these facts has been devised for the estimation of thorium. The solution of sulphates from the monazite decomposition is treated with sufficient hydrochloric acid to make the solution have a total acidity of 0·3N. A solution of sodium pyrophosphate is added slowly, and the solution boiled gently for 5 minutes. The precipitate is allowed to settle for 5-10 minutes and filtered. The precipitate contains thorium pyrophosphate, $ThP_2O_7$, along with the pyrophosphates of zirconium and any quadrivalent cerium which may be present. In this method it is essential to keep the acidity at about the figure mentioned; if it is less than 0·3N some of the thorium may not be precipitated owing to the formation of the soluble double salt, $Na_4P_2O_7,ThP_2O_7,2H_2O$, and if more concentrated than 0·3N some thorium pyrophosphate may be dissolved. The precipitate is washed with slightly acidulated (HCl) water and heated with sulphuric acid and a little sodium perchlorate until all organic matter has been destroyed. Water is slowly added and the solution of sulphate poured into a solution of sodium hydroxide. The precipitated thorium hydroxide is boiled with dilute hydrochloric acid, sulphur dioxide is passed in to reduce traces of cerium to the cerous condition, and the solution again precipitated with sodium pyrophosphate. The precipitate is again treated with sulphuric acid as before and the solution of the hydroxide in hydrochloric acid precipitated with oxalic acid. The oxalate is filtered, washed, and ignited to thorium dioxide which is weighed. Several other methods have been proposed for the gravimetric estimation of thorium which, although, not to be specially recommended for one reason or another are distinctly interesting, and may be briefly enumerated here.

A separation of thorium from the rare earths has been based on the solubility of thorium carbonate or thorium oxalate in excess of ammonium carbonate or ammonium oxalate solution. The cerium earths are practically all precipitated when the solution is treated with an excess of either reagent, but the yttrium

earths are only incompletely precipitated, so that a rigid and complete separation of the thorium cannot be achieved. The method was first proposed and used by Glaser,[124] but was soon shown to be unworkable, for the reasons stated, by Hintz and Weber,[894] Drossbach[892] and Benz.[896] Dennis[901] precipitates the thorium as hydroxide by means of potassium azide. This effects a complete separation of the thorium from a neutral solution but it also precipitates the cerium, and a separation of this element cannot be effected by reprecipitation. The reagent is difficult to obtain in the pure condition and is very expensive. This at once rules it out for commercial work. Giles[902] makes use of lead carbonate as the precipitating agent. This substance is intimately mixed with a neutral solution of the rare earths when the quadrivalent elements cerium (ceric), thorium, and zirconium are precipitated as hydroxides. To prevent the precipitation of the cerium, it must previously be reduced from the ceric to the cerous state by sulphur dioxide. The zirconium is removed from the precipitate as described above. The precipitate is washed, dissolved in hydrochloric acid, and treated with hydrogen sulphide to remove the lead. The thorium is then precipitated as hydroxide by ammonia. The objections to this method, which is apparently quite good, are the difficulty of obtaining pure lead carbonate and the troublesome separation of the lead as sulphide.

Metzger[903] proposes to precipitate the thorium from a 40 per cent. alcohol solution by means of fumaric acid. Neish[904] and Kolb and Ahrle[304] suggest precipitating it by *m*-nitrobenzoic acid from boiling aqueous solution, and James and Smith[306] suggest the use of sebacic acid with boiling solutions.

A volumetric method has been described recently for the estimation of thorium.[905] It is based on the fact that ammonium molybdate precipitates thorium as normal molybdate, but has no action with the cerium and yttrium earths. A solution of the mixed nitrates in 1 : 15 acetic acid to which a little sodium acetate has been added is titrated cold with a standard solution of ammonium molybdate using a solution of diphenyl carbazide as outside indicator. This indicator gives a deep rose coloration with the first drop of ammonium molybdate in excess.[906, 907] The colour is somewhat evanescent, remaining only about 15 seconds. The indicator should be made up at least fourteen days before use.

For approximate analysis of thorium minerals the hydrofluoric acid method may be used. This method may only be used when the other rare earths are absent or when they are present in so small a quantity that the sum of the oxides does not differ much from that of the thorium oxide, e.g. in a uranium ore. In these cases the solution is treated with ammonia and the precipitate of hydroxide washed into a platinum dish and heated with aqueous hydrofluoric acid on the water-bath until nearly dry. A little dilute hydrofluoric acid is added and the impure fluorides filtered from the solution and washed with very dilute hydrofluoric acid. The precipitate is transferred to a platinum dish and treated with concentrated sulphuric acid. The sulphates thus obtained are dissolved in hydrochloric acid and precipitated as hydroxides with ammonia. The filtered and washed hydroxides are dissolved in hydrochloric acid, evaporated to dryness, and warmed with a little concentrated oxalic acid solution. The oxalates are filtered and ignited.

## Spectra of Thorium.

Thorium salts, being colourless, give no visible absorption spectrum.

The spark spectrum has been measured by Eder and Valenta,[673] Leonard,[909] and Exner and Haschek.[504, 508] It is made up of a very large number of lines.

The arc spectrum has been measured by Eder and Valenta,[908] Cooper,[503] and Exner and Haschek.[504, 508] The most intense lines are 4863·38 and 4919·99 of intensity 10, 5989·2 of intensity 8, and 3188·2, 3511·76, 3741·36, 4019·29, 4382·02, 4391·29, 4752·60, 5017·39, 5049·93, and 6462·83 of intensity 5.

The Zeeman effect on the lines of the thorium spectrum has been studied by Moore.[910] He shows that a large number of the lines are unsymmetrical in intensity and sharpness, and the stronger component is always a little displaced. Some of the lines change their appearance in the magnetic field without being separated.

The high frequency spectrum of thorium has been examined and described by Siegbahn and Friman.[1025, 1026, 1027]

# CHAPTER VIII.

## ATOMIC WEIGHT DETERMINATIONS.

THE great similarity of the metals of the rare earths, coupled with the difficulty experienced in completely separating them from one another, makes the determination of the atomic weights of these elements one of the most laborious and tedious of all chemical operations. Many times in the history of these substances it has happened that a product has been regarded as homogeneous, only after years to be shown to be a mixture of compounds of two or more elements. It will, therefore, be clear that many atomic weight determinations have been made with material contaminated either by unknown elements or by known elements which it was not possible, at the time, to remove completely. Again, it has not always been possible to be really sure that a given compound is homogeneous, on account of the great similarity of the elements. Strictly speaking, it is only since the introduction of the spectroscope that certain knowledge of the entire absence of known elements from the rare earth compounds has been possible. Hence, in the present chapter, it is proposed to describe and discuss only those atomic weight determinations in which the approximate purity of the material used is established or probable. This will imply that, except in very few cases, the atomic weight determinations made prior to the introduction of the spectroscope will be omitted.

### Cerium Earths.

The tervalent character of the elements, lanthanum, neodymium, praseodymium, samarium, and cerium (in the cerous compounds) has been substantiated in the following way :—

(i) The molecular weight of the anhydrous chlorides of these elements, as determined in non-ionising solvents [620, 911, 912] is in agreement in every case with the formula $MCl_3$.

(ii) The behaviour of the salts of these elements in aqueous solution points to the presence of a tervalent cation. For example, the difference $\lambda_{1024} - \lambda_{32}$ in the case of chlorides is very near to the value 30, which, in accordance with the Walden rule, indicates tervalent ions.

(iii) A number of the compounds of these elements are isomorphous with analogous compounds of other elements of undoubted tervalent character. Thus the octohydrates of the sulphates of samarium, neodymium, and praseodymium are isomorphous with the octohydrate of yttrium sulphate. The selenites of lanthanum, cerium, and the "old didymium" are isomorphous with the selenites of chromium, iron, and aluminium.[467, 913]

(iv) The atomic heat of the metals, in all cases where the specific heat has been determined, is approximately 6·4 if the atomic weight used in the calculation is that based on the assumption that the elements are tervalent. Thus, in the case of cerium, the specific heat is 0·0448, which if 140 is chosen as the atomic weight leads to an atomic heat of 6·3. Furthermore, the value 140·25 which is based on the tervalency of cerium in the cerous compounds, places cerium in group IV of the periodic system. A position which is, in all probability, the correct one, as can be seen from the analogy between cerium, in its quadrivalent compounds, and thorium and zirconium. Lanthanum has a specific heat 0·0464, which if the atomic weight is 139 leads to an atomic heat 6·43. The atomic weight 139 depends on the assumption that lanthanum is tervalent, and it places lanthanum in group III of the periodic system, a position fully in accord with its properties.

## Cerium.

The atomic weight determinations of cerium, of which a very large number have been made, have all been based on the analysis or synthesis of three salts: the sulphate, chloride, and oxalate. In the case of the sulphate the ratios

$$Ce_2(SO_4)_3 : 2CeO_2;\ Ce_2(SO_4)_3 : 3BaSO_4;^{914}\ Ce_2(SO_4)_3,8H_2O : 8H_2O;$$
$$Ce_2(SO_4)_3,8H_2O : 2CeO_2;\ \text{and}\ Ce_2(SO_4)_3 : Ce_2O_3$$

have been determined and the atomic weight calculated from them. Of these ratios, that involving the precipitation of barium

sulphate is the least reliable since it has been shown that barium sulphate carries down some of the cerium salt with it.

In the case of the oxalate, the atomic weight has been determined from the ratios

$$Ce_2(C_2O_4)_3 : 2CeO_2 ; \quad Ce_2(C_2O_4)_3 : 6CO_2 ; \text{ and } 2CeO_2 : C_2O_3,$$

whilst in the case of the chloride the ratio $CeCl_3 : 3Ag$ has been used.

In 1884 Robinson[430] converted highly purified cerous oxalate into the anhydrous chloride by heating it in a current of hydrogen chloride and carbon dioxide. The chloride was preserved in a vacuum desiccator over chalk for some time to remove any free hydrogen chloride which might conceivably be contained in the salt. A solution of the salt in water was titrated with a silver solution of known concentration and the atomic weight calculated from the ratio $CeCl_3 : 3Ag$. As a mean of seven experiments the value Ce = 140·259 was obtained. This value is slightly too low, for the author failed to correct the quantity of silver used for the solubility of silver chloride in the solution, and consequently a slightly larger amount of silver solution was used than was necessary to complete the double decomposition.

In the following year Brauner[78] prepared pure cerium compounds by the repeated hydrolysis of a mixture of ceric sulphate and nitrate. This was finally converted into cerous sulphate which was dissolved in ice-cold water and precipitated by alcohol. After two such treatments, the sulphate was again dissolved in ice-cold water and precipitated as hydrated salt by warming the solution. The hydrated salt was then placed in a platinum crucible and dehydrated in a sulphur bath (see Chap. IV., p. 59). After weighing, it was replaced in the sulphur bath and converted into oxide by steadily raising the temperature. The ratio

$$Ce_2(SO_4)_3 : 2CeO_2$$

was thus obtained, and as a mean of twenty-three experiments the atomic weight of cerium was found to be 140·22.

Ten years later Brauner[86] published the results of an analysis of cerous oxalate, and from the ratio $2CeO_2 : C_2O_3$ calculated the atomic weight to 140·01.

In 1897 Wyrouboff and Verneuil[407] determined the atomic weight of cerium from analyses of the octohydrate of cerous sulphate. Three sets of experiments were performed :—

(i) The ratio $Ce_2(SO_4)_3,8H_2O : 8H_2O$ was determined by heating the hydrated salt to 250°. From ten experiments the mean value Ce = 139·21 was obtained. This value is doubtless inaccurate since Brauner has shown that 250° is not high enough to expel completely the water, amounts up to 0·2 per cent. remaining.

(ii) The anhydrous sulphate obtained in the previous determinations was raised to a white heat and the ratio

$$Ce_2(SO_4)_3 : 2CeO_2$$

obtained, from which as a mean of ten experiments Ce = 139·50.

(iii) The octohydrate was converted directly into the dioxide by ignition at a white heat and the ratio

$$Ce_2(SO_4)_3,8H_2O : 2CeO_2$$

obtained, from which as the mean of ten experiments Ce = 139·21.

In 1903 Brauner and Batěk [434] made determinations by two methods:—

(i) The anhydrous sulphate was converted into the dioxide, and the ratio $Ce_2(SO_4)_3 : 2CeO_2$ determined, whence from seven experiments Ce = 140·21.

(ii) The hydrated oxalate was analysed in the following way: The oxalate was ignited and the weight of dioxide formed determined. A second portion of the oxalate was dissolved in dilute sulphuric acid and titrated with standard potassium permanganate whereby $3C_2O_3$ was determined. Hence the ratio

$$2CeO_2 : 3C_2O_3$$

was known, and from fourteen experiments Ce = 140·265.

In the same year Brauner [490] published the results of a most complete series of atomic weight determinations. Three methods were employed:—

(i) Analysis of cerous oxalate. The ratio $2CeO_2 : 3C_2O_3$ was determined by the method of Brauner and Batěk; from five experiments Ce = 140·246.

(ii) Cerium dioxide preserved from the 1885 experiments was analysed iodometrically and its composition determined. The data thus obtained, combined with the 1885 data, showed that anhydrous cerous sulphate contained 57·7641 per cent. $Ce_2O_3$ and that it yielded 60·5729 per cent. $CeO_2$. Hence from the ratio $Ce_2(SO_4)_3 : Ce_2O_3$ the value Ce = 140·24 was obtained.

(iii) The octohydrate of cerous sulphate was ignited to

dioxide. In these experiments it was found that the weight of the oxide was a function of the time which had elapsed between the end of the ignition and the time of weighing. This increase in weight was due to surface condensation on the dioxide. Consequently the weighings were always made 30 minutes after the heating ceased, and the weight of the dioxide at the moment the ignition ceased determined by graphic extrapolation. It was shown that the weight increased 0·033 per cent. on standing 30 minutes in the desiccator. As a mean of seven experiments from the ratio $Ce_2(SO_4)_3,8H_2O : 2CeO_2$ the atomic weight Ce = 140·25 was obtained.

The value accepted by the International Atomic Weight Committee is Ce = 140·25 (1918).

## Lanthanum.

A very large number of determinations of the atomic weight of lanthanum have been made with widely divergent results. Consequently only those determinations made since 1893 will be considered here. Since this date much more concordant values have been obtained, due no doubt to improvements in the methods of purification of the material and in the analytical technique.

In 1893 Gibbs,[915] using material prepared by the recrystallisation of the double ammonium nitrate, analysed lanthanum oxalate. The amount of oxide was obtained by ignition and the amount of $C_2O_3$ by titration with standard potassium permanganate solution. In this way the ratio $La_2O_3 : 3C_2O_3$ was obtained and the atomic weight La = 139·70 calculated.

Schützenberger[916] determined the ratio $La_2O_3 : La_2(SO_4)_3$ by synthesising the sulphate from the oxide and found the atomic weight La = 138·0.

In 1902 Brauner and Pavlíček,[281, 347] made a very complete study of the atomic weight of lanthanum, and examined, in great detail, the conditions under which lanthanum oxide is converted into lanthanum sulphate. They found that two causes were mainly responsible for the results (generally too low) of previous experimenters.

(i) The difficulty of completely expelling the last traces of free sulphuric acid from the sulphate without effecting a decomposition. In this connection it is shown that a temperature of

about 600° is necessary to expel completely the acid, and this temperature is very near the temperature of decomposition of the normal sulphate.

(ii) The difficulty in weighing lanthanum sulphate which is an exceedingly hygroscopic substance.

The first difficulty was overcome in the following way. The lanthanum sulphate was heated to about 600°, and this was followed by a further heating at the same temperature in the dissociation products of ammonium carbonate. A portion of the lanthanum sulphate after cooling, as described below, was dissolved in cold water to which a few drops of methyl orange solution were added. From the colour of the solution it was immediately known whether all the free acid had been expelled or whether the neutral sulphate had been decomposed. In the former case the solution would be acid and the acidity was determined by titration with $\frac{N}{20}$ sodium hydroxide. In the latter case the solution would be alkaline and the alkalinity was determined by titration with $\frac{N}{20}$ sulphuric acid. The correction to be applied was therefore known and was made use of in all determinations.

To remove the error due to the absorption of water by the sulphate, a small specially constructed desiccator was employed, which contained phosphoric anhydride. The crucible containing the lanthanum sulphate was placed, whilst hot, inside a stoppered weighing bottle and the whole allowed to cool in the desiccator. Moisture was therefore prevented from coming into contact with the sulphate. Making use of these experimental refinements the authors determined the ratio $La_2O_3 : La_2(SO_4)_3$, and found as a mean of seven experiments La = 139·03.

In a second series of experiments the ratio $La_2(SO_4)_3 : La_2O_3$ was found by igniting the anhydrous sulphate to oxide. It was observed in these experiments that the oxide absorbed oxides of sulphur from the furnace gases and in consequence pure lanthanum oxide was never obtained. The value La = 139·14 was obtained in this series. In a final set of twenty-three experiments the ratio $La_2O_3 : 3C_2O_3$ was obtained, the former quantity by ignition of the oxalate to oxide and the latter by titration with standard potassium permanganate solution. Fluctuating results were obtained, due in all probability to the hydrolysis of lanthanum

oxalate when washed with water. The mean value La = 139·07 resulted from this series of experiments.

In the same year Jones [348] determined the atomic weight of lanthanum by the synthesis of the sulphate from the oxide and as a mean of twelve experiments the value La = 138·77 was obtained. Brauner [917] thereupon pointed out that he had obtained the same value in his preliminary experiments where the special precautions for preventing the absorption of water were not taken.

In 1906 Brill [349] determined the atomic weight of lanthanum by the sulphate method. A small quantity of lanthanum oxide, 2-3 mgm., was treated with sulphuric acid in a small platinum capsule and heated to 500°-550°. This expelled the excess of acid and did not decompose the normal sulphate. The weighings were made by means of a microbalance and the results La = 139·5 and 139·8 obtained. Whilst these results cannot claim to have the accuracy of those of Brauner on account of the relatively large error in the weighing, yet they probably indicate that Brauner's value is more accurate than Jones' value.

Feit and Przibylla [352] in 1906 determined the atomic weight of lanthanum by dissolving the oxide in a known excess of $\frac{N}{2}$ sulphuric acid and titrating the excess acid with $\frac{N}{10}$ alkali using methyl orange as indicator. They obtained the value

$$La = 139{\cdot}17.$$

The value accepted by the International Atomic Weight Committee is La = 139·0 (1918).

## Praseodymium.

The atomic weights of praseodymium and neodymium were first determined in 1885 by Auer von Welsbach,[55] who from the ratio $X_2O_3 : X_2(SO_4)_3$ obtained the values Pr = 143·6 and Nd = 140·8. Brauner,[578] who in 1898 determined the atomic weight of praseodymium, by the analysis of the oxalate and the sulphate, got the value Pr = 140·95. Consequently, he concludes that in some way the atomic weights of neodymium and praseodymium found by von Welsbach have been transposed and that in reality Pr = 140·8 from von Welsbach's experiments.

In 1898 Jones[614] prepared praseodymium sesquioxide from the dioxide by reduction in hydrogen. This he converted into the sulphate by dissolving in dilute sulphuric acid. As a mean of twelve experiments the value Pr = 140·46 was obtained from the ratio, $Pr_2O_3 : Pr_2(SO_4)_3$. Using identically the same method, von Scheele[223] obtained the value Pr = 140·53, whilst by the oxalate method—ignition to oxide and titration with potassium permanganate—he got values varying between 139·72 and 140·15.

An extensive series of experiments was made by Brauner[912] in 1901 to determine the atomic weight of praseodymium. Four distinct series of experiments were carried out. In the first place it was shown that the reduction of the black oxide of praseodymium cannot be effected quantitatively to the sesquioxide. In all experiments the material employed was shown to be pure by both the spark spectrum and the absorption spectrum.

(i) In the first series of experiments the crystallised octohydrate of praseodymium sulphate was heated to 500° to expel the water of crystallisation. The ratio $Pr_2(SO_4)_3,8H_2O : 8H_2O$ was thus obtained and from two experiments Pr = 141·09.

(ii) In the second series the anhydrous sulphate was converted into sesquioxide by ignition and the ratio $Pr_2(SO_4)_3 : Pr_2O_3$ obtained. From two experiments Pr = 140·95.

(iii) In the third series of experiments the ratio $Pr_2O_3 : 3C_2O_3$ was determined from the oxalate; the sesquioxide by ignition and the oxalate by titration with potassium permanganate solution. A mean value, Pr = 140·98, was obtained.

(iv) The final series of experiments was based on the synthesis of the sulphate whereby the ratio $Pr_2O_3 : Pr_2(SO_4)_3$ was obtained. The percentage of praseodymium sesquioxide in the oxalate was first determined, then accurately weighed quantities of the oxalate were carefully ignited and the residue reduced in hydrogen. This was dissolved in dilute nitric acid and evaporated with dilute sulphuric acid and the residue heated to 500°-600° in the presence of the decomposition products of ammonium carbonate. After weighing, the acidity of the solution of the product was determined as is described in the case of lanthanum (*q.v.*). These experiments give as a mean

$$Pr = 140{\cdot}96.$$

In 1903 Auer von Welsbach[918] published the value

$$Pr = 140{\cdot}57$$

as a mean, although no details of the work on which this value is based are available.

In 1906 Feit and Przibylla [352] dissolved accurately weighed quantities of praseodymium oxide in a measured excess of $\frac{N}{2}$ sulphuric acid. The excess of acid was titrated with $\frac{N}{10}$ alkali using methyl orange as indicator. The value Pr = 140·62 was obtained.

In 1915 Baxter and Stewart [919] determined the atomic weight of praseodymium by the analysis of the chloride. The pure chloride was gently heated to remove water and finally fused to remove the last traces of moisture. It was found in the experiments that sometimes a small amount of an insoluble oxychloride, PrOCl, was produced. The quantity of this substance produced increases with length of time during which the material is fused, and it was shown that by making the period of fusion one minute, the last trace of moisture can be expelled and the amount of PrOCl kept below the quantity 1·0 mgm., per 5 grams of material. Weighed quantities of anhydrous praseodymium chloride were treated with silver nitrate solution and the silver chloride collected and weighed. The ratio $PrCl_3 : 3AgCl$ thus obtained gave the value Pr = 140·92.

The value adopted by the International Atomic Weight Committee is Pr = 140·9 (1918).

## Neodymium.

The first atomic weight determination of neodymium was made in 1885 by Auer von Welsbach [55] who obtained the value Nd = 143·6 (see praseodymium). In 1898 Brauner [578] obtained the value Nd = 143·63 and Boudouard [920] by analysis of the sulphate obtained Nd = 143·05. By the synthesis of the sulphate, Jones [614] determined the ratio $Nd_2O_3 : Nd_2(SO_4)_3$, and as a mean of twelve experiments obtained the value Nd = 143·63. In these experiments, material was used which was considerably purer than that used by Auer von Welsbach. The results were also corrected for the small amount of praseodymium contained in the material.

In 1901 Brauner [580] synthesised the sulphate and obtained the ratio $Nd_2O_3 : Nd_2(SO_4)_3$, from which Nd = 143·89. In 1903

from the same ratio Auer von Welsbach[921] obtained the value Nd = 144·54 (three experiments).

In 1905 Feit and Przibylla,[229, 352] by dissolving the sesquioxide in dilute sulphuric acid and titrating the excess acid with standard alkali, obtained the value Nd = 144·52. A repetition of the work in 1906 gave Nd = 144·60.

In 1907 Holmberg,[922] using very pure material, obtained the value Nd = 144·11; in this work the anhydrous sulphate was ignited and the ratio $Nd_2(SO_4)_3 : Nd_2O_3$ obtained.

Baxter and Chapin[923] have determined the atomic weight from the chloride. This salt was dissolved in water and the solution treated with silver nitrate. The silver chloride was collected and weighed, and the ratio $NdCl_3 : 3AgCl$ obtained, from which Nd = 144·272 as the mean of fifteen experiments which gave values lying between 144·250 and 144·286. A series of seven titration experiments gave from the ratio $NdCl_3 : 3Ag$, Nd = 144·268; the experimental values lying between 144·249 and 144·283

Comparatively recently, Baxter, Whitcomb, Stewart, and Chapin[924] have made a further series of atomic weight determinations of neodymium. The nitrate was purified by a prolonged series of recrystallisations from nitric acid. This was converted in order into the oxalate, oxide, and chloride. The chloride was analysed by comparison with silver. From the experimental results, Nd = 144·261.

The value adopted by the International Atomic Weight Committee is Nd = 144·3 (1918).

## Samarium.

Samarium compounds were first obtained pure in 1900 by Demarçay,[356] and by Urbain and Lacombe[647] in 1904. Consequently the atomic weight of this element can only be regarded as approximate in the case of all determinations made prior to these dates. The material used contained, in all cases, at least some europium compounds. A large number of determinations were made prior to 1900 by Delafontaine, Marignac,[50] Brauner,[53] Cleve,[649] Bettendorff,[573] and Koppel,[925] with results, in most cases, which do not differ much from the values obtained with the pure material.

In 1900 Demarçay[356] determined the ratio $Sa_2O_3 : Sa_2(SO_4)_3$

by synthesising the sulphate from the oxide. Results were obtained which gave values for the atomic weight of samarium varying between 147·2 and 148·0.

In 1904 Urbain and Lacombe[647] carried out a number of experiments with material prepared from various sources, and quite free from gadolinium and europium. The determinations were made with different fractions of the material, all of which gave the same value for the atomic weight, thus demonstrating the uniformity of the material. The method adopted consisted in dehydrating the octohydrate of the sulphate by cautious heating and converting the anhydrous sulphate into oxide by strong ignition. The following ratios were thus determined and the atomic weight calculated :—

(i) $Sa_2(SO_4)_3,8H_2O : Sa_2(SO_4)_3$; Sa = 150·314;
(ii) $Sa_2(SO_4)_3 : Sa_2O_3$; Sa = 150·533;
and (iii) $Sa_2(SO_4)_3,8H_2O : Sa_2O_3$; $Sa_2$ = 150·484.

In 1906 Feit and Przibylla[352] determined the atomic weight by their titration method and obtained the value Sa = 150·56.

Matignon[275] determined the atomic weight by converting the basic sulphate into the normal sulphate. In this way the ratio $Sa_2O_3,SO_3 : Sa_2O_3,2SO_3$ was obtained from which Sa = 150·6.

Stewart and James[1028] starting with pure samarium oxide prepared the anhydrous chloride. The crystallised chloride was first obtained and heated to 100° until most of the water had been expelled. The temperature was then raised to 180° and finally to 300°, a current of hydrogen chloride being passed over the material the whole time. The anhydrous salt was cooled, powdered, and heated to the melting-point in hydrogen chloride which was expelled by nitrogen and finally by air. Using this material the atomic weight was determined by measuring the ratio $3Ag : SaCl_3$. As a mean of eight determinations the value Sa = 150·43 was obtained. The value adopted by the International Atomic Weight Committee is

Sa = 150·4 (1918).

## Yttrium Earths.

As far as solutions of the salts of the members of the yttrium earths have been examined, ample evidence is forthcoming to indicate the tervalent character of the cation. Thus the electro-

conductivity of salts of gadolinium, yttrium, and the mixture of ytterbium and lutecium indicates the presence of tervalent ions. The octohydrates of the sulphates of europium, gadolinium, erbium, yttrium, and probably lutecium and ytterbium are isomorphous with the corresponding compounds of the elements of the cerium group. In the case of the other earths the general similarity is so great that it is to be inferred that they also are tervalent.

The purity of the material used in the atomic weight determinations of several members of this group is still very doubtful, and this coupled with the fact that not much of it is available has had as a result that not much work has been possible in these cases. The values, therefore, which have been obtained must be accepted with considerable caution.

## Scandium.

The atomic weight of scandium was first determined by Cleve,[264] who used both the analytical and the synthetic sulphate methods. The former method gave the value Sc = 45·20, whilst the latter method gave the value Sc = 44·96. In 1880, using a purer specimen of the scandium compound, Nilson [686] determined the atomic weight by the synthetic sulphate method and obtained the value 44·13. Meyer and Winter, using a scandium preparation, which had been purified by the sodium carbonate method obtained the value Sc = 45·0. This material when converted into the acetylacetonate and twice crystallised gave the same atomic weight, whilst after six recrystallisations from alcohol the atomic weight became quite constant at Sc = 44·9 By purifying scandium by the double ammonium tartrate, Meyer and Goldenberg obtained a material which gave the value

$$Sc = 43·9.$$

The results quoted above make it very obvious that a great deal of work is necessary on the atomic weight and purification of scandium before it will be possible definitely to fix the most probable value of the atomic weight. The value adopted by the International Atomic Weight Committee is Sc = 44·1 (1918).

## Yttrium.

In 1883 Cleve [926] determined the atomic weight of yttrium from experiments on the synthesis of the anhydrous sulphate.

The material used was very carefully purified from terbium earths. The ratio $Yt_2O_3 : Yt_2(SO_4)_3$ was obtained from twelve experiments and the value Yt = 89·11 calculated. Probably the best atomic weight of yttrium is that recorded by Brauner.[927] This value has been calculated by Brauner from the data YtO = 75·25 which he took from the label of a bottle in Marignac's collection which contained pure yttria. This oxide was doubtless obtained from the sulphate, and according to Brauner must have been obtained between 1880 and 1887. From the data Brauner has calculated the atomic weight Yt = 88·88. In 1895 Jones[928] determined the atomic weight by both the analytical and the synthetic sulphate methods. The material used in these experiments was purified by fractional precipitation with potassium ferrocyanide. By the former method the value Yt = 88·97 was obtained, whilst by the latter method Yt = 88·95. In 1901 G. and E. Urbain[242] gave the value 88·6 without any details of the method used in procuring it. Using their titration method, Feit and Przibylla[352] found the value 89·40. In 1913 Egan and Balke[274] converted yttrium sesquioxide into the anhydrous chloride in a quartz flask, and from three perfectly concordant experiments of a preliminary nature they have determined the ratio $Yt_2O_3 : YtCl_3$ and obtained the value Yt = 90·12. The material used in these experiments was not quite pure and was estimated to contain 0·5 per cent. of erbia. Meyer and Wourinen,[275] using material purified by the iodate method, determined the ratio $Yt_2(SO_4)_3 : Yt_2O_3$, from which Yt = 88·60. Meyer and Weinheber[698] from a series of determinations by both the synthetic and analytical sulphate methods obtained by the former method the value Yt = 88·72 (limits 88·71-88·73) and by the latter method Yt = 88·735 (limits 88·71-88·76). They consider from these experiments that the accepted atomic weight of yttrium (89·0) is too high, and that the most probable value is 88·7 with some doubt as to the second decimal. Hopkins and Balke[929] criticise adversely the sulphate method for the determination of the atomic weight of yttrium, first because the value found varies widely with the time and temperature employed in igniting the oxide, and also because the salt $Yt_2(SO_4)_3,8H_2O$ is too unstable for accurate work. Using the same method as Egan and Balke,[274] they have determined the ratio

$$Yt_2O_3 : 2YtCl_3,$$

from which the atomic weight 88·9 has been calculated. The experiments gave values which varied from 88·80 to 89·06. The value adopted by the International Atomic Weight Committee is Yt = 88·7 (1918).

## Europium.

The atomic weight of europium was first determined in 1904 by Urbain and Lacombe.[232] A small quantity of europium oxide, free from samarium and gadolinium, was obtained by the careful fractionation of the material lying between the samarium and gadolinium fractions. The oxide was converted into the octohydrate of the sulphate, which was heated at 375° to render it anhydrous and at 1600° to convert it into the oxide. The following ratios and atomic weights were obtained :—

| | | |
|---|---|---|
| $Eu_2(SO_4)_3,8H_2O : Eu_2(SO_4)_3$ | (5 experiments) | Eu = 151·826 |
| $Eu_2(SO_4)_3 : Eu_2O_3$ | (5 ,, ) | Eu = 151·790 |
| $Eu_2(SO_4)_3,8H_2O : Eu_2O_3$ | (5 ,, ) | Eu = 151·796 |

Previous to these determinations, Demarçay[357] in 1900 had determined the atomic weight of the substance ΣZ which in 1901 was named europium. The method used consisted in synthesising the anhydrous sulphate from the oxide. From the ratio $Eu_2O_3 : Eu_2(SO_4)_3$; Eu = 151·0, Feit and Przibylla[352] by their titration method obtained the value Eu = 152·66, whereas in 1908 Jantsch[930] by the same method as Urbain and Lacombe obtained the mean value 152·03 ± 0·02. The value adopted by the International Atomic Weight Committee is

Eu = 152·0 (1918).

## Gadolinium.

Up to the year 1905 the atomic weight of gadolinium had been determined by many chemists, who obtained values which were near the figure 156·5. Thus we find in 1880 Marignac[50] obtained the value 156·75; Lecoq de Boisbaudran[931] in 1890 found 155·33-156·12; Bettendorf[932] in 1891 found 156·72; Benedicks[730] in 1900 found 156·38, and Marc[933] in 1904 got the value 156·33. All these values were obtained by the synthetic sulphate method, and in all cases are too low. A series of very careful and trustworthy experiments was carried out by

Urbain[236] in 1905 which gave the value Gd = 157·24. The material used was gadolinium oxide obtained from the products of fractional crystallisation of the double nickel nitrate. A large number of fractions were obtained and of these, numbers 18-23 were identical and gave values for the atomic weight varying between 157·36 and 157·05, which leads to the mean value 157·24. The fractions 35-39 gave the value 157·25, the extreme values being 157·04 and 157·45. The mean value from the whole eleven fractions is therefore 157·25. The experimental method adopted in these experiments consisted in igniting the octohydrate of the sulphate to oxide to determine the ratio $Gd_2(SO_4)_3,8H_2O : Gd_2O_3$. Feit and Przibylla[352] using their titration method find the value Gd = 157·47. The value adopted by the International Atomic Weight Committee is

Gd = 157·3(1918).

## Terbium.

The atomic weight of terbium has been variously determined to values fluctuating between 113 (Delafontaine, 1864) and 163·1 (Lecoq de Boisbaudran, 1886). These widely varying values are explained by the non-homogeneous character of the material employed. The first material which may be regarded as pure was obtained in 1905 by Urbain ;[341, 718, 740] this was prepared by the fractional crystallisation of the double nickel nitrate and precipitation with ammonia. In this way 7 grams of the pure oxide were obtained. This was converted into the octohydrate of the sulphate in which the water was estimated. Hence from the ratio $Tb_2(SO_4)_3,8H_2O : Tb_2(SO_4)_3$ the value Tb = 159·22 was obtained as the mean of figures which lay between 159·17 and 159·30. The value adopted by the International Atomic Weight Committee is Tb = 159·2 (1918).

## Dysprosium.

In 1905 [341, 359] Urbain succeeded in preparing relatively pure dysprosium compounds, and from fourteen successive fractions he obtained values between 162·64 and 162·28 for the atomic weight. In 1906 Urbain and Demenitroux,[752] using material obtained from repeated recrystallisation of the nitrate, arrived at the value Dy = 162·52 as the mean of six determinations of the ratio $Dy_2(SO_4)_3,8H_2O : Dy_2O_3$. The extreme values of this

series were 162·29 and 162·75. The material was then subjected to a further purification by recrystallising as the ethyl sulphate. Six experiments with the purified material gave values between 162·36 and 162·63, from which the mean value Dy = 162·54 is obtained. At a later date the same chemists extracted dysprosium from the earth fraction between yttrium and terbium, by the ethyl sulphate method, and found that after fourteen crystallisations a material with a constant spectrum was obtained. This material gave the atomic weight Dy = 162·49, this being the mean of values lying between 162·64 and 162·28. Hinrichs [934] has applied his method of calculating atomic weights to Urbain's figures and finds the value Dy = 162·5.

In 1918 Kremers, Hopkins, and Engle [995] submitted very pure dysprosium material to a prolonged purification by the ethyl sulphate and bromate methods. With this material the atomic weight has been obtained from the ratios:—

(i) $Dy_2(SO_4)_3,8H_2O : Dy_2O_3$; (ii) $Dy_2O_3 : 2DyCl_3$;
and (iii) $DyCl_3 : 3Ag$.

In the case of the ratio $Dy_2(SO_4)_3,8H_2O : Dy_2O_3$ it is shown that the octohydrate is not constant in composition when dried over sulphuric acid, and consequently this ratio does not give trustworthy results. The value Dy = 163·83 was obtained as the mean of nine experiments from the ratio $2DyCl_3 : Dy_2O_3$, but since on further investigation it was shown that the oxide prepared for these experiments from the oxalate was not constant in composition this value is rejected. Further, an oxide, which would yield concordant results from this ratio, could not be prepared. Eight determinations of the ratio $DyCl_3 : 3Ag$ lead to the value 162·52. The value adopted by the International Atomic Weight Committee is Dy = 162·5 (1918).

## Holmium.

In 1879 Cleve [44] separated holmium and thulium from the erbium earths, and found for holmium the atomic weight 160-161. Hofmann and Krüss [282] fractionated a mixture of earths containing holmium in the way described for erbium (p. 210), and found the atomic weight of the various holmium fractions fluctuated between 158·5 and 169·4. Urbain [935] is of the opinion that the atomic weight of holmium lies between 162·5 and 167, but he is also of the opinion that the homogeneous character

of holmium has not yet been established. This view is confirmed by some experiments of Holmberg,[756] who after a prolonged purification of holmium material found the atomic weight 144. Further purification raised the value to 150, and finally a partial precipitation by aniline raised the value to 156. At a later date Holmberg[936] obtained material which contained only the merest traces of erbium and dysprosium, and from six experiments with this material the value Ho = 163·5 was obtained. The value adopted by the International Atomic Weight Committee is 163·5 (1918).

## Erbium.

The first comparatively pure erbium compounds were obtained by Bahr and Bunsen[22] in 1866, and these chemists by synthesising the anhydrous sulphate from the oxide obtained the ratio $Er_2(SO_4)_3 : Er_2O_3$ and from it the value Er = 169·08.

By the same method Cleve and Höglund[23] obtained the value 170·59, whilst Humpidge and Burney[937] by analysis of the anhydrous sulphate determined the ratio $Er_2O_3 : Er_2(SO_4)_3$ and from it the value Er = 171·62. In 1880 Cleve[938] prepared erbium compounds which had a rose-red colour, and these were entirely free from ytterbium. Using this material the atomic weight was determined by the synthetic sulphate method and the value Er = 166·25 obtained. In 1893 Hofmann and Krüss,[939] using an erbium preparation which gave an atomic weight 166-167, carried out a long series of fractionations, partly by the basic nitrate method and partly by aniline precipitation. A large number of fractions were obtained which gave atomic weights varying between 165·4 and 172·4. Brauner[927] employed the same method as Cleve in 1905, but used more highly purified material. He obtained the value Er = 167·14 which indicates that Cleve's material was mixed with earths of lower atomic weight. Hofmann and Burger[244] in 1908 obtained the value Er = 167·38, whilst in 1910 with still purer material Hofmann[246] obtained the value 167·68. The value adopted by the International Atomic Weight Committee is Er = 167·7 (1918).

## Thulium.

When Cleve[44] first separated thulium from the mixture of the erbium earths he found the value Tm = 170·7 as its atomic

weight. Apparently no atomic weight determinations have been made with pure material. Urbain [940] considers that the value of the atomic weight cannot be higher than 168·5, and this value has been adopted by the International Atomic Weight Committee.

## Ytterbium.

Since the "old ytterbium" has been resolved into its constituent elements, the "atomic weight" of this substance has ceased to have anything but an historical interest. A short list of the investigators, together with the atomic weight values obtained by them, may, however, not be entirely devoid of interest. Marignac [42] (1878) found Yb = 172·5; Nilson [211] (1880) Yb = 173·16; A. Cleve [783] (1902) 173·11; and Brauner (1904) 173·08. The method adopted in every case was that of converting the oxide into the anhydrous sulphate.

## Ytterbium. Lutecium. Celtium.

From the fractions obtained by the nitrate method of separation of the constituents of the old ytterbium, Urbain [89] obtained the atomic weights 170·1 and 173·4 for the most soluble fraction (Yb) and the least soluble fraction (Lu) respectively. At a later date from fractions obtained from 15,000 crystallisations of the nitrate, he got the respective values 170·66 and 174·04 by the analysis of the octohydrates of the sulphates. From the fractions of the double oxalate crystallisation von Welsbach [90] obtained the values 172·9 and 174·23 for ytterbium and lutecium respectively by ignition of the sulphate to oxide. At a slightly later date,[90] with more highly purified material, he obtained the values

$$Yb = 173{\cdot}0 \text{ and } Lu = 175{\cdot}0.$$

In this case the method employed was to convert the sulphate into oxalate and this by ignition into oxide. Blumenfeld [989] and Urbain in more recent work find the value Yb = 173·54 although no details are given.

The element celtium has not yet been obtained pure, and no atomic weight determinations of any kind are to be found in the literature of this element.

The values adopted by the International Atomic Weight Committee are Yb = 173·5; Lu = 175·0 (1918).

## Thorium.

Berzelius (1828) ascribed the formula ThO to thoria on account of its analogies with CeO, LaO, and DiO, these oxides having been given their formulæ from their resemblance to magnesia. The correct formula $ThO_2$ was first indicated by Delafontaine[33] in 1863 on account of the isomorphism of this substance with stannic oxide ($SnO_2$) and rutile ($TiO_2$), and also on account of the analogy between the double potassium fluorides with those of zirconium; $2KF,ZrF_4 : 2KF,ThF_4,4H_2O$ and

$$KF,ZrF_4,H_2O : KF,ThF_4,\tfrac{1}{2}H_2O.$$

These analogies would demand for thorium an atomic weight of the order 232 and not 116 as is implied by Berzelius' formula for the oxide. The crystalline relationships all indicate that thorium is a quadrivalent element and not bivalent as the earlier formula of the oxide implied. This view is confirmed by the vapour density of the tetrachloride, by the electroconductivity and hydrolysis of aqueous solutions of thorium salts. An atomic weight of 232 leads to the value 6·41 for the atomic heat of the metal, and this value places thorium in the 4th group of the periodic system where it is obviously correctly placed, whilst the value 116 would place it in the same position as tin, a situation which would not agree so well with the properties of the element.

An extremely large number of atomic weight determinations of thorium have been carried out, of which, in all probability, those due to Nilson[791] and Krüss[786] are the most trustworthy. The earliest determinations were made in 1829 by Berzelius,[127] who precipitated the thorium in thorium sulphate as hydroxide, and, after filtration, precipitated barium sulphate in the filtrate and weighed it. From the ratio $ThO_2 : 2BaSO_4$ he got the values Th = 240·1 and 236·0 in two different series of experiments. He also analysed the double thorium potassium sulphate and got the following values from $ThO_2 : 2BaSO_4$; Th = 240·7 and from $ThO_2 : 2K_2SO_4$; Th = 236·9. In 1861 from the analysis of the sulphate, Chydenius[127] obtained the value 237·3, the analysis of thorium potassium sulphate gave 236·1, analysis of the acetate gave 237·3, analysis of the formate 241·2, and of the oxalate 231·4. In 1863 Delafontaine[33] ignited the enneahydrate and from the ratio $Th(SO_4)_2,9H_2O : ThO_2$ obtained the value Th = 232·35.

In 1874 Cleve,[941] by ignition of the anhydrous sulphate, obtained the value 234·03, and by the ignition of the oxalate and determination of the percentage of thoria, water, and carbon dioxide obtained the value Th = 233·97. In 1882 Nilson,[791] by ignition of the anhydrous sulphate, determined the ratio

$$ThO_2 : 2SO_3 \text{ from which Th} = 232{\cdot}16.$$

He also determined the ratios

$$ThO_2 : Th(SO_4)_2,9H_2O \text{ and } Th(SO_4)_2 : 9H_2O,$$

and obtained from them the values Th = 232·51 and Th = 233·75 respectively.

In 1887, by the same method, Krüss and Nilson[786] determined the ratio $ThO_2 : 2SO_3$ and from it the value Th = 232·49. Some ten years later Brauner,[578] by ignition of the oxalate and by titration with potassium permanganate obtained the ratio

$$ThO_2 : 2C_2O_3 \text{ from which Th} = 232{\cdot}39\text{-}232{\cdot}21.$$

In 1900, by ignition of the anhydrous sulphate, Urbain[942] got the value Th = 233·79 and by ignition of the octohydrate of the sulphate Th = 232·64. In 1905 Meyer and Gumperz,[948] by ignition of the anhydrous sulphate got the value 232·2-232·7. Finally in 1916 Hönigschmidt and Horovitz[944] criticise adversely the sulphate method of determining the atomic weight of thorium. They prepared thorium tetrabromide in a quartz flask and sublimed it into a weighing tube. This weighed quantity of bromide was then analysed by comparison with silver by the Richards' method. Two series of experiments were completed and the following results obtained:—

1st series : Th = 232·15 ± 0·016 (12 experiments).
2nd series : Th = 232·12 ± 0·014 (15 „ ).

The value accepted by the International Atomic Weight Committee is 232·4 (1918).

# CHAPTER IX.

## RARE EARTHS AND THE PERIODIC SYSTEM.

THE correct allocation of the metals of the rare earths in the periodic classification is a matter attended with considerable difficulty, and one which cannot, as yet, be regarded as definitely and finally achieved. The difficulty experienced here arises from three distinct causes:—

(i) The uncertainty which still exists as to the individuality and uniformity of many of the members of this group;

(ii) The lack of sufficient knowledge of the compounds and properties of many of the elements; and

(iii) The large number of elements with atomic weights of nearly the same value and with very similar properties.

The consideration of the position of these elements will, in all probability, best be made on the basis of the periodic classification in the form introduced by Mendeléeff. Consequently, this system is reproduced here, without the elements under discussion, to aid the present consideration.

MENDELÉEFF'S TABLE.

| Series. | 0. | I. | II. | III. | IV. | V. | VI. | VII. | VIII. |
|---|---|---|---|---|---|---|---|---|---|
| | | A. B. | A. B. | A. B. | A. B. | A. B. | A. B. | A. B. | |
| 1 | H | — | — | — | — | — | — | — | — |
| 2 | He | Li | Gl | B | C | N | O | F | — |
| 3 | Ne | Na | Mg | Al | Si | P | S | Cl | — |
| 4 | A | K Cu | Ca Zn | — Ga | Ti Ge | V As | Cr Se | Mn Br | Fe Co Ni |
| 5 | — | Rb Ag | Sr Cd | — In | Zr Sn | Nb Sb | Mo Te | — I | Ru Rh Pd |
| 6 | Kr | Cs | Ba | — | — | — | — | — | — |
| 7 | — | — | — | — | — | — | — | — | — |
| 8 | X | — | — | — | — | Ta Bi | W — | — — | Os Ir Pt |
| 9 | — | — | — | — | — | | | | |
| 10 | — | — | — | — | — | | | | |
| 11 | — | Au | Hg | Tl | Pb | | | | |
| 12 | — | — | Ra | — | — | — | U | — | — |

Of the eighteen elements to be considered, three—scandium, yttrium, and thorium—are by no means difficult to place in the system, and it will probably be well to deal with these elements first. But the remaining fifteen elements, whose atomic weights lie between 139 and 175·0, are extremely difficult to place in the system, and very many views have been put forward as to the positions which must be given to these elements.

*Scandium.*—This element is of more than ordinary interest, since it is without doubt the ekaboron predicted by Mendeléeff,[676] in 1871. The hydrogen equivalent of scandium has been found to be 14·7; and if it is assumed that scandium is a tervalent element then it must have an atomic weight of 44·1 and occupy a position in the periodic classification between calcium (40) and titanium (48). This position until the discovery of scandium was vacant. Consequently, it would seem probable that scandium will be correctly placed in group III, series 4. However, before an element can be finally placed in any position in the periodic classification, it must be definitely shown that the element has physical and chemical properties which are in accordance with the characteristics of the group selected. The tervalency of scandium is definitely proved by the molecular weight determinations of the acetylacetonate in both benzene and chloroform solutions. These determinations indicate that this compound has the formula $Sc(CH_3COCHCOCH_3)_3$ and consequently scandium must be tervalent. On this basis the oxide becomes $Sc_2O_3$ and the chloride $ScCl_3$, formulæ in accord with the position allotted to the element. Scandium oxide is weakly basic, a property in keeping with its position between the strongly basic calcium oxide and the weakly acidic titanium oxide. The density of scandium oxide (3·86) also lies between the densities of calcium oxide (3·30) and titanium oxide (3·95). When scandium chloride is dissolved in water it is hydrolysed to a considerable extent, and in this respect it is similar to aluminium chloride and intermediate between calcium chloride which is not hydrolysed and titanium chloride which is completely hydrolysed. All the derivatives of scandium have properties which are strictly in accord with the position allotted to scandium in group III.

*Yttrium.*—This element is shown to be tervalent by the isomorphism of its selenite and platinochloride with the corresponding salts of chromium, aluminium, indium, and iron,[541, 761] and

also by the isomorphism of the octohydrate of the sulphate, $Yt_2(SO_4)_3,8H_2O$, with the corresponding salts of neodymium, praseodymium, and erbium. The electroconductivity of solutions of the sulphate also show the presence of the tervalent ion. Since, therefore, yttrium is tervalent and has a hydrogen equivalent of 29·6 it follows that its atomic weight must be about 89, a value which would place it in group III, series 6, between strontium (87·6) and zirconium (90·6).

That yttrium is correctly placed in group III is definitely shown by the properties of its oxide. Yttrium oxide is more basic than scandium oxide which is situated immediately above it, and its basicity is intermediate between that of strontium and zirconium which occupy positions on either side of it in series 6. Yttrium compounds like those of scandium and aluminium show a great tendency to form complex derivatives.

*Thorium.*—Berzelius attributed to thoria the formula ThO from the analogy which exists between this oxide and those of lanthanum, didymium, and cerium. At this period the elements just enumerated were regarded as bivalent, and consequently the oxides had the formulæ LaO, DiO, and CeO respectively. According to this view, thorium was a bivalent element with an atomic weight of 116, a value which could not possibly be fitted into group II of the periodic classification where such an element would naturally belong. In 1863 Delafontaine,[83] on account of the isomorphism of thoria with tin oxide and rutile, gave thoria the formula $ThO_2$. This led to thorium being recognised as a quadrivalent element with atomic weight 232, and in consequence it was placed in group IV, series 12, of the periodic classification. Confirmation of this view was furnished by the analogy between the double fluorides of potassium and zirconium on the one hand with those of potassium and thorium on the other. This analogy is not as complete as might be desired, for the two sets of salts differ in respect of the water content.

| | |
|---|---|
| $2KF,ZrF_4$ | $2KF,ThF_4,4H_2O$ |
| $KF,ZrF_4,H_2O$ | $KF,ThF_4,0{\cdot}5H_2O$. |

Metallic thorium has a specific heat of 0·0278 which, in accordance with Dulong and Petit's law, leads to an atomic weight of about 230, a value already obtained experimentally on the basis of the quadrivalency of the element. The vapour

density of thorium chloride, according to Troost,[945] indicates that the chloride has a molecular weight corresponding to $ThCl_2$, but further determinations by Krüss and Nilson [786, 787] show that at high temperatures thorium chloride dissociates, and that at temperatures 1050°-1100° the vapour density corresponds to that required by the formula $ThCl_4$.

VAPOUR DENSITY OF THORIUM CHLORIDE.

| Theory for $ThCl_4$ = 12·93. | | | | Theory for $ThCl_3$ = 9·6. | | |
|---|---|---|---|---|---|---|
| Temperature . . | 1057° | 1102° | 1140° | 1270° | 1400° |
| D . . . . | 12·43 | 12·41 | 11·56 | 11·23 | 9·83 |

Against this interpretation of the experimental results, Biltz [946] suggests that at 1400° the molecular weight corresponds to $ThCl_3$ whilst at lower temperatures $Th_2Cl_6$ represents the molecule. This view is, however, most seriously discounted by the value of the molecular weight obtained for the acetylacetonate by the boiling-point method. The value thus obtained agrees absolutely with that demanded by the formula

$$Th(CH_3COCHCOCH_3)_4.$$

Hence it may be taken that the quadrivalency and the position of thorium in group IV, series 12, are firmly established.

The properties of thorium and its compounds fully confirm the correctness of this position. It is found in group IV that the acidic character of the dioxide decreases with increase of atomic weight, thus titanium dioxide and zirconium dioxide are both amphoteric oxides, but the acidic tendencies of titanium dioxide are greater than those of zirconia. Thorium oxide would, therefore, not be expected to have any acidic properties at all, and this is in keeping with fact. The hydroxide of the elements of group IV can all be readily converted into gels and sols, a property which thorium shares with the other elements. The salts of thorium are hydrolysed less than those of any other element of the group. This is quite clear from the fact that the chloride, nitrate, and sulphate of thorium may be crystallised from water solution, whereas the compounds of the other elements cannot owing to hydrolysis. This fact can be illustrated best by considering the chlorides; in the presence of water no definite chloride of titanium can be prepared, whilst the compound $ZrOCl_2,8H_2O$ is obtained in the case of zirconium only by the use of the most concentrated acid, and thorium

chloride can be crystallised from aqueous solution without any particular difficulty.

The properties of the remaining elements of the rare earths may now be considered together, but at the outset cerium shows itself to be different from the others inasmuch as it forms a stable dioxide and an unstable sesquioxide, whilst the other elements possess stable sesquioxides and no dioxides or at best only very unstable ill-defined dioxides. It will, therefore, probably be well to consider the position of cerium first.

Cerium compounds occur in two stages of oxidation, cerous and ceric. The salts of the lower stage of oxidation in aqueous solution give rise to tervalent ions $Ce^{\cdots}$ and the molecular weights of these salts in non-ionising solvents agree with formulæ of the type $CeX_3$. Hence in this stage the metal has a hydrogen equivalent of 46·75 which leads to an atomic weight of about 140. In the higher state of oxidation the hydrogen equivalent is 35·1, which gives an atomic heat of 6·3 if the metal is quadrivalent and has an atomic weight of 140. The atomic weight of cerium is insufficient to place cerium in the periodic classification, since just in the position where it would fall, there are many vacant spaces and a great deal of uncertainty exists as to which of the spaces are really free to take it. The properties of the element and its compounds, however, serve sufficiently well to place it in group IV, series 8. The great stability of the dioxide and its other properties, of necessity, place cerium in group IV. The elements in the *A* sub-group would then, in order of atomic weight, read Ti,Zr,Ce,—,Th. Consideration of the dioxides of this group shows that those of titanium and zirconium are acid forming, whilst that of thorium is entirely basic. From the position of cerium in the group it might reasonably be expected to show some acidic properties and some basic properties. Cerium dioxide has weak basic properties, but it has not been definitely shown to have acidic properties. That cerium dioxide has weak acidic properties may be deduced from the following considerations.[420] Perfectly pure cerium dioxide is attacked by acids only with the greatest difficulty, but oxide mixtures containing not more than 40-50 per cent. of cerium dioxide are readily attacked. Minerals containing cerium dioxide are readily attacked by hydrochloric acid and the cerium dissolved. It may be taken for proved that

the minerals are not simply mixtures of the rare earth oxides but rather salts, of the nature of manganites and chromites, in which cerium dioxide plays the part of the acid. This being so, cerium must be regarded as an amphoteric oxide with very weak acidic properties.

Ceric nitrate, although unknown in the free condition, forms a series of derivatives which are analogous with similar derivatives of thorium. Thus the following series are known :—

$Ce(NO_3)_4,2M'NO_3$. $Th(NO_3)_4,2M'NO_3$ where $M' = NH_4$, K, Na, Rb. . .

$Ce(NO_3)_4,M''(NO_3)_2,8H_2O$. $Th(NO_3)_4,M''(NO_3)_2,8H_2O$ where $M'' = Mg$, Zn, Ni, Co, Mn.

The chlorides of cerium and thorium of the type $MCl_4$ form a series of compounds with organic bases, of which the following may be quoted :—

$CeCl_4,2(C_5H_5N,HCl)$, $ThCl_4,2(C_5H_5N,HCl)$,
$CeCl_4,2(C_9H_7N,HCl)$, $ThCl_4,2(C_9H_7N,HCl)$.

Further evidence in support of the position of cerium in group IV, A, is found in a comparison of the physical properties of the four elements. All four elements when heated in nitrogen form nitrides and with the exception of titanium when heated in hydrogen form hydrides, titanium merely absorbs the gas and forms no compounds, facts which are in keeping with its small atomic weight and its proximity to carbon and silicon. The nitrides are all decomposed by steam with the formation of ammonia.

The following table of physical constants also supports the position :—

| | Ti. | Zr. | Ce. | — | Th. |
|---|---|---|---|---|---|
| Atomic weight . | 48·1 | 90·6 | 140·25 | — | 232·4 |
| Density . . . | 4·87 | 6·4 | 7·04 | — | 12·6 |
| Melting-point . . | not melted | 1530° | 623° | — | 1450° |
| Specific heat . . | 0·1288 | 0·0666 | 0·0448 | — | 0·0278 |

As far as these physical properties go they are in accord with the position allotted to cerium. The melting-point alone does not run regularly with the atomic weight, and here the figures indicate that there is a steady fall from titanium to cerium

followed by a rise. This is exactly what is found in other cases, and in particular the same thing occurs in group IV, B,

Ge 900°, Sn 232°, Pb 326°.

Further all these elements are paramagnetic, and quite recently cerium has been brought further into line with the other elements by the preparation of the oxychloride, $CeOCl_2$,[947] a type of compound which has long been known for the other elements.

There still remain fourteen elements which may be regarded as sufficiently characterised for consideration in the present connection. These include lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium, and celtium, a group of elements which are very similar in their properties and as far as is known analogous in all respects. Since many of them exist in such small amounts and are so difficult to obtain pure, the valency of the commoner members alone has been determined experimentally, whilst that of the less common elements is, by analogy, accepted as the same as that of the better-known elements.

At the time the periodic classification was introduced by Mendeléeff, only six of these elements (La, Ce, Di, Yt, Er, Tb) were identified, and these, from their strong basicity and apparent similarity to the metals of the alkaline earths, were assumed to be bivalent and to possess oxides of the type MO. This view would seem to be confirmed by the isomorphism which exists between calcium tungstate and didymium tungstate, and between the silicotungstates of cerium, lanthanum, thorium, didymium, and calcium. In this connection, however, it must be remembered that with molecules of such a large size the heavy acid radical probably exerts the predominating influence on the crystallographic configuration.

Mendeléeff at first tentatively placed lanthanum, didymium, and erbium in group VIII, but later he rejected the idea that these elements were bivalent, and placed them in the periodic classification as indicated below :—

| Series. | Group. | | | | | |
|---|---|---|---|---|---|---|
| | II. | | III. | | IV. | |
| 4 | Ca | | Ekaboron | | Ti | |
| 5 | | Zn | | — | | — |
| 6 | Sr | | Yt | | Zr | |
| 7 | | Cd | | — | | Sn |
| 8 | Ba | | Di? | | Ce | |
| 9 | | — | | — | | — |
| 10 | — | | Er | | La? | |
| 11 | | Hg | | — | | Pb |

This choice was no doubt very much influenced by the lack of sufficient space in group II for the accommodation of these elements. Of the five elements thus placed, two (Yt and Ce) occupy the same positions as are now allotted to them. Mendeléeff was doubtful about the positions of lanthanum and didymium, and further he was of the opinion that the latter substance was a mixture.

All the work since the time of Mendeléeff has substantiated his view that the elements of the rare earths are tervalent. This evidence may now be considered under various headings.

## 1. Specific Heat of the Metals.

Although comparatively few of the metals of the rare earths have been prepared, and these not always very pure, the evidence obtained from the specific heats indicates that these elements are tervalent. Take the case of lanthanum as an example; this element has a specific heat of 0·04637, and since the equivalent of lanthanum has been found to be 46·3 it follows from the Dulong and Petit law that the valency must be 3.

$$46{\cdot}3 \times x \times 0{\cdot}04637 = 6{\cdot}4$$
$$x = 2{\cdot}99.$$

## 2. Molecular Weight Determinations.

Molecular weights of compounds of the rare earths have been carried out by the boiling-point method, and in all cases the results have been such as to confirm amply the tervalency of these elements. The molecular weights of the chlorides of lanthanum, praseodymium, and neodymium have been determined in absolute alcohol solution and in all cases values corresponding with the formula $MCl_3$ have been obtained. The molecular weights of

the acetylacetonates of praseodymium and samarium have been determined in carbon disulphide solution and that of neodymium in ethyl sulphide solution. In all cases, formulæ corresponding to the bimolecular formula $M_2(CH_3COCHCOCH_3)_6$ have been obtained. This last result is not quite in keeping with the tervalency of the elements, but when the nature of the solvent is considered it is clear that in reality it confirms the tervalency of the elements of the rare earths, particularly when it is remembered that the scandium compound gives the single molecular weight in chloroform and benzene solutions.

### 3. Isomorphism of Salts.

The octohydrates of the sulphates, $M_2(SO_4)_3,8H_2O$, of yttrium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, erbium, and ytterbium all crystallise in the monoclinic system and are isomorphous. Scandium and lanthanum do not form octohydrates and the cerous compound crystallises either triclinic or rhombic. The ethyl sulphates [665] of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, thulium, erbium, and ytterbium of the general formula $M_2(EtSO_4)_6,18H_2O$ form a perfectly isomorphous series of the hexagonal bipyramidal system. The acetylacetonates of scandium, indium, and iron are also isomorphous. The nitrates of the rare earths form several series of isomorphous double salts of the types,

| | |
|---|---|
| $R(NO_3)_3,2M'NO_3,H_2O$ | : R = Ce, La, Pr, Nd, M′ = Na |
| $R(NO_3)_3,2M'NO_3,2H_2O$ | : R = La, M′ = K . Cs |
| $R(NO_3)_3,2M'NO_3,4H_2O$ | : R = Ce, La, Pr, Nd, M′ = Rb, Tl, $NH_4$ |
| $2R(NO_3)_3,3M''(NO_3)_2,24H_2O$ | : R = La, Pr, Nd, Sa, Gd, M″ = Mg, Ni, Co, Zn, Mn. |

It is also interesting and important in connection with the tervalency of the rare earth metals that the last series of double nitrates, mentioned above, are isomorphous with a series of bismuth double nitrates, $2Bi(NO_3)_3,3M''(NO_3)_2,24H_2O$ in which M″ = Mg, Co, Ni, Mn, and Zn.

Another interesting case of isomorphism is found in the replacement of tervalent cerium in the acid sulphate,

$$HCe^{III}(SO_4)_2,Ce^{IV}(SO_4)_2,24H_2O,$$

by the elements lanthanum, praseodymium, and neodymium.

In addition to the cases quoted, there is a general isomorphism, which need not be emphasised here, between the various rare earth elements in their chlorides, nitrates, sulphates, selenates, and double platinum compounds.

## 4. Electro-conductivity Measurements.

The measurement of the equivalent conductivity of a series of sulphates and chlorides of the rare earths, at 25°, give values which are in accord with the presence of tervalent cations.

| (i) Sulphates. | | | Δ. |
|---|---|---|---|
| $Ce^{III}$ | $\lambda_{33}$ 45·66 | $\lambda_{1056}$ 100·90 | 55·24 [591] |
| La | $\lambda_{32}$ 40·72 | $\lambda_{1024}$ 87·84 | 47·12 [911] |
| Nd | $\lambda_{33\cdot4}$ 40·61 | $\lambda_{1071}$ 95·95 | 55·34 |
| Sa | $\lambda_{31\cdot3}$ 31·17 | $\lambda_{1003}$ 89·24 | 58·07 |
| Cr | $\lambda_{32}$ 63·0 | $\lambda_{1024}$ 119·8 | 56·6 |
| Al | $\lambda_{32}$ 47·8 | $\lambda_{1024}$ 87·8 | 52·5 |

The value of $\Delta = \lambda_{1024} - \lambda_{32}$ for a tervalent cation and a bivalent anion should, according to the Ostwald-Walden rule, have the value 60, but this value is rarely reached as will be seen in the case of aluminium and chromium; the most usual value is about 56.

| (ii) Chlorides. | $\lambda_{32}$. | $\lambda_{1024}$. | Δ. |
|---|---|---|---|
| La | 105·8 | 131·5 | 25·7 |
| $Ce^{III}$ | 107·8 | 135·2 | 27·6 |
| Pr | 105·5 | 135·9 | 30·4 |
| Nd | 103·8 | 134·3 | 30·5 |
| Yt | 98·8 | 123·4 | 24·6 |
| Yb | 107·4 | 140·4 | 33·0 |
| Al | 99·9 | 138·0 | 38·1 |

In this case it is clear that $(\lambda_{1024} - \lambda_{32})/10 \doteq 3$, which, according to the Ostwald rule, indicates a tervalent cation if the anion is univalent.

From the foregoing it is fully established that the fourteen elements under consideration are tervalent. These elements have atomic weights which lie between La = 139 and Lu = 175, hence they must be fitted into the periodic system in the space available between barium and tantalum. Of the positions available for these elements it will be seen, since they are tervalent, that only three are suitable, namely, group III in series

8, 9, and 10. Hence fourteen elements are known with only three available positions in the periodic system, and it is in this very point that the difficulty of placing the rare earth metals in the periodic system lies.

An examination of the properties of these elements and their compounds shows that no very marked differences exist between them. If the elements are taken in ascending order of atomic weight it is found that the properties of the element of lowest atomic weight reappear very slightly modified in the second element, and so on until in the element of highest atomic weight they are still present and not very much changed. This will be obvious from a consideration of a few of the properties. Consider first the basicity of the hydroxides.

The hydroxides are moderately strong bases, the strength of which lies between that of the hydroxides of the alkaline earth metals and that of the hydroxides of group III,

$$[Al(OH)_3,\ In(OH)_3,\ Tl(OH)_3].$$

The rare earth hydroxides all liberate ammonia from ammonium salts and their salts with strong acids are only slightly hydrolysed. Commencing with the strongest base the elements follow the order: La, $Ce^{III}$ Pr, Nd, Yt, Eu, Gd, Sa, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, $Ce^{IV}$. This series is the result of experiments on the order in which the hydroxides are precipitated by alkalis, and shows a decreasing basicity with increasing atomic weight, except in the case of Yt, Sc, and $Ce^{IV}$. These three elements, however, do not concern us in the present discussion for they have already been placed in the periodic system.

The atomic volumes of the elements are very close to one another as the following series shows:—

La (22·6), Ce (20·3), Pr (21·8), Nd (20·7), Sa (19·5), Yt(23·3), Yb(19·8).[948]

A similar condition is found when the molecular volumes of the chlorides are considered.

La 63·8, $Ce^{III}$ 62·9, Pr 60·8, Nd 60·6, Sa 57·5, Gd 58·3, Tb 61·1, Dy 73·3[948].

With regard to the solubility of the salts it is found that the differences between the corresponding salts of the various elements are very slight. The following examples sufficiently prove this

point, although the difficulty of separating the various elements is in itself sufficient proof.

SOLUBILITY OF RARE EARTH SALTS.

| | La. | Ce. | Pr. | Nd. | Sa. | Gd. | Yt. | Yb. | |
|---|---|---|---|---|---|---|---|---|---|
| Oxalates in water . | 0·62 | 0·41 | 0·74 | 0·49 | 0·54 | — | 1·0 | 3·34 | mgm. per litre |
| Oxalates in $\frac{N}{10}H_2SO_4$ | 0·034 | 0·0215 | — | 0·055 | 0·094 | — | — | — | ,, ,, ,, |
| Double magnesium nitrates in $HNO_3$ (1·325 gr. per litre) | 0·0382 | 0·0418 | 0·0503 | 0·0635 | 0·0583 | 0·2252 | — | — | moles. per litre |

The molecular volumes and densities of the double magnesium nitrates show much the same picture as the solubilities.

DOUBLE MAGNESIUM NITRATES.

| | Ce. | La. | Pr. | Nd. | Sa. | Gd 451. |
|---|---|---|---|---|---|---|
| $d_4^{0°}$ . . . | 2·002 | 1·988 | 2·019 | 2·020 | 2·088 | 2·163 |
| Molecular volume . | 764·2 | 768·3 | 758 | 761·2 | 742·4 | 723·0 |

Considering the properties of these elements generally it is found that the metals also have very similar properties; they burn brightly when heated in oxygen at about 250°, they dissolve readily in dilute acids and decompose water, and they form hydrides and nitrides when heated in hydrogen and nitrogen respectively. In general it will be found that the similarity persists with all the compounds. One point of marked difference must, however, be noted. Two of these elements samarium and europium can function as bivalent elements, inasmuch as chlorides $SaCl_2$ and $EuCl_2$ have been prepared. The existence of these chlorides does not, however, in any way prevent these elements being placed in group III, for the chloride $InCl_2$ is already known in this group.

Having seen that the rare earths constitute a series of tervalent elements of very similar properties, the actual fitting into the periodic system may now be considered.

In 1881 Brauner suggested that lanthanum belongs to group III, series 8, and cerium to group IV, series 8, whilst the other

elements were placed in various positions in series 8, 9, and 10 as shown in the diagram :—

| Series. | Groups. | | | | | | |
|---|---|---|---|---|---|---|---|
| | II. | III. | IV. | V. | VI. | VII. | VIII. |
| 6 | Sr | Yt | Zr | Nb | Mo | — | Ru Rh Pd |
| 7 | Cd | In | Sn | Sb | Te | I | — |
| 8 | Ba | La | Ce | Pr | Nd | Sa | Eu |
| 9 | — | Gd | Tb | Dy | Er | — | — |
| 10 | — | — | — | Ta | W | — | Os Ir Pt |

This view, however, he apparently abandoned, for in 1902 [617] he considered that the rare earths from cerium to ytterbium must be regarded as forming a zone of elements in group IV of the periodic system and at the same time he indicates the existence of eight undiscovered rare earth elements, as shown in the table below. This, as will be seen, entirely removes from the periodic table the empty ninth series. In some respects this idea conforms with the character of the elements.

EXTRACT FROM BRAUNER'S TABLE (1902).

| Series. | Groups. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0. | I. | II. | III. | IV. | V. | VI. | VII. | VIII. |
| 6 | Kr | Rb | Sr | Yt | Zr | Nb | Mo | — | Ru Rh Pd |
| 7 | — | Ag | Cd | In | Sn | Sb | Te | I | — |
| 8 | X | Cs | Ba | La | Ce Pr Nd —<br>— Sa Eu —<br>— Gd — —<br>Tb Ho Er —<br>Tm Yb — — | Ta | W | — | Os Ir Pt |
| 9 | — | Au | Hg | Tl | Pb | Bi | — | — | — |
| 10 | — | — | Ra | — | Th | — | U | — | — |

Soddy is of much the same opinion as Brauner, but he objects to this arrangement because it destroys the continuity of the

system, and he describes a helical arrangement in which the first two short series are represented on single helices which by their shape indicate the relatively rapid change in the properties of the elements. These are followed by two double helices on which the first and second long series are placed. A small helix of entirely different shape follows; this indicates a slow rate of change, and on this the elements of the rare earths are situated. The remaining elements follow on a third double helix of the same type as the others. (A diagram representing this system is given in "Chemistry of the Radio-elements," F. Soddy, in this series of monographs.)

The view put forward by Benedicks [949] is to a certain extent like the foregoing. On account of the very slow change in atomic volume he places the elements from lanthanum to ytterbium in the space which would normally be occupied by groups III and IV, and at the same time he removes series 9 in the same way as Brauner. From considerations of isomorphism, Retgers [951] places the elements La, Ce, Di, Sa, Er, and Yb in group III, series 8, whilst Biltz [950] does practically the same thing except that he places no element separately but regards them as one element for this purpose and writes ΣCe in group III, series 8. Perhaps one of the most hopeful suggestions in this matter has come from R. J. Meyer.[952] He, on the basis of the properties of the rare earths in general, has decided that cerium must occupy the position which has been allotted to it in group IV and that the other elements all belong to group III and occupy the place which has generally been given to lanthanum despite the fact that cerium thereby falls out of the atomic weight order. He then subdivides the elements into three sub-groups of five elements each which implies that two elements are still unknown. These he places between thulium and ytterbium. One of these missing elements is doubtless the newly discovered celtium. The following diagram shows group III, series 8, of the periodic system according to Meyer.

GROUP III, SERIES 8.

| | | | | |
|---|---|---|---|---|
| La | Pr | Nd | Sa | Eu |
| Gd | Tb | Dy | Ho | Er |
| Tm | — | — | Yb | Lu |

Hence it may be taken that the rare earths with the exception of scandium, yttrium, and cerium form a minor periodic system among themselves which has its position in group III.

In 1908 Brauner [953] abandoned the views put forward in 1902 and reverted to the views of 1881 which are modified slightly and amplified in the following table:—

| Series. | Groups. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | O. | I. | II. | III. | IV. | V. | VI. | VII. | VIII. |
| 6 | Kr | Rb | Sr | Yt | Zr | Nb | Mo | — | Ru Rh Pd |
| 7 | — | Ag | Cd | In | Sn | Sb | Te | I | —— |
| 8 | X | Cs | Ba | La | Ce | Pr | Nd | Sa | Eu — — |
| 9 | — | — | — | Gd | Tb | Dy | Ho | Er | Tm Yb — |
| 10 | — | — | — | Lu | — | Ta | W | — | Os Ir Pt |

Brauner justifies this arrangement by the fact that some of the elements appear to be able to form higher oxides in the presence of oxygen carriers. Further he points out that the rare earth elements can be divided into two series based on the strength of the hydroxides and also on their power of forming complexes. These facts serve to place one group in series 8 and the other in series 9.

These two series are:—

La, Ce, Pr, Nd, Sa. 8th series.
Gd, Tb, Er, Yb. 9th series.

The elements placed in the 8th series decrease in basicity with increasing atomic weight and also decrease in their tendency to form complexes. Those placed in series 9 increase in their tendency to complex formation but decrease in basicity with increase of atomic weight. The elements scandium, yttrium, lanthanum, gadolinium, and lutecium are regarded as tervalent and placed in group III. The rest are placed according to their valency which Brauner deduces from the hydrides, and as an example quotes the 8th series thus:—

| I. | II. | III. | IV. | V. | VI. | VII. | VIII. |
|---|---|---|---|---|---|---|---|
| CsH | $BaH_2$ | $LaH_3$ | $CeH_4$ | $PrH_3$ | $NdH_2$ | (SaH) | $Eu(H_0)$. |

From a discussion of the atomic volumes of the elements, Baur [954] shows that the Lothar Meyer atomic volume curve, which

as is well known breaks off at barium after a series of crests and troughs and then after the break ends with one more crest, does not form a crest in the open space as has been generally anticipated. The rare earth metals lie in this region and these instead of forming a crest form a zig-zag line which commences at lanthanum just below barium and after lutecium drops suddenly to tantalum. From this, Baur concludes that lanthanum belongs to group III, series 8, cerium to group IV, series 8, and the remainder belong to no group. He therefore places them between groups III and IV in series 8. Stefan Meyer [955] puts forward a similar arrangement except that he includes lanthanum and cerium with the other rare earths in a group which lies between barium and tantalum.

Vogel [956] maintains that the rare earth metals cannot be correctly placed in any of the groups of the periodic system and he is of the opinion that they occupy a position intermediate between the 3rd and 4th groups. To represent this without destroying the symmetry of the periodic system, he suggests that the elements be arranged on an ascending spiral in the order of their atomic numbers. Each turn of the spiral accommodates one short period of eight elements and elements of the same group lie vertically above one another. After passing barium the spiral changes its course and develops a subsidiary loop, which after making rather more than a complete turn rejoins the original path at tantalum and then proceeds normally. The sixteen rare earth metals are crowded on to this subsidiary loop in such a way that the elements lanthanum and cerium lie very close to the vertical lines drawn through the elements of group III and IV respectively. Vogel bases his views on the assertion made by Tammann [957] that metals in the same group of the periodic system should exhibit little or no chemical affinity for one another, or conversely if two metals form a stable compound they cannot belong to the same group of the periodic system. Vogel, himself, has prepared the compounds $CeAl_2$, $CeAl_4$, $Ce_2Sn$, $Ce_4Bi_3$, and $LaAl_4$, and the compounds $Ce_4Mg$, $CeMg$, $CeMg_3$, and $CeMg_9$ have also been isolated and, consequently, on the basis of Tammann's statement, cerium and lanthanum and by analogy the remainder of the rare earth metals find groups II, III, IV, and V closed to them. Further, in support or perhaps in *extenuation* of this view, Vogel states that the crystallographic and chemical

evidence, in favour of placing lanthanum and cerium in groups III and IV respectively, is very slight, and that in any case the valency of an element and the isomorphism of its salts are very uncertain guides to its relationships with other elements. These propositions cannot be maintained even by the most prejudiced supporter of Vogel's views; few elements possess such sound crystallographic and chemical evidence for placing them in a group of the periodic system as do the metals of the rare earths. The difficulty here is not the chemical characteristics but the large number of elements. Further, to state that valency is an uncertain quantity on which to base relationships of the elements is to destroy at a blow one of the fundamentals of the periodic system. This criticism in no way denies or attempts to deny the difficulty of placing these elements, which may, as Vogel and others have affirmed, have to be grouped outside the ordinary groups of the periodic system. But it can be taken as definitely proved that the elements scandium, yttrium, lanthanum, and cerium now occupy their proper positions; and making use of the general principles of the periodic system it seems extremely likely that the remaining elements will find a place in either groups III or IV (probably group III), much in the same way as the elements of group VIII.

An analogy between the rare earth elements and those of Mendeléeff's eighth group has often been suggested. Many seem inclined to think that this analogy indicates the method of arranging the elements. Steele,[958] from a consideration of the atomic volumes and magnetic properties of the rare earths points out an analogy between these elements and those of group VIII. The main points on which this analogy is founded are: (i) The difficulty of separating the elements of each group from one another, the members of the three triads Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt—are more difficult to separate from one another than is the case with any of the other elements except the rare earths; (ii) The atomic volumes of the members of group VIII are the smallest of all the common elements; and (iii) these elements are the most strongly paramagnetic of all the elements. In all these points strict analogy is found with the rare earth metals. They are undoubtedly difficult to separate from one another, they have small atomic volumes, and they are strongly paramagnetic. Steele, therefore, proposes to revert to the arrange-

ment of Julius Thomsen [959] in order to include the rare earths in the periodic system. He proposes (ignoring the inert gases) to write the elements in two series of seven elements each, these to be followed by two series of seventeen elements each. In each of the long series the three central elements constitute an interperiodic group. Just as the periodicity of the two short series undergoes a change on passing to the third series so the fourth series undergoes a change in periodicity on passing to the next series; the change in this case being brought about by the introduction of an interperiodic group—the group of the rare earth metals. The last series differs again from the preceding series in its periodicity, and at present consists only of the two elements thorium and uranium. Steele, however, does not indicate into which group or series he proposes to place the rare earth elements, and consequently, for the present purpose, his views do not carry the matter much forward.

Werner has amplified the idea put forward by Steele, and expresses his views in a table which also serves the purpose of exposing the weakness of the idea. The elements are arranged in order of the atomic weight in series according to Steele's idea, but the arrangement is arbitrary so that the groups of the original Mendeléeff system may be maintained. The interperiodic elements in this scheme do fall in the centre of their series, but the diagram does not represent the regular change in properties so well as the usual method of representation. That is, whilst the method of Steele and Werner modifies the periodic system to accommodate the rare earth metals, at the same time it destroys the simplicity and regularity.

WERNER'S PERIODIC TABLE.

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| — | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | |
|

weight except for praseodymium and neodymium where it is found that the two elements appear to be reversed.

| | La. | Pr. | Nd. | Sa. |
|---|---|---|---|---|
| Atomic weight . . . . | 139 | 140·9 | 144·3 | 150·4 |
| Melting-point . . . . | 810° | 940° | 840° | 1300°-1400° |
| Equivalent heat of formation of oxide . . . . . | 74·1 K | 68·9 K | 72·5 K | — |
| Heat of combustion . . . | 1602·1 K | 1466·8 K | 1506 K | — |

This is particularly interesting when it is remembered that cobalt and nickel present a similar anomaly, and that the crystallised salts of nickel and praseodymium are green whilst those of cobalt and neodymium are red, and further, the colours of both pairs Ni, Co and Nd, Pr are complementary. Werner[960] shows that the four abnormalities which occur in the periodic system are themselves periodic. Four such cases, where the elements do not follow the order of their atomic weight, are known (A, K); (Te, I); (Co, Ni); and (Pr, Nd). There are 6-7 elements between the first and second pair, and also the same number between the third and fourth pair.

# CHAPTER X.

## USES OF THE RARE EARTHS.

IN the present chapter it is proposed to give a brief survey of the various uses which have been made of the rare earths. A large number of proposals have been put forward but many of these have received no attention; some of the proposals will be briefly noticed here. Neither the uses nor the proposals will be dealt with in detail, the present object is merely to give a general survey of the subject.

### Thorium.

The most important use of the rare earth elements is found in the manufacture of mantles for incandescent lighting. The incandescent mantle as purchased consists of a skeleton composed of a mixture of oxides of thorium (99 per cent.) and cerium (1 per cent.) held together by asbestos or metal struts and stiffened by impregnation with collodion. Earlier mantles contained lanthana, zirconia, magnesia, and yttria, but these were all abandoned when Auer von Welsbach showed that the most brilliant illumination was obtained from a mixture of 99 per cent. thoria and 1 per cent. ceria.

Cotton fibre was originally used in the manufacture of mantles but this was supplanted by ramie fibre and artificial silk (vicose or nitrocellulose silk). The fibre is woven into tubes of the required size and then washed to remove fatty material and to reduce the ash. The process differs in the various cases; ramie fibre web is soaked for about 12 hours in 2 per cent. nitric acid, centrifuged to remove excess of acid and then washed with distilled water. Cotton web is first washed in 3-5 per cent. sodium hydroxide and then in 1-3 per cent. hydrochloric acid at about 50°. Silk web requires no preliminary water washing. The web is then dried in a current of hot air. Cotton and ramie webs are cut into the requisite size at this stage. The web is then soaked for 2 minutes, in the case of cotton and ramie, and 5 hours in the case of silk in a solution con-

sisting of 1000 gm. thorium nitrate, 10 gm. cerium nitrate, 5 gm. glucinum nitrate, and 1·5 gm. magnesium nitrate in 2 kilos of water. Cotton and ramie webs are now passed between rollers to remove the excess of solution, the silk web is centrifuged. The web is then dried at 30°, cotton and ramie stretched on glass cylinders, silk on wooden rollers. After drying, the mantles are formed, fitted with asbestos loops and other supports, and strengthened by coating the top and bottom with thorium solution containing salts of calcium, aluminium, and magnesium. At this stage the mantle may be branded by stamping with a paste of 1 kilogm. didymium nitrate, 200 gm. glycerine, 25 gm. methylene blue, 300 gm. 96 per cent. alcohol, and 300 gm. distilled water. The mantle is now shaped on a wooden form and burnt off with a Bunsen flame starting at the top.

The next process is that of hardening, which is carried out by raising the mantle to a high temperature for a few minutes. The mantle is now finished, but so fragile that any movement is likely to break it. Consequently, before it can be put on the market it must be strengthened. This is done by immersing it in a solution of 100 gm. 4 per cent. collodion, 40 gm. ether, 6·5 gm. camphor, and 3·5 gm. castor oil, and then drying at 50°-60°.

A few modifications in the above process are made when nitrocellulose is used. In this case the fibre must be denitrated before burning off; with vicose this is unnecessary.

Silk web after being washed in ether containing a little carbon disulphide is impregnated in the usual way, and after drying, the mantle is denitrated by immersion in 95 per cent. alcohol containing a little hydrofluoric acid. The other points are in general much like those in the case of ramie and cotton mantles.

Thoria is an extremely valuable catalyst in certain organic reactions, some of which may be noted here. Sabatier, Mailhe, and Senderens [962] have shown that by using thoria as a catalyst, symmetrical and unsymmetrical ketones may be prepared directly from monocarboxylic acids. Thus butyric acid gives a fair yield of butyrone.[1029] Alcohols are converted into ethers or olefines according to the temperature employed.

$$2C\,H_{2n+1}OH + ThO_2 = ThO(OC_nH_{2n+1})_2 + H_2O$$
$$ThO(OC_nH_{2n+1})_2 = ThO_2 + (C_nH_{2n+1})_2O$$
$$ThO(OC_nH_{2n+1})_2 = ThO_2 + H_2O + 2C_nH_{2n}.$$

Benzyl alcohol in the presence of thoria reacts with formic acid, acetic acid, propionic acid, isobutyric acid, and benzoic acid to give esters. When ammonia and alcohols are passed over thoria at 360°, olefines and primary amines are produced.[833] The vapours of esters when passed over heated thoria are decomposed according to the equation—

$$2C_pH_{2p+1}COOC_nH_{2n+1} = (C_pH_{2p+1})_2O + C_nH_{2n} + C_nH_{2n+1}OH + CO_2.$$

Thorium compounds find use in several devices for intense illumination. Thus small cylinders, after the nature of the "limes" used in limelight lanterns, made of thoria mixed with a little ceria, are used for the headlights of motor cars and also for searchlights.

Thorium tungstate,[963] chromate, and other salts[964, 965] are mixed with powdered magnesium in the production of flashlight powders. These powders when fired do not emit so much smoke as the simple magnesium powders, and on that account are to be preferred. The filament of the later forms of the Nernst lamp is composed of mixtures of thoria, yttria, and zirconia, to which small quantities of ceria are sometimes added. Alloys of thorium and tungsten [966] are used in the production of filaments for electric lamps. The filaments are obtained by squirting a colloidal mixture of the two metals. Finally, thorium compounds have a considerable use in radiology.

## Cerium Earths.

Cerium earths have found their most important use in the manufacture of pyrophoric alloys. These alloys are utilised in the manufacture of automatic gas lighters, petrol lighters, and for indicating the path of bullets and shells in the so-called "tracer" shells and bullets. The alloy of the mixed cerium earth metals is an extremely powerful reducing agent and is used on the small scale to produce the metals niobium, tantalum, zirconium, iron, cobalt, nickel, chromium, manganese, vanadium, tungsten, and uranium, and the non-metals boron and silicon from their oxides.

Alloys prepared from mixtures of the cerium earths were shown by Auer von Welsbach [967] to give off showers of sparks when filed. This discovery led to the establishment of the automatic lighter industry. It was soon found that if the alloys

were to be kept active the oxidised surface must be repeatedly renewed. This was troublesome and many patents were granted for devices designed to overcome the difficulty. It was found that an alloy of the cerium metals with iron, nickel, cobalt, or manganese emitted sparks continuously when filed, and required no treatment on the surface to keep it active. The most reliable alloy is one containing 35 per cent. of iron and 65 per cent. of the cerium metals. This alloy is known as Auer metal, and constitutes the material from which the automatic lighters at present in use are made.

The alloy of cerium metals is produced from the rare earth mixture left after the extraction of thorium from monazite which consists, on the average, of 45 per cent. ceria, 25 per cent. lanthana, 15 per cent. neodymia, and small quantities of yttria and samaria. The mixture is converted into anhydrous chlorides by solution in hydrochloric acid, evaporation to dryness with an excess of ammonium chloride and subsequent heating until the whole of the ammonium chloride is volatilised. The mixed chlorides are melted in a graphite crucible and electrolysed by a heavy current using a large iron cathode.

To obtain the required alloy the cerium alloy is then melted with the required quantity of iron or other metal. This is generally carried out in a vacuum on account of the very reactive nature of the rare earth metals.

A pyrophoric alloy known as Kunheim[968] is produced by mixing aluminium and magnesium with the cerium earth alloy and heating the mixture at 500° in hydrogen to convert it into hydrides. This alloy is stated to be quite stable in air, and has the composition: cerium 36 per cent., lanthanum, neodymium, etc., 49 per cent., magnesium 10 per cent., aluminium 1 per cent., iron 0·5 per cent., hydrogen 1·3 per cent., and silicon 0·5 per cent.

Other pyrophoric alloys containing in addition to the cerium metals, silicon, titanium, boron, cadmium, zinc, tin, lead, manganese, or antimony have been described, and are covered by patents.

The addition of 0·2 per cent. of the cerium metals to aluminium [969] has the effect of improving the physical properties of the metal. The addition is best effected by adding a small quantity of rare earth fluorides to the cryolite melt from which the aluminium is obtained.

Cerium fluoride and cerium titanofluoride with other salts have been used as the carbon core in the manufacture of flaming arcs. Tungstate and molybdate[970] of lanthanum, cerium, and didymium in arc carbons produce a much more brilliant light than the carbons alone.

The cerium earths have found a number of uses in textile industries, in glass and porcelain manufacture, in photographic processes, and in medicine; also as catalysts and oxidising agents. These may now be considered under separate headings.

### (i) Textile Industries.

Variegated colours are produced[971] by treating yarn with a solution of cerous chloride (specific gravity 1·16-1·26), drying, passing through a strongly alkaline solution of hypochlorite and again drying. This treated yarn is then woven with untreated yarn. The fabric is then treated with a direct cotton dye and run through an acid bath when the treated fibre loses its colour whilst the untreated fibre retains it, thus producing a variegated pattern. If "vat" or "thio" colours are used the reverse process takes place; the treated fibre retains the colour whilst the untreated fibre loses its colour. Garelli[927, 928] describes processes whereby cerium earth salts may be used in tanning and also as mordants in the dyeing of leather. These produce much the same results as aluminium salts. Oxides of the cerium earths may be used to replace tin oxide[974] in the weighting of silk, but it is found that by using cerium earths alone the colours are not so bright. This difficulty is surmounted by adding a little stannic chloride to the rare earth chloride solution before use.

Cerium earth carbonates form good bases for dyeing with alizarin colours. The double sodium cerium nitrate is pressed on to the fabric as a paste and after drying treated with a boiling solution of sodium carbonate whereby the cerium is deposited in the fibre as an insoluble double sodium cerium carbonate. Fabrics thus treated are extremely easily dyed by alizarin colours.[975]

### (ii) Glass and Porcelain Industries.

The cerium earths find a certain use in the glass and porcelain industries as colouring materials. When 1 per cent. of ceria is added to potash glass a bright yellow colour is produced,

whilst larger quantities give shades down to brown. Lime soda glass in which a portion of the lime is replaced by cerium oxide not only has the colours stated above but also the properties of a potash glass.

Neodymium compounds added in small quantities to glass produce blue optical glasses.[976] Such glass exhibits, without any special apparatus, the characteristic neodymium absorption spectrum.

If an excess of cerium dioxide is fused with an opaque glass melt a beautiful yellow enamel is produced.[977]

Many derivatives of the cerium earths possess fire stable colours which may be used for colouring porcelain.[610] Among these may be noted, neodymium phosphate and praseodymium phosphate which give an amethyst-red and a bright green colour respectively. Suitable mixtures of these two salts produce many intermediate shades which are very useful in decorating porcelain. Ceric titanate produces a shining yellow colour, ceric molybdate a beautiful bright blue, ceric tungstate a bluish-green, and cerium mangani-titanate an orange-yellow colour; neodymium tungstate produces a bluish-red colour.

### (iii) Photographic Processes.

Proposals, covered by patents, have been made to use cerium compounds in colour photography and in general photographic processes. Whether these have been much used or not is unknown. An acidified solution of ceric sulphate has been suggested for reducing the density of over-exposed negatives.[978] A paper soaked in cerous sulphate or nitrate is sensitive to light and the image produced may be developed as a positive by either phenol or *p*-amino benzoic acid.[979]

### (iv) Medicinal Uses.

Mixed cerium earth oxalates have been used, in doses of 0·05-0·2 gram, to prevent nausea in cases of stomach catarrh, sea-sickness, epilepsy, megrim, and hysteria. In all these cases it has been shown that the mixture of cerium earth oxalates has exactly the same action as the separate oxalates individually.

Didymium salicylate is sold under the name "Dymal" as a non-irritant antiseptic dressing for wounds. Cerium phenolate [980] is recommended as a disinfectant which, while possessing

the same efficiency as phenol, is less toxic. Ceric double sulphates have been sold in Italy under the name "Ceriform" as an antiseptic which is particularly useful in the treatment of wounds.

Proposals have been made to use cerous bromide in place of alkali bromides, whilst the chlorides of the rare earth metals have the same effect as ferric chloride in stopping bleeding.

### (v) Catalytic Action.

Crude cerium earths constitute an efficient catalyst in the contact process for the manufacture of sulphuric acid;[981] the catalytic material is prepared by soaking pumice in a solution of the mixed sulphates and strongly igniting. Cerium sulphate is the active medium in this action, but the presence of the other rare earth sulphates increases its activity.

The copper chloride catalyst,[982] used in the Deacon chlorine process may be replaced by the cerium earth chlorides. With these substances the reaction takes place most efficiently at 350°-480°.

Double alkali sulphates of cerium are the best catalysts for the production of aniline black by the action of potassium chlorate or chromate on aniline.[983]

Cerium hydride and nitride, according to Lipski and Whitehouse,[984] act as catalysts in the combination of nitrogen and hydrogen to form ammonia, but the catalyst very soon loses its activity.

### (vi) Oxidising Actions.

Acid solutions of ceric salts are strong oxidising agents, and those solutions are claimed to be more efficient oxidising agents than chromates. They have been used for the production of aldehydes and quinones from aromatic hydrocarbons. Thus, using crude 70 per cent. cerium dioxide to prepare a solution of the sulphate, benzaldehyde, naphthoquinone, and anthraquinone were obtained in good yields from toluene, naphthalene, and anthracene respectively. By carrying out these reactions in an electrolytic cell the cerous sulphate, produced by the reaction, is immediately reoxidised to ceric sulphate, which makes the reaction continuous.[985] In this way, with a 20 per cent. acid solution of ceric sulphate, toluene is converted into tolyl phenylmethane and anthraquinone, *m*-xylene into tolyl aldehyde, and naphthalene into phthalic acid and naphthoquinone.

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