THE RARE EARTHS

THEIR OCCURRENCE, CHEMISTRY, AND TECHNOLOGY

BY

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PREFACE

During the thirty years which have elapsed since Dr. Auer's application of the rare earths to the production of artificial light, the incandescent mantle industry has developed to an extent which gives it a prominent place among those chemical industries which may be considered essential to modern civilisation. This technical development has in turn assisted and stimulated the scientific examination of the elements of this group, with the result that ordered and accurate knowledge is beginning to replace the confused and uncertain data which had been collected by earlier workers in the field. These advances have served to emphasise the scientific interest and importance of the rare earth group, and the difficulty of bringing it into relation with the other elements. The relatively scant attention devoted to the study of this province of inorganic chemistry by teachers and students in England is probably due no less to the difficulty in classification, and the uncertainty with regard to the homogeneity and individuality of the various members of the family—an uncertainty by no means entirely removed even now—than to the fact that the very extensive literature on the subject is somewhat confused and difficult of access, especially to those unfamiliar with the French and German languages.

The present work is intended to give a general but fairly comprehensive account of the rare earth group. In accordance with general usage, the elements zirconium and thorium have been included, though these are now recognised as falling outside the limits of the rare earth group proper. The inclusion of titanium, which chemically is so far removed from the cerium and yttrium elements, has been considered desirable, not only on account of its general occurrence in the rare earth minerals, and its position in Group IVB with zirconium, cerium, and thorium, but also on account of its increasing chemical and technical interest, and its use in the ordinary quantitative laboratory operations.

Though the nature of the matter embraced has rendered the division into three parts desirable, the whole subject has been treated primarily from the chemical standpoint. In view, however, of the occurrence of considerable quantities of monazite within the British Empire, and of the possibility that in the near future the Brazilian fields will not remain the sole source of thorium nitrate, stress has been laid on the technical aspect, which is more especially developed as regards the production of monazite and the incandescent mantle industry in Chapters VII and XVII–XX.

In the preparation of Part I full use has been made of Dana's indispensable 'System of Mineralogy,' as well as of the encyclopædic 'Handbuch' of Hintze, whilst for Part II the excellent monograph of R. J. Meyer, in Abegg's 'Handbuch,' Vol. III, Div. I, and the work of the same author and Hauser, 'Die Analyse der seltenen Erden und der Erdsäuren,' Vols. XIV–XV of 'Die Chemische Analyse,' have been of service.

I have great pleasure in expressing my gratitude to Mr. A. Hutchinson, of Pembroke College, Cambridge, who has kindly read for me the manuscript of Part I, and suggested improvements; to Dr. H. J. H. Fenton, of Christ's College, who has given me similar assistance in Part II; and to Dr. S. Ruhemann, of Gonville and Caius College, who has read Parts II and III. I am also greatly indebted to Mr. E. J. Holmyard, of Sidney Sussex College, who helped me with the preparation of Part II; and to Mr. H. M. Spiers, of Gonville and Caius College, who read the proofs for me with special thoroughness and care.

I have also to thank Professor Soddy and his publishers, Messrs. Longmans, Green & Co., for kind permission to reproduce from 'The Chemistry of the Radio-Elements' the diagram on p. 138.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES

Abstr. Chem. Soc.	Abstracts in Journal of the Chemical Society.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Astrophys. J.	Astrophysical Journal.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Berz. Jahres.	Berzelius' Jahresbericht über die Fortschritte der Chemie und Mineralogie.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. franc. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. franc. Photog.	Bulletin de la Société française de Photographie.
Bull. U. S. Geol. Survey	Bulletin of the United States Geological Survey.
Cass. Mag.	Cassier's Magazine.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Paläontologie.
Chem. Eng.	Chemical Engineer.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Zeitg.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. Polyt. J.	Dingler's Polytechnisches Journal.
D. R. P.	Deutsche Reichspatentschrift.
E.	English Patent Specification.

Elect. chem. Ind.	Electrochemical Industry (since 1904, Electrochemical and Metallurgical Industry).
F.	Brevet d'Invention de la République Française.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Gasbel.	Journal für Gasbeleuchtung.
J. Gaslighting	Journal of Gaslighting.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. pr. Chem.	Journal für practische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Met. Chem. Eng.	Metallurgical and Chemical Engineering.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monats.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Phil. Mag.	Philosophical Magazine.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Pogg. Ann.	Poggendorff's Annalen der Physik und Chemie.
Proc. Amer. Acad.	Proceedings of the American Academy.
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Prog. Age	Progressive Age (now Gas Age).
Publ. Astrophys. Observ. Potsdam	Publikationen des Astrophysikalischen Observatoriums zu Potsdam.
Schweigg. J.	Schweigger's Journal für Chemie und Physik.
Sitzungsber. kaiserl. Akad. Wiss. Wien	Sitzungsberichte der kaiserlich Akademie der Wissenschaften zu Wien.
Sitzungsber. königl. Akad. Wiss. Berlin	Sitzungsberichte der königlich Preussischen Akademie der Wissenschaften zu Berlin.
Stahl Eisen	Stahl und Eisen.
Trans. Amer. El. chem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Chem. Soc.	Transactions of the Chemical Society

Tsch. Min. Mitt.	Tschermak's Mineralogische Mittheilungen.
U. S. Geol. Survey	United States Geological Survey—Mineral Resources of the United States.
U. S. P.	United States Patent Specification.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. pr. Geol.	Zeitschrift für praktische Geologie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.

INTRODUCTION

By Sir William Crookes, O.M., F.R.S.

The mysterious group of substances to which have been given the title of "rare earths" has long been the subject of my special study, and no one knows better the magnitude of the difficulties encountered in the investigation, or realises more clearly the comparative insignificance of the knowledge we have acquired. The rare earths constitute the most striking example of the association of chemical substances with others which are closely allied to themselves, and from which they are separable only with extreme difficulty. They form a group to themselves, sharply demarcated from the other elements, and it is my belief that by following the study of them to the utmost limits, we may arrive at the explanation of what the chemical elements really are and how they originated, and discover the reasons for their properties and mutual relations. When this knowledge has been wrested from Nature chemistry will be established upon an entirely new basis. We shall be set free from the need for experiment, knowing *a priori* what the result of each and every experiment must be; and our knowledge then will as much transcend our present scientific systems as the knowledge of the skilled mathematician of the present day exceeds that of primitive man, counting upon his fingers. The great problem of the nature and genesis of the elements is approaching solution, and when the consummation is reached it will undoubtedly be found that the study of the rare earths has been an important factor in bringing it about.

There has long been a need for a work in the English language dealing historically and descriptively with these substances, and Mr. Levy's book is well fitted to fill the gap. The chapters on the technical applications of the rare earths are particularly valuable, and the chemical aspect of the incandescent lighting industry is admirably treated. The author is to be congratulated upon having successfully achieved an important and useful piece of work.

WILLIAM CROOKES.

December 1914.

THE RARE EARTHS

PART I

OCCURRENCE OF THE RARE EARTHS

CHAPTER I

THE NATURE OF THE MINERALS AND THEIR MODE OF OCCURRENCE

The history of the rare earth minerals begins in the year 1751, when the Swedish mineralogist Cronstedt described a new mineral, which he had found intimately mixed with chalcopyrite[1] in the quarry of Bastnäs, near Ryddarhyttan, in the province of Westmannland, Sweden. Cronstedt gave the mineral the name Tung-sten (heavy stone); but as the name Tenn-spat (heavy spar, or heavy mineral) had already been selected by Wallerius (1747) for a new species from Bohemia, believed to contain tin, the choice was not a happy one. More than fifty years after its discovery, a new earth, now known as ceria, was isolated from Cronstedt's mineral, for which at the same time the name Cerite was proposed.[2] Meanwhile, however, the Finnish chemist Johann Gadolin had observed, in the year 1794, a new earth in a mineral discovered by Arrhenius at Ytterby in Sweden in 1788; he called the new oxide Ytterbia, and the mineral in which he observed it, Ytterbite. The discovery was confirmed in 1797 by Ekeberg, who suggested the names Yttria and Gadolinite for the oxide

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[1] Chalcopyrite, or Copper pyrites, is a mixed sulphide of iron and copper, of the approximate formula $CuFeS_2$.

[2] For the history of the name Tungsten, see under the mineral Cerite, Ch. II.

and mineral respectively; these names were accepted by Klaproth, and soon came into general use.[1] Whilst then Cerite was the first of the rare earth minerals to be discovered, it was in Gadolinite that new elements were first recognised, and the chemistry of the rare earths began in 1794 with Gadolin's observation.

During the nineteenth century a considerable number of rare earth minerals was discovered and analysed; the quantities of the minerals observed, however, were so small that the name 'Rare earths,' applied to the new oxides found, was in every sense justified. Until the year 1885, though by that time the scientific interest of the group had been fully demonstrated by the discovery of several new elements, it was supposed that the minerals were almost entirely confined to a few scattered localities in Scandinavia and the Ural mountains. In that year Dr. Auer von Welsbach announced his application of the rare earths to the manufacture of incandescent mantles. Immediately there was a great demand for raw material for the preparation of thoria and ceria. The agents of the Welsbach Company visited all the important mining centres of Europe and America, intent on a search which shortly made it clear that the metals of the so-called 'rare earths' are really quite widely distributed in nature. The chief commercial deposits are the monazite sands of the Carolinas, the Idaho basin, and Brazil, the gem-gravels of Ceylon, and the remarkable deposits of gadolinite and allied minerals at Barringer Hill in Texas.

Whilst deposits of commercial importance are not very common, improved scientific methods and more careful search have shown that in traces the rare earths are of exceedingly wide distribution. Sir William Crookes has shown that yttria earths are often present in calcite and in coral; whilst Headden[2] noted that quite considerable amounts (up to 0·03 per cent.) were present in a yellow phosphorescent variety of calcite from Colorado. Similarly Humphreys[3] found that fluorspar usually contains traces of yttrium, whilst one or two phos-

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history of these names will be found somewhat more fully under Ch. II.

J. Sci., 1906, [iv.], 21, 301. [3] *Astrophys. J.*, 1904, 20, 266.

phorescent varieties contain quantities varying up to 0·05 per cent. The presence of yttria elements in phosphorescent varieties of calcite is interesting, and some connection has been suggested; there is, however, no positive ground for the belief in such a relation.

More recently Eberhard[1] has found very considerable quantities of rare earths in cassiterite (tin dioxide, SnO_2) and wolframite [an iron manganese tungstate, $(Fe,Mn)WO_4$]. A specimen of wolframite from the Erzgebirge was found to contain nearly 0·4 per cent. of rare earths, over half of this quantity being scandium oxide. A process which is readily susceptible of commercial application has been worked out by R. J. Meyer,[2] for the extraction of scandia and the yttria earths from the mixed oxides left after the treatment of wolframite for tungstic acid.

Using the spectroscopic method, which is capable of detecting one part of scandia in twenty thousand, Eberhard (*loc. cit.*) has found that minute quantities of scandia and yttria earths are present in almost all the commoner rocks and minerals. The minerals richest in scandium were beryl, cassiterite, wolfram, the zircon minerals, and the titanates and columbates of the ceria and yttria oxides. These results are in agreement with the observations of Sir William Crookes,[3] who has made the study of scandium especially his own. From the fact that scandium was often observed unaccompanied by any other member of the rare earth group, Eberhard rather favours Urbain's conclusion[4] that scandium may not be a member of the rare earth family. Spectroscopic examination has also shown the existence of some of the rare earth elements in the sun and stars (see Europium, p. 189).

In view of this extraordinarily wide distribution of the rare earths in the mineral world, it is but natural that they should be found also in the vegetable and animal kingdoms. Tschernik[5] found 10 per cent. of rare earths in the ash of a coal from Kutais, in the Caucasus, and smaller quantities

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[1] *Sitzungsber. königl. Akad. Wiss. Berlin*, 1908, 851; 1910, 404.

[2] Meyer, *Zeitsch. anorg. Chem.*, 1908, **60**, 134. Meyer und Winter, *ibid.*, 1910, **67**, 398.

[3] *Phil. Trans.* 1910, A, **210**, 359.

[4] See under Scandium in Pt. II.

[5] See Abstr. in *Zeitsch. Kryst. Min.*, 1899, **31**, 513.

have been found in the ashes of various plants; members of the group have also been identified in the human body.

Apart from the general occurrence in traces throughout the mineral kingdom, the minerals in which the rare earths occur are not very common; and though of fairly wide distribution, they are found usually only in small quantities. The earliest known locality, and the most fruitful in regard to number of species, has been the southern part of the Scandinavian peninsula;[1] the minerals occur in the numerous pegmatite veins traversing the granitic country-rock. The mining district round Miask, in the Ural mountains, has also long been known as a fruitful source. Other districts in Europe are the Harz and Erzgebirge, the Laacher See in Prussia, Joachimsthal in Bohemia, Dauphiné, Cornwall, etc. In the United States numerous localities are known; the chief are in the Carolinas and Georgia, Idaho, Oregon, California, Texas, Colorado, Virginia, Pennsylvania and Connecticut. Many of the southern provinces of Brazil also furnish important sources; the famous diamond fields of Minas Geraes, Matto-Grosso, Goyaz and the surrounding provinces yield numerous species, whilst the sands along the southern coasts of Bahia are rich in monazite, and form to-day the most important source of the mineral. Monazite, as well as other rare earth minerals, occurs also in South Africa. An interesting species, plumboniobite (*q.v.*), has recently been found in German East Africa. From Australia numerous occurrences are reported, whilst in Canada only a few districts are known to yield members of the group. In Asia important localities are Ceylon—the famous gem-gravels being the most accessible source—and one or two districts in Japan; monazite has been reported recently in considerable quantities near Travancore, India.[2] A more extended search will doubtless show that they occur in many other places.

For several reasons, the rare earth minerals[3] form a group

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[1] See Brögger, *Die Mineralien der Sud-Norwegische Granit- Pegmatitgänge*, Christiania, 1906.

[2] *Bull. Imp. Inst.*, 1911, vol. ix: No. 2, p. 103.

[3] The phrase 'rare earth minerals' will be used whenever it is desired to indicate collectively those minerals of which the yttria and ceria earths form

of the highest scientific interest. In the first place, they are generally of very complex composition, more especially with regard to their rare earth content. Thus, whilst it sometimes happens that one or other of the two groups of oxides (the ceria and yttria groups) may predominate to the complete exclusion of the second, it is no uncommon thing for a species to contain almost all the elements of the rare earth family. On the other hand, it is very uncommon for as much as 50 per cent. of the rare earth content to consist of any one oxide. The usual case is that a mineral contains chiefly yttria earths with some ceria earths, or *vice versâ*, the two sub-groups being almost always complex mixtures of several oxides, in which occasionally one may predominate. The remarkable similarity in chemical behaviour of the rare earth elements, and the difficulty of separating them, correspond to this peculiarity in their occurrence.

A second point of even greater interest is that the rare earth minerals are as a general rule strongly radio-active; further, it only occasionally happens that any mineral in which the rare earths do not form an important constituent has more than the feeblest activity; the exceptions being, of course, those uranium minerals which do not contain rare earths. The connection may be pushed even further; for whilst it appears that hardly any rock or mineral possesses absolutely no radio-activity, it is equally worthy of notice that traces of the rare earths, if not quite universal in the mineral world, are yet normally found in the majority of common minerals. As a natural consequence of their activity, the rare earth minerals are also as a rule rich in helium. These facts and the problems which they open up will be treated more fully in a later chapter.

A point of further interest is that of the age of the rare earth minerals. Except in a few cases where they are obviously of secondary formation, these minerals are among the oldest

an important constituent, as contrasted to those in which only traces of these oxides occur. Such minerals may often contain titanium, zirconium, or thorium, and, for convenience, the term may be taken to include the commoner zirconium and thorium minerals, but not the commoner titanium minerals.

known to us. They occur usually in igneous rocks, particularly in granites which have been considerably metamorphosed. Where erosion has occurred, they are found in deposits of such a nature as to leave very little doubt that the original rock was of plutonic formation and of very considerable age. Whilst it is true, however, that the rare earth minerals are generally of very great antiquity (none of the primary minerals being of more recent date than the palæozoic age), Eberhard has pointed out that the age and nature of common rocks seem to have absolutely no influence on the traces of scandia and yttria oxides which they contain. The geological evidence shows that the rare earth minerals are on the whole exceedingly stable, and that they have been generally formed during the pegmatitic alteration of granites. As early as the year 1840, Scheerer drew attention to these facts, and to the extreme age of the rare earth minerals; but so far his observation seems to have attracted little attention, and no explanation has been put forward.

In the following chapters no attempt is made to treat the rare earth minerals fully. An alphabetical list of all the minerals of any importance which contain rare earths, titanium, zirconium or thorium is given, and of these several are selected for fuller treatment. The basis of selection has been somewhat arbitrary. Those species which are of mineralogical importance, as well as those to which any special historical, scientific or commercial interest attaches, have of course been singled out; in addition, the more recently discovered species have occasionally been considered worthy of separate mention.[1]

It is now being realised that some knowledge of crystallography is essential to the chemist, and for this reason short accounts of the crystallography of the selected types have been given. Apart from this, every effort has been made to render the mineralogy intelligible to the student of chemistry who has devoted no attention previously to this subject, and also to stimulate an interest in the problems of mineral

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[1] A full list of the minerals containing rare earths known up to 1904, with an account of their properties and very full references, will be found in the work of Dr. J. Schilling, *Das Vorkommen der Seltenen Erden im Mineralreiche*, 1904.

chemistry, unfortunately too often ignored by our present-day teachers. The rare earth minerals afford good examples of some phenomena of great interest to the chemist, as, *e.g.* Isomorphism and Solid Solution, Dimorphism, Isodimorphism, and Molecular Change, and in one or two cases these are treated rather fully.

No special advantages are claimed for the system of classification, which is merely one of convenience. The minerals are divided into five groups:—

(1) The Silicates, which are grouped into three sub-divisions.
(2) The Titano-silicates and the Titanates.
(3) The Tantalo-columbates, sub-divided into those free from titanium and those in which titanium is present.
(4) The Oxides and Carbonates.
(5) The Halides and Phosphates.

A separate chapter has been devoted to the monazite sands, and another to the radio-active properties of the minerals.

ALPHABETICAL LIST OF MINERALS CONTAINING TITANIUM, ZIRCONIUM, THORIUM, OR ELEMENTS OF THE CERIUM AND YTTRIUM GROUPS.

The following list contains all but a few entirely unimportant members of these classes of minerals. The names of those species selected for fuller treatment are printed in heavy type, whilst names of those not so selected, which for convenience are included under the generic term 'Rare earth mineral,' *i.e.* roughly all those containing Thorium, or elements of the Cerium and Yttrium groups, and the commoner Zirconium minerals, as distinguished from minerals containing Titanium, are printed in italics. (See footnote on p. 4.) Their properties are given in the following order:—

Chemical Composition and Rare Earth Content.
Crystallographic Data.
Physical Properties.
Locality, etc.

The following contractions are employed:

E = any element or elements of the cerium or yttrium groups.
Cer = oxides of the cerium metals.
Yttr = oxides of the yttrium metals.
G = Specific Gravity.
H = Hardness.

Aenigmatite.

A Titanosilicate of Fe″ and Na, with small proportions of Fe‴ and Al‴. Closely allied to the amphiboles. $TiO_2 = 7–8$ %.

Anorthic. Habit prismatic.

G = 3·80–3·86. H = 5½. Black; pleochroism strong.

Greenland and S. Norway.

Aeschynite

A Titanocolumbate of Cerium metals, with Th, Fe, Ca, Mn, aq. Cer = 19·4–24·1 ; Yttr = 1·1–3·1 ; $ThO_2 = 15·7–17·6$; $TiO_2 = 21–22$ %.

Rhombic, holosymmetric. Habit prismatic or tabular.

G = 4·9–5·7. H = 5·6. Black; opaque.

Hitterö, Norway; Miask, Urals; also in Germany and Brazil.

Allanite (Orthite).

H_2O, $4R''O$, $3R'''_2O_3$, $6SiO_2$, where R″ = Ca, Fe″, Be, and R‴ = Al, Fe,‴E. An epidote containing rare earths. Cer = 3·6–51 (usually 10–25); Yttr = 0–8 (usually < 3); $ThO_2 = 0–3·5$ %.

Monoclinic; isomorphous with epidote.

G = 3·5–4·2. H = 5½–6. Brown to black; opaque.

Widely distributed in Greenland and Scandinavia.

Alvite (Anderbergite).

Silicate of Zr and E, with Ca, Mg, Be, Al, Cu, Zn, and aq. in small quantities. Cer → 3·98 ; Yttr → 22 ; $ZrO_2 = 30·5–61·4$ %.

Tetragonal; optically isotropic. Pseudomorphous after zircon.

G = 3·3–4·3. H = 5–6. Yellowish brown; transparent.

Ytterby, Sweden; Arendal, Norway; various localities in N. America.

Anatase (Octahedrite).

Titanium dioxide. $TiO_2 = 97–100$ %.

Tetragonal; habit octahedral.

G = 3·82–3·95. H = 5½–6. Transparent to opaque; brown to black.

Dauphiné; Bavaria; Cornwall; Norway; Brazil, etc.

Ancylite.

$4Ce(OH)CO_3 + 3SrCO_3 + 3H_2O$; with Fe, Mn, Ca, F, traces. Cer = 46·3 %.

Rhombic; prismatic.

G = 3·95. H = 4½. Brown; translucent.

Plain of Narsarsuk, Greenland.

Annerödite.

A parallel growth of Columbite on Samarskite, once believed to be a new species.

Corresponding to Columbite.

Arfvedsonite.

Metasilicate of Na, Ca, Fe'', Zr; approximately $4Na_2O,3CaO,14FeO,(Al,Fe)_2O_3,21SiO_2$. $ZrO_2 = 1–6$ %.

Monoclinic—an amphibole.

G = 3·44. H = 6. Black; pleochroism strong.

S. Greenland and S. Norway.

Arizonite.

Ferric metatitanate, $Fe_2O_3,3TiO_2$ or $Fe_2(TiO_3)_3$. $TiO_2 = 36·7$ %.

Uncertain; apparently monoclinic.

G = 4·25. H = 6–7. Dark steel-grey; opaque.

Hackberry, Arizona.

Arrhenite.

Silico-tantalate of Yttrium metals, with Ce, Al, Fe, Ca, Be, aq. Yttr = 33·2; Cer = 2·6; $ZrO_2 = 3·4$ %.

Amorphous.

G = 3·68. Red; translucent to opaque.

Ytterby, Sweden.

Astrophyllite.

Titano-silicate of Fe, Al, Mn, Zr, K, Na, with aq. $ZrO_2 = 1·2–4·5$; $TiO_2 = 7–14$ %.

Rhombic. Cleavage (010) perfect.

G = 3·2–3·4. H = 3. Golden to bronze yellow; strongly pleochroic.

Brevik, Norway; El Caso Co., Colorado; Greenland.

Auerbachite.

An impure hydrated form of Zircon, $ZrSiO_4$. $ZrO_2 = 55·2$ %.

Tetragonal; isotropic. Pseudomorphous after zircon.

G =4·06. H = 6. Brownish-grey; translucent to opaque.

Alexandrovsk, Russia.

Auerlite.

$3ThO_2,[3SiO_2,P_2O_5]6H_2O$; traces of Fe, Ca, Mg, Al, CO_2, etc. SiO_2 replaced by $\frac{P_2O_5}{3}$? $ThO_2 = 69·2–72·2$ %.

Tetragonal; probably a pseudomorph after Thorite.

G = 4·4–4·8. H = 2–3. Yellowish to orange-red.

Henderson Co., N. Carolina.

Baddeleyite.

ZrO_2, with small amounts of SiO_2, Fe_2O_3, Al_2O_3, CaO, etc. ZrO_2 = 96·5 %.

Monoclinic.

G = 4·4–6·0. H = 6½. Brown; pleochroic.

São Paulo, Brazil; Rakwana, Ceylon.

Bagrationite.

A variety of Allanite (orthite) with no important chemical difference.

Monoclinic; habit prismatic.

G = 3·84. H = 6½. Black; translucent to opaque.

Achmatovsk, Urals.

Bastnäsite (Harmatite).

Hydrated fluocarbonate of Cerium metals, $\dot{E}(F)CO_3$. Cer = 64–93·5; ThO_2 = 0–10 %.

Hexagonal prisms, pseudomorphous after Tysonite (*q.v.*); or massive.

G = 4·9–5·2. H = 4–4½. Yellow to brown; transparent.

Bastnäs, Sweden; Pike's Peak, Colorado.

Beckelite.

Zirconosilicate of rare earths and lime, $Ca_3E_4(Si,Zr)_3O_{15}$. Cer = 59·7; Yttr = 2·8; ZrO_2 = 2·5 %.

Cubic, in octahedra and dodecahedra. Cubic cleavage.

G = 4·15. Brown; transparent.

Near Sea of Azov, Russia.

Benitoite.

A Titano-silicate of barium, $BaTiSi_3O_9$. TiO_2 = 20·1 %.

Rhombohedral.

H = 6½–7. Colourless to blue; transparent; pleochroism strong.

Source of San Benito River, California.

Blomstrandine.

Dimorphous with Polycrase (*q.v.*), and of same composition.

Orthorhombic; isomorphous with priorite (*q.v.*).

G = 4·5–5·0; H = 6½. Bright black; translucent.

Hitterö and Arendal, Norway.

Blomstrandite.

Hydrated titano-columbate of U, with some Fe and Ca. TiO_2 = 10·7%.

Massive.

G = 4·17–4·25. H = 5½. Black; opaque

Nohl, Sweden.

Bodenite.

A variety of Allanite (*q.v.*), rich in Al and Ca, with no Be. Yttr = 17; Cer = 18 %.

Monoclinic.

As Allanite.

Boden, near Marienburg.

Britholite.

A basic phosphosilicate of cerium metals, with Fe, Ca, Mg, Na, F. Cer = 60·5–60·9 %.

Hexagonal; habit prismatic.

G = 4·446. H = 5½. Brown; transparent.

Naujakasik, Greenland.

Bröggerite.

A variety of Uraninite (*q.v.*), with rare earths, Th, Pb, Fe, Ca, Si, aq., etc. Cer = 0·4; Yttr = 1·4–4·3; ThO_2 = 4·7–6·1 %. Traces of ZrO_2.

Cubic, in octahedra and dodecahedra.

G = 8·7–9·0. H = 5–6. Black; translucent to opaque.

Anneröd, near Moos, Norway.

Brookite.

Titanium dioxide, TiO_2 = 99–100 %; trimorphous with Anatase and Rutile.

Orthorhombic.

G = 3·87–4·01. H = 5½–6. Brown; opaque.

Dauphiné; Urals; Switzerland; Magnet Cove, Arkansas.

Calciothorite.

A variety of Thorite containing lime—$5ThSiO_4, 2Ca_2SiO_4 + 10H_2O$. ThO_2 = 59·3 %.

Completely amorphous.

G = 4·114. H = 4½. Deep red; translucent.

Islands of Läven and Arö, Langesund Fiord, Norway.

Cappelenite.

A borosilicate of rare earth metals and barium, with traces of Th, Ca, K, Na, aq. Approximately $BaSiO_3, YBO_3$. Cer = 4·2; Yttr = 52·5 %.

Hexagonal; habit prismatic.

G = 4·407. H = 6–6½. Greenish brown; translucent.

Island of Klein-Arö, Langesund Fiord, Norway.

Caryocerite (Karyocerite).

Complex fluosilicate of E, with Ta, Th, Ca; also CO_2, P_2O_5, B, Al, Fe, Mn, U, Mg, Na, aq, etc. Approaching **Melanocerite**, (*q.v.*), but richer in Th. Very complex. Cer = 41·8; Yttr = 2·2; ThO_2 = 13·6; ZrO_2 = 0·5%.

Rhombohedral, but isotropic; apparently a pseudomorph after Melanocerite (*q.v.*)

G = 4·295. H = 5–6. Nut brown; translucent. Faces very brilliant, but striated. Lustre vitreous to resinous.

Various rocks and shoals round Arö Island, Langesund Fiord, Norway.

Castelnaudite.

A variety of Xenotime (*q.v.*) containing Zr. Yttr = 60·4; ZrO_2 = 7·4 %.

Tetragonal.

G = 4·5. H = 4–5. Greyish white to pale yellow

Diamond sands of Brazil.

Cataplejite (Kataplejite).

$H_4(Na_2,Ca)ZrSi_3O_{11}$. ZrO_2 = 29·6–40 % (usually 30–33 %).

Monoclinic, pseudohexagonal. Becomes truly hexagonal at 140° C.

G = 2·8. H = 6. Yellow to brown; transparent to opaque. A blue variety is known which contains no calcium.

Islands of Langesund Fiord, Norway; Narsarsuk, Greenland.

Cerite.

A basic silicate of Cerium metals, with Ca and Fe. Approximately $H_3(Ca,Fe)Ce_3Si_3O_{13}$. Cer = 50·7–71·8 %. In a variety from Batoum, Tschermak reports Yttr = 7·6 and ZrO_2= 11·7 %.

Orthorhombic; usually massive or granular.

G = 4·9. H = 5–6. Brown to red; translucent to opaque.

Ryddarhyttan, Sweden; Batoum, Caucasus?

Chalcolamprite.

A silico-columbate of E, Zr, Ca, Fe, Na, K; $R_2Cb_2F_2SiO_9$, where R represents various metals. E = 3·41; ZrO_2 = 5·7 %.

Cubic, in small octahedra.

G = 3·77. H = 5½. Greenish brown; opaque. Metallic lustre (χαλκός = Copper, λαμπρός = lustre).

Narsarsuk, S. Greenland.

Churchite.

Hydrous phosphate of Cerium metals and Ca. Cer = 51·87 %.

Monoclinic? Aggregations only.

G = 3·14. H = 3½. Greyish; transparent to translucent.

Cornwall.

Cleveite

A variety of Uraninite (*q.v.*) rich in rare earths and helium. Cer = 2·3–2·9; Yttr = 10·0–10·3; ThO_2 = 4·6–4·8 %.

Cubic; usually massive.

G = 7·49. H = 5½. Black; opaque.

Arendal, Norway.

Cordylite

Fluocarbonate of Cerium metals and Ba; $E_2F_2Ba(CO_3)_3$. Cer = 49·4 %.

Hexagonal; isomorphous with Parisite (*q.v.*).

G = 4·31. H = 4½. Yellow; transparent.

Plain of Narsarsuk, Greenland.

Cossyrite.

A variety of Aenigmatite (*q.v.*) of very complex composition. TiO_2 = 6–8 %.

Anorthic.

G = 3·74. H = 5. Black; opaque.

Island of Pantellaria (formerly Cossyra).

Cyrtolite.

A pseudomorph after zircon, allied to Alvite (*q.v.*).

Tetragonal.

See Alvite.

Various localities in Scandinavia, and U.S.A.

Davidite.

A Titanate of Fe, U, V, Cr, and E—uncertain formula. $TiO_2 > 50$; E_2O_3 = 5–10 %.

Cubic—in grains and rounded crystals.

G = 4 about. Black, with brilliant lustre.

Olary, S. Australia.

Delorenzite.

$2FeO,UO_2,2Y_2O_3,24TiO_2$. Yttr = 14·63; TiO_2 = 55 %.

Rhombic; habit prismatic.

G = 4·7. H = 5½–6. Black; translucent to opaque; lustrous.

Craveggia, Piedmont, Italy.

Derbylite.

$FeO,Sb_2O_5 + 5FeO,TiO_2$? TiO_2 = 35 % about.

Orthorhombic; habit prismatic.

G = 4·53. H = 5. Pitch black; opaque; lustre resinous.

Tripuhy, Minas Geraes, Brazil.

Dysanalyte (Perovskite).
Approximately $6RTiO_3,R(Cb,Ta)_2O_6$, where $R = Ca, Fe''$. Believed by Hauser to be merely an impure Perovskite (*q.v.*). Cer = 0–5·1; TiO_2 = 41·5–59·3 %.
Cubic.
G = 4·13. H = 5–6. Black; opaque.
Vogtsburg, near Baden, Germany.

Elpidite.
$Na_2Zr(Si_2O_5)_3$, $1\frac{1}{2}H_2O$. ZrO_2 = 20·5 %.
Orthorhombic.
G = 2·52–2·56. H = 7–8. Colourless to red; translucent.
Various localities in Greenland.

Endeiolite.
$R''Cb_2O_6(OH)_2 + R''SiO_3$ (cf. Chalcolamprite). E_2O_3 = 4·43; ZrO_2 = 3·78 %.
Cubic.
G = 3·44. H = 4. Dark chocolate-brown; transparent.
Narsarsuk, Greenland.

Erdmannite (Michaelsonite).
A silicate of E and Ca, with Zr, Be, Th, Al, Fe, aq., etc. An altered Homilite? Cer = 17·7–34·9; Yttr = 1·4–2·1; $ThO_2 + ZrO_2$ = 0–12 %.
Amorphous; isotropic.
G = 3·01–3·39. H = $4\frac{1}{2}$. Brown to leek-green.
Near Brevig, Norway.

Erikite.
A phosphosilicate of E, Ca, Al, K and Na, with ThO_2, H_2O, etc. Cer = 40·5; ThO_2 = 3·3 %.
Orthorhombic.
G = 3·473. H = $5\frac{1}{2}$–6. Brown; opaque.
Julianehaab, Greenland.

Eucolyte.
$R'_4R''_3Zr(SiO_3)_7$. where R' = K, Na, H, and R'' = Ce(OH), Fe, Mn, Ca, and Zr(OCl) may replace SiO_2? A very complex mineral. ZrO_2 = 10·9–20; Cer = 0–5·2 %.
Rhombohedral.
G = 3·0–3·1. H = 5–$5\frac{1}{2}$. Red to brown; translucent. Double Refraction strong, — ve.
Various localities in Norway.

Eucrasite.

An altered Thorite (*q.v.*) containing E, Ca, Fe, Mn, Na, Ti, H_2O, etc. Cer = 14; Yttr = 5·9; ThO_2 = 36·0; ZrO_2 = 0·6 %.

Rhombic (Paijkull). Amorphous, isotropic (Brögger).

G = 4·39. H = 4½–5. Brownish black; opaque.

Near Brevig, Norway.

Eudialite.

A variety of Eucolyte (*q.v.*) of the same composition.

As Eucolyte.

G = 2·92. Double Refraction strong, +ve. Otherwise as Eucolyte.

Greenland; Lapland; Arkansas, U.S.A.

Euxenite.

$E(CbO_3)_3,E_2(TiO_3)_3,1\frac{1}{2}H_2O$; with U and Zr. Cer = 2·3–8·4; Yttr = 13·2–34·6; TiO_2 = 20–23 %. $ThO_2 + ZrO_2$ usually in traces.

Orthorhombic; usually massive.

G = 4·6–5·0. H = 6½. Brownish-black; translucent to opaque.

Hitterö, Brevig, Jolster, Arendal, Norway; Cooglegong, Australia; N. Carolina.

Fergusonite.

Approximately $E_2O_3,(Cb,Ta)_2O_5$, with U, Fe, Ca. Cer = 0·5–13·9; Yttr = 27·9–47·1; $ThO_2 + ZrO_2$ = 0–7 %. [Berzelius found Cer = 36·3; Yttr = 0 % in one specimen.]

Tetragonal, polar.

G = 5·84–4·3 when largely hydrated. H = 5·6. Brown to black.

Norway; Australia; Texas, etc.

Florencite.

A silico-phosphate of E and Al. Cer = 28 % approximately.

G = 3·6. H = 5. Yellow to red. Resinous lustre.

Minas Geraes and diamond localities in Brazil.

Fluocerite.

Basic fluoride of rare earth metals, E_2O_3, $4EF_3$. Cer = 81·4–82·6; Yttr = 1·1–4·3 %.

Massive. Original hexagonal mineral of Berzelius and Haidinger, probably Tysonite (*q.v.*).

G = 5·7–5·9. H = 4. Reddish yellow; opaque.

Österby, Sweden.

Freyalite.

Silicate of E and Th, with Al, Fe, Mn, Na, aq., etc. Cer = 31·3; ThO_2 = 28·4; ZrO_2 = 6·3 %.

Amorphous.

G = 4·06–4·17. H = 6. Brown; opaque; lustre resinous.

Brevig, Norway.

Gadolinite.

FeO, 2BeO, Y_2O_3, $2SiO_2$, where Y = yttrium metals. Cer = 3·4–51·5 (usual 6–20); Yttr = 5–60 (usual 35–48) %.

Monoclinic; habit prismatic. Often amorphous and isotropic.

G = 4·0–4·5. H = 6½–7. Brown and green. Double Refraction strong, + ve.

Ytterby and Fahlun, Sweden; Hitterö and Malö, Norway; Llano Co., Texas; Colorado, etc.

Geikielite.

$(Mg,Fe'')TiO_3$. TiO_2 = 56·1–64·8 %. Specimens rich in iron are called Picroilmenite.

Massive.

G = 4 about. H = 6. Purplish or brownish black.

Ceylon.

Gorceixite.

An alumino-phosphate of alkaline and ceria earths. Cer = 0–3 %.

Microcrystalline.

G = 3. H = 6. White to brown. Translucent.

Diamond sands of Brazil.

Guarinite.

Formerly supposed to be dimorphous with Titanite (*q.v.*); shown by Zambonini and Prior (1909) to be identical with Hiortdahlite (*q.v.*).

Hainite.

Tantalo-silicate and titanate of Zr, Ca, Na. ZrO_2 = 29–32 %.

Anorthic.

G= 3·2. H = 5. Colourless to yellow; transparent.

Bohemia.

Hellandite.

$3H_2O$, $2R''O$, $3R'''_2O_3$, $4SiO_2$, where R'' = Ca, Mg, $\frac{Th}{2}$; R''' = E, Al, Fe, Mn. E_2O_3 = 40 %.

Monoclinic; habit prismatic.

G = 3·70. H = 5½. Reddish-brown when fresh.

Lindvikskollan and Kragerö, Norway.

Hiortdahlite

$3CaSiO_3,Ca(F,OH)NaZrO_3$. $ZrO_2 = 21{\cdot}5$; $TiO_2 = 1{\cdot}5$ %.
Anorthic; habit tabular.
G = 3·27; H = 5–5½. Yellow, with weak pleochroism.
Island of Låven, Langesund Fiord, Norway.

Hjelmite (Hielmite).

A stanno-tantalate of Ca, Mn, Fe, E, related to Yttrotantalite (*q.v.*). $E_2O_3 = 1$–6 %.
Orthorhombic.
G = 5·82. H = 5. Black; lustre metallic.
Fahlun, Sweden.

Homilite.

$(Ca,Fe)_3(BO)_2(SiO_4)_2$. Sometimes with ceria earths, 0–2·6 %.
Monoclinic—isomorphous with Gadolinite (? Brögger).
G = 3·34–3·38. H = 4½–5. Black; pleochroic.
Islands of Lanegsund Fiord, Norway.

Hussakite (Xenotime).

A prismatic form of Xenotime (*q.v.*), erroneously supposed to contain > 6 % SO_3.
Diamond sands of Brazil.

Hydrotitanite.

An altered Perovskite (*q.v.*) with Fe‴ and aq. $TiO_2 = 82{\cdot}8$ %.
Amorphous.
G = 3·68. H = 1–2. Yellowish grey.
Magnet Cove, Arkansas.

Ilmenite.

$FeTiO_3$; composition varies widely. $TiO_2 = 3{\cdot}5$–$52{\cdot}3$ %.
Rhombohedral.
G = 4·5–5. H = 5–6. Black; opaque. Slightly magnetic.
Norway; Dauphiné; Bohemia; Cornwall, etc.

Ilmenorutile.

$FeO,Nb_2O_5,5TiO_2$? $TiO_2 = 66$–75 %.
Tetragonal, very near to Rutile (*q.v.*).
G = 4·3–5·0. H = 6–7. Brown to black; opaque.
Ilmen Mountains, Russia.

Johnstrupite.

Silico-titanate of E, Al, Mg, Ca, Na, etc., with F and aq. Cer = 13·5; Yttr = 1·1; $TiO_2 = 7$–8; $ThO_2 + ZrO_2 = 3{\cdot}6$ %.
Monoclinic, very close to Epidote.
G = 3·19–3·29. H = 5. Brownish green; weakly pleochroic.
Islands of the Langesund Fiord, Norway.

Kainosite (Cenosite).
$CaY_2(SiO_3)_4,CaCO_3,2H_2O$, where Y = Yttrium metals. Yttr = 30–37 %.
Uncertain; pseudo-hexagonal.
G = 3·38–3·41. H = 5–6. Yellowish brown.
Hitterö and province of Nordmark, Norway.

Keilhauite (Yttrotitanite).
An isomorphous mixture of Titanite (*q.v.*) with $(E,Al,Fe)SiO_5$. E_2O_3 = 5–12; TiO_2 = 26–30 %.
Monoclinic; isomorphous with Titanite.
G = 3·52–3·77. H = 6½. Brown to black.
Various localities in Norway.

Kischtimite.
A fluocarbonate of the Cerium metals, near Parisite (*q.v.*). Cer = 74·2 %.
Massive.
G = 4·78. H = 4½. Yellowish brown; translucent.
Barsovka River, Kyshtymsk, Urals.

Knopite.
A variety of Perovskite (*q.v.*) containing E and Fe. Cer = 4–7; TiO_2 = 55 %.
Pseudo-cubic.
G = 4·2. H = 5½. Grey; opaque; lustre metallic.
Alnö, Sweden.

Kochelite.
A columbate of E, Fe, Zr; with ThO_2, SiO_2, Ca, aq., etc. Allied to Fergusonite (*q.v.*). Yttr = 17·22; ZrO_2 = 12·8; ThO_2 = 1·23 %.
Doubtful; may be tetragonal.
G = 3·74. H = 3–3½. Brown to honey yellow; translucent.
The Kochelweise, near Schreiberhau, Silesia.

Koppite.
Columbate of E, Ca, Fe, Th, K, Na, etc. Near Pyrochlore (*q.v.*). Cer = 4–10; ZrO_2 = 0–5 %.
Cubic; in dodecahedra.
G = 4·45–4·46. H = 5–6. Brown; transparent.
Schelingen, Black Forest Mountains, Germany.

Lanthanite.
Hydrated carbonate of Cerium metals, especially La; $E_2(CO_3)_3,9aq$. Cer = 54·9 %.
Orthorhombic; habit tabular.

G = 2·6–2·7. H = 2. White; opaque.
With Cerite (*q.v.*) at Bastnäs, Sweden; Bethlehem, Pennsylvania, U.S.A.

Lavenite.
$(Mn,Ca,Fe)(ZrOF)Na(SiO_3)_2$? ZrO_2 = 28·8–31·6 %.
Monoclinic; habit prismatic.
G = 3·51–3·55. H = 6. Brown to yellow; translucent.
Langesund Fiord, Norway; the Ardennes, France.

Leucosphenite.
$BaO,2Na_2O,2(Ti,Zr)O_2,10SiO_2$. TiO_2 = 13·2; ZrO_2 = 3·5 %.
Monoclinic; wedge-shaped.
G = 3·05. H = 6½. White; transparent.
Naisarsuk, Greenland.

Lewisite.
$3R''Sb_2O_6,2R''TiO_3$, where R = Ca, Fe″ and Mn. TiO_2 = 11–12 %.
Cubic; in small octahedra.
G = 4·95. H = 5½. Yellow to brown; translucent.
Tripuhy, Minas Geraes, Brazil.

Loranskite.
Tantalate of E, Zr, Fe, etc. Yttr = 10; Cer = 3; ZrO_2 = 20 %.
Massive.
G = 4·6. H = 5. Black; opaque. Metallic lustre.
Finland.

Lorenzenite.
Titano-silicate of Na and Zr; TiO_2 = 35; ZrO_2 = 12 %.
Orthorhombic; acicular.
G = 3·4. H = 6. Colourless; transparent.
South Greenland.

Mackintoshite.
Mixture of oxides, chiefly of Th and U; also Fe, Ca, Mg, Pb, Na, B, Ta, etc. Composition very complex. ThO_2 = 45·3; E_2O_3 = 1·9; ZrO_2 = 1 %.
Tetragonal, resembling thorite (*q.v.*).
G = 5·42. H = 5½. Black; opaque.
Bluffton, Llano Co., Texas.

Malacone.
An altered Zircon (*q.v.*), with E, Ca, Fe, H_2O, etc. ZrO_2 = 47–67 %.
Tetragonal; pseudomorphous.
G = 3·9–4·1. H = 6. Brown, often dull white internally.
Hitterö, Norway; Haute Loire, France; and in U.S.A.

Mauzeliite.
Very similar to Lewisite (*q.v.*), with Pb. $TiO_2 = 8$ %.
Cubic.
G = 5·11. H = 5–6. Brown; translucent.
Jakobsberg, Sweden.

Melanocerite.
Very complex fluosilicate of E and Ca, chiefly. Cer = 48; Yttr = 9·2; $ThO_2 + ZrO_2 = 2$ %.
Rhombohedral; habit tabular.
G = 4·13. H = 5–6. Deep brown to black. Transparent.
Langesund Fiord, Norway.

Microlite.
Complex columbate of Ca, E, Fe, etc., with F and H_2O. $E_2O_3 \rightarrow$ 8 %.
Cubic; habit octahedral.
G = 5·48–5·56. H = 5–5½. Red to yellow.
Stockholm, Sweden; Island of Elba; and in U.S.A.

Molengraafite.
Titano-silicate of Ca, Na, Fe, Al, Mn, etc. $TiO_2 = 28$ %.
Monoclinic; in small prisms.
Yellow. High refraction and birefringence.
Pilandsberg, Transvaal.

Monazite.
Phosphate of E, with Th and SiO_2. Cer = 49–74; Yttr = 1 4; $ThO_2 = 1–20$ %.
Monoclinic.
G = 4·9–5·3. H = 5–5½. Red to brown and yellow; translucent.
The Carolinas; Idaho; Brazil; Scandinavia, etc.

Mosandrite.
In composition identical with Johnstrupite (*q.v.*).
Isomeric with Johnstrupite (*q.v.*).
G = 2·93–3·03. H = 4. Reddish brown; translucent.
Langesund Fiord, Norway.

Muromontite.
A variety of Allanite (*q.v.*), rich in yttria earths and Be, but poor in Al and ceria earths. Cer = 9·1; Yttr = 37·1 %.
See Allanite.
G = 4·263. H = 7. Black to greenish black.
Mauersberg, Erzgebirge, Saxony.

Naegite.

A silicate of Zr, $ZrSiO_4$, with E, Th, U, Cb, etc. $ZrO_2 = 55{\cdot}2$; Yttr $= 9{\cdot}12$; $ThO_2 = 5{\cdot}01$ %.

Tetragonal; in globular aggregates.

G = 4·091. H = 7½. Dark green or brown; dull.

Gravel-tin of Japan.

Narsarsukite.

$Na_4FeTi_2Si_{12}O_{32}F$. $TiO_2 = 14$ %.

Tetragonal. Habit tabular.

G = 2·75. H = 7–7½. Yellow to reddish-brown; pleochroic.

Plain of Narsarsuk, Greenland.

Neptunite.

$(K,Na)_2(Fe,Mg,Ca,)_2(Ti,Si)_4O_{12}$. $TiO_2 = 18$ %.

Monoclinic. Habit prismatic.

G = 3·23. H = 5½. Black, red in flakes. Translucent to opaque.

Narsarsuk, Greenland.

Nivenite.

A variety of Cleveite (*q.v.*), readily soluble in dilute acids.

Cubic; crystallisation indistinct.

G = 8·01. H = 5½. Velvet black; opaque.

Bluffton, Llano Co., Texas.

Nohlite.

A variety of Samarskite (*q.v.*) containing water (→ 4·6 %).

Massive, without cleavage.

G = 5·04. H = 4½–5. Brownish black; opaque.

Nohl, near Kongelf, Sweden.

Oerstedite.

A variety of Zircon (*q.v.*), poor in SiO_2. $ZrO_2 = 69$ %.

Tetragonal; angles exactly those of Zircon.

G = 3·629. H = 5½. Reddish-brown; adamantine lustre.

Arendal, Norway.

Orangite.

$ThSiO_4$, usually with Fe, Ca, H_2O in traces. $ThO_2 = 71{\cdot}2$–$73{\cdot}8$ %.

Tetragonal. Habit prismatic.

G = 5·19–5·40. H = 4½–5. Orange yellow; lustrous.

See under Thorite.

Parisite.

$E_2CaF_2(CO_3)_3$. Cer $= 50{\cdot}8$–$64{\cdot}4$; Yttr $= 0$–$2{\cdot}5$ %.

Hexagonal. Habit pyramidal.

G = 4·36. H = 4½. Yellow to red; transparent.

Muso Valley, Columbia; Montana, U.S.A.; Greenland; Norway; the Urals, etc.

Perovskite.

$CaTiO_3$, with traces of Fe″. $TiO_2 = 58·9$ %.
Pseudo-cubic ? Optically biaxial.
G = 4·017. H = 5½. Yellow; transparent to opaque.
The Urals; Switzerland; Tyrol, etc.

Pilbarite.

$PbO,UO_3,ThO_2,2SiO_2,2H_2O + 2aq$. $ThO_2 = 31·3$ %. Cer and Yttr—traces.
Amorphous.
G = 4·4–4·7. H = 2½–3. Bright yellow; opaque.
Pilbara goldfields, West Australia.

Pitchblende.

A mixture of oxides, chiefly UO_2 and UO_3, but without E_2O_3 or ThO_2.
Amorphous.
G = 5–6·5. H = 3–4. Black; resinous lustre.
Bohemia; Cornwall; Carolina; Norway, etc.

Plumboniobite.

A variety of Samarskite (*q.v.*) containing Pb; $R''_2Cb_2O_7$, $R'''_4(Cb_2O_7)_3$, where $R'' = Fe$, Pb, Ca, UO, $R''' = E$, Al. Yttr = 14·3 %.
Massive, isotropic.
G = 4·80–4·81. H = 5–5½. Dark brown to black.
Morogoro, Uluguru Mountains, German E. Africa.

Polycrase.

A titano-columbate of E and U; Yttr = 19·5–32·5; TiO_2 = 25–33 %. Cer and ThO_2 traces. Isomorphous with Euxenite.
Orthorhombic.
G = 4·0–4·8. H = 6. Black; vitreous lustre.
Norway.

Priorite.

Dimorphous with Euxenite (*q.v.*).
Orthorhombic; isomorphous with Blomstrandine.
G = 4·6–5·0. H = 6. Black; transparent in flakes.
Swaziland, S. Africa.

Pseudobrookite.

$Fe_4(TiO_4)_3$, ferric orthotitanate. $TiO_2 = 44–53$ %.
Orthorhombic.
G = 4·39–4·98. H = 6. Dark brown to black.
Norway; France.

Pyrochlore.

A columbate of Ca and E, with Th, Fe, Ti, F, etc. $E_2O_3 \rightarrow 18$; $TiO_2 = 5$–14 %.
Cubic.
G = 4·2–4·36. H = 5–5½. Dark brown.
Scandinavia ; the Urals ; Tasmania, etc.

Pyrophanite.

$MnTiO_3$, with traces of SiO_2. $TiO_2 = 50$–53 %.
Rhombohedral ; isomorphous with Ilmenite.
G = 4·537. H = 5. Deep blood-red ; translucent ; lustrous.
Pajsberg, Sweden.

Retzian.

Hydrated arsenate of Mn″, Ca, E. Cer + Yttr = 8–11 %.
Orthorhombic, usually in prisms.
G = 4·15. H = 4. Brown ; pleochroic ; transparent.
Province of Nordmarken, Sweden.

Rhabdophane (Scovillite).

Hydrated phosphate of E, Al, Fe, Mg, etc., with SiO_2. Cer = 53·8–57 ; Yttr = 2·1–10·0 %.
Massive.
G = 3·94–4·01. H = 3½. Brown to yellow ; translucent.
Cornwall ; Scoville, Connecticut, U.S.A.

Rhōnite.

$(Na,K,H)_2Ca_8(Fe'',Mg)_{15}(Al,Fe''')_{16}(Si,Ti)_{21}O_{90}$. $TiO_2 = 9{\cdot}5$ %.
Anorthic, isomorphous with Aenigmatite.
G = 3·5–4·3. Brown, with strong pleochroism.
Rhōn Mountains, Saxony.

Rinkite.

A titanosilicate closely allied to Mosandrite and Johnstrupite (*q.v.*)—$Na_9Ca_{11}Ce_3(Ti,Th)_{41}Si_{12}O_{48}$? Cer = 21 ; Yttr = 0·4–1·4 ; $TiO_2 = 13$–14 %.
Monoclinic, very close to Johnstrupite.
G = 3·46. H = 5. Yellow, pleochroic ; translucent.
Kangerdluarsuk, Greenland.

Risörite.

An yttria columbate, near Fergusonite, but with no U and considerable TiO_2 ; Yttr = 37 ; Cer = 2·9–4·0 ; $TiO_2 = 6{\cdot}5$ %.
No data yet determined. Isotropic.
G = 4·179. H = 5½. Yellowish brown.
Norway.

Rogersite.

Hydrated yttria columbate. Yttr=60·12 %. A weathered Samarskite ?

Amorphous, mamillary.

G = 3·313. H = 3½. White.

Mitchell Co., N. Carolina.

Rosenbuschite.

Titanosilicate of Ca, Zr, Na, E, Fe, Mn, with F. ZrO_2 = 18·7–20 ; Cer = 0·3–2·4 %.

Monoclinic, in spherical aggregates.

G = 3·30–3·31. H = 5–6. Orange-grey.

Near Brevik, Sweden.

Rowlandite.

Silicate of E, with Th, Ti, Fe, etc.—$2Y_2O_3$, $3SiO_2$. Cer = 14·4 ; Yttr = 47·7 ; ThO_2 = 0·6 %.

Massive.

G = 4·515. H = 6. Pale dull green.

Llano Co., Texas.

Rutile.

Titanium dioxide ; TiO_2 = 98–100 %

Tetragonal ; habit prismatic.

G = 4·18–4·25. H = 6–6½. Reddish-brown to black.

Very widely in Europe and America.

Samarskite.

$R''_3R'''_2(Cb,Ta)_6O_{21}$, where R'' = Fe, Ca, UO_2 ; R''' = E. Cer = 1·2–6·4 ; Yttr = 4·72–21·2 ; $ThO_2 + ZrO_2 \rightarrow 7$ %.

Orthorhombic ; usually massive.

G = 5·6–5·8. H = 5–6. Deep velvet black ; opaque.

Miask ; Urals ; Mitchell Co., N. Carolina.

Schorlomite.

A titaniferous Garnet—$3CaO,(Fe,Ti)_2O_3,3(Si,Ti)O_2$. TiO_2 = 12·5–22 %.

Cubic ; usually massive.

G = 3·81–3·88. H = 7–7½. Black ; transparent in flakes.

Magnet Cove, Arkansas.

Senaite.

$(Fe,Mn,Pb)O,TiO_2$, cf. Ilmenite. TiO_2 = 49–52 %.

Rhombohedral ; isomorphous with Ilmenite, Geikielite, etc.

G = 5·3 (to 4·2 when weathered). H = 6½. Black.

Diamantina, Minas Geraes, Brazil.

Sipylite.

Columbate of E, Zr, Fe, U, Sn, etc. ; near Fergusonite (*q.v.*).

Cubic, in octahedra. Usually granular.

$G = 4·89$. $H = 6$. Brownish-black; translucent.
Amhurst Co., Virginia.

Steenstrupine.
A silicate of E, Fe, Na, Th, Mn, Al, Ti, H_2O, etc.; near Melanocerite. Cer = 14·4–32·5; Yttr = 0–15·9; ThO_2 = 2·1–7·1 %.
Rhombohedral.
$G = 3·38$. $H = 4$. Brown; faces dull.
Kangerdluarsuk, Greenland.

Strüverite.
$FeO,(Nb,Ta)_2O_5,4TiO_2$. TiO_2 = 69–71 %.
Tetragonal; angles very close to those of rutile.
$G = 5·0$. $H = 6–7$. Black; opaque.
Craveggia, Piedmont, Italy; and in Madagascar.

Tachyaphaltite.
An altered zircon, containing H_2O. ZrO_2 = 40–50 %.
Tetragonal; very close to Zircon.
$G = 3·6$. $H = 5\frac{1}{2}$. Dark brown.
Kragerö, Norway.

Tengerite.
Hydrated carbonate of E, Be, Ca, etc.; a weathered Gadolinite (*q.v.*). E_2O_3 = 39·2–47·8 %.
Amorphous.
White; opaque; very soft.
Llano Co., Texas.

Thalenite.
$H_2E_4Si_4O_{15}$, with traces of Fe''' and Al. Yttr = 58·6–63·9 %.
Monoclinic.
$G = 4·23$. $H = 6\frac{1}{2}$. Bright red and yellow.
Österby, Sweden.

Thorianite.
Mixed $ThO_2 + UO_2$, with E, Pb, Zr, Si, Fe, etc. ThO_2 = 72–79; Cer = 1–8 %.
Rhombohedral; pseudocubic.
$G = 8·0–9·7$. $H = 7$. Jet black; bright resinous lustre.
Gem-gravels of Ceylon.

Thorite.
$ThSiO_4$, with H_2O, U, Fe, E, Ca, Al, etc. ThO_2 = 41·4–57·9; E_2O_3 = 0–6 %.
Tetragonal; habit prismatic.
$G = 4·4–4·8$; $H = 4\frac{1}{2}–5$. Brown to black.
Various localities in Scandinavia.

Thorogummite.

$UO_3,3ThO_2,3SiO_2,6H_2O$? An altered Mackintoshite (*q.v.*) ? $ThO_2 = 41·4$; $E_2O_3 = 6·7$ %.

Usually massive; sometimes in crystals resembling Zircon.

G = 4·43–4·54. H = 4–4½. Dull brown; opaque.

Llano Co., Texas.

Thortveitite.

$E_2O_3,2SiO_2$, with Fe‴, Al, Mn‴ traces; E = chiefly Sc. Yttr = 54·5 %.

Orthorhombic, in radial aggregates.

G = 3·571. H = 6–7. Greyish green; translucent.

Iveland, Sätersdalen, Norway.

Titanite (Sphene, Grothite).

$CaSiTiO_5$, with Fe″, Mn″. $TiO_2 = 34–45$ % (usually 41 %).

Monoclinic; wedge-shaped.

G = 3·40–3·56. H = 5–5½. Yellow, green, or brown; pleochroism strong; lustre resinous.

Widely distributed in Europe and N. America.

Titanium Olivine.

$(H_2,Fe'',Mg)_2(Si,Ti)O_4$; Mn and F in traces. $TiO_2 = 3–12$ %.

Orthorhombic.

G = 3·25–3·27. H = 6½–7. Deep red to yellow; pleochroic.

Pfunders, Tyrol; Zermatt, Switzerland.

Tritomite.

A fluo-borosilicate of E, Th, Ca, with Zr, Na, H_2O, etc. Cer = 44·2–59·2 ; Yttr = 0·4–4·6 ; $ThO_2 + ZrO_2 = 0–10·6$ %.

Rhombohedral; in crystals resembling regular tetrahedra.

G = 4·15–4·25. H = 5½. Dark brown; transparent to opaque.

Langesund Fiord, Norway.

Tscheffkinite.

Titano-silicate of E, Th, Fe, Ca, etc. Cer = 23–47 ; Yttr = 0–3·4 ; $ThO_2 + ZrO_2 = 0–20$; $TiO_2 = 16–21$ %.

Massive, amorphous.

G = 4·26–4·55. H = 5–5½. Velvet black.

Ilmen Mountains; Nelson Co. and Bedford Co., Virginia, U.S.A.

Tysonite.

Fluoride of E, with Th, H_2O, CO_2, etc. Cer = 69·2–70·6 ; $ThO_2 = 0–31$ %.

Hexagonal; in thick prisms.

G = 6·12–6·14. H = 4½–5. Wax yellow; transparent to translucent.

Fahlun and Osterby, Sweden; Pike's Peak, Colorado.

Uhligite.

Titanate of Zr, Ca, Al; $Ca(Zr,Ti)O_3 + Al(Ti,Al)O_3$? $TiO_2 = 48$; $ZrO_2 = 22$ %.

Cubic; near to Perovskite (*q.v.*).

H = 5–6. Black. Transparent in flakes.

Lake Magad, E. Africa.

Uraninite.

Oxides of U (60–75 %), with PbO_2, ThO_2, ZrO_2, E_2O_3, Fe_2O_3, etc. Cer. = 0–2·7; Yttr = 0–10·2; ThO_2 = 1·6–11·1; ZrO_2 = 0–8·1 %.

Cubic, usually massive; alters to amorphous pitchblende.

G = → 6·4 (massive); → 9·7 (crystalline). H = 5½. Black; transparent in splinters.

Norway; Bohemia; Saxony; Cornwall; Carolina, etc.

Vietinghofite.

A hydrated ferruginous samarskite (*q.v.*). $E_2O_3 = 8·2$; $ZrO_2 = 1·0$ %.

Amorphous.

G = 5·53. H = 5½–6. Dull black; opaque.

Lake Baikal, Siberia.

Warwickite.

$6MgO,FeO,2TiO_2,3B_2O_3$? $TiO_2 = 23·5$ %.

Orthorhombic; habit prismatic, elongated.

G = 3·35–3·36. H = 3–4. Dark brown to black; pleochroic. Double refraction strong, +ve.

Edenville, New York State.

Weibyite.

Carbonate of E, with Ca, Sr, F, and H_2O; allied to Bastnäsite (*q.v.*). Cer = 66·96 % ?

Orthorhombic; in pyramids resembling those of Zircon.

Crystals are small, and covered with a thin yellow crust; they are intergrown with Parisite (*q.v.*)

Langesund Fiord, Norway.

Wiikite.

Titano-tantalo-silicate of Zr, Th, E, Fe, U, with Cb_2O_5, H_2O, etc. Cer = 2·5; Yttr = 7·6; Sc_2O_3 = 1·2; ThO_2 = 5·5; $ZrO_2 + TiO_2$ = 23·4 %.

Perfectly amorphous.

G = 4·85. H = 6. Black; opaque; infusible.

Impilaks, Lake Ladoga, Finland.

Wöhlerite.

Silicate and columbate of Ca, Zr, Na; $Si_{10}Zr_3Cb_2O_{42}F_3Ca_{10}Na_5$? ZrO_2 = 15·2–22·7 %. Cer, traces.

Monoclinic; prismatic or tabular habit.

G = 3·41–3·44. H = 5½–6. Light yellow; pleochroic.

Langesund Fiord.

Xenotime.

Phosphate of E, with ThO_2, SiO_2, Zr, etc. Cer = 0–11; Yttr = 54·1–64·7; ThO_2 = 1–5 %.

Tetragonal; isomorphous with Zircon?

G = 4·45–4·56. H = 4–5. Brown to yellow; opaque.

Diamond sands of Brazil; Norway.

Yttrialite (Green Gadolinite).

A weathered gadolinite (*q.v.*)—$E_2O_3,2SiO_2$. Cer = 6·6–8·2; Yttr = 43·4–46·5; ThO_2 = 10·8–12·8 %.

Amorphous, massive.

G = 4·6. H = 5½. Green to brown; translucent.

Bluffton, Llano Co., Texas.

Yttrocerite.

$Ca_3E_2F_{12}$, $1\frac{1}{2}H_2O$. Cer = 9·3–18·2; Yttr = 8·1–29·4 %.

Massive, granular.

G = 3·45. H = 4½. White to violet blue or brown.

Various localities in Scandinavia.

Yttrocrasite.

$(Ca,Pb)O,(Th,U)O_2,3E_2O_3,16TiO_2,6H_2O$. Yttr = 25·7; Cer = 2·9; ThO_2 = 8·7; TiO_2 = 49·7 %.

Orthorhombic; axial ratios unknown.

G = 4·80. H = 5½–6. Black; lustrous.

Burnet Co. Texas.

Yttrofluorite.

$nCaF_2 + mYF_3$ in isomorphous mixture? Yttr = 20-25; Cer = 1–2 %.

Cubic.

G = 3·54–3·56. H = 4½. Closely resembles fluorspar, except in badness of cleavage.

Northern Norway

Yttrogarnet.

A variety of garnet with E and Zr. Yttr = 1–6·7; ZrO_2 = 0–3 %.

Cubic (cf. Garnet).

Dark reddish brown (cf. Garnet).

Stockö, Norway; Schreiberhau, Germany.

Yttrogummite.

$UO_3, 3ThO_2, 3SiO_2, 6H_2O$? $E_2O_3 = 6{\cdot}7$; $ThO_2 = 41{\cdot}4$ %.
Tetragonal; angles near Zircon. Usually massive
G = 4·43–4·54. H = 4–4½. Yellowish brown.
Llano Co., Texas.

Yttrotantalite.

$R''R'''_2(Cb,Ta)_4O_{14} + 4H_2O$; R″ = Fe″, Ca; R‴ = E; Cer = 0–2·4; Yttr = 17·2–38·3 %.
Orthorhombic; isomorphous with Samarskite (*q.v.*).
G = 5·5–5·8. H = 5–6. Yellow to black.
Ytterby, Sweden; South Norway.

Zircon.

$ZrSiO_4$, with Fe, Th, etc., in traces. $ZrO_2 = 61{\cdot}0–70{\cdot}0$ %.
Tetragonal; habit prismatic.
G = 4·68–4·70. varying considerably. H = 7½. Colour very variable.
Widely distributed as a rock mineral, in sands, etc.

Zirkelite.

(Ca, Fe) $(Zr, Ti, Th)_2O_5$, with E, U, Mg, etc. $ZrO_2 = 48{\cdot}9–52{\cdot}9$; $ThO_2 = 0–7{\cdot}3$; $TiO_2 = 14–15$; $E_2O_3 = 0–3$ %.
Cubic; in twinned octahedra.
G = 4·7. H = 5. Black; transparent in thin flakes.
Jacupiranga, São Paulo, Brazil.

CHAPTER II

THE SILICATES

(a) Silicates of the Yttrium and Cerium Metals

Cerite.—Cerite is a silicate of the cerium metals, with small amounts of lime, ferrous oxide and water. Hintze gives the formula $H_3(Ca,Fe)Ce_3Si_3O_{13}$,[1] which Groth interprets as a basic metasilicate $(Ca,Fe)[CeO]Ce_2(OH)_3(SiO_3)_3$, *i.e.* a basic salt of the acid $H_6Si_3O_9$, a polymer of metasilicic acid, H_2SiO_3.

Crystals are not very common, the mineral usually occurring granular or massive.

> Crystals, orthorhombic, holosymmetric; $a:b:c = 0{\cdot}9988:1:0{\cdot}8127$. Usual forms—the Pinakoids *a*, *b*, and *c* {100}, {010} and {001}, prisms *m* {110} and *q* {130}, domes *u* {101}, *t* {301} and *n* {011}, and some pyramids {hkl}.
>
> Angles, $a \wedge m = 44° 58'$, $u \wedge c = 39° 8'$, $n \wedge c = 39° 6'$.
>
> The crystals usually occur as short prisms. No cleavage. Optical constants unknown. In flakes the absorption spectrum of didymium can be observed.
>
> The mineral is brittle; hardness 5 to 6 on Moh's scale; sp. gr. varies a little about 4·9. Fracture splintery; lustre dull, resinous. Colour brown to red and greyish-red, streak greyish-white. The mineral is almost opaque.

Cerite is infusible before the blowpipe. It is attacked

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[1] The symbol (Ca,Fe) here indicates that the iron and calcium occur in variable proportions, the variation however occurring in such a way that the equivalent of the two taken together is always the same, *i.e.* the iron can replace the calcium, or *vice versa*, atom by atom. The recognition of this possibility of 'Vicarious Replacement' between similar elements first brought order into the confused field of mineral chemistry, and allowed a systematic classification of minerals according to chemical composition to be made. Iron and calcium, or, according to the more convenient nomenclature of the mineralogists, lime and ferrous oxide, are here vicarious constituents.

The symbol Ce here stands for elements of the cerium group, which are never found singly.

readily by sulphuric acid, less easily by hydrochloric acid, with which it gives a gelatinous mass. Rammelsberg[1] found that the silica left behind on treatment of the powdered granular variety with the latter acid contained a variable proportion of bases, which he obtained and estimated after fusing the siliceous residue with sodium carbonate. From the different proportions of the earths in the part attacked by the acid and that left in the silica, he remarks, 'It would almost appear that Cerite is a mixture of silicates which are not all attacked with the same ease by hydrochloric acid.' Apparently without previous knowledge of this observation, Welsbach[2] noticed the same thing in 1884. He concluded that ordinary granular 'cerite' is a mixture of several minerals, among which there are at least two which contain rare earths. Of these, one, the chief constituent of the aggregate, is probably identical with the crystallised mineral, and is characterised by the readiness and completeness with which it is attacked by hydrochloric acid. The other does not react with hydrochloric, but is readily attacked by sulphuric acid; it contains yttria earths, in addition to the ceria earths. In the extraction of ceria earths from the mineral aggregate, Welsbach used hydrochloric acid, so leaving this second mineral unchanged; but to avoid loss of the rare earths, sulphuric acid is more commonly employed for the decomposition.

Though of great historical interest, cerite is of very small importance for the extraction of rare earths at the present time, on account of its very rare occurrence. The mineral seems to be almost entirely confined to the Bastnäs quarry near Ryddarhyttan, Sweden, where it is found with the rare earth silicate allanite (*q.v.*), biotite, hornblende, bismuth glance, chalcopyrite, etc. Here it was observed in 1751 by Cronstedt, who called it Tungsten (*vide supra*, p. 1). In 1781 Scheele examined a specimen of Wallerius's 'Tenn-spat' from Bipsberg, Dalecarlia, and found Tungstic Oxide (Acid), WO_3, in it.[3] After Scheele's work, the Ryddarhyttan mineral

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[1] *Pogg. Ann.*, 1859, **107**, 631.

[2] *Monats.*, 1884, **5**, 512.

[3] This mineral, which Scheele knew as Tungstein, is now called Scheelite.

was known as Red Tungsten, until Bergmann (1780) and d'Elhuyar (1784) showed that the two minerals were chemically distinct. They considered the red variety to be a silicate of iron and calcium, the rare earths being mistaken for lime. In 1804 Klaproth examined it, and found a new earth; he called the mineral 'Ochroite,' from its colour. In the same year, but independently of Klaproth, Berzelius and Hisinger made the same discovery; they called the mineral Cerite and the new metal Cerium, in honour of the discovery of the minor planet Ceres by Piazzi in 1801.

The analyses of cerite made in the earlier part of the nineteenth century resulted in some confusion. Klaproth in 1807 found 34·5 per cent. SiO_2 in a specimen (his Ochroite); Vauquelin in 1805, and Hisinger in 1810, found 17·0 and 18·0 per cent. respectively.[1] Hermann[2] called attention to this discrepancy in 1843 (and again in 1861), and declared that the two could not be the same. For Klaproth's mineral he proposed to revive the name Ochroite, whilst from his own analyses he proposed for the cerite of Berzelius the name Lanthanocerite, having found carbon dioxide and lanthanum, with much less cerium, in the latter.[3] In 1861 Kenngott partly explained these results by showing that the sample of cerite which Hermann had analysed contained Lanthanite[4]; but the extraordinarily high percentage of silica obtained by Klaproth remained unexplained. It may have been due to impurities of high silica content in the specimen he examined.

Cerite contains from 59·4 to 71·8 per cent. of rare earths (oxides), the amount and nature of which vary with the precise locality. The oxides consist chiefly of ceria, lanthana, and didymia (praseodymia and neodymia), the complexity of the so-called ceria having been shown by Mosander in the case of ceria separated from gadolinite as well as from cerite; but yttria earths are also found to a small extent in the mineral.

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[1] *Vide* Hintze, *Handbuch der Mineralogie*, Leipzig, 1897, ii. 1329.

[2] Hermann, *J. pr. Chem.* 1843, **30**, 194, and 1861, **82**, 406.

[3] The announcement of the discovery of Lanthanum by Mosander was made in 1839.

[4] Lanthanite (see list) is an hydrated carbonate, $R_2O_3,3CO_2,9H_2O$, where R = cerium metals, chiefly Lanthanum.

It is remarkable that neither thorium nor uranium has been found in cerite, which is thus practically unique among the rare earth minerals.

This anomaly becomes even more marked in view of the very high percentage of inert gases found by Tschernik[1] in a related mineral from Batoum. This is a very complex mineral in which the basic part is represented by rare earths, chiefly ceria earths (50·8 per cent.) with water (3·4 per cent.), and oxides of iron, calcium and copper (6·8 per cent.); the acidic oxides being silica (6·6 per cent.), zirconia (11·6 per cent.), and titanium dioxide (14·7 per cent.), with phosphorus pentoxide (3·2 per cent.), and sulphuric anhydride (1·7 per cent.). Traces of thoria are present, but no uranium; very considerable quantities (up to 1 per cent. ?) of helium were found.

It is somewhat heavier than cerite (sp. gr. 5·08), but otherwise resembles it closely.

Gadolinite (Ytterbite).—Gadolinite is a silicate of iron, beryllium, and the yttria earths, of the formula $2BeO,FeO,Y_2O_3,2SiO_2$, which may be written $FeBe_2Y_2Si_2O_{10}$. According to Groth, it is a basic orthosilicate, $Be_2Fe(YO)_2(SiO_4)_2$, derived from the acid $H_8Si_2O_8$. The beryllium content varies considerably, and some authors recognise two varieties of the mineral, one rich, and one poor in beryllium; but Scheerer pointed out in 1840 that iron and beryllium are probably vicarious constituents.

Analysis gives silica 21·8 to 25·3 per cent.; yttria earths 22 to 47 per cent.; ceria earths 5 to 31 per cent. In a variety from Ytterby, the rare earth Scandia was first found, forming up to 0·02 per cent. of the mineral. Small quantities of thoria, ThO_2 may be present, and traces of helium were found by Ramsay, Collie, and Travers. According to Strutt it contains also uranium and radium. Like cerite, it does not often occur crystalline, being usually found in amorphous masses.

The crystals are monoclinic; $a : b : c = 0·6273 : 1 : 1·3215$; $\beta = 89° 26\frac{1}{2}'$.

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[1] G. Tschernik, *J. Russ. Phys. Chem. Soc.* 1896, **28**, 345; 1897, **29**, 291. Abstracts in *Zeitsch. Kryst. Min.* 1899, **31**, 513 and 514.

Common forms are—Ortho-, clino-, and basal pinakoids, a {100}, b {010}, and c {001}, hemi-prisms m {110}, v {120}, clino-prisms w {012}, q {011}, and many others; and various hemi-pyramids {hkl} and {$\bar{h}$kl}.

Angles $a \wedge m = 32^\circ 6'$, $c \wedge q = 52^\circ 53'$, $c \wedge (101) = 64^\circ 9'$.

Crystals commonly prismatic, terminated by c. Faces rough and coarse; lustre vitreous to greasy, seen only on freshly-broken surfaces. Brittle. No cleavage. Fracture conchoidal to splintery. Hardness 6½–7; sp. gr. 4·0–4·5.

Colour black, greenish- and brownish-black; green and transparent in flakes. The crystalline variety has strong positive birefringence, with the plane of the optic axes parallel to (b), the plane of symmetry; the amorphous variety is of course isotropic. The brown variety shows very distinct pleochroism, *i.e.* the colour as seen by transmitted light varies with the direction in which the light traverses the crystal; the green kinds have much weaker pleochroism.

Gadolinite is of common occurrence in the pegmatite veins of the Scandinavian granite. It was first found in a felspar quarry on the island of Ytterby, near Stockholm, by a Lieutenant Arrhenius[1]; it is also found, together with a large number of other rare earth minerals, at Fahlun. It occurs in Norway on the islands of Hitterö and Malö, and in Germany in the Riesengebirge and the Harz. Probably the largest deposit is that in Texas, at Barringer Hill, near Bluffton, on the west bank of the Colorado River, Llano County, now owned and worked by the Nernst Light Company of Pittsburg; in 1904 a mass of very pure gadolinite weighing 200 lb. was found here.[2]

In the same place a decomposition product of gadolinite was discovered by Hidden and Mackintosh in 1889. They named it Yttrialite or Green Gadolinite. It contains no beryllium, and twice as much silica as the parent mineral, and approximates to the formula $R_2O_3,2SiO_2$, where R_2O_3 is chiefly yttria oxides; it is thus similar in composition to the newly found scandium silicate, Thortveitite (*q.v.*). It is amorphous and massive, and is often found in continuous growth with gadolinite. Pieces up to 10 lb. in weight have been obtained.

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[1] *Vide* Geijer, *Crell's Chemische Annalen*, 1788, 1, 229.

[2] See *U.S. Geol. Survey* (*Minerals*), 1904, 1213.

As stated above, Gadolinite was discovered by Arrhenius in 1788. Geijer examined it in the same year, and described it as a black zeolite. In 1794 it was analysed by Gadolin, who declared it to be a silicate of iron, aluminium, and a new element which he called Ytterbium. In 1797 Ekeberg examined it, and confirmed the discovery. He proposed the name Gadolinite for the mineral, and Yttria for the new earth; these names were accepted by Klaproth, who examined it with Vauquelin in 1800, and by the French crystallographer Haüy. In 1802 Ekeberg showed that the oxide originally taken for alumina was in reality beryllia; in 1816 Berzelius showed that ceria was present with the yttria.[1] About 1838 Mosander began his classical work on the earths in gadolinite. In that year he announced the separation of Lanthana,[2] and in 1842 that of Didymia, which he had actually discovered eighteen months earlier. In the latter year he announced [3] the separation of erbia and terbia. In 1842 also Scheerer [4] declared that the yttria from gadolinite was a mixture of earths, from its different behaviour on heating in closed and open vessels; but when Mosander announced the discovery of didymia (the announcement appears to have been hastened indeed by Scheerer's observation) it was agreed that the colouration observed was probably due to that earth. The further history of these earths must be continued elsewhere (*vide* p. 111).

The behaviour of gadolinite on heating is of great interest. When heated uniformly, in closed or open vessels, the mineral suddenly glows very strongly at a definite temperature (according to Hofmann and Zerban [5] at 430° C.), with considerable alteration in properties. The amorphous variety exhibits the phenomenon much more markedly than the crystalline form. The change in the two cases is entirely distinct, the only effect in common being that both varieties are rendered insoluble in acids after the glowing. The amorphous variety, in the act of glowing, changes to the crystalline form.

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[1] *Schweigg. J.*, 1816, **16**, 405.

[2] Berzelius (a letter to Pelouze), *Pogg. Ann.*, 1839, **46**, 648.

[3] *Berz. Jahres.*, **23**, 145; **24**, 105.

[4] *Pogg. Ann.*, 1842, **56**, 483.

[5] *Ber.*, 1903, **36**, 3095.

This phenomenon of phosphorescence, or glowing, on heating, with a change in properties, was first observed by Berzelius in 1816. He found that the oxides of many metals, *e.g.* chromium, tantalum, and rhodium, became denser and insoluble in acids after being heated. Later in the same year he observed the glowing, with a similar change in properties, in the case of a gadolinite from Fahlun.[1] Apparently without knowledge of this observation, Wollaston published a similar account of the glowing of a gadolinite in 1825. In 1840 Scheerer noted an almost identical change in the case of the mineral allanite (*q.v.*). Scheerer made a careful study of the phenomena in the cases of allanite and gadolinite.[2] In each case he found that the variety of lower specific gravity showed, on heating, a very strong phosphorescence, accompanied by change of colour and optical properties, and a marked increase of specific gravity. Gadolinite suffered no appreciable loss of weight, but allanite had lost a little water after the change. Careful measurement of the specific gravity before and after the change showed, in the case of two varieties of gadolinite and one of allanite, that the volume had decreased in the ratio 1 : 0·94. Scheerer assumed that this ratio was constant for all such cases, and advanced a general explanation. We know now that numerous cases of similar phenomena occur, in which the change of volume is quite different; but Scheerer's explanation is so ingenious, and so foreshadows some modern theories, that it is given here in full.

He ascribes the alteration to 'interatomic change, involving change of relative position of atoms and decrease of interatomic distances.' (Scheerer and the chemists of that period understood by atoms the ultimate particles of a body, making no distinction between elements and compounds; in this case he meant by atoms what we mean by molecules, and the word 'molecule' has therefore been substituted for 'atom' in what follows.) The change is simply one of closer packing of the molecules, which take up a more stable position with liberation of energy as heat and light. He imagines

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[1] *Schweigg. J.*, 1816, **16**, 405.
[2] *Pogg. Ann.*, 1840, **51**, 493.

his molecules as uniform spheres arranged in horizontal layers, as shown in Fig. 1. In placing one layer vertically over another there are three possible arrangements, of which only two concern us. In the arrangement for closest packing, B, say, a molecule of any one layer touches three molecules in each of the layers above and below, which with the six it touches in its own layer make twelve altogether. In the next closest arrangement, A, say, a molecule of any one layer touches only two molecules in each of the layers above and below it, so that one molecule is in contact with ten others altogether.

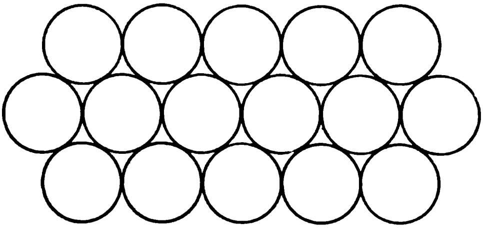

Fig. 1

Now it can be shown that the volumes of equal numbers of molecules in the arrangements A and B will be to one another as the height, H, of an equilateral triangle, to the height, *h*, of a regular tetrahedron whose edges are equal to the sides of the triangle, a length R (which will be equal to the diameter of a molecule).

$$\text{Then } H = \tfrac{1}{2}R\sqrt{3}, \quad h = R\sqrt{\tfrac{2}{3}}.$$

Then vol. in arrangement A : vol. in arr. B :: $H : h$

i.e. :: $\frac{\sqrt{3}}{2} : \sqrt{\frac{2}{3}}$

:: $1 : 0{\cdot}943$.

That is, the volume changes in the ratio 1 to 0·943, the amorphous variety of gadolinite consisting of molecules in arrangement A, which go over to the closer packed arrangement B in the change to the crystalline form.

More extended work has shown that this ingenious and interesting explanation is not of general application. Thus

H. Rose[1] found that samarskite (*q.v.*) exhibited the phenomenon of glowing, but that the specific gravity was actually less after the change than it was before, *i.e.* there was an increase of volume. Damour observed glowing in the case of zircon from Ceylon (*q.v.*) with increase of density, the volume change being from 1 to 0·922, *i.e.* even greater than for gadolinite. Again, Hauser[2] observed in the case of his new rare earth mineral risörite a sudden change at a red heat, the mineral losing water, becoming very brittle, and increasing very considerably in specific gravity (the volume changing from 1 to 0·90 approximately), but without glowing. Ramsay and Travers[3] found that fergusonite (*q.v.*) glowed strongly when heated to 500°–600°, with decrease of specific gravity (5·62 before to 5·37 after), evolution of all its helium, and very considerable evolution of heat; they suggested that helium was present in combination, in an endothermic compound decomposed by heat, but in view of the properties of helium, this hypothesis seems hardly tenable.

It appears unlikely that any one explanation can cover all these interesting facts; there are in each case peculiar factors to be taken into account. In 1841, Regnault,[4] considering the case of the oxides observed by Berzelius, inferred that the development of light and heat denoted that the bodies possessed a lower specific heat after the change than before. The experimental difficulties encountered in attempting to dry the oxides prevented him from confirming this view. He measured the specific heats of the minerals calcite and aragonite ($CaCO_3$), and of the two allotropic modifications of phosphorus, but could observe no appreciable differences. H. Rose (*vide supra*) showed by experiment that considerable heat was evolved on the glowing of gadolinite, with a decrease of about one-fourteenth in the specific heat. In the case of samarskite there was, however, no appreciable evolution of heat, nor could he determine any difference in the specific heats before and after glowing.

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[1] *J. pr. Chem.* 1858, **73**, 391.

[2] *Ber.* 1907, **40**, 3118.

[3] *Zeitsch. physikal. Chem.* 1898, **25**, 568.

[4] *Pogg. Ann.* 1841, **53**, 249.

Probably the only inference that can be safely drawn is that in most cases the change is due to some molecular re-arrangement. The evolution of water, helium, etc., in some cases, may possibly be due to intramolecular change, but on the one hand the current view at present is that the helium is mechanically held in radio-active minerals, and on the other hand it is not known that the water evolved is water of constitution; in an intermolecular change at fairly high temperature, these might be evolved without disruption of the true mineral molecules. The question of the energy involved, and consequently of the specific heats, appears to depend on factors peculiar to each case, of which at present no accurate conception can be formed; and the change in specific gravity is probably bound up with these. The loss of solubility in acids is a factor not always connected with glowing, as it is frequently observed in the laboratory after ignition of compounds, but here again no adequate explanation is forthcoming.

The possibility of chemical change in one or two cases, however, must not be ignored. Thus ammonium magnesium phosphate, NH_4MgPO_4, on heating glows, and is converted to magnesium pyrophosphate, according to the equation:

$$2NH_4MgPO_4 = Mg_2P_2O_7 + H_2O + 2NH_3$$

A case possibly analogous to this is that of the mineral sipylite (*q.v.*), $R'''_2Cb_2O_8$, with 'basic water' (*i.e.* R''' partially replaced by H). Before the blowpipe this decrepitates with loss of water, and glows brilliantly. The specific gravity after the change does not appear to have been determined. Mallet explains the glow as due to a change to the pyrocolumbate.

Similar explanations may possibly hold in the cases of allanite and risörite, but it must be remembered that we are really ignorant of the part played by the water in these minerals.

Allanite.—Allanite, or Orthite, as it is often called, is a mineral of the epidote family, containing rare earths. The general formula for Epidote is $H_2O,4R''O,3R'''_2O_3,6SiO_2$, where R'' is a divalent and R''' a trivalent metal, or vicarious series of metals. In the case of Allanite, $R'' = (Fe'',Ca)$, $R''' = (Al,Fe''',E)$, where E stands for metals of the cerium and yttrium groups (Engström's formula). Groth formulates it as a basic salt, $R'''_3(OH)R''_2Si_3O_{12}$, of the acid $H_{12}Si_3O_{12}$ ($= 3H_4SiO_4$).

Crystals are fairly common, but the mineral usually occurs massive or in rounded grains.

Crystals—Monoclinic, holosymmetric; $a : b : c = 1{\cdot}5509 : 1 : 1{\cdot}7691$, $\beta = 64° 59'$.

Common forms—Ortho- and basal pinakoids *a* {100} and *c* {001}; *m* {110} and other prisms, *e* {101} and other hemi-ortho-prisms, *o* {011}, *d* {111} and other hemi-pyramids.

Angles, $(100) \wedge (110) = 54° 34'$; $(001) \wedge (101) = 63° 24'$; $(001) \wedge (011) = 58° 3'$.

Tabular, parallel to *a*, or long and slender by elongation parallel to axis *b*.

Birefringence weak, variable. Refraction strong. Colour brown to brownish-black; almost opaque. In flakes very strongly pleochroic, the colours for light parallel to the three vibration directions **c**, **b** and **a** being brownish-yellow, reddish-brown, and greenish-brown respectively.

Brittle. Hardness 5½–6; sp. gr. 3·5–4·2.

On heating, allanite becomes amorphous and isotropic with increase of specific gravity (cf. Gadolinite). Before the blowpipe it loses water, and melts to a black magnetic glass, many varieties phosphorescing strongly (*vide supra*). With hydrochloric acid it gelatinises, unless previously heated strongly, in which case it is not attacked.

Analyses show that the rare earth content varies considerably (vicariously as regards ferric iron and aluminium), ceria earths varying from 3·6 to 51·1 per cent. and yttria earths from traces up to 4·7 per cent.[1] Thoria is usually present, 0 to 3·5 per cent. In 1909 Fromme[2] found small quantities of beryllia in the mineral, and in 1911 Meyer[3] found amounts of scandium oxide up to 1 per cent. It contains traces of uranium, and is weakly radioactive. Ramsay, Collie and Travers found no helium (1895), but in 1905 Strutt found

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[1] *Vide* Schilling, pp. 70–75 for analyses of this mineral.

[2] Fromme, *Tsch. Min. Mitt.* 1909, 28.

[3] Meyer, *Sitzungsber. königl. Akad. Wiss. Berlin*, 1911, 379.

radium in it, so that the presence of helium seems *a priori* probable.

Many varieties of the mineral are known, differing in habit, colour, water content, specific gravity, etc., and the percentage composition varies very much by reason of vicarious replacement of the bases. Goldschmidt[1] has found 'Epidote-orthites' which are isomorphous mixtures of orthite with an iron epidote; he concludes that most orthites are probably similar solid solutions, and in this way accounts to a large extent for the varying composition.

Allanite is of very wide distribution, though it is not often found in large quantities. The usual occurrence in pegmatitic veins in granites, syenites and other acid plutonic rocks has been often noted, *e.g.* in many parts of Sweden and Norway. It is found also in the extinct crater now forming the Laacher See, near Coblenz, Germany, and at Impilaks, near Lake Ladoga, on the border of Finland; a mass of the pure mineral weighing 300 lb. was recently discovered at Barringer Hill, (cf. under Gadolinite), and it occurs in large quantities in Amherst Co., Virginia. It is an accessory constituent of many acid volcanic and hypabyssal rocks, and has been found also in limestone, and in magnetic iron ores. On account of its exceedingly wide distribution, and the variations in appearance and composition, it has been repeatedly described under various names, varieties being constantly mistaken for new mineral species.

Its history is rather curious.[2] In 1806 the Danish mineralogist Giesecke made a protracted voyage to Greenland, collecting minerals and rocks; he remained there until 1813. In 1808 he sent off his first collection by ship to Copenhagen; on the voyage the ship was taken by an English privateer, and the cargo landed and sold at Leith. The minerals were bought by Allan, a Scotch mineralogist, who recognised that they were from Greenland by the presence of cryolite, at that time only known to occur in Greenland. He mistook the mineral subsequently named after him for gadolinite, and sent it to

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[1] *Centr. Min.* 1911, 4.

[2] *Vide* Schilling, pp. 75–76, where full references are given.

Thomson for analysis.[1] Thomson recognised it as a new mineral, and named it Allanite (1810). In 1815 Hisinger described a mineral from Ryddarhyttan, Sweden, which he called Cerin; Leonhard (1821) and Hauy (1822) showed that this was identical with Allanite. In 1818 Berzelius described two varieties of a mineral from Finbo, near Fahlun, Sweden, which he called Orthite, and Pyrorthite; these were eventually shown by Scheerer (1844) to be varieties of Allanite. In 1824 the French mineralogist Lévy described a mineral from Arendal, Norway, which he named Bucklandite, in honour of the English naturalist; in 1825 this was identified with a 'black zeolite' from the Laacher See by G. Rose, and in 1828 both were shown by Hermann to have the same composition as orthite or allanite. The list might be extended at will; the Tautolite of Kokscharow (1847), the Bodenite of Breithaupt (1844), the Muromontite of Kerndt (1848), and the Vasite of Bahr (1863) have all been shown to be varieties of the same bewildering mineral.

Hellandite.—Hellandite[2] is a mixed silicate of rare earths with lime, magnesia, alumina, ferric and manganic oxides, with considerable quantities of water. The formula approximates to $3H_2O,2R''O,3R'''_2O_3,4SiO_2$, where $R'' = (Ca,Mg,\frac{Th}{2})$—Thorium being able to replace two atoms of calcium or magnesium—and $R''' = (Al,Fe''',Mn'''$ and rare earth metals). This may be written as a basic orthosilicate, $R''_2[R'''(OH)]_6(SiO_4)_4$, a basic salt of the acid $H_{16}Si_4O_{16}$ $(= 4H_4SiO_4)$. This composition puts it in the class containing topaz and some rarer silicates.

The mineral is crystalline, the crystals being well developed, but often dull and opaque by alteration (hydration).

> Crystal system—Monoclinic, holosymmetric, $a:b:c = 2{\cdot}0646:1:2{\cdot}1507$. $\beta = 109°\,45'$. Habit usually prismatic, with $\{100\}$, $\{010\}$, and several prisms $\{hko\}$, terminated by various pyramid forms.

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[1] See Kobell's *Geschichte der Mineralogie*, 1864, p. 679.

[2] Brögger, *Zeitsch. Kryst. Min.* 1906, **42**, 417.

Angles (100)∧(001) = 70° 32′; (100)∧(110) = 62° 22′; (010)∧(110) = 27° 14′; (110)∧(1$\bar{1}$0) = 125° 0′.

Twinned on (001), twin plane (001), forming knee-shaped twins. Hardness varies from 5½ in the least altered to 1 in the most altered specimens; sp. gr. 3·70 in least altered specimens, decreasing with hydration. Colour of fresh crystals, reddish-brown; on alteration they become brownish-black, yellow, or even white.

The mineral dissolves easily in hydrochloric acid, with evolution of chlorine; it is less soluble in nitric and sulphuric acids. It readily fuses to a yellow mass.

It was first discovered by Brögger at Lindvikskollan, in 1903, and later, in larger quantities, at Kragerö in Norway. It occurs in pegmatite veins in granite.

Thalénite.[1]—A silicate of yttria earths with water and small quantities of alumina, ferric oxide, carbon dioxide and alkalies. The ratio of rare earths to silica gives the formula $R_2O_3,2SiO_2$, or $R_2Si_2O_7$; if the water be included, the formula becomes $H_2R_4Si_4O_{15}$. The presence of both water and carbon dioxide indicates, however, that the mineral has been somewhat altered, and the simpler formula $R_2Si_2O_7$ (cf. Thortveitite, below) probably expresses the composition of the original mineral. It contains considerable quantities of nitrogen and helium, though uranium and thorium appear to be absent.

Monoclinic; $a : b : c = 1·154 : 1 : 0·602$. $\beta = 80° 12'$.

Common forms are the pinakoids {100} and {010}, hemi-prism {110}, hemi-pyramids {111} and {11$\bar{1}$}, and others, and the hemi-dome {021}.

Angles, (100)∧(010) = 91° 0′; (100)∧(110) = 48° 9′; (100) : (111) = 59° 4′.

Double refraction weak. No cleavage. Brittle. Hardness 6½. Colour, bright flesh-red; translucent, with greasy lustre; sp. gr. 4·227, increasing to 4·29 after ignition. A yellow variety has sp. gr. 4·11–4·16, and is transparent.

The 'average atomic weight' of the rare earth metals is 99, from which it appears that these consist chiefly of yttrium, with a smaller quantity of the metals of higher atomic weight.

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[1] Benedicts, Abstract in *Zeitsch. Kryst. Min.* 1900, 32, 614.

It was discovered in 1898 by Benedicts, accompanying fluocerite (*q.v.*) in a quartz quarry at Oesterby in Dalekarlia.

Thortveitite.[1]—A silicate of yttria earths, chiefly scandia, of the formula $R_2O_3,2SiO_2$. Scandia forms about 37 per cent. of the whole (R. J. Meyer); yttria with small quantities of the other yttria earths forms the bulk of the remainder of the bases, the ceria group being almost completely absent. Ferric oxide (with traces of manganic oxide and alumina) forms about 3 per cent. Thorium is present only in traces, and radioactivity is barely perceptible.

Thortveitite is the first mineral to be discovered in which the content of scandia is greater than 2 per cent.; in 1908 Crookes[2] examined a very large number of yttria minerals for scandia, and finally chose for extraction of the earth Wiikite (*q.v.*) which has a scandia content of 1·2 per cent.[3]

Thortveitite is orthorhombic; $a:b:c = 0{\cdot}7456:1:1{\cdot}4912$; commonly combinations of pyramids *o* {111} and *s* {211} with prism *m* {110}, in radial aggregates of crystals elongated parallel to the *c* axis. Cleavage parallel to *m*, fair. Twin plane *m* (110), twinning very common.

Refraction strong; birefringence strong, negative. Acute bisectrix perpendicular to (001), plane of the optic axes (010). Hardness, 6–7; sp. gr. 3·571. Extremely brittle; lustre brilliant, vitreous to adamantine. Colour, greyish-green, white to reddish-grey on alteration; in transmitted light yellowish-green, after ignition, reddish; the change being probably due to presence of oxides of iron.

It is fusible with difficulty, and only partially attacked by hydrochloric acid. It was found by Thortveit, in 1910, in a pegmatite vein in granite, at Iveland, Sätersdalen, S. Norway, accompanied by euxenite, monazite, beryl, and the usual vein-materials (quartz, felspar, etc.). It was analysed and recognised as a new mineral by Schetelig (*loc. cit.*).

The following minerals, of which particulars will be found in the alphabetical list, also belong to this class:

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[1] J. Schetelig, *Centr. Min.* 1911, 721.

[2] *Phil. Trans.* 1908, A, **209**, 15.

[3] According to Eberhard, some varieties of Wiikite have a much lower scandia content.

Bagrationite, Bodenite, and *Muromontite,* varieties of allanite with differences in composition and physical properties.

Yttrialite, a weathered variety of gadolinite.

Elpidite, Erdmannite and *Cainosite,* more complex silicates.

Rowlandite, a comparatively simple silicate of the yttrium metals.

Yttrogarnet, a variety of garnet containing yttrium metals.

(*b*) SILICATES OF THORIUM AND ZIRCONIUM

Thorite.—Thorite and its variety Orangite are somewhat altered forms of a pure silicate of thorium, $ThSiO_4$, containing also small quantities of water, usually uranium, and often rare earths, with iron, lead, calcium, and aluminium. Orangite differs from thorite in its beautiful orange colour and greater specific gravity. Both varieties are radio-active.

When unaltered, the crystals are tetragonal and uniaxial, the pure mineral $ThSiO_4$ being isomorphous with zircon, $ZrSiO_4$ (*q.v.*). By alteration they become isotropic.

Crystals are tetragonal, holosymmetric; $c = 0{\cdot}6402$; $p \wedge p' = 56° 40'$.

Common forms are the prism m {110} with the pyramids p {111} and z {311}.

Hardness 4½–5; sp. gr. 4·4 to 4·8 for thorite, 5·2 to 5·4 for orangite.

Thorite contains from 1·4 to 3·1 per cent. of rare earths. According to Nilson and Blomstrand, the uranium is present as uranium dioxide, UO_2 replacing thoria, ThO_2, but Dunstan and Blake state that the two oxides are isomorphous (see under Thorianite, p. 74), and so they might be expected to be vicarious. Thorite was discovered by Esmark in 1828, and first analysed by Berzelius,[1] who announced the discovery of a new earth in it in 1829. The name Thorite is from Thor, the god of Scandinavian mythology.

Thorite is a member of a peculiarly interesting series of isomorphous minerals, which includes Cassiterite (SnO_2), Rutile (TiO_2), Zircon ($ZrSiO_4$), and most probably the allied silicate Naegite, and the rare earth phosphate Xenotime

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[1] *Pogg. Ann.*, 1829, **16**, 385.

(*q.v.*), which are very similar in forms and angles. The oxide TiO_2 is itself trimorphous, being known in the three crystallographically different forms, Rutile, Anatase, and Brookite (*q.v.*). On account of the isomorphism of cassiterite and rutile with the two silicates, it has been suggested that the oxide formulæ be doubled and written $Sn(SnO_4)$ and $Ti(TiO_4)$ respectively,[1] to show the analogy with $Th(SiO_4)$ and $Zr(SiO_4)$. Consideration of the molecular volumes (obtained by dividing molecular weight by specific gravity, *i.e.* multiplying by specific volume) lends a certain amount of support to this view. It has often been observed that isomorphous compounds, and many compounds which occur in parallel growth to one another, have nearly equal molecular volumes; there are, however, many exceptions. Taking molecular volumes for the series under consideration, we have, using approximate numbers only—

	Mol. Wt.	Sp. Gr.	Mol. Vol.
Cassiterite, SnO_2 . .	151	6·9	22
Rutile, TiO_2 . . .	80	4·2	19
Zircon, $ZrSiO_4$ . . .	182	4·7	39
Thorite, $ThSiO_4$ . .	325	5·4 (Orangite)	60
Xenotime, XPO_4 . .	184	4·5	41

It will be seen that if the numbers for cassiterite and rutile be doubled, four out of the five show very fair approximation to the constant value 40. The number 60 for thorite is quite irreconcilable with the values obtained from the other members; of course pure silicate of thorium, $ThSiO_4$, is not known as a mineral, but it is most unlikely that the relatively small amount of impurity in the densest specimens of orangite should have depressed the specific gravity by over two units, as would be required if the molecular volume of thorite were to show even the most approximate semblance of agreement with the others. It cannot be too often remarked, however, that very little indeed is known of the molecular formulæ of minerals, and that very little reliance can be placed on such

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[1] This isomorphous series has recently been extended by Zambonini, and also by Schaller, by the inclusion of minerals containing Columbium and Tantalum; see under Ilmenorutile and Struverite, end of Ch. IV., p. 71.

figures as the above. On the contrary, it is hardly conceivable that amphoteric oxides like those of tin and titanium, occurring in the form of heavy crystalline minerals, should have molecular formulæ only double the empirical formulæ. Where agreements of the kind do occur, they must be taken as indicating approximately equal degrees of molecular complexity in the minerals concerned, rather than as affording any real insight into the molecular condition.

Zircon.—Zircon is a silicate of zirconium, $ZrSiO_4$, with small quantities of other elements. Most varieties contain ferric oxide and thoria; more rarely small proportions of the yttria earths may be present. All varieties contain traces of a large number of the common metals. Traces of radium are usually present, with helium and neon,[1] and the mineral is strongly radioactive.

> System tetragonal, holosymmetric sub-class. $c = 0{\cdot}6404$; $(001) \wedge (101) = 32° 38'$.
>
> Usual forms—Prisms *a* {100} and *m* {110}; pyramids *e* {101}, *p* {111}, *u* {221} and *x* {311}, etc. The basal pinakoid *c* {001} is rare. The usual combination is one or both of the prisms *a*, *m*, with one or two pyramids. Twinning is rare, the twin plane being *e* (101), giving knee-shaped twins similar to those so characteristic of cassiterite and rutile. Cleavage ‖ *m* imperfect, ‖ *p* bad.
>
> Brittle; conchoidal fracture. Hardness 7½; sp. gr. usually 4·68–4·70, but varying from 4·2 to 4·86. Adamantine lustre. Clear and colourless to yellow-, red- or greenish-brown. Transparent to opaque. Refraction and double refraction strong, double refraction positive ($\omega = 1{\cdot}924$, $\epsilon = 1{\cdot}968$, for sodium light); on heating it becomes biaxial, and occasionally is found biaxial in nature. By alteration it becomes isotropic.

It is infusible before the blowpipe, but loses its colour; some varieties glow and increase in density (see p. 38). In some varieties also the colour changes or disappears rapidly on exposure to sunlight, and is often restored on keeping in the dark. These phenomena of colour change have been

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[1] Strutt, *Nature*, 1906, 102.

attributed variously to alteration in the state of oxidation of the iron present, and to the presence of organic matter. It seems probable that either cause or even both may be at the root of the change in particular cases.

On account of the hardness, unalterability, and strong refraction and double refraction, good crystals of zircon are used as gems. The two gem varieties, Hyacinth and Jargon, are found chiefly in the gem gravels of Ceylon. It was in a zircon from Ceylon that Klaproth discovered the new earth, Zirconia, in 1789.[1] In 1795 he found the same earth in hyacinth, and so showed the two to be identical.

Artificial crystals of zircon have been obtained by the action of silicon tetrachloride and silicon tetrafluoride on zirconia, and by the action of zirconium tetrafluoride on silica at high temperatures.

Zircon is one of the most widely distributed minerals known, though usually it occurs in very small quantities. Good crystals have been found in New Zealand, in Ceylon, at Miask in the Urals, and in North Carolina. This last deposit has been worked commercially for the extraction of zirconia for Nernst lamps (*vide* p. 320). It occurs in a decomposed felspar in a pegmatite dyke in the Archæan gneiss near Zirconia, Henderson Co., and can be easily extracted by picking or washing, after crushing if necessary. Should there ever be a considerable demand for zirconia, it could doubtless be saved as a by-product in the extraction of thoria from monazite sands (*q.v.*), zircon being very generally found in those sands (see below).

Zircon is common in crystalline rocks, limestones, schists, syenites, granites, etc. It is a constant accessory constituent in the acid igneous rocks, especially in the more acid eruptive rocks. It is readily detected under the microscope by the pleochroic haloes with which the tiny crystals are surrounded; these have been shown by Joly to be due to alteration of the surrounding rock by the radiations emitted by the radio-active constituents of the zircon. It also occurs as a constituent of those sands which are formed by the erosion of the igneous

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[1] *Schriften der Gesellschaft naturförschender Freunde in Berlin*, 1789, vol. 9.

rocks in which it is enclosed, and hence it almost invariably accompanies monazite in the so-called monazite sands.

Zircon is one of the least easily altered minerals; by the prolonged action of chalybeate and other waters, during many geological ages, however, it gradually changes, losing silica and gaining lime, oxides of iron, and water. Some of these altered varieties have received special names, as, *e.g.* Auerbachite, Malacone, Cyrtolite, and Alvite; but none of them is of special interest.

Naegite.[1]—This rare mineral is a silicate closely related to zircon, but of rather more complex composition. It may be represented as silicate of zirconium, $ZrSiO_4$ (zirconia = 55·3, silica = 20·6 per cent.), with rare earths (chiefly yttria, 9·1 per cent.), uranium (UO_3 = 3 per cent.), and thorium (ThO_2 = 5·0 per cent.), partly as silicates, partly as columbates and tantalates ($(Cb,Ta)_2O_5$ = 7·7 per cent.).[2]

It is tetragonal, usually occurring in globular aggregates of crystals. The measurable angles are extremely close to those of zircon, and it is probable that naegite is isomorphous with the series mentioned above under Thorite.

The hardness is 7½, the sp. gr. 4·091. The colour is dark green or brown, becoming dull by weathering. The double refraction is extremely weak.

So far it has only been found in the 'placer' tin deposits or 'gravel tin' of Japan.

The following minerals (see list) are also to be included in this sub-class:

Alvite (Anderbergite or Cyrtolite), *Auerbachite, Malacone Oerstedite* and *Tachyaphaltite,* altered varieties of zircon.

Calciothorite, Eucrasite and *Freyalite,* altered varieties of Thorite.

Pilbarite, Thorogummite and *Yttrogummite,* hydrated silicates of thorium with uranium and other metals.

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[1] *Beiträge zur Mineralogie von Japan,* 1906, 2, 23.

[2] An earlier analysis (*Abstr. Chem. Soc.* 1905, 88, [ii.], 177) gave over 20 per cent. of uranous oxide, UO_2; the greater part of this appears to have been zirconia, ZrO_2.

(c) COMPLEX SILICATES

Eudialyte (Eucolyte).—This is a complex silicate of alkalies, lime, ferrous oxide, rare earths, etc., containing chlorine and a high proportion (up to 17 per cent.) of zirconia. The empirical formula is given by Dana as $Na_{13}(Ca,Fe)_6Cl(Si,Zr)_{20}O_{52}$. Brögger gives the simpler metasilicate formula $R'_4R''_3Zr(SiO_3)_7$, where $R = (Na,K,H)$, $R'' = (Ca,Fe,Mn,CeOH)$, and Zr(OCl) may partly function as an acid in place of SiO_2. The true formula, however, is quite uncertain, as the zirconia may function either as an acidic or basic oxide. The fact that a mineral of such exceedingly complex composition occurs in perfectly well-defined crystals indicates the intricate nature of the problems to be solved in mineral chemistry.

The crystals are rhombohedral, $a : c = 1 : 2{\cdot}1116$.

Common forms are—the pinakoid *c* {111}, prisms *a* {101}, and *m* {211}, and pyramids *r* {100} and *e* {110}. $c \wedge r = 31° 22'$. Habit tabular parallel to *c*, rhombohedral with *e* prominent, or prismatic with *a* prominent.

Cleavage $\parallel c$ very good, $\parallel a$ difficult.

The colour is brown or red to brownish- or bluish-red. Brittle. Hardness 5 to 5½; sp. gr. 2·92 for eudialyte, 3·0 to 3·1 for eucolyte.

The double refraction is strong, being positive for eudialyte, negative for the Norwegian variety, eucolyte. From careful microscopic examination, Ramsay has found that zones of positive and negative birefringence, as well as isotropic (singly-refracting) zones can occur on the same crystal, and he suggests that the mineral is really composed of two isomorphous compounds forming mixtures. In view of the continuous variation of optical properties in an isomorphous series like the felspars, such an explanation seems doubtful. The optical behaviour of minerals is very often anomalous, and the phenomena in this case are probably due to repeated twinning, with some alteration in the double refraction, or to the lamellar intergrowth of two varieties having slightly different optical properties.

On heating, the mineral evolves moisture and readily fuses. It is easily attacked even by dilute acids, being named by Strohmeyer (1819) on account of this property. The dilute hydrochloric acid solution reddens turmeric paper—a test for the presence of zirconium.

It is found in Greenland, usually embedded in felspar, in Norway, in Lapland and in Arkansas, being generally associated with minerals rich in alkalies, *e.g.* ægirine, elæolite, nepheline, sodalite, arfvedsonite, etc.

Beckelite.—This is a mineral similar in composition to eudialyte, though not so complex, and of more recent discovery.[1] It is a silicate of ceria earths and lime, in which zirconia replaces silica; the oxygen ratio (*i.e.* ratio of oxygen in basic oxides to oxygen in acid oxides) is 3 : 1, and the formula $Ca_3R'''_4(Si,Zr)_3O_{15}$, where $R =$ rare earth metals, chiefly of the cerium group. It is thus a salt of an acid $H_{18}Si_3O_{15}$ [$= 3H_6SiO_5 = 3(3H_2O,SiO_2)$] with zirconium and silicon vicarious.

The crystals appear to belong to the cubic system, occurring in cuboid grains, and in octahedra and dodecahedra. It is brown, and isotropic, with cubic cleavage. Sp. gr. = 4·15.

It is soluble in hot hydrochloric acid, even after ignition; the solution gives the turmeric test for zirconium.

It was found in a dyke in an elæolite syenite, near the Sea of Azov.

The following minerals (see list) are also to be placed in the class of mixed silicates:

Arfvedsonite and *cataplejite*, complex zircono-silicates.

Hiortdahlite (Guarinite) and *Lavenite*, zircono-silicates with fluorine.

Caryocerite, *Melanocerite* and *Steenstrupine*, complex fluosilicates.

Auerlite, *Britholite*, *Erikite* and *Florencite*, phospho-silicates.

Cappelenite, *Homilite* and *Tritomite*, boro-silicates.

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[1] *Abstr. Chem. Soc.* 1905, 88, ii, 177.

CHAPTER III

THE TITANO-SILICATES AND TITANATES

(a) THE TITANO-SILICATES

Yttrotitanite or Keilhauite.—A titano-silicate of calcium, aluminium, iron and yttrium metals. The mineral is isomorphous with titanite, CaO,TiO_2,SiO_2 (*q.v.*), and is itself probably an isomorphous mixture of titanite with the silicate $(Y,Al,Fe)_2SiO_5$, where Y = yttrium metals. Its composition will then be represented by the formula $m\ (Y,Al,Fe)_2(SiO_5) + n\ CaTi(SiO_5)$.

> It is monoclinic, with axial ratios and angles very close to those of titanite. Usual forms—pinakoids *a* {100} and *c* {001}, hemi-prism *m* {110}, hemi-pyramids *n* {111}, *e* $\{\bar{1}11\}$ and *l* $\{\bar{1}12\}$. Cleavage ‖ *n* distinct. Birefringence weak, +ve. Colour brown to brownish-black. Hardness 6½; sp. gr. 3·52 to 3·77.

The mineral is fusible before the blowpipe, and is decomposed by hydrochloric acid.

It was named by Scheerer in 1844 from its composition, and by Ekeberg in the same year in honour of the Norwegian geologist Keilhau.

Titanite or Sphene.—This species, important as an accessory mineral of many rocks, is a titano-silicate of calcium, generally containing small quantities of aluminium and iron. The approximate formula usually given, $CaTiSiO_5$, is unsatisfactory; some specimens contain as much as 7 per cent. of ferric oxide, others up to 2 per cent. of manganese, whilst the percentage of titanium oxide, TiO_2, varies very considerably (30 to 45 per cent.). Zambonini and Nickolan have independently analysed specimens for which no satisfactory formulæ could be deduced. For specimens containing trivalent metals, Groth considers the mineral to be an isomorphous mixture of $CaTiSiO_5$ and R'''_2SiO_5 (see under Yttrotitanite, above); Blomstrand, however, advances the formula $2(R''R'''_2O_2,TiO)O,SiO_2$, where TiO is basic, and the trivalent metals occur in the divalent group R'''_2O_2; this formula is also supported by Zambonini.

More recently the problem of the constitution has been attacked by Bruckmoser, using Tschermak's method of determining the nature of the salts present in silicates. In this method, the mineral is digested with hydrochloric acid, at a temperature not greater than 60°, until decomposition is complete; the silicic acid formed is washed by decantation, and dried in air at a constant temperature; it is weighed at regular intervals until the weight is constant. It is stated that if a curve of times and weights be plotted, a break is observed at the point where drying ceases (for the acid is of course wet) and decomposition begins; the composition at this point, which is taken as the composition of the acid required, can be determined from the weight of the acid, and the weight of anhydrous silica present, which is determined by ignition after the weight has become constant.

Employing this method in the case of titanite, Bruckmoser claims to have obtained the acids $H_2Si_2O_5$ and $H_2Ti_2O_5$. He therefore concludes that the constitution of the mineral is represented by the formula Si_2O_5,Ti_2O_5Ca, which presumably may be written $Ca(Ti,Si)_2O_5$.

Crystal system—monoclinic; $a : b : c = 0{\cdot}7547 : 1 : 0{\cdot}8543$. $\beta = 60° 17'$.

Common forms (Des Cloizeaux's orientation)—the pinakoids *a* {100} and *c* {001}, with *m* {110}, *s* {021}, *x* {$\bar{1}$02}, *n* {111}, and many others.

$(100) \wedge (110) = 33° 14\tfrac{1}{2}'$; $(001) \wedge (\bar{1}01) = 65° 57'$; $(001) \wedge (011) = 36° 34'$.

The habit is very varied, the commonest being the wedge form, elongated || *c*. Twinning is fairly common, especially

> on the law—Twin plane || *a*, which gives both contact and interpenetrant twins. Cleavage || *m*, fairly distinct. Hardness 5 to 5½; sp. gr. 3·40 to 3·56. Lustre adamantine to resinous. The colour varies very much, doubtless with the content of iron and manganese; it is commonly yellow, green, or brown. Pleochroism is very distinct. The refraction and dispersion are very high, giving the facetted stone a 'fire' inferior only to that of diamond. Birefringence positive, strong; the axial angles vary very widely in different specimens.

It is fusible with difficulty before the blowpipe. Hot concentrated hydrochloric acid decomposes it partially, with separation of silica; boiling sulphuric acid, or, better, fused potassium hydrogen sulphate, decomposes it completely.

On account of the high dispersion and refractive index, clear specimens of sphene make very beautiful gems, but the stone is not sufficiently hard to stand much wear.

The mineral was discovered in Chamouni by Pictet in 1787, and was named Pictite by Delamètherie (1797). In 1795 Klaproth analysed a specimen from Passau, and, observing the presence of titanium (which he had just discovered in rutile), proposed the name Titanite. The mineral described by de Saussure (1796) as 'Schorl rayonnante,' and afterwards by Hauy (1801) as Sphene (σφήν = a wedge), was shown to be identical in composition with titanite by Cordier, and also by Klaproth (1810); the crystallographic identity was proved by G. Rose (1820).

On account of the difference in colour and composition, a large number of varieties are distinguished. The ordinary yellow and brown varieties are known indifferently as sphene or titanite. *Ligurite* has an apple-green colour; *Semeline* is a greenish form named from a fancied resemblance to flax seed. *Lederite* is a brown variety of tabular habit; *Greenovite* is rose-coloured, and contains manganese. *Alshedite* and *Eucolite-Titanite* are rich in the trivalent metals; *Grothite* is a brown variety containing a considerable percentage of ferric iron. *Yttrotitanite,* which contains a high proportion of rare earths, is usually treated as a separate species (see above).

Titanomorphite and *Leucoxene* are white amorphous varieties chiefly produced by alteration of rutile and ilmenite.

Titanite is a fairly widespread mineral; as an accessory rock constituent it is common in the massive plutonic rocks in tiny crystals, readily distinguished under the microscope by the high refraction and birefringence, whilst in large embedded crystals it occurs in many granular limestones, and in plutonic acid, as well as in some metamorphic rocks. In good crystals it is found in many parts of Switzerland and the Alps, in Dauphiné, the Tyrol, Piedmont, the Urals, South Norway, and other European localities; it is also widely distributed in the United States and Canada.

The mineral is important as a valuable source of titanium.

The class of Titano-silicates is a very large one, and might be extended almost at will by the inclusion of the numerous silicates which contain titanium. Owing to the frequency with which small quantities of silica are replaced by titanium dioxide, almost all the commoner silicate minerals contain the latter oxide, so that titanium is one of the most widely distributed of the elements. Relatively very few, however, of the titanium-bearing minerals contain the element in considerable quantities, and only two or three have any importance as commercial sources of titanium compounds.

Only those additional titano-silicates which contain titanium as an important constituent are mentioned below; short accounts will be found in the alphabetical list.

Johnstrupite, Mosandrite, Rinkite, Rosenbuschite and *Tscheffkinite* are complex titano-silicates containing yttrium or cerium metals.

Astrophyllite, Leucosphenite, Molengraafite, Neptunite and *Rhōnite* are complex titano-silicates free from rare earth elements.

Benitoite is a simple titano-silicate of barium; *Ænigmatite* and *Narsarsukite* contain iron and sodium; *Lorenzenite* has sodium and zirconium. *Schorlomite* is a titaniferous garnet. A variety of olivine rich in titanium (*Titanium Olivine*) is also known.

(*b*) The Titanates

Yttrocrasite.[1]—This is a complex titanate of rare earths (chiefly yttria earths) with lime, thoria, and oxides of lead, iron, uranium, etc.; it has a considerable water content. An approximate formula is $R''O,R^{iv}O_2,3R'''_2O_3,16TiO_2,6H_2O$, where $R'' = (Ca,Pb,Fe)$, $R^{iv} = (Th,U)$, and $R'''_2O_3 =$ rare earths. No constitutional formula can be given; it will be noticed that the amount of titanium dioxide is considerably more than is required to combine with the bases present (cf. also Delorenzite below). It is radioactive.

Imperfect crystals only were found, apparently belonging to the orthorhombic system. No crystallographic data could be determined.

The mineral is black, closely resembling polycrase and euxenite (*q.v.*) in appearance. Hardness 5½–6; sp. gr. 4·80.

It is infusible, and not easily soluble in acids. Hydrofluoric acid decomposes it, and the powdered mineral is also slowly attacked by boiling concentrated sulphuric acid.

It was found in 1904 by Barringer, in Burnet Co., Texas.

Delorenzite.[2]—A compound similar to the above, but even richer in titanium dioxide, which amounts to 66 per cent. Tin dioxide is also present, with traces of columbic anhydride. The bases are the yttria earths (almost free from ceria earths), uranium dioxide, and some ferrous oxide, the formula being $2FeO,UO_2,2Y_2O_3,24TiO_2$, with a little SnO_2 replacing TiO_2. It is strongly radioactive. Its closest chemical neighbour is yttrocrasite, but in appearance and angles it closely resembles polycrase (*q.v.*). Its discoverer, Zambonini, therefore formulates it as a metatitanate with titanium acting also as a base—polycrase is a mixed metatitanate and metacolumbate—thus, $2FeTiO_3 + U(TiO_3)_2 + 2Y_2(TiO_3)_3 + 7(TiO)TiO_3$.

The crystals occur in aggregates of numerous individuals in sub-parallel growth. The system is orthorhombic;

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[1] Hidden and Warren, *Amer. J. Sci.* 1906, [iv.], 22, 515; also *Zeitsch. Kryst. Min.* 1907, **43**, 18.

[2] Zambonini, *Zeitsch. Kryst. Min.* 1908, **45**, 76.

$a : b : c = 0{\cdot}3375 : 1 : 0{\cdot}3412$. Usual forms—the pinakoids a {100} and b {010} with prism m {110}, dome d {201}, etc. Habit prismatic, elongated ‖ c axis. Hardness 5½–6; sp. gr. about 4·7.

It was found with struvite in a pegmatite at Craveggia, Piedmont, Italy.

Ilmenite or Menaccanite (Specular Iron Ore, Titaniferous Ironstone, etc.).—This is a titanate of iron, usually written $FeTiO_3$. Its constitution has given rise to very considerable discussion[1]; not only do the relative proportions of iron and titanium vary greatly, but the iron is undoubtedly present in both the ferrous and the ferric states, and in the former state is partly replaced in some specimens by manganese and magnesium. In 1829 Mosander put forward the view that the mineral consisted of $FeTiO_3$, ferrous titanate, with varying proportions of ferric oxide, the forms and angles of ilmenite being very similar to those of hæmatite, Fe_2O_3. This view was disputed by H. Rose, who concluded that the mineral must have been originally an isomorphous mixture of ferric oxide, Fe_2O_3, and titanic oxide, Ti_2O_3, which on exposure to high temperature in the earth's crust would change according to the equation

$$Fe_2O_3 + Ti_2O_3 = 2TiO_2 + 2FeO$$

so that the proportion of ferrous iron increases with the proportion of titanium dioxide, as is actually found to be the case. This condition, however, is also satisfied by Mosander's view. The latter view was also supported by Rammelsberg, who pointed out that the presence of magnesium indicated the existence of ferrous iron as a primary constituent. Additional support is lent to this view by the discovery of Pyrophanite, $MnTiO_3$ (see list), which is found to be isomorphous with ilmenite, so that there can be little doubt that $MgTiO_3$, which can be only a titanate, would, if it existed in the crystalline form (see Geikielite in list), also be isomorphous with ilmenite. Friedel and Guérin (1876) prepared artificial titanium sesqui-

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[1] For a full account of the earlier work on the constitution of ilmenite *vide* Hintze, i. 1858 *et seq.*

oxide, Ti_2O_3, and found it to be isomorphous with hæmatite, Fe_2O_3; they concluded that $FeFeO_3$, $FeTiO_3$ and $TiTiO_3$ formed an isomorphous series, and that ilmenite was a mixture of the second with the other two. In 1890 Hamberg pointed out that there was no reason to suppose that hæmatite, Fe_2O_3, contains ferrous iron, *i.e.* has the constitution $Fe''Fe^{iv}O_3$, analogous to $Fe''Ti^{iv}O_3$, since in corundum, the analogous compound of aluminium, Al_2O_3, divalent aluminium can hardly exist; nevertheless, strict analogy of constitution is not necessary for isomorphism, as shown by the case of potassium nitrate, KNO_3, and aragonite, $CaCO_3$, so that hæmatite, Fe_2O_3, and ferrous titanate, $FeTiO_3$, might form solid solutions in varying proportions without the strictly analogous formula $FeFeO_3$ being true for the former. The balance of opinion inclines to the constitution ($mFeTiO_3 + nFe_2O_3$ in isomorphous mixture) originally proposed by Mosander. The evidence in support of this view has been greatly strengthened by the recent work of Manchot,[1] which has proved the absence of titanium sesquioxide, Ti_2O_3; the mineral is therefore to be regarded as a titanate.

Crystal system—rhombohedral; in forms and angles very close to hæmatite, but the two differ in symmetry (hæmatite has t, 3δ, c, 3π; ilmenite has only t, c).

$c = 1{\cdot}38458$; $(111) \wedge (100) = 57° 58\tfrac{1}{2}'$; habit, tabular, thick; or in thin laminæ. Usually in embedded grains or rolled crystals in sand.

Hardness 5 to 6; sp. gr. 4·5 to 5·0, increasing with percentage of ferric oxide. Iron black, opaque; streak black to brownish-red. Lustre sub-metallic. Slightly magnetic.

The mineral is infusible; when powdered, it dissolves slowly in boiling hydrochloric acid, the filtered yellow solution giving the characteristic blue colouration of titanium salts on addition of tinfoil. In fused potassium hydrogen sulphate it dissolves readily. The variation in composition can be judged from the following limits:

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[1] *Zeitsch. anorg. Chem.* 1912, **74**, 79.

TiO_2	Fe_2O_3	FeO	
3·5	93·6	3·3	per cent.
52·3	1·2	46·5	„

Ilmenite is a widely distributed mineral. In crystals it occurs chiefly at Kragerö and Arendal in Norway, at Miask in the Ilmen mountains, in Dauphiné, the St. Gothard, etc.; in the massive form at Bay St. Paul, Quebec, and other localities in America; and in sands at Menaccan in Cornwall, Iserwiese in Bohemia, Puy de Dôme, dép. Haute Loire, France, and in Brazil, Australia, and New Zealand.

The mineral was discovered at Menaccan in Cornwall by McGregor, about 1790. He described it as containing iron and a new oxide; the unknown oxide was obtained in 1795 from rutile by Klaproth, who gave the name Titanium to the new metal it contained.

Short descriptions of the following titanates are also given (see list):

Davidite and *Knopite*; these are complex titanates containing elements of the cerium and yttrium groups.

Arizonite and *Pseudobrookite*—ferric titanates.

Perovskite, calcium titanate, and its variety *Hydrotitanite*.

Pyrophanite, a manganese titanate isomorphous with ilmenite, and *Senaite*, a species intermediate in composition between these two.

Geikielite, the magnesium analogue of ilmenite, with the variety *Picroilmenite*, which is rich in iron.

Uhligite, a titanate of zirconium, calcium and aluminium.

Derbylite, *Lewisite* and *Mauzeliite*, an interesting series of titano-antimonates.

Warwickite, a boro-titanate.

CHAPTER IV

THE TANTALO-COLUMBATES

(*a*) TANTALO-COLUMBATES CONTAINING NO TITANIUM DIOXIDE

Samarskite, Yttro-ilmenite or Eytlandite (Urano-tantalite).—Samarskite is a tantalo-columbate[1] of the rare earth metals, with iron, calcium, and uranium.

Rammelsberg gives the formula $R''_3R'''_2(Cb,Ta)_6O_{21}$, where $R'' = (Fe'',Ca,UO_2)$, and $R''' =$ rare earth metals. Groth regards it as essentially a pyrocolumbate (tantalate) of rare earth metals $R_4[(Cb,Ta)_2O_7]_3$ the iron, calcium and uranium being more or less accessory constituents. Des Cloizeaux considers the formula indefinite. The mineral has also been found to contain tin, thorium, germanium, and helium. The yttria earths usually predominate (11·9 to 18·9 per cent.), the percentage of ceria earths being low (2·4 to 5·2 per cent.). The yttria earths contain the very rare oxide samaria.

The mineral is radio-active.

Crystal system—orthorhombic; $a : b : c = 0·5456 : 1 : 0·5178$.

Forms—macro- and brachy-pinakoids *a* {100} and *b* {010}; prisms *m* {110} and *h* {120}, the macrodome *e* {101}, and pyramids *p* {111} and *v* {231}.

Angles—$(100) \wedge (110) = 28° 37'$; $(001) \wedge (101) = 43° 30'$; $(001) \wedge (011) = 27° 22\frac{1}{2}'$.

Habit usually prismatic, with *e* prominent; sometimes

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[1] In this and all similar minerals, columbium (niobium) and tantalum are to be regarded as vicarious; they replace each other in all proportions. It seldom happens that a pure columbate is found free from tantalum, or *vice versa*; one or other may predominate, but the two are almost always found together.

tabular parallel to *a* or *b*. Cleavage || *b*, imperfect. The faces are usually rough. The mineral commonly occurs massive, and in flattened grains embedded in granite. Conchoidal fracture. Brittle. Hardness 5 to 6; sp. gr. 5·6 to 5·8.

Colour velvet-black, streak reddish-brown. Opaque even in thin films.

Before the blowpipe it fuses at the edges; with borax it gives an iron bead. It is decomposed by boiling concentrated sulphuric acid, better by fusion with potassium hydrogen sulphate, and leaching the residue with dilute hydrochloric acid—this leaves the insoluble oxides Cb_2O_5 and Ta_2O_5. On heating it glows, with decrease in specific gravity (cf. p. 38).

Samarskite occurs with other columbo-tantalates in felspar, or in veins in granite, near Miask in the Urals, near Quebec in Canada, and in Mitchell County, North Carolina. From the last-named locality, masses up to twenty pounds in weight have been obtained.

The mineral was first discovered in the Urals by Ewreinoff, captain of a corps of Russian mountain engineers. He sent a specimen for identification to the mineralogist Gustave Rose, who pronounced it to be a tantalate of uranium containing manganese, and called it Urano-tantalite.[1] In 1847 the chemist Heinrich Rose, brother of Gustave, in the course of his researches on tantalic 'acid' (oxide), analysed a specimen. He found the composition given above, and renamed it Samarskite,[2] in honour of the Russian engineer who furnished him with the specimen for analysis.

In 1907, Brögger [3] announced that *Annerödite*, of which he had published an account as a new species in 1881, was a parallel growth of the mineral columbite, $(Fe,Mn)Cb_2O_6$, on samarskite.

Both minerals are orthorhombic, but they are not isomorphous. The mistake was due to the fact that whilst the crystallographic data were determined from the upper crystals of columbite, the crystals of samarskite were used for analysis.

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[1] *Pogg. Ann.* 1839, **48**, 555.

[2] *Ibid.*, 1847, **71**, 157.

[3] *Abstr. Chem. Soc.*, 1907, **92**, ii. 885.

Plumboniobite.[1]—This is a recently discovered mineral closely related to samarskite and yttrotantalite (*q.v.*). It is essentially a columbate[2] of yttrium metals, lead and uranium, with water, ferrous oxide, titanium dioxide, stannic oxide, alumina, lime, and cuprous oxide. The formula given is $R''_2Cb_2O_7,R'''_4(Cb_2O_7)_3$, where $R'' = (Fe,Pb,Ca,UO)$, and $R''' = Al$ and yttria metals, with isomorphous (?) metatitanate. The mineral is radio-active, and gives considerable quantities of gas on being heated with sulphuric acid (carbon dioxide 0·19, helium and nitrogen 0·22 per.cent.). The yttria earths are rich in the oxides of gadolinium and samarium, and the mineral should prove a valuable source of these elements. It is remarkable that the ceria earths are almost entirely absent.

The mineral is massive, with some indication of crystalline structure. It is dark brown to black, transparent in flakes, and under the microscope is seen to be isotropic, with doubly-refracting inclusions, undoubtedly of a secondary nature. Hardness 5 to 5½; sp. gr. 4·80 to 4·81. Unlike samarskite, it does not glow on ignition.

It occurs with mica and pitchblende in pegmatite veins in granite, at Morogoro, in the Uluguru Mountains, German East Africa.

Yttrotantalite.—This is a tantalo-columbate similar in composition to Samarskite, and isomorphous with it; though, as the name implies, the acidic oxide is chiefly tantalum pentoxide, the percentage of columbic anhydride being much lower than in the latter mineral. It is a pyro-salt of the formula $R''R'''_2(Cb,Ta)_4O_{14} + 4H_2O$,[3] where $R'' = (Fe,Ca)$ and R''' = rare earth (chiefly yttrium) metals (Rammelsberg). Strutt found thorium and radium in it. The manner in which the water is combined in this, as in many other minerals, is at present undetermined.

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[1] Hauser u. Finch, *Ber.* 1909, 42, 2270; Hauser, *ibid.*, 1910, 43, 417.

[2] It is to be understood that small quantities of columbium are replaced by tantalum.

[3] Dana gives $R''R'''_2(Cb,Ta)_4O_{15} + 4H_2O$; this appears to be an error.

Crystal system—orthorhombic; $a:b:c = 0{\cdot}5411:1:1{\cdot}1330$. Common forms—pinakoids *b* {010} and *c* {001}, prisms *m* {110}, *o* {210}, *p* {120}, domes *s* {201} and *β* {011}. Habit, prismatic with *m* and *b* prominent, or tabular parallel to *b*. Colour yellow to black, white after strong ignition.

It is found at Ytterby in Sweden, and in South Norway.

Fergusonite, Tyrite, or Bragite.—A columbate and tantalate of the rare earth metals, with uranium, iron, calcium, etc. The general formula is that of an ortho-compound, $R_2O_3,(Cb,Ta)_2O_5$ or $R(Cb,Ta)O_4$, where R = metals of the rare earths, chiefly of the yttrium group. Brögger includes the other constituents in the more complex formula $(Th,U)(Si,Sn)O_4 + 12R(Cb,Ta)O_4$; but the simpler formula agrees quite well with specimens from the most widely separated localities, and is usually adopted. The mineral is radio-active and contains helium.

Tetragonal, polar (with tetrad axis of symmetry only). $c = 1{\cdot}4643$. $(001) \wedge (101) = 55° \; 40'$. Common forms—Basal pinakoid *c* {001}, tetragonal prism *g* {320}, pyramids *s* {111}, *z* {321}. Brittle. Hardness 5 to 6; sp. gr. 5·84, decreasing on hydration. Lustre dull, brilliantly vitreous on broken surfaces. Colour brownish-black. Translucent to opaque.

Fergusonite was discovered by Hartwell. It occurs with samarskite, and often with gadolinite and allanite, in Norway and Sweden, the Carolinas, Texas, the Urals, W. Australia, etc.

On heating it glows suddenly between 500° and 600° C.,[1] losing all its helium, and with decrease in density (5·619 to 5·375). At the same time it gives out a considerable amount of heat—8·09 C.[2] for 1 gm. (see p. 38).

Sipylite.—Essentially a columbate of rare earth metals, with oxides of tantalum, tungsten, zirconium, uranium, iron

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[1] Ramsay and Travers, *Zeitsch. physikal. Chem.* 1898, 25, 568.

[2] The heat of combustion of a gram of hydrogen is 342 K.

and calcium, and some water. Mallet, the discoverer, gives the formula as R_2O_3,Cb_2O_5, the basic oxides including, besides the rare earths, Cb_2O_5 with Ta_2O_5 and WO_3, and some water. An alternative formula, making it a complex pyro-salt, is also given, but from its great similarity in form and angles to fergusonite, the first formula is preferred. Strutt finds that it contains not only uranium, radium and helium, but also thorium in considerable quantity ($ThO_2 = 4{\cdot}9$ per cent.), a fact which had been overlooked by Mallet. The rare earths contain a high proportion of erbia.

> It is tetragonal, $c = 1{\cdot}4767$, $(001) \wedge (101) = 55° \ 54'$. The crystals are octahedral, with the form p $\{111\}$; $p \wedge p' = 79° \ 15'$, $p \wedge p'' = 128° \ 50'$. Cleavage distinct $\parallel p$. It is usually granular and amorphous. Colour brownish-black to brownish-red, lustre resinous. Brittle. Hardness 6; sp. gr. 4·89. Translucent.

Its behaviour on heating has been already mentioned (see p. 39); it is infusible. Boiling hydrochloric acid partially dissolves it; the solution gives the turmeric test for zirconium, and on diluting and adding metallic tin a sapphire-blue colour is developed, due to the columbium present. Boiling concentrated sulphuric acid decomposes it slowly.

It is found in Amhurst Co., Virginia, adherent to the allanite which occurs there in large quantities. It was discovered there by Mallet in 1877, who named it, on account of the columbium (niobium) present, from Sipylus, one of the sons of Niobe.[1]

In this class, also, are to be included the following minerals (see list):

Nohlite and *Vietinghofite*, varieties of Samarskite.

Hjelmite and *Kochelite*, minerals closely related to Yttrotantalite and Fergusonite respectively.

Koppite, *Loranskite*, *Microlite* and *Rogersite*, complex tantalo-columbates containing elements of the cerium or yttrium groups.

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[1] See Mallet, *Amer. J. Sci.* 1877, [iii.], **14**, 397.

(*b*) TANTALO-COLUMBATES CONTAINING TITANIUM DIOXIDE

Æschynite.—A columbate and titanate of the cerium metals, with thorium, calcium, iron, etc. From the results of an analysis on a specimen from Hitterö, Norway, Tschernik proposed the rather formidable formula

$$2(2Ce_2O_3,3TiO_2),4(ThO_2,TiO_2),Y_2(CbO_3)_6,3(CaO,TiO_2),\\ 3Fe(CbO_3)_2,Fe(TaO_3)_2,6TiO_2.$$

This can be simplified to $Y(CbO_3)_3 + ThTiO_4 + \frac{3}{2}TiO_2$, in which Y represents rare earth metals partially replaced (2 atoms) by ferrous iron (3 atoms), whilst thorium can be partially replaced by (2 atoms of) ferrous iron or calcium. Strutt found it to contain the uranium-radium combination and helium.

The crystals are orthorhombic, holosymmetric; $a : b : c = 0{\cdot}4866 : 1 : 0{\cdot}6737$.

Common forms—brachy- and basal pinakoids *b* {010} and *c* {001}, prisms *m* {110} and *r* {120}, domes *d* {101} and *v* {021}, with pyramid *o* {111}.

$(100) \wedge (110) = 25° 57'$; $(001) \wedge (101) = 54° 9'$; $(001) \wedge (011) = 33° 58'$.

Habit prismatic, vertically striated, or tabular parallel to *b* with horizontal striations. Brittle. Hardness 5 to 6; sp. gr. 4·9 to 5·7. Colour nearly black. Nearly opaque.

It occurs at Miask, in the Urals, at Hitterö in Norway, and at Fredriksvarn. The variety from the last locality is called Polymignite; it was shown by Rose to be probably identical with Æschynite. Æschynite was discovered by Berzelius at Miask and named by him from the Greek *αἰσχύνη*, shame, from the fact that its composition could not at that time be determined.

If the ceria earths be largely replaced by yttria earths, a variety very similar in appearance and angles, but approximating to polycrase (*q.v.*) in composition, is obtained. This mineral was found in 1879, and referred to Æschynite; analysis subsequently showed its true composition, and it was named Blomstrandine (*q.v.*) by Brögger in 1907.

The Isodimorphous Series Euxenite, Polycrase, Blomstrandine, and Priorite.

Euxenite and Polycrase are members of an isomorphous series and vary considerably in composition. The composition of the series is that of mixed columbates and titanates of yttria earths (with, as usual, some ceria earths), with uranium and zirconium, and water. Before the isomorphous relation was recognised, Rammelsberg gave for Euxenite the formula $R'''(CbO_3)_3,R'''_2(TiO_3)_3,1\frac{1}{2}H_2O$. The ratio of the acidic oxides, $Cb_2O_5 : TiO_2$, is here 1 : 2. This is the greatest value of the ratio, which varies for the series between 1 : 2 and 1 : 5.[1] The end members, the pure metacolumbate and pure metatitanate respectively, are unknown; all the members occurring in nature are to be regarded as mixtures of these within the limits set by the ratios ½ and ⅕. Brögger[2] suggests that the name Euxenite be retained for all members for which the ratio is between ½ and ⅓, whilst for those minerals in which it is less than ¼ the name Polycrase be kept; these views have been supported by Lange, who has analysed members of the series.

The members of this isomorphous series, however, are themselves dimorphous, that is, can each crystallise in two different ways. The second form corresponding to the Euxenites is known as Priorite, whilst that corresponding to Polycrase is known as Blomstrandine; and these second forms are themselves members of a parallel isomorphous series of the same chemical composition, of course, as the first series. It is, perhaps, undesirable to cite this as a typical example of an isodimorphous series, since no end members of unmixed composition are known. A perfect example of such a series is furnished by the oxides of antimony and arsenic. Each of these compounds exists in two distinct crystalline varieties, antimony trioxide, Sb_2O_3, as Valentinite (orthorhombic) and Senarmontite (cubic), arsenic trioxide, As_2O_3, as Claudetite (orthorhombic) and Arsenolite (cubic); and these two modi-

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[1] Lange (*Abstr. Chem. Soc.* 1911, **100**, ii. 499) gives the limits ½ and ⅙.

[2] *Abstr. Chem. Soc.* 1907, **92**, ii. 885.

fications are isomorphous with one another, senarmontite with arsenolite, and valentinite with claudetite.

In the case we are considering, the name Euxenite is applied to one crystalline modification (A) of a number of isomorphous compounds within certain limits of composition, the name Priorite to the second crystalline modification (B) of the same compounds; the name Polycrase is applied to compounds having the crystal form A, and a composition varying within a second set of limits in the same chemical series, whilst this second set of compounds in the crystalline form B is known as Blomstrandine.

Stated as concisely as possible, the relationship is as follows: Each member of this chemical series of continuously varying composition can crystallise in two forms, which are the same for every member. The two varieties at one end of the series are called euxenite and priorite, at the other end polycrase and blomstrandine.

Thus, whilst euxenite and priorite, at the one end, and polycrase and blomstrandine at the other, have the same compositions, euxenite and polycrase have the same crystalline form, whilst priorite and blomstrandine have the same second crystalline form.

All four minerals have the same bright black appearance, and bright conchoidal fracture; they are all four isotropic, probably as a result of hydration. All are orthorhombic, but the measurements for euxenite and polycrase are different from those for blomstrandine and priorite. The two latter are not so widely distributed as the two former. Blomstrandine occurs at Hitterö, Arendal, and other localities in Norway; priorite is found in Swaziland, South Africa.

The crystal system of the Polycrase-Euxenite series is orthorhombic, but Dana gives slightly different axial ratios for the two minerals. This, though Brögger gives the same values for both, is by no means incompatible with isomorphism, as a glance at the axial ratios for the minerals aragonite, strontianite, witherite, etc., of the series of the orthorhombic carbonates, will show.

Brögger's ratios for the two are $a:b:c = 0{\cdot}3789:1:$

0·3527; Dana gives for polycrase 0·3462 : 1 : 0·3124, for euxenite 0·364 : 1 : 0·303.

Euxenite.

> This species occurs usually in the massive form as a bright brownish-black mineral, of hardness 6½, and sp. gr. 4·6 to 5·0. The crystals are prismatic in habit; the common forms are the pinakoids *a* {100} and *b* {010}, the prism *m* {110}, the unit pyramid *p* {111}, and the dome {201}. Ramsay, Collie and Travers found no helium in it; Boltwood found uranium, radium and helium, and Strutt found in addition to these thorium. As early as 1879, Blomstrand had observed zirconium in euxenite.

The mineral is infusible and with difficulty soluble in acids. It occurs in many localities in Scandinavia (Hitterö, Arendal, Brevig, etc.), in North Carolina, South Australia, etc. It was discovered by Scheerer at Jölster, in Norway, in 1839.

The Euxenite-Polycrase series was studied by Hauser and Wirth in 1909,[1] in an endeavour to establish their theory that the proportions in which the various earths and acids occur in this group of minerals is subject to definite laws beyond the ordinary laws of combination. Thus of the erbia earths they state that the proportion of holmia and dysprosia increases relatively to erbia as titanium dioxide increases, *i.e.* as we pass from the euxenites to the polycrases; at the same time scandia and yttria increase relatively to the other yttria earths (the terbia group), whilst in the ceria group samaria and praseodymia decrease relatively to the others. Thus samaria is found in appreciable quantities only when the titanium content is low. The original paper must be consulted for full details.

It was stated above that zirconium was found in euxenite in 1879. In 1901 Hofmann and Prandtl[2] declared that zirconia was an unfailing constituent of the mineral, and that it was always accompanied by a new oxide, which they named Euxenia ('Euxenerde'). This was characterised by the solubility of its oxalate in acid solutions, the insolubility of

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[1] *Ber.* 1909, **42**, 4443.

[2] *Ibid.* 1901, **34**, 1064.

the precipitated hydroxide in excess of alkali, and the gradual precipitation by hydrogen peroxide from a slightly acid solution of its salts. In their paper quoted above, Hauser and Wirth state that zirconia is never present in typical euxenites. In a second paper[1] they state that after exhaustive treatment of every known zirconia mineral, they can find no trace whatever of the 'new earth,' and conclude that Hofmann and Prandtl must have made some experimental error. During this examination, they observed radioactivity in some minerals which contained no traces of uranium or thorium.

Risörite.[2]—A columbate of yttria earths, with titanium; ferric oxide, alumina, lime and lead monoxide are present in small quantities. It resembles fergusonite in composition, but differs in the almost complete absence of uranium, the high loss on ignition, and the amount of titanium present, which is here considerable ($TiO_2 = 6{\cdot}5$ per cent.). Hauser regards it as an orthocolumbate, $R'''(Cb,Ta)O_4$, with an isomorphous admixture of metatitanate, $R'''_2(TiO_3)_3$.

The rare earths are chiefly yttria, with some erbia earths and a little terbia; ceria, lanthana and didymia are also present. The mineral contains a considerable amount of helium, which is remarkable in view of the very small content of uranium and thorium (cf. Thalenite). It is radioactive, the active constituent being precipitated with the lead (and to a very small extent with the rare earths).

It is infusible, but at a red heat it loses much water, and becomes very brittle, with increase of specific gravity; no glowing is observed. It is attacked by boiling concentrated sulphuric acid, and by fused potassium bisulphate; also by hydrofluoric acid (40 per cent.), with separation of the insoluble rare earth fluorides.

No good crystals have been found, and no crystallographic data are known; examined by polarised light it appears isotropic, but this may be due to alteration. Colour, yellowish- to greenish-brown. Streak, yellowish-white.

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[1] *Ber.* 1910, **43**, 1807.

[2] Hauser, *Ber.* 1907, **40**, 3118; *Zeitsch. anorg. Chem.* 1908, **60**, 230.

Hardness 5½; sp. gr. 4·179, increasing to 4·678 after ignition (cf. p. 38).

The mineral was found in a granite-pegmatite at Risör, South Norway.

Wiikite.[1]—A mineral of very complex composition, for which no definite formula can be assigned. Its chemical nature may be understood from the following analytical data:

Columbic and tantalic anhydrides = 16·0; Dioxides of titanium and zirconium = 23·4; Silica = 17·0; Ceria = 2·5; Yttria = 7·6; Scandia = 1·2; Thoria = 5·5; Ferrous oxide = 15·5; Uranic oxide = 3·6; water (and gas) = 5·8 per cent.

Traces of lime, magnesia, stannic oxide and sulphur are also present.

The mineral is infusible; on heating, helium, sulphuretted hydrogen and water vapour are given off, and a white sublimate is formed. The evolution of gas is almost explosive, the mineral breaking with a curious fracture.

It is black and perfectly amorphous, showing no trace of crystalline structure or action on polarised light. Hardness, 6; sp. gr. 4·85.

Wiikite is partially attacked by acids, readily by fused potassium bisulphate. It is radioactive.

The mineral was found with monazite in a felspar quarry at Impilaks, Lake Ladoga, Finland. It is important as the source of scandium used by Sir William Crookes in his investigations of that element; some specimens of the mineral contain over 1 per cent. of the oxide (see p. 44).

The following related minerals, of which descriptions are given in the alphabetical list, are to be included here:

Arrhenite, *Chalcolamprite*, *Endeiolite* and *Wöhlerite*, are complex tantalo-columbates containing silica.

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[1] Crookes, *Phil. Trans.* 1908, A, **209**, 15.

Hainite contains both silicon and titanium.

Dysanalyte is a titano-columbate believed by Hauser[1] to be merely an impure form of perovskite (see p. 14).

Ilmenorutile and *Strüverite* are closely allied minerals believed by Prior[2] and Schaller[3] to be isomorphous mixtures of rutile with Tapiolite or Mossite (ferrous tantalo-columbates).

Pyrochlore is a complex titano-columbate containing elements of the cerium or yttrium groups.

Blomstrandite is an hydrated titano-columbate of rare earth elements, with calcium and uranium; it must not be confused with blomstrandine.

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[1] Vide *Zeitsch. anorg. Chem.* 1908, **60**, 237.

[2] *Min. Mag.* 1908, **15**, 78.

[3] *Abstr. Chem. Soc.* 1912, **102**, ii. 773.

CHAPTER V

THE OXIDES AND CARBONATES

(*a*) The Oxides

Uraninite or Pitchblende.—Uraninite consists essentially of oxides of uranium ($UO_2 + UO_3 = 75$ to 85 per cent.), associated with thoria, zirconia, rare earths, beryllia, and oxides of lead. Traces of lime, iron oxides, silica, bismuth, and arsenic are also sometimes present, with water in widely varying quantities. Nitrogen and helium are always found in it, and, of course, radium. Groth regards pitchblende as uranous uranate $U^{iv}(U^{vi}O_4)_2$, the uranium in the acidic radicle being hexavalent and in the basic radicle tetravalent, and in the latter condition partially replaced by lead, thorium, and rare earths.

Szilard[1] regards it rather as a loose compound or even a solid solution of oxides of thorium and uranium,[2] with small quantities of other oxides, he having obtained apparently homogeneous (though non-crystalline) bodies by dissolving thorium hydroxide in solutions of uranium salts and evaporating to dryness.

The cubic form of the crystalline varieties has been taken as indicating that the mineral is really a spinel,[3] but it is difficult to see how the general formula of that group can be considered comparable to the uranyl uranate formula, UO_2,UO_3, for pitchblende.

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[1] *Compt. rend.* 1907, **145**, 463.

[2] See under Thorianite, *infra*.

[3] The Spinels are an isomorphous family of cubic minerals of the general formula $R''O,R'''_2O_3$, where $R'' =$ Be, Fe, Mg, Ca, etc., and $R''' =$ Fe, Al, Cr, etc.

Crystals are rare, and belong to the cubic system, the common forms being the octahedron $o\{111\}$ and the dodecahedron d $\{110\}$; the cube a $\{100\}$ is sometimes present. The mineral is massive, usually botryoidal. The crystalline or primary form is black, with hardness 5½, sp. gr. 9·0 to 9·7; the altered varieties are grey to greenish- and brownish-black, sp. gr. 5·0 to 6·4.

It is infusible before the blowpipe, but readily soluble in nitric acid.

The mineral occurs both as a primary and secondary constituent of rocks; as a primary mineral it is found in Norway, North Carolina, etc.; as a secondary species it occurs in the massive and hydrated form, with ores of lead, silver, tin, etc., in Saxony and Cornwall, and at the celebrated mine of Joachimsthal, in Bohemia. The latter deposits, consisting of the massive and altered varieties, for which the name Pitchblende is generally reserved, have been much used as a source of radium, especially those at Joachimsthal, and the Cornwall ore.

Several varieties of uraninite have been distinguished by special names. Crystalline varieties from Anneröd and Arendal in Norway are known as Bröggerite and Cleveite respectively; Nivenite is a third form. In these varieties uranium oxides have been replaced to a considerable extent by the rare earths and thoria. An amorphous variety of doubtful composition, produced by alteration, is known as Gummite; Uranosphærite is a similar altered form.

Thorianite.[1]—This interesting mineral consists chiefly of thoria, ThO_2 (55–79 per cent.), with oxides of uranium (11–32 per cent.), and ceria oxides (1–8 per cent.); oxides of lead and iron are also present in small quantities, and zirconia with silica, probably due to associated zircon.

Helium is present, and the mineral is strongly radioactive. A careful analysis by Hahn[2] shows traces of many metals; the same chemist has also separated an extremely active

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[1] Dunstan and Blake, *Proc. Roy. Soc.* 1905, A, 76, 253; Dunstan and Jones, *ibid.*, 1906, A, 77, 546.

[2] Hahn, *ibid.*, 1907, A, 78, 385.

component, 250,000 times as active as thorium nitrate, which he calls Radiothorium.

The composition has been accounted for (Dunstan and Jones, *loc. cit.*) on the hypothesis that thoria (ThO_2) and uranous oxide (UO_2) are isomorphous, the mineral being really a solid solution. Whilst, however, the crystal system of the natural body is really rhombohedral (*vide infra*) the two pure oxides appear to be cubic. Thus Troost and Ouvrard[1] obtained artificial thoria in minute octahedra; and, similarly, Hillebrand[2] obtained uranous oxide in octahedra by reduction of uranyl chloride, UO_2Cl_2, though his work seems to be open to objection. On the other hand, the same author[3] found that uranous oxide and thoria, fused together in almost any proportions, gave a homogeneous body crystallising in octahedra (cf. Szilard, *Compt. rend.* 1907, **145**, 463, quoted under Uraninite). The probability of the isomorphism of the oxides is strengthened by the observation of isomorphism in the sulphates. As early as 1886, Rammelsberg showed that uranous sulphate, $U(SO_4)_2$, crystallises with nine molecules of water and is isomorphous with the corresponding thorium sulphate, $Th(SO_4)_2,9H_2O$; and six years later, Hillebrand and Melville[4] obtained mixed crystals of the two sulphates which were exceedingly close in forms and angles to those of pure uranous sulphate. It is then at least probable that the two oxides are isomorphous, though the point cannot be regarded as satisfactorily proved, by reason of the anomalous crystal forms of the naturally occurring mixtures, thorianite and uraninite. The recent results of Kobayashi[5] point to the conclusion that different varieties of thorianite may exist, in each of which the oxides of thorium and uranium bear definite simple ratios to one another.

Thorianite occurs in jet-black crystals with a bright resinous lustre. They are pseudocubic, and the twinning resembles that of the cubic mineral fluorspar—interpenetrant

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[1] *Compt. rend.* 1882, **102**, 1422.
[2] *Zeitsch. anorg. Chem.* 1893, **3**, 243.
[3] *Bull. U.S. Geol. Surv.* No. 113, 1893.
[4] *Ibid.* No. 90, 1892, p. 30.
[5] *Abstr. Chem. Soc.* 1912, **102**, ii. 1181.

cubes, twin axis a cube diagonal. Close examination shows, however, that twinning can only take place about one of the four diagonals, and an optical examination makes it clear that the symmetry is really rhombohedral. The case is exactly analogous to that of the mineral chabazite, a zeolite which occurs in rhombohedra of which the angles differ but little from those of the cube, and which also forms the interpenetrant twins. In view of the fact that both uranous oxide and thoria have been obtained as octahedra, whilst a fused mixture of the two on cooling forms cubic crystals, it seems not unlikely that at high temperatures the pseudo-cubic thorianite would become truly cubic; but no experiments in this direction seem to have been tried.

The crystals are brittle; hardness 7; sp. gr. 8·0–9·7.

Thorianite is infusible, incandescing before the blowpipe. When powdered, it dissolves readily in nitric and sulphuric acids, with evolution of helium. Gray[1] has shown that the helium content can be reduced by 28 per cent. by fine grinding, thus showing that part at least of the gas must be mechanically held.

Thorianite was found in Ceylon, being originally mistaken for pitchblende. A sample was supplied by the discoverer, Mr. Holland, to the officers of the Mineral Survey, by whom it was sent to London for examination. Its composition was determined by Dunstan, who named it. It was found in the river gravels (gem-gravels), the matrix being a pegmatite granite. It is a valuable source of thorium nitrate for incandescent mantles, one ton of the mineral (with thoria content of 70 per cent.) having been sold for £1500; but the supply is small and unreliable.

Baddeleyite.[2]— Baddeleyite consists of almost pure zirconia ($ZrO_2 = 96{\cdot}5$ per cent.) with small quantities of ferric oxide, alumina, lime, magnesia, alkalies and silica. Thoria and rare earths are present in traces, uranium is absent; the mineral is not radioactive, and contains only traces of helium.

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[1] *Proc. Roy. Soc.* 1908, A, 82, 306.

[2] *Vide* Fletcher, *Min. Mag.* 1893, 46, 10, 148; Hussak, *Zeitsch. Kryst. Min.* 1895, 24, 164, and 25, 298.

Monoclinic—$a : b : c = 0{\cdot}9871 : 1 : 0{\cdot}5114$. $\beta = 98° \; 45\frac{1}{2}'$.

Common forms—all three pinakoids, $a \{100\}$, $b \{010\}$, and $c \{001\}$, with the hemi-prisms $m \{110\}$, $k \{120\}$, and $l \{230\}$, and various pyramids and domes.

Angles—$(100) \wedge (110) = 44° \; 17\frac{1}{2}'$; $(100) \wedge (001) = 81° \; 14\frac{1}{2}'$; $(100) \wedge (101) = 55° \; 33\frac{1}{2}'$.

Cleavage || *c* and || *b*, parting || *m* due to repeated twinning. Twinning is exceedingly common; of many hundred crystals examined by Hussak, only three were found untwinned. Twin planes *m* (110), *a* (100), and *x* (201).

Colour brown, varying in zones by twinning, with distinct pleochroism. Hardness 6½; sp. gr. varies from 4·4 to 6·0, being about 5·5 to 5·6 for fairly pure material. Double refraction negative, 2 E = 70–75°. Acute bisectrix nearly coincident with *c* axis, plane of the optic axes *b*, (010).

The mineral is insoluble in acids, readily soluble in fused potassium hydrogen sulphate. Before the blowpipe it is almost infusible; it dissolves in the fused borax bead, rapid cooling causing separation of crystals. If a bead containing zirconia be heated until the borax is partially volatilised, zirconia crystallises on cooling in tetragonal crystals, isomorphous with those of rutile.[1]

The mineral was discovered in 1892 by Hussak and L. Fletcher independently. The former, who obtained it from the pyroxenite sand of São Paulo, South Brazil, believed it to be a tantalo-columbate, and called it Brasilite. Fletcher found it in a gem-gravel from Rakwana, Ceylon, and named it Baddeleyite. An analysis by Blomstrand of Hussak's mineral showed it to be identical with the Ceylon mineral, and Hussak withdrew his name and accepted Fletcher's. It has recently been found [2] in a corundum-syenite, near Bozeman, Montana, U.S.A.

The mineral now comes on the market in commercial quantities; pure zirconia almost entirely free from iron can be obtained by leaching with acids. The pure oxide is extraordinarily refractory, and promises to be of great use for crucibles, furnace linings, etc. (*vide* p. 324).

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[1] Nordenskiöld, *Pogg. Ann.* 1861, **114**, 625; for tetragonal zirconia see also Troost and Ouvrard, *Compt. rend.* 1888, **102**, 1422.

[2] Rogers, *Amer. J. Sci.* 1912, [iv.], **33**, 54.

Rutile.—Titanium dioxide, TiO_2, occurs crystallised in nature in the three minerals Rutile, Brookite, and Anatase (Octahedrite), which therefore form a trimorphous series. They are all stable minerals, though rutile appears the most stable, being occasionally found in pseudomorphs after the other two. The family is remarkable in that it is not unusual to find two of them occurring together—an uncommon phenomenon with polymorphous minerals.

Rutile often contains small quantities of iron and chromium. The ferriferous varieties are distinguished as Nigrine, which is black, with 2–3 per cent. ferric oxide, and Ilmenorutile, with up to 10 per cent. of ferric oxide, and specific gravity up to 5·13.

Crystal system — tetragonal, holosymmetric; $c = 0{\cdot}6442$; $(001) \wedge (101) = 32° 47'$.

Common forms—prisms *a* {100}, *m* {110}, and *l* {310}; pyramids *e* {101}, *s* {111}, and many others. The basal pinakoid *c* {001} is very rare. Habit, prismatic, with vertical striations; or in slender needles. Twinning very common and varied; usually on the cassiterite law—twin plane *e* (101)—forming the knee-shaped twins, and irregular rosettes by repetition, and many contact twins. Contact twins on the law—twin plane *v* (301) are less common.

Cleavage ‖ *a* (100) and *m* (110), distinct. Hardness 6–6½; spr. gr. 4·18–4·25, and up to 5·2 if much iron is present. Colour reddish-brown to black, with good metallic lustre; transparent to opaque. The refraction and double refraction are very high—$\omega = 2{\cdot}6158$, $\epsilon = 2{\cdot}9029$ for sodium light—and allow the crystals to be readily distinguished in rock-sections.

The mineral is insoluble in acids, but can be dissolved after fusion with alkalies or alkali carbonates.

Rutile is a member of the isomorphous series, cassiterite, zircon, etc. (see under Thorite), and in particular it has the colour, appearance, and twinning of cassiterite, from which, however, it is readily distinguished by its lower specific gravity. In this connection it is interesting to note that an apparently pure specimen, quite free from inclusions, was found (1904) to contain 1·7 per cent. of tin dioxide.[1]

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[1] Friedel et Grandjean, *Bull. Soc. franc. Min.* 1909, **32**, 52.

As an accessory rock mineral, and also as an important constituent of many sands, rutile is of very wide distribution. It occurs, usually imbedded in quartz or felspar, in many granites, syenites, gneisses, slates, and allied rocks ; in acicular crystals penetrating quartz it forms the 'Veneris Crinis' of Pliny. At Risör and other localities in Norway, it is found in the massive form, and it is largely worked at Risör as a source of titanium. It occurs in all the countries of Europe, and largely in America. Arendal, Kragerö, and Risör, in Norway, the Binnenthal, the Urals, the St. Gothard, Castile, Magnet Cove in Arkansas, Alexander Co. in N. Carolina, Barre and Shelburne in Massachusetts, and Chester Co. in Pennsylvania are the chief localities.

It was in this mineral that the element titanium was first recognised by Klaproth (1795).

Anatase (Octahedrite) is the second crystalline modification of titanium dioxide.

Tetragonal $c = 1{\cdot}7771$. $(001) \wedge (101) = 60° \, 38'$, $(111) \wedge (1\bar{1}1) = 82° \, 9'$.

Common forms—Prisms *a* {100} and *m* {110}, pyramids *p* {111}, *e* {101}, and many other complex forms; the basal plane *c* {001} is occasionally found. Habit usually octahedral, with *p* or *v* prominent ; sometimes tabular with *c*, more rarely prismatic with *a* well developed. Cleavage ‖ *c* and *p* perfect. Hardness 5½–6; sp. gr. 3·82–3·95, usually increasing after heating. Lustre adamantine, so splendent that in Brazil detached crystals have been mistaken for diamonds. Colour, some shade of bluish-black to brown ; by transmitted light, greenish-yellow. Transparent to opaque. Double refraction negative, strong; for sodium light $\omega = 2{\cdot}554$, $\epsilon = 2{\cdot}493$.

It is found at Bourg d'Oisans in Dauphiné, and in Norway, the Urals, Brazil, etc. In Switzerland it occurs as the variety Wiserine, which was at one time believed to be xenotime. It was named Octahedrite by de Saussure, in 1796, from the prevailing habit, and Oisanite, from its occurrence in Dauphiné, by Delamètherie, in 1797. The name anatase (ἀνάτασις =

erection) was proposed by Haüy, being intended to denote that the vertical axis ($c : a$) is greater than that of rutile, the other tetragonal modification of the dioxide.

Brookite, the third form of this compound, is orthorhombic.

$a : b : c = 0{\cdot}8416 : 1 : 0{\cdot}9444$.

Common forms—the three pinakoids *a* {100}, *b* {010}, and *c* {001}, prisms *m* {110}, *l* {210}, pyramids *e* {122}, *z* {122}, and numerous others.

Angles — (100) ∧ (110) = 40° 5′; (001) ∧ (100) = 48° 18′; (001) ∧ 011) = 43° 22′.

The habit is varied; it occurs usually in bipyramids with *e* and *m* or prismatic with *m*, *a*, and terminating pyramids. Cleavage ‖ *m* indistinct, ‖ *c* very poor.

Hardness 5½–6; sp. gr. 3·87–4·01. Lustre metallic. Colour brown to reddish- and yellowish-brown and black. The optical behaviour is interesting. The acute bisectrix is perpendicular to *a* (100), but while for red light the plane of the optic axes is (001), for blue it is (010); for an intermediate light, therefore ($\lambda = 5550\ \mu\mu$), the mineral appears uniaxial.

The chief localities are Bourg d'Oisans, Miask, the St. Gothard, the Tyrol, Magnet Cove in Arkansas, and Tremadoc in Wales.

Titanium dioxide can be obtained crystalline by the action of steam on titanium tetrafluoride, TiF_4, at high temperatures; it is stated that by varying the temperature of the reaction, any one of the three crystalline modifications can be obtained.

The only other minerals which need be mentioned in this class (see list) are:

Zirkelite, a complicated mixture of oxides, in which thoria, zirconia, and titanium dioxide act as acidic oxides, and

Mackintoshite, a mixture of several oxides, of which those of thorium and uranium are the most important.

(*b*) THE CARBONATES

Lanthanite, Hydrocerite.—This mineral is a carbonate of ceria earths, chiefly lanthana, of the formula $La_2(CO_3)_3,9H_2O$.

Orthorhombic; $a:b:c = 0{\cdot}9528:1:0{\cdot}9023$. Common forms—the pinakoids a {100} and c {001}, with m {110} and o {111}.

Angles—(100) $\wedge$ (110) = 43° 37′; (001) $\wedge$ (101) = 43° 26½′; (001) $\wedge$ (011) = 42° 3½′.

Habit tabular, parallel to c; cleavage perfect, $\parallel c$.

Double refraction negative; optic axis plane a (100).

Usually amorphous, being probably an alteration product of a mineral rich in lanthanum. Hardness 2; sp. gr. 2·6–2·7.

Colour white to yellowish-white, usually opaque; infusible before the blowpipe (being converted to the oxide), readily soluble in acids.

Lanthanite occurs with cerite at Bastnäs, and at Bethlehem, Pennsylvania.

Morton[1] states that he prepared a crystalline didymium carbonate in the laboratory, of the formula $Di_2(CO_3)_3,8H_2O$, which was isomorphous with lanthanite; he concluded that the latter had only eight instead of nine molecules of water.

Parisite (Synchisite), and **Cordylite.**—*Parisite* is a fluocarbonate of calcium and cerium metals; *Cordylite* is an analogous compound in which barium replaces calcium, and is isomorphous with Parisite. The formula of Parisite is $CaR_2F_2(CO_3)_3$, where R = cerium metals. Groth formulates this as $(CaF)(RF)R(CO_3)_3$, Penfield and Warren as $(RF)_2Ca(CO_3)_3$, whilst Schilling gives $Ce_2(CO_3)_3,CaF_2$. Analogous formulæ may be proposed for Cordylite, $BaR_2F_2(CO_3)_3$. Since the two minerals are very similar in crystallographic properties, one description will be sufficient for both. The following are Dana's data for Parisite:

Hexagonal, $c = 3{\cdot}2891$. (0001) $\wedge$ $(10\bar{1}1)$ = 75° 15′.

Forms are extremely numerous, and have remarkably high indices. Among the simplest are the base c {0001}, the prism m $\{10\bar{1}0\}$, pyramids q $\{10\bar{1}2\}$, and h $\{11\bar{2}2\}$; the other forms are chiefly rhombohedra and pyramids. The usual habit is that of an acute double hexagonal pyramid, with form o $\{20\bar{2}1\}$, terminated by c. Cleavage $\parallel c$, perfect.

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[1] See abstract in *Zeitsch. Kryst. Min.* 1886–87, 12, 518.

It is brownish-yellow to red. Hardness 4½; sp. gr. 4·36. The double refraction is strong, positive. Soluble in hydrochloric acid with effervescence.

Both minerals are characteristic pneumatolytic species of the riebeckite-ægirine rocks. Parisite was discovered by Paris in the emerald mines of the Muso valley, Colombia, in 1835, and first correctly analysed by Bunsen in 1845. Before the blowpipe it glows, remaining infusible (the glow does not appear to have been investigated in this case).

Cordylite was discovered by Flink in 1900, in Greenland.

It is yellow to brownish-yellow and colourless. Hardness 4½; sp. gr. 4·31. Before the blowpipe it decrepitates, and is infusible; moistened with hydrochloric acid, it gives the characteristic barium flame.

The so-called Synchisite was discovered by Nordenskiöld who correctly described it as Parisite. Flink found it in Greenland, and announced it as a new species, with the formula $R_2F_2Ca_2(CO_3)_4$, *i.e.* the formula for parisite plus one molecule of calcium carbonate, $CaCO_3$. From its extraordinary resemblance to parisite in physical and crystallographic properties, Palache and Warren[1] believe that the specimens selected by Flink for analysis must have consisted, in reality, of parisite with admixed calcium carbonate. This conclusion has now been confirmed by Quercigh, by a careful comparison of the optical properties.[2] The minerals are usually found together, the chief localities being S. Norway, the gold districts of the Urals, Narsarsuk in S. Greenland, and Montana, U.S.A.

The following rare earth carbonates are described in the alphabetical list:

Ancylite, a basic hydrated carbonate.

Tengerite, a hydrated carbonate formed by the weathering of gadolinite.

Kischtimite, a fluo-carbonate related to parisite.

Bastnäsite (Harmatite) and *Weibyite*, hydrated fluo-carbonates of the cerium elements.

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[1] *Amer. J. Sci.* 1911, [iv.], 31, 533.

[2] *Abstr. Chem. Soc.* 1912, 102, ii. 773.

CHAPTER VI

THE PHOSPHATES AND HALIDES

(a) The Phosphates

Monazite, Phosphocerite.—Monazite, by far the most important, commercially, of all the rare earth minerals, is essentially an orthophosphate of the ceria earths, of the formula $R'''PO_4$.[1] The yttria earths are usually present in small quantities. Silica and thoria, in quantities varying from traces up to 6 per cent. of the former and from 1 to 20 per cent. of the latter, are invariable constituents; it is almost entirely to the percentage of thoria that the mineral owes its commercial value. The following also are common constituents, though usually in very small quantities only—stannic, ferric and manganous oxides, alumina, lime, magnesia, zirconia and water. Helium was observed in it by Tilden, and by Ramsay, Collie and Travers.[2] Boltwood[3] and Zerban[4] found uranium in it; the latter attributed this to impurities, the former regarded it as an essential constituent. Strutt[5] found uranium in a pure monazite. Haitinger and Peters[6] detected radium, their result being confirmed by Boltwood and Strutt.

Monazite occurs in small crystals belonging to the monoclinic system. $a : b : c = 0{\cdot}9693 : 1 : 0{\cdot}9256$, $\beta = 76° 20'$. These values vary slightly with different specimens. Common forms—Ortho- and clino-pinakoids *a* {100}, *b* {010}, hemi-prisms *m* {110}, and *n* {120}, hemi-ortho-

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[1] For the composition of the earths in monazite, see James, *J. Amer. Chem. Soc.* 1913, **35**, 235.

[2] *Trans. Chem. Soc.* 1895, **67**, 684.

[3] *Phil. Mag.* 1905, [vi.], **9**, 599.

[4] *Ber.* 1905, **38**, 557.

[5] *Proc. Roy. Soc.* 1905, A, **76**, 88 and 312.

[6] *Sitzungsb. kaiserl. Akad. Wiss. Wien*, May, 1904.

prisms *w* {101} and *x* {$\bar{1}$01}, hemi-clino-prism *e* {011}, hemi-pyramid *v* {$\bar{1}$11}, etc.; the basal pinakoid *c* {001} is rare.

Angles—$a \wedge m = 43° 17'$, $c \wedge w = 37° 8'$, $c \wedge e = 41° 58'$.

Habit tabular, parallel to *a*, needle-shaped by elongation parallel to *b* axis, or prismatic by good development of *v*.

Cleavage || *c*, perfect, || *a*, distinct, || *b*, difficult.

Twin plane *a* (100). Birefringence moderate, positive; plane of optic axes perpendicular to *b*, nearly parallel to *a*. Acute bisectrix inclined to *c* at angle of 1°–4°. Dispersion feeble, $\rho < v$. Brittle. Hardness 5–5½; sp. gr. 4·9–5·3; conchoidal fracture. Lustre resinous. Colour, red to brown, yellow, yellowish- and greenish-brown. Transparent when pure; more often translucent to opaque.

Monazite is with difficulty soluble in acids; before the blowpipe it is infusible; when moistened with sulphuric acid it colours the flame greenish-blue.

The mineral often occurs massive, yielding angular fragments, but is most common in rolled grains. It occurs in the gneiss of the Carolinas and Georgia, and in sands derived from the gneiss, in Idaho and many of the Pacific States; in Brazil, at various localities in the provinces of Minas Geraes, Bahia, Espirito Santo; in Queensland, Australia; in Madagascar; in Ceylon; near Travancore in India; in the Urals; in Scandinavia, etc. The deposits of commercial value will be treated more fully in the next chapter. It is of wide distribution as an accessory constituent of granites, diorites, and gniesses.

Monazite was first described, under the name Turnerite, by Lévy,[1] in 1823; the specimen was from the collection of the English chemist Turner, who thought it a variety of sphene (titanite), and was named after him at the suggestion of the mineralogist Heuland. The specimen was stated to have been found in Dauphiné, but in spite of considerable examination of the question, the precise locality is still unknown. The resemblance between Turnerite and the mineral later described as monazite (μονάζειν = to be solitary) was pointed out by

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[1] *Annals of Philosophy*, 1823, 21, 241.

Dana in 1866, and confirmed by Pisani, 1877. The name Monazite was first used by Breithaupt[1] in describing a mineral found by Menge (1826) accompanying zircon in a granite from Miask in the Urals. Breithaupt concluded, from the high specific gravity, that the mineral contained a heavy metallic oxide. It was again described as Mengite by Brooke[2] in 1831. It was re-discovered by Shephard[3] in South Carolina in 1837, and described by him under the name Edwardsite, a variety from Connecticut being called Eremite. To Shephard belongs the honour of having discovered its true nature; after analysis he described it as a 'Basic Sesquiphosphate of the Protoxide of Cerium,' giving the formula (modern notation) $3CeO,2P_2O_5$, and finding also zirconia, alumina, and silica in it (his specimen was probably very impure). Gustav Rose[4] showed this to be identical with monazite in 1840. In 1846 Wöhler described, under the name Cryptolite, a variety of tetragonal habit closely resembling zircon. This occurs at Arendal in Norway, enclosed by apatite, in the granite; it may be obtained by treatment with dilute nitric acid, which dissolves the apatite.

The question of the manner in which the thorium is combined in monazite is of considerable importance, in view of the fact that it is to this element that the mineral owes its commercial value. The amount present varies from traces up to over 20 per cent., but the usual value is between 5 and 7 per cent. The first explanation of its presence was advanced by Dunnington[5] who suggested, on the result of only one analysis, that orangite ($ThSiO_4$) was present mechanically mixed with the monazite. Penfield[6] supported this suggestion, and stated that in three analyses of pure material he found the ratio of rare earths to phosphorus pentoxide and that of thoria to silica exactly equal to unity, though the actual amounts of thoria varied considerably. He also quotes

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[1] *Schweigg. J.* 1829, **55**, 30.
[2] *Phil. Mag.* 1831, [ii.], **10**, 139.
[3] *Amer. J. Sci*, 1837, **32**, 162.
[4] *Pogg. Ann.* 1840, **49**, 223.
[5] *Amer. Chem. J.* 1882, **4**, 138.
[6] *Amer. J. Sci.* 1882, [iii.], **24**, 250; 1888, **36**, 322.

an analysis made by Rammelsberg in 1877, in which no thoria was found, to show that it is not an essential constituent. In a microscopic examination he found dark resinous particles scattered throughout the section; after moistening with hydrochloric acid, warming, and washing, these dark spots became white, and could be stained with fuchsine, the monazite remaining unaffected throughout. He concluded that these particles were thorite or orangite.

Blomstrand[1] disputed Penfield's conclusions. In twelve analyses of monazite from various parts of Scandinavia he never once found either thoria or silica absent. Of these twelve analyses, two give the ratio of thoria to silica, ThO_2 : SiO_2, exactly unity, in seven cases the ratio is not greater than 1·25, in five cases it varies considerably. He summed up his results in three statements:

(*a*) Silica is never absent; its amount depends not on the amount of thoria, but on the amount of phosphorus pentoxide present.
(*b*) The thoria which is always present is combined partly with silica, partly with phosphorus pentoxide.
(*c*) In most cases, the rare earths alone are insufficient to satisfy the ratio $R_2O_3 : P_2O_5 = 1$.

An exhaustive examination of the question has been made more recently by Kress and Metzger.[2] They made in all over fifty analyses, using thirty different specimens of monazite; they estimated silica both as quartz and as silicate silica, and determined thorium by the fumarate method—the other investigators had used the thiosulphate method of Hermann (*vide* p. 286). Their results may be summarised as follows:

(i.) Silica is always present.
(ii.) The amount of silica usually increases with the thoria, but not regularly.
(iii.) By far the majority of cases showed insufficient total silica to combine with the thoria present.
(iv.) In about 9 per cent. of the cases, the thoria present was insufficient to combine with the silicate silica,

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[1] *J. pr. Chem.* 1890, **41**, 266.
[2] *J. Amer. Chem. Soc*, 1909, **31**, 640.

from which it follows that some foreign silicate must be at least occasionally present.

(v.) A careful microscopic examination showed conclusively that no thorite ($ThSiO_4$) was present, the silicate being biaxial; quartz is present as such.

They conclude that thorium is present as phosphate, and is an essential constituent, but that there is always some admixed silicate, most probably a felspar.

Xenotime.—Chemically this mineral is closely allied to monazite, being an orthophosphate of rare earths, containing silica and thoria; whereas, however, in monazite the content of yttria earths does not rise above 4 per cent., in xenotime these constitute by far the greater part of the bases, the content of ceria earths ranging from 8·2 to 11 per cent. The yttria earths, chiefly oxides of yttrium and the erbium group, vary from 54·1 to 64·7 per cent. There are traces of zirconia; Ramsay, Collie and Travers detected helium, whilst Boltwood, and also Strutt, found uranium and radium. It also appears to contain traces of sulphuric anhydride.

The crystals are tetragonal, holosymmetric. $c = 0{\cdot}6187$; $(001) \wedge (101) = 31^\circ\ 45'$.

Common forms are the prisms *a* {100} and *m* {110}, the basal pinakoid *c* {001}, the pyramids *e* {101}, *f* {201}, *z* {111}, etc.

Cleavage ∥ *m*, perfect. Uniaxial, double refraction strong, positive. Transparent to opaque. Colour, brown to reddish-brown and yellow. Hardness 4–5; sp. gr. 4·45–4·56.

It is insoluble in acids, and infusible before the blowpipe; when moistened with sulphuric acid, however, it turns the flame bluish-green, like most mineral phosphates (*vide* monazite).

It is not so widely distributed as monazite, but is not uncommon. It often occurs with zircon—to which it is very closely allied in crystal form, if the two are not actually isomorphous—in parallel growth, in granitic rocks. The diamond sands of Diamantina, Brazil, form the richest source of the mineral, but it is also found in Scandinavia, at Hitterö, Åro, etc.

The mineral is of considerable importance, chemically, on account of the high percentage of erbia earths.

In the works of Bauer, Rosenbusch, Weinschenk, Schilling and Iddings will be found accounts of a mineral named 'Hussakite.' These accounts rested on the work of Kraus and Reitinger,[1] who in 1901 announced the discovery of a new species. The crystals were obtained as a specimen of xenotime by Prof. Muthmann from Dr. E. Hussak, in São Paulo, and had the crystallographic properties of that mineral. On analysis, the amount of sulphur trioxide present was found to be remarkably high (6·3 per cent.), and Kraus and Reitinger concluded that the substance was distinct from xenotime. They announced it as a new mineral, with the name Hussakite, and the formula $3R_2O_3,3P_2O_5,SO_3$ or $6RPO_4,SO_3$, and stated that by the action of dilute alkalies the sulphur trioxide could be easily and completely removed. They therefore regarded xenotime as a pseudomorph[2] after hussakite, the sulphur trioxide having been removed from the latter by the action of the alkaline waters of the earth's crust. In support of this view, they gave analyses of opaque crystals from a Bahia sand represented as containing 2·6 to 2·7 per cent. of sulphur trioxide, and so as being intermediate forms produced during the change.

The latter conclusion was quickly challenged by Brögger, who found no sulphur trioxide in a perfectly fresh and transparent xenotime from Àro in Scandinavia. Brögger concluded that the Hussakite of Kraus and Reitinger was an independent species of the formula $5YPO_4,(YSO_4)PO_3$, and that xenotime was not derived from it.

Basing his work on the barium chloride test given by Kraus and Heitinger (see below) Rösler[3] declared that 'Hussakite' was a common accessory constituent of igneous rocks, having been previously mistaken for zircon, which it resembles in appearance and optical properties.

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[1] *Zeitsch. Kryst. Min.* 1901, **34**, 268.

[2] One mineral is said to be pseudomorphous after another when the first is produced from the second by a chemical change which proceeds so slowly that the original structure and crystalline form are unaltered (*i.e.* a change proceeding molecule by molecule). The pseudomorph is usually opaque and shows clear signs of the alteration.

[3] *Zeitsch. Kryst. Min.* 1902, **36**, 258.

In 1907 Hussak[1] published a paper in which he showed that the mineral named after him was not a new species at all, but a xenotime of prismatic habit. Analyses made at his request by Florence in Brazil, G. T. Prior in London, and Tschernik in St. Petersburg, confirmed the original values given by Gorceix (sulphur trioxide up to 0·25 per cent.). He mentions Brögger's analysis of the Norwegian specimen in which Kraus and Reitinger had found 2–3 per cent. of sulphur trioxide, but in which Brögger found none. He explains the results of Kraus and Reitinger as due to the addition of barium chloride to the acidified solution of the carbonate fusion of the mineral, by which barium phosphate was precipitated; this was dried and weighed as barium sulphate. Rösler's tests are declared doubtful; xenotime is not a widely spread rock constituent, the mineral in question being really zircon.

In face of these results, there can be little doubt that the name 'hussakite' is unnecessary and undesirable, since the mineral to which it was applied is proved to be xenotime.

In the alphabetical list, particulars of the following rare earth phosphates will be found:

Castelnaudite, a variety of xenotime containing zirconia.

Churchite and *Rhabdophane* (Scovillite), hydrated phosphates.

Gorceixite, an alumino-phosphate of alkaline and ceria earths.

Retzian, an hydrated arsenate of manganese, calcium and rare earth metals.

(*b*) THE HALIDES

Yttrocerite.—This mineral is a fluoride of calcium and rare earth metals, with water. A recent analysis by Tschernik[2] gives the formula $Ce_2F_6,2Y_2F_6,9CaF_2,2H_2O$. Putting the rare earth metals together, this gives $6RF_3,9CaF_2,2H_2O$, or $R_2Ca_3F_{12},\frac{2}{3}H_2O$. Yttrocerite is of interest since it was probably in the analysis of this mineral by the discoverers, Berzelius and Gahn, that the double sulphate method of separating the yttria from the ceria earths was first employed[3] (*vide* p. 156).

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[1] *Centr. Min.* 1907, 533.

[2] *Abstr. Chem. Soc.* 1907, **92**, ii. 362.

[3] *Schweigg. J.* 1816, **16**, 244.

It is found only massive or granular. Colour usually white to violet-blue, sometimes reddish-brown. Hardness 4½; sp. gr. 3·45. Infusible, but loses colour before the blowpipe. When powdered, it dissolves completely in boiling hydrochloric acid, and readily in sulphuric acid with evolution of heat. It has been found at various localities in Scandinavia.

Yttrofluorite.[1]—This is a fluoride of varying composition, very similar to yttrocerite, but characterised by the absence of water, and the very small ceria content (1·7 per cent.). It is thus a fluoride of calcium and the yttrium metals.

Cubic, with poor octahedral cleavage. Colour, yellow to brown and yellowish-green; transparent to translucent, bleached by weathering. Very brittle. Hardness 4½; sp. gr. 3·54–3·56.

It is very similar to fluorspar (except that the octahedral cleavage of the latter is very good), and is regarded by Vogt as an isomorphous mixture of the latter with yttrium fluoride (or with a double yttrium calcium fluoride, which is less probable). This view would account for the variations in composition, and also for the remarkable frequency with which traces of rare earths are found in fluorspar (*vide* p. 2). Yttrocerite is regarded as a similar isomorphous mixture, but containing cerium metals in addition to the yttrium group.

Yttrofluorite occurs in pegmatite veins in granite in Northern Norway, with gadolinite, fergusonite, allanite, fluorspar, and the usual vein minerals.

The other members of this family (see list) are:

Fluocerite, a basic fluoride of yttrium and cerium metals.

Tysonite, a hydrated fluoride containing carbonates.

It is to be noticed that fluorine is the only member of the halogen family which occurs in nature in combination with rare earth elements. This fact is possibly connected with the great age of the rare earth minerals, and their formation during pneumatolytic metamorphism of plutonic rocks (*vide* Chapter I).

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[1] T. Vogt, *Centr. Min.* 1911, 373.

CHAPTER VII

THE MONAZITE SANDS

It has been stated that monazite is a not uncommon accessory constituent of many rocks, particularly of granites, gneisses, diorites, etc. The crystalline material, of which an account has been given, is found sometimes in veins in these rocks, more often in tiny crystals disseminated throughout the mass. Most of these monazite-bearing rocks are extremely old, belonging to the Archæan or pre-Cambrian age, and probably none are of secondary (Mesozoic) or later age. It follows, then, that they have been subjected to erosion during practically the whole immense period of which geology can give us any detailed knowledge. Heat, frost, wind, the action of vegetation and of percolating water, the innumerable weathering agents known to the geologist, have been at work on them during countless ages, breaking, crushing, dissolving; rains, brooks, rivers, even ocean-waves have dissolved or washed away the fragments, sorted them out unerringly according to density, and re-deposited them, now in a river-bed, now at the base of some sea cliff, now in a wide alluvial plain from which the water has long since retired. It is in deposits of this nature that the monazite has been concentrated. Its relatively high specific gravity (about 5·0) has secured its separation from the lighter mica, quartz, and felspar of the parent-rock; but the heavier vein or accessory minerals have, of course, been concentrated with it. Zircon is an invariable constituent of these 'monazite sands,' as such deposits are called; and others almost as frequently found are rutile, ilmenite, sphene (titanite), and apatite. Common, too, are the characteristic minerals of the metamorphic rocks, garnet, epidote, sillimanite, tourmaline, etc. Rare earth minerals found in the monazite sands include xenotime, fergusonite, samarskite, gadolinite, and allanite. The remaining minerals are oxides of iron and tin, with, of course, a considerable amount of quartz.

It is apparent, from what has been said above, that monazite will be concentrated with the heaviest constituents of the rocks from which it is derived. Very often, indeed usually, these rocks are precisely those in which gold occurs, disseminated sometimes in tiny particles, sometimes collected into nuggets in veins of quartz and pegmatitic minerals. The erosion of these rocks concentrates the gold with the heaviest minerals ; and hence it happens that monazite is an almost universal constituent of the gold- and gem-bearing sands and gravels. In the Carolinas and in Brazil, monazite is found in the gold washings ; and though in the past the two have always been extracted separately, the gold first and the monazite from the washings or tailings, there appears to be no reason why a system calculated to extract both—where, of course, the content is high enough—should not be put into operation in the future.

A chemical test affords the only reliable method of detecting monazite in a sand. A little of the sand is washed with water to remove the lighter minerals and warmed with concentrated sulphuric acid. A few drops of the liquid are poured off, evaporated to small bulk, and one drop placed on a glass plate. This is placed under a microscope and one drop of a concentrated solution of sodium acetate is added. If monazite is present in the sand, tiny pointed oval crystals of sodium cerium sulphate will separate.

On the commercial scale, monazite is extracted from the sands only, in the manner described below. An effort was made in North Carolina in 1906 by the British Monazite Company, representing the South Metropolitan Gas Light Company of London, to extract monazite from the rock in which it occurs disseminated. The rock was crushed and powdered, and the monazite separated by washing off the lighter particles on concentration tables (see below). In the same year, however, the price of thorium nitrate was suddenly lowered 50 per cent. by the German Thorium Syndicate, which largely controls the Brazilian output of monazite, and the British company stopped operations in 1907. At present it may be said that only the sands are available for profitable extraction.

Up to 1895, the Carolina deposits, which were worked chiefly by the Welsbach Light Company of New York, either directly or indirectly, supplied all the demand, but in that year the Brazilian sands were first worked, and a keen struggle commenced for the market. The American companies, after keeping up a considerable output for some years, were forced to suspend operations in May 1910. The Brazil deposits, worked by the German Thorium Syndicate and the Austrian Welsbach Company, which have an agreement, now meet practically the whole demand. The Brazilian sand occurs chiefly along the shores of the southern provinces, having been concentrated by the action of the tides from the products of erosion of the cliffs; it is very uniform and considerably richer than the Carolina sand, and owing to its occurrence on the sea-shore, the cost of transporting it is very low. It is exported chiefly to Germany, recently also to the United States, and to a small extent lately to England. The method of working it is similar to that employed in Carolina—namely, concentration by washing and magnetic separation.

THE NORTH AMERICAN DEPOSITS[1]

There are two important regions in North America within which monazite sands occur; one extends over the Carolinas, and the north-western part of Georgia, the other over the Idaho basin and neighbouring counties of the Pacific Slope. It will be best to treat these separately, as the deposits are somewhat different in character.

(*a*) **The Carolina Deposits,** including the unimportant Georgia deposits, which belong to the same field, occur over an area approaching 4000 square miles. The area is occupied chiefly by the Piedmont plateau, which is drained by a number

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[1] See Nitze, *Bull.* No. 9, *N. Carolina Geol. Survey*, 1895; also Test, *Colorado School of Mines Bull.* Vol. IV. No. 2, p. 125, Jan. 1908.

of streams rising in the South Mountains, an eastern outlier of the Blue Ridge; it is in the basins and valleys of these streams, particularly at the head-waters, that the monazite is chiefly found. The geology of the district is very complicated,[1] the rocks being very highly altered granites. The chief bed is known as the Carolina gneiss, and includes several types of gneiss, usually very much weathered. The sands, which average about 1 per cent. of monazite, are worked in and near the stream beds; they occur in the beds, and in layers 1 to 2 feet in thickness a few feet below the surface of the surrounding soil.

Concentration was formerly effected chiefly by a crude process of washing. In this process the sand is thrown on to a sort of sieve, fixed over the upper end of a long wooden trough, by one workman; a jet of water is directed on to the sieve, washing the sand through it. The heavier particles fall to the bottom of the trough, whilst the lighter are washed right through. A second workman continually turns over the sand left in the box and on the sieve; at the end of a day's work the 'concentrate' is collected. This averages from 15 to 70 per cent. of monazite, according to the nature and amount of the heavy minerals accompanying it in the sand. The concentrate is dried either on rubber or oiled cloths in the sun, or on an iron plate covering a trough in which a fire is lighted. The iron minerals are then picked out by means of a magnet, and the sand filled into sacks for transport.

Before treatment for thorium nitrate, the sand is at the present day further concentrated by powerful magnetic separators. In a few cases the older method of concentration by hand-washing has been abandoned for machine concentration, the Wilfley table being sometimes employed. The principle here is exactly the same, the sand being fed into a hopper by means of a moving belt and thence on to a machine-shaken table from which running water constantly removes the particles, sorting them according to their specific gravity.

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[1] See Sterret, *U.S. Geol. Survey* (*Minerals*), 1906, p. 1195.

Further separation of the dried concentrate has been effected by three kinds of separators.[1] The first was of the Edison, or fall-and-deflection type; in this the sand is allowed to flow in a thin vertical stream past a horizontal magnet, which deflects the minerals containing iron; these fall on one side of a partition, the part richer in monazite on the other. The second was an electrostatic machine; the heated sand is borne on a moving belt underneath a rotating vulcanite cylinder, excited by felt-covered rubbers; the lighter particles are attracted to the cylinder, and dropped on one side, the heavier passing on. Neither of these machines is of much value in effecting concentration, and neither is in general use.

The third, and by far the most efficient and most widely-used machine, is known as the Wetherill electro-magnetic separator. It depends on the principle, first applied by the American engineer Wetherill, that not only the iron minerals, but a large number of other minerals may be attracted if the magnetic field be sufficiently strong. In all types of this machine used in cleaning monazite concentrates, four magnetic fields of increasing intensity are traversed by the sand; the first removes magnetite, ilmenite, and the larger fragments of garnet; the second removes all the remaining garnet and ilmenite; the third removes the coarser, and the fourth the finer monazite, tailings of zircon, rutile, and silica passing on. Careful adjustment of the magnetic fields will readily give a 97–99 per cent. monazite.

Two types of this machine are in common use. In the first the magnetic fields are obtained by four successive electro-magnets, arranged so that a broad horizontally-moving belt passes between the poles of each in succession. The upper poles are ground down to a fine edge perpendicular to the direction of the belt, to secure a more powerful field. Just beneath these edges, and just above the broad belt are four rapidly driven horizontal belts moving at right angles to the first or main belt; these carry off and deposit in separate bins the minerals attracted by their respective magnets. This type is known as the Rowand separator.

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[1] See Pratt and Sterrett, *Trans. Amer. Inst. Min. Eng.* 1909, 40, 313.

In the second type four horizontal belts are arranged in the form of descending steps, as shown in the diagram (Fig. 2). The magnets are placed at the end of each belt, and within it. The attracted mineral is held to its own belt, whilst the remainder drops on to the next; the attracted mineral falls into a bin as soon as its belt carries it out of the magnetic field. The sand to be cleaned is fed on to the first belt by means of a hopper.

The almost pure monazite so obtained is now treated chemically for its thorium. The processes proposed and in use are described in Chapter XVIII.

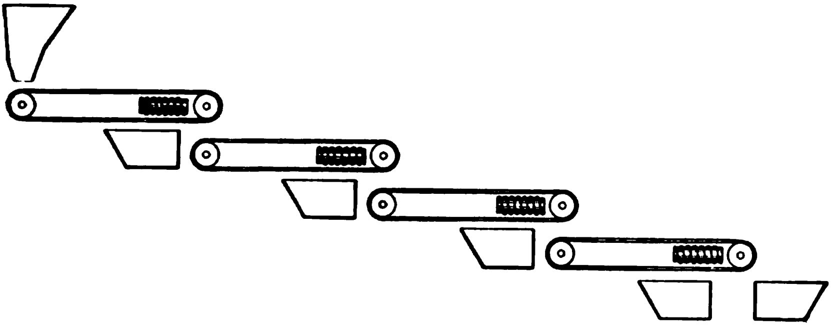

FIG. 2.

As already stated, the extraction of monazite in the United States has practically ceased; but the processes outlined above, which were first brought into use in the Carolinas, have been adopted for the treatment of the Brazilian sands.

(*b*) **The Idaho Deposits.**—Monazite was first observed in placer-gold deposits in the vicinity of Boise city near the Snake river. This deposit was a gold-bearing sand derived from granite. Later the gold-bearing sands of Oregon were also found to contain monazite; these sands are rich in zircon, and contain platinum and allied metals as well as gold. The sands of the Pacific slope are the so-called black sands, derived from hornblende, and augite-granites, usually porphyritic, which are much weathered at the surface. The soil is loose and is largely composed of granite fragments; the rain and streams constantly bring it down to the valleys, and continually renew the deposits. The concentrates obtained by washing are rich in well-crystallised zircon, with titanite and garnet.

In 1906 a company was formed to extract monazite from the black sand residues left after the extraction of gold. By 1909 they had erected plant and commenced operations at Centerville, and proposed to work the poorer auriferous sands for gold during the monazite washing. This, it was expected, could be done by washing the sands in boxes lined with amalgamated copper plates, which would retain the gold. Considerable amounts of monazite had already been extracted from the tailings when a disastrous fire put a stop to the operations in 1910.

Since then the production of monazite in the United States has practically ceased.

THE BRAZILIAN DEPOSITS

Brazil first became a serious competitor in the world's market with the United States, for the supply of monazite, in 1895. The greater percentage of thorium, the more even quality of the sands, and above all the occurrence on the sea-coast, rendered the Brazilian monazite cheaper from the beginning, so that it soon ousted the Carolina sand, and since 1910 has supplied the whole demand. The deposits at present worked lie along the coasts of Bahia, Minas Geraes and Espirito Santo, and whilst they are very rich in monazite, there is the disadvantage that their position and extent, and so also the possibility of working them, depend very largely on the variations in the tides, etc. The largest of these deposits is on the shores of a bay near the island of Alcobaca, on the southern coast of Bahia.

Monazite also occurs to a considerable extent in the diamond sands and gold-bearing sands of many of the interior provinces. In Minas Geraes it has long been known to occur at the celebrated mining centres of Diamantina and Ouro Preto, where xenotime and other rare earth minerals are also found; it is also known at various localities in the surrounding mining provinces of São Paulo, Goyaz, and Matto Grosso. More recently, extensive inland deposits have been found by Freise, in the province of Espirito Santo.[1] In the plateau-basin of the Muriahé and Pomba rivers he found a sand known locally as 'catalco' which carries an average of 2·1 per cent. of monazite and a gold-content of 1·75 grams per ton. In the Aymoré's mountains he found monazite, both massive and granular, in pegmatite veins in granite; analysis showed a thoria content of 9·23 per cent., which is very high. These deposits would form a very valuable and extensive source of thoria, if the difficulties of transport could be overcome.

At present, as stated above, only the beach deposits are worked. The Brazilian Government has laid a very heavy tax on all monazite exported; it is stated[2] that the German Thorium Syndicate pays 50 per cent. of its profits in royalties to the Government. In spite of this, the high quality of the sand and the low cost of transport have enabled this combine to lower the price of thorium nitrate to a point at which the Carolina sands cannot be worked, and it appears probable that the world's markets will be supplied for some time, at least, entirely from Brazil. The methods employed in working the sand are similar to those already described.

In the last few years monazite deposits have been found in various places, notably in Australia, India, and Ceylon. In the latter locality it occurs sparingly in the gem-gravels, in association with the much more valuable thorianite and thorite, but the supply is uncertain, and the minerals cannot be worked regularly. In Australia it occurs in Victoria and in Queensland. In Victoria the deposits are poor in monazite —about 0·025 per cent.—so that working is not profitable. In Queensland it occurs in beach sands on the southern coast, with gold, platinum, and cassiterite; there seems to be no reason why these deposits should not be profitably worked when sufficient labour is forthcoming. It also occurs in North

[1] *Zeitsch. pr. Geol.* 1909, 17, 514; *ibid.*, 1910, 18, 143.
[2] *U.S. Geol. Survey* (*Minerals*), 1906, p. 1195.

Queensland, on the Walsh and Tinaroo mineral fields; here it is found massive and granular in veins in granite, associated with wolframite, molybdenite, and cassiterite.

Quite recently, deposits of considerable extent have been found near Travancore, India.[1] These sands contain about 46 per cent. of the mineral, which is itself very rich in thoria, containing about 10 per cent. of the oxide; the unconcentrated sand is therefore as valuable as a source of thorium nitrate as the ordinary Brazilian concentrates, which average 4 per cent. or less of the oxide.

Monazite has also been observed in the tin-bearing sands of Embabaan, Swaziland, South Africa, and in the province of Ottawa, Canada.

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[1] *Bull. Imp. Inst.* 1911, vol. ix., No. 2, p. 103.

CHAPTER VIII

RADIOACTIVITY OF THE MINERALS

In the present chapter no attempt will be made to give a complete account of all the phenomena of radioactivity which have been observed in the mineral world. There are, however, a few problems of the highest scientific interest which centre about the rare earth minerals, and mention of these can hardly be avoided in a work which professes to give a general account of the rare earth group. It is obvious that a detailed treatment cannot be given without entering into phenomena which would be quite beyond the range of the present work, and an excuse is hardly needed, therefore, for the fragmentary and abbreviated account which follows. The reader's acquaintance with the general phenomena of radioactivity is of necessity assumed.

Radioactivity (the spontaneous emission of special radiations) was first observed by Becquerel, in 1896, in the case of potassium uranyl sulphate, and was soon found to be common to all uranium compounds, and to the metal itself. Mme. Curie showed that whilst in uranium salts the degree of activity varies directly with the percentage of uranium, in minerals containing the element the same rule does not hold. The observation that pitchblende is considerably more active than the uranium it contains led to the discovery of polonium[1] and radium in 1898. Exactly analogous phenomena were shown to hold for thorium salts and thorium-containing minerals by Mme. Curie and Schmidt in 1898, and in 1905 Hahn separated Radio-thorium from thorianite.

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[1] Polonium, which was named by Mme. Curie in honour of her native country, has been shown to be identical with Marckwald's 'Radio-tellurium,' which was named by Rutherford 'Radium F'; it is one of the degradation products of radium.

In 1899 Debierne discovered that the rare earths precipitated from the solution obtained on treatment of pitchblende are associated with another extremely active body, which he named Actinium ; Giesel found that in the separation of the rare earths this remains with lanthanum. In 1903 Ramsay and Soddy experimentally confirmed the prediction of Rutherford and Soddy, that radium would be found to produce helium continuously. The discovery of these remarkable phenomena has modified many fundamental physical conceptions, and has opened up a new field of scientific enquiry, which is being developed with unexampled rapidity.

It has been mentioned, in the accounts of the rare earth minerals given above, that almost all these minerals are radioactive, *i.e.* have the property of emitting specific radiations. Moreover, radioactivity, to any considerable extent at least, is, with a few important exceptions, confined to the minerals which have been already described. It has been shown by many investigators, chief amongst whom are Strutt and Boltwood, that the activity is usually due to the presence of uranium or thorium, or both.[1]

After the discovery of helium in Cleveite (a variety of pitchblende, *vide* p. 13) in 1895 by Ramsay, a large number of minerals were examined for this gas, and it was found that almost all the rare earth minerals contain helium. The fact that these minerals are also for the most part radioactive, naturally suggested some relation between the activity and the presence of helium, and led directly to the discovery that radium is continuously producing helium; and it became apparent that helium has been accumulating in these minerals since their formation, by the decay of radioactive elements. The question of the origin of helium in minerals will be touched on again.

In 1904 Boltwood advanced the theory that radium is produced by the degradation of uranium, the parent-element having, however, a much greater half-life period. If uranium continuously produces radium, whilst the latter decays much

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[1] Hauser and Wirth (*Ber.* 1910, 43, 1807) observed activity in some zirconium minerals containing neither thorium nor uranium.

more rapidly than the former, it must follow that in minerals containing uranium a state of equilibrium is reached between uranium and radium, and the ratio of these two in all minerals should therefore be constant, and independent of the geological age. Boltwood examined a number of the minerals of which descriptions have been given in the preceding chapters, and found the ratio to be surprisingly constant.[1] Strutt also examined a large number of minerals,[2] and whilst on the whole his results seemed to support the theory, his values for the ratio were by no means so constant as those of Boltwood. Strutt included in his examination the interesting radium-containing mineral observed by Danne at Issy l'Evêque.[3] This was a pyromorphite (lead chlorophosphate) containing neither uranium nor thorium. Danne suggested that the radium was not an original constituent, but had been introduced by the action of percolating waters. This view was confirmed by McCoy and Ross,[4] who found that the activity was entirely confined to the surface layer.

Mlle. Gleditsch has also examined the question of the uranium-radium ratio in minerals. Her earlier work [5] gave ratios which, whilst constant for each mineral species, varied in much the same manner as Strutt's for different species, and afforded very little support to Boltwood's theory. Her more recent results,[6] however, are much more closely in accord with the theory, which has been still further strengthened by the work of Pirret and Soddy [7] and of Marckwald and Russell.[8] It may now be regarded as firmly established that radium is in the line of direct descent from uranium.

Boltwood had assumed that the helium in radioactive minerals is produced from the uranium, during its disintegration. Strutt, however, disputed this; his experiments showed that very little helium is found even in the richest radium-

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[1] *Amer. J. Sci.* 1904, [iv.], **18**, 97; *Phil. Mag.* 1905, [iv.], **9**, 599.

[2] *Proc. Roy. Soc.* 1905, A, **76**, 88 and 312. *Ibid.* 1907, A, **80**, 56.

[3] *Compt. rend.* 1905, **140**, 241.

[4] *J. Amer. Chem. Soc.* 1907, **29**, 1698.

[5] *Compt. rend.* 1909, **149**, 267; *Le Radium*, 1909, **6**, 165.

[6] *Le Radium*, 1911, **8**, 256.

[7] *Phil. Mag.* 1911, [vi.], **21**, 652.

[8] *Ber.* 1911, **44**, 777.

uranium minerals unless thorium is also present. Thus pitchblende contains a very high percentage of uranium, but relatively little helium (there is usually a considerable thorium percentage here too, so that nothing conclusive can be deduced from this). Adams [1] found that carnotite, a mineral very rich in uranium, but containing no thorium, contains no helium at all; he explained its absence by the very loose texture and permeability of the mineral, which would allow the gas to escape. Strutt concluded that whilst helium is undoubtedly produced by disintegration in the uranium series, in minerals it is produced more by thorium or, as more recent work indicates, by radio-thorium, than by uranium.

The question of the origin of helium in minerals is, however, not definitely settled, for several anomalous cases are known. Thus the yttria silicate, Thalénite (*q.v.*), contains quantities of helium, but no uranium or thorium is given in the analyses. Similarly, Risörite contains a relatively large quantity of helium, but only traces of uranium and thorium. In the last mineral, the active constituent is precipitated with the lead, so that no radio-thorium appears to be present. Further, Thomsen analysed a fluorspar from Ivitgut in Greenland which he found to contain 27 c.c. of helium per kilogram. This specimen contains no uranium, but gives off the thorium emanation in quantities which suggest the presence of radio-thorium; moderate quantities of thorium are also present. Since the α particle has been definitely identified as a positively charged helium atom, it appears certain that disintegration in all three series (uranium, actinium, and thorium series) produces helium, and a mineral containing a member of any of these series (which gives α rays or α ray-giving products) would also contain helium.

Even so, there is a case in which the helium content is anomalous, if not altogether beyond explanation at the present stage. In examining a large number of minerals for helium, Strutt [2] found that some samples of beryl, a beryllium aluminium silicate, contain a relatively very large amount of helium, but only traces of thorium, and was altogether

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[1] *Amer. J. Sci.* 1905, [iv.], **20**, 256.

[2] *Proc. Roy. Soc.* 1908, A, **80**, 572.

inactive. The absence of any active constituent renders untenable the ordinary explanations of the presence of such a surprising quantity of helium. Boltwood has put forward a suggestion which in the present state of our knowledge must be regarded as a provisional explanation. He conceives that in the concentration of beryllium from the parent magma, it may have become associated with some short-lived intermediate radioactive element, which had been altogether separated from its long-lived parent element in the process of concentration; this intermediate element, having collected in the crystallised beryl, decayed completely in the course of the great period which must have elapsed, leaving the helium to which it had given rise during its disintegration enclosed in the mineral. It is difficult to see how two substances which must be so intimately connected as a parent-element and its product could be completely separated in the process of cooling of a magma; but since so little is known of the process of crystallisation of minerals, the suggestion can hardly be rejected on geological grounds. In any case, we have here only one strongly marked exception to the very definite rule that in all cases in which helium occurs in minerals, it is accompanied by and undoubtedly produced from, a radioactive element or elements; and in the majority of cases, the helium in minerals is produced by disintegration of uranium or thorium and their products.

Strutt found that traces of helium are universal in the mineral world. His method of determining helium was approximate only. He obtained the gas content by heating the powdered mineral—a method which, as Wood has shown,[1] will only give all the gas when very high temperatures (up to 1000° C.) are employed. The gases were freed from oxygen and hydrogen by passing over a heated, partially oxidised, copper spiral, and from carbon dioxide by means of potash. Nitrogen was removed by sparking with excess of oxygen and shaking over potash; the excess of oxygen was removed by melted phosphorus. The inert gases so obtained were freed from all impurities by the use of the liquid alloy of sodium

[1] *Proc. Roy. Soc.* 1910, A, **84**, 70.

and potassium for the electrodes of the spectrum tube in which the gases were examined spectroscopically.[1] Argon, if present—it seems to be a universal constituent of igneous rocks, into which it may have been absorbed from the air—was removed by charcoal at a temperature of – 80° C. The helium so left was examined spectroscopically, and measured in a MacLeod gauge.

As stated, helium was found in traces in nearly all minerals, and its presence is to be attributed to traces of radium, which also appears universal. In minerals containing uranium or thorium, or rare earths (the latter are almost always accompanied by uranium and thorium), helium is found to a much greater extent, and Ramsay considers it possible that some fraction of the helium content may arise from the rare earth metals. There is, however, no positive evidence to support the conjecture. He found that the helium ratio, *i.e.* the volume of helium per gram of uranous oxide, UO_2, varies with the amount of thoria present; but where the latter is absent the variations are much less marked. If helium were produced in a mineral from uranium alone, and none escaped, it is obvious that the helium ratio would depend only on the age of the mineral. For minerals of about the same age, and containing no thorium, the helium ratio would be roughly constant, if no disturbing factor required consideration.

In 1905 Strutt pointed out that in all the minerals he had examined, thorium was never present unless accompanied by uranium and radium, whilst uranium and radium often occurred without thorium. He suggested that the present atomic weight of thorium, 232·5, was too low, and that it was really the parent of uranium (at. weight 238·5); he further supposed that the next permanent member in the line of descent was one of the cerium metals. These suggestions have been negatived by later work of Boltwood and Holmes. The former pointed out[2] that it was far more likely that thorium is a disintegration product of uranium of considerably

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[1] As soon as the discharge is started in such a tube, all the gases present other than those of the helium family are absorbed by these electrodes.

[2] Boltwood, *Amer. J. Sci.* 1905, [iv.], 20, 256.

longer life. On the whole, however, there is very little positive evidence to connect thorium with uranium.

In the same year Boltwood (*loc. cit.*) drew attention to the persistent appearance of traces of lead, bismuth, barium, etc., in the radioactive minerals, and also pointed out that the variations of the ratio of helium to uranium in pitchblende might be used to determine the age of the mineral. In 1907 he suggested [1] that lead was the final product of the degradation of uranium, from which it follows that the ratio of uranium to lead should be constant for minerals of the same age (since lead decays, if at all, at an infinitely slower rate than uranium). He collected all the available analyses, and classified the minerals dealt with into six groups according to the value of the ratio. The order given by the ratio was declared to be in accordance with the order of age as given by geological evidence.

Holmes [2] has further extended this work. He examined a number of rare earth and allied minerals from the Christiania district, which Brögger considers to be of approximately Lower Devonian age, and found the ratio of lead to uranium to approximate quite closely, for almost all the minerals examined, to 0·045. Representing the change in the usual way as

$$\begin{array}{c} \mathrm{U} \longrightarrow 8\mathrm{He} + \mathrm{Pb} \\ 238{\cdot}5 \longrightarrow 31{\cdot}92 + 207{\cdot}1 \end{array}$$

and using the data calculated by Rutherford and others for the rates of decay, he gives the age of Lower Devonian strata as about 370 million years. This figure is about twice as great as that deduced by palæontologists from the flora and fauna, and greater still than the times based on physical data, *e.g.* rates of cooling, precession and nutation, etc. His figures for pre-Cambrian rocks, based on the same ratio, range between 1000 and 1640 million years, the later being deduced from a thorianite from the Archæan rocks of Ceylon. Strutt's figure for Archæan rocks is about 700 million years; this was derived from work on the helium ratio, which must now be considered.[3]

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[1] *Amer. J. Sci.* 1907, [iv.], 23, 77.

[2] *Proc. Roy. Soc.* 1911, A, 85, 248.

[3] See Strutt, *Proc. Roy. Soc.* 1908, A, 82, 166; 1909, 83, 96; 1909, 83, 298; 1910, 84, 194.

In 1898 Travers[1] had examined the effect of heat on cleveite and fergusonite, and found that about half the total helium, together with hydrogen, is given off at a bright red heat. He considered it likely that the helium was combined with a metal (though he recognised no distinction between occlusion and combination) and remarked: 'The results of such experiments cannot therefore serve as a basis for speculation as to the origin or history of the substances in question.' The chemical inactivity of helium, however, as well as the experiments of Moss and Gray, who showed that helium was evolved on grinding the materials,[2] indicate that the gas is mechanically bound only. This, however, introduces the difficulty, if an attempt be made to use the helium-uranium ratio to calculate the age of minerals, that the gas would be expected to escape from a porous material, so that its amount is never so great as it should be. Strutt himself found that helium escapes rapidly from powdered monazite, whilst even the solid mineral was found to evolve helium at a rate much in excess of the probable rate of production by radioactive changes. Similar results were found with thorianite, and the only conclusion, since helium is found in the minerals, is that under the conditions under which these minerals exist in the earth's crust, this escape is checked or altogether prevented. It follows, however, that any age determined from the helium ratio must be a minimum age, since there is always the chance of loss; this of course is not the case—except where the minerals have suffered chemical changes—with the lead ratio, and may account for the discrepancies observed.

Strutt's earlier work on the helium ratio was made with phosphate minerals (coprolites and fossil bones) of known ages. The ratios found were not in order of age, the minerals being very permeable, so that helium had probably been lost. He next turned his attention to igneous rocks, and selected zircon for the work. Here he obtained some sort of regularity in the order of age and the order given by the ratio, and assumed

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[1] *Proc. Roy. Soc.* 1898–99, **64**, 140.

[2] *Vide* Gray, *Proc. Roy. Soc.* 1908, A, **82**, 306.

that if helium were lost at all, it must be lost in roughly proportional amounts by reason of the similarity in conditions. Geological criticism tends to lessen the trustworthiness of the conclusions ; it is pointed out that the age of a specimen of zircon is not necessarily that of the rock in which it occurs, for zircon is an extremely stable mineral, and might survive unchanged several fusions and re-crystallisations of the magma. Strutt replies to this that at the temperature of fusion of a rock, zircon would certainly give up its accumulated helium, so that the age determined from the helium content would be that of the last fusion, *i.e.* the age as given by geological data. On the other hand, our ignorance of the real mechanism of the crystallisation of a magma, and especially of the amount and effect of the pressures obtaining, robs this reply of its force, and the objection must be counted valid.

In still later work Strutt used sphene and thorianite, and his results agree as well as can be expected. The sphenes used were all from Archæan rocks, except one, which was from a Tertiary volcanic deposit of the Laacher See, near Coblenz (the lake is in the crater of an extinct volcano). In this case the helium ratio was very much smaller (about $\frac{1}{1000}$ of the values for Archæan rocks) indicating the (comparatively) extremely recent formation of the deposit.

The most recent results in the study of radioactivity point to the conclusion that elements which differ in atomic weight and radioactive properties may be chemically identical, or at least chemically inseparable ; such elements have been termed isotopes. The end product of the thorium series of radio-elements should have an atomic weight of about 208·4, and it has been suggested that the element actually produced in this series of changes may be bismuth. The latest results, however, rather point to the conclusion that disintegration in the thorium series gives rise to an isotope of lead. If this hypothesis be true, the lead derived from a mineral rich in thorium and poor in uranium should have an atomic weight appreciably higher than that of ordinary lead. Experiments to test this conclusion have recently been carried out by Soddy and Hyman.[1]

[1] *Proc. Chem. Soc.* 1914, 30, 134.

These authors have made analyses of Ceylon thorite, which they find to contain 0·35 per cent. of lead; from the ratio of thorium to uranium in the mineral, they calculate that the lead should have an atomic weight of 208·2, that of ordinary lead being 207·1. Preliminary comparative experiments on 1 gram of pure lead chloride extracted from the mineral point to an atomic weight for the thorite lead of 208·4, a result surprisingly in accord with theory. More extended experiments on this most interesting question are in progress.

The present chapter would be incomplete without a reference to the interesting work of Goldsmidt on radioactivity as an aid in identifying mineral species.[1] He describes a simple method by which the activity of a mineral may be rapidly and easily measured to a sufficient degree of approximation, and shows how the determination enables a line to be drawn on a diagram already mapped out; this line will intersect an area on the diagram which corresponds to the particular mineral. Owing to lack of analytical data, and to the great difficulty of determining with accuracy small quantities of uranium and thorium, the method is at present of scientific interest only; but it is capable of development, and its development would be of undoubted value in the further study of this branch of radioactivity.

In order to make this part of the subject as clear as possible, the chief points in this chapter are summarised as follows:

1. Radioactivity is only observed to an appreciable extent in some rather rare minerals. These minerals as a rule contain radium, uranium, thorium, rare earths, and helium.

2. The helium has been produced during geological time by the degradation of one or more members of the three series of active elements (the Uranium, Actinium, and Thorium series).

3. Radium is a degradation product of uranium, and itself is degraded continuously; the final product of degradation is probably lead.

4. The age of minerals has been calculated from the ratio

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[1] *Zeitsch. Kryst. Min.* 1907–8, **44**, 545; *ibid.* 1908, **45**, 490.

of lead to uranium ; the figures obtained are much greater than those put forward by geologists and physicists.

5. The helium ratio has also been used, but appears less trustworthy, owing to escape of helium, and uncertainty as to geological age of the minerals employed.

6. Some connection between radioactivity and the presence of the yttrium or cerium metals appears highly probable, but no satisfactory theories have been advanced on this point ; it has been shown that actinium is very closely allied to lanthanum.

PART II

THE CHEMISTRY OF THE ELEMENTS

CHAPTER IX

GENERAL PROPERTIES OF THE CERIUM AND YTTRIUM GROUPS

THE chemistry of the rare earth elements begins in the year 1794, with Gadolin's discovery of the new oxide 'Ytterbia,' for which the name Yttria was subsequently proposed by Ekeberg, and generally adopted (see Chapter I, and under Gadolinite, p. 35). The discovery of Ceria followed in 1804 (see under Cerite, p. 32). The classical work of Mosander, carried out between 1838 and 1842, showed the complex nature of the new oxides. From ceria he separated three new earths, Ceria proper, Lanthana, and Didymia. Yttria was shown to be a mixture of at least three oxides, for which the names Yttria, Erbia, and Terbia were proposed. These oxides were believed to have the general formula RO, by analogy with the alkaline earths, which they were found to resemble in many respects, notably in their strongly basic character.

The properties of the new oxides were examined during the next twenty years by many chemists, the chief workers being Marignac, Rammelsberg, and Hermann, but the next important advance was the investigation of the absorption spectra of solutions of the rare earth salts, first suggested by Gladstone in 1856, and developed more fully by Bunsen and Kirchhoff in 1860 and the following few years. The introduction of the methods of spectrum analysis furnished a very delicate and valuable method of examining and identifying the various oxides, and so greatly assisted the laborious processes of separation.

Sixteen elements (excluding thorium and zirconium) are at the present time recognised as belonging to the rare earth group. With one or two exceptions, these show the closest resemblance to one another, both in chemical behaviour and in the properties of their compounds, so that the difficulties of separating and purifying them are very great. They may be said to form a series, in which the properties vary continuously but gradually from member to member, so that no sharp differences are anywhere perceptible. The method of division into groups is, therefore, almost entirely one of convenience, and has arisen from the course which the separations have followed.

The elements are divided into two chief families or groups, that of the cerium metals and that of the yttrium metals respectively. The cerium elements are separated by a process depending on the relative insolubility of their alkali double sulphates; in this group are included cerium, lanthanum, praseodymium, neodymium, and samarium. The yttrium family is further divided into four sub-groups: the first consists of scandium and yttrium; the second or terbium group of europium, gadolinium, and terbium; the third or erbium group of dysprosium, holmium, erbium, and thulium; and the fourth or ytterbium group of ytterbium and lutecium—the element celtium, recently discovered by Urbain, will also fall into this sub-group, but the discovery awaits confirmation. Whilst scandium and yttrium fall into somewhat abnormal positions, corresponding to their low atomic weights, the terbium elements occupy an intermediate position between the cerium elements and the remaining yttrium elements, or yttrium group proper, and so are frequently classified as a third or intermediate group.

This list does not include all the names which have been put forward to designate what have been claimed from time to time as new elements; whilst the individuality of some of those included is not yet fully established, and the homogeneity of others has been called in question. The uncertainty is more pronounced among the yttrium elements than among the cerium elements; owing to the opportunities for investigation furnished by the commercial treatment of monazite, the chemistry of the cerium group may be regarded as complete.

In the following table the elements are arranged in order of increasing atomic weight, and it can be seen at once how closely the division into groups follows this order:

	Element	Atomic Wt.	Colour of Salts
	Scandium, Sc.	44·1	Colourless
	Yttrium, Yt	89·0	Colourless
Cerium Group.	Lanthanum, La	139·0	Colourless
	Cerium, Ce	140·25	Cerous, colourless; ceric, orange to red
	Praseodymium, Pr	140·6	Green
	Neodymium, Nd	144·3	Red to reddish-violet
	Samarium, Sa	150·4	Topaz yellow
Terbium Group.	Europium, Eu	152·0	Faint rose
	Gadolinium, Gd	157·3	Colourless
	Terbium, Tb	159·2	Colourless
Erbium Group.	Dysprosium, Dy	162·5	Bright green
	Holmium, Ho	163·5	Yellow to orange
	Erbium, Er	167·7	Deep rose
	Thulium, Tm	168·5	Bluish-green
Ytterbium Group.	Ytterbium, Yb	172·0	Colourless
	Lutecium, Lu	174·0	Colourless

In their chemical relations, the rare earth elements may be placed between the metals of the alkaline earths, and the trivalent metals iron, aluminium, and chromium. With the exceptions of cerium in the ceric salts, and of samarium and europium in the recently discovered dichlorides, they are uniformly trivalent, but the oxides are very strong bases, and the salts very slightly hydrolysed in dilute solutions; generally, therefore, they resemble the calcium family rather than the aluminium group. Among the common salts, the oxalates, phosphates, chromates, iodates, fluorides, carbonates, tartrates, and borates are almost insoluble; the sulphates are only sparingly soluble at ordinary temperatures. Among the double salts, the alkali double sulphates are of great importance from their employment for separations; the tendency to the formation of complex salts is greater among the yttrium than among the cerium elements, increasing with the atomic weight, and with the decrease in basic strength of the oxides.

The great similarity in chemical behaviour of the rare earth elements is apparent not only in the similarity in composition, solubility and chemical properties of the salts—which is so great that the general account of the compounds which follows applies almost in its entirety to each member of the group—but also in the crystallographic relations between corresponding compounds. Many of the salt hydrates form isomorphous series; the sulphate octohydrates, for example, appear to be isomorphous throughout the whole group, and probably the relation would be found to apply even more completely than is generally accepted, if the necessary data were forthcoming. Of great interest and practical importance is the isomorphism between the nitrates and double nitrates of the cerium elements and bismuth, which has been utilised with such valuable results in the processes of fractional crystallisation.

The Metals.—The earlier attempts to reduce compounds of the rare earth elements to the metallic condition, by means of metallic sodium or potassium, did not yield pure products; nor did the use of aluminium or magnesium lead to results of practical importance. The metals were first obtained in a coherent physical condition by Hillebrand and Norton,[1] by electrolysis of the fused chlorides. These investigators obtained cerium, lanthanum, and the so-called didymium, and measured their specific heats; their results confirmed the atomic weights assigned to the elements by Mendelejeff, except in the case of lanthanum. Their method has since been elaborated by Muthmann, Hofer and Weiss,[2] who have

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[1] *Pogg. Ann.* 1875, **155**, 631; **156**, 466.

[2] *Annalen*, 1902, **320**, 231; see also Muthmann and Weiss, *ibid.* 1904, **331**, 1.

prepared large quantities of the cerium elements in the pure state. More recently, Hirsch has prepared metallic cerium in large quantities,[1] and has studied its properties.

By electrolytic reduction of the mixed chlorides of the cerium elements, a mixture known as 'Misch metal' is obtained; this has powerful reducing properties, and, like aluminium, reduces the oxides of iron, chromium, etc., with great development of heat.[2] The yttrium metals have not yet been obtained in the pure state, the electrolytic method giving unsatisfactory results on account of the high melting-points of the metals, and the volatile nature of their chlorides.

The cerium metals are white or slightly yellowish in colour, and are moderately stable in dry air. In moist air they tarnish slowly, lanthanum, as the most positive, being most readily oxidised. The melting-points and specific gravities are as follows:

Element	Melting-point	Specific Gravity
Cerium	623°	7·0242
Lanthanum	810°	6·1545
Praseodymium	940°	6·4754
Neodymium	840°	6·9563
Samarium	1300°–1400°	7·7–7·8

The metals decompose water slowly in the cold, but rapidly at the boiling-point, with evolution of hydrogen. They have a great affinity for oxygen, the heats of formation of the oxides being of the order of those of alumina and magnesia:

	Heat of Formation per Equivalent Weight of Oxide[3]
$\frac{1}{6}La_2O_3$	74·1 K
$\frac{1}{6}Nd_2O_3$	72·5 ,,
$\frac{1}{6}Pr_2O_3$	68·7 ,,
$\frac{1}{4}CeO_2$	56·1 ,,
$\frac{1}{6}Al_2O_3$	64·3 ,,
$\frac{1}{2}MgO$	71·9 ,,

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[1] *Met. Chem. Eng.* 1911, 9, 543.

[2] A full account of the properties and preparation of the cerium metals and their alloys will be found in the monograph of Kellermann, '*Die Ceritmetalle und ihre pyrophoren Legierungen*, Wilhelm Knapp, Halle, 1912.

[3] Muthmann and Weiss, *loc cit.*; K = 1 kilogram-calorie, or 1000 cal.

In consequence of the high values of the heats of combustion, the metals have powerful reducing properties.

The cerium metals form alloys with magnesium, zinc, aluminium, and iron, and combine with boron and silicon. The alloys of cerium, and the metal itself, are remarkable for their property of emitting brilliant sparks when scratched (see Chapter XXI). Cerium also forms an amalgam with mercury.

The metals burn brilliantly when heated in oxygen, and dissolve readily in dilute mineral acids. When heated to a temperature of 200°–300° in a current of hydrogen, they absorb the gas very readily, forming the *hydrides*. These compounds are also obtained by heating the oxides with magnesium in a current of hydrogen. They were first prepared by Winkler,[1] who deduced from his analyses the general formula RH_2; the more recent work of Muthmann and Beck,[2] however, points to the formula RH_3.

If nitrogen be substituted for hydrogen in either of the above methods of preparation, *nitrides* of the general formula RN are obtained; cerium nitride, however, cannot be obtained by heating the element in the gas.[3] These compounds are also obtained when the carbides are heated in ammonia. They are amorphous solids, which yield ammonia when acted upon by water.

Hydroxides. — The hydroxides are thrown down as gelatinous precipitates on the addition of alkalies to hot dilute solutions of the salts; precipitation in the cold, or in strong solution, usually gives a basic salt, or an hydroxide mixed with a large quantity of basic salt. The hydroxides are insoluble in excess of precipitant, but the precipitation is inhibited by the presence of some organic hydroxy-acids.[4]

The hydroxides are insoluble in water, but dissolve very readily in acids. The most basic of them absorb carbon dioxide from the air; lanthanum hydroxide is exceptional in that it colours litmus blue.

Whilst hydrogen peroxide in neutral solution does not

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[1] *Ber.* 1890, **23**, 2642; 1891, **24**, 873.

[2] *Annalen*, 1904, **331**, 58.

[3] Dafert and Miklanz, *Monats.* 1912, **33**, 911.

[4] For effect of tartaric acid, see p. 133.

react with rare earth salts,[1] alkalies in presence of this reagent precipitate gelatinous hydrated peroxides, which are very unstable, decomposing on standing, or on treatment with acids, with evolution of oxygen. The general formula $R_4O_9 + xH_2O$ was proposed for these compounds by Cleve, but more recently the formula $R(OOH)(OH)_2$ has been advanced.[2]

Oxides.—In their most stable state of oxidation, the rare earth elements are generally trivalent. In the case of cerium, the dioxide, CeO_2, is more stable than the sesquioxide Ce_2O_3, but the ceric salts are unstable, and are very readily reduced to cerous compounds, corresponding to the oxide Ce_2O_3. Higher oxides are known with certainty among the other elements only in the cases of praseodymium and terbium, but these do not give rise to salts.

The oxides R_2O_3 are fairly strong bases, being comparable in strength to the alkaline earths, and far more strongly basic than alumina and oxides of other trivalent elements; thus they liberate ammonia from ammonium compounds, whilst the salts they form with strong acids are not easily hydrolysed. Their relative strengths as bases are expressed in the following series, in which the elements are placed in order of diminishing electropositive character:[3]

La, Ce''', Pr, Nd, Yt, Eu, Gd, Sa, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Ce^{iv}.

It will be seen that, with the exception of scandium and yttrium, the metals of the cerium and yttrium groups become less electropositive as the atomic weight increases.

This arrangement is obtained by ascertaining the order in

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[1] Compare behaviour of thorium and zirconium, Ch. XVI.

[2] Melikoff and Pissarjewski, *Zeitsch. anorg. Chem.* 1899, 21, 70; Melikoff and Klimento, *Chem. Zentr.* 1902, 1, 172.

[3] The position of yttrium in this series is not known with certainty; it is probably as positive as neodymium. It is usually stated (see Meyer and Hauser, pp. 32–33) that the terbia oxides are intermediate in basic strength between the ceria and yttria earths, though the arrangement into two series, consisting of the cerium and yttrium groups respectively, is generally adopted; the electropositive character of the elements in each series then weakens as the atomic weight rises, scandium being of course exceptional.

which the various hydroxides are precipitated from a solution by gradual addition of a dilute solution of a strong base. The weakest base is precipitated first, and the strongest last; those intermediate in strength are thrown down in ascending order of strength. Similar results may be obtained by the fractional decomposition of the nitrates by heat; in this case the nitrate of the weakest base is decomposed at the lowest temperature. This order is also confirmed, as far as the data are available, by measurements of the equivalent conductivities of solutions of the salts (see, for example, p. 122).

Quite recently, a very different order has been obtained from a consideration of the dissociation tensions, and of the heats of dissociation of the anhydrous sulphates.[1] In the following table the elements are arranged in the order of the increase of the dissociation tension (T) measured at 900°, which is the same as the order of decrease of the heats of dissociation (Q):

Element	At. Wt.	T. (Mm. Hg.)	Q.
La	139·0	2	59·8
Yt	89·0	3	58·9
Lu	174·0	3·5	58·5
Yb	172·0	4	58·2
Er	167·7	5	57·6
Pr	140·6	5·5	57·4
Nd	144·3	6	57·2
Gd	157·3	7	56·9
Sa	150·4	8	56·5
Sc	44·1	11	54·5
Ce	140·25		52·4

It will be observed that the order is very different from the order of increase of atomic weight, the positions of lutecium and ytterbium being especially surprising; these elements are generally considered to be among the least electropositive of the whole series. The anomalous position of cerium is probably due to the fact that the sulphate on decomposition leaves the

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[1] Wöhler and Grünzweig, *Ber.* 1913, 46, 1726.

dioxide, and not the sesquioxide, as with the other elements; this would undoubtedly affect the values. The heats of dissociation are the greatest yet observed for the sulphates of trivalent metals, a further evidence of the strongly basic nature of the oxides.

Ignited lanthana resembles quicklime in that it readily absorbs carbon dioxide from the air, and hisses when slaked with water; as the basicity becomes weaker, the affinity for water and carbon dioxide becomes less marked. All the oxides are soluble in dilute acids, even after prolonged ignition; but the ease with which solution occurs is naturally much influenced by the treatment to which the oxide has been subjected, as well as by its strength as a base.

The rare earth oxides are capable of existing in more than one modification, the compounds obtained by ignition of the hydroxides differing in appearance and reactivity from those prepared by ignition of the oxalates or nitrates, and so on; they are probably highly polymerised. Cerium dioxide, CeO_2, is remarkable for its power of combining with the other oxides, R_2O_3, of the rare earth metals. The pure dioxide is insoluble in nitric acid, but mixtures of earths containing up to 50 per cent. of the dioxide dissolve readily. The various colours of mixtures of the ceria earths may sometimes be attributed to a similar combination,[1] and there can be little doubt that the dioxide sometimes functions as an acid in the rare earth minerals.

Sulphides.—These compounds cannot be prepared in the wet way, that is, by the action of hydrogen sulphide or ammonium sulphide on the salts in solution; the former reagent gives no precipitate, the latter throws down the hydroxides. In this behaviour, the rare earth elements resemble aluminium and chromium.

The normal sulphides, R_2S_3, are obtained by reduction of the anhydrous sulphates, or from the oxides at high tempera-

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[1] The brown colour of a mixture of ceria oxides containing praseodymium is generally attributed to the presence of the strongly coloured peroxide of that element.

tures, by treatment with hydrogen sulphide. They are strongly coloured compounds, fairly stable towards cold water, but readily hydrolysed on boiling.

Disulphides, RS_2, are known in the cases of cerium, lanthanum, and praseodymium; these are to be regarded as polysulphides, since on treatment with dilute acids they yield hydrogen persulphide, H_2S_2.

Carbides.—By reduction of the oxides with carbon in the electric furnace, Moissan obtained the carbides in the form of microscopic yellow crystals. They have the general formula RC_2, and are attacked by water and dilute acids, with evolution of very complex mixtures of gases.[1] The principal product is acetylene, with various higher homologues, and in smaller quantities ethylene and ethane and their homologues. No methane is formed,[2] but hydrogen is always present, the olefines and paraffins probably arising from its action on the acetylenic hydrocarbons. The relation of the rare earth elements to the calcium group is here very close; calcium carbide when attacked by water yields pure acetylene, whereas aluminium carbide gives pure methane.

Halogen Salts.—The halides of the rare earth elements show a close analogy with the corresponding compounds of the alkaline earth elements. The *fluorides* are insoluble in water and dilute mineral acids, and are obtained as gelatinous precipitates by the addition of hydrofluoric acid, or a soluble fluoride, to solutions of the salts. They may be prepared in the crystalline condition by heating the carbides in a stream of fluorine, or by the action of hydrofluoric acid upon the hydroxides in aqueous suspension. The rare earth elements, as well as thorium, may be separated from zirconium by taking advantage of the insolubility of their fluorides in excess of hydrofluoric acid or alkali fluorides, since zirconium fluoride

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[1] Damiens, *Compt. rend.* 1913, 157, 214.

[2] Moissan stated that 24–30 per cent. of methane was formed in this action; compare *Compt. rend.* 1900, 131, 595.

is readily soluble in excess of the precipitant. The solubility of the fluorides in a large excess of concentrated acid increases with the electropositive character of the metal, the fluorides of the more negative elements being the least soluble. Thorium and scandium may, therefore, be concentrated to a large extent by repeated precipitation with hydrofluoric acid in acid solution.

The *silicofluorides* of the rare earth elements have been used by R. J. Meyer in the extraction of scandium from wolframite (see Chapter I and under Scandium, p. 215). They are thrown down as gelatinous precipitates on addition of potassium or sodium silicofluoride to boiling, neutral solutions of rare earth salts. In presence of mineral acids, however, they are not thrown down in the cold ; on boiling, the cerium metals are precipitated as fluorides, by hydrolysis of the silicofluorides—the yttrium elements, with the exception of scandium, being held in solution by the mineral acid.

With the exception of the fluorides, the halogen salts of the rare earth metals are readily soluble in water, and crystallise from the concentrated solutions in the hydrated form. The bromides and iodides have not been so fully studied as the chlorides ; they are hygroscopic salts, and decompose rather easily. The iodides have been obtained by Moissan in the anhydrous state, by the action of iodine vapour on the carbides at high temperature.

The anhydrous *chlorides* may be obtained by the application of any of the ordinary methods, *e.g.* by heating the oxides with carbon in a stream of chlorine, by heating the carbides in the same gas, by heating the sulphides or hydrated chlorides in hydrogen chloride, or by evaporating the solutions of the hydrated salts to dryness in presence of ammonium chloride, and then igniting till the latter has all been removed. As obtained by any of these methods, they are fusible at a red heat, but only slightly volatile ; they are easily soluble in water or alcohol, with disengagement of heat. They are insoluble in most organic solvents, but dissolve to some extent in some bases ; the chlorides of the yttrium elements, for example, are readily soluble in pyridine. With such solvents, the chlorides form compounds which may be considered as derived from the hydrated forms, by replacement of the so-called water of crystallisation by the organic base.

Conductivity measurements show that the salts are not perceptibly hydrolysed in moderately dilute aqueous solutions, though the values for the equivalent conductivities vary somewhat with the variations in the electropositive character of the elements. In the following table, the equivalent conductivities of the chlorides in solutions of dilution 32 and 1024 at 25°C. are given. It will be seen that the value $(\lambda_{1024} - \lambda_{32}) \div 10$ is in all cases (except for the highly hydrolysed scandium salt) very close to 3, an experimental proof of the trivalent nature of the elements. The values for the chlorides of iron, aluminium and chromium are included; it will be seen that these elements are considerably less positive than the rare earth metals (with the exception, of course, of scandium).

Salt	λ_{32}	λ_{1024}	$\lambda_{1024}-\lambda_{32}$
$LaCl_3$	105·8	131·5	25·7
$CeCl_3$	107·8	135·2	27·6
$PrCl_3$	105·5	135·9	30·4
$NdCl_3$	103·8	134·3	30·5
$YtCl_3$	98·8	123·4	24·6
$YbCl_3$	107·4	140·4	33·0
$ScCl_3$	116·9	257·9	141·0
$AlCl_3$	99·9	138·0	38·1
$CrCl_3$	98·4	152·6	54·2
$FeCl_3$	117·2	200·7	83·5

From aqueous solutions the chlorides crystallise with six molecules of water, except praseodymium chloride, which has seven. The hydrated salts, when heated to 120° in the air, form insoluble oxychlorides of the general formula ROCl.

The chlorides do not show a great tendency to form double salts with other metallic chlorides; on the other hand, they readily form complex compounds with the chlorides of the less electropositive metals, *e.g.* tin, bismuth, gold, and platinum.

Subchlorides of samarium and europium have recently been obtained; in these compounds, for the first time, rare earth metals have been shown to be capable of functioning as divalent elements.

Cyanides of the rare earth elements are not known; addition of potassium cyanide to solutions of the salts throws down the hydroxides. The *platinocyanides* may be obtained by double decomposition of the sulphates with barium platinocyanide. They are very stable and characteristic bodies, of the general formula $R_2[Pt(CN)_4]_3$, with 18 or 21 molecules of water. The compounds of the cerium elements are yellow, with a strong blue fluorescence; they crystallise in the monoclinic system. The platinocyanides of the yttrium metals are red or crimson, with a splendid green fluorescence, and crystallise in the rhombic system. Scandium platinocyanide is of great interest from the fact that it exists in two modifications, which show the characteristic appearance of the two groups of compounds respectively.

Potassium ferrocyanide precipitates *potassium earth ferrocyanides* of the general formula $KR(FeC_6N_6),3H_2O$, from neutral solutions;[1] the precipitate is somewhat soluble in excess. The ferrocyanides have been proposed for the purification of yttrium; the method is useful where rapid concentration of the element is required, yttrium ferrocyanide being far more soluble than the analogous compounds of the erbium and ytterbium metals, but the precipitates are gelatinous, and very difficult to handle.

Halogen Oxy-salts.—*Perchlorates* and *periodates* of the rare earth elements, of the general formula $R(XO_4)_3,xH_2O$, have been obtained. The existence of *chlorates* has been observed only in the yttrium group; yttrium chlorate, $Yt(ClO_3)_3,8H_2O$, has been prepared by double decomposition of the sulphate with barium chlorate. The *bromates* are also prepared in this way. They are readily soluble compounds, of which several hydrated forms are known. They are of considerable importance for purposes of separation in the yttrium group.

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[1] Compare Astrid Cleve, *Zeitsch. anorg. Chem.* 1902, **32**, 129.

The *iodates* are sparingly soluble bodies, precipitated by addition of the alkali compound to solutions of the rare earth salts. The rare earth iodates are soluble in nitric acid, the solubility increasing as the electropositive character of the element becomes stronger. A method for the purification of yttrium has recently been based upon this property of the iodates, whilst the fact that thorium iodate is completely insoluble in nitric acid allows of the easy separation and estimation of thorium in minerals or mixtures containing rare earth elements.

Sulphates.—The sulphates of the rare earth elements are obtained by dissolving the oxides or hydroxides in sulphuric acid. From the solutions so obtained, various hydrated salts separate according to the temperature of crystallisation. By heating the hydrated salts to a temperature of 300°–400°, the anhydrous salts are prepared. These are extremely soluble in water at 0°, having a great tendency, which is indeed to be observed in the hydrated forms also, to form supersaturated solutions. When the temperature of such a solution is allowed to rise, larger or smaller quantities of an hydrated form separate out, the differences of solubility among the sulphate hydrates of the various elements being sometimes considerable.

The hydrated sulphates of the cerium elements have been very closely studied in connection with the purification of thorium. Cerium sulphate itself forms hydrates with 12, 9, 8, 5, and 4 molecules of water, but sulphates of the other elements generally form fewer hydrates; the commonest have 12, 8, or 4 molecules of water, and numerous cases of isomorphism are known among them. The solubility curve of the cerium sulphate hydrates is shown in the diagram, Fig. 3. The sulphates of the yttrium elements have not yet been systematically investigated, and in most cases only the octohydrates are known. Scandium sulphate is notably different from the other sulphates, in that it is considerably more soluble, and crystallises with six molecules of water.

It is an important characteristic of the rare earth elements that the solubility of the sulphates diminishes rapidly as the temperature rises. The study of the various equilibrium conditions is greatly complicated by the tendency to form

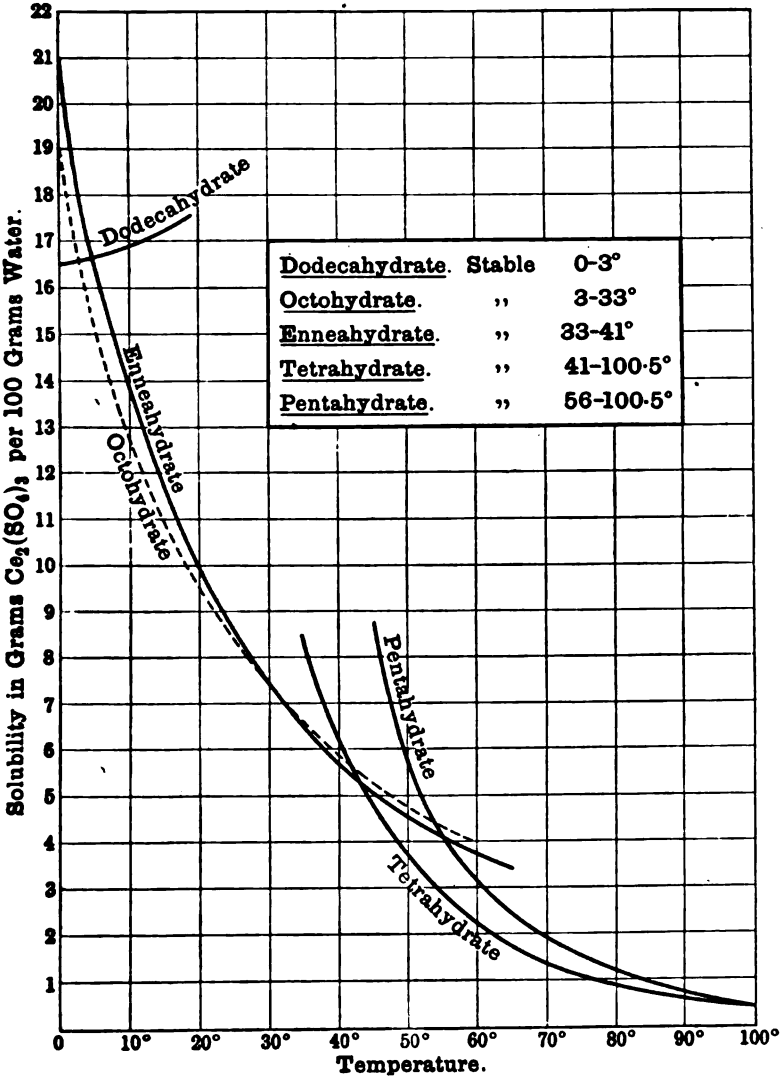

Fig. 3.

supersaturated solutions, and the fact that many hydrates can exist throughout considerable ranges of temperature in the metastable condition; in consequence of this, also, the solubilities of many hydrates are known for temperatures far beyond the transition points. Foreign elements may be separated by taking advantage of the very great solubility of the anhydrous sulphates at 0°, and the rapid decrease in solubility with rise of temperature. For this purpose, a solution of the anhydrous sulphates saturated at 0° is prepared, and after filtration is slowly allowed to come to room temperature; the hydrated rare earth sulphates then separate, leaving in solution the foreign sulphates. This method may indeed be used instead of the oxalate separation (see p. 147).

In presence of excess of sulphuric acid, *acid sulphates* of the general formula $R(HSO_4)_3$ are formed. These are fairly stable, and must be heated to a temperature of 400°–500° to decompose them completely to the normal salts; even at that temperature, traces of acid are tenaciously retained, a fact which renders the determination of the equivalents by the sulphate method unreliable, unless special precautions are taken. On further heating, the normal sulphates pass into *basic salts*, R_2O_3,SO_3, and finally, at the temperature of the blowpipe flame, into the oxides. The temperatures at which these decompositions occur vary with the positive character of the elements; the most basic oxide clings most tenaciously to sulphuric anhydride, and forms the most stable acid salt. Lanthanum sulphate, for example, requires to be heated for a considerable time at a white heat if the pure oxide is required, whilst the sulphates of the less positive elements are easily decomposed at a red heat. The order of basic strength of the oxides, as determined by the ease with which the sulphates are decomposed, seems, however, to be very different from the order determined by decomposition of the nitrates (see p. 118).

With the alkali sulphates, the sulphates of the rare earth elements readily form *double salts*, which are of great importance in separation, on account of the great differences in solubility. The double sulphates of the cerium group are almost insoluble in excess of alkali sulphate, whereas the yttrium double sulphates, with the exception of those of the terbium metals, which occupy an intermediate position, are very easily soluble. This method of separating the elements into the two main groups was first employed by Berzelius, and though a century has elapsed, it remains to-day the most efficient method of effecting the separation.

The *ethylsulphates* have been employed by Urbain and others in effecting separations, especially in the erbium and terbium groups. The solubilities of these salts are in the same general order as those of the alkali double sulphates, and they are especially convenient for separating the metals into the three groups of the cerium, terbium, and yttrium elements respectively. They may be prepared by double decomposition of the rare earth sulphates with barium ethylsulphate, but on account of the ease with which the alkylsulphates are hydrolysed by acids, it is essential that the solutions should be quite neutral. A more convenient method, according to James, is the treatment of the anhydrous chlorides in alcohol solution with sodium ethylsulphate dissolved in the same medium; sodium chloride is precipitated, whilst the ethylsulphates of the rare earth elements remain in solution.

The *sulphites* of the rare earth elements are sparingly soluble crystalline salts, of the general formula $R_2(SO_3)_3,xH_2O$. They are obtained by passing sulphur dioxide into a suspension of the hydroxides in water, or by double decomposition of soluble salts with alkali sulphite. They dissolve in excess of sulphurous acid, and on evaporation of the solution are deposited unchanged. They are distinguished from thorium sulphite by the fact that they form no alkali double salts. The strongly electropositive character of the rare earth metals is shown by the fact that they form normal and not basic sulphites.

The *thiosulphates* are readily soluble, crystalline bodies. With the exception of the ceric and scandium salts, they are not hydrolysed in boiling solution, a fact which allows of a complete separation from the readily hydrolysed thiosulphates of zirconium and thorium.

Dithionates of the commoner rare earth elements, of the general formula $R_2(S_2O_6)_3,xH_2O$, have been prepared by double decomposition of the sulphates with barium dithionate. They are readily soluble, crystalline salts.

The *selenates* are soluble, crystalline salts, which separate from aqueous solutions in various hydrated forms. They resemble the sulphates in being less soluble in hot than in cold water, and numerous cases of isomorphism have been observed among the corresponding sulphate and selenate hydrates. Several alkali double selenates have been described; they show a close resemblance to the analogous double sulphates.

The *selenites* are amorphous, insoluble compounds, obtained by the action of selenious acid on the carbonates, or on solutions of neutral salts. Basic and acid selenites are also known.

Nitrates. — The nitrates are crystalline, deliquescent compounds, readily soluble in water and alcohol, but less easily in nitric acid, a fact which has been of considerable importance for purposes of separation. The solubility is greatest in the case of lanthanum nitrate, diminishing through the cerium group to a minimum in gadolinium nitrate, and then increasing again. They separate from aqueous solution in the form of crystalline hydrates; in the cerium group, these have commonly the formula $R(NO_3)_3,6H_2O$, whilst the nitrates of the yttrium elements usually crystallise with 3 or 5 molecules of water. By carefully heating the hydrated salts, basic nitrates may be obtained, which in the yttrium group are soluble in water, and may be obtained crystalline; in the cerium group, the basic nitrates are insoluble. By further heating, insoluble 'superbasic salts,' and finally the oxides, are obtained in all cases. The temperatures at which these basic and superbasic compounds are formed vary with the electropositive character of the element; this fact affords a method of separation which has been very frequently employed.

An interesting series of addition compounds of the rare earth nitrates with antipyrine (dimethylphenylpyrazolone, $C_{11}H_{12}ON_2$) has been described recently by Kolbe.[1] Those of the cerium metals have the general formula $R(NO_3)_3,3C_{11}H_{12}ON_2$;

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[1] *Zeitsch. anorg. Chem.* 1913, 83, 143

the yttrium nitrates appear to combine with four molecules of the base.

The tendency to form double nitrates with nitrates of the metals of Group IA and Group IIA also varies with the basic strength of the hydroxides. In the most positive elements of the cerium group, the tendency is very pronounced, and there are a large number of stable, crystalline double salts; but the stability decreases rapidly as the atomic weight of the element rises, and in the terbium and yttrium groups crystallised double nitrates cannot be obtained. The solubility of these double salts increases rapidly in the same direction, the lanthanum double nitrates being the least soluble. For this reason, these compounds are of great importance for the purpose of separation, especially in the cerium group. Bismuth nitrate and the various bismuth double nitrates are isomorphous with the corresponding compounds of the cerium group, and the double bismuth ammonium and bismuth magnesium salts have been largely used by Urbain in the separation of samarium and the elements of the terbium group.

Phosphates.—Addition of phosphoric acid, or an alkali phosphate to solutions of rare earth salts throws down the phosphates as gelatinous precipitates, which slowly become crystalline on standing. The precipitate is soluble in excess of phosphoric acid, and in other mineral acids, a fact of great importance in the commercial treatment of monazite. The composition of the precipitate is not known with certainty; both neutral and acid phosphates can probably be obtained according to the conditions. Double salts with the alkali phosphates can be prepared by fusion methods. The naturally occurring phosphates, monazite and xenotime, are mixtures of the orthophosphates of the cerium and yttrium elements respectively.

Phosphites are known in a few cases only; *arsenates* and *arsenites* of lanthanum have been prepared. *Vanadates* of some of the rare earth elements have been described.

Chromates.—The rare earth chromates are, as a rule, sparingly soluble in water, and show considerable differences of solubility amongst themselves; for this reason, they have been of some use in the separation of the cerium elements.[1] They are obtained by addition of potassium chromate to neutral solutions of rare earth salts as crystalline precipitates, of the general formula $R_2(CrO_4)_3,8H_2O$; with a large excess of alkali chromate, double chromates are obtained, which are more readily formed, and more soluble, in the yttrium series than in the cerium group. Addition of chromic acid or alkali bichromate to solutions of the soluble salts gives no precipitate, a fact which allows of the separation of zirconium and thorium, and of cerium in the tetravalent state, since the tetravalent elements are precipitated by both these reagents.

Ammonium molybdate throws down from neutral solution of rare earth salts gelatinous precipitates of the *molybdates*; the formula $La_2(HMoO_4)_6$ is assigned to the lanthanum compound obtained in this way. No precipitation occurs if the solution be strongly acid; on this fact a process has recently been based for the volumetric estimation of thorium, in presence of rare earth salts, by means of ammonium molybdate (see p. 289).

Various *silicotungstates* and *double tungstates* have been described.

Carbonates.—The more pronounced electropositive character of the rare earth elements, as contrasted with other trivalent metals, is well illustrated by the fact that they form stable neutral carbonates of the formula $R_2(CO_3)_3,xH_2O$. These may be obtained by passing a current of carbon dioxide through an aqueous suspension of the hydroxides, or by addition of an alkali carbonate to neutral solutions of the salts. Basic carbonates are known in the case of the less positive yttrium elements only; both these and the neutral carbonates are insoluble in water.

In presence of a large excess of alkali carbonate, double carbonates are formed. The stability as well as the solubility of these compounds increases in passing from the cerium to

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[1] Muthmann and Böhm, *Ber.* 1900, **33**, 42; Böhm, *Zeitsch. angew. Chem.* 1904, **15**, 372 and 1282.

the yttrium group, *i.e.* as the electropositive character becomes weaker. The double carbonates of the cerium elements are sparingly soluble, and are decomposed by water, especially on warming; they may, however, be recrystallised from alkali carbonate solution. The sodium and ammonium double salts are less soluble than the potassium compounds. The latter have the general formula $R_2(CO_3)_3,K_2CO_3,12H_2O$, and are of considerable importance in many processes of separation. The yttrium elements can be separated from the cerium metals, and the latter from one another, by taking advantage of the differences of solubility shown by the potassium double carbonates. If a concentrated solution of the salts in potassium carbonate solution be fractionally diluted with water, the cerium elements separate in the order: lanthanum, praseodymium, cerium, neodymium, and samarium; the more soluble yttrium compounds remain in the solution. Thorium forms double alkali carbonates which are very readily soluble in excess of alkali carbonate; this property is of great importance for the technical separation of the element.

Oxalates.—The oxalates of the rare earth elements are of the greatest importance, on account of the fact that they are not only insoluble in water, but are also very sparingly soluble in dilute mineral acids, and in excess of oxalic acid. They can be completely precipitated even from strongly acid solutions by addition of sufficient excess of oxalic acid, or alkali oxalate, and thus afford a means of easily and completely separating the rare earth group from the commoner elements.

They are thrown down by addition of oxalic acid, or alkali oxalate, as amorphous precipitates, which rapidly become crystalline, especially if the solution is warmed. From water at normal temperatures they usually separate as the decahydrates, $R_2(C_2O_4)_3,10H_2O$, but hydrates with 7, 9, and 11 molecules of water of crystallisation are also known. From strongly acid solutions, mixed oxalo-salts of the general formula $R(C_2O_4)X$, where $X = Cl, NO_3, HSO_4$, etc., may be obtained. These mixed salts may also be prepared by dissolving the oxalates in concentrated solutions of the chlorides, nitrates, etc., whilst nitro-sulphates, $R(SO_4)NO_3$, have been obtained by recrystallising the sulphates from strong nitric acid. The tendency to form salts with mixed acid radicles appears to be general.[1]

The solubilities of the oxalates in mineral acids of various concentrations have been examined by Hauser and Wirth.[2] Whilst the solubilities in water are exceedingly slight, and increase with increasing atomic weight of the elements, *i.e.* from the cerium to the yttrium group, in mineral acids of concentration 3–4N the solubility becomes noticeable, and is greatest for the oxalates of the most positive elements. The solubility is greatly lessened, however, if considerable excess of oxalic acid be present.

Double oxalates with the alkali oxalates can be obtained with the salts of the yttrium elements only, the oxalates of the cerium elements being almost insoluble in excess of alkali oxalate in the cold. Of the alkali double oxalates, the potassium compounds are the most soluble, but the ammonium compounds show the greatest differences in solubility ; von Welsbach has employed the method of fractional crystallisation of these salts from a saturated solution of ammonium oxalate for separations in the yttrium group. The sodium double oxalates are the least soluble of these double salts.

Since the rare earth elements are almost always separated in the form of the oxalates, the methods for transforming these into soluble compounds become important. They may be ignited to oxides, and these dissolved in nitric acid ; if the content of ceria is very high, the oxide mixture may become insoluble, but this difficulty may be overcome by addition of a reducing agent—hydrogen peroxide is very convenient for this purpose. The oxalates may also be dissolved directly in fuming nitric acid, care being taken to avoid loss ; if the mixture contains cerium, the oxidation is hastened, ceric salts having the property of acting as oxygen carriers. By boiling for a short time with potash, the oxalates may be easily transformed into the hydroxides, which can be dissolved in dilute acids.

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[1] See Meyer and Marckwald, *Ber.* 1900, **33**, 1003 ; also Matignon, *Ann. Chim. Phys.* 1906, [viii.], **8**, 243.

[2] *Zeitsch. anal. Chem.* 1908, **47**, 389.

Formates.—On account of the considerable differences in solubility by which they are characterised, these salts have been employed for separations. The formates of the cerium group are considerably less soluble than those of the yttrium group. They may be partly precipitated from solutions of rare earth salts by addition of alkali formate—formic acid itself causes precipitation only with salts of weak acids, *e.g.* the acetates—but are best prepared by dissolving the oxides in formic acid ; on concentration of the solution, the formates of the cerium and terbium elements successively separate, the salts of the yttrium group remaining in solution. The separation of the terbium earths by this method was attempted by Delafontaine ; his 'new' element, Philippium, obtained from the mother-liquors, was in reality a mixture of the terbium and yttrium elements, which cannot be completely separated by the formate method.[1]

The *acetates* are readily soluble in water, the yttrium salts being rather less easily soluble than those of the cerium group. They are therefore obtained by dissolving the oxides in acetic acid ; addition of alkali acetate to a solution of a rare earth salt gives no precipitate, even on boiling, behaviour which is in marked contrast to the ease with which the salts of other trivalent metals are hydrolysed under these conditions. In this respect the rare earth elements differ also from the tetravalent elements zirconium and thorium (and from cerium in the tetravalent state) ; soluble salts of the latter, on boiling with sodium acetate, give insoluble basic acetates. Even sparingly soluble compounds of the rare earth elements are as a rule taken into solution by digestion with ammonium acetate.

Tartrates.—Addition of ammonium tartrate to a neutral solution of rare earth salts throws down an amorphous precipitate, which dissolves easily in acids, and in excess of the precipitant. In the presence of tartaric acid, precipitation of the earths by addition of sodium hydroxide is completely inhibited. Potassium hydroxide under these conditions gives a precipitate in the case of the yttrium elements, though only

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[1] See Urbain, *Ann. Chim. Phys.* 1900, [vii.], **19**, 184.

on boiling; ammonia gives a crystalline precipitate even in the cold with this group. These precipitates are alkali double tartrates of the yttrium metals; the cerium elements give no precipitate at all. In all cases, therefore, the precipitation of the hydroxides is inhibited by the presence of tartaric acid.

A very large number of organic salts of the rare earth elements has been prepared and examined during the past two decades, in the endeavour to find some class of compounds which will allow of an easy separation of the group. The *benzoates*, *succinates*, *hippurates*, *citrates* and similar relatively simple salts first received attention, but less common acids, as *e.g.* the hydroxynaphthalenesulphonic acids, have also been employed.[1] The use of various organic acids for the separation and estimation of thorium in presence of the rare earths is outlined in that connection (see p. 288). More recently, the glycollates and cacodylates have been prepared. The *glycollates*[2] of the cerium elements have the general formula $R(C_2H_3O_3)_3$, and crystallise in crusts; they are more soluble than the yttrium compounds, which have the formula $R(C_2H_3O_3)_3,2H_2O$, and crystallise in needles. The *cacodylates*,[3] $R_2[As(CH_3)_2O_2]_6$, crystallise with 16 or 18 molecules of water, and have similar solubility relations.

The *phthalates* of the yttrium group have been found to be very valuable for purposes of separation by Meyer and Wuorinen.[4] The salts are readily obtained in solution by shaking together cold aqueous suspensions of the rare earth hydroxides, and phthalic acid; the clear solutions when warmed become cloudy. the organic salts hydrolysing very easily, with separation of the hydroxides. The most positive elements naturally remain longest in the solution, the weakly basic oxides accumulating in the first precipitates.

An organic compound which has proved very useful

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[1] Erdmann and Wirth, *Annalen*, 1908, **361**, 190; see also Pratt and James, *J. Amer. Chem. Soc.* 1911, **33**, 1330; Baskerville and Turrentine, *ibid.*, 1904, **26**, 46; James, Hoben and Robinson, *ibid.*, 1912, **34**, 276, etc.

[2] Jantsch and Grünkraut, *Zeitsch. anorg. Chem.* 1913, **79**, 305.

[3] Whittlemore and James, *J. Amer. Chem. Soc.* 1913, **35**, 627.

[4] *Zeitsch. anorg. Chem.* 1913, **80**, 7.

in the treatment of the rare earths is acetylacetone, $CH_3.CO.CH_2.CO.CH_3$.[1] In its enolic form, this substance forms salts with metals, which in the case of the rare earth elements are especially characterised by the ease with which they may be obtained, and their high crystallising power. They may be prepared by double decomposition of neutral solutions of rare earth salts with ammonium acetylacetone, and crystallise readily from dilute alcohol. They have been used by Urbain in the fractionation of the yttrium group, and for determination of molecular weights by the boiling point method; Biltz[2] has shown that in solution they generally have the double formula $R_2(C_5H_7O_2)_6$.

THE RARE EARTH ELEMENTS, AND THE PERIODIC CLASSIFICATION

At the time of the introduction of the periodic classification the rare earth elements were generally believed to be divalent. This belief, which has persisted until quite recently,[3] was based chiefly on the electropositive character of the metals, and their general chemical resemblance to the elements of the alkaline earths; the isomorphism of the tungstates of calcium and the cerium elements, and of the molybdates of lead and the cerium elements, also supports this view. The physical evidence in favour of Mendelejeff's view, however, is quite overwhelming; the specific heats of the metals, the equivalent conductivities of the chlorides, and molecular weight determinations by means of vapour densities and the boiling point method, prove beyond doubt that the elements are in fact trivalent.

In deciding in favour of the trivalent nature of the rare earth metals, Mendelejeff was influenced chiefly by the fact that there was no room in the table for divalent elements with the equivalent weights then assigned to the cerium and yttrium

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[1] Urbain, *Bull. Soc. chim.* 1897, [iii.], **17**, 98; Urbain and Budischofsky, *Compt. rend.* 1897, **124**, 618; Biltz and Clinch, *Zeitsch. anorg. Chem.* 1904, **40**, 218.

[2] *Annalen*, 1904, **331**, 334.

[3] See Wyrouboff, *Bull. Soc. franc. Min.* 1896, **19**, 219; Wyrouboff and Verneuil, *Compt. rend.* 1897, **124**, 1230 and 1300; *ibid.*, 1899, **128**, 1573; etc.

elements. At that time, only the six oxides obtained by Mosander were known; of these the accepted equivalents and atomic weights were as follows:

Element.	Equivalent.	Atomic Weight.
Lanthanum . . .	46	92
Cerium . . .	46	92
Didymium . . .	48	96
Yttrium . . .	31	62
Erbium . . .	56	112

the values for terbium being uncertain. If cerium be considered trivalent in the cerous salts, its atomic weight becomes 138, that of barium being 136. Mendelejeff placed cerium in Group IV, series 8, in the position which it still occupies; he pointed out that the accepted equivalent must be too low, and suggested that the atomic weight should be at least 140, almost exactly the value accepted to-day.

This choice left the positions in Group III, series 8, horizontally before cerium, and in Group IV, series 10, vertically below it (see figure), to be filled by the two elements, lanthanum and didymium. No chemical evidence being available to decide the choice, he provisionally assigned didymium to the first (Group III, series 8), and lanthanum to the second (Group IV, series 10) position, at the same time expressing the opinion that didymium was probably a mixture of closely related elements. Yttrium then fell into place in Group III, series 6, above didymium, and erbium in Group III, series 10, below it. To the vacant space above yttrium in Group III, series 4, he assigned the hypothetical element Eka-boron, with atomic weight 44; this space is now occupied by scandium, which corresponds almost exactly in properties to the metal described by the Russian chemist. A part of the table illustrating these positions is shown in Fig. 4.

The determination of the specific heats of the metals by Hillebrand and Norton in 1875, whilst confirming the trivalency of the elements, rendered it necessary to alter the position of lanthanum, which was placed in Group III, series 8, instead of didymium, which was thus left without a place. This first indication that all the rare earth elements could not be fitted into the table without difficulties was soon followed by the discovery of several other members of the group, for which places could not easily be found.

It was first pointed out by Brauner in 1881 that, with the exception of scandium (44·1) and yttrium (89·0), the rare earth elements form a zone of increasing atomic weight between barium (137·37) and tantalum (181·5). In 1902 he proposed[1] to consider the rare earth metals as a kind of zone or belt among the elements, comparable to the asteroids in the solar system, extending from cerium in Group IV to tantalum in Group V in a continuous series. The suggestion seems at

Group	O	I		II		III		IV		V
		A	B	A	B	A	B	A	B	A
Series 1		H								
„ 2		Li		Be		B		C		
„ 3		Na		Mg		Al		Si		
„ 4		K		Ca		*Eka-boron*		Ti		
„ 5			Cu		Zn					
„ 6				Sr		Yt		Zr		
„ 7			Ag		Cd				Sn	
„ 8				Ba		Di ?		Ce		
„ 9										
„ 10						Er		La ?		
„ 11			Au		Hg				Pb	
„ 12								Th		

FIG. 4.—PART OF THE PERIODIC TABLE, SHOWING THE POSITIONS ORIGINALLY ASSIGNED TO THE RARE EARTH ELEMENTS BY MENDELEJEFF

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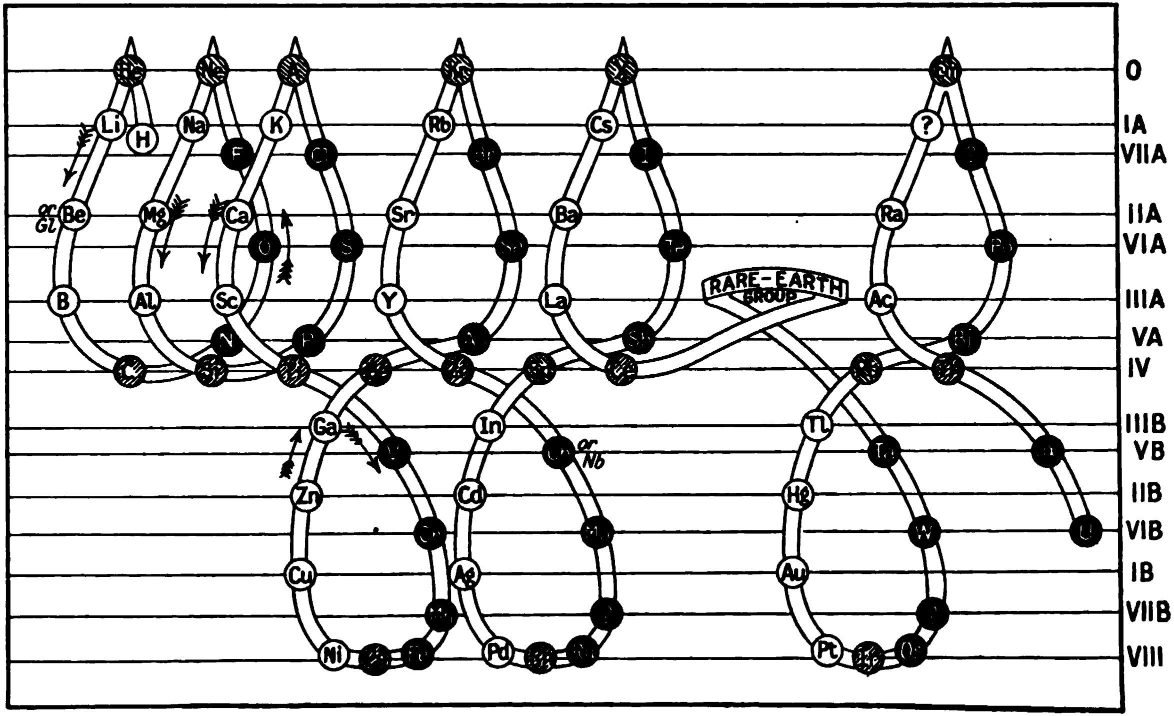
[1] *Zeitsch. anorg. Chem.* 1902, 32, 1.

FIG. 5.—HELICAL REPRESENTATION OF THE PERIODIC LAW



Electropositive Elements, above plane of paper, black letters on white ground. Electronegative Elements, below plane of paper, white letters on black ground. Intermediate Elements, in plane of paper, black letters on sectioned ground.

first sight contrary to the whole principle of periodic classification, but it accords very well with the anomalous position of the rare earth group among the other elements; it is very well illustrated in the accompanying Fig. 5, which shows an helical or space representation of the table.

Brauner's conception is also in accord with the physical properties of the elements and their compounds. These vary continuously throughout the group, and show nowhere the sudden transitions which are characteristic of other series in the table. Benedicts[1] has collected all the data bearing on the atomic volumes, and finds that those also vary continuously, with rise in the atomic weights, within quite small limits, all lying between the values for barium and tantalum. In face of all the evidence furnished by physical and chemical properties, however, Brauner[2] has recently reverted to an idea which he put forward in 1881, according to which lanthanum and cerium are placed as usual in Groups III and IV, series 8, whilst the other elements are distributed in order throughout the remaining groups, as shown in Fig. 6.

Group	III.		IV.		V.		VI.		VII.		VIII.
	A	B	A	B	A	B	A	B	A	B	
Series 6	Yt		Zr		Cb		Mo				Ru Rh Pd
„ 7		In		Sn		Sb		Te		I	
„ 8	**La**		**Ce**		**Pr**		**Nd**		**Sa**		**Eu**
„ 9		**Gd**		**Tb**		**Dy**		**Ho**		**Er**	**Tm** **Yb**
„ 10	**Lu**				Ta		W				Os Ir Pt
„ 11											

FIG. 6.—PART OF THE PERIODIC TABLE, SHOWING THE POSITIONS ASSIGNED TO THE RARE EARTH ELEMENTS BY BRAUNER IN 1908

In support of this arrangement, he quotes the fact that

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[1] *Zeitsch. anorg. Chem.* 1904, **39**, 41.

[2] *Monats.* 1881, **3**, 1; *Zeitsch. Elektrochem.* 1908, **14**, 525.

some of the elements appear to be able to form higher oxides in the presence of other oxides, which act as oxygen carriers (see pp. 174, 177–8), though these higher oxides are certainly not salt-forming. He also deduces, from the rates of hydrolysis of the sulphates, that the elements fall into two parallel series, according to the strengths of the hydroxides as bases, on which ground he justifies the distribution throughout series 8 and 9. There can be no doubt, however, that this disposition is far less in accordance with the behaviour and properties of the rare earth elements than is the first arrangement, which places them in a transition zone between barium and tantalum; it is impossible, for example, to reconcile the properties of praseodymium with those of columbium and tantalum, or to find the slightest analogy between neodymium and molybdenum or tungsten, as the second arrangement requires.

The analogy of the rare earth group to the elements of Group VIII has been pointed out by many authors.[1] On the ground that the rare earth elements cannot be spread over the table in series 8–10, Steele [2] favours the early classification of Thomsen, according to which the elements are divided into three groups. The first, corresponding to Groups I and II of Mendelejeff's table, consists of two sub-groups, each containing seven elements [3]; the second, corresponding to the first two long series of the periodic table, has two sub-groups, each of seventeen elements, of which the first and last seven are analogous—these elements fall into the same groups in the periodic table—whilst the middle three are interperiodic. These interperiodic elements are those which Mendelejeff places in Group VIII. The third division consists of one (or two) group(s) of thirty-one elements; here again, the first and last seven are analogous, whilst the interperiodic elements, which are seventeen in number, include the rare earth metals.

Steele's idea has been extended by Werner,[4] who has drawn up a table to illustrate it. In this classification, the elements are arranged in order of atomic weight, but arbitrary gaps are left in such a way that similar elements may fall

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[1] Compare Biltz, *Ber.* 1902, **35**, 562.

[2] *Chem. News*, 1901, **84**, 345.

[3] The inert gases are not included.

[4] *Ber.* 1905, **38**, 914.

into the same vertical columns, as in the periodic table. The arrangement has the advantage that the interperiodic elements, consisting of the rare earth elements and the elements placed in Group VIII of the periodic table, here do fall in the middle of their respective periods, but it has several drawbacks, and does not represent the transition of properties from element to element so well as the helical representation of the periodic table, which brings out most clearly the true relations between the elements, and the anomalous position of the rare earth metals.

Mention must be made at this point of the theory of 'Meta-elements' put forward in 1888 by Sir William Crookes.[1] From his work on the cathode luminescence of some of the oxides (see next chapter), that author was led to the conclusion that several of the then-accepted rare earth elements, notably samarium and yttrium, were in reality heterogeneous, consisting of large numbers of very closely related bodies, differing so very slightly in properties that only the most refined methods could perceive the variations; for these he proposed the name Meta-elements. Though it has been proved that the differences observed by Crookes in the luminescence spectra were really due to the presence of very small quantities of impurities, his paper is of great interest, in that it contains a theory of evolution of the elements, and postulates the possibility of their decay. Modern developments in radioactivity have not only lent a curious force to these speculations, but even support his contention that a chemical element, in the ordinary sense of the word, is not necessarily homogeneous.[2] In the field of the rare earths, also, the homogeneity of elements is even now continually being called into question (see Thulium, p. 204). In any case, we have in the rare earth elements a series of bodies in which the change of properties from one member to another—and the consequent possibility of easy separation—is so very slight, and so far without parallel in the whole field of chemistry, that we are at least justified in asking whether some extension of our ordinary conception of an element is not required.

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[1] *Trans. Chem. Soc.* 1888, **53**, 487.

[2] See Soddy, *The Chemistry of the Radio-Elements*, Part II., Introduction.

CHAPTER X

GENERAL METHODS OF SEPARATION

THE chemist who sets out to prepare a pure compound of a rare earth element is faced by a great difficulty. The rare earth compounds occur in nature, as one might expect from their great similarity, as mixtures of very complex composition. After the relatively simple separation from foreign elements has been accomplished, the enormously greater difficulty of separating the elements from one another has to be encountered. So great is this difficulty, by reason of the fact that, with the sole exception of cerium, the elements show no variation in property sufficient to allow of the use of ordinary analytical methods, that even at the present day it is extremely doubtful if all the elements in the yttrium group are known to us.

The methods which can be adopted in attempting a separation are of two kinds. The first includes those processes which take advantage of the gradual variation in basic strength of the hydroxides as the atomic weight changes; the most important of these are fractional precipitation of the hydroxides, and fractional decomposition of the nitrates. Fractional precipitation of the hydroxides is generally effected by gradual addition of ammonia, soda, magnesia, or other base, to a solution of the mixed salts; such a solution may also be digested with the oxides obtained by ignition of another fraction of the rare earth compounds. If the digestion be sufficiently complete, the precipitate in each case will be richer in the less basic hydroxides, whilst the solution will be richer in the salts of the more electropositive elements.

The fractional decomposition of the nitrates is based on the fact that when a mixture of the salts is heated gradually, the nitrate of the least positive element begins to decompose first. The temperature is maintained for some time at the point at which decomposition begins; when nitrous fumes cease to be evolved the mixture is cooled, and extracted with water or dilute acids. The insoluble portion—basic or superbasic nitrate (see p. 128)—will then be richer in the less electropositive elements; the solution is evaporated, and the solid so obtained subjected to a somewhat higher temperature, and the process repeated several times. In this way, a series of fractions is obtained, in which the elements tend to distribute themselves in order of electropositive character. By a sufficient number of systematic repetitions of such steps, the elements may eventually be obtained in the form of compounds of approximate purity, which may then be refined by one of the methods of the second kind described below. Experience has shown, however, that a quicker and more complete separation may generally be effected by combining two or more methods of separation; one method will give the best separation up to certain limits, but then becomes much less valuable; the separation at this point is therefore taken up by another process. A process depending on differences of basic strength of the hydroxides is generally supplemented by a method of the second class, *i.e.* a process of fractional crystallisation; where the basicity method is not used (as, for example, in most of the recent processes for separation of the cerium elements), two or more different methods of fractional crystallisation will supplement one another.

The methods of the second class, which are processes of fractional crystallisation, depend on the differences in solubility which are observed in analogous compounds in passing from one member of the group to another. The value of these methods, as opposed to the methods depending on differences in basic strength, was clearly shown by Auer von Welsbach, who in 1885 succeeded in resolving Mosander's 'Didymium' into two new elements, praseodymium and neodymium, by fractional crystallisation of the ammonium double nitrates;

since that date, much attention has been devoted to the task of finding rare earth compounds which will lend themselves to such processes. The method is extremely laborious, and may involve several thousand recrystallisations, in consequence of the generally very slight differences of solubility, and the ease with which the rare earth compounds, being almost always isomorphous with one another, form mixed crystals.

Whilst the method of fractional crystallisation has come into general use for the separation of one element from another only within the last thirty years, processes for the separation of the cerium group from the yttrium elements, depending on differences of solubility, have long been known and used. The most important of these, the double sulphate method, depends on the fact that the potassium double sulphates of the cerium metals are almost insoluble, whilst those of the terbium group are sparingly, and of the yttrium group readily soluble in a concentrated solution of potassium sulphate. The cerium elements may be thus completely removed from a solution of mixed salts by addition of a crust of potassium sulphate crystals, or of an hot concentrated solution of the same reagent. In other cases, *e.g.* in the double carbonate and double oxalate processes, separation is effected by taking advantage of the greater tendency to the formation of double salts possessed by the yttrium metals.

In effecting a separation of closely related bodies by fractional processes, in which a large number of repetitions of the same operation are necessary, only the most careful and systematic procedure can avoid much waste of valuable material; in these processes, the object of the chemist is to obtain pure end fractions, whilst keeping the middle fractions as small as possible. One method of procedure generally adopted is illustrated in Fig. 7, which represents a fractional crystallisation of a mixture of four or five substances, α, β, . . . ϕ; the separations being usually conducted in such a way that subgroups of three, four or five elements are first obtained, these being then further fractionated to obtain the pure elements. In the diagram, crops of crystals are represented by crosses, the mother-liquors by circles; for the sake of illustration, the process is made to appear as simple as possible.

The mixture is dissolved up, and allowed to crystallise; the crystals are filtered off, the filtrate concentrated, and a second crop obtained; this is repeated until five or six crops of crystals have been obtained. These, with the mother-liquor, constitute series A. The first fraction is now recrystallised; it yields a crop of crystals, fraction 1 of series B,

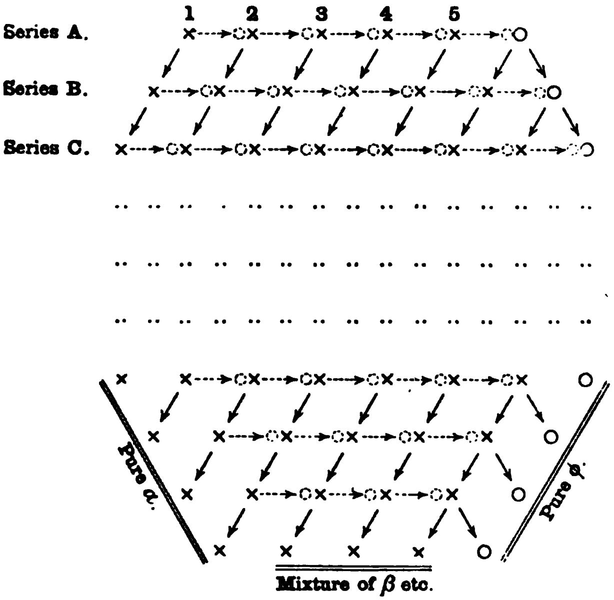

Fig. 7

and a mother-liquor, which is added to fraction 2 of series A, as indicated by the dotted arrow and circle; on recrystallisation of this mixture, a crop of crystals, fraction 2 of series B, is obtained, together with a mother-liquor, which is recrystallised with fraction 3 of series A. In this way, by continued repetition, series are obtained, of which each contains one fraction more than its predecessor; the least soluble constituent is thus concentrated in the fractions represented on the left of the diagram, whilst the most soluble accumulates in the mother-liquors. After a greater or smaller number of series have been traversed, according to the differences in solubility, the end fractions in each series will be pure. These are no longer fractionated, and the number of fractions in each series begins to diminish, as shown on the diagram. The middle fractions will contain the compounds of intermediate solubility; these may be separated by further fractionation on the same lines, or may perhaps be better treated by a different or modified process.

In a modification of the method, each fraction of series A is recrystallised separately, yielding a crop of crystals, and a mother-liquor; series B is then built up by adding to the crystals from fraction 2 the mother-liquor from fraction 1, to the crystals from fraction 3 the mother-liquor from fraction 2, and so on; the fractions in this series are then recrystallised separately, and the third series built up by the similar combination of the crystals and mother-liquors.

Similar systematic methods of procedure must be adopted in working out any method of fractional separation; it can at once be seen that where, as in the rare earth group, only small variations in properties exist, much time and care must be expended, if pure products are required.

Since the development of the methods of spectrum analysis, the difficulty of testing the efficiency of a method of separation, and of examining the purity of the products obtained, has been greatly lessened. The only reliable test at the disposal of the earlier chemists was the determination of the equivalent weight, which still constitutes an important check on the modern methods. Some account of the methods available for the control of the methods of separation is essential in a general account of the rare earths; but before describing these, it will be convenient to give a short description of the methods used in the extraction of the elements from the rare earth minerals.

EXTRACTION OF THE RARE EARTHS FROM MINERALS

With the exception of those containing large proportions of columbium, tantalum, and titanium, the rare earth minerals are easily decomposed by acids. The silicates, as a general rule, can be satisfactorily treated with hydrochloric acid in the ordinary way, but for large quantities, the use of sulphuric acid is more desirable. The more refractory minerals are completely decomposed by fused alkali hydrogen sulphate; sodium bisulphate is more suitable for this purpose than the potassium compound, the sodium double sulphates of the rare earth elements being more soluble than the potassium salts. Hydrofluoric acid also attacks the refractory minerals very readily; the rare earths, in this case, are left as the insoluble fluorides.

After decomposition with sulphuric acid or bisulphate, the cold residue is extracted with water, the rare earth sulphates or double sulphates being removed in solution. Digestion with nitric acid may be necessary at this stage, if titanium, columbium, etc., are present; after filtration, the solution is evaporated to dryness, and the residue extracted with dilute hydrochloric acid. The solution is saturated with sulphuretted hydrogen to remove lead, copper, bismuth, molybdenum, etc., and treated in the usual way with ammonium chloride and ammonia. The precipitate is washed, and dissolved in hydrochloric acid, the solution heated to about 60°, and the rare earths precipitated by addition of excess of oxalic acid, which holds in solution any zirconium which may be present. In the presence of phosphates, *e.g.* in the treatment of monazite or xenotime, the precipitate of oxalates should be ignited to the oxides, these dissolved in acid, and a second precipitation with oxalic acid effected; this treatment is necessary to remove phosphoric acid completely.

Preliminary examination of the earth mixture.—Before a method of separation can be decided upon, some knowledge of the composition of the mixture to be treated must be obtained. The nature of the mineral used for the extraction will, as a rule, afford useful information. It is known that in some minerals the cerium group, in others the yttrium group, predominates more or less completely; certain minerals, also, are known to be rich in elements of one or another subgroup. An approximate knowledge of the relative proportions of the cerium, terbium, and yttrium groups will be afforded by a rough double sulphate separation; thorium, zirconium, and scandium come down with the cerium earths. For approximate separation, Urbain[1] proposes the use of the ethylsulphates. The yttrium elements can be quickly separated in an approximate manner by fractional precipitation of the hydroxides with magnesia. The successive fractions obtained by these methods are examined spectroscopically; from the results, the composition of each, and so of the original mixture, may be roughly deduced.

THE SPECTRUM EXAMINATION

In no department of chemistry have the methods of spectrum analysis proved of more value than in the field of the rare earths. They provide the chemist with a means of following and controlling his processes of separation which is far more delicate and decisive than the older method of determining the equivalent weight. Whilst the examination of emission spectra, and especially of arc spectra, is of decisive value in every case, it has the disadvantage of requiring delicate and complicated apparatus and great experimental skill; wherever possible, therefore, the examination of the absorption spectra is preferred, though this is useful only for a few of the elements, and varies considerably with the conditions employed.

The Absorption Spectra.—Absorption in the visible region of the spectrum is observed only with those rare earth compounds which are coloured, and is of value, therefore, chiefly for identification in the case of praseodymium and neodymium among the cerium elements, and of erbium among the yttrium metals; these give characteristic absorption bands, even in dilute solution. The absorption spectra of the rare earth compounds are highly characteristic, the bands being well defined and sharply bounded, whereas coloured compounds of the common elements show general absorption, or at best diffuse bands, under the same conditions.

In observing an absorption spectrum, the light from a

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[1] *Ann. Chim. Phys.* 1900, [vii.], 19, 184.

Nernst lamp, or incandescent burner, is passed through a layer of a suitable solution of the coloured compound, of known concentration and thickness, and after collimation is analysed by a suitable prism; the spectrum is observed by a telescope in the ordinary way. Where accurate readings are not required, as, for example, in testing for the presence or absence of a particular element, the position of the bands may be read to a sufficient degree of accuracy by means of a scale, the image of which is adjusted to coincide with the spectrum as seen through the eyepiece; but in mapping a spectrum accurately, more refined methods must of course be used. The photographic method, in which a photograph of the spectrum is taken on a plate which bears, for purposes of measurement, a comparison spectrum of known lines, is very convenient for examining the absorption in the violet and ultraviolet regions.

The intensity, and to some extent also the position, of bands in an absorption spectrum may vary considerably, according to the conditions employed. Of the various factors which must be considered, the concentration of the solution, the thickness of the layer used, the nature of the solvent, and of the acid radicle, and the presence of other earths are the most important. The concentration of the solution, and the thickness of the layer, which together constitute the Optical Density, must be so adjusted that the absorption is neither too strong nor too weak; in the first case the sharp bands tend to merge into broad diffusion areas, and details are obscured, whilst in the second case the presence of coloured compounds which do not show strong absorption bands may be overlooked.

The nature of the acid radicle has considerable influence on the position of the absorption maxima, the general rule being that the bands are shifted towards the red end of the spectrum as the molecular weight of the compound used increases. Naturally, also, the nature of the solvent has an important effect, all the usual phenomena which must be considered in the measurement of the physical properties of substances in solution coming into play; electrolytic dissociation, hydration, dissociation and the formation of complexes, for example, are all important factors. The presence of colourless earths has also been found to cause important differences. It follows, therefore, that for the chemist, the absorption spectra can be considered as a valuable aid only in detecting the presence or absence of the three elements which give the strongest and most characteristic absorption bands, viz. praseodymium neodymium, and erbium, and that conclusions regarding the quantitative composition of mixtures must be drawn with the utmost caution.

The Emission Spectra: Spark Spectra.—The factors which tend to limit the value of the absorption spectra for analytical purposes, for the most part disappear when the emission spectra are employed. In the case of the spark spectra, indeed, great differences are observed according to the conditions and method of experiment; but the arc spectra are practically invariable under all conditions, and hence they constitute the ultimate test in all cases. The spark spectra are observed when one terminal—the cathode—of an induction coil is embedded in the oxides to be examined, and the discharge then passed. The discharge is also frequently passed between platinum poles partly immersed in a strong solution of a salt of the element under examination; a form of apparatus very suitable for this method of observation has been described by Sir W. Crookes.[1] The spectra so obtained are in a high degree characteristic, but they vary very considerably with the form and dimensions of the coil, the length and cross-section of the wires, the potential difference employed, and so on. An entirely new spectrum also is obtained in many cases by mere reversal of the current; under these conditions, a phosphorescent appearance is observed, the spectrum of which—reversed spark spectrum of de Boisbaudran—has been found in many cases to resemble the cathode luminescence spectra of Crookes.

The Arc Spectra.—The final criterion of purity in the examination of a rare earth element is in almost all cases the

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[1] *Proc. Roy. Soc.*, 1903, **72**, 295.

arc spectrum. Since for some of the elements, especially in the yttrium group, the entire spectrum has not yet been accurately mapped out, spectra are generally observed frequently throughout the course of a fractionation ; by this means, the separation can be followed by the disappearance of some lines, and the appearing or strengthening of others, and such examinations have led occasionally to the discovery of new elements (see, for example, under Separation of ytterbium earths, p. 205). Such determinations, however, require much time and extensive and complicated apparatus.

Carbon electrodes are generally employed, and it is immaterial in this case which is the anode, and which the cathode. The lower carbon is hollowed out, and the space filled with the oxide or sulphate of the element or mixture to be examined ; or the electrode may be impregnated with a concentrated solution of a salt. The light is examined by means of a diffraction grating, and the spectrum photographed on a plate which bears a comparison spectrum for measurement. The lines are most numerous in the violet and ultraviolet regions, and the most characteristic spectra are given by the colourless earths. The method is naturally more delicate for some elements than for others ; the great persistency of the scandium line 3613·984, for example, was found very valuable by Crookes and by Eberhard in the examination of various rocks and minerals for that element, whilst other intense and persistent lines have served for the detection of various rare earth elements in the sun and many stars.

The Cathode Luminescence Spectra.—The phenomenon of cathode luminescence, which was observed and very fully investigated by Sir William Crookes, and which led that author to his theory of Meta-elements, is one of the greatest scientific interest. Crookes observed that certain of the rare earths, when subjected to the action of cathode rays in a vacuum tube, exhibit a brilliant phosphorescence, which, when examined by the spectroscope, show characteristic spectra, which differ greatly for fractions of apparently identical chemical composition, and are otherwise distinguishable by physical properties. The researches of Lecoq de

Boisbaudran, and the more recent work of Baur and Marc,[1] have shown that this luminescence is observed when a small quantity of a coloured earth is present with a very large quantity of a colourless earth, the maximum phosphorescence being produced by about 1 per cent. of the coloured earth, or 'phosphorogen.' The question has recently been very fully examined by Urbain.[2] He shows that the sensitiveness of the phenomenon is so great that it cannot be employed for the ordinary purposes of chemical analysis, one part in a million of the phosphorogen being sufficient to cause a clearly perceptible luminescence in a pure colourless oxide.

The Magnetic Susceptibility.—The fact that the rare earths differ very considerably from one another in their magnetic properties has been known for several years,[3] and has recently been employed by Urbain and Jantsch[4] as a means of identification, and a test of purity, and for following processes of fractionation. The magnetic susceptibility reaches a minimum at samarium, and rises very sharply on either side of that element, so that the presence of the closely related elements, neodymium on the one side, and europium and gadolinium on the other, which differ only very slightly from samarium in atomic weight and solubility, can easily be detected by this means. The property is highly additive, and can be used, therefore, to estimate the relative proportions of two oxides in a mixture; the determinations are said to be easily and quickly carried out.

When the elements are considered in order of atomic weight, the coefficient reaches a maximum at neodymium in the cerium group, and again at dysprosium (or holmium) in the yttrium group:—[5]

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[1] *Ber.* 1901, **34**, 878.

[2] *Ann. Chim. Phys.* 1909, [viii.], **18**, 222; see also *Introduction à l'étude de la Spectrochimie*, pp. 145 *et seq.*

[3] See Meyer, *Monats.* 1898, **20**, 369 and 793.

[4] *Compt. rend.* 1908, **147**, 1286; see also Urbain, *ibid.*, 1910, **150**, 913.

[5] See Urbain and Jantsch, *loc. cit.*; the values for lanthana, scandia, and yttria were determined by Wedekind (see Meyer and Wuorinen, *Zeitsch. anorg. Chem.* 1913, **80**, 7).

Element.	Atomic Weight.	Coefficient of magnetisation for the oxide. $x \times 10^{-6}$
Scandium . .	44·1	$-0·05$
Yttrium . .	89·0	$-0·14$
Lanthanum . .	139·0	$-0·18$
Neodymium . .	144·3	33·5
Samarium . .	150·4	6·5
Europium . .	152·0	33·5
Gadolinium . .	157·3	161
Terbium . .	159·2	237
Dysprosium . .	162·5	290

Erbium, thulium, ytterbium, and lutecium appear in descending order at the end of the series, but no figures are given.

The most interesting application of the property has been Urbain's discovery of the new element Celtium (see p. 207).

THE EQUIVALENT WEIGHT DETERMINATION

The determination of the mean equivalent weight, which was for the earlier chemists the only reliable method of controlling their fractionations, is still of considerable importance for this purpose, especially in the yttrium group, in which the differences in atomic weights are more considerable than among the cerium metals. Great importance, moreover, still attaches to these determinations, since they serve to fix the atomic weights; save that the methods used in an atomic weight determination are somewhat more elaborate and refined than those used when it is desired merely to test a fractionation, the same processes apply in both cases.

The methods which have been most commonly used are those based on a determination of the ratio $R_2O_3 : R_2(SO_4)_3$, and these are of two kinds, the synthetic and the analytical. The first, in which a known weight of the oxide is converted into the sulphate, has been most used for the most strongly basic oxides, since with these it is difficult to remove the last traces of sulphuric anhydride from the oxide by heat. The oxides are best obtained from the oxalates, which are precipitated from an acid solution of the nitrates, washed thoroughly with water, alcohol and ether in succession, dried, and ignited in a tarred platinum crucible. The oxide is best dissolved in dilute hydrochloric or nitric acid on the waterbath, a slight excess of sulphuric acid being added only when a clear solution has been obtained; the liquid is then heated gradually to 300°, and finally in the electric furnace at 450° – 550° until constant in weight. If sulphuric acid be added directly to the weighed oxide, particles of the latter may become completely coated with the insoluble sulphate, and so escape the action of the acid.

In the analytical method, a known weight of sulphate is ignited to the oxide, and weighed as such. This method is most suitable for the less basic members of the yttria earths, of which the sulphates can be completely decomposed without difficulty at a red heat. By the use of the microbalance, a sufficiently accurate determination can be carried out by either of these methods in little more than half an hour, as the chemical changes are exceedingly rapid where only small quantities are employed, and no time is required to allow the vessels and solids to cool. Using the microbalance, Brill[1] has carried out a series of experiments to determine the limits of temperature within which the various steps of the process should be carried out. He finds that a temperature of 400° – 550° is required to decompose the last traces of acid sulphate, and give the pure neutral sulphate. Between the temperatures of 850° and 950°, basic salts are formed, from which the last trace of sulphuric anhydride is expelled at 900° – 1150°; the precise temperature required in each case depends, of course, on the basic strength of the oxide in question.

The determination of equivalents by means of the ratio $R_2O_3 : R_2(C_2O_4)_3$, has been brought to a high degree of accuracy by Brauner.[2] A weighed quantity of the carefully prepared oxalate is ignited, with suitable precautions, to the oxide, in a tarred platinum crucible. A second weighed specimen of the same oxalate preparation is dissolved in dilute sulphuric acid, and titrated at 60° with permanganate, which is standardised against pure ammonium oxalate.

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[1] *Zeitsch. anorg. Chem.* 1905, **47**, 464.

[2] *Ibid.* 1903, **34**, 103, 207.

Of the methods of volumetric analysis which have been proposed, that put forward by Feit and Przibylla appears to be the most suitable. A convenient quantity of oxide, which has been ignited until constant in weight, is dissolved by gently heating with a known excess of $\frac{N}{2}$ sulphuric acid, in a conical flask of Jena glass. The excess of acid is titrated with $\frac{N}{10}$ sodium hydroxide, using methyl orange as indicator. This method, which has the advantages of ease and quickness, is very reliable, if suitable precautions are taken, in the case of the more strongly basic oxides; but with the least strongly basic members of the yttria group, the erbia and ytterbia oxides, the end point is not very sharp, whilst with the weakly basic scandia, the method breaks down entirely.

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[1] *Zeitsch. anorg. Chem.* 1905, **43**, 202; 1906, **50**, 249.

CHAPTER XI

THE CERIUM GROUP—CERIUM

The extraction of the rare earth elements from minerals, by which they are obtained in the form of the oxalates, and the methods of bringing these into solution, have already been described. From the solution, before any separation of the rare earths is attempted, thorium should be removed; for this purpose, any of the methods described under estimation of thorium (see p. 286) may be used, the most convenient being the peroxide precipitation of Wyrouboff and Verneuil.

The solution is then treated with potassium sulphate until the absorption bands of didymium (praseodymium and neodymium) can no longer be observed, or appear only very faintly, when a layer of the solution is examined with a spectroscope; the precipitate then consists of the potassium double sulphates of the cerium with some of the terbium elements. If the mixture is very rich in the cerium elements, and correspondingly poor in the yttrium elements—as, for example, the mixture of earths obtained from monazite—Drossbach[1] recommends a preliminary separation by means of the double carbonates; the double sulphate method may then be employed to remove the last of the yttrium and most of the terbium elements. The sparingly soluble double sulphates of the cerium metals may be transformed into the hydroxides by digestion with potassium hydroxide, and these taken into solution, after washing, by hydrochloric or nitric acid.

Cerium, Ce = 140·25

Of all the rare earth elements, cerium, by virtue of its property of forming ceric salts corresponding to the dioxide

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[1] *Ber.* 1900, 33, 3506.

CeO_2, is the one most easily separated and obtained in the pure state. In those compounds in which it is tetravalent, cerium functions as a much less strongly electropositive element than in the cerous compounds, and all the methods of separation are based on this fact. Mosander, who first demonstrated that the old 'ceria' was a mixture, separated the element by treating a suspension of the hydroxides in potassium hydroxide with chlorine; yellow ceric hydroxide remains undissolved, whilst the other elements go into solution as the chlorides and hypochlorites. This method was extensively used until quite recently; it has the advantage of separating the cerium completely, but the product is very impure, and several repetitions are required to give good results. The basic nitrate method, which is now used on the commercial scale in extracting cerium from monazite (see p. 284), is also due to Mosander, though it has been employed subsequently by many workers.

Several methods take advantage of the ease with which the ceric salts, as compared with salts of the trivalent elements, may be hydrolysed. Brauner[1] dissolves the oxides in nitric acid, and after removal of excess of acid, boils with a large volume of water—basic ceric nitrate is thrown down, the other elements remaining in solution as nitrates. The precipitate is redissolved, and the process repeated until the cerium is found spectroscopically to be free from didymium. The hydrolysis of the ceric salt may be effected more quickly and completely by the addition of ammonium sulphate or magnesium acetate.[2] James[3] boils the solution of the nitrates with potassium bromate, keeping the whole neutral by addition of powdered marble; the cerium is completely and very quickly precipitated as basic nitrate.

An interesting method is due to Koppel[4]; the oxides are dissolved in a solution of hydrogen chloride in methyl alcohol, and treated with pyridine, when the sparingly soluble double

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[1] *Trans. Chem. Soc.* 1885, **47**, 879.

[2] Meyer and Koss, *Ber.* 1902, **35**, 672.

[3] *J. Amer. Chem. Soc.* 1912, **34**, 757; this paper gives a complete scheme for a full separation of all the elements.

[4] *Zeitsch. anorg. Chem.* 1898, **18**, 305.

chloride, $(C_5H_5NH)_2CeCl_6$, separates, and may be obtained pure by recrystallisation from alcohol and ether. The permanganate method of Drossbach, which is used on the commercial scale, is described on p. 285.

The cerium compounds obtained by these methods are purified by transformation into the anhydrous sulphate, which is dissolved in ice-water; when this solution is allowed to come slowly to room temperature, the pure octohydrate separates. Pure cerium salts should show no trace of absorption when concentrated solutions are examined spectroscopically; on ignition, the oxide obtained should be almost colourless, having at most a faint yellow tinge. A reddish or brownish-red shade indicates the presence of praseodymium. An arc spectrum examination will generally show the presence of lanthanum, which occurs in traces even in the most carefully purified cerium preparations.

The preparation and properties of metallic cerium have already been described (see p. 114); for an account of the pyrophoric alloys, see p. 314.

THE CEROUS COMPOUNDS

The salts of trivalent cerium are very similar to those of the other rare earth elements, and a detailed description of them is therefore unnecessary. The *sesquioxide*, Ce_2O_3, cannot be obtained by ignition of the oxalate, nitrate, or other similar salt, since these decompose at high temperatures with formation of the dioxide, CeO_2. It has been prepared by the reduction of the dioxide with calcium;[1] it has a great affinity for oxygen, and readily absorbs the gas when exposed to moist air. *Cerous hydroxide*, $Ce(OH)_3$, obtained by addition of alkali to solutions of cerous salts, has also strong reducing properties,[2] and can only be prepared and preserved when oxygen is carefully excluded. It has been obtained as a perfectly white solid by the action of water on the carbide;[3] when dried in an inert atmosphere, it yields a perfectly white oxide. In presence of

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[1] Burger, *Ber.* 1907, **40**, 1652.

[2] Dennis and Magee, *J. Amer. Chem. Soc.* 1894, **16**, 649; also Biltz and Zimmerman, *Ber.* 1907, **40**, 4979.

[3] Damiens, *Compt. rend.* 1913, **157**, 214.

air, it darkens, assuming a reddish-violet colour, which passes into yellow as the oxidation becomes complete. The oxidation proceeds more quickly in presence of potash or soda, ceric hydroxide, $Ce(OH)_4$, being formed; in presence of potassium carbonate, however, a dark-coloured peroxyhydrate is formed by autoxidation. The colour so produced disappears on shaking if an 'acceptor' is present, ceric hydroxide being left; if the acceptor cannot reduce this, the solution after shaking loses the power of re-forming the dark peroxide, but if the acceptor can reduce the ceric compound to cerous hydroxide, the solution after shaking regains the power of forming the peroxide which is a property of the lower hydroxide.

Cerous nitride, CeN, has been prepared by Moissan[1] by the action of ammonia on the heated carbide; it can also be obtained by heating the hydride in a stream of nitrogen.[2] Muthmann and Kraft also state[3] that it can be prepared by heating metallic cerium in the gas, the metal burning with the liberation of much energy in the form of heat and light; but Dafert and Miklanz[4] deny that it can be obtained in this way. Cerium nitride is a lustrous, brass yellow to bronze coloured solid, stable in dry air, but at once attacked by moist air, with evolution of ammonia, and formation of the dioxide. When moistened in air with a few drops of water, the substance reacts violently, becoming heated to redness. Alkalies and acids decompose it, with formation of cerous compounds.

The *sulphide*, Ce_2S_3, has been prepared by Biltz[5] by heating the sulphate to a red heat in a current of sulphuretted hydrogen; he describes it as a red powder. The *chloride*, $CeCl_3$, combines with ammonia with evolution of heat even at a temperature of $-80°$. Five additive compounds are described;[6] they are white powders, decomposed by water.

The solubility curve of the various *sulphate hydrates* has already been given (see p. 125). Various *double sulphates* with ammonium sulphate, and the sulphates of sodium, potassium,

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[1] *Compt. rend.* 1900, 131, 865.
[2] Dafert and Miklanz, *Monats.* 1912, 33, 911.
[3] *Annalen*, 1902, 325, 261.
[4] *Loc. cit.*
[5] *Ber.* 1908, 41, 3341.
[6] Barre, *Compt. rend.* 1913, 156, 1017.

thallium and cadmium are known. The cadmium double compound has the composition $Ce_2(SO_4)_3,CdSO_4,6H_2O$, and is prepared by mixing solutions of the simple salts in presence of sulphuric acid. Many *double nitrates* have been prepared; these are for the most part stable, highly crystalline compounds, easily soluble in water and alcohol. With the nitrates of the common divalent metals, cerous nitrate forms a series of double salts of the general formula $2Ce(NO_3)_3,3R(NO_3)_2,24H_2O$, where $R = Mg, Mn, Co, Ni,$ or Zn; these form an isomorphous series, crystallising in the hexagonal system. The *acetylacetone compound* melts at 131°–132°.

In the presence of hydrogen peroxide in the cold, ammonia throws down from solutions of cerous salts a reddish-brown peroxyhydrate, $Ce(OOH)(OH)_3$,[1] which on heating loses oxygen, and yields ceric hydroxide. The reaction is very delicate, and may be used as a test for cerium. If the precipitate be treated with acids in the cold, ceric salts are first obtained, but these are at once reduced, in the acid solution, by the hydrogen peroxide formed, so that cerous salts remain; ceric salts may be obtained by first boiling the suspension of the peroxyhydrate and treating the ceric hyroxide so obtained with acids.

THE CERIC COMPOUNDS

The ceric salts are much more readily hydrolysed than the cerous salts, and show a great tendency, in dilute solution, to pass over into the latter. So great is this tendency that a solution of a ceric salt acts as if it were supersaturated with oxygen; ceric sulphate, for example, in dilute solution slowly evolves oxygen, whilst the chloride evolves chlorine. In consequence of this behaviour, ceric compounds have a very powerful oxidising action. The ceric salts are yellow to red in colour; their solutions are strongly acid, owing to the ease with which the salts hydrolyse, and on boiling deposit insoluble basic salts.

Beside the methods which have already been mentioned, ceric compounds may be prepared from cerous by oxidation

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[1] Pissarjewski, *Zeitsch. anorg. Chem.* 1902, 31, 359.

with sodium peroxide, bismuth tetroxide, ammonium persulphate, etc. In electrolysis of cerous salts, also, ceric compounds are obtained at the anode.

Ceric hydroxide, $Ce(OH)_4$, is obtained as a gelatinous yellow precipitate on the addition of alkali to a solution of a ceric salt, or by the oxidation of cerous hydroxide. The freshly prepared precipitate dissolves in nitric acid with a reddish colour ; hydrochloric acid reduces it, with evolution of chlorine, and formation of cerous chloride, whilst sulphuric acid dissolves it with partial reduction, oxygen being evolved. If a solution of a ceric compound be dialysed for some days, a clear neutral solution is obtained, which contains the hydroxide in the colloidal condition; by evaporation of the solution, a gummy mass is obtained, which dissolves again in water to a clear solution. Electrolytes rapidly cause coagulation.

Cerium dioxide, CeO_2, is obtained by the ignition of any salt of cerium with a volatile acid, or by burning the element in oxygen ; the latter reaction produces a very intense and blinding light, on account of which cerium compounds are often suggested for use in flashlight powders (see p. 319). The pure oxide should be almost white, or at most a very faint yellow, but the exact shade and appearance vary according to the method and temperature employed in preparation, doubtless by reason of the possibility of different degrees of polymerisation.[1] The oxide can act as an oxygen carrier towards other substances, notably towards other oxides of the rare earth group,[2] but the phenomena have not been fully elucidated. In virtue of this property, the dioxide has been proposed as a substitute for platinised asbestos in Dennstedt's method for the combustion of organic bodies.[3]

The ignited oxide is soluble in nitric or hydrochloric acid only in presence of a reducing agent. Concentrated sulphuric acid converts it into ceric sulphate ; fused bisulphate attacks it more readily. In the crystalline form, obtained by fusing

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[1] See in this connection Wyrouboff and Verneuil, *Compt. rend.* 1898, **127**, 863; *ibid.* 1899, **128**, 501; and in *La chimie des terres rares*, 'Conférences de la Société chimique de Paris,' Paris, 1903.

[2] See Meyer and Koss, *Ber.* 1902, **35**, 3740.

[3] Bekk, *Ber.* 1913, **46**, 2574.

the amorphous form with borax, or a suitable salt,[1] it is extremely resistant to acids and to alkalies.

By heating the dioxide in a stream of hydrogen, care being taken to exclude air, a dark blue oxide, of which the composition corresponds approximately to that required by the formula Ce_4O_7, is obtained.[2] This substance has strong reducing properties; when warmed in air, it glows, forming the dioxide, and reduces carbon dioxide when heated in a current of that gas. This *intermediate oxide* is said to correspond in composition to the violet hydroxide which is obtained as an intermediate product in the oxidation of cerous to ceric hydroxide, and which is said to yield the blue oxide, Ce_4O_7, when dried *in vacuo*.

The *disulphide*, CeS_2, has been obtained by Biltz[3] by prolonged heating of anhydrous cerous sulphate in a current of sulphuretted hydrogen at a dull red heat; it is a dark, yellowish-brown, crystalline solid, which on treatment with hydrochloric acid yields hydrogen persulphide.

Halogen salts.—No halogen compounds are known in the free state, except the *fluoride*, CeF_4,H_2O, which was obtained by Brauner as a yellowish-brown mass, by the action of hydrofluoric acid on the hydroxide. A *double fluoride*, $2CeF_4,3KF,2H_2O$, was prepared by the same author by dissolving the hydroxide in potassium hydrogen fluoride; it is insoluble in water. By dissolving a ceric salt in concentrated hydrochloric acid, a dark red solution is obtained, which is believed to contain the unstable complex acid, H_2CeCl_6; this decomposes slowly in the cold, more quickly on warming, with evolution of chlorine, and formation of cerous chloride. Several double compounds of ceric chloride with hydrochlorides of organic bases have, however, been obtained.

Ceric sulphate, $Ce(SO_4)_2$, is obtained by the action of concentrated sulphuric acid on the dioxide. It is a deep yellow crystalline powder, dissolving readily in water to a brown solution, which has a strongly acid reaction; on warming or

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[1] See, *e.g.* Sterba, *Ann. Chim. Phys.* 1904, [viii.], **2**, 193.

[2] Sterba, *Compt. rend.* 1901, **133**, 221; Meyer, *Zeitsch. anorg. Chem.* 1903, **37**, 378.

[3] *Ber.* 1908, **41**, 3341.

diluting, a basic sulphate separates. The solution slowly evolves oxygen, and therefore always contains cerous compounds. On evaporation, a *cero-ceric acid sulphate* of the formula $\mathrm{HCe^{iii}Ce^{iv}(SO_4)_4,12(13\,?)H_2O}$ first separates; the hydrated sulphate $\mathrm{Ce(SO_4)_2,4H_2O}$, being more soluble, separates on further concentration.[1] The relative amounts of the two compounds obtained depends on the temperature and the concentration of acid in the solution ; if both these factors are kept low, the almost pure hydrated suphate can be at once obtained. This separates in yellow crystals belonging to the rhombic system ; it is readily soluble in water. The mixed acid salt is less soluble, and forms orange prisms and needles, which cling tenaciously to sulphuric acid. Other complex and double salts have also been obtained. When, for example, silver nitrate is added to a warm solution of the sulphate in concentrated sulphuric acid, a bright orange-yellow precipitate of the salt $\mathrm{10Ce(SO_4)_2,6Ag_2SO_4}$ is obtained.[2]

Neutral ceric nitrate is unknown. A *basic nitrate*, $\mathrm{Ce(NO_3)_3OH,3H_2O}$, is obtained in red crystals by evaporation of a solution of ceric hydroxide in strong nitric acid. The solid is readily soluble in water, forming a yellow, acid solution, which becomes paler by hydrolysis, on warming or on standing. The course of the hydrolysis is also indicated by the action towards acids, and towards hydrogen peroxide.[3] A freshly prepared ceric salt, on addition of acid, becomes immediately much darker in colour, whereas the colour change is very slow, if considerable hydrolysis has occurred. Similarly, hydrogen peroxide at once reduces a freshly prepared solution, forming colourless cerous salts, whilst if much hydrolysis has occurred, deeply coloured higher oxidation products are at first formed, and these lose their colour only slowly.

The *double ceric nitrates* [4] are a large and very important class of compounds ; they are the most stable of the ceric salts. With nitrates of the monovalent metals, ceric nitrate

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[1] See Meyer and Aufrecht, *Ber.* 1904, **37**, 140; Brauner, *Zeitsch. anorg. Chem.* 1904, **39**, 261.

[2] Pozzi-Escot, *Compt. rend.* 1913, **156**, 1074.

[3] Meyer and Jacoby, *Zeitsch. anorg. Chem.* 1901, **27**, 359.

[4] Meyer and Jacoby, *loc. cit.*

forms double nitrates of the type $R_2Ce(NO_3)_6$; these are deep red hygroscopic substances, crystallising in the monoclinic system, readily soluble in water and alcohol, but dissolving only sparingly in nitric acid. The ammonium salt is important for the separation of cerium. A series of double nitrates with the nitrates of manganese, magnesium, zinc, nickel, and cobalt has the general formula $RCe(NO_3)_6,8H_2O$, but these are much less stable in solution than the alkali double salts.

ATOMIC WEIGHT OF CERIUM

No less than twenty-eight separate determinations of the atomic weight of cerium have been carried out. The earlier determinations are rendered unreliable by the almost certain presence of other elements, and Brauner[1] has shown that some of the methods employed in later work give erroneous results.

A very careful determination was made by Robinson in 1884.[2] Cerium oxalate was heated in a stream of dry hydrogen chloride, mixed with carbon dioxide, and the anhydrous chloride freed from traces of acid in a vacuum over chalk. The weighed chloride was then dissolved in water, and titrated with silver nitrate. He obtained the value 140·26; recalculation from his data with the modern values for silver and chlorine give 140·19. Brauner points out that this result is too low, since no account was taken of the solubility of silver chloride in water. In the following year, Brauner[3] determined the ratio $Ce_2(SO_4)_3 : 2CeO_2$, and obtained the atomic weight 140·22. Wyrouboff and Verneuil[4] in 1897 disputed Brauner's work, and as a result of several determinations gave the values 139·21, 139·48, and 139·50; their determinations, however, varied very considerably, and the work has been severely criticised by Brauner. In 1903, the latter author and Batěk[5] obtained the values 140·21 and 140·27 by the sulphate and oxalate methods respectively; whilst in the

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[1] *Trans. Chem. Soc.* 1885, 47, 879; also *Zeitsch. anorg. Chem.* 1903, 34, 207.
[2] *Proc. Roy. Soc.* 1884, 37, 150.
[3] *Loc. cit.*
[4] *Compt. rend.* 1897, 124, 1300.
[5] *Zeitsch. anorg. Chem.* 1903, 34, 103.

same year, using the same methods, Brauner[1] obtained from three independent series of determinations the values 140·25, 140·24, and 140·25.

The International Atomic Weight Committee have accepted the value 140·25 since 1904.

DETECTION AND ESTIMATION OF CERIUM

The detection of cerium in a mixture of earths is a comparatively simple matter, as it has several distinctive reactions. The brown colour of the peroxy-compounds has been suggested as a convenient test by several authors. This may be observed when ammonia is added to a cerous salt in presence of hydrogen peroxide. In the presence of a large excess of foreign earths, very dilute ammonia should be added, drop by drop, with continuous shaking, until a small permanent precipitate remains; this will be rich in the weakly basic ceric hydroxide, and on addition of the peroxide solution will show the colour clearly.[2] For very small quantities of cerium, the neutral solution is added to warm concentrated potassium carbonate solution, and one or two drops of dilute hydrogen peroxide added to the clear liquid; the yellow colour is then very characteristic.[3]

Biltz and Zimmerman[4] employ the reducing powers of cerous hydroxide; ammoniacal silver nitrate is added to the neutral solution of the cerous salt, and the mixture warmed. Dilute solutions (1–2 mgms. per litre) give a brown colour, concentrated solutions a black precipitate. The oxidation of an ammoniacal solution of the tartrate by air or hydrogen peroxide, by which an intense yellowish brown colour is developed, has been recently suggested by Wirth[5] as a very delicate test for the element.

Spectrum analysis.—Cerous salts show no absorption, ceric salts general absorption of the violet end of the spectrum. Arc spectrum—see Exner and Haschek,[6] Eder and Valenta,[7]

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[1] *Zeitsch. anorg. Chem.* 1903, **34**, 207.

[2] Marc, *Ber.* 1902, **35**, 2370.

[3] Meyer, *Zeitsch. anorg. Chem.* 1904, **41**, 94.

[4] *Ber.* 1907, **40**, 4979.

[5] *Abstr. Chem. Soc.* 1913, **104**, ii. 712.

[6] *Die Spektren der Elemente, etc.*, Leipzig and Vienna, 1911.

[7] *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, **119**, II*a*, 531.

and Cooper.[1] The emission spectrum of cerium is especially rich in lines ; for identification, the following may be used :

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
5512·72

The *estimation* of cerium cannot be carried out accurately by gravimetric methods in the presence of other earths ; volumetric methods, however, will give reasonably accurate results, if the necessary precautions are taken. In Bunsen's method the ignited oxides are treated with hydrochloric acid in presence of potassium iodide, the iodine set free from the hydriodic acid by reduction of the cerium dioxide being estimated by means of sodium thiosulphate, in the usual way. This method gives very inaccurate results, since in the presence of cerium dioxide, other oxides of the group can be converted into higher oxides which will also liberate iodine under these conditions.

The most reliable method is that of v. Knorre.[2] The solution to be estimated is acidified with sulphuric acid, and oxidised by means of ammonium persulphate. The excess of the oxidising agent having been destroyed by boiling, the cooled solution is treated with a slight excess of hydrogen peroxide, which reduces the ceric salt according to the equation :

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

The excess of hydrogen peroxide is then estimated by means of a dilute permanganate solution. Permanganate is itself reduced by the cerous salt formed, but the action is so slow in acid solution at the ordinary temperature that the excess of peroxide can be accurately determined without unduly hurrying the titration. In this form the method is generally employed for the estimation of cerium in monazite sands, and in the incandescent mantle industry. The greatest difficulty is the adjustment of the concentration of the sulphuric acid required. If this be too low, basic

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[1] *Astrophys. J.* 1909, **29**, 352.

[2] *Ber.* 1900, **33**, 1924.

ceric sulphate separates on boiling, and the estimation fails; if it be too high, oxidation to the ceric salt is hindered, and may even be inhibited. This difficulty disappears in the modified method of Waegner and Muller,[1] in which the oxidation to the ceric condition is effected by means of bismuth tetroxide in nitric acid solution. A similar method, in which reduction to the cerous state is effected by a ferrous salt, in place of hydrogen peroxide, has been employed by Metzger.[2]

Many attempts have been made to estimate cerium compounds by means of permanganate, which in alkaline solution oxidises cerous salts to the ceric condition, but the autoxidation of cerous hydroxide in the air introduces errors, unless suitable precautions are taken. Meyer and Schweitzer[3] show that if the solution of the cerous salt be added, with constant shaking, to a known volume of a standard permanganate solution, in presence of excess of magnesia, the liquid being kept warm, this difficulty is overcome; the results are usually a little high, however, probably by reason of the oxidising action of the cerium dioxide on the other oxides present.

Good results have also been obtained by the use of potassium ferricyanide in alkaline solution,[4] oxidation taking place according to the equation:

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

The ceric hydroxide is filtered off, and the ferrocyanide formed estimated by means of permanganate in acid solution.

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[1] *Ber.* 1903, **36**, 282 and 1732.

[2] *J. Amer. Chem. Soc.* 1909, **31**, 523; see also Metzger and Heideberger, *ibid.* 1910, **32**, 642.

[3] *Zeitsch. anorg. Chem.* 1907, **54**, 104; see also Roberts, *ibid.* 1911, **71**, 305.

[4] Browning and Palmer, *Zeitsch. anorg. Chem.* 1908, **59**, 71.

CHAPTER XII

CERIUM GROUP (*continued*)

LANTHANUM, PRASEODYMIUM, NEODYMIUM, AND SAMARIUM

IN his examination of the ceria earths in 1839, Mosander discovered a new constituent, which he called Lanthana; the new oxide was removed in solution when the ignited mixture was extracted with dilute nitric acid, which leaves cerium dioxide undissolved. On examination, the new oxide was found to be heterogeneous; by fractional precipitation with ammonia, and subsequent recrystallisation of the sulphates, he obtained two oxides, which he called respectively Lanthana (*λανθάνειν*, to be hidden), from the absence of colour and specific reactions, and Didymia, *δίδυμοι*, twins) from their similarity and the occurrence of the two together.

Samaria was isolated by Lecoq de Boisbaudran, in 1879, from a specimen of didymia extracted from the mineral samarskite. Two years previously, Delafontaine had shown that the didymia separated from this mineral was not spectroscopically identical with the oxide obtained from other sources, and in 1878 had isolated an oxide which he called Decipia; this was shown later, however, to be a mixture of which samaria was one component. The samaria obtained by de Boisbaudran was by no means pure, being associated with terbia earths; several investigators claimed to have separated from it new oxides, most of these being proved afterwards to have been more or less impure specimens of Europia.

In 1885, Auer von Welsbach[1] employed for the first time the method which has now become of paramount importance for the separation of the cerium group, viz. the fractional crystallisa-

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[1] *Monats.* 1885, **6**, 477; *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1885, **92**, II, 317.

tion of the double nitrates. By this method he succeeded in resolving Mosander's didymia into two new oxides, for which he proposed the names Praseodidymia (πράσινος, leek-green), from the colour of the salts, and Neodidymia

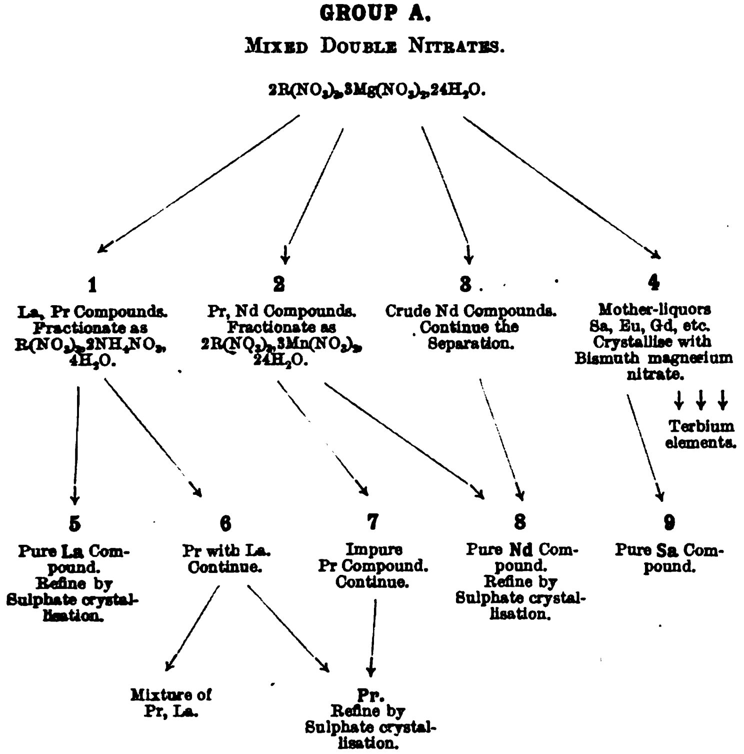

Fig. 8.—Separation of the Cerium Elements

respectively; the shorter names praseodymia and neodymia are, however, now generally adopted.

Separation

The modern methods for the separation of these elements are based almost entirely on the differences in solubility of the various double nitrates.[1] The mixed double sulphates separated

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[1] The following scheme is largely from James, 'The Separation of the Rare Earths,' *J. Amer. Chem. Soc.* 1912, **34**, 757.

by saturation of a solution of the chlorides with sodium sulphate, which contain the cerium and most of the terbium elements, are transformed into nitrates, and the neutral solution boiled with potassium bromate, in presence of powdered marble, till all the cerium is precipitated as basic ceric nitrate. From the filtered solution the other elements are thrown down as oxalates, transformed into the magnesium double nitrates (A in Fig 8), and fractionated from nitric acid solution[1] until a rough separation has been effected (fractions·1, 2, 3, and 4). The separation, which is somewhat long and tedious, is followed by means of the absorption spectra, and by the colour changes of the fractions. Fraction 1, containing lanthanum and some praseodymium, should be faint green to colourless; fraction 2 is colourless by the complementary action of the coloured salts of neodymium and praseodymium; fraction 3, which should contain the crude neodymium salt, is amethyst; and fraction 4, the mother-liquor, is yellow from the presence of the samarium compound.

Fraction 1 is now converted to the double ammonium nitrates, which allow of a readier separation at this stage; two fractions are obtained, of which the less soluble, fraction 5, is the fairly pure lanthanum compound, whilst the more soluble, fraction 6, contains the praseodymium with a little lanthanum. The lanthanum ammonium nitrate, fraction 5, is converted into the anhydrous sulphate, which is dissolved in ice-water; when the solution is gradually warmed, the enneahydrate, $La_2(SO_4)_3,9H_2O$, separates, and may be obtained perfectly pure by recrystallisation. It is of interest that the radioactive element actinium is chemically very similar to lanthanum, and follows it closely through the process of separation.

The mixed praseodymium and neodymium magnesium nitrates which constitute fraction 2 are transformed into the double manganese nitrates, and the crystallisation from nitric acid continued.[2] The less soluble part, fraction 7, is fairly free from neodymium, and the separation is continued with that of

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[1] See Demarçay, *Compt. rend.* 1900, 130, 1019 and 1185; also Drossbach, *Ber.* 1902, 35, 2826, and Muthmann and Weiss, *Annalen*, 1904, 331, 1.

[2] Cf. Lacombe, *Bull. Soc. Chim.* 1904, [iii.], 31, 570.

fraction 6, until both lanthanum and neodymium have been completely removed. The more soluble part, fraction 8, yields the pure neodymium compound, as does also the crude neodymium magnesium nitrate which constitutes fraction 3, if the crystallisation be continued.

The mother-liquors, fraction 4, are treated with bismuth magnesium nitrate,[1] which is intermediate in solubility between the analogous compounds of samarium and europium, and the crystallisation continued. The less soluble fraction contains the samarium compound, in which bismuth is the only impurity; this is easily removed by treatment with sulphuretted hydrogen. The remaining fractions are used as a source of the terbium elements (see p. 186).

The double carbonate method[2] is very suitable for the preparation of pure lanthanum compounds after the removal of cerium. The mixture of salts is added to a warm 50 % solution of potassium carbonate, and to the clear liquid, water is added gradually, with constant stirring. The double carbonates of the most positive elements are the least soluble, and are first thrown down, so that the precipitate is rich in lanthanum; it is collected and washed with a 25 % potassium carbonate solution, and the process repeated. A few repetitions suffice to separate lanthanum completely from the other members of the group. The method may also be used for the purification of praseodymium salts.

Lanthanum, La = 139·0

As the most electropositive element of the rare earth group, lanthanum is the most similar in its chemical properties to the metals of the alkaline earths. The *metal* itself (see p. 115) oxidises even in dry air, and in moist air rapidly becomes coated with a white layer of hydroxide; it attacks water, and burns vigorously when heated in the air. An alloy with aluminium, of the formula $LaAl_4$, has been prepared by Muthmann and Beck[3]; it forms lustrous white crystals, very stable in the air and very resistant towards acids.

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[1] See Urbain and Lacombe, *Compt. rend.* 1903, 137, 792; *ibid.* 1904, 138, 84 and 1136.

[2] Meyer, *Zeitsch. anorg. Chem.* 1904. 41, 94.

[3] *Annalen*, 1904, 331, 46.

The *hydroxide* is of interest from the fact that, if precipitated under suitable conditions, it has the power of taking up solid iodine to form a deep blue adsorption compound[1]; colloidal solutions of basic lanthanum acetate are also coloured blue by addition of a few drops of iodine solution. If precipitation with alkali be carried out in presence of hydrogen peroxide, an hydrated *peroxide* of the composition La_2O_5,nH_2O is obtained.[2] This compound partially decomposes with evolution of oxygen at ordinary temperatures; towards carbon dioxide and acids it acts as a true peroxide, with formation of hydrogen peroxide.

The *oxide* is colourless, and forms colourless salts with those acids in which the anion is not coloured. The oxide is distinguished from the other rare earth oxides in that it turns moistened litmus paper blue; it resembles lime in hissing when slaked, absorbing carbon dioxide from the air, and liberating ammonia from ammonium salts. By fusion with alkali carbonates, and by digestion with concentrated alkali hydroxides, Baskerville and Catlett[3] claim to have obtained lanthanates and metalanthanates, but their work has not yet been confirmed.

The *sulphate*, $La_2(SO_4)_3,9H_2O$, is the least soluble of all the rare earth sulphates. The enneahydrate is the only form stable at ordinary temperatures,[4] though under special conditions, hydrates with 6 and with 16 molecules of water of crystallisation have been obtained. It separates in needles belonging to the hexagonal system; 100 parts of water dissolve at 0°, 3·01, and at 100°, 0·69 parts of the salt. The *acetylacetone compound* melts at 185°.

A large number of other lanthanum compounds have been prepared, but these are so typical of the rare earth salts generally that no detailed treatment is required; for a full account of them, the reader is referred to Abegg's classical handbook.

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[1] Damour, *Compt. rend.* 1857, **43**, 976; see also Biltz, *Ber.* 1904, **37**, 719

[2] Melikoff and Pissarjewski, *Zeitsch. anorg. Chem.* 1899, **21**, 70.

[3] *J. Amer. Chem. Soc.* 1904, **26**, 75.

[4] Muthmann and Rölig, *Ber.* 1898, **31**, 1718.

Atomic Weight.—A large number of determinations of this constant have been made, but the results even of recent investigations do not agree so closely as might be desired. The value adopted by the International Committee, 139·0, is based on the work of Brauner and Pavlíček,[1] carried out in 1902. These authors give an account of all the determinations made up to that date, with critical discussion of the methods employed and the possible sources of error. The more important investigations have been based on the ratio $La_2O_3 : La_2(SO_4)_3$, for the determination of which the most stringent precautions must be taken. The synthetic method has generally been employed, on account of the tenacity with which the oxide clings to traces of sulphuric anhydride. In this method, the total decomposition of the acid sulphate, and the protection of the very hygroscopic sulphate, $La_2(SO_4)_3$, from atmospheric moisture, constitute the chief difficulties. By this method, H. C. Jones[2] in 1902 obtained a result (138·76) considerably lower than the value found by Brauner and Pavlíček (*loc. cit.*) A later research by Brill,[3] who carried out a synthetic sulphate determination on a minute scale, using a Nernst microbalance, gave the value 139·5, which, whilst considerably higher than either of the other figures, shows that Brauner and Pavlíček's number can hardly be too high.

Detection.—Pure lanthanum compounds show no absorption in the visible region, and the pure oxide gives no cathode luminescence. The emission spectra show very characteristic lines in the violet and ultraviolet. The chief lines are:

3949·27	4238·55	6250·14	6394·46
3988·69	4333·98	6262·52	

For arc spectra see Exner and Haschek; Eder and Valenta.[4]

Praseodymium, Pr = 140·6

This element occurs only in small quantities in the commoner rare earth minerals, and its separation in the pure state is in

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[1] *Trans. Chem. Soc.* 1902, 81, 1243.
[2] *Amer. Chem. J.* 1902, 28, 23.
[3] *Zeitsch. anorg. Chem.* 1906, 47, 464.
[4] *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, 119, IIa, 39.

consequence a matter of very great difficulty. The salts and their solutions have a characteristic green colour. The salts are derived from the sesquioxide, Pr_2O_3, but a dioxide, PrO_2, and an intermediate oxide of uncertain composition are known. The absorption spectrum has five absorption bands, one of which coincides with a band in the absorption spectrum of neodymium ; this fact has been interpreted as an indication of the non-elementary nature of both metals.[1] Difference in the absorption spectra have been put forward by several workers as indicating the complex nature of praseodymium, but an exhaustive examination by Stahl[2] in 1909 showed that there is no reason to doubt that the metal is really an element.

The *metal* is prepared by electrolysis of the fused chloride ; in order to attain the temperature required to fuse the element, a very thin cathode is employed ; if too powerful a current be used, the dioxide is formed. The metal is purified by remelting it in crucibles of magnesia, under a layer of anhydrous barium chloride. It has a yellowish shade, and is more stable in the air than lanthanum and cerium. For physical properties, see p. 115. No alloys have been prepared.

The *hydroxide* is thrown down by alkalies as a gelatinous green precipitate ; in the presence of hydrogen peroxide, an hydrated peroxide, which closely resembles the corresponding lanthanum compound, is thrown down.

The *Oxides.*—By ignition of salts of volatile acids, Auer von Welsbach[3] obtained an oxide to which he assigned the formula Pr_4O_7. More recent work[4] has shown that the composition of the oxide obtained depends upon the conditions under which the various salts are decomposed. By fusing the nitrate in presence of potassium nitrate at 400–450° C., Meyer obtained the dioxide, PrO_2; at higher temperatures this decomposes, giving the intermediate oxides. The formation of the dioxide is greatly influenced by the presence of other oxides,[5]

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[1] Auer von Welsbach, *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1903, **112**, II*a*, July; also Urbain, *Ann. Chim. Phys.* 1900, [vii], **19**, 184.

[2] *Le Radium*, 1909, **6**, 215.

[3] *Monats.* 1885, **6**, 477.

[4] See, *e.g.* Meyer, *Zeitsch. anorg. Chem.* 1904, **41**, 94.

[5] Brauner, *Monats.* 1882, **3**, 1; Marc, *Ber.* 1902, **35**, 2370; Meyer and Koss, *ibid.* 3470.

—ceric oxide, acting as an oxygen carrier, favouring whilst the other oxides hinder. The pure dioxide is a brownish-black powder, which resembles manganese dioxide, but is less stable. It liberates halogens from the halogen acids, and oxidises manganese salts to permanganates, but does not completely oxidise ferrous or stannous salts, losing instead a part of its oxygen in the gaseous form. The dioxide cannot be obtained in the wet way.

When heated in a stream of hydrogen, the dioxide yields the *sesquioxide*, Pr_2O_3, as a greenish-yellow powder, which readily absorbs oxygen from the air, becoming brown, with formation of the intermediate oxide.

The *chloride*, $PrCl_3,7H_2O$, forms large green prisms, very readily soluble in water; 100 parts of the solvent at 13° take up 334·2 parts of the hydrated salt, the solution having the specific gravity 1·687. The anhydrous chloride is a pale green deliquescent powder, which melts at a red heat to a clear green liquid; ebullioscopic measurements show that in alcoholic solution it has the simple molecular formula $PrCl_3$.

The *Bromate*, $Pr(BrO_3)_3,9H_2O$, has been obtained by James and Langelier[1] by dissolving the oxide in aqueous bromic acid, and also by double decomposition. It forms greenish hexagonal prisms, melting at 56·5°, and is readily soluble; 100 parts of water dissolve 190 parts of this salt at 25°. At 100° it loses five molecules of water, forming the tetrahydrate $Pr(BrO_3)_3,4H_2O$, which loses all its water at 130°. The anhydrous salt begins to decompose at 150°.

The *sulphate* crystallises with 8 molecules of water of crystallisation at ordinary temperatures, but hydrates with 15½, 12, and 5 molecules of water respectively have been described. The octohydrate is considerably more soluble than lanthanum sulphate enneahydrate. The anhydrous salt is a bright green powder.

Praseodymium acetylacetone melts at 146°.

Atomic Weight.—The value 140·6, adopted by the International Committee, is based on the work of Jones, v. Scheele,

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[1] *J. Amer. Chem. Soc.* 1909, 31, 913.

Auer von Welsbach, and Feit and Przibylla; the work o Brauner, however, points consistently to a higher atomi weight. Most of these investigators have used the sulphat method. The first determinations of von Welsbach for the newly discovered element[1] gave the value 140·8 (see p. 179); another series of determinations published in 1903[2] gave the mean value 140·57. Jones[3] obtained the sesquioxide for the synthetic sulphate operation by reduction of the peroxide in a current of hydrogen; according to Brauner, this method gives an oxide which is not perfectly pure, probably by absorption of water vapour and carbon dioxide from the air. Jones' mean value was 140·466. v. Scheele[4] used the same method, as well as a combined oxalate-sulphate method; his figures vary considerably, the mean value being 140·55. Feit and Przibylla,[5] using their volumetric method, obtained the value 140·54.

Brauner's earlier work,[6] carried out in 1898, gave the value 140·95. In 1901 this author[7] carried out an extensive research on the atomic weight of praseodymium, employing four different methods with spectroscopically pure material; the mean value of his very concordant results was 140·97, almost the value he obtained in 1901. A further investigation into the value of this constant appears desirable.

Detection.—The maxima of the absorption bands are given by Rech[8] as follows:

Yellow	596·4 and 588·2, weak.
Blue	481·3 very intense.
	468·3 coincident with a neodymium band.
Violet	444·2

The arc spectrum is very rich in lines.[9] The most intense, which may be used also for identification, are the following:

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[1] *Monats.* 1885, 6, 477.

[2] *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1903, 112, 1037.

[3] *Amer. Chem. J.* 1898, 20, 345.

[4] *Zeitsch. anorg. Chem.* 1898, 17, 310.

[5] *Zeitsch. anorg. Chem.* 1906, 50, 249.

[6] *Proc. Chem. Soc.* 1898, 14, 70.

[7] *Ibid.* 1901, 17, 65; see also Abegg, III, i. 263.

[8] *Zeitsch. wiss. Photochem.* 1906, 3, 411.

[9] Exner and Haschek; Bertram, *Zeitsch. wiss. Photochem.* 1906, 3, 16; Eder and Valenta, *Sitzungsber. kaiserl. Akad. Wiss. Wien.* 1910, 119, IIa, 65.

4008·90
4100·91
4118·70
4143·33
4179·60
4189·70
4206·88
4223·18
4225·50
4241·20
4305·99
4429·38
4496·60
4510·32

Neodymium, Nd = 144·3.

Neodymium is, after cerium, the commonest constituent of the cerium group in the more important rare earth minerals, and its separation is therefore by no means so difficult as that of praseodymium. The compounds of the element obtained by von Welsbach in 1885 were not pure, being admixed with samarium compounds which had not been completely separated. Neodymium salts were first prepared free from samarium by Demarçay [1] in 1898; they are of a violet-rose colour, and show in solution a well-marked and characteristic absorption spectrum, the bands being very numerous and sharply defined, and extending over the whole optical region. In chemical as well as in physical and crystallographic properties, they show an extremely close resemblance to the compounds of praseodymium.

On account of the high melting-point, the preparation of the *metal* presents the same difficulties as that of praseodymium. A current of 90–100 ampères is employed at a potential difference of 15–22 volts; this suffices to raise the thin carbon cathode to a bright white heat, and to fuse the liberated metal. For the properties of the element, see p. 115.

The *sesquioxide*, Nd_2O_3, when perfectly pure, has a light blue or lilac colour, with a faint reddish fluorescence; the shade varies somewhat according to the method of and temperature employed for the preparation. A bluish or violet-red fluorescence is highly characteristic of the salts, and is particularly noticeable if the powdered recrystallised oxalate be viewed in a good light. The greyish or brownish colour of the oxide observed by some authors is probably due to traces of impurity.[2] The existence of higher oxides of the formulæ Nd_2O_4 and Nd_2O_5

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[1] *Compt. rend.* 1898, **126**, 1039.

[2] See Waegner, *Zeitsch. anorg. Chem.* 1904, **42**, 118; also Baxter and Chapin, *J. Amer. Chem. Soc.* 1911, **33**, 1.

respectively, which Brauner[1] put forward, has been disputed by other writers, though it is found[2] that in the presence of ceria and praseodymia, the sesquioxide can take up more oxygen. Waegner[3] claimed to have obtained the compound Nd_4O_7 by heating the oxalate in a stream of oxygen, though his material, as well as that of Brauner, contained praseodymia. More recently, Joye and Garnier[4] have shown that the spectrum attributed by Waegner to the hypothetical Nd_4O_7 was in reality that of an hydrated oxide, $2Nd_2O_3,2H_2O$; these authors have also prepared a second hydrated oxide of the formula $2Nd_2O_3,3H_2O$.

The *chloride*, $NdCl_3,6H_2O$, is obtained by crystallisation from aqueous solutions; it is also precipitated by addition of water to an alcoholic solution. It forms large deliquescent rose-coloured crystals; 100 parts of water at 13° dissolve 246·2 parts of the salt, the saturated solution having the density 1·741; at 100°, 511·6 parts are dissolved. The solution resembles those of the other chlorides of the group in that it readily dissolves the rare earth oxalates. When heated in a current of hydrogen chloride of 130°, the hexahydrate yields a monohydrate, $NdCl_3,H_2O$; at 160° the anhydrous chloride is obtained as a very deliquescent rose-coloured powder, which melts at a red heat to a clear red liquid. The anhydrous chloride forms an additive compound $NdCl_3,12NH_3$, when exposed to the action of ammonia at low temperatures;[5] by gradually heating this, a large number of other additive compounds are formed, containing smaller quantities of ammonia.

The anhydrous *iodide*, NdI_3, has been obtained[6] by passing hydrogen iodide over the heated anhydrous chloride, and also by heating the carbide in iodine vapour. It fuses to a black liquid, which at a higher temperature suddenly becomes transparent.

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[1] *Chem. News*, 1898, **77**, 161; *ibid.* 1901, **83**, 197.

[2] See Meyer and Koss, *Ber.* 1902, **35**, 3740; and Marc, *ibid.* 2370.

[3] *Loc. cit.*

[4] *Compt. rend.* 1912, **154**, 510.

[5] Matignon and Trannoy, *Compt. rend.* 1906, **142**, 1042.

[6] Matignon, *ibid.* 1905, **140**, 1637.

The *bromate*, $Nd(BrO_3)_3,9H_2O$, which is exactly similar to the analogous compound of praseodymium, forms rose-coloured hexagonal prisms, melting at 66·7°.

The *sulphate*, $Nd_2(SO_4)_3,8H_2O$, is isomorphous with the corresponding salt of praseodymium, but is considerably less soluble. Only the one hydrate is known.

The *nitrates* show an interesting case of isomorphism with the corresponding bismuth nitrate hydrates.[1] The stable form of the neodymium salt is the hexahydrate, $Nd(NO_3)_3,6H_2O$, whilst the pentahydrate, $Nd(NO_3)_3,5H_2O$, is labile. Of the bismuth salts, on the other hand, the pentahydrate is stable whilst the hexahydrate is labile; but mixed crystals of both pairs may be obtained, the stable neodymium hexahydrate with the unstable bismuth compound, and the stable bismuth pentahydrate with the labile neodymium salt.

Many *double carbonates* are obtained by dissolving the normal carbonate in excess of the precipitant. The absorption spectra of these solutions, which have a blue colour, are abnormal and very intense, and have been suggested as a basis of quantitative estimation.[2]

The *acetylacetone derivative* forms violet crystals, melting at 144°–145°.

A large number of *organic salts* of neodymium have been prepared by James, Hoben, and Robinson.[3]

Atomic Weight.—The earlier determinations of this constant were carried out by the sulphate method, the synthetic process being usually employed. Auer von Welsbach, at the time of the discovery of praseodymium and neodymium,[4] gave the values 143·6 and 140·8 respectively for their atomic weights. Brauner, who carried out a determination in 1898,[5] showed that these numbers should be interchanged, and gave the value 143·63 for neodymium. Boudouard,[6] employing the analytical sulphate method, obtained the value 143·05, whilst

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[1] Bodman, *Ber.* 1898, **31**, 1237.

[2] Muthmann and Stutzel, *Ber.* 1899, **32**, 2653.

[3] *J. Amer. Chem. Soc.* 1912, **34**, 276.

[4] *Loc. cit.*

[5] *Proc. Chem. Soc.* 1898, **14**, 70.

[6] *Compt. rend.* 1898, **126**, 900.

in the same year Jones[1] gave the value 143·6. A second determination by Brauner[2] gave the value 143·89. All these values are undoubtedly too low, the material being probably contaminated with other earths.

In his second determination in 1903, Auer von Welsbach[3] gave the value 144·54 as the mean of three determinations. Feit and Przibylla,[4] using their volumetric method, gave the value 144·52, whilst Holmberg,[5] using material which he considered to have been the purest obtained up to that time, obtained the figure 144·11. More recently, Baxter and Chapin[6] have made determinations by treating the chloride with pure silver nitrate, and weighing the precipitated silver chloride, as well as by titration. The mean value obtained by the first method—ratio $NdCl_3 : 3AgCl$—was 144·272 (extremes 144·250 and 144·298), and by the second method—ratio $NdCl_3 : 3Ag$—was 144·268 (extremes 144·249 and 144·283), giving the mean value for the whole series of 144·270.

The value adopted by the International Committee is 144·3.

Detection.—The absorption spectra of neodymium compounds have been examined by Demarçay, Forsling, von Welsbach, Rech, Schäfers, and Baxter and Chapin, with concordant results. The positions of the absorption maxima as given by Holmberg[7] from the measurements of Forsling are as follows, the weaker bands being omitted :

677·5		532·3	In concentrated solution these give one intense band.
621·7		521·6	
578·5	In concentrated solution these give the intense absorption region in the yellow.	520·4	
575·4		512·4	
573·5		508·7	
571·6		474·5	
		468·7	
		461·0	
		427·1	

The arc spectrum is given by Exner and Haschek,

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[1] *Amer. Chem. J.* 1898, **20**, 345.
[2] *Proc. Chem. Soc.* 1901, **17**, 66.
[3] *Loc. cit.*
[4] *Zeitsch. anorg. Chem.* 1905, **43**, 202; *ibid.* 1906, **50**, 249.
[5] *Ibid.* 1907, **53**, 124.
[6] *Proc. Amer. Acad.* 1911, **46**, 215.
[7] *Zeitsch. anorg. Chem.* 1907, **53**, 83.

Bertram,[1] and Eder and Valenta.[2] The most intense lines are as follows:

3863·52
3951·32
4061·27
4156·30
4247·54
4282·67
4303·78
4325·87
4375·11
4385·81
4400·96
4446·51
4451·71
4463·09
4920·84
5923·35
5319·98
5594·58
5620·75
6310·69
6314·69
6385·32

Samarium, Sa = 150·4

The samarium of the earlier chemists (see p. 168) contained a large proportion of the terbium elements, from which a fairly complete separation was first effected by Demarçay in 1900.[3] By the fractional crystallisation of the double magnesium nitrate in presence of bismuth magnesium nitrate, Urbain and Lacombe [4] succeeded in preparing samarium compounds, which were shown by spectroscopic examination [5] to be free from other earths. The element is intermediate in electropositive character and in the solubility relations of its salts between neodymium and the terbium earths; its salts are topaz-yellow in colour, and in concentrated solutions show absorption in the blue and violet regions. The oxide is almost white in colour, with only a faint yellow tinge. A systematic investigation of samarium compounds was carried out by Cleve,[6] but his work was vitiated by the fact that his material was very impure. More recently, the pure salts have been examined by Matignon and his pupils.

The melting-point of the *metal* lies between 1300° and 1400° C., so that its preparation by the electrolytic method is a matter of great difficulty. A mixture of the chloride with one-third of its weight of barium chloride is electrolysed by means of a current of 100 ampères, using a cathode of

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[1] *Zeitsch. wiss. Photochem.* 1906, **3**, 16.

[2] *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, **119**, II*a*, 554.

[3] *Compt. rend.* 1900, **130**, 1185.

[4] *Ibid.* 1904, **138**, 84 *and* 1166.

[5] Eberhard, *Zeitsch. anorg. Chem.* 1905, **45**, 374.

[6] *Trans. Chem. Soc.* 1883, **43**, 362; *Bull. Soc. Chim.* 1885, [ii.], **43**, 53; *Chem. News*, 1886, **53**, 30, 45, 67, 80, 91, 100.

only 2·5 mm. thickness; the metal so obtained is greyish white in colour, and is the hardest of the cerium elements.

The *chloride* separates from aqueous solution as the hexahydrate, $SaCl_3,6H_2O$, in large tabular yellow crystals. The anhydrous chloride is white, but fuses to a chocolate-brown liquid; it forms a large number of additive compounds with ammonia. When heated in an atmosphere of dry hydrogen or ammonia, air and moisture being carefully excluded, it yields the *subchloride,*[1] $SaCl_2$, as a dark brown crystalline solid, insoluble in alcohol and all organic solvents. Samarous chloride dissolves in water, forming a deep brownish-red solution, which rapidly becomes colourless, with evolution of hydrogen, and precipitation of the oxide and oxychloride. *Samarous iodide,* SaI_2, may be obtained by a similar process, and closely resembles the chloride.

The *bromate,* $Sa(BrO_3)_3,9H_2O$, melts at 75°, and closely resembles the corresponding compounds of the didymium metals. The *sulphate* crystallises with 8, and the *nitrate* with 6 molecules of water. The *carbonate,* $Sa_2(CO_3)_3,3H_2O$, can be obtained only by passing carbon dioxide through an aqueous suspension of the hydroxide; addition of alkali carbonate to a solution of a samarium salt precipitates hydrated double carbonates.

The *acetylacetone compound* melts at 146°–147° C.

Many organic salts have been prepared by James, Hoben, and Robinson (*loc. cit.*).

Atomic Weight.—The earlier determinations of this constant were carried out with material not entirely free from europium. Demarçay[2] carried out a synthetic sulphate operation with the material which he obtained free from europium in 1900, and found values between the limits 147·2 and 148·0. The International Committee has adopted the value 150·4, which is based on the work of Urbain and Lacombe[3] in 1904. These authors made determinations of three series of ratios, obtained by (*a*) conversion of sulphate octohydrate to anhydrous sulphate, (*b*) conversion of anhydrous sulphate to oxide, and (*c*)

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[1] Matignon and Cazes, *Compt. rend.* 1906, **142**, 83.

[2] *Loc. cit.*

[3] *Compt. rend.* 1904, **138**, 1166.

conversion of sulphate octohydrate to oxide; these gave the values 150·314, 150·533, and 150·484 respectively, from which the mean atomic weight is 150·44.[1]

Detection.—The absorption spectrum of samarium compounds is only visible in fairly concentrated solutions, so that the element cannot usually be detected in a mixture by this means. The position of the maxima of the strongest bands (Demarçay, *loc. cit.*) are:

476	417
463	402

These are all in the blue and violet regions; the first and second are in the neighbourhood of neodymium and europium bands (*q.v.*), and in concentrated solutions the bands would partially coincide. Since these are the two elements from which the separation is most difficult, and are moreover the most constant in their occurrence with samarium, the absorption spectrum is of very little use as a test.

The arc spectrum is very rich in lines,[2] of which the most intense are:

3739·30	4319·12	4424·55	4519·80
4152·38	4329·21	4434·07	4524·08
4203·18	4334·32	4434·52	4544·12
4225·48	4347·95	4452·92	4566·38
4229·83	4391·03	4454·84	4577·88
4236·88	4420·72	4458·70	4642·41
4256·54	4421·32	4467·50	4674·79

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[1] These numbers are calculated by Brauner (Abegg's *Handbuch*, III. i. p. 285) on the basis O = 16, S = 32·06, H = 1·0076, and are somewhat higher than those given by Urbain and Lacombe, who used the round numbers O = 16, S = 32, and H = 1.

[2] Exner and Haschek; Eder and Valenta; Rütten and Mersch, *Zeitsch. wiss. Photochem.* 1905, 3, 181.

CHAPTER XIII

THE TERBIUM GROUP

In his examination of the yttria earths in 1842, Mosander described two new oxides isolated from the old yttria. To one of these, an orange-yellow earth which yielded colourless salts, he gave the name Erbia; the second earth, which was colourless and gave rose-coloured salts, he called Terbia. Bahr and Bunsen examined the yttria oxides in 1866, and obtained only the latter earth, which gave rose-coloured salts; to this they applied Mosander's name Erbia, and stated that the earth to which Mosander had given that name had no existence. Delafontaine, however, confirmed Mosander's work, showing that the orange-yellow earth which yielded colourless salts (Mosander's Erbia) had been fractionated out of their material by Bahr and Bunsen in the double sulphate separation of the cerium group; to avoid further confusion, however, he proposed to give to this oxide (Mosander's Erbia) the name Terbia, leaving for the colourless oxide, which forms rose-coloured salts (which Mosander had called Terbia) the name Erbia applied to it by Bahr and Bunsen. This reversed nomenclature has been generally accepted.

Delafontaine,[1] continuing his work on the earths from samarskite (see p. 168) announced in 1878 the discovery of a new oxide, Philippia, intermediate between terbia and yttria; but this was subsequently shown to be a mixture of yttria and terbia (see p. 133). In the same year, Lawrence Smith[2] announced the discovery of another oxide, Mosandria, from the samarskite earths; this was afterwards shown by Lecoq de Boisbaudran to be a mixture of terbia with gadolinia.[3] In 1880

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[1] *Compt. rend.* 1878, **87**, 559.

[2] *Ibid.* 1878, **87**, 146.

[3] *Ibid.* 1886, **102**, 647.

Marignac[1] announced the discovery of two more new oxides, Y_α and Y_β, from the same mineral; Y_β was afterwards found to be identical with samaria, whilst Y_α was subsequently separated from the old terbia earths by Lecoq de Boisbaudran, who proposed, with the assent of Marignac, the name Gadolinium.[2] The terbia left after removal of the erbia earths and gadolinia was believed by that author to be still a mixture, a conclusion supported by the work of Hofmann and Kruss in 1893.[3]

In 1886 Demarçay[4] isolated from samaria a new oxide, which he designated S_1. From his work on this oxide in 1892–1893, de Boisbaudran[5] concluded that samaria consisted of at least three oxides, samaria proper, and two new oxides Z_ξ and Z_ϵ. In 1896, Demarçay[6] separated an earth Σ, which showed the spark-spectrum of Z_ϵ and the reversal spectrum of Z_ξ, and finally in 1901[7] he obtained the new oxide in a fairly pure condition, and gave it the name Europia.

The complicated history of the terbium group has been entirely cleared up by the work of Urbain and his co-workers during the early years of the present century, and processes have been devised by which the separation of the three members of the group from one another, and from the related elements of the erbium group on the one side, and samarium on the other, can be satisfactorily accomplished. The chemistry of this group, therefore, may be regarded as satisfactorily settled, though relatively little is known of the properties of the elements and their compounds.

In their general chemical relations, elements of the terbium group occupy an intermediate position between the cerium group and the elements of the yttrium group in the narrower sense. In the solubility relations of the double salts, they are bounded on the one side by samarium and the less soluble cerium group, on the other by dysprosium and holmium and the more soluble yttrium group. They show only very slight

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[1] *Compt. rend.* 1880, **90**, 899.

[2] *Loc. cit.*

[3] *Zeitsch. anorg. Chem.* 1893, **4**, 27.

[4] *Compt. rend.* 1886, **102**, 1551.

[5] *Ibid.* 1892, **114**, 575; *ibid.* 1893, **116**, 611 and 674.

[6] *Ibid.* 1896, **122**, 728.

[7] *Ibid.* 1901, **132**, 1484.

differences in electropositive character, and methods based on differences in basic strength of the oxides, therefore, are of very little use for separating them from one another. Fractional precipitation with ammonia separates them in the order terbium, samarium, gadolinium, and europium—samaria being less strongly basic than the oxides of gadolinium and europium; this constitutes an exception to the general rule regarding the solubilities of the double nitrates and sulphates with increasing electropositive character.[1] The difficulties of separation are greatly increased by the very small proportions in which the elements are usually found in rare earth minerals. Gadolinium usually occurs in the largest quantities; in consequence of this, there is little doubt that most of the material described by the earlier workers as terbia consisted very largely of gadolinia.

The group is not characterised by well-marked absorption spectra; europium and terbium show weak absorption in the blue region Terbium, of which the salts are colourless, forms a very strongly coloured peroxide, analogous to that of praseodymium; small quantities of this give to the mixed oxides obtained by ignition the characteristic yellow colour, whilst mixtures richer in the peroxide become correspondingly darker and darker.

SEPARATION

In the double sulphate separation of the yttrium and cerium groups, the terbium elements divide themselves between the soluble and the insoluble portions; if the separation is made as complete as possible by addition of a large excess of alkali sulphate under suitable conditions, the larger part of the compounds of the group will be precipitated with the cerium elements. In the separation of the cerium elements the terbium elements collect in the most soluble fractions, and the mother-liquors of the double nitrate crystallisations therefore form a very convenient source of these elements. A considerable proportion, however, will usually remain in solution with the double sulphates of the yttrium group; in

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[1] See Lecoq de Boisbaudran, *Compt. rend.* 1890, 111, 394.

the bromate separation of these (see p. 198), the terbium elements collect in the least soluble fractions. By careful fractionation under suitable conditions, the double sulphate method may be used to separate the terbium group completely from the cerium and yttrium elements. A very convenient method of separating the terbium group from a rare earth mixture is the ethylsulphate process of Urbain. By fractional crystallisation of these salts from alcohol or water, the separation into three groups can be satisfactorily accomplished.

For the separation of the terbium elements from one another, the nitrate and double nitrate methods are most suitable. Samarium can readily be separated by crystallisation of the double magnesium nitrates in presence of bismuth magnesium nitrate ; by continuing the fractionation, europium magnesium nitrate can be separated in a pure state, as there is a considerable difference between the solubility of this salt and the corresponding compound of gadolinium ;[1] the process, however, is somewhat long and tedious. For the separation of gadolinium and terbium, the double nitrates are converted into the simple nitrates, and these fractionated from nitric acid in presence of bismuth nitrate. The gadolinium nitrate separates before the bismuth nitrate, and may be obtained fairly pure in this way, though the process is extremely tedious, and several thousand recrystallisations are required.[2] Terbium nitrate has almost the same solubility as bismuth nitrate, and the two separate together in the middle fractions. The more soluble nitrates of the erbia earths collect in the mother-liquors.

Europium, Eu = 152·0

This element is one of the rarest of the whole group, and occurs only in extremely small quantities. Monazite sand is said to contain about 0·002 per cent. of the oxide, though on account of the remarkable intensity of some of the stronger lines in the arc spectrum, Eberhard[3] was able to detect europium

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[1] James (*J. Amer. Chem. Soc.* 1912, **34**, 757) employs at this stage the fractional crystallisation of the double nickel nitrates.

[2] See Urbain, *Compt. rend.* 1904, **139**, 736.

[3] *Zeitsch. anorg. Chem.* 1905, **45**, 378.

with ease in a mixture of rare earth oxides from that mineral, after the separation of cerium. The *oxide* has a pale rose colour; the salts are also faintly coloured, and in solution show weak absorption bands.

Europium sulphate, $Eu_2(SO_4)_3,8H_2O$, separates in pink crystals, which are completely dehydrated at 375°; *europic chloride*, $EuCl_3$, in the anhydrous state forms fine yellow needles; *europium oxychloride*, EuOCl, prepared by heating europic chloride in dry air to 600°, is a white solid, insoluble in water, but soluble in strong acids; *europous chloride*, $EuCl_2$, prepared by reduction of the higher chloride in hydrogen, is a white amorphous solid, soluble in water to a neutral solution, which on boiling throws down the oxide, Eu_2O_3.[1] Several organic salts have been prepared by James and Robinson.[2]

Atomic Weight.—Using the material isolated from samaria, Demarçay [3] in 1900, by the synthetic sulphate method, found the atomic weight of europium to be about 151. Urbain and Lacombe [4] determined the value in 1904, with material free from gadolinium and samarium, using the three ratios which they employed in the case of the latter element (see p. 182); their values, corrected by Brauner, were 152·00, 151·93 and 151·94 respectively. Another series of determinations was carried out by Jantsch [5] in 1908, the same method being employed; he obtained the mean value 152·03, with an error of ±·02. The International Committee have adopted the value 152·0.

Detection.—The absorption spectrum was determined by Demarçay,[6] but is not sufficiently intense or characteristic for ordinary purposes of detection. The spark spectrum has been investigated by the same author (*loc. cit.*); it is very bright, and shows the three blue rays which characterised Lecoq de Boisbaudran's Z_ε. The reversal spectrum shows the characteristic band of Z_ζ.

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[1] Urbain and Bourion, *Compt. rend.* 1911, **153**, 1155.

[2] *J. Amer. Chem. Soc.* 1913, **35**, 754.

[3] *Compt. rend.* 1900, **130**, 1469.

[4] *Ibid.* 1904, **138**, 627.

[5] *Ibid.* 1908, **146**, 473.

[6] *Ibid.* 1900, **130**, 469.

The pure oxide, according to Urbain,[1] shows no luminescence under the influence of cathode rays, but when impure, or very largely diluted with lime or gypsum, it gives very bright and characteristic spectra.

The arc spectrum [2] is very characteristic, and contains some exceedingly intense lines, by means of which Lunt [3] has detected europium in the sun and in many stars. The lines most suited for identification of the element are the following:

3688·57
3725·10
3819·80
3907·28
3930·66
3972·16
4129·90
4205·20
4435·75
4522·76
4594·27
4627·47
4662·10
6645·44

Gadolinium, Gd = 157·3.

Gadolinia is the commonest of the terbia oxides, and occurs in considerable quantities in some of the rare earth minerals, notably in samarskite and gadolinite; its separation from the neighbouring oxides, europia and terbia, is, however, exceedingly difficult, and has only been satisfactorily accomplished in recent times. The gadolinium compounds prepared and examined by the earlier workers, as appears from the atomic weight determinations, must have been associated with earths of lower atomic weight, and undoubtedly also with small quantities of terbium. After the isolation of Marignac's Y_α, and the examination of the element by Lecoq de Boisbaudran, to whom the name gadolinium is due, further investigations were carried out by Bettendorff [4] and by Benedicts.[5] Pure gadolinia was probably first obtained by Demarçay,[6] by fractional crystallisation of the magnesium double nitrate; the oxide obtained by Urbain and Lacombe [7] by crystallisation of the nitrates in presence of bismuth nitrate, was proved to be spectroscopically pure by Eberhard.[8]

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[1] *Ibid.*, 1906, **142**, 205, 1518.

[2] Exner and Haschek; Eder and Valenta, *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, **119**, II*a*, 31.

[3] *Proc. Roy. Soc.* 1907, **79**; A, 118.

[4] *Annalen*, 1892, **270**, 376.

[5] *Zeitsch. anorg. Chem.* 1900. **22**. 393.

[6] *Compt. rend.* 1900, **131**, 343; *ibid.* 1901, **132**, 1484.

[7] *Ibid.* 1905, **140**, 583, etc.

[8] *Zeitsch. anorg. Chem.* 1905, **54**, 374

The gadolinia obtained by ignition of the salts of volatile acids should be perfectly white; presence of terbia causes it to assume a yellow colour.[1] The salts are colourless, and their solutions show no absorption in the visible region, though Urbain[2] has shown that there are four strong bands in the ultraviolet.

The *hydroxide*, $Gd(OH)_3$, is a gelatinous precipitate with strongly basic properties, rapidly absorbing carbon dioxide from the air. The *oxide*, Gd_2O_3, also absorbs carbonic anhydride from the air, and is easily soluble in acids, even after strong ignition. The element is therefore strongly electropositive. Its position among the yttrium elements, however, is justified by the properties of the *platinocyanide*, $2Gd(CN)_3,3Pt(CN)_2,18H_2O$, which forms long, pointed red crystals, with a green metallic lustre, belonging to the rhombic system, and isomorphous with the corresponding yttrium and erbium salts; the cerium elements, on the other hand, give yellow platinocyanides, with a blue metallic lustre, which crystallise in the monoclinic system.

The *nitrate*, $Gd(NO_3)_3,6H_2O$, separates from aqueous solutions at the ordinary temperatures in large crystals belonging to the anorthic system, and is isomorphous with the corresponding compounds of praseodymium and neodymium.[3] From solutions in strong nitric acid, a pentahydrate is obtained, which melts at 92°; the hexahydrate melts at 91°. The *sulphate* separates from aqueous solution as the octohydrate, $Gd_2(SO_4)_3,8H_2O$, isomorphous with the corresponding salts of both groups. The anhydrous sulphate is much less soluble in water at 0° than the corresponding compounds of the cerium elements. The *selenate* forms hydrates with 10 and 8 molecules of water of crystallisation respectively; these are isomorphous with the corresponding selenates of yttrium and the erbium metals.

Atomic Weight.—The determinations of this constant made by the earlier workers were all carried out with impure

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[1] Eberhard (*loc. cit.*) has shown that even in the perfectly white oxide, traces of terbia can be distinguished by spectroscopic examination.

[2] *Compt. rend.* 1905, **140**, 1233.

[3] Lang and Haitinger, *Annalen*, 1907, **351**, 450.

material and gave results which were considerably too low. The International Committee have adopted the value 157·3, which is based on the work of Urbain.[1] In employing the analytical sulphate method, that author observed that the anhydrous sulphate did not remain constant in weight when allowed to remain in a desiccator, and that it could not be accurately weighed. He therefore determined the ratio $Gd_2(SO_4)_3 8H_2O : Gd_2O_3$, by converting the octohydrate directly to oxide, and obtained the mean value 157·24.

Detection.—Pure gadolinium compounds show no absorption in the visible spectrum, but there are four strong bands[2] in the ultraviolet, viz. 311·6 – 310·5; 306·0–305·7; 305·6–305·5; and 305·4–305·0. The arc spectrum[3] is very rich in lines, of which the most intense are the following:

3082·15
3100·66
3422·62
3545·94
3549·52
3585·12
3646·36
3671·39
3719·63
3743·68
3768·60
3796·62
3814·18
3852·65
3916·70
4037·49
4050·05
4063·62
4070·51
4073·99
4085·73
4098·80
4130·59
4184·48
4251·90
4262·24
4325·83
4327·29
4342·35
6114·26

The spark spectra have been examined by Demarçay,[4] Baur and Marc,[5] Urbain[6] and Crookes.[7]

Terbium, Tb = 159·2

Terbia occurs among the rare earth oxides in exceedingly small quantities, and its separation has in consequence presented such great difficulties that only within the last few years have terbium compounds been completely freed from gadolinium and neighbouring elements. In 1886 Lecoq de Boisbaudran,[8] by fractional precipitation of the hydroxides with ammonia, and subsequent fractional crystallisation of the double sulphates, obtained an oxide much richer in terbia

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[1] *Compt. rend.* 1905, **140**, 583.

[2] Urbain, *ibid.* 1905, **140**, 1233.

[3] Exner and Haschek; Eder and Valenta, *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, **119**, IIa, 21.

[4] *Compt. rend.* 1900, **131**, 343.

[5] *Ber.* 1901, **34**, 2460.

[6] *Loc. cit.*

[7] *Proc. Roy. Soc.* 1905, **74**, 420.

[8] *Compt. rend.* 1886, **102**, 395, 483.

than any specimen previously prepared; it was dark yellow in colour. In 1902 Marc[1] obtained from monazite a very dark oxide containing about 15 per cent. of terbia, whilst Feit[2] in 1905 obtained a dark brown oxide consisting of gadolinia with about 13 per cent. of terbia. Pure terbium compounds were obtained by Urbain in 1904,[3] by fractional crystallisation of the nitrate from nitric acid, in presence of bismuth nitrate, and by crystallisation of the double nickel nitrates, and precipitation with ammonia; he showed that the element was identical with the Z_δ and Z_β of de Boisbaudran,[4] with the Γ of Demarçay,[5] and with the G_β and possibly the G_ζ of Crookes[6] (see p. 193).

The element gives the white *sesquioxide*, Tb_2O_3, and colourless salts.[7] The *peroxide*, of which the composition corresponds approximately to the formula Tb_4O_7, is obtained as a brownish-black powder by ignition of suitable salts. Its presence, even in small quantities, gives so deep a colouration to the other earths that some kind of salt formation seems probable. It is insoluble in cold acids; it dissolves in hot nitric acid with evolution of oxygen, forming a solution from which the *nitrate*, $Tb(NO_3)_3,6H_2O$, melting at 89·3°, separates on cooling. In hot hydrochloric acid, the peroxide dissolves with evolution of chlorine, forming solutions from which the *chloride*, $TbCl_3,6H_2O$, can be isolated with difficulty; this salt is extremely deliquescent, and easily forms supersaturated solutions. The *sulphate*, $Tb_2(SO_4)_3,8H_2O$, can be precipitated from a sulphuric acid solution of the oxide by addition of considerable quantities of alcohol; it is isomorphous with the other sulphate octohydrates, and is completely dehydrated at 360°.

Atomic Weight.—The value adopted by the International Committee is 159·2, which was obtained by Urbain in 1905

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[1] *Ber.* 1902, **35**, 2382.

[2] *Zeitsch. anorg. Chem.* 1905, **43**, 267.

[3] *Compt. rend.* 1904, **139**, 736; 1905, **141**, 521; 1909, **149**, 37.

[4] *Ibid.* 1895, **121**, 709; 1904, **139**, 1015.

[5] *Ibid.* 1900, **131**, 343.

[6] *Trans. Chem. Soc.* 1889, **55**, 258.

[7] The terbium compounds here described have been prepared by Urbain (*loc. cit.*) from carefully purified material; other compounds have been described by Potratz (*Chem. News*, 1905, **92**, 3), but her material contained a large proportion of gadolinium.

(*loc. cit*) from the ratio $Tb_2(SO_4)_3,8H_2O : Tb_2(SO_4)_3$. This is the only determination on which reliance can be placed, as the material of the earlier workers was seldom even approximately pure.

Detection.—Solutions of terbium salts show only one band in the visible spectrum, at 487·7 in the blue. This band was observed by Lecoq de Boisbaudran in a specimen of terbia containing dysprosia, and assumed by him to belong to a new element, Z_δ (*loc. cit*). In the ultraviolet nine absorption bands have been observed (Urbain, *loc. cit.*)

The spark spectrum shows the lines observed by Demarçay in 1900, and attributed by him to the new element Γ. Lecoq de Boisbaudran's element Z_β showed a green fluorescence with the reversed spark, a phenomenon which Urbain has found to be exhibited by pure terbium compounds.

The arc spectrum of Urbain's pure terbia was examined by Eberhard[1]—see also Exner and Haschek, and Eder and Valenta.[2] The element may be detected in minerals and earth mixtures by the following lines:

3523·82
3676·52
3703·05
3704·01
4005·62
4278·71

The chief lines in the arc spectrum (Exner and Haschek) are the following:

3324·53
3509·34
3531·86
3561·90
3568·69
3600·60
3628·53
3650·60
3659·02
3704·10
3711·91
3848·90
3874·33
3899·34
3925·60
3939·75
3977·01
3982·07
4005·70
4012·99
4278·70
4752·69

Pure terbia does not exhibit the phenomenon of cathode luminescence, but gadolinia containing a trace of terbia shows a marked green fluorescence, which was attributed by Crookes to a new Meta-element, G_β. A trace of terbia in aluminium oxide causes the latter to exhibit a highly characteristic intense white luminescence.

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[1] *Sitzungsber. königl. Akad. Wiss. Berlin*, 1906, 18, 385.

[2] *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, 119, IIa, 14.

CHAPTER XIV

THE ERBIUM AND YTTERBIUM GROUPS—YTTRIUM AND SCANDIUM

In his examination of the 'Yttria' of Gadolin and Ekeberg, during the years 1839 to 1843, Mosander, by methods based on differences in strength of the oxides as bases, separated the earth into three new oxides, yttria proper, the most strongly basic, terbia, intermediate in strength, and erbia,[1] the least basic. No further separation was effected until 1878, when Marignac, by fractional decomposition of the nitrates, separated from erbia a new oxide, for which he proposed the name Ytterbia; the new oxide was the least basic of the erbia earths. In the following year, Nilson[2] isolated from ytterbia a still less basic oxide, by the same method; he proposed the name Scandia, to recall the fact that it occurred in gadolinite and euxenite, which up to that time had been found only in Scandinavia. In 1879 also, Soret[3] announced the discovery of a new element X, evidence for the existence of which he had obtained during a spectroscopic examination of a mixture of erbia and terbia earths; the oxide of X was isolated in the same year by Cleve[4] from the old erbia, by fractional decomposition of the nitrates, and the name Holmium, from the town of Stockholm, was proposed for the new element. The same investigation led to the discovery of Thulium, which derives its name from Thule, an old name for Scandinavia.

Lecoq de Boisbaudran[5] in 1886 showed Cleve's Holmia to be a mixture of at least two oxides; he retained the name Holmium for the element which gave the most characteristic

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[1] The reversed nomenclature of Delafontaine is here employed (see p. 184).

[2] *Compt. rend.* 1879, **88**, 642, 645.

[3] *Ibid.* 1879, **89**, 521.

[4] *Ibid.* 1879, **89**, 478, 708.

[5] *Ibid.* 1886, **102**, 1003, 1005.

absorption bands of the old holmium, and proposed the name Dysprosium (from δυσπρόσιτος, difficult of access) for the second element. The name Erbia was retained for the oxide remaining after the removal of holmia, thulia, and dysprosia from the old erbia; the homogeneity of this erbia has been called in question, but is now fairly firmly established. The individuality of dysprosium[1] and holmium[2] may also be regarded as definitely established; that of thulium remains doubtful (see p. 204).

The homogeneity of ytterbia was questioned by Auer von Welsbach[3] in 1906; by fractionation of the ammonium double oxalates, that author isolated the oxides of two new elements, for which he proposed the names Aldebaranium and Cassiopeium. By fractionation of the nitrates from nitric acid solution, Urbain[4] arrived at the same result, and proposed the names Ytterbium (Neoytterbium) and Lutecium, which have been adopted by the International Committee. The latter author, employing the same method in the fractionation of the gadolinite earths, has recently obtained very strong evidence of the existence in this group of another element, for which he proposes the name Celtium;[5] the discovery, however, awaits confirmation.

SEPARATION

In the separation of the yttrium elements, methods based on differences in electropositive character are of much greater importance than in the separation of the cerium and terbium groups, and the method of nitrate fusion has been very largely employed even in comparatively recent work. This method, which was introduced by Berlin in 1860, has been of great value in the separation of yttrium and the ytterbium elements from the erbium group; it was employed in the isolation of ytterbium by Marignac, and of scandium by Nilson.

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[1] Urbain, *Compt. rend.* 1906, **142**, 785.

[2] Holmberg, *Zeitsch. anorg. Chem.* 1911, **71**, 226.

[3] *Monats.* 1906, **27**, 935; 1908, **29**, 121.

[4] *Compt. rend.* 1907, **145**, 759.

[5] *Ibid.* 1911, **152**, 141.

If a concentrated solution of the nitrates be evaporated down, and the syrupy residue subjected to gradually increasing temperature, the nitrates of the ytterbium elements and scandium are converted first into the basic nitrates; at somewhat higher temperatures the erbium salts are decomposed, whilst yttrium nitrate and the nitrates of any cerium elements present are the last to break up. If the mixture of basic and neutral nitrates be dissolved in boiling water, the former, being less soluble, crystallise out on cooling, and may be separated by this means, the process being repeated with the filtrate containing the unchanged nitrates. In this way, the weakly basic scandia and ytterbia quickly collect in the first fractions, whilst the oxides of the erbia group are easily separated from the more strongly basic yttria. The presence of the intermediate terbium group renders the process much less easily workable.

The process may be modified by raising the temperature to such an extent that the soluble basic nitrates are converted into insoluble superbasic nitrates, the temperatures at which this change occurs increasing from element to element as the positive character becomes more marked; the mixture of basic and superbasic salts is then extracted with dilute nitric acid which leaves that latter undissolved and removes the more positive elements in solution.

Fractional precipitation of the hydroxides by means of ammonia, alkalies, or alkaline earths has also been frequently employed. A modification of this process is the precipitation with aniline, carried out by Kruss;[1] in this method, the solution of the chloride in warm dilute alcohol is treated with an alcoholic solution of the organic base. Another modification is the 'Oxide process' employed by Auer von Welsbach[2] for the separation of the cerium elements, and by Drossbach[3] in the yttrium group. The concentrated solution of the mixed salts is thoroughly digested with the oxides obtained by precipitating a fraction of the earths; the more strongly basic oxides tend to displace the less basic, so that these accumulate

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[1] *Zeitsch. anorg. Chem.* 1893, **3**, 108, 353.

[2] *Monats.* 1883, **4**, 630.

[3] *Ber.* 1902, **35**, 2826.

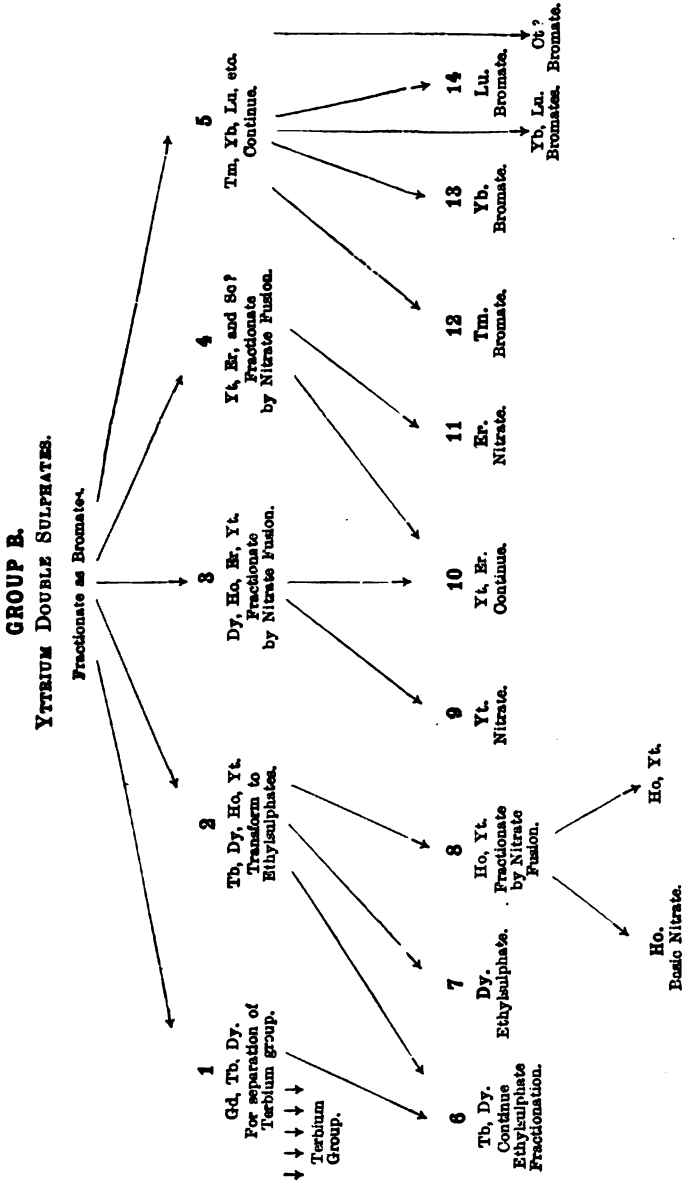

FIG. 9.—SEPARATION OF THE YTTRIUM ELEMENTS

in the insoluble part. The solution is filtered from the undissolved oxides, another fraction precipitated, and the oxides obtained from the precipitate digested with the concentrated solution as before.

The more modern methods of separation combine the above processes with the methods of fractional crystallisation, for which the bromates and alkylsulphates of these elements are well adapted, The procedure[1] which experience shows will lead to a fairly rapid separation is roughly represented in Fig 9. The double sulphates (B), left in solution after removal of the cerium and part of the terbium group, are transformed into the bromates, which are separated by fractional crystallisation into five main fractions. The least soluble portion, fraction 1, contains the terbium elements with some dysprosium; in the fractionation of the terbium group by means of the nitrates and double nitrates, the dysprosium, with some terbium, collects in the final fractions (fraction 6). Fraction 2 contains terbium, dysprosium, holmium, and yttrium as the bromates; these are converted into the anhydrous chlorides, from which, by treatment with sodium ethylsulphate in alcoholic solution, the ethylsulphates are obtained. By fractional crystallisation, dysprosium may be obtained in a fairly pure condition (fraction 7), the least soluble part (fraction 6) containing the terbium with some dysprosium. Holmium and yttrium collect in the most soluble part (fraction 8), from which pure holmium can be obtained by the method of nitrate fusion. Fraction 3 contains yttrium and erbium, with small quantities of dysprosium and holmium; the latter are readily separated by the nitrate fusion, which will also allow of a fairly complete separation of yttrium (fraction 9). Fraction 4 contains yttrium and erbium; scandium if present will also collect here. Erbium can be obtained pure by the nitrate fusion; the second fraction from this process contains both yttrium and erbium, and may be further worked up with the fraction of similar composition (fraction 10) from fraction 3.

The mother-liquors from the bromate separation (fraction 5)

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[1] James, *J. Amer. Chem. Soc.* 1912, **34**, 757.

contain thulium and the ytterbium elements; the crystallisation is continued, and allows of complete separation of thulium and ytterbium, and probably of lutecium, though the most soluble fractions do not seem to have been fully separated.

THE ERBIUM GROUP

The oxides of this group, as contrasted with the ytterbia oxides, give rise to coloured salts, which in solution show definite absorption spectra in the optical region; the spectrum of erbium salts is particularly definite and characteristic. Erbium has among the yttrium elements the place of neodymium among the cerium elements; after yttria, erbia is the commonest oxide of the yttria group, though on account of the difficulties of separation the chemistry of erbium is by no means so complete and definite as that of neodymium. The oxides in order of decreasing basicity, as shown by the order in which they are thrown down by ammonia, are: dysprosia, holmia, erbia, thulia; the electropositive character becomes weaker, therefore—as generally in the rare earth series—as the atomic weight of the elements increases.

Dysprosium, Dy = 162·5

Compounds of this element were probably prepared in the pure state for the first time by Urbain[1] in 1906, by the fractional crystallisation of the ethylsulphate. He showed that after fourteen recrystallisations, the absorption spectrum of the salts and the mean atomic weight of the element remain unaltered, and that after removal of terbium by the very efficient ethylsulphate method, all remaining traces of yttrium could be rapidly removed by crystallisation of the nitrate. The salts have generally a more or less pronounced yellow colour.

The *oxide*, Dy_2O_3, is a white powder which does not alter in composition when strongly heated in reducing or oxidising atmospheres. It is remarkable in that it is the most strongly paramagnetic oxide known, having a coefficient of susceptibility

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[1] *Compt. rend.* 1906, 142, 785.

much greater than that of ferric oxide.[1] The *chloride* crystallises with 6, the *sulphate* with 8, and the *nitrate* with 5 molecules of water of crystallisation. The *bromate*, $Dy(BrO_3)_3 9H_2O$,[2] obtained by double decomposition, melts at 78°. The *platinocyanide*, $Dy_2[Pt(CN)_4]_3,21H_2O$, forms bright red cubic crystals, with greenish fluorescence.

Several other salts are described by Urbain, and by Jantsch and Ohl (*loc. cit.*).

Atomic Weight.—Urbain and Demenitroux[3] determined this constant from the ratio $Dy_2(SO_4)_3,8H_2O : Dy_2O_3$. The mean value of six determinations carried out with material obtained by fractional crystallisation of the nitrate was 162·52 ; with material purified by the ethylsulphate crystallisation, the mean of six determinations gave the value 162·54. The International Atomic Weight is 162·5.

Detection.—Lecoq de Boisbaudran[4] and Urbain[5] give the position of the following absorption maxima in the visible and ultraviolet regions respectively :

753	368·5	338
475	379·5	332·5
451·5	365	
427·5	351	

The arc spectrum of Urbain's material was examined by Eberhard,[6] who gives as most suitable for detection of the element in a mineral or oxide mixture the following lines :

3385·16
3531·86
3536·17
3645·54
3898·69
3944·83
4000·59
4078·11
4187·00
4211·82

See also Exner and Haschek, and Eder and Valenta.[7]

The ultraviolet arc spectrum and the cathode phosphorescence have also been examined by Urbain.[8]

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[1] *Compt. rend.* 1908, **146**, 922.

[2] Jantsch and Ohl, *Ber.* 1911, **44**, 1274.

[3] *Compt. rend.* 1906, **143**, 598.

[4] *Ibid.* 1886, **102**, 1003.

[5] *Ibid.* 1906, **142**, 785.

[6] *Publ. astrophys. Observ. Potsdam*, 1909, **20**, No. 60.

[7] *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, **119**, II*a*, 9.

[8] *Loc. cit.*

Holmium, Ho = 163·5

The individuality of this element can hardly be regarded as perfectly established, though Holmberg[1] has prepared salts which in solution show only faint indications of erbium and dysprosium, when tested spectroscopically. That author fractionated the yttrium elements obtained from euxenite by a long process of separation, which involved crystallisation of the *m*-nitrobenzenesulphonates, of the simple nitrates (two series), of the double ammonium oxalates, and finally fractional precipitation of the hydroxides by ammonia.

He determined the *Atomic Weight* as 163·5, which is the value accepted by the International Committee, and mapped the absorption spectrum. The *oxide*, Ho_2O_3, is a pale yellow powder; the *salts* are yellow, with a faint orange tinge.

Erbium, Er = 167·7

Although erbia was separated by Mosander seventy years ago, it is doubtful if the perfectly pure oxide has ever been prepared. Whilst the individuality of the element is well established, its homogeneity has frequently been called in question. The name 'Neo-Erbia' was given by Cleve[2] to the residue left after the separation from the old erbia of ytterbia, scandia, thulia, and holmia (with which dysprosia (*q.v.*) was also separated), but the spectrum examination of Kruss and Nilson[3] led them to regard Cleve's oxide as still complex. Their results, however, were explained by the work of Hofmann and his pupils,[4] who consider erbia to be a homogeneous product; the homogeneity of the element, therefore, may be considered as established, though it would be strengthened by a more complete knowledge of the neighbouring elements, holmium and thulium.

The element forms a rose-coloured oxide, and rose-coloured salts, which give to the compounds of the mixed erbia earths their characteristic colour. The oxide gives a very definite

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[1] *Zeitsch. anorg. Chem.* 1911, **71**, 226; see also Langlet, *Abstr. Chem. Soc.* 1907, **92**, ii. 955.

[2] *Loc. cit.*

[3] *Ber.* 1887, **20**, 2134.

[4] *Ber.* 1908, **41**, 308; also Hofmann, *ibid.* 1910, **43**, 2631.

and characteristic reflection spectrum, but the salts do not possess this property;[1] the reflection spectrum remains unchanged in the presence of foreign oxides, provided no combination occurs. From the atomic weight determinations, it seems clear that the salts described by Cleve and his pupils[2] were not pure erbium compounds; a few salts only appear to have been recently obtained in the pure state for the atomic weight determination (*q.v.*).

The *sulphate* separates from aqueous solutions at ordinary temperatures as the octohydrate, $Er_2(SO_4)_3,8H_2O$, which forms rose-coloured monoclinic crystals isomorphous with the corresponding sulphates of the whole group. The anhydrous sulphate is formed by long heating at 400°, more quickly at 475°, and can be heated to 630° without decomposition. At 845° a basic salt, Er_2O_3,SO_3, is formed, which begins to decompose at 950°; at 1055° the transformation to the oxide is complete. The ammonium and potassium double sulphates are easily soluble in cold water.

The *oxalate* is thrown down in rosettes of bright rosy plates, which according to Hofmann[3] have the formula $Er_2(C_2O_4)_3,10H_2O$, even when dried in the air. Cleve believed the salt to be thrown down as the enneahydrate. When kept *in vacuo* over phosphoric anhydride, the decahydrate passes into the trihydrate, which when heated decomposes, passing into the oxide at a temperature of 575°. The *nitrate*, $Er(NO_3)_3,5H_2O$, separates from aqueous solution as the pentahydrate, in large stable red crystals. The *platinocyanide*, $Er_2[Pt(CN)_4]_3,21H_2O$, has the characteristic red colour with green fluorescence. The *formate*, $Er(HCOO)_3$—Cleve, *loc. cit.*—is a red powder, obtained by dissolving the oxide in formic acid; it crystallises from water as the dihydrate.

Atomic Weight.—The determinations of the earlier workers, being carried out with impure material, gave results which differ very widely, and are quite unreliable. Cleve's value of 1880, for material free from ytterbia, but not apparently

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[1] See Kruss and Bugge, *Ber.* 1908, **41**, 3783.

[2] See *Compt. rend.* 1880, **91**, 381.

[3] *Loc. cit.*

free from earths of lower equivalent, was 166·25; Brauner,[1] using the same material in 1905, obtained the much higher value 167·14. The determinations of Hofmann and Burger[2] in 1908 gave the mean value 167·38; with purer material, Hofmann in 1910[3] obtained the mean value 167·68, on which is based the value accepted by the International Committee, 167·7.

Detection.—Salts of erbium give in solution absorption spectra which are well defined and highly characteristic, though not so intense as those of praseodymium and neodymium. Hofmann and Bugge[4] give the following absorption maxima for a 10 per cent. solution of their pure nitrate in a layer of 15 mm. thickness:

667 weak
654 strong
541 very weak
523 very strong
519 shadowy
492
487 strong
450
442 weak

The arc spectrum has been mapped by Eder and Valenta[5] and Exner and Haschek. The following lines are used by Eberhard[6] for purposes of detection:

3230·73
3264·91
3312·56
3372·92
3499·28
3692·85
3896·40
3906·47
3938·79

Thulium, Tm= 168·5

The thulia isolated in 1879 was described by Cleve[7] as pale rose in colour; in the following year, having obtained it in larger quantity, he found that it was white, and dissolved in acids to form colourless solutions which showed absorption bands in the red and blue. The spectra of the thulium compounds prepared by Cleve were examined by Thalèn,[8] who concluded that a new element was certainly present, though it had not been freed from ytterbium and erbium. Incidental

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[1] Abegg, III. i. 318. [2] *Loc. cit.* [3] *Loc. cit.* [4] *Ber.* 1908, 41, 3783.
[5] *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, 119, II*a*, 18.
[6] *Publ. astrophys. Observ. Potsdam*, 1909, 20, No. 60.
[7] *Loc. cit.* [8] *Compt. rend.* 1880, 91, 376.

observations on the new oxide were made by various investigators, but no extensive researches were carried out upon it until 1911, when James[1] published an account of the separation and purification by the bromate method, stating that after some 15,000 operations, his products remained unaltered; he gives, however, no spectroscopic determinations, though part of his material, spectroscopically examined by Sir William Crookes, was described as 'Very good thulium, with a trace of ytterbium.' In the same year Auer von Welsbach[2] published an account of a spectroscopic investigation, as a result of which he concludes that thulium is a mixture of at least three elements, of which the second, Tm II, agrees fairly well in properties, so far as the two accounts allow of comparison, with the thulium of James.

Thulia is described by James as a dense white powder, with a greenish tinge, which 'emits a carmine coloured glow, when carefully made to incandesce.' The salts have a greenish tint, very susceptible to traces of erbium; addition of erbium compounds turn the solution first yellowish-green, then colourless, and finally pink. von Welsbach describes Thulium II as forming an almost white sesquioxide, which, when heated in the flame, gives a purplish light quickly succeeded by a splendid characteristic glow; the salts are pale yellowish-green by daylight, emerald-green by artificial light, the colour being almost complementary to that of erbium salts. In solution, salts of Tm II give the bands at 685 and 464 ascribed by James and other workers to thulium.

Until further researches on these interesting results are published, the elementary nature of thulium cannot be considered definitely settled; it appears probable, however, that homogeneous salts of a definite element were obtained by James. The following salts are described by James (*loc. cit.*).

The *chloride*, $TmCl_3,7H_2O$, separates at ordinary temperatures from the concentrated solution of the oxide in hydrochloric acid as greenish crystals, very soluble in alcohol and water. The *bromate*, $Tm(BrO_3)_3,9H_2O$, forms pale bluish-

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[1] *J. Amer. Chem. Soc.* 1911, **33**, 1333.

[2] *Zeitsch. anorg. Chem.* 1911, **71**, 439.

green hexagonal prisms, isomorphous with the analogous salts of the group. The *sulphate* and *nitrate* separate as the octohydrates. The precipitated *oxalate* has the formula $Tm_2(C_2O_4)_3,6H_2O$, and is soluble in excess of alkali oxalate. The *acetylacetone derivative* was prepared by dissolving the precipitated and well-washed hydroxide in alcoholic acetylacetone; it recrystallises from absolute (?) alcohol as the dihydrate, $Tm_2(C_5H_7O_2)_6,2H_2O$. The *phenoxyacetate*, $Tm_2(C_6H_5{\cdot}O{\cdot}CH_2{\cdot}COO)_6,6H_2O$, was obtained in a similar manner by addition of the hydroxide to a solution of phenoxyacetic acid in dilute alcohol.

Atomic Weight.—Cleve gave the value 170·7 for this constant, but his material was very impure. In a footnote to a paper published in 1907, Urbain[1] pointed out that the value could not be above 168·5. Analyses of the salts prepared by James agree fairly well with the theoretical values calculated on this basis, but a systematic determination with pure material has not yet been made. The International Committee (1912) have adopted the value 168·5.

Detection.—The element can be detected in solution by its absorption spectrum, the most intense bands being in the neighbourhood of $\lambda = 685$, and $\lambda = 464$. For provisional arc spectra see Exner and Haschek, and for spark spectra Auer von Welsbach (*loc. cit.*) and Eder and Valenta.[2]

Ytterbium (Neoytterbium, Aldebaranium), Yb = 172·0.
Lutecium (Cassiopeium), Lu = 174·0.

The first indication of the complexity of Marignac's Ytterbium was furnished on spectroscopic grounds by Auer von Welsbach in 1905;[3] he showed that a separation could be effected by the fractional crystallisation of the ammonium double oxalates from concentrated ammonium oxalate. Three years later[3] he published a full account of his method, gave atomic weight determinations, and mapped the spectra of the two new elements. In 1907, Urbain[4] independently effected

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[1] *Compt. rend.* 1907, **145**, 760.

[2] *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, **119**, II*a*, 103.

[3] See *Monats.* 1908, **29**, 204.

[4] *Compt. rend.* 1907, **145**, 759.

a separation by the fractional crystallisation of the nitrates from nitric acid, and proposed the names Lutecium (from the old name for Paris) and Neoytterbium for the elements.

The two new elements resemble one another so closely in chemical properties that the account given by Astrid Cleve in 1902[1] of the compounds of the old ytterbium applies in practically every detail to the new elements. The oxides are white, and yield colourless salts, showing in solution no absorption bands in the visible region.

The *oxides*, R_2O_3, though perfectly white, are coloured yellow or brown by the faintest traces of thulium. They are attacked by acids only slowly in the cold, but dissolve readily on warming; lutecia is slightly the less strongly basic. The *chlorides* crystallise with six molecules of water, and are extremely soluble and deliquescent; when heated in a stream of hydrogen chloride, they form oxychlorides of the type ROCl. The *platinocyanides* crystallise with 18 molecules of water, and have the characteristic appearance of the analogous compounds of the yttrium elements. The *sulphates* crystallise at all temperatures as the normal octohydrates, and are moderately easily soluble in water; conductivity measurements show that they are partially hydrolysed in solution. The *nitrates* crystallise from concentrated aqueous or nitric acid solutions as the tetrahydrates; by evaporation of the aqueous solutions over sulphuric acid, the trihydrates are obtained. These compounds are anomalous among the rare earth nitrates, by reason of their low water content. The neutral *carbonates* are thrown down by ammonium carbonate as the tetrahydrates; if a stream of carbon dioxide be led into aqueous suspension of the hydroxides, *basic carbonates* of the formula $R(OH)CO_3,H_2O$, are obtained. The *oxalates* are precipitated as the decahydrates; they are readily soluble in excess of alkali oxalate.

Many other salts of the old ytterbium have been prepared.

Atomic Weights.—The values determined by Urbain (*loc. cit.*) for the fractions obtained by the nitrate method

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[1] *Zeitsch. anorg. Chem.* 1902, **32**, 129.

gave the number 170·1 for the least soluble fraction free from terbium, and 173·4 for the most soluble fraction. Auer von Welsbach (*loc. cit.*) obtained the values 172·9 and 174·2 for the least soluble and most soluble fractions from the double oxalate crystallisation respectively. More recently[1] he has determined these constants with highly purified material, employing a modified method. The weighed anhydrous sulphates are transformed into the oxalates, which are then ignited to the oxides. He obtained the values Yb = 173·00, Lu = 175·00.

The values adopted by the International Committee are Yb = 172·0 and Lu = 174·0.

Spectra.—The spark spectra are of more use in distinguishing the two elements than the arc spectra. The spark spectrum of the old ytterbium was mapped by Exner and Haschek,[2] and of the two compounds by both discoverers (*loc. cit.*). See also Eder and Valenta.[3]

The arc spectra have been mapped by Eder and Valenta (*loc. cit.*) and by Exner and Haschek; the latter authors give as the most intense lines the following:

Yb	Lu		
3031·26	2615·50	3397·21	4124·87
3107·99	2911·53	3472·65	4184·40
3289·50	3077·75	3507·57	4518·74
3464·47	3198·27	3508·55	5476·88
3988·16	3254·45	3554·58	5983·92
5556·67	3281·89	3568·00	5984·32
	3312·30	3624·10	6222·10
	3359·74	3636·41	6463·40
	3376·69	3876·80	

Celtium

The separation of Marignac's ytterbium into the two elements described above was accomplished by Urbain with the yttria earths extracted from xenotime. In carrying out

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[1] *Monats.* 1913, **34**, 1713.

[2] *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1899, **108**, II*a*, 1123.

[3] *Ibid.* 1910, **119**, II*a*, 3.

the same process with the ytterbia earths from gadolinite, that author[1] obtained from the mother-liquor an earth for which the coefficient of magnetisation was found to be $4{\cdot}1 \times 10^{-6}$; lutecia has a coefficient three to four times as great. A spectroscopic examination revealed the presence of lines which did not correspond with those of any known body, and Urbain considered that a new element, for which he proposed the name Celtium, with the symbol Ct, must be present. Lutecia from xenotime shows no trace of the new element.

Spectroscopic evidence for the existence of a third ytterbium element had previously been brought forward by Auer von Welsbach[2] and also by Exner and Haschek.[3]

The new element appears to be intermediate between lutecium and scandium, and therefore may be expected to have a higher atomic weight than the former element. Its chloride is more volatile than that of lutecium, less volatile than that of scandium; its hydroxide is more feebly basic than that of lutecium, but more strongly basic than that of scandium.

Urbain (*loc. cit.*) gives the following as the principal lines in the spectrum; strong lines are denoted by a single, very strong by a double, asterisk:

2459·4
2469·3
2481·6 *
2536·9 *
2677·7
2685·2 **
2729·1 *
2737·9
2765·8 **
2834·3 *
2837·3 *
2845·2 *
2870·2
2885·1 *
2903·9 *
2931·9
2949·5 *
3080·7 **
3118·6 **
3171·4 *
3197·9 **
3326·0 *
3391·5 *
3665·6

Yttrium, Yt = 89·0

Since the separation of yttria proper from the old yttria earths by Mosander, in 1842, the individuality of yttrium has been well established. The yttria of the workers of the

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[1] *Compt. rend.* 1911, **152**, 141. [3] *Monats.* 1908, **29**, 204.

[2] Exner and Haschek, *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, **119**, II*a*, 771.

sixties and seventies, to judge from the atomic weight determinations, must have been very impure, but no doubts were raised as to its homogeneity. By examination of the cathode luminescence spectra, Crookes[1] concluded that the oxide was of a complex nature; Lecoq de Boisbaudran, however, showed that the phenomena observed by Crookes were due to traces of impurity in his material, a conclusion confirmed by the work of Baur and Marc.[2]

The oxide is the most strongly basic of all the yttria earths; in the basicity methods of separation, therefore, it collects in the end fractions, and is easily separated from the erbia and ytterbia earths by the nitrate fusion and similar processes. The terbia earths, however, which are comparable to it in basic strength, cannot be easily separated by such methods; processes of fractional crystallisation are very convenient in this case, since yttrium falls, with regard to the solubility of its simple salts, among the erbium group—between holmium and erbium generally—which is easily separated from the less soluble terbium elements. The separation of yttrium, therefore, affords an example of the combination of methods of both kinds.

The methods for the separation and purification of yttrium have recently been exhaustively examined by Meyer and Wuorinen.[3] They consider the chromate method suitable only if the terbium elements have already been removed. The ethylsulphate method is said to be tedious, whilst the ferrocyanide method indeed effects very rapid concentration, but with great loss. For purposes of concentration they find the most suitable method in the fractional hydrolysis of the phthalates; these salts are soluble in cold water, but hydrolyse when the solution is warmed, the most positive elements remaining of course longest in solution. For the final purification, they recommend fractional precipitation of the iodate from nitric acid solution; yttrium iodate being more soluble than the iodates of the erbium and ytterbium group, the latter collect in the first precipitates.

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[1] *Trans. Chem. Soc.* 1889, **55**, 255.

[2] *Ber.* 1901, **34**, 2460.

[3] *Zeitsch. anorg. Chem.* 1913, **80**, 7; Meyer and Weinheber, *Ber.* 1913, **46**, 2672.

Pure yttria is quite white, and gives rise to colourless salts, which in solution show no absorption spectrum in the visible region. A very large number of yttrium compounds have been prepared, of which sufficiently detailed accounts have been given in the general description of rare earth compounds. For an exhaustive treatment, the reader is referred to Abegg's 'Handbuch.'

The *metal* has probably not been obtained in the pure state; impure yttrium has been obtained by Winkler[1] by the action of magnesium on the oxide, and by Cleve[2] by the action of sodium on a mixture of the chloride with common salt, and by electrolysis of the mixture of fused chlorides. It is described as a greyish metal, resembling iron in appearance; it oxidises in the air and readily decomposes boiling water. The *hydroxide* is thrown down as a gelatinous precipitate by alkalies; ammonia throws down basic salts, but in presence of hydrogen peroxide an hydrated *peroxide* is obtained. The *oxide* absorbs carbon dioxide from the air, and liberates ammonia from ammonium salts.

The anhydrous *chloride* has been prepared by many authors; it melts at a relatively low temperature, 680°, and is the most easily volatilised of all the rare earth chlorides. After fusion, it forms a mass of brilliant white lamellæ.[3] It is characterised by the ease with which it dissolves in pyridine. From aqueous solution it separates as the hexahydrate, $YtCl_3,6H_2O$, which melts at 160°. The *bromide* separates from solution as the enneahydrate, $YtBr_3,9H_2O$; the *bromate*[4] also separates with 9 molecules of water of crystallisation.

The *nitrate* cannot be obtained anhydrous; the normal hydrate, $Yt(NO_3)_3,6H_2O$, loses 3 molecules of water at 100°, but further heating converts it into basic salts. A *basic nitrate*, $3Yt_2O_3,4N_2O_5,20H_2O$, is described by James and Pratt[5] as stable at ordinary temperatures, and in contact

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[1] *Ber.* 1890, **23**, 772.

[2] *Bull. Soc. Chim.* 1874, [ii.], **21**, 344; Cleve and Höglund, *ibid.* 1873, [ii.], **18**, 193; see also Popp, *Annalen*, 1864, **131**, 359.

[3] *Compt. rend.* 1902, **134**, 1308.

[4] James and Langelier, *J. Amer. Chem. Soc.* 1909, **31**, 913.

[5] *J. Amer. Chem. Soc.* 1910, **32**, 873.

with solutions of the normal nitrate. The *sulphate* octohydrate is isomorphous with analogous compounds of the rare earth elements, and with the *selenate*, $Yt_2(SeO_4)_3,8H_2O$; the latter compound can also form an enneahydrate. The *phosphate*, $YtPO_4$, occurs in nature in the mineral xenotime, and has been obtained in the laboratory in the crystalline form; many other phosphates have been prepared. The *platinocyanide*, $Yt_2[Pt(CN)_4]_3,21H_2O$, has the characteristic red colour with greenish-blue fluorescence.

Many *organic yttrium salts* have been prepared by James and Pratt[1] and by Tanatar and Voljanski.[2]

Atomic Weight.—The numbers obtained by the investigators who have determined this constant vary to such an extent that considerable uncertainty attaches to the value, 89·0, at present accepted by the International Committee. The determinations carried out prior to 1870 gave such diverse results that they are of little use in fixing the constant; since that date, all the investigations, with the exception of the most recent, have given values below 90, the sulphate method being generally employed.

Cleve and Höglund,[3] in 1883, carried out six determinations by the synthetic method; their results were concordant, and gave the mean value 89·57. Brauner considers this result if anything too low, as traces of undecomposed acid sulphate may have been present in the anhydrous sulphate. The same method was employed again by Cleve in 1884;[4] the mean of twelve very concordant results gave the number 89·11.

Much stress is laid by Brauner[5] on an unpublished determination of Marignac, carried out with material entirely free from terbia, which gave the value 88·88. H. C. Jones in 1895[6] carried out two series of determinations with material purified by Rowland's method, *i.e.* precipitation with potassium

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[1] *J. Amer. Chem. Soc.* 1911, **33**, 1330.

[2] *Vide Abstr. Chem. Soc.* 1910, **98**, i. 809.

[3] *Loc. cit.*

[4] *Compt. rend.* 1883, **95**, 1225.

[5] Abegg's *Handbuch*, III. i. 328.

[6] *Amer. Chem. J.* 1895, **17**, 154.

ferrocyanide;[1] the results in both series were very concordant, the synthetic method giving the value 88·95, the analytical method the value 88·97. This work has been taken by the International Committee as the basis for the accepted value. According to Brauner, the ferrocyanide method does not give perfectly pure material.[2]

Egan and Balke[3] have recently found the ratio $Yt_2O_3 : 2YtCl_3$ to be very suitable as a basis for atomic weight determinations; the oxide is converted into the anhydrous chloride in a quartz flask. In a preliminary experiment, they obtain as a mean of three consistent determinations the provisional value 90·12; the yttria employed was considered to contain not more than one-half per cent. of erbia.

Recent work by Meyer and his co-workers[4] indicates that the accepted value is too high. Preliminary work with the synthetic sulphate method gave the values (corrected) 88·71 and 88·73; the mean value of six analytical sulphate determinations, made on material carefully purified by the iodate method, was 88·75, the extreme values being 88·71 and 88·76. They consider that the true atomic weight is 88·7, the value of the second decimal figure being a little uncertain.

Detection.—The spark spectrum of yttrium has been examined by many authors, and the ultraviolet as well as the visible regions have been mapped; *vide* Exner and Haschek; Eder and Valenta, also Becquerel.[5]

The arc spectrum has been examined by Kayser, Eberhard,[6] and Eder and Valenta;[7] Exner and Haschek give the following as the most intense lines:

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[1] Rowland, *Chem. News*, 1894, **70**, 68; compare also Crookes, *ibid.* **70**, 81–82. Bettendorff (see Böhm, *Die Darstellung der seltenen Erden*, I. 480) has also used the method.

[2] See also Meyer and Wuorinen (*loc. cit.*).

[3] *J. Amer. Chem. Soc.* 1913, **35**, 365.

[4] Meyer and Wuorinen; Meyer and Weinheber, *loc. cit.*

[5] *Compt. rend.* 1908, **146**, 683.

[6] *Zeitsch. wiss. Photochem.* 1909, **7**, 245.

[7] *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, **119**, IIa, 1.

3216·83
3242·42
3328·02
3600·92
3611·20
3621·10
3633·28
3664·78
3710·47
3774·52
3788·88
3950·52
3982·79
4077·54
4102·57
4128·50
4143·03
4177·74
4302·45
4309·79
4348·93
4375·12
4883·89
6191·91
6435·27

Pure yttrium compounds should be colourless, show no absorption in the visible region, and yield a perfectly white oxide.

Scandium, Sc = 44·1

The scandia obtained by Nilson in 1879 was isolated from the minerals gadolinite and euxenite; it consisted very largely of ytterbia, as shown by spectrum examination[1] and by atomic weight determinations, which gave the value 90. In the same year[2] Cleve prepared the oxide in a much purer state, using as his source the minerals gadolinite and keilhauite; he described several salts, carried out atomic weight determinations by the analytical and synthetic sulphate methods, and showed that scandium corresponds with the Eka-boron of which the existence was predicted by Mendelejeff in 1871.[3] Starting from a large quantity of euxenite, Nilson[4] in the following year prepared several grams of approximately pure scandia, which contained only traces of ytterbium.

The investigation of scandium, which occurs only in extremely small quantities in the minerals employed by Nilson and Cleve, and was therefore believed to be exceedingly rare, was not continued until 1908, when Sir William Crookes[5] made a systematic investigation of a large number of minerals in order to find a convenient source of the element. He showed that scandium is present in many rare earth minerals, and selected as the most suitable for the extraction of the element a complex mineral named Wiikite, some specimens of

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[1] Thalén, *Compt. rend.* 1879, **88**, 642; 1880, **91**, 45.

[2] *Compt. rend.* 1879, **88**, 419.

[3] See also Mendelejeff, *Ber.* 1881, **14**, 2821.

[4] *Ber.* 1880, **13**, 1439.

[5] *Phil. Trans.* 1908, A, **209**, 15.

which he found to contain over 1 per cent. of scandia (see p. 70). The mineral was decomposed by fusion with potassium hydrogen sulphate, and scandia extracted from the rare earths by the nitrate fusion. The separation effected on these lines was very thorough, Crookes considering a specimen of scandia unsatisfactory if it showed any trace of the dominant ytterbium line, 3694·344, on an over-exposed plate, or if it gave an atomic weight for the element higher than 44·1.

A systematic investigation of the common rocks and minerals for scandium was carried out by Eberhard in 1908, as a result of which processes for the extraction of the oxide from wolframite were worked out by R. J. Meyer (see pp. 3, 131). Wolframite is a tungstate of iron and manganese, containing, in addition to other oxides, small quantities of the rare earths, of which considerable proportions are found to be scandia. The mineral is fused with soda in the usual way, and the rare earths concentrated by the oxalate method. Scandium is precipitated as the fluoride by addition of sodium silicofluoride to the boiling acid solution, and purified by precipitation as the double ammonium tartrate.[1]

Whilst the researches of Crookes and Eberhard have shown how widely distributed the element really is, the minerals which they found richest in scandium still contained extremely small quantities of the oxide. The discovery of the mineral Thortveitite (see p. 44), which contains about 37 per cent. of scandia, is therefore of the greatest scientific interest, and will doubtless allow of a very searching examination of the properties of this interesting element.

Whilst the low atomic weights of scandium and yttrium place them, to some extent, apart from the other rare earth elements, the latter element at least is so closely allied in properties to the other members of the group that yttria is one of the typical oxides of the family. Scandium and its compounds, however, present many peculiarities of behaviour when compared with the typical members, on the grounds of which Urbain[2] has contended that scandia should not be

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[1] Meyer and Goldenberg, *Chem. News*, 1912, **106**, 13.
[2] *Chem. News*, 1905, **90**, 319.

classed among the rare earths at all. Whilst this contention is perhaps rather extreme, especially in view of the fact that in nature scandia always occurs with other yttria oxides, it must be admitted that in many respects the element is anomalous. The oxide is the weakest base of the whole group, yet the oxalate is comparatively readily soluble in mineral acids (compare p. 132), and the potassium double sulphate is almost insoluble in potassium sulphate. The sulphate is altogether exceptional in that it is very easily soluble in water, and crystallises out with 6 molecules of water of crystallisation. The fluoride and the carbonate both dissolve readily in excess of precipitant, whilst sodium thiosulphate precipitates a basic salt from neutral solutions.

Meyer has pointed out the close resemblance between beryllium and scandium. The oxide and salts are colourless; the latter have a peculiar sweet astringent taste, and readily yield basic salts.

The *hydroxide*, $Sc(OH)_3$, is thrown down by alkalies as a bulky white gelatinous mass; the *oxide* is a white powder, less readily soluble in dilute acids than most of the rare earths. The *fluoride* is important on account of its insolubility in mineral acids, which exceeds that of all the other rare earth fluorides, and approaches that of thorium. It is thrown down from neutral or acid solutions by addition of hydrofluoric acid or a soluble fluoride; if the solution be boiled, a soluble silicofluoride will also precipitate scandium fluoride, though no precipitate is obtained in the cold. This behaviour is due to the ease with which the silicofluoride is hydrolysed at high temperatures, according to the equation:

$$Sc_2(SiF_6)_3 + 6H_2O = 2ScF_3 + 3SiO_2 + 6H_2F_2$$

and is of great value in separating scandium from the other earths. The fluoride is extremely resistant to acids, being completely decomposed only by fused bisulphate. In the absence of acids, the freshly precipitated fluoride dissolves in excess of concentrated alkali fluoride, forming double salts; in this behaviour, scandium resembles zirconium, but differs from thorium and the cerium and yttrium elements.

The *chloride* separates from solution at ordinary temperatures as the dodecahydrate, $Sc_2Cl_6,12H_2O$, which loses 9 molecules of water when kept for six hours at 100°. The trihydrate $Sc_2Cl_6,3H_2O$, is converted into scandia at a red heat, with the loss of 6 molecules of hydrogen chloride. The *iodate*, $Sc(IO_3)_3,18H_2O$, is obtained as an almost insoluble white crystalline powder by addition of ammonium iodate to a salt in solution; hydrates with 15, 13, and 10 molecules of water are known, and at 250° the anhydrous compound is obtained. It resembles the iodates of the cerium and yttrium group in being soluble in strong nitric acid, but the separation of thoria and scandia by this method is tedious and unsatisfactory.[1]

The *platinocyanide*, $Sc_2[Pt(CN)_4]_3,21H_2O$, was obtained by Crookes [2] by double decomposition of the sulphate with barium platinocyanide, in crimson monoclinic prisms, with a green fluorescence. It dissolves in water to a colourless solution. Orlov [3] shows that it can occur also in a second form, stable at higher temperatures; this is yellow, with a blue fluorescence and crystallises with 18 molecules of water. The two modifications resemble respectively the platinocyanides of the yttrium and of the cerium elements; in this respect, therefore, scandium occupies an intermediate position between the two groups.

The *sulphate*, $Sc_2(SO_4)_3$, is obtained anhydrous by evaporating the excess of acid from a solution of the oxide in the concentrated acid, care being taken to avoid too high a temperature. The compound dissolves very easily in water, and slowly hydrates itself with evolution of heat; no crystals can be obtained from the solution until it has been concentrated to the consistency of a syrup, when on cooling it slowly deposits the hexahydrate. This effloresces in a dry atmosphere, forming the pentahydrate, which appears to be the most stable hydrate at ordinary temperatures. According to Nilson, the hexahydrate loses 4 molecules of water when maintained at 100°. At 250° it becomes anhydrous; above that temperature, basic salts are formed. The *potassium double sulphate*, $3K_2SO_4,Sc_2(SO_4)_3$, was shown by Nilson to resemble

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[1] Meyer, Winter and Speter, *Zeitsch. anorg. Chem.* 1911, **71**, 65.

[2] *Phil. Trans.* 1910, A, **210**, 359.

[3] *Abstr. Chem. Soc.* 1913, **104**, i. 27.

the analogous cerium compounds in being insoluble in a saturated solution of potassium sulphate. The *nitrate*, $Sc(NO_3)_3,4H_2O$, separates from concentrated solutions over sulphuric acid as the tetrahydrate ; it is very soluble in water and alcohol, and extremely deliquescent.

The *carbonate*, $Sc_2(CO_3)_3,12H_2O$, is thrown down by addition of ammonium carbonate as a bulky white precipitate, easily soluble in a hot solution of the precipitant; the solubility in excess may be used in the separation of scandia from yttria. Addition of water to such solutions causes separation of a basic carbonate, but crystalline *double carbonates* may be obtained by evaporation of concentrated solutions containing a large excess of alkali carbonate. The sodium compound, $Sc_2(CO_3)_3,4Na_2CO_3,6H_2O$, is very sparingly soluble, and has been used in the separation from thorium. The *oxalate*, $Sc_2(C_2O_4)_3,5H_2O$, differs from other oxalates of the group, which generally separate with 10 molecules of water of crystallisation, not only in its water content, and in its solubility in acids, but also in the ease with which it forms double oxalates soluble in excess of alkali oxalate ; in this latter property it shows a further resemblance to zirconium and thorium. The *formate* and *acetate* have the formulæ $Sc(OH)(HCOO)_2,H_2O$ and $Sc(OH)(CH_3COO)_2,2H_2O$, respectively. A large number of organic salts have been described by Sir William Crookes.[1]

Atomic Weight. — The mean values obtained by Cleve[2] in 1879 were 44·96 and 45·20 by the analytical and synthetic sulphate methods respectively. In the following year Nilson,[3] using purer material, obtained the value 44·13 by the synthetic method. Meyer and others (*loc. cit.*) have criticised Nilson's estimation on the ground of his empirical method of obtaining the neutral anhydrous sulphate. Determinations made with material purified from thorium by the iodic acid method gave the values 44·11, 44·11, 44·20 ; material purified by the double ammonium tartrate method gave the atomic weight 43·90. Meyer has shown that small quantities of thoria in the oxide

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[1] *Loc. cit.*; see also Meyer, *Zeitsch. anorg. Chem.* 1908, **60**, 134; Meyer and Winter, *ibid.* 1910, **67**, 398.

[2] *Loc. cit.*

[3] *Loc. cit.*

cannot be detected spectroscopically; the value of the magnetisation coefficient, however, showed the oxide obtained by the last method to be free from thoria, and he considers another determination of the atomic weight to be necessary.

The value accepted by the International Committee is **44·1**.

Detection.—Scandium gives no absorption spectrum in the visible region. The spark spectrum has been examined by Thalèn (*loc. cit.*) and Nilson;[1] see also Exner and Haschek, Lockyer and Baxendall,[2] and Crookes (*loc. cit.*). The arc spectrum has been examined by Fowler,[3] Eder and Valenta,[4] and Exner and Haschek.

The most intense lines of the arc spectrum are the following:

3353·90
3372·33
3558·69
3567·89
3572·73
3576·53
3614·00
3630·93
3642·99
3907·69
3912·03
4020·60
4023·88
4247·02
4314·31
4320·98
4325·22
4374·69
4400·63
4415·78
6305·94

Fowler (*loc. cit.*) examined the arc spectrum with reference to solar spectra. For detection of the element in minerals see Crookes (*loc. cit.*) and Eberhard (*loc. cit.*).

The purity of scandium preparations may be determined by the following tests:

(1) Precipitation with thiosulphate in boiling solution should remove all the rare earth content from solution.
(2) The iodate test for thorium should give no result.
(3) The oxide must be perfectly white, and salt solutions show no absorption.
(4) R. J. Meyer has found that whilst 0·5 per cent. of thoria cannot be detected spectroscopically in scandia, the magnetisation coefficient affords an exceedingly delicate test. The value for pure scandia is $-0·12 \times 10^{-6}$, the oxide being diamagnetic; for scandia with 0·5 per cent. thoria the cofficient was found to be $+0·04 \times 10^{-6}$, the mixture being paramagnetic.

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[1] *Compt. rend.* 1880, **91**, 56, 118.

[2] *Proc. Roy. Soc.* 1905, **74**, 538.

[3] *Phil. Trans.* 1908, **A, 209**, 47.

[4] *Sitzungsber. kaiserl. Akad. Wiss. Wien*, 1910, **119**, IIa, 576.

CHAPTER XV

THE GROUP IVA ELEMENTS—TITANIUM

THE oxides zirconia and thoria were generally classed among the rare earths by the earlier chemists. This view was based partly upon the mode of occurrence of the oxides, which are very generally associated in nature with rare earths, and were believed to be equally sparingly distributed, and partly on fallacious chemical analogies. Thus Berzelius regarded thoria as a monoxide, ThO, and classed it with the other earth oxides, magnesia, lime, ceria, lanthana, etc., to all of which the general formula RO was assigned. Zirconia was regarded as a sesquioxide, Zr_2O_3, analogous to alumina, Al_2O_3, which in turn showed many points of resemblance to the rare earths. The introduction of the periodic classification, and a wider knowledge of the chemical properties of the oxides, have gradually altered the older conceptions, and zirconia and thoria are now only classed under the head 'Rare Earths' when that term is used in its widest sense. More generally, the term is restricted to the oxides of the cerium and yttrium elements, which, whilst they cannot all be placed in Group III of the table, yet constitute a series with properties which entitle them to be considered in that relation.

The elements which fall into group IVA of Mendelejeff's classification are titanium, zirconium, cerium, and thorium; the elements of lower atomic weight, carbon and silicon, are placed by some authors in Group IVB, by others in Group IVA. It is a feature of the periodic system that the members of the A and B families show great differences in the end groups, I and VII, II and VI, which disappear as the middle groups are approached; in group IV the families A and B show only slight differences in properties, corresponding to their amphoteric character and electrochemical indifference, so that the elements carbon and silicon may be placed as well in the one as in the other. Generally they are placed in family B.

In its tetravalent condition, titanium shows a close relationship to silicon; the similarity is manifested by the ease with which the dioxide replaces silica in many minerals, and the isomorphism of many titanates with corresponding silicates. Yet the strengthening of electropositive character, which always accompanies the change in atomic weight in descending a vertical column of the table, is very apparent in the case of titanium, and its ability to form salts in the tetravalent state is a very important property. This strengthening of the electropositive character is still more marked in the case of the succeeding elements. The salts of zirconium are highly hydrolysed in solution, but they are considerably more stable than those of tetravalent titanium; the ceric salts show the same change, whilst thorium salts are comparatively stable in solution, and can be recrystallised from water without change. Zirconium hydroxide will not dissolve in alkalies, though zirconates may be obtained in the dry way; thorium hydroxide shows no acidic properties whatever.

The change in electrochemical character is accompanied by corresponding changes in physical properties of the elements and their compounds. With the exception of cerium, which has a very low melting-point (623°), the elements fuse only at high temperatures; titanium is the most refractory, zirconium melts at over 1500°, and thorium at about 1450°. The boiling-points of the chlorides rise as the series is descended; titanium tetrachloride boils at 136°, zirconium and thorium chlorides at 400°–450° and 950° respectively; zirconium chloride partly sublimes, whilst ceric chloride decomposes when heated.

The elements of Group IVA are distinguished from the rare earth elements by their much less strongly marked electropositive character. This is apparent not only in the amphoteric nature of the oxides, and in the ease with which the salts are hydrolysed in solution, but in the more pronounced tendency to the formation of complex salts. The complex fluorides of the type K_2RF_6 are peculiarly characteristic, and in the case of titanium and zirconium have been very important for purposes of analysis and atomic weight determination. The solubility of zirconium and thorium salts in excess of alkali oxalate or carbonate is also in harmony with the less pronounced electropositive character of these elements. The sulphates of titanium and zirconium appear to be of complex constitution, whilst their neutral chlorides cannot be obtained from solution. As is to be expected from its high atomic weight, thorium approaches most nearly to the rare earths in chemical properties; thus it forms stable double nitrates of the type $R_2Th(NO_3)_6$ and its salts, especially the sulphate, resemble those of the rare earth elements in their solubility relations.

The elements titanium, zirconium, and thorium are distinguished also by the fact that they form no definite hydroxides. The precipitates thrown down from solutions of the salts, on addition of alkali, are hydrated oxides, which lose water continuously when dried, giving rise to no definite chemical individuals until constant weight is reached with the anhydrous oxides. The hydroxides have the further characteristic, common also to the other members of Group IV, of readily forming colloidal solutions and gels, a property possessed to some extent also by the elements themselves, and particularly by zirconium, which, when reduced from its compounds, shows a great tendency to go into colloidal solution merely on washing. Highly characteristic also is the property of forming 'meta'-oxides (acids) and 'meta'-salts, which is common to all the Group IV elements which have solid oxides.

In presence of hydrogen peroxide, alkalies throw down characteristic hydrated peroxides, which have definite acidic properties in the case of titanium: the zirconium compound is less strongly acidic, the cerium compound shows no tendency to salt formation, whilst if hydrogen peroxide be added to a neutral or faintly acid solution of a thorium salt, the precipitate is a peroxy-salt, containing some acid grouping, *e.g.* SO_4,NO_3.

With regard to valency, the elements in the typical compounds are tetravalent. Titanium forms three series of salts, in which the element is respectively di-, tri, and tetravalent; salts of the first two series have powerful reducing properties, and the compounds in which the metal is tetravalent are most stable. Zirconium is always, with the doubtful exception of its peroxy-compounds and the lower oxides, tetravalent. Cerium, as already described, can form two series of compounds, in which it is respectively tri- and tetravalent; thorium, like zirconium, is always tetravalent.

Titanium, Ti = 48·1

Though generally classed among the rare elements, titanium is probably at least as widely distributed in nature as most of the common metals. It occurs as the dioxide in small quantities in all the common silicate rocks and minerals, and in traces in the animal and vegetable kingdoms; the element has been identified in the sun and in many stars, and has been found in meteorites. Probably the commonest mineral in which the element occurs in quantity is ilmenite, or titaniferous ironstone, which occurs in enormous quantities in many parts of the world (see p. 57). The pure dioxide occurs in the three forms Rutile, Brookite, and Anatase (*q.v.*), in which it is said to be isotrimorphous with tin dioxide. Other important titanium minerals are Perovskite, Titanite or Sphene, the Euxenite series, and other minerals of the tantalo-columbate group (see Part I).

The commercial sources of titanium compounds are the minerals rutile and ilmenite. These may be opened up by fusion with alkali or alkali carbonate; the residue after extraction with water is dissolved in acid, and precipitated with ammonia; the mixture of iron and titanium oxides thrown down may be separated by one of the methods outlined on p. 339. Fusion with potassium bisulphate has also been employed. A very satisfactory method is that of Stähler,[1] in which the ore is fused with carbon in the electric furnace. The carbides so obtained are heated in a stream of chlorine, when the volatile titanium tetrachloride distils over, and may be obtained quite pure by redistillation; by appropriate methods, the required compounds may be obtained from this. (See also pp. 326–7.)

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[1] *Ber.* 1904, **37**, 4405; 1905, **38**, 2619.

The Metal.—The difficulty of isolating metallic titanium in the pure state is very great, on account of its great affinity for nitrogen, oxygen, hydrogen, carbon, etc., the ease with which it forms alloys with all the common metals; and the extremely high melting-point; in consequence, it is only within recent times that the element has been obtained in a state approximately approaching purity, and the accounts given of its physical properties vary very widely.

Berzelius prepared an impure titanium (Ti = 85 per cent.) by reduction of potassium titanofluoride with potassium; the method was modified by Wöhler, who heated a tube containing two boats, of which one was filled with the fluoride, the other with sodium, reduction being effected by the sodium vapour. Many authors have attempted the reduction of titanium tetrachloride by means of hydrogen. By heating the tetrachloride with sodium in a cast iron bomb, Nilson and Pettersson obtained a product containing 95 per cent. of the element. Reduction of the dioxide by means of sodium, magnesium, silicon, or aluminium has not been found to yield good results, by reason of the ease with which titanium alloys with these elements. Reduction of the dioxide with carbon yields good results only when precautions are taken to avoid the formation of the compound which the element so readily forms with carbon and nitrogen. Moissan [1] found that if temperatures high enough to decompose this compound were used, the product contained as the only impurity carbon, which could be partly removed by fusing with the dioxide; the product then contained 98 per cent. of titanium.

The element has been obtained in the fused condition by Weiss and Kayser,[2] who pressed the amorphous form into sticks, under a pressure of 70,000 atmospheres, and employed these as pencils for the electric arc *in vacuo*; the metal fused, forming globules on the ends of the electrodes, which were detached after the apparatus had been allowed to cool.

The amorphous element is a dark powder, resembling finely divided iron (Ferrum reductum), of density 3·5–3·6.

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[1] *Compt. rend.* 1895, **120**, 290.

[2] *Zeitsch. anorg. Chem.* 1910, **65**, 388.

The specific heat rises rapidly with the temperature, so that the atomic heat has the values 5·40 between 0° and 100°, 6·18 between 0° and 210°, 7·13 between 0° and 300°, and 7·77 between 0° and 440°. The amorphous element is said to be paramagnetic.

The fused carbonaceous product of Moissan formed an extremely brittle mass, with a shining white lustre on the fractured surface, sufficiently hard to scratch quartz and steel; its density was determined as 4·87. The product of Weiss and Kayser was also extremely hard and brittle; when rubbed against steel, it gave bright sparks. Its density was found to be 5·174, and the heat of combustion for the gram-atom, 97·79 K.

The amorphous variety is fairly stable in air, but burns vigorously when heated in air, oxygen, or halogens. Heated in nitrogen or ammonia, it reacts vigorously, forming the nitride TiN; if carbon is present, a peculiar substance of uncertain composition, known as *titanium cyanonitride*, is formed. This substance is also obtained when air is passed over a heated mixture of the dioxide with coke, and is found in blast-furnaces in which ores containing small quantities of titanium are worked; it forms brilliant red cubes, which are extremely hard and resistant to acids. This substance, as well as the nitride itself, yields ammonia when heated in steam, and has been proposed as a medium for 'fixing' atmospheric nitrogen (see p. 337).

The amorphous element also absorbs hydrogen, when heated in the gas, but no definite hydride is known. It combines when heated with almost all the known non-metals, and forms alloys with all the common metals. Moissan[1] claims to have prepared a compound as hard as diamond by heating titanium with boron in the electric furnace. The element attacks steam at a red heat.

The element is fairly resistant to acids in the cold, but is readily attacked, with evolution of hydrogen, on warming. Hot dilute hydrochloric acid gives the trichloride; but dilute sulphuric acid is variously reported to give the di- and

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[1] *Loc. cit.*

tri-salt. Hot nitric acid oxidises it readily, forming the so-called metatitanic acid. Hydrofluoric acid attacks it very readily, forming the tetrafluoride.

COMPOUNDS OF DIVALENT TITANIUM.

The compounds of divalent titanium show resemblances to those of divalent iron, chromium and vanadium, but on account of the great difficulty of preparing them and protecting them from oxidation, little is known of their properties and behaviour; even the colour of the salts in solution is not known with certainty. In its divalent state, the element does not appear to act as a strongly positive metal; the salts in solution are said to show an acid reaction, whilst the precipitates thrown down with alkali oxalates and acetates are soluble in excess of the precipitant, forming deeply coloured solutions. With sodium phosphate the soluble salts give a bluish-black precipitate, with potassium ferrocyanide and ferricyanide, dark brown and reddish-brown precipitates respectively. They are distinguished from salts of the higher oxides of titanium by the brown colouration produced by potassium thiocyanate in presence of hydrochloric acid.[1]

The *hydroxide* is thrown down from solutions by addition of alkali, alkali carbonate, alkali cyanide, or ammonium sulphide, as a black precipitate. It cannot be transformed to the corresponding oxide by drying, since it attacks the water with evolution of hydrogen, forming the dioxide. The *monoxide*, TiO, has probably never been obtained in the pure state; it is formed by reduction of the dioxide with zinc or magnesium. Moissan[2] obtained it in the form of black prismatic crystals by treating the dioxide with the calculated amount of charcoal in the electric furnace. The *sulphide*, TiS, is an extremely stable compound; it can be prepared by heating the higher sulphides in a stream of hydrogen to a very high temperature, and then forms pseudomorphs after these.[3] It is a dark red metallic mass, which reacts in the air only when heated, forming

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[1] v. d. Pfordten, *Annalen*, 1886, **234**, 257; 1887, **237**, 201; see also *Ber*. 1889, **22**, 1485.

[2] *Loc. cit.*

[3] See v. d. Pfordten (*loc. cit.*); Thorpe, *Chem. News*, 1885, **51**, 260.

the dioxide; dilute acids and alkalies have no action on it, concentrated nitric acid oxidises it slowly.

The *dichloride*, $TiCl_2$, is obtained in the impure state as a black powder by decomposition of the trichloride at a red heat; the tetrachloride is formed at the same time, and volatilises.[1] According to v. d. Pfordten,[2] it is obtained by reduction of the tetrachloride by sulphuretted hydrogen or sodium amalgam in the cold. The latter author states that it dissolves in alcohol or water in absence of air to a dark brown solution; Friedel and Guèrin, however, state that it acts energetically on these solvents with evolution of hydrogen, forming a yellow solution. When heated in the air it burns, evolving fumes of the tetrachloride and leaving a residue of the dioxide. The *iodide*, TiI_2, has been obtained by Defacq and Copaux [3] by reduction of the tetraiodide with silver or mercury, as a black, lustrous, infusible sublimate. It is insoluble in organic solvents, but reacts with water and aqueous alkalies, and is readily attacked by acids. Hydrogen at a bright red heat reduces it to amorphous titanium.

COMPOUNDS OF TRIVALENT TITANIUM.[4]

These salts are obtained when the element is dissolved in hydrochloric and sulphuric acids, and by reduction of the compounds of tetravalent titanium in solution by means of zinc and hydrochloric acid, or by electrolysis. According to Diethelm and Forster [5] the reduction may also be effected by hydrogen in presence of finely divided platinum. The salts have strong reducing properties, transforming nitro-bodies to amines and decolourising azo-derivatives very rapidly; they reduce unsaturated bodies, and reduce dyes to the leuco-bases; they reduce sulphurous acid to sulphur, precipitate gold, silver

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[1] Friedel and Guèrin, *Compt. rend.* 1875, **81**, 889; 1876, **82**, 509, 872.

[2] *Loc. cit.*

[3] *Compt. rend.* 1908, **147**, 65.

[4] Compounds of trivalent titanium are frequently referred to in English chemical and technical literature as 'Titanous Compounds,' the salts of the tetravalent element being tacitly recognised as 'Titanic Compounds.' In view of the existence of compounds of divalent titanium, to which the name 'Titanous Compounds' might be more logically applied, the former nomenclature cannot be regarded as altogether satisfactory, and it is therefore not adopted here.

[5] *Zeitsch. physikal. Chem.* 1908, **62**, 129.

and mercury from their salts, and reduce cupric and ferric salts to cuprous and ferrous compounds respectively. The salts are green or violet in solution, showing the phenomenon of hydrate-isomerism which is exhibited by the chromic salts; they are to some extent hydrolysed in aqueous solution, as shown by the acid reaction of the chloride. They resemble the salts of ferric iron and aluminium in giving precipitates of basic salts when boiled with sodium acetate or sodium formate, and in giving no precipitate with alkalies in the presence of organic hydroxy-acids. Ferrocyanide and ferricyanide give brown precipitates.

The *hydroxide*, $Ti(OH)_3,xH_2O$, is thrown down as a dark precipitate with strong reducing properties; it attacks water with evolution of hydrogen, forming the dioxide; when an aqueous suspension is shaken with air, autoxidation occurs, hydrogen peroxide being formed. The *sesquioxide*, Ti_2O_3, has been prepared by Friedel and Guèrin[1] by heating the dioxide to a white heat in a current of hydrogen and titanium tetrachloride; it forms black lustrous crystals, isomorphous with hæmatite. The *sulphide*, Ti_2S_3, is best obtained by reduction of the disulphide, at a moderate temperature, in a stream of hydrogen or nitrogen, but is also prepared by the action of a mixture of carbon disulphide and sulphuretted hydrogen on the dioxide at a high temperature. It is a dark grey metallic powder, stable towards air, water, alkalies and dilute acids.

Titanium Nitride, TiN, is obtained in all reduction processes in which titanium compounds are used, if air or nitrogen is admitted; it is formed when the element is heated in nitrogen, and by the action of ammonia on the chloride. It forms lustrous, bronze-coloured leaflets, which appear blue or violet when powdered. It is extremely hard, and very stable, but is attacked by alkalies with evolution of ammonia. It reduces the oxides of copper and lead in the fused state. Ruff and Eisner have shown that it is a true nitride of the trivalent element, and that only one nitride exists.[2]

The *fluoride*, TiF_3, has been obtained as an insoluble violet powder by reduction of potassium titanofluoride, K_2TiF_6, with

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[1] *Loc. cit.*

[2] *Ber.* 1905, **38**, 742; 1908, **41**, 2250.

hydrogen. From a solution it may be obtained by reduction of the same salt with zinc and hydrochloric acid, or sodium amalgam. It forms complex salts with alkali or ammonium fluoride, of which the compound $(NH_4)_3TiF_6$ is an example; this salt appears to be isomorphous with the analogous compounds, $(NH_4)_3VF_6$, $(NH_4)_3CrF_6$, and $(NH_4)_3FeF_6$. By autoxidation in the air, the solutions form fluoroxypertitanates. The complex salts appear to exist in two forms, a violet insoluble form and a green soluble modification.

The *chloride*, $TiCl_3$, is obtained anhydrous by reduction of the tetrachloride—mercury, silver, and hydrogen being the most suitable agents. Heated in hydrogen, it breaks up, forming the tetrachloride and the dichloride; heated in air it burns, evolving the tetrachloride and leaving a residue of dioxide. In solution, in combination with alkali chlorides, and as the solid hydrate, it exists in the green and violet forms. Concentrated aqueous solutions deposit the violet hexahydrate, $TiCl_3,6H_2O$. If such a solution be covered with ether, and saturated at 0° with hydrogen chloride, the green modification is formed, and may be extracted by the ether; it is stable only in the presence of hydrochloric acid. In the violet form, all the chlorine is in the ionic condition, and can be removed by silver nitrate; similar determinations have not been made with the green form, but it is most probable, as in the case of the analogous chromic salts, that only part of the chlorine content can be removed by silver nitrate. Böck and Moser[1] have recently described a brown substance, obtained by the action of the silent electric discharge on a mixture of hydrogen and the vapour of titanium tetrachloride at the ordinary temperature, which they believe to be a monotropic modification of the ordinary violet trichloride; the change of this brown form to the violet form is irreversible.

The *bromide* and *iodide* resemble the chloride, but are very unstable.

The *sulphate*, $Ti_2(SO_4)_3$, is obtained as a green crystalline powder by heating with sulphuric acid the violet solution obtained by reduction of a solution of the dioxide in sulphuric

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[1] *Monats.* 1912, **33**, 971; 1913, **34**, 1825

acid. It dissolves in dilute acids, forming violet solutions. With alkali sulphates it forms *titanium alums,* which can be recrystallised from dilute sulphuric acid, and have the general formulæ, properties, and crystal form of the other alums. An *acid sulphate,* $3Ti_2(SO_4)_3,H_2SO_4,25H_2O$, is obtained by electrolytic reduction of a strongly acid solution of the dioxide in sulphuric acid, or by treating the chloride repeatedly with hot dilute sulphuric acid. It forms a crystalline violet powder, with silky lustre, insoluble in alcohol, ether, and 60 per cent. sulphuric acid; it dissolves slowly in water, forming a violet solution. When the aqueous solution is treated with excess (2½ molecules) of alkali sulphate, it forms sparingly soluble *double sulphates,* which separate in bright blue crystals; the compounds $Ti_3(NH_4)(SO_4)_5,9H_2O$, and $Ti_3Rb(SO_4)_5,12H_2O$, have been obtained in this way.

The Use of Salts of Trivalent Titanium in Volumetric Analysis.—Owing to their powerful reducing properties, these salts have been proposed as very convenient reagents in volumetric analysis,[1] the chloride being most useful in this respect. The estimations must be carried out in absence of air, to avoid atmospheric oxidation; generally the apparatus is filled with carbon dioxide. The titanium solutions for use must also be preserved from the oxidising action of the air.

For estimation of ferric salts, an aliquot quantity is titrated directly with the titanium solution, ammonium thiocyanate being used as indicator. Ferrous salts and ferric salts in the same solution are easily estimated by titrating the former with permanganate solution, or better with hydrogen peroxide, and then estimating the total ferric salt with the titanium solution. Oxidising agents like nitrates and chlorates can be estimated in acid solution by treatment with an excess of a ferrous salt, and estimation of the ferric compound formed by means of titanium. Azo-bodies and organic dyes can be titrated directly, if soluble in hydrochloric acid, the disappearance of colour marking the end of the reaction; nitroso-compounds can also be estimated in this way. If the compound is

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[1] See Knecht, *Ber.* 1903, **36**, 166; Knecht and Hibbert, *ibid.* 1903, **36**, 1549; 1905, **38**, 3318; 1907, **40**, 3819.

insoluble, it may be reduced in hydrochloric acid suspension with excess of the titanium salt, and the excess then determined by means of ferric iron. Insoluble dyes may also be converted into soluble sulphonic acids, and estimated directly in solution. Ammonium persulphate may be estimated by reduction with excess of the chloride, and back titration of the excess with ferric iron. Hydrogen peroxide may be estimated directly, the disappearance of the yellow colour formed at the first addition marking the end of the reaction. Tin may be estimated by addition of an excess of a ferric salt, and estimation of the excess by titanium in the usual way. Cupric salts also may be estimated directly,[1] the end point being reached when the bluish-green solution becomes colourless.

COMPOUNDS OF TETRAVALENT TITANIUM

The compounds of tetravalent titanium are much more stable than the compounds in which the element has a lower valency, and are very readily formed from them. The dioxide is amphoteric in character, and acts as a weak acid as well as a weak base; the salts it forms with acids as well as those it forms with bases are very easily hydrolysed, with separation of the hydrated oxide. Titanium salts, therefore, can only be held in solution by a considerable excess of acid. The tendency to the formation of complex compounds is very pronounced, particularly in the case of the fluoride, oxalate and tartrate.

The *hydroxide*, or *hydrated oxide*, is capable of existing in two modifications, according to the conditions under which it is thrown down, though the two can hardly be said to be very definitely differentiated. The α or ortho form is obtained as a voluminous white precipitate by the addition of ammonia or alkali hydroxide in the cold to a freshly prepared solution of a titanium salt. It is insoluble in water and alcohol, but dissolves readily in dilute mineral acids, and to some extent also in dilute alkalies. The water content is very variable, and no definite hydrate or hydroxide can be prepared; when the substance is heated, it loses water continuously, and at a

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[1] Moser, *Chem. Zeitg.* 1912, **36**. 1126.

definite temperature glows, doubtless by reason of some polymeric change. If it be maintained for some time at a temperature somewhat below the normal temperature of glowing, this phenomenon no longer occurs when the temperature is further raised.

The β modification, or metatitanic acid, as it is called, is obtained by hydrolysis of the salts by boiling, or by addition of alkali at 100°, as a fine white precipitate. It is almost insoluble in dilute acids and alkalies, but dissolves in water to a colloidal solution; when heated it does not glow. The β form is also obtained when the metatitanates are treated with water; these compounds hydrolyse very readily, but the precipitated dioxide carries down alkali by adsorption.

The *dioxide*, TiO_2, occurs crystalline in nature in the three forms Rutile, Brookite, and Anatase, all of which can be prepared by laboratory methods;[1] the amorphous form is obtained by ignition of the hydrated oxide, and of suitable salts. The oxide melts at 1560°, forming a mobile (?) liquid of density 4·1; for the physical properties, see the accounts of the naturally occurring forms in Chapter V. When heated in a current of hydrogen or carbon monoxide, it gives rise to intermediate oxides, Ti_3O_4, Ti_7O_{12}, etc., which are not very well known, and are of doubtful individuality. It reacts when heated in chlorine, and with many non-metallic chlorides, forming the tetrachloride; with carbon disulphide at high temperatures it gives the disulphide, ammonia at a red heat forms the nitride. It is exceedingly resistant to acids, but is attacked slowly by boiling sulphuric acid, more quickly by fused bisulphate.

Titanium disulphide, TiS_2, is obtained in the pure state when a mixture of the vapour of the tetrachloride and sulphuretted hydrogen is led through a strongly heated porcelain tube. It is a fairly stable substance, forming metallic crystals which yield the dioxide when heated in air. When heated in a stream of hydrogen or nitrogen it yields one or other of the lower sulphides according to the temperature employed. It is not attacked by water, but dissolves in acids, and is

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[1] See p. 79; also Hautefeuille, *Ann. chim. phys.* 1863, [iv.], 4, 129.

decomposed by boiling potash, forming a titanate; it is insoluble in alkali sulphides.

The *carbide*, TiC, was prepared by Moissan by heating the oxide with carbon in the electric furnace; any excess of carbon separates on cooling as graphite. It has the density 4·25, and resembles the fused element in appearance. It dissolves in nitric but not in hydrochloric acid.

Titanium tetrafluoride, TiF_4, is obtained by the action of fluorine on the element or the carbide, and by the action of anhydrous hydrofluoric acid on the element or the tetrachloride. It is a white powder, and boils at 284°; it is very hygroscopic, and dissolves easily in alcohol and water, showing little tendency to form basic salts. From the concentrated aqueous solution it separates as the dihydrate, $TiF_4,2H_2O$; basic salts are obtained only by repeated evaporation with water. The anhydrous compound forms additive products with ammonia and with pyridine.

With aqueous hydrofluoric acid it forms the complex H_2TiF_6, as shown by conductivity measurements, and the fact that only a slow and incomplete precipitation of the hydroxide is effected by addition of ammonia. The solution dissolves metallic oxides and carbonates, forming *titanofluorides*, which are for the most part isomorphous with the corresponding silicofluorides, stannofluorides, and zirconofluorides. They are very stable crystalline salts, of the general formula R'_2TiF_6; many salts of the types $R''TiF_6$, R'_3TiF_7, etc., have been prepared. The most important is the potassium salt, K_2TiF_6, which crystallises from acid solutions in monoclinic tablets; from aqueous solution it separates as the monohydrate, K_2TiF_6,H_2O, isomorphous with the compounds K_2CbOF_5,H_2O and $K_2WO_2F_4,H_2O$. The hydrate loses its water at 100°, and melts at a white heat without decomposition. It is moderately soluble in hot, very sparingly soluble in cold water, and hence is readily recrystallised.

The *tetrachloride*, $TiCl_4$, is important, on account of its low boiling-point, for the separation and purification of titanium compounds. In physical as well as chemical properties, it resembles the chloride of a non-metallic element rather than a normal salt, and is distinguished by the ease with which it combines or reacts with the most widely differing organic compounds. It is prepared by the action of chlorine upon the element, the carbide, or a mixture of the dioxide with carbon, and by the action of chloroform or carbon tetrachloride upon the dioxide at a bright red heat. It is a colourless, transparent liquid, of density 1·76 at 0° ; it freezes at —23°, and boils at 136° under atmospheric pressure. In moist air it fumes excessively, yielding hydrogen chloride by hydrolysis : $TiCl_4 + H_2O = TiOCl_2 + 2HCl$, and is decomposed by water with separation of the hydrated oxide. If the compound be added slowly to a large quantity of cold water, and the clear solution warmed, the oxide formed by hydrolysis remains in colloidal solution.

The chloride dissolves in fuming hydrochloric acid, forming a deep yellow solution, which becomes colourless when diluted. The solution appears to contain the unstable complex acid H_2TiCl_6, or its ions ; by addition of ammonia, or organic bases, salts of the type $(NH_4)_2TiCl_6$ can be obtained as yellow crystalline solids. An interesting property of the chloride is its ability to form stable additive compounds with the chlorides of negative elements. A long series of these are known, of which the compounds $TiCl_4,PCl_3$, $TiCl_4,PCl_5$, $TiCl_4,POCl_3$, and $TiCl_4,2POCl_3$ may be considered examples ; for the most part, they can be distilled without decomposition. A very long series of compounds, partly additive and partly condensation products, with all kinds of organic substances, is also known.

A series of *oxychlorides*, or *basic chlorides*, $TiCl_3(OH)$, $TiCl_2(OH)_2$, and $TiCl(OH)_3$, has been obtained by addition of hydrochloric acid, in certain quantities and concentrations, to the chloride ; they are amorphous solids, of which little is known.

The *tetrabromide*, $TiBr_4$, is a yellow crystalline solid, melting at 39° and boiling at 230°. Its solutions in concentrated hydrobromic acid are of a blood-red colour, and by treatment with ammonia and organic bases yield deep red crystalline salts of the type $(NH_4)_2TiBr_6$. The *tetraiodide*, TiI_4, is a reddish-brown metallic-looking solid, melting at 150°, and boiling at 360°; no complex salts are known.

The sulphates.—Many compounds of doubtful composition and individuality have been described as titanium sulphates, but relatively little is known with certainty of this class of derivatives. The most stable seems to be the *titanyl sulphate*, $TiOSO_4$, obtained as a white powder, which is slowly hydrolysed by water, by evaporating a solution of the dioxide in concentrated sulphuric acid. Under suitable conditions, *e.g.* when separated from acid or alcoholic solutions, it is said to form hydrated compounds; the mono-, di- and penta-hydrate have been described. When solutions of this compound in concentrated sulphuric acid are treated with concentrated aqueous solutions of alkali suphates, salts of the formulæ $(NH_4)_2TiO(SO_4)_2,H_2O$ and $K_4(TiO)_3(SO_4)_5,10H_2O$, are obtained. By treating solutions of the dioxide in a large excess of concentrated acid with solutions of calcium or strontium sulphate in sulphuric acid, salts of the type $R''Ti(SO_4)_3$ are obtained; the barium salt has the formula $3Ti(SO_4)_2,2BaSO_4$. All these compounds are rapidly hydrolysed by water.

Phosphoric Acid Derivatives.—Solutions of titanium compounds are completely precipitated by the addition of phosphoric acid, or soluble phosphates, even in presence of a large excess of mineral acid, but the composition of the precipitate obtained is unknown. By heating the oxide with orthophosphoric acid, a crystalline compound, TiO_2,P_2O_5, is obtained, and various alkali double phosphates may be prepared by suitable fusions.

Concentrated aqueous oxalic acid solutions readily dissolve one equivalent of titanium dioxide, forming greenish-yellow solutions which contain *titanyl oxalate*, $TiO(C_2O_4)$. From alcoholic solution, this substance can be precipitated by ether as the alcoholate, $TiO(C_2O_4),C_2H_5OH$, a micro-crystalline precipitate soluble in water and alcohol. *Titanyloxalic acid*, $TiO(HC_2O_4)_2,H_2O$, and its salts are stable compounds; the latter are obtained by dissolving the dioxide in alkali binoxalate, the acid itself being obtained by treatment of the sparingly soluble barium salt with sulphuric acid.

Complex acids are also formed with tartaric acid, and other organic hydroxy-acids ; from its solutions in these acids, the dioxide cannot be again precipitated by boiling, or by addition of alkalies.

Titanates and Pertitanates.—On account of the weakly acid character of the dioxide, stable titanates can be prepared only in the dry way. The dioxide resembles silica in the conditions under which it forms salts, and in the nature, and generally the crystallographic properties, of the products obtained. The commonest salts are the metatitanates of the formulæ R'_2TiO_3 and $R''TiO_3$, which are obtained by fusing the dioxide with metallic oxides and carbonates, sometimes with addition of a suitable agent to act as a crystallising medium, *e.g.* sodium tungstate, calcium chloride, magnesium chloride, etc. Calcium metatitanate, $CaTiO_3$, prepared by heating titanium dioxide with calcium carbonate in presence of calcium chloride, is identical in properties with the naturally occurring compound, Perovskite (*q.v.*). Orthotitanates of divalent metals only are known ; these have the general formula R''_2TiO_4, and are prepared by similar methods. The iron compound $FeTiO_3$ is also identical in properties with the mineral ilmenite, and isomorphous with the sesquioxides Fe_2O_3, Ti_2O_3. Magnesium titanates of both the ortho type (Mg_2TiO_4) and the meta type ($MgTiO_3$) have been prepared in the laboratory ; the latter is identical with the mineral Geikielite (*q.v.*).

The compounds prepared in this way are all insoluble in water, doubtless by reason of the slowness with which such compact solids can be attacked ; they dissolve easily in dilute acids. The weakly acid character of titanium dioxide is shown by the fact that if the fusion with metallic carbonates be carried out in vessels so adjusted that the carbon dioxide exerts a pressure of one atmosphere, a condition of equilibrium is reached, in which a considerable part of the carbonate remains unattacked. In the presence of hydrogen peroxide, however, the acidic properties are considerably strengthened, and the per-salts can be obtained in the wet way.

Addition of hydrogen peroxide to a neutral or acid solution of a titanium compound gives a yellow colour, due to the formation of a peroxide, TiO_3,aq. Such solutions have the same oxidising powers as hydrogen peroxide, but do not give the blue colouration with chromium salts. By treatment of the solution with dilute alkalies, an hydrated peroxide is thrown down, which, when dried over phosphoric anhydride, has the formula $TiO_3,3H_2O$, and forms a yellow, horny mass. The freshly precipitated peroxide dissolves in acids and alkalies; from the latter solutions, by addition of hydrogen peroxide and alcohol, pertitanates of various composition can be obtained, of which the following are examples: $Na_2O_2,TiO_3,3H_2O$; $(NH_4)_2O_2,TiO_3,H_2O_2$; $BaO_2,TiO_3,5H_2O$; $K_2O_4,K_2O_2,TiO_3,10H_2O$, etc. These salts lose hydrogen peroxide when treated with dilute acids, and their constitutions are unknown.

An interesting series of fluoroxypertitanates has been prepared by oxidation of the solution of titanium dioxide in hydrofluoric acid with hydrogen peroxide, and addition of metallic fluorides. The ammonium compound, $(NH_4)_3TiO_2F_5$, crystallises in yellow octahedra, isomorphous with the salts $ZrF_4,3NH_4F$ and $CbOF_3,3NH_4F$. The potassium salt, $K_2TiO_2F_4$, crystallises well from water, and is easily obtained in the pure state; various barium salts are known. Similar compounds with oxalic acid have also been prepared.

Atomic Weight of Titanium.—The first reliable determinations of this constant were carried out by H. Rose in 1829. He determined the ratio $TiCl_4 : 4AgCl$, by dissolving the pure tetrachloride, weighed in sealed glass bulbs, in water in closed flasks, precipitating the dioxide by ammonia, and weighing the silver chloride obtained by adding silver nitrate to the filtered and acidified solution. He obtained the values 48·27 and 48·13, which agree very well with the accepted value, 48·1. In the same year, Mosander, using a method not specified, obtained the value 47·15. Determinations carried out by Pierre (1847) and Demoly (1849) led to widely varying results. A series of determinations carried out by Thorpe during the years 1883–1885 gave consistent results The method used was the precipitation of silver halide from the tetrachloride and tetrabromide, and the mean value of seven series of determinations gave the number 48·08. The International Committee have adopted this result as the basis of the accepted value, 48·1.

Detection.—The specific reactions for the element are frequently masked by the presence of other metals, especially of iron, columbium, tantalum, and vanadium, which most frequently accompany it in nature, and from which a quantitative separation is frequently very difficult (see p. 338). The most characteristic reactions are the following:

(1) Reduction in acid solution by means of tin or zinc gives an intense violet colour, due to the formation of trivalent titanium salts. Various colours are given by vanadium, columbium, and tungsten, so that the test is not decisive if these are present.

(2) Hydrogen peroxide in acid solution gives a reddish-yellow colour, which is very delicate, and is used in quantitative estimation; vanadium compounds interfere.

(3) In sulphuric acid solution, characteristic colours are obtained with many phenolic compounds; thymol gives a blood-red colour which is exceedingly intense.

(4) A very characteristic and intense colour is given in acid solution on the addition of 1:8-dihydroxynaphthalene-2:4-disulphonic acid (chromotropic acid).

The methods for the estimation of titanium are given in Chapter XXII.

CHAPTER XVI

THE GROUP IVA ELEMENTS (*continued*)—ZIRCONIUM AND THORIUM

Zirconium, Zr = 90·6

THE oxide zirconia was isolated as a new earth from zircon from Ceylon by Klaproth in 1789 ; six years later the new earth was obtained also from hyacinth, the gem-variety of the same mineral. The new oxide was examined in 1818 by Berzelius, who pointed out its resemblance to alumina, and gave it the formula Zr_2O_3 ; during the next two decades he thoroughly investigated its properties, preparing the element itself, and determining its equivalent. In 1857 a determination of the vapour density of the chloride, by Deville and Troost, showed that the element is really tetravalent, and that the formula ZrO_2 must be assigned to the oxide ; this formula was shown to accord with the isomorphism of rutile (TiO_2) and zircon (ZrO_2,SiO_2) by Rose in 1859, whilst in the following year Marignac observed the isomorphism between the fluozirconates of zinc and nickel and the fluosilicates, fluotitanates, and fluostannates of these metals. The homogeneity of the oxide has been questioned ; Svanberg in 1845 considered it to be a mixture of at least three earths, whilst Sorby and Forbes in 1869 claimed to have discovered in it a new oxide, 'Jargonia.' These claims, however, have been shown to have been founded on inaccurate experimental work, and the individuality of the element is at the present time considered to be well established.

Zirconium is fairly widely distributed in nature, but generally in very small quantities, and can be rightly classed as one of the rarer elements. It occurs in some silicates, and in small quantities in almost all the rare earth minerals. The most important source of the element and its compounds was until quite recently the mineral Zircon, with its gem-varieties Hyacinth and Jargon, and the large number of secondary altered zircon minerals. Since its discovery in 1892, however, the naturally occurring oxide, Baddeleyite,[1] has become increasingly important for the extraction of zirconium compounds, especially for the preparation of the pure oxide for fire-resistant materials.

The minerals may be treated by any of the usual methods. Zircon may be fused with alkali or alkali carbonate; the cooled melt is extracted with water, and the insoluble alkali zirconate decomposed by dilute acids; from the solution, zirconia is thrown down by alkalies. Potassium hydrogen fluoride and potassium hydrogen sulphate may be used for the treatment either of zircon or of baddeleyite; in the first case, the potassium fluozirconate formed may be dissolved by boiling with dilute hydrofluoric acid, and separates out readily on cooling, whilst the fluosilicate formed is not dissolved; the second treatment yields the sulphate, which may also be dissolved out by dilute acid. A very convenient method consists in reducing with carbon, either alone or in presence of lime, at the temperature of the electric arc; the infusible zirconium carbide is formed, whilst silica, if present, is reduced to the carbide, which is volatile at that temperature and is therefore driven off. The zirconium carbide may be dissolved in warm aqua regia.

In all these methods the compounds obtained are contaminated with iron, which clings to zirconium very tenaciously. Many methods have been devised for its removal. A very suitable method is the thiosulphate precipitation. Zirconia is thrown down quantitatively, mixed with sulphur, from a not too strongly acid solution by addition of sodium thiosulphate at the boiling-point, sulphur dioxide being at the same time evolved, by decomposition of the potential thiosulphuric acid

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[1] For accounts of the zircon minerals, see pp. 47 and 75, and the alphabetical list.

formed by hydrolysis. Thorium and titanium accompany the zirconium, but iron, aluminium, and the rare earths remain in solution. Another method depends on the fact that zirconium is not precipitated from alkaline solution by ammonium sulphide in the presence of tartaric acid, whereas this reagent does not inhibit the precipitation of ferrous sulphide. Iron may also be removed from a solution in concentrated hydrochloric acid by means of ether, in which medium ferric chloride is easily soluble. Zirconium compounds may be obtained free from iron by repeated crystallisations of the oxychloride.

Zirconium forms only one series of compounds, in which the metal is tetravalent. Its chemical behaviour accords well with its position in the periodic classification. It is somewhat more electropositive than titanium, as shown by the fact that the hydroxide will not dissolve in alkalies, though zirconates may be obtained by the fusion methods ; the oxide, however, is still a weak base, and the salts are to a large extent hydrolysed in solution. The formation of a stable oxychloride, which can be recrystallised without change in composition, shows clearly the strengthening of the electropositive character. It has still, however, in a high degree, the property of forming complex salts, which is characteristic of the less electropositive metals.

The group relations are borne out by the isomorphism of many related salts. The hydroxide and oxide show polymeric modifications, and the former has the usual tendency of compounds of this group to form colloidal solutions, a tendency which extends to the element itself. The metal resembles titanium in the eagerness with which it combines with other elements, especially with oxygen, nitrogen, and carbon, whilst the chloride closely resembles titanium tetrachloride in general properties, and in the ease with which it forms addition and condensation products with other substances.

The Metal.—All the difficulties which attend the attempts to prepare metallic titanium in the pure state have to be encountered in the preparation of metallic zirconium. The attempts which have been made have used the same methods, and obtained much the same kind of result as those employed in the case of titanium.[1] The reduction of potassium fluozirconate by metallic potassium, first employed by Berzelius, gives an amorphous product of unknown metal-content; it certainly contains a considerable percentage of oxygen. The monoxide is obtained when zirconia is reduced by magnesium (Winkler's method). The reduction of the fluozirconates of potassium by means of sodium gives better results if the reaction is carried out in presence of sodium chloride in a sealed iron bomb; the product after careful washing contains 97–98 per cent. of the metal. Reduction with aluminium leads to the formation of alloys; Weiss and Neumann[2] have used these in the form of pencils as electrodes between which they pass the electric arc *in vacuo,* and so obtain an almost pure zirconium. The 97–98 per cent. amorphous product obtained by the sodium reduction also yields the practically pure metal when treated in this way (compare Titanium, p. 223). A very pure zirconium has been obtained by Wedekind[3] by heating the oxide with fine calcium turnings in an evacuated iron tube; the powdered product is washed, in absence of air, and heated in an evacuated porcelain tube to 800°–1000°, at which temperature the powder sinters into lumps which take a brilliant polish and contain 99·1 per cent. of the metal. Attempts to prepare a purer product from this by the method of Weiss and Neumann were unsuccessful.

The amorphous metal is a dark powder, which when washed with water on the filter paper passes through as a dark blue colloidal solution; it burns readily when heated in the air. According to Wedekind and Lewis,[4] amorphous zirconium is really the colloidal form of the metal. The fused metal is very hard (7–8, Moh's scale—it scratches quartz but not topaz) and very brittle; it has the density 6·4, and is of a whitish colour, with good metallic lustre on freshly broken surfaces. The atomic heat is abnormally high, being approximately 7·3; the element is paramagnetic. The melting-point

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[1] For a detailed account of these, see Lewis, *Studien über das elementare Zirconium*, Stuttgart, 1912.

[2] *Zeitsch. anorg. Chem.* 1909, **65**, 248.

[3] *Annalen*, 1913, **395**, 149.

[4] *Ibid.* 1910, **371**, 367.

was given by Wedekind and Lewis[1] as 2330°–2380°, but later work of the former author[2] gives the much lower value of 1530°, which seems more probable in view of the fact that the element cannot be employed for electric lamp filaments (see p. 322).

Metallic zirconium is highly resistant to acids; it is attacked only by hydrofluoric acid and by aqua regia. In the compact form it burns in the air only at very high temperatures, though when powdered it glows in the air at a red heat, forming probably a mixture of lower oxides. It is attacked by chlorine and by hydrogen chloride at a red heat, with formation of the chloride; fused potash also oxidises it, with evolution of hydrogen. When heated in a current of hydrogen at a red heat, it forms the *hydride*, ZrH_2,[3] as a velvet-black powder, which burns with an intense bluish flame in oxygen, forming the sesquioxide, Zr_2O_3. When heated in nitrogen or ammonia, amorphous zirconium yields *nitrides*, which are also obtained when any attempt is made to reduce zirconium compounds to the metal in air. The most definite is the compound Zr_2N_3,[3] which forms a bronze-coloured powder, resistant to all mineral acids except hydrofluoric acid. Chlorine and bromine transform this to the halide.

The *hydroxide* is of doubtful individuality, since on drying it loses water progressively as the temperature is raised, no definite stable compound being known; in this respect zirconium resembles titanium. When heated to 100°, its composition corresponds approximately with that required by the formula ZrO_2,H_2O, but the percentage of water varies with the history of the specimen. When precipitated by alkalies in the cold, it forms the so-called α or ortho modification, which, like the analogous titanium compound, is readily soluble in dilute acids, and glows when heated. By precipitation at the boiling point, the β form is obtained; this is less soluble in acids, and does not glow when heated. The differences between the two forms are by no means sharply marked; they are rather the limiting forms of a continuously varying series than distinct chemical individuals, and the

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[1] Weiss and Neumann, *loc. cit.*; also Wedekind, *loc. cit.*

[2] *Annalen*, 1913, **395**, 149.

[3] Wedekind and Lewis, *Annalen*, 1910, **371**, 367.

properties of any hydroxide precipitate depend very largely on the conditions under which it is thrown down.

The hydroxide is insoluble in water, but can be obtained in colloidal solution after it has been repeatedly heated with dilute acids, which serve to break down the molecular complexes; it can be also readily obtained in colloidal solution by dialysis of the nitrate, chloride, or acetate. In these solutions it is positively charged; electrolytes precipitate it with great ease. The gel has a very high power of forming adsorption products. When thrown down from solution by soda or potash, it carries down considerable quantities of alkali, to which it clings so tenaciously that the most careful washing cannot entirely remove them. If the gel be placed in contact with an ammoniacal solution of a cupric compound, it removes the cuprammonium complex entirely from the solution, becoming itself deep blue in colour, and leaving the liquid quite clear and colourless. In colloidal solution it forms adsorption compounds with negatively charged colloids, especially metals, the gels obtained from such solutions containing both colloids.

In the presence of hydrogen peroxide, ammonia throws down an hydrated peroxide, which is also obtained [1] by electrolysis of a brine solution in which the hydroxide is suspended, oxidation being effected by the sodium hypochlorite formed. This reaction is expressed by the equation:

$$Zr(OH)_4 + NaOCl = Zr(OOH)(OH)_3 + NaCl$$

It is an endothermic compound, and is very unstable, losing oxygen on standing; by the action of acids it gives hydrogen peroxide. It dissolves in alkalies containing hydrogen peroxide; from such solutions, alcohol precipitates salts of the formula $R'_4Zr_2O_{11},9H_2O$.

Zirconium oxide, ZrO_2, occurs in nature; it can be obtained in the laboratory as a voluminous white powder by ignition of the hydroxide or a suitable salt. The physical properties are described under the mineral Baddeleyite (p. 75) and in Chapter XXI (p. 323), in which an account of its technical

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[1] Pissarjewski, *Zeitsch. anorg. Chem.* 1900, **25**, 378.

applications is given. The melting-point is probably about 2700° ; at 3000° it begins to volatilise. It dissolves readily in mineral acids, unless previously ignited very strongly ; all specimens dissolve easily in hydrofluoric acid, and are readily converted by concentrated sulphuric acid into the sulphate.

When fused with metallic oxides or carbonates, it gives crystalline *zirconates*, of which a large number have been prepared ; the calcium compound, $CaZrO_3$, is said to be isomorphous with perovskite, $CaTiO_3$.

A *suboxide*, ZrO, of somewhat doubtful individuality,[1] is said to be obtained when the dioxide is reduced with magnesium ; it forms a dry black powder, which is not attacked by acids, and when heated glows, forming the dioxide. A *sesquioxide*, Zr_2O_3, is obtained as a greenish powder when the hydride is burnt in oxygen ; when heated in the air, it oxidises very slowly, forming the dioxide.

An *oxysulphide*, ZrOS, is obtained when the anhydrous sulphate is heated in a current of sulphuretted hydrogen ; it is a bright yellow powder, which ignites spontaneously in the air. No disulphide is known. The *carbide*, ZrC, is obtained, according to Moissan and Lengfeld,[2] when the oxide is heated with carbon in any proportions, excess of carbon separating on cooling as graphite ; the process is hastened by addition of lime. It is a hard, dark-grey solid, and is a very good conductor of electricity. When heated in oxygen or nitrogen, it reacts readily, forming the oxide and nitride respectively ; halogens attack it at quite low temperatures (250°–400°), forming the halide compounds, which are indeed best prepared in this way. Strong mineral acids, with the exception of hydrochloric acid, attack it, and fused alkalies dissolve it readily.

The *fluoride*, ZrF_4, is best obtained by the action of anhydrous hydrofluoric acid on the chloride. It forms a white crystalline mass, which readily sublimes, and is soluble in hydrofluoric acid ; from the solution it crystallises as the

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[1] Wedekind and Teletow (*Annalen*, 1913, **395**, 149) have recently denied the existence of this oxide.

[2] *Compt. rend.* 1896, **122**, 651.

trihydrate, $ZrF_4,3H_2O$. The anhydrous substance is very slightly soluble in water in the cold; when warmed, it hydrolyses, forming the hydroxide. The solution in hydrofluoric acid dissolves metallic carbonates and oxides, forming the numerous *fluozirconates* or *zirconofluorides*.

There are many types of these compounds, of which the potassium salt, K_2ZrF_6, is the most important. The solubility of this salt increases very rapidly with the temperature; 100 parts of water dissolve, at 15°, 1·41 parts, at 100°, 25 parts of the compound. It has been frequently used for the purification of zirconium compounds, for the preparation of the element, and for analytical determinations. Other potassium salts, K_3ZrF_7 and $KZrF_5,H_2O$, are obtained by using a large excess of potassium fluoride and zirconium fluoride respectively. The ammonium compounds are analogous in composition to the potassium salts, but the sodium salt, Na_5ZrF_9, is obtained from mixtures of the components in all proportions; on account of its very low solubility, it can be obtained by double decomposition of the potassium salt with sodium chloride. Of the salts with divalent metals, the types $R''ZrF_6,xH_2O$ and R''_2ZrF_8,xH_2O, are the most common.

The *chloride*, $ZrCl_4$, is known, on account of the ease with which it hydrolyses, in the anhydrous state only. It can be obtained by all the usual methods, of which perhaps the action of chlorine on the carbide, and of carbon tetrachloride, or a mixture of chlorine and sulphur monochloride, on the oxide, are the most convenient; an interesting method consists in heating the oxide with phosphorus pentachloride in a closed tube at 190°. It forms a volatile white sublimate, which fumes strongly in air, and reacts vigorously with water; it is soluble in ether. It forms a series of addition compounds with ammonia and organic bases, as well as with the chlorides of non-metallic elements; warmed with phosphorus pentachloride, it forms a stable solid, $2ZrCl_4,PCl_5$, which melts at 240°, and boils at 345°. With organic compounds, especially with esters, acids, and phenols, it forms a long series of addition and condensation products, of which the compounds $ZrCl_4(C_6H_5{\cdot}COOC_2H_5)_2$ and $ZrCl_2[O{\cdot}C_6H_5{\cdot}CHO]_2$ may be taken as examples. By addition of organic bases to a solution of the chloride in alcoholic hydrogen chloride, double chlorides of the type $(C_5H_5NH)_2ZrCl_6$ are obtained.

The *oxychloride*, $ZrOCl_2,8H_2O$, separates in characteristic tetragonal prisms when the tetrachloride is dissolved in water or hydrochloric acid of any concentration. It is readily soluble in water and alcohol, but sparingly soluble in hydrochloric acid, from which therefore it is generally recrystallised. According to Chauvenet,[1] it effloresces in dry air, forming the hexahydrate, $ZrOCl_2,6H_2O$; when dried in a vacuum, it forms the hydrate, $ZrOCl_2,3\frac{1}{2}H_2O$, whilst the dihydrate, $ZrOCl_2,2H_2O$, is obtained by heating at 100°–105° in hydrogen chloride. When the dihydrate is heated to 230°, it forms another basic chloride, $ZrOCl_2ZrO_2$,[2] which is stable up to 600°; above this temperature, it breaks up, forming the volatile tetrachloride, and leaving a residue of the dioxide.

By repeated evaporation of the oxychloride with small quantities of water, a 'metazirconium chloride' is obtained, which dissolves in water to a colloidal solution, and on dialysis yields a colloidal solution of 'metazirconic acid.'

The *bromide*, $ZrBr_4$, very closely resembles the chloride; when treated with water it forms the oxybromide, which separates from solution according to the conditions in various hydrated forms, of which the commonest is the octohydrate, $ZrOBr_2,8H_2O$. The *iodide*, ZrI_4, is a very reactive body, which closely resembles the preceding; it forms an oxyiodide, $ZrOI_2,8H_2O$.

Zirconyl chlorate, $ZrO(ClO_3)_2,6H_2O$, is obtained from the sulphate by double decomposition with barium chlorate; it forms very soluble colourless needles. Alkali iodates or iodic acid throw down a voluminous *oxyiodate*, very sparingly soluble, like the corresponding ceric and thorium salts, in water and acids.

The Sulphates.—When zirconium dioxide is dissolved in concentrated sulphuric acid, and the excess of acid removed by heating to 400°, the 'neutral' sulphate, $Zr(SO_4)_2$, remains. The compound dissolves in dilute sulphuric acid to form solutions which contain various 'complexes,' as shown by

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[1] *Compt. rend.* 1912, **154**, 821.

[2] *Ibid.* 1234.

conductivity measurements, and the behaviour towards oxalic acid. Whilst solutions of the nitrate or chloride give immediate precipitates with this reagent, solutions of the 'sulphate' give no precipitate, or at most a very gradual one; moreover, addition of sulphuric acid or of alkali sulphates to other zirconium salts inhibits the oxalate precipitation. These facts are explained by regarding the 'neutral' sulphate, $Zr(SO_4)_2,4H_2O$, as zirconylsulphuric acid, $ZrOSO_4,H_2SO_4,3H_2O$, which in solution ionises to $2H^{\cdot}$ and $ZrOSO_4,SO_4''$. This conclusion is confirmed by the fact that whilst in solutions of the chloride in hydrochloric acid, zirconium goes on electrolysis to the cathode, on addition of sulphuric acid to the solution it travels to the anode. The anhydrous compound and the hydrate are extremely soluble in water, but much less readily soluble in dilute sulphuric acid. Probably in solution more complex salts are formed by further hydrolysis, for by addition of concentrated alkali sulphate solution in the cold, double salts of the formula $Zr_2O_3(RSO_4)_2,8H_2O$ are obtained. When the solution is kept for some time at 39°–40°, a basic sulphate, $4ZrO_2,3SO_3,14H_2O$, separates slowly. When concentrated solutions are boiled, a salt, $2ZrO_2,3SO_3,5H_2O$, separates as a crystalline precipitate; in contact with water it slowly hydrates itself to the compound $2ZrO_2,3SO_3,14H_2O$; when heated to 300°, it becomes anhydrous without further change. Various other basic, acid and complex salts have also been described.

The *nitrate*, $Zr(NO_3)_4,5H_2O$, separates from concentrated solutions of the oxide in nitric acid by evaporation over sulphuric acid and sodium hydroxide; it is believed to be a zirconylnitric acid, $ZrO(NO_3)_2,2HNO_3,4H_2O$ by analogy with the sulphate. When its aqueous solutions are warmed, basic salts separate. Kolbe[1] has described an additive compound with antipyrine, $Zr(NO_3)_4,6C_{11}H_{12}ON_2$, which is soluble in water, and melts at 217°–218°.

When phosphoric acid or a soluble phosphate is added to a solution of a zirconium salt, *zirconium phosphates* of doubtful composition are thrown down; by fusion methods, various double phosphates have been prepared. A *hypophosphate*,

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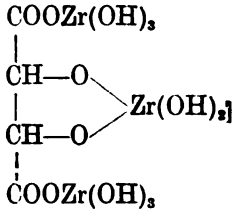
[1] *Zeitsch. anorg. Chem.* 1913, 83, 143.

$Zr(PO_3)_2,H_2O$, has recently been obtained by Hauser and Herzfeld[1] by precipitation. The same authors have prepared a *hypophosphite*, which is sensitive to light. When hypophosphorous acid, H_3PO_2, is added to a solution of zirconium nitrate, a precipitate is obtained, which dissolves in excess of the acid; by addition of alcohol to the clear solution, the hypophosphite, $Zr(H_2PO_2)_4,H_2O$, is thrown down in colourless, highly refracting prisms, which on exposure to sunlight for a short time become deep violet, without further perceptible change.

Zirconium carbonate has recently been obtained by Chauvenet.[2] Addition of sodium carbonate precipitates a basic orthocarbonate, $ZrCO_4,ZrO_2,8H_2O$, soluble in excess; when dried *in vacuo*, the precipitate loses water, forming the dihydrate, $ZrCO_4,ZrO_2,2H_2O$. When the latter compound is treated with carbon dioxide at a pressure of 30–40 atmospheres, the neutral orthocarbonate, $ZrCO_4,2H_2O$, is formed. When the compounds are heated, other basic salts are obtained.

Zirconyl oxalate, ZrO,C_2O_4, is obtained in the hydrated form when oxalic acid is added to a zirconium salt in the presence of hydrochloric or acetic acid. It is a white powder, soluble in oxalic acid, and easily hydrolysed by water. If an aqueous solution of oxalic acid be saturated with zirconium hydroxide, an acid oxalate, $ZrOH(HC_2O_4)_3,7H_2O$, is obtained on evaporation. Double oxalates are readily obtained by dissolving zirconium hydroxide in solutions of alkali hydrogen oxalates, the general form being $Zr(C_2O_4R')_4,xH_2O$. The *tartrate* precipitated when tartaric acid is added to a zirconium salt in solution probably has the cyclic structure, 

as shown by the great rise in the specific rotatory power of solutions of alkali oxalates on addition of zirconium compounds. The precipitate dissolves readily in alkalies, and various

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[1] *Zeitsch. anorg. Chem.* 1913, 84, 92.

[2] *Bull. Soc. Chim.* 1913 [iv.], 13, 454.

double alkali tartrates have been prepared; the potassium salt, $ZrO(C_4H_4O_6K)_2,3H_2O$, is analogous to the thorium alkali tartrates. The solubility in alkalies is of great importance for the separation of iron and zirconium.

Atomic Weight of Zirconium.—The value of this constant is not very accurately known. The International Committee has adopted the value 90·6, but there is some uncertainty as to the value of the decimal fraction. Berzelius in 1825 employed the analytical sulphate method, and found Zr = 88·47. The numbers of Hermann (1844), obtained by the analysis of the oxychloride, $2ZrOCl_2,9H_2O$,[1] were very discordant, the mean giving the value 89·56. Marignac in 1860 analysed the potassium salt, K_2ZrF_6; this he heated with strong sulphuric acid, the residue being ignited until all the zirconium sulphate was transformed to oxide; the weighed mixture was then freed from potassium sulphate, and the residual oxide dried and weighed. From the three ratios $K_2ZrF_6 : ZrO_2$, $K_2ZrF_6 : H_2SO_4$, and $K_2SO_4 : ZrO_2$, he obtained the mean values 90·02, 91·55, and 90·68 respectively. Weibull in 1881–1882 determined the ratios $Zr(SO_4)_2 : ZrO_2$ and $Zr(SeO_4)_2 : ZrO_2$ by ignition of the sulphate and selenate respectively; he obtained the values 89·55 and 90·81.

Bailey carried out a series of analytical sulphate determinations in 1890, obtaining the mean value 90·656. Brauner criticises the method on the ground that the preparation of the pure neutral anhydrous sulphate is almost impossible; the sulphate heated to 400° is not yet anhydrous, so that Bailey's result, on this ground, is probably too low. Venable in 1898 analysed the oxychloride; he claimed to have obtained the compound $ZrOCl_2,3H_2O$, by heating the crystallised salt at 100°–125° in hydrogen chloride, a method which Chauvenet (*loc. cit.*) has found to lead to the dihydrate, $ZrOCl_2,2H_2O$. His value was 90·803.

Detection and Estimation.—The following reactions may be employed to distinguish zirconium:

(1) The oxalate precipitated from neutral or faintly acid

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[1] Chauvenet (*loc. cit.*) could not confirm the existence of this hydrate.

solution dissolves readily in excess of oxalic acid; the oxalates of thorium and of the rare earth elements are practically insoluble under these conditions. The fluoride also dissolves in excess of hydrofluoric acid or of alkali fluoride, behaviour characteristic of this element alone among the group.

(2) By fusion with sodium carbonate in the oxidising flame, a bead is obtained, which, when dissolved in boiling hydrochloric acid, forms a solution which gives a voluminous precipitate on addition of disodium hydrogen phosphate, if zirconium is present. Iron, aluminium, titanium, thorium, and rare earths have no influence on the test.[1]

(3) A solution of a zirconium salt in hydrochloric acid gives an orange colouration with curcuma paper. Ferric and titanium salts, if present, must be reduced by means of zinc before the test is applied.

The *estimation* of zirconium is complicated by the difficulty of separating it from the accompanying elements. The solubility of the oxalate in oxalic acid allows of a rapid and easy separation from thorium and rare earth elements, so that iron, aluminium, and chromium only remain to be removed. Iron may be separated by the thiosulphate method, or other processes mentioned on p. 338; when free from that element, zirconium may be separated from aluminium and chromium by precipitation with alkali iodate in presence of the least possible excess of acid. The precipitates in the thiosulphate and iodate methods may be washed, and ignited directly to the dioxide, which is weighed as such; if the zirconium is left after separation in solution, it may be precipitated with ammonia,[2] and after washing and drying, ignited and weighed as dioxide.

Thorium, Th = 232·4

The name Thoria (thorina) was proposed by Berzelius in 1817 for what appeared to be a new earth, but which in 1824 was recognised as a basic yttria phosphate. In 1828 a new mineral was discovered by Esmark near Brevig in Norway;

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[1] Biltz and Mecklenburg, *Zeitsch. angew. Chem.* 1912, **25**, 2110.

[2] On account of the adsorption of alkalies by the zirconium oxide gel, potash or soda is never used for this precipitation.

to the oxide isolated from this, Berzelius gave the name thoria, from its resemblance to the substance he had obtained in 1817. The homogeneity of the new element was questioned by Bergmann in 1857, and also by Bahr in 1862, but the conclusions of those authors have been shown to be quite unfounded.

Thorium occurs in traces in a large number of common minerals, and in varying quantities in most of the uranium and rare earth minerals. Its occurrence in monazite, and the distribution of the latter mineral, have already been dealt with; the commercial treatment of monazite is described in Chapter XVIII. The oxide forms the chief constituent in Thorite, with its gem-variety Orangite, and the various secondary minerals, and in the mineral Thorianite, in which the only other important constituent is uranous oxide. The extraction from these minerals is a comparatively simple matter. Decomposition is easily effected by hydrochloric or sulphuric acid, thorianite dissolving easily also in nitric acid; the solutions obtained, after appropriate treatment to remove silica, excess of acid, etc., are treated with sulphuretted hydrogen, to remove lead, bismuth, and similar foreign metals, and freed from the rare earths by the carbonate, oxalate, or sulphate methods. The last depends on the fact that thorium sulphate and its hydrates are much less soluble than corresponding compounds of the rare earth elements; the first two on the fact that thorium salts dissolve readily in excess of alkali carbonates or oxalates, whilst the rare earth compounds are much less easily soluble.

Thorium, like zirconium, forms only one series of salts, in which the metal is tetravalent. The formula ThO was originally put forward by Berzelius for the oxide, from its resemblance to the ceria and yttria oxides, and its general occurrence with these. The true formula was deduced, when the valency of zirconium had been decided by the vapour density experiments of Troost and Deville, in 1857, from the isomorphism of zircon and thorite, and the close relationship between the compounds of the two elements, especially among the double fluorides, and was confirmed by a determination of the specific heat of the metal by Nilson in 1883.

In its chemical relations, the element resembles zirconium, though, as is to be expected from the high atomic weight, it shows a much more marked electropositive character, approaching in this respect the elements of the yttrium group. The oxide has no longer acid properties, and the neutral salts, though they hydrolyse readily and are therefore acid to indicators in solution, may be recrystallised unchanged from aqueous solution. The tendency to form double salts is still present, though diminished; the oxalate is soluble in a large excess of alkali oxalate, but not in oxalic acid, and the double fluorides are less numerous and varied than those of zirconium and titanium. On the other hand, it forms a well-crystallised and characteristic series of double nitrates, $R'_2Th(NO_3)_6$, isomorphous with the analogous ceric salts. In the behaviour of its sulphate it differs markedly from zirconium, and closely approaches the rare earth elements. The hydroxide has the characteristic tendency to form colloidal solutions and gels.

Thorium is peculiar, among the elements which have been considered, through its property of giving characteristic radiations, and disintegrating with formation of a whole family of new elements; or, as it is commonly expressed, through its radioactive properties.[1] The element has a half-life period of the order of 4×10^{10} years; in the course of decay, it gives rise to mesothorium 1, which is rayless, but decays to mesothorium 2, with its product radiothorium, both of which give powerful radiations. Mesothorium 1 of course occurs in all thorium-containing minerals, and may be separated from monazite by addition of a barium compound during the sulphuric acid decomposition; in consequence of the powerful radiating properties of its products, it is itself of considerable importance, and proposals for extracting it from monazite in the preparation of the thorium nitrate of commerce have been put forward (see p. 276).

Mesothorium appears to be chemically identical with radium; since monazite, like all other thorium-bearing minerals,

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[1] The nature of the present work allows only the briefest reference to be made to the exceedingly interesting phenomena which centre about this subject; for a more complete account, the student should consult Soddy, *The Chemistry of the Radio-Elements*, Part I, 1911.

contains uranium and radium, the latter element is separated with the mesothorium, and indeed, having a very much larger half-life period, constitutes by far the greater part of such 'mesothorium' preparations. On account of the great activity of the mesothorium products, the best preparations from monazite, though estimated to contain only 1 per cent. of mesothorium to 99 per cent. radium, are said to be four times as active as pure radium compounds. The chemical identity of the two products seems to preclude any possibility of determining the physical properties and constants of mesothorium.

The element radiothorium, which was discovered by Hahn in 1905, in the mineral thorianite, is chemically identical with the parent element thorium, but can be separated by means of the intermediate element, mesothorium 1. The latter is readily separated by the sulphate precipitation, and the radiothorium to which it gives rise may be separated by precipitation with ammonia. Thorium is also chemically identical with ionium, the parent of radium, and the thorium nitrate of commerce therefore contains important quantities of ionium—important that is, in view of the high radiating power of the latter element. The study of these relationships constitutes one of the most important and interesting fields in the province of radioactivity.

The Metal.—Elementary thorium has not yet been obtained in the pure state, owing to the ease with which it forms compounds and alloys with all the common elements, and to its great affinity for oxygen; the high melting-point also increases the difficulty of obtaining the pure metal. Berzelius attempted to reduce the alkali double fluorides and double chlorides with sodium or potassium; Nilson carried out the same reaction in a closed iron cylinder, but his product still contained 20 per cent. of thoria. Reduction of the oxide with magnesium is never complete, and the carbon method gives only a mixture of carbide and metal. Electrolytic methods give no better results, since the metal liberated at the cathode always encloses oxide and other impurities. Moissan and Hönigschmid in 1906, by heating the carefully purified anhydrous chloride with sodium in a sealed glass tube from which air and moisture had been removed, claim to have obtained a product containing only 3 per cent. of the oxide. The element has recently been prepared in leaf form by forcing the amorphous product into the bore of a copper tube, hammering into sheets, and removing the copper by dilute nitric acid.[1]

The amorphous impure metal is a dark grey powder, of specific gravity 11·3; the hammered and strongly heated leaf has the density 12·16. It burns readily in air with great brilliance, and when finely powdered ignites if crushed or rubbed. When heated in the electric furnace, it melts, according to von Bolton,[1] at about 1450°; von Wartenburg[2] found the melting-point to be about 1700°; the fused beads resemble platinum in physical properties. It is somewhat resistant to acids, dissolving easily only in aqua regia, and more slowly in fuming hydrochloric acid. It combines directly when heated in sulphur or halogens, and in nitrogen and hydrogen.

The *hydride*, ThH_4, is best obtained by heating the metal in hydrogen, an energetic reaction taking place at a red heat. Winkler observed that a mixture of the dioxide with magnesium absorbs hydrogen readily when heated. The hydride is a stable greyish-black powder, not attacked by water, but dissolving readily in hydrochloric acid, with evolution of hydrogen. The *nitride*, Th_3N_4, is prepared by heating the metal in the gas, or the carbide in a stream of ammonia. It is a brown powder, decomposed by water with evolution of ammonia and formation of the dioxide. The *azide* has been used for purposes of detection and estimation, since in boiling solution it is hydrolysed with separation of the hydroxide; zirconium and ceric salts also show this reaction, but the rare earth salts give no precipitate.

The *hydroxide*, $Th(OH)_4,xH_2O$, is precipitated from solutions of thorium salts by alkalies or ammonia, as a gelatinous white precipitate, insoluble in excess. It dissolves readily in mineral

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[1] v. Bolton, *Zeitsch. Elektrochem.* 1908, **14**, 768.

[2] *Ibid.* 1909, **15**, 866.

acids or in alkali carbonates. Hydrogen peroxide and ammonia throw down an hydrated *peroxide*, Th_2O_7; from neutral solutions hydrogen peroxide alone throws down *peroxy-salts*, which contain acid groups. This peroxide may also be obtained by the action of sodium hypochlorite or hydrogen peroxide on the hydroxide, as in the case of the zirconium compound. It readily gives up oxygen, passing into the more stable peroxide, ThO_3. Since in neutral or faintly acid solutions zirconium and the rare earths give no precipitate with hydrogen peroxide, the reaction is extremely useful in the detection and estimation of thorium.

Thorium dioxide, ThO_2, is obtained by the ignition of the hydroxide or of suitable salts as a white powder, of which the properties and appearance depend largely on the method and temperature used in its formation. Whilst the residue obtained by ignition of the nitrate is an extraordinarily voluminous and light flaky mass, the sulphate yields a dense thick powder; the nitrate was therefore always preferred in the manufacture of incandescent mantles (*q.v.*), as it was thought that the oxide obtained from it was the most suitable for illumination. In the crystalline form the oxide has been obtained in the laboratory by fusion with borax and with potassium phosphate. The first method gives tetragonal crystals, probably isomorphous with those of rutile and cassiterite; the phosphate fusion is said to give cubic crystals (see p. 74). The oxide is insoluble in acids, but can be transformed into the sulphate by evaporation with concentrated sulphuric acid, or fusion with alkali bisulphate. It does not liberate carbon dioxide when fused with alkali carbonates.

By repeated evaporation with small quantities of acids, thoria can be transformed into a gel soluble in water (thorium meta-oxide). The sol is an opalescent fluid, orange-red by transmitted light, and contains small quantities of the acid employed. The hydroxide may also be obtained in this form by carefully washing it, and boiling with small quantities of acids, or with thorium or other salts, or even by long continued washing with pure water; similarly, continued dialysis of thorium salts eventually yields such gels. The colloid is positively charged, and resembles the zirconium oxide gel in its relation to negatively charged colloids. The gel is easily precipitated by electrolytes.

Ignited thorium oxide has found considerable application in recent years as a catalyst in the preparation of ketones by the contact method of Sabatier and Senderens.[1] By passing mixtures of the vapours of appropriate acids over the catalyst heated to the necessary temperature, good yields of the required ketones are obtained.[2]

The *sulphide*, ThS_2, is obtained, together with the oxysulphide, ThOS, according to Duboin,[3] by passing a current of sulphuretted hydrogen over a mixture of thorium chloride with excess of sodium chloride, at a red heat. The former forms large brown crystals, from which the small orange-yellow crystals of the oxysulphide may be separated by means of a sieve; the latter is purified by treatment with warm nitric acid, which dissolves the sulphide very readily. The oxysulphide is also obtained when the anhydrous sulphate is heated in sulphuretted hydrogen.[4]

The *carbide*, ThC_2, is obtained by the action of carbon on the oxide in the electric furnace; it is a yellow crystalline mass, decomposed slowly by water, energetically by dilute acids in the cold, with evolution of a complex mixture of hydrogen and hydrocarbons, in which many members of the paraffin, olefine and acetylene series have been observed.[5] Hydrogen constitutes over 50 per cent. of the mixture, the next most important constituents being the acetylenic hydrocarbons, followed by ethane.

Thorium fluoride, ThF_4, is obtained anhydrous by passing hydrogen fluoride over the anhydrous chloride or bromide at a temperature of 350°–400°. The tetrahydrate, $ThF_4,4H_2O$, is precipitated by addition of hydrofluoric acid to a solution of a thorium salt, or by the action of the acid on the hydroxide. Hydrofluosilicic acid also throws down the fluoride, even in

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[1] Cf. Senderens, *Ann. Chim. Phys.* 1913 [viii.], **28**, 143.

[2] Cf. Pickard and Kenyon, *Trans. Chem. Soc.* 1913, **103**, 1923.

[3] *Compt. rend.* 1908, **146**, 815.

[4] Hauser, *Zeitsch. anorg. Chem.* 1907, **53**, 74.

[5] Lebeau and Damiens, *Compt. rend.* 1913, **156**, 1987.

the cold, from solutions of thorium salts. The fluoride is insoluble in water and mineral acids, as well as in excess of precipitant; this behaviour allows of a complete and easy separation of thorium from titanium and zirconium. The rare earth fluorides are also much more easily soluble in concentrated mineral acids than thorium fluoride, so that this compound may also be used in the separation from the rare earths. When heated in a stream of the acid to 800°, the hydrated salt yields the oxyfluoride, $ThOF_2$; ignited in the air, it leaves the dioxide. Precipitation with potassium fluoride gives the *double fluoride*, $KThF_5,H_2O$, which may be obtained anhydrous by fusion of the mixed fluorides; it is insoluble. An amorphous insoluble compound, $K_2ThF_6,4H_2O$, is obtained by boiling the hydroxide with a mixture of potassium hydrogen fluoride and hydrofluoric acid. Sodium and ammonium fluorides throw down the simple fluoride.

Thorium chloride, $ThCl_4$, is obtained in the anhydrous form by all the usual methods, the most convenient being perhaps the action of chlorine and sulphur monochloride on the heated dioxide. It almost invariably contains small quantities of oxychloride. When pure, it forms colourless needles fairly stable in dry air; the impure product gradually darkens in colour. It dissolves in water with considerable evolution of heat, and is soluble also in alcohol and moist ether. It melts at about 820°, and sublimes unchanged at somewhat higher temperatures; the vapour begins to dissociate at about 1050°, the dissociation increasing rapidly as the temperature rises. It resembles zirconium chloride in the ease with which it forms additive compounds with ammonia and organic bases, and addition and condensation products with organic oxygen-compounds; many *double* and *complex chlorides* are also known, among which the platinum compounds $ThPtCl_8,12H_2O$ and $Th_2Pt_3Cl_{14},24H_2O$, and the pyridine salt $(C_5H_5NH)_2ThCl_6$ may be mentioned.

From aqueous solution the octohydrate, $ThCl_4,8H_2O$, separates at ordinary temperatures; a heptahydrate and an enneahydrate have been described as precipitated from the alcoholic solution by addition of water. The *basic salts*,

$Th(OH)Cl_3,7H_2O$ and $Th(OH)_2Cl_2,5H_2O$, have been obtained by addition of the hydroxide to alcoholic hydrogen chloride. The *oxychloride*, $ThOCl_2$, may be obtained by the carefully regulated action of carbon tetrachloride on the dioxide, according to the equation :

$$ThO_2 + CCl_4 = ThOCl_2 + COCl_2$$

It is a colourless crystalline solid, which takes up moisture from the air, forming the hexahydrate.

Thorium bromide, $ThBr_4$, is a volatile solid which boils at 725° ; it closely resembles the chloride. The *iodide* and a *basic iodide*, $Th(OH)I_3,10H_2O$, are known.

No cyanide of thorium is known, addition of potassium cyanide merely causing separation of the hydroxide. A *ferrocyanide*, $Th[Fe(CN)_6],4H_2O$, is thrown down as a white powder by potassium ferrocyanide; with potassium ferricyanide no precipitate is obtained. The *platinocyanide*, $Th[Pt(CN)_4]_2,16H_2O$, is obtained by double decomposition in yellowish-brown prisms.

Among the halogen oxysalts, the *perchlorate*, *chlorate*, *bromate*, and *iodate* were prepared by Cleve. The iodate is of great importance for purposes of detection and estimation, from the fact that, in presence of a large excess of alkali iodate, it is insoluble in strong nitric acid, whilst the analogous compounds of the rare earth elements dissolve readily in that solvent.

The *sulphate*, $Th(SO_4)_2$, is obtained anhydrous by evaporating the excess of acid from a solution of the dioxide in oil of vitriol, or by heating the hydrates. It resembles the sulphates of the rare earth elements, in that it dissolves in water at 0° to form a highly supersaturated solution, from which the hydrated forms separate out almost quantitatively when the temperature is allowed to rise. The solubility relations of the various hydrates, on account of their commercial importance, are somewhat fully treated in Chapter XVIII. A dihydrate, $Th(SO_4)_2,2H_2O$, is obtained by keeping the tetrahydrate at 110°. The ennea- and octohydrates are isomorphous with the corresponding thorium selenate hydrates, and the ennea- and tetrahydrates with the analogous uranous sulphate hydrates. The hydrates yield the anhydrous salt when heated to 400°; the anhydrous sulphate has already a considerable dissociation tension (15 mm.) at 575°. By treatment with excess of acid, and subsequent heating to 130° *in vacuo*, the *acid sulphate*, $Th(SO_4),H_2SO_4$, is obtained. An insoluble *basic salt*, $ThOSO_4,2H_2O$, is formed by continued boiling of the tetrahydrate in dilute solution, or more quickly by heating the solution in a closed tube to 120°–125°; a monohydrate, $ThOSO_4,H_2O$, is also known. Halla[1] has recently obtained the hydrate, $ThOSO_4,5H_2O$, by boiling a solution of the neutral sulphate with magnesium sulphate, and also by treating the anhydrous sulphate with a little water in presence of magnesium carbonate.

By precipitation with potassium sulphate the *double salt*, $Th(SO_4)_2,2K_2SO_4,2H_2O$, is formed; this is soluble in water but insoluble in potassium sulphate solution. The analogous sodium and ammonium salts are soluble both in water and excess of the corresponding alkali sulphate.

The *sulphite*, $Th(SO_3)_2,H_2O$, is obtained as a white amorphous precipitate by warming a solution of a thorium salt with sulphurous acid. Basic sulphites and double sulphites are also known; the precipitates obtained by addition of alkalki sulphite dissolve readily in excess. The hydroxide is almost insoluble in sulphurous acid, behaviour which distinguishes thorium (and zirconium) from all the trivalent metals. No *thiosulphate* is known, the hydroxide being thrown down from boiling solution by addition of sodium thiosulphate: this method of precipitation was formerly much used for purposes of estimation, but it is more tedious and less accurate than the modern methods.

Thorium nitrate, $Th(NO_3)_4,12H_2O$, crystallises at ordinary temperatures in large hygroscopic tablets, very soluble in water and alcohol. The hydrates, $Th(NO_3)_4,6H_2O$ and $Th(NO_3)_4,5H_2O$, have been obtained from hot solution and from nitric acid solution respectively. Thorium is employed in commerce almost entirely in the form of this salt, which is dehydrated until it contains about 48 per cent. ThO_2, which

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[1] *Zeitsch. anorg. Chem.* 1912, **79**, 260.

approximates to the formula $Th(NO_3)_4,4H_2O$; the commercial product, however, is not a definite hydrate. Kolbe[1] has described the additive product with antipyrine, $2Th(NO_3)_4,5C_{11}H_{12}ON_2$, which melts at 168°. The extent to which thorium salts are hydrolysed in solution is very considerable, as is evident from the fact that the nitrate may be titrated with standard potash in presence of phenolphthalein as indicator; the solution first becomes alkaline to this reagent when 3·5 molecules of potash have been added for each molecule of thorium nitrate present.[2] Of the large number of *double nitrates* which have been prepared, the general types $R'_2Th(NO_3)_6$, where $R' = NH_4,K,Rb,Cs$, and $R''Th(NO_3)_6,8H_2O$, where $R'' = Mg,Mn,Zn,Ni,Co$, are the most important.

Thorium phosphates.—The precipitates obtained by addition of phosphoric acid or alkali phosphates to solutions of thorium salts are gelatinous solids of doubtful composition; they dissolve in mineral acids and in alkali carbonates, and their behaviour is of great importance in the technical treatment of monazite. Various phosphates and *double phosphates* are obtained by fusion methods, but none of these are important. The *phosphite*, $Th(HPO_3)_2,3H_2O$, and *hypophosphite*, $Th(H_2PO_2)_4$, are insoluble solids obtained by double decomposition. The *hypophosphate* $ThP_2O_6,11H_2O$, is of great importance for purposes of detection and estimation, since it is thrown down quantitatively from strongly acid solutions; under these conditions the rare earths remain in solution.

No neutral *carbonate* of thorium is known. Alkali carbonates precipitate a basic salt, which dissolves readily in excess; this fact is of very great importance in the commercial extraction of thorium, the sodium and ammonium double carbonates of the cerium elements being almost insoluble in alkali carbonates. Addition of alcohol to the solution throws down double carbonates, which can be washed with ice water. The salts $K_6Th(CO_3)_5,10H_2O$, $Na_6Th(CO_3)_5,12H_2O$, and $(NH_4)_2Th(CO_3)_3,6H_2O$ have been obtained in this way; they dissolve readily in water or dilute alkali carbonate, though

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[1] *Zeitsch. anorg. Chem.* 1913, 83, 143.

[2] Halla, *loc. cit.*

on warming or diluting the solution, the hydroxide separates. The thallium compound, $Tl_6Th(CO_3)_5$, is sparingly soluble, and is thrown down from a solution of the ammonium compound on addition of a thallium salt; it has been proposed for the microchemical detection of thorium. The quantitative separation of thorium by means of pure moist lead carbonate has been proposed for the purpose of estimation (see p. 288).

Thorium oxalate, $Th(C_2O_4)_2,6H_2O$, is precipitated quantitatively by means of oxalic acid, even in presence of considerable quantities of mineral acids. It is less soluble in sulphuric acid than any of the rare earth oxalates,[1] and is not attacked, as are the latter compounds, by concentrated nitric acid. In hydrochloric acid the solubility first increases rapidly with the concentration of the acid, and then suddenly decreases; this behaviour is due to the formation of an *oxalochloride*, $3Th(C_2O_4)_2,ThCl_4,20H_2O$. When the amorphous oxalate obtained by precipitation is allowed to remain for a considerable time in contact with acids, it forms characteristic tetragonal prisms of the more stable form. The dihydrate, $Th(C_2O_4)_2,2H_2O$, is obtained when the hexahydrate is dried over sulphuric acid, or heated to 100°. The salt dissolves easily in excess of alkali oxalate, but is precipitated from the solutions by mineral acids, a fact which allows of another means of separation from zirconium, the double oxalates of which are much more stable towards acids. The solubility of the oxalate in alkali oxalate allows of separation from the rare earth elements, whilst its insolubility in excess of oxalic acid can be used for the separation from zirconium.

The *formate* and *acetate* can be obtained in the form of neutral salts by the action of the acids on the hydroxide; by double decomposition, amorphous precipitates of basic salts are obtained. With *tartaric acid* stable complex compounds are formed, as shown by the fact that alkalies will not precipitate the hydroxide from a solution in presence of that reagent, and by the elevation of the specific rotatory power. Many *complex salts* are known, the simplest having the

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[1] Hauser and Wirth, *Zeitsch. anorg. Chem.* 1912, 78, 75.

composition $ThO(C_4H_4O_6R')_2,8H_2O$, where $R'=K,Na,NH_4$; these are obtained by dissolving thorium hydroxide in concentrated solutions of alkali hydrogen tartrates. *Thorium acetylacetone*, $Th(C_5H_7O_2)_4$, is precipitated by addition of ammonia to an aqueous solution of the nitrate mixed with acetylacetone dissolved in ammonia; the solid is recrystallised from alcohol, and melts at 171°.

Atomic Weight of Thorium.—The value adopted by the International Committee (1914) is 232·4, but most of the determinations carried out within the last thirty years show considerable discrepancies. The earlier work of Berzelius (1829) and Chydenius (1861) led to very widely varying results, and for the same reason little reliance can be placed on the results of Delafontaine (1863) and Hermann (1864). In 1874 Cleve determined the constant by ignition of the sulphate, obtaining the mean values 234·03 and 233·97; the figure 234 based on these results was for many years accepted as the true atomic weight. A series of determinations carried out by Nilson in 1882 led to much lower results. He employed the sulphate ennea- and octohydrates, first dehydrating these, and then igniting to oxide, and showed that Cleve's value must be too high on account chiefly of the hygroscopic nature of the ignited oxide, which increases in weight when kept; but his own values show considerable discrepancies. The ratio $Th(SO_4)_2,9H_2O - ThO_2 : ThO_2$ (enneahydrate converted to oxide) gave the figure (corrected to vacuo) 232·51, whilst the ratio $ThO_2 : 2SO_3$ (anhydrous sulphate to oxide) gave 232·16; the ratio $Th(SO_4)_2 : 9H_2O$ (hydrate to anhydrous salt) gave, however, 233·75. The value obtained for the ratio $ThO_2 : 2SO_3$ for anhydrous sulphate prepared from the octohydrate was 232·49 (corrected to vacuo). Five years later, Krüss and Nilson prepared the anhydrous sulphate from the pure octohydrate, and ignited this to the oxide. The ratio $ThO_2 : 2SO_3$ gave as a mean of very concordant results the figure 232·49.

Brauner criticises these values on the ground that no details are given as to the temperature required to obtain the anhydrous salt from the hydrates, and that probably some traces of sulphate must be decomposed at the temperatures required (450°–500°) to drive off all the water. The results obtained from the enneahydrate are to a great extent invalidated by the doubts as to the purity of the hydrate, completeness of dehydration, etc., which arise from the discrepancies in the values deduced from the three ratios. He accepts, however, the figure 232·49 obtained by Nilson and by Krüss and Nilson from material separated as octohydrate, with some uncertainty as to the second decimal figure.

Brauner himself employed the oxalate method in 1898; the purified hexahydrate was used, the percentage of thoria being determined by ignition, and of (C_2O_3) by titration with permanganate. The ratio $ThO_2 : 2C_2O_3$ gave results varying from 232·21 to 232·29, but as the value rose continuously as purification was carried further and further, he did not feel justified in taking a mean value. In 1900 Urbain determined the constant with material purified by the acetylacetone method. He prepared the octohydrate, heated it for ten hours in a bath of sulphur vapour at 440°, and ignited the anhydrous salt so obtained at a white heat. The ratio $ThO_2 : 2SO_3$ gave the result (corrected to vacuo) Th = 233·67. Brauner criticises the value on the ground that the hydrated salt was heated in a vessel open to the air, and that at the high temperature obtained, traces of moisture gaining access to the sulphate caused hydrolysis, with loss of sulphuric acid; this would cause the results to be too high. In 1905 Meyer and Gumperz employed the same method, and obtained values varying from 232·2 to 232·7, with the mean 232·47. Finally Brauner carried out an extended investigation to disprove the heterogeneity of thorium which had been 'discovered' by Baskerville (1904), in the course of which he showed the atomic weight of the element to lie between the limits 232·34 and 232·52.

Detection of Thorium.—The element is best detected in a mixture of earths by the following reactions:

(1) Precipitation with hydrogen peroxide from warm, faintly acid solution.

(2) Precipitation with sodium hypophosphate, $Na_2H_2P_2O_6$, in concentrated hydrochloric acid solution. On boiling, a

perceptible precipitate is obtained if only traces of thorium are present; but ceric and zirconium salts and titanium must be absent. The latter element gives no precipitate under these conditions if hydrogen peroxide is present; ceric salts may be decomposed by boiling. The possible presence of zirconium renders it necessary to boil the hypophosphate precipitate with nitric acid; on addition of oxalic acid to the clear solution, thorium is precipitated, whilst zirconium remains in solution, and may be detected.

(3) Potassium azide, KN_3, throws down thorium hydroxide from boiling neutral or faintly acid solutions. Ceric salts if present must be previously reduced; zirconium must be previously removed by oxalic acid.

(4) Precipitation may be effected with potassium iodate in strong nitric acid solution. Here also ceric salts must be reduced before applying the test. Zirconium also gives the test; the precipitate must therefore be washed and warmed with oxalic acid, in which thorium iodate is insoluble, whilst zirconium iodate is soluble.

The methods of estimating thorium are given in Chapter XVIII.

PART III

THE TECHNOLOGY OF THE ELEMENTS

CHAPTER XVII

THE INCANDESCENT MANTLE INDUSTRY—HISTORICAL AND GENERAL INTRODUCTION

THE group of elements which we are considering can be divided, from the point of view of technical application, into two classes. The first of these contains one element only, titanium, which in its technology, as in its chemistry, stands apart from the others; it will, accordingly, be treated in a separate chapter. The second class contains the yttrium and cerium metals, with zirconium and thorium; the technical importance of these elements is due chiefly to the use of their oxides in illumination, to a small extent in Nernst lamps, and to a much greater extent in the so-called Incandescent Lighting. The manufacture of incandescent mantles[1] is a large and ever-extending industry, intimately bound up with the older process of coal-distillation, with its innumerable ramifications; indeed, it may be said that but for the ingenious invention of Dr. Auer, illumination by means of coal-gas would to-day have been almost obsolete. The discovery which resulted in the production of the familiar incandescent mantle of the present day may be regarded as the culmination of a century's effort

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[1] The term 'incandescent mantle' is not, perhaps, scientifically very desirable. It is used here, not only on account of its general acceptance, but also because there seems to be no brief and convenient term which might be used in its stead.

to increase the value of coal-gas as an illuminating agent. In the present chapter it is proposed to outline the history of these endeavours, and to give a short general account of Auer's work and its results.

Soon after the introduction of gas as an illuminating agent it was realised that the luminosity of the flame is dependent on the presence of solid particles, which by the heat of combustion of the gas are raised to a temperature at which they emit radiations of wave-lengths corresponding to the 'luminous rays' of the spectrum. A non-luminous flame of sufficiently high temperature, therefore, can be rendered luminous by the introduction of suitable solids, and numberless investigators have striven, during the past century, to discover the most suitable method of increasing the luminosity of a flame in this way. The luminosity of the ordinary 'bats-wing' or 'flat' flame, now so rapidly going out of use, is due to the presence in the outer zone of the flame of heated particles of carbon, produced by the decomposition—or partial combustion—of 'dense' hydrocarbons, *i.e.* of hydrocarbons having a high percentage of carbon. Ordinary coal-gas consists largely of a mixture of hydrogen and methane, both of which burn with practically non-luminous flames, with small quantities of olefines, acetylenes, etc., to which the luminosity is chiefly due. It would appear, then, that by the introduction of dense hydrocarbons, a gas of poor illuminating power might be made much more valuable as a source of light. On the other hand, it is also apparent that the same end might be achieved by the introduction into a non-luminous or feebly luminous flame of an altogether foreign substance, introduced as such, and not continuously consumed, as is the carbon in the former method. Both these directions of improvement have been followed; since, however, the results achieved by the latter method have become recently of far greater importance, the applications of the first method will be dismissed quite briefly, and the history of the second will then be treated somewhat fully.

The first important attempt to increase the illuminating power of gases burning with feebly luminous flames was that of Faraday, who in the course of an investigation into the causes of the variations in luminosity of 'portable gas,' discovered benzene, or bicarburet of hydrogen, as he called it, in 1826. In 1830 an engineer named Dunnovan undertook to illuminate Dublin by means of water-gas[1] which he 'carburised' by addition of dense hydrocarbons. During the latter half of the nineteenth century this method became of some importance. It has been applied, in particular, to enrich the 'natural gas' of Ohio, North America. The dense hydrocarbons necessary for this purpose are obtained by the process known as 'cracking.' The viscous residues from the distillation of the mineral oil of the district are allowed to drop into a brick chamber, of which the walls are raised to a bright red heat, and the dense hydrocarbons which are evolved are removed by a current of the gas to be enriched. In this way a gas of relatively high illuminating power is obtained.

In the year previous to that in which Faraday first carburised water-gas, Berzelius had observed that thoria and zirconia, when heated in a non-luminous flame, emit an intense white light. Similar behaviour had long before been observed in the cases of magnesia, alumina, lime, zinc oxide, etc. The first practical application of this property of the oxides was that of Drummond, who in 1826 heated a pencil of lime in the oxy-hydrogen flame and obtained the intense white light which has since become so familiar as the Drummond or 'lime-light.' A further development in this direction was due to du Motay and Maréchal, who in 1867 illuminated the Place de Tuileries and the Hôtel de Ville in Paris by means of pencils of compressed zirconia—magnesia was also used—heated by means of oil vapour and oxygen.

The use of non-luminous flames to secure illumination, by raising the temperature of solids suspended in them to the point of incandescence was proposed in 1839 by Cruickshank, who used a mantle of platinum wire, covered with lime and rare earths, which he heated by means of water-gas. In 1846

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[1] Water-gas is a mixture of equal volumes of carbon monoxide and hydrogen, obtained by blowing steam through a glowing coke furnace. At intervals the steam is shut off, and air is blown through to raise the temperature of the coke.

Gillard employed mantles of platinum wire, raised to incandescence in the flame of burning hydrogen, which he obtained by passing steam over heated iron wire; later he used water-gas (1848), his lamps with this modification being employed in Paris and in Philadelphia. Narbonne was later illuminated (1856–1865) by a similar device, but permanent success could hardly be obtained in view of the cost of the platinum mantles, which lasted only a few months. The same mantle was proposed in 1882 by Lewis, the ordinary Bunsen flame being suggested as the source of heat. In the same year Popp exhibited at the Crystal Palace lamps in which a platinum mantle was raised to incandescence by means of a flame of coal-gas and heated air. These attempts, however, served only to show that no permanent advance could be made in this direction.

A new development was made in 1880 by Clamond. He prepared a paste by grinding up calcined and powdered magnesia with a concentrated solution of magnesium acetate; by forcing this through a press he obtained a ribbon which was then wound crosswise on a wooden shaper, dried carefully, and ignited. In his later experiments twenty per cent. of zirconia was added to the magnesia. The mantle was supported in a platinum cage and heated in the flame of a mixture of coal-gas and heated air. This mantle gave an intense light, but was too fragile for extended use. In the following year, Lundgren patented a process by which lime, magnesia, and zirconia, made into a paste by the addition of gum, were forced through a press, and the resulting thread wound on a graphite-covered shaper. The mantle so obtained was stable, and gave an intense white light, but after having been heated for some time the oxides crumbled to powder. A modification of this process was introduced by Knöfler in 1894, in an attempt to use a cellulose solution containing rare earth salts; this was forced through jets, and the cellulose precipitated as a continuous thread from which the mantle was made. A further modification of Knöfler's process by Plaisetty in 1901 was technically successful; but these developments must be taken up in a later chapter (*vide* p. 307).

In 1883 a process was patented by Fahnehjelm in Stockholm, by which for the first time a cheap and stable mantle of considerable efficiency was produced, and which, but for the advent of the Auer mantle, would undoubtedly have been commercially successful. Fahnehjelm's mantle consisted of an arrangement of needles or lamellæ of magnesia, lime, zirconia, etc., suspended over a burner. The plates and needles were usually arranged in the form of a comb of suitable shape, and were found to give an intense light, and to be long-lived. In later forms the combs were made of rods of magnesia dipped into solutions of chromium salts. The great disadvantage of this invention lay in the fact that the combs required to be heated in the flame of water-gas, in order to secure a good incandescence; had it been possible to attain a sufficiently high temperature by the use of coal-gas, it is doubtful whether the Auer mantle would have ever been evolved.

The more important attempts to secure arrangements by which the radiations of heated solids could be used for illumination have now been outlined and the ground cleared for the consideration of the work of Baron von Welsbach. There remain yet to be mentioned, however, two attempts which are of especial interest in view of that work. The first is that of Frankenstein, who in 1849 made use of a 'Light-multiplier' obtained by impregnating gauze with a paste of chalk and magnesia ground with water. The second is that of Edison, who proposed (1878) to utilise the observations of Bahr and Bunsen (1864) and of Delafontaine (1874), of the remarkable incandescence exhibited by the yttria and erbia earths, and the terbia earths, respectively, when heated; he suggested the employment of a mantle of platinum wire covered with zirconia and the oxides of the rare earth metals, a proposal similar to that put forward nearly forty years earlier by Cruickshank.

About the year 1880 Dr. Carl Auer began the study of the rare earth elements. The chemical aspect of his work has already been dealt with (*vide* p. 168); but the results obtained by the technical application of his observation that threads of cotton, impregnated with a solution of salts of the elements, leave after ignition a coherent ash of oxide, which glows brightly when heated, have been of far greater importance than the purely scientific aspect, valuable though that is. A series of experiments soon showed that a fabric of suitable shape, impregnated with a solution of nitrates or acetates of the rare earth elements, after being dried and drawn together at one end by means of a platinum wire, can be ignited in a Bunsen flame in such a way as to leave a coherent skeleton of the earth oxides, which can be formed and hardened by suitable manipulation with a high temperature burner; the mantle so prepared, when suspended from a lateral support in a Bunsen flame, gives a light of considerable intensity, the colour varying with the oxides employed from green to orange tints.

The earlier mantles, which were placed on the market about 1883, consisted chiefly of oxides of lanthanum and zirconium, with smaller quantities of the other oxides, selected according to the shade of light desired. These mantles were protected by patents taken out in France in 1884, and in Germany in 1885 and the following years. The process[1] was briefly the following: A vegetable fibre, of cylindrical form, woven from threads of about 0·22 mm. diameter, is washed with dilute hydrochloric acid, then with distilled water, and impregnated with a 30 per cent. solution of the selected salts. The fabric is then wrung out and dried, and cut into suitable lengths, allowance being made for subsequent shrinkage. One end of each cylinder is then drawn together by means of a platinum wire, and the mantle hung from a side support over a burner and incinerated. The head is then treated with a solution of aluminium and magnesium nitrates (beryllium nitrate and the corresponding phosphates are also specified) to strengthen it, and the mantle dried, and 'formed' by means of a very hot flame. This first patent protected several definite mixtures of salts, chosen so that the mantle should emit light of a definite known tint. The chief oxides employed were lanthana, yttria, magnesia, and zirconia. A German patent granted in 1886[2] protects the use of thorium salts,

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[1] *Vide D. R. P.* 39162. Granted September 23, 1885.

[2] *D. R. P.* 41945.

and a long list of salts of the elements with numerous acids; an important advance mentioned in this specification is the process of collodinisation of the finished mantle, by dipping in a solution of rubber in benzene or of collodion (cellulose nitrate) in ether and alcohol, which renders the product strong enough for transport. From 1885 to 1891 numerous improvements were effected; asbestos threads were substituted for plantinum wire, central rods of magnesia replaced the lateral platinum support, and various mixtures of oxides were tried. None of the innumerable mixtures employed, however, was successful in establishing the struggling industry on a firm basis in face of the vigorous competition of the electric lamp, and it was not till 1891 that the introduction of the final 'Auer Mixture,' which is in use at the present day, gave the welcome assurance of a certain success to von Welsbach and his assistants. The discovery of this mixture was a result of the examination of a quantity of impure thoria; it was found that mantles made from the nitrate gave a light which steadily decreased in intensity as the impurities were removed. It needed only the observation that the impurities consisted chiefly of cerium compounds to turn the long and arduous investigation in the direction of final success, and our present mantles, which consist approximately of 99 per cent. thoria and 1 per cent. ceria, were placed on the market in 1891, the composition being announced by patent in 1893.[1]

The effect of increasing or decreasing the ratio of the two oxides, and the theories which have been advanced to account for the results, must be referred to in a later chapter (*vide* p. 294). It may be mentioned here, however, that practically no other known mixture gives such satisfactory results, though mantles have been manufactured of alumina with small quantities of chromic oxide, and 'inverted' mantles made of these oxides with zirconia have recently been advocated by Professor Lewes,[2] an authority on gas lighting. Mixtures of alumina and uranium oxide have also been patented, but no mantles appear to have been manufactured according to the

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[1] *Vide*, *e.g.* Moeller, *E.* 124, 1893.

[2] *Vide D. R. P.* 218333 of January 1910.

specifications. In this connection, also, may be mentioned the various attempts to evade the Auer patents by taking advantage of the 'discovery' of 'new' elements. One enterprising firm, after having an account of a 'new' element, Lucium, inserted in a well-known scientific periodical, put salts on the market, and proceeded to manufacture mantles from what were proved by analysis to be cerium compounds. Similar 'new' elements were Russium, Kosmium, and Neo-kosmium, names which covered various mixtures of thorium and cerium compounds with other salts.

After the introduction in 1891 of the final Auer mixture, progress became rapid. The original mantles, made from cotton, had many disadvantages; thus after being in use for some time they were found to shrink considerably, with marked decrease in strength and light-giving power. Once the success of the new form of lighting was assured, numberless investigations were undertaken to lengthen the life and increase the efficiency of the mantles. The most important of these were connected with the endeavour to replace cotton by some fabric which on ignition would leave the oxide skeleton in a harder, more coherent and more elastic condition. The first great advance in this connection was the introduction of Ramie fibre by Buhlmann in 1898. Ramie, China-grass, or grass-cloth, as it is sometimes termed, is a fabric made from the fibres of the tschuma plant of the Yang-tse-kiang valley and other parts of Asia; mantles made from it last longer and maintain their efficiency much better than the earlier cotton mantles, which they have very largely displaced. The use of artificial silk was patented by De Mare in 1894, but his process was unworkable; it was an effort to adapt to the purposes of incandescent lighting the nitro-cellulose process introduced by Chardonnet in 1890 for the manufacture of artificial silk. In 1897 De Lery and in 1900 Plaisetty made further efforts in this direction, and finally in 1902–1903 the latter worked out a process by which mantles were made directly from the spun fabric. These mantles are superior in every way to the earlier ramie or cotton kinds, and are rapidly coming into general use, especially for lamps using high-pressure gas. Numberless patents for the manufacture and improvement of this kind of mantle have been taken out during the last ten years; the most important of these will be dealt with in a later chapter.

Attempts have been made to secure greater strength and toughness in mantles in other directions also. The use of metallic wires in the fibre has been suggested; numerous patents deal with mantles 'strengthened' by doubling the thread at intervals, and by special methods of weaving the fibre. One method, which follows on the lines of Clamond and Lundgren, proposes[1] the use of mantles made from various oxides mixed with silica, the whole being worked into a paste by use of a gum or soap, from which threads are prepared by pressure; mantles made from these threads are said to be very strong and porous. Another patent[2] protects the manufacture of 'incandescence bodies' made from plates or combs prepared from a thread obtained in a rather similar way. A third of these innumerable suggestions recommends a preliminary impregnation of the fabric with an aluminium or magnesium salt,[3] from which the oxide is precipitated on the fabric by a suitable means, impregnation with the ordinary 'lighting fluid' being effected after drying. Quite an early patent[4] proposes the impregnation of the prepared mantle, either after or just before burning off, with an alcoholic solution of an organic silicon compound, so that when the mantle is in use a skeleton of silica is formed to 'strengthen' the oxide ash. No useful purpose can be served by extending the list of these proposals; enough has been said to indicate the various directions in which so many vain attempts at improvement have been made.

From the mechanical and physical side the recent developments have been very marked. The introduction of the 'inverted' lamp was a tremendous step forward, and paved the way to the second great improvement, the use of 'high-pressure' gas, with which such successful results are being obtained. The form of lamp now coming into use for street lighting gives 1500

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[1] Laigle, *D. R. P.* 216871 of December, 1909; see also *D. R. P.* 216877 and 219640.

[2] Michaud and Delasson, *D. R. P.* 210640, June, 1909; see also *D. R. P.* 227257.

[3] Zdanowich, *E.* 27755, 1908.

[4] Jasper, *E.* 30145, 1897.

candle-power per mantle, and usually carries three mantles; each lamp thus develops 4500 candle-power. The purely mechanical devices which are now used to secure 'automatic' lighting are rapidly bringing this form of lamp into favour for street illumination. A full account of these developments would be entirely beyond the scope of the present work. In the following chapters, therefore, no complete treatment of the incandescent lighting industry can be given; but whilst the chemical aspect is treated at some length, many points of more purely technical character, which are connected with this, have also been included.

CHAPTER XVIII

THE CHEMICAL TREATMENT OF MONAZITE

It has been stated in the previous chapter that the first Auer mantles were made of mixtures of various rare earth oxides, the mixture of thoria with 1 per cent. of ceria being first employed in October, 1891. The impetus given to the mantle industry by the success of the new mixture caused an immediate demand for thoria, which was at that time extracted from thorite (see p. 43). A 'thorite-fever' broke out along the coasts of Scandinavia, and the price of orangite rose to 600 marks per kilogram (about £13 10*s*. per pound avoirdupois), sinking again shortly to 80 marks[1] (about £1 16*s*. per lb). The discovery of the monazite sands of the Carolinas and Brazil, which at the present rate of consumption may be considered to be, for all practical purposes, inexhaustible, placed the industry on a firm basis, and the pure monazite, extracted from these deposits by the methods outlined in Chapter VII, is now almost the sole source of the thorium nitrate of commerce. Small quantities are obtained from thorianite, the separation of the pure material presenting, in this case, very little difficulty by reason of the solubility of the mineral in acids and the very high percentage of thoria.

The extraction of pure thorium compounds from monazite is a process of very great technical difficulty. The percentage of thoria is small, whereas that of the ceria oxides is high. The mineral is almost always decomposed by heating with concentrated sulphuric acid, and when the resulting pasty mass is taken up with water, a large amount of free sulphuric acid must be present in order to hold the rare earth phosphates in solution.

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[1] *Vide* Böhm, 'Die Thorium Industrie,' *Chem. Ind.* 1906, **29**, 450 and 488.

For the separation of thoria from ceria and yttria compounds in acid solution no processes were known until quite recently. When it is remembered that the thorium nitrate used for the manufacture of mantles must be of a degree of purity which very few commercial products ever approach, some idea of the difficulties of the extraction may be obtained.

Decomposition of the Monazite.—Two processes have been used for the working up of monazite. The first of these consists in fusing the mineral with soda, and extracting the sodium phosphate with water; the earths may then be taken into solution with acid, and the separation effected as outlined below. This method is very rarely used. A process has been proposed, in which the monazite is fused with carbon in an electric furnace; the cooled mass is treated with mineral acids, which take the earths into solution free from phosphoric acid. No technical application has so far been made of this proposal.

The method commonly used is that in which the sand is decomposed by means of sulphuric acid. The charge usually employed, about two to three hundred kilograms, requires from four to six hours' heating, about twice the weight of concentrated acid being needed. The operation is carried out in cast-iron vessels, and an efficient draught must be maintained to remove the acid fumes; the factories are usually isolated. The treatment with sulphuric acid converts the phosphates chiefly into sulphates; when the reaction is finished, the liquor fumes strongly and begins to thicken, heating being stopped when a thick broth is obtained. The cooled mass is extracted with water, care being taken to maintain a degree of acidity sufficient to prevent any precipitation of the phosphates.

It has been already stated in Part I (*vide* p. 73) that a strongly radioactive product, Radiothorium, has been obtained from the mineral thorianite. This body is produced by the atomic degradation of thorium, and an intermediate body, mesothorium, has been found to be formed during the change. Mesothorium is a substance which, though it appears to be chemically identical with radium, has an activity equal to three hundred times that of radium, and when in equilibrium with its degradation products the 'rays' it emits are very similar to those of the latter element. Since mesothorium is a degradation-product of thorium, it occurs in minute quantities in all thorium minerals, and by reason of the possibility of using it as a substitute for radium, its extraction becomes a matter of importance. Soddy[1] has shown that if a barium compound be added to monazite before the treatment with sulphuric acid, the mesothorium remains with the barium sulphate; this is readily separated from the heavy unchanged grains of sand, and is purified, and finally obtained as chloride by treating the solution with hydrogen chloride. On recrystallisation of the barium chloride, the active products are concentrated in the less soluble part, and it is possible to prepare on the commercial scale a mixture which, though it contains only 0·25 per cent. of mesothorium, has an activity equal to that of pure radium bromide. This mixture contains 25 per cent. of radium compounds, radium being present as an original constituent of monazite; owing to the chemical identity of radium and mesothorium,[1] the latter cannot be separated, but Soddy, by removal of much of the barium compound in the laboratory, has obtained a product four times as active as the pure radium salt.

It is probable that the treatment of monazite will in the future be modified by the addition of barium sulphate before the sulphuric acid decomposition, to allow of the commercial extraction of its mesothorium.

Separation of Thorium.—The separation of a crude thorium product from the acid solution obtained after decomposition of the mineral can be effected in two ways, both of which are based on the fact that thoria is less basic than the oxides of the cerium and yttrium metals. In the first, the rare earth elements, including thorium, are precipitated as oxalates by the addition of oxalic acid to the acid solution. These are again taken into solution by the action of hydrochloric acid on the hydroxides, obtained by prolonged digestion of the

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[1] *Proc. Chem. Soc.* 1910, **26**, 336, and *E.* 25504, November, 1910. See also Hahn, *Chem. Zeitg.* 1911, **35**, 845.

oxalates with sodium hydroxide; the acid solution is then treated carefully with sodium hydroxide, or pure powdered magnesia, until about one-sixth of the bases has been precipitated, the liquid being constantly stirred. Thorium hydroxide being very weakly basic is precipitated before the other hydroxides, and the precipitate obtained, after one or two repetitions, contains most of the thorium originally present in the monazite. In the second process, thorium is partially separated from the other metals by adding gradually to the solution obtained after the treatment of the mineral with sulphuric acid, the quantity of magnesia calculated to precipitate a suitable fraction of the earths, with constant stirring; this throws down a mixture of phosphates containing almost all the thorium and some of the other elements. The slimy phosphate precipitate is dissolved in hydrochloric acid, and the earths precipitated as oxalates; the precipitate must be washed thoroughly in order to remove phosphoric acid. It will be seen that these two methods differ only in that in the first the phosphoric acid is removed before the precipitation of thorium, whereas in the second the thorium is precipitated as phosphate, and this transformed into oxalate.

Quite recently, methods have been proposed by which the thorium can be separated in a fairly pure condition from the acid solution obtained from the sulphuric acid treatment. Rosenheim, Meyer and Koppel[1] protect the use of hydrofluosilicic acid (H_2SiF_6), and its salts, for this purpose. The sodium salt, added to the hot acid liquid, produces a quantitative separation of thorium silicofluoride; the precipitate is washed by decantation, and treated with sulphuric acid, the thorium sulphate being then purified directly by the sulphate method described below. A second method proposes to make use of the insolubility of thorium hypophosphate, $ThP_2O_6,11H_2O$, which was found by Kaufmann in 1899 to be insoluble in water, and in acids and alkalies. This method has already been in use for some years for analytical work;[2] it appears to be readily susceptible of adaptation

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[1] *D. R. P.* 214886, October, 1909.

[2] Rosenheim, *Chem. Zeitg.* 1912, 36, 821; also Koss, *ibid.* 986

for the technical extraction,[1] the sodium hypophosphate, $Na_2H_2P_2O_6,6H_2O$ required as the precipitating agent being obtainable in large quantities by the electrolytic oxidation of copper phosphide, employed as the anode in an electrolytic cell.[2] This method also gives a thorium compound sufficiently free from other earths to be subjected at once to the refining process ; the hypophosphate has in fact been suggested as a very suitable compound for the impregnation of artificial silk mantles directly. The thorium nitrate of commerce, however, is still prepared almost entirely from the crude product obtained by one or other of the two methods of fractional precipitation first described, so that it becomes necessary to outline the method generally employed for separating from this a compound pure enough to be suitable for the final refining process.

The crude oxalate or hydroxide is thoroughly digested with a concentrated solution of sodium carbonate. The carbonates of the cerium elements are much less soluble in sodium carbonate solution than is thorium carbonate. After thorough digestion the liquid is filtered from the undissolved carbonates. The thorium is reprecipitated from the filtrate, either as oxalate, by the addition of hydrochloric acid (if the crude material was in the form of oxalate), or as hydroxide, by the addition of sodium hydroxide. The process is again repeated, and a final digestion is then made with ammonium carbonate ; addition of an alkali to the clear filtrate now gives thorium hydroxide sufficiently pure to be used for the last refining.

Purification of the Thorium Compounds.—The object of this last stage is to remove from the thorium compound small quantities of cerium and yttrium salts which cannot be separated by the carbonate method. The chief process is the sulphate crystallisation, the principles underlying which have been thoroughly examined in the patient researches of Koppel and Holtkamp.[3] Since the process is based on the solubilities

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[1] Wirth, *Zeitsch. angew. Chem.* 1912, 25, 1678.

[2] Rosenheim and Pinsker, *Ber.* 1910, 43, 2003.

[3] *Zeitsch. anorg. Chem.* 1910, 67, 266.

of the various thorium sulphate hydrates, it is necessary to consider these in some detail.

The solubility-curve of thorium sulphate was examined by Demarçay and by Roozeboom. Three important hydrates are known, viz. $Th(SO_4)_2,9H_2O$, $Th(SO_4)_2,8H_2O$, and $Th(SO_4)_2,4H_2O$, other unstable intermediate compounds being said to exist. From a study of the diagram it will be seen that the hydrate with 8 molecules of water is labile, whilst the 9-hydrate and the 4-hydrate have a transition temperature at 43°C., the transition temperature of the 8-hydrate and the 4-hydrate being just below this.

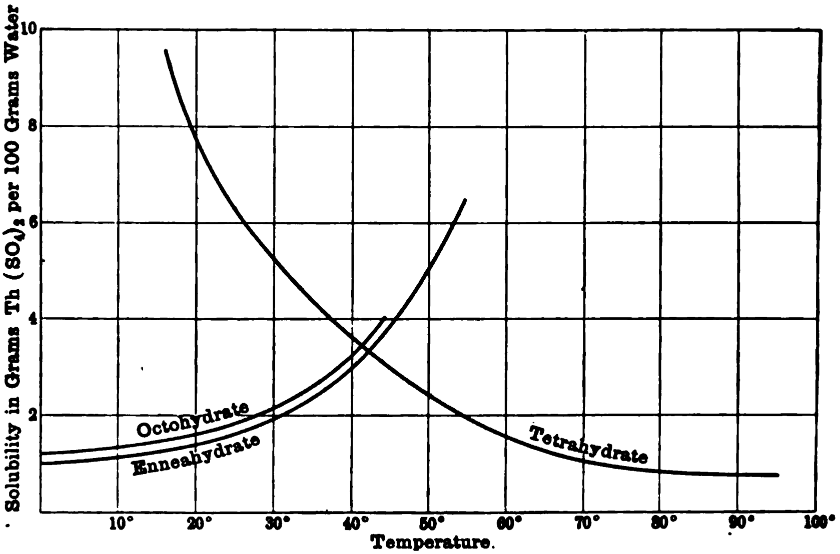

FIG. 10

Since the 8-hydrate is labile with regard to the 9-hydrate, and the transition temperatures are so near, the former will be formed first as a solution cools, and by reason of the great similarity of the solubility-curves for the 9- and 8-hydrates the rate of change of this to the 9-hydrate will be very slow. In practice, therefore, it is always the 8-hydrate which is formed, and it is on the separation of this compound that the success of the process depends. The anhydro-compound, $Th(SO_4)_2$, which can be obtained by heating any of the hydrates to 300°–400°C., is very soluble at 0°, but slowly hydrates itself and separates from the solution as the 8-hydrate, which has a very low solubility. The sulphates of the cerium metals, compounds of which form the chief impurities to be removed, are considerably more soluble, and can be separated by repeated crystallisations.

The thorium hydroxide to be purified is dissolved in sulphuric acid, and in the first form in which the method was employed, the thorium sulphate obtained by evaporation of the solvent was heated until it became anhydrous. This was dissolved to saturation at 0°, and the solution raised to the boiling-point, the 4-hydrate being precipitated; this treatment was repeated several times. It was pointed out by Bunsen, from theoretical grounds, that this method could never yield a pure thorium salt, and Krüss and Nilson accordingly introduced a modification. The impure sulphate, after dehydration, as before, is dissolved at 0°, and allowed to come to ordinary room temperature, 20°; the hydrate which separates (the 8-hydrate) is collected and dried at high temperature and the crystallisation repeated. This method gives a fairly pure salt after three recrystallisations, but the process is very tedious, owing to the time required for drying and heating the hydrate. For this reason the method was further modified by Cleve and Witt. The crude sulphate is boiled with ammonia, and the hydroxide obtained dissolved in hydrochloric acid; addition of sulphuric acid to the concentrated solution in the cold transforms the chloride into the sulphate, which separates as the 8-hydrate at ordinary temperatures. Three repetitions give a satisfactory product, and in this form the method is now much used.

The work of Koppel and Holtkamp referred to above has placed the process on a sound basis. These authors have examined the solubilities of the various hydrates in presence of hydrochloric, nitric, and sulphuric acids, and mixtures of these, at different temperatures. They find that hydrochloric acid is to be preferred to nitric acid, in the process of Cleve and Witt, as besides its lower price, its use involves less loss than that of the latter acid; excess of hydrochloric acid is not harmful within wide limits, whilst a slight excess of sulphuric acid over the quantity required to form the sulphate is desirable, to secure the greatest yield. Finally, the temperature at the addition of the sulphuric acid must not be allowed to rise above 25°, for in the presence of so much acid the transition temperature to the 4-hydrate, normally 42°, is considerably lowered ; it is necessary to avoid separation of the 4-hydrate, which is a flocculent unworkable precipitate.

Recently it has been proposed to carry out the purification by use of alkyl hydrogen sulphates,[1] as it is stated that the differences of solubilities of the alkyl sulphates of thorium and the cerium metals are greater than in the case of the sulphates themselves. It is also claimed that the presence of a small quantity of the alkyl sulphate in the thorium nitrate which forms the final product has a good effect on the quality of the mantles made from it.

Another process of purification which has found considerable commercial application is the acetate crystallisation, thorium acetate being considerably less soluble than the acetates of the cerium elements. The impure hydroxide is dissolved in acetic acid and the solution evaporated to dryness ; repeated washing with small quantities of water removes the cerium acetates, and a fairly pure salt is obtained. This is repeatedly damped with nitric acid and heated to dryness, but even after this treatment a certain amount of unchanged thorium acetate is usually present.

In a second form of this method, due to Haber, the impure hydroxide is dissolved in hydrochloric acid, and the acetate precipitated by addition of sodium acetate. The precipitate is filtered off and re-dissolved in acid, and the acetate again thrown down by means of sodium acetate. The precipitate is then dissolved in nitric acid, and the solution evaporated to dryness. In this form the method gives very good results, even from a comparatively crude product; but the process is, of course, considerably more expensive than the sulphate purification.

The high price of the necessary reagents, again, is a bar to the technical application of the very simple and efficient process of Wyrouboff and Verneuil. These authors suggest

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[1] **Kreidl u. Heller, *D. R. P.* 233023, March, 1911 ; *F.* 414463, June, 1910.**

the precipitation of thorium peroxide from a warm dilute neutral solution by means of hydrogen peroxide, a process which is quantitative and yields a very pure product. The last traces of the cerium metals can be completely removed by a second precipitation. The cost of hydrogen peroxide is too high, however, to allow of its employment on such a large scale, and the method has not, in consequence, come into general use.

The thorium nitrate obtained after purification by the sulphate method, or by the less generally employed acetate method, is usually considered sufficiently pure for technical purposes. Even now, however, it may contain traces of sulphate, of iron, of alkalies, and of cerium metals. If absolute purity is desired, the salt may be dissolved, and freed from all impurities, except the cerium compounds, by precipitation with ammonium oxalate and thorough washing; the oxalate may then be dissolved in chromic acid, and potassium chromate solution added drop by drop; the precipitated thorium chromate is nearly free from other rare earth compounds, and repetition of the process will give a pure salt. The separation from cerium metals may also be effected by the hydrogen peroxide process. If the technical processes are carefully carried out, however, a thorium nitrate of a very high degree of purity may be obtained, and the laboratory purification need only be undertaken if material is needed for very accurate quantitative work.

Preparation of Thorium Nitrate from Mantle-ash. — Since the ordinary incandescent mantle, in use, consists only of the pure thoria and ceria, with small quantities of alumina, lime, and magnesia, which have been employed to strengthen the 'head,' the working-up of mantle-ash gives an easy means of obtaining the nitrates, and high prices are accordingly paid for the ash in quantity. At one period of great competition between rival manufacturers, canvassers went from house to house in many large towns buying up mantle residues, to be used for the extraction of the thorium for 'lighting-fluid.'

For this purpose, the oxides are treated with hot concentrated sulphuric acid, the cooled residue dissolved in water, and the thorium and cerium precipitated free from compounds of aluminium, magnesium, and calcium by oxalic acid. If pure thorium nitrate, free from cerium, is required, the oxalates are added to the last precipitate from the double carbonate purification in the treatment of monazite (*vide supra*), and the ordinary processes of refinement continued; more often, however, the mixed nitrate for impregnation of the mantle-fabric is required, and this is obtained by ignition of the oxalates and solution of the oxides so obtained in nitric acid, more cerium nitrate being added if necessary.

Extraction of Cerium Nitrate.—Since monazite is primarily a phosphate of the cerium metals, the percentage of thoria being usually quite low (*vide* Monazite, Chapter VI), very large quantities of compounds of the cerium group of elements are annually produced in the process of extraction of thorium. There is at present a very limited demand for these compounds (*vide* Chapter XXI), no important uses having yet been found for them. In the ordinary process of extraction of the thorium, these elements remain as the sparingly soluble double carbonates, whilst the thorium double carbonate is removed in solution. From the mixed salts which contain 50–60 per cent. of the cerium compound, the cerium nitrate required for the manufacture of mantles is prepared, but the amount so used is a small fraction of the whole, and large quantities of compounds of cerium and the allied elements are available as soon as profitable uses can be found.

Three processes are in general use for the preparation of cerium nitrate from the mixed carbonates; all of these are based on the fact that cerium can become tetravalent, forming in this condition compounds which can readily be separated from those of the allied elements, which can be obtained only in the trivalent condition. When ceria is dissolved in hot nitric acid, ceric nitrate, $Ce(NO_3)_4$, is formed, though the action of nitric acid on cerous carbonate or oxalate gives rise to cerous nitrate. Two of the three processes are based on this reaction, and for these the mixed carbonates are dissolved in hydrochloric acid, freed from foreign elements by precipitation with oxalic acid, and the oxalates ignited to the oxides, which are then dissolved in the required quantity of nitric acid. In the first process the cerium is precipitated from this solution by merely pouring it into a large excess of very dilute nitric acid, when a yellow basic ceric nitrate is precipitated ; this is washed with dilute nitric acid by decantation, dissolved in concentrated acid, and purified by a second precipitation in the same way. In the second process, separation is effected by addition to the nitric acid solution of the calculated quantity of ammonium nitrate ; the solution is concentrated to incipient crystallisation, and on cooling the double ceric ammonium nitrate, $Ce(NO_3)_4,2NH_4NO_3$, separates. This is collected, washed with dilute nitric acid, and recrystallised until a pure salt is obtained. The double nitrate can be readily decomposed by ignition, leaving ceria, which is dissolved in nitric acid ; the nitrate is obtained by evaporation.

The third method, due to Drossbach, is based on the oxidation of cerium salts in neutral solution by potassium permanganate. The mixed carbonates are dissolved in hydrochloric acid, a further quantity of the carbonates stirred in, to neutralise excess of acid, and a solution of the required quantity of potassium permanganate added. The reaction is said to proceed according to the equation :

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

The precipitated solid is separated, and dissolved in acid ; the cerium is then precipitated as the oxalate, which is transformed into nitrate in the usual way. The solution contains the other elements of the cerium group, which are precipitated by means of sodium hydroxide. The yield obtained by this method is very good, practically the whole of the cerium being separated without loss ; whilst it has the further advantage that the remaining elements of the group can be precipitated at once after the separation.

Analysis of a Monazite or Monazite Sand for Thorium.—Since the commercial value of a monazite sand or concentrate, or of the pure mineral, depends, at present, entirely on the percentage of thoria, it is important to have a rapid and reliable method of estimating this constituent. The only reliable methods of quantitatively decomposing the mineral, however, all involve acid treatment, and excess of acid must always be present to prevent precipitation of phosphates. Until recently, no way was known for estimating thorium in an acid solution, and all the earlier methods therefore involved tedious processes for complete removal of phosphoric acid, so that the salts could be obtained in neutral solution. This was usually effected by precipitation of the whole rare earth content with oxalic acid, and thorough washing of the oxalates ; these can then be dissolved directly in fuming nitric acid on the water-bath, or ignited to the oxides, which may then be dissolved in the same reagent. The solution of nitrates is evaporated to dryness, to effect removal of the excess of acid, the nitrates dissolved in water, and the thorium estimated in the neutral solution.

Among the earliest methods employed for the estimation in neutral solution was the thiosulphate precipitation.[1] Thorium thiosulphate is not known ; when sodium thiosulphate is added to a neutral solution of a thorium salt, a precipitate of thoria mixed with sulphur is obtained, by hydrolysis of the potential thiosulphate, and decomposition of the unstable thiosulphuric acid. The method, however, leaves much to be desired ; other earths are partly precipitated, and the separation of thoria is not complete. For analytical purposes the precipitate obtained is redissolved in hydrochloric acid, and a second precipitation with thiosulphate effected. The filtrates from the two precipitations are collected, and the whole earth-content precipitated from these with ammonia ; the hydroxides are dissolved in hydrochloric acid, and again treated with thiosulphate to throw down any thoria which has escaped the previous precipitations. The three precipitates of thoria are then collected, dried, and ignited for weighing as pure thorium dioxide, ThO_2.

Even more tedious and unsatisfactory is the method based on the solubility of thorium oxalate in excess of ammonium oxalate in neutral solution. The solution is boiled, ammonium oxalate added, and after some moments a small quantity of

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[1] Full accounts of this and the two following methods will be found in an important paper by Benz, *Zeitsch. angew. Chem.* 1902, 15, 297

ammonium acetate solution. On cooling, the oxalates of the cerium metals separate, and can be collected; thoria is precipitated from the filtrate by addition of ammonia. The process must be repeated two or three times, the solution being allowed to stand for one or two days each time, and finally the thoria must be precipitated by thiosulphate to remove traces of the other bases before it can be weighed. Benz (*loc. cit.*) gives a complete account of this method, and quotes numerous analyses carried out to test its accuracy.

Far more satisfactory than either of the above is the peroxide method used by de Boisbaudran and Cleve, and later by Wyrouboff and Verneuil.[1] Thorium is completely precipitated as a 'peroxide salt' (Th_2O_7,SO_3 or Th_2O_7,N_2O_5 respectively) from warm neutral solutions of the sulphate or nitrate on addition of dilute hydrogen peroxide, a second precipitation being necessary to free it from cerium compounds. Wyrouboff and Verneuil state that the process is rendered difficult by the fact that the peroxide cannot be converted into the dioxide by heating, either alone or with acids, as decrepitation takes place and may cause loss; they accordingly reduce the compound in presence of hydrochloric acid by ammonium iodide, and precipitate thorium hydroxide by ammonia. Benz (*loc. cit.*) does not find this difficulty; he states that small quantities of the peroxide dissolve easily in acids without loss, and further finds that if an ammonium salt be added to the neutral solution of the thorium compound before addition of hydrogen peroxide, the precipitate forms much more readily and is very easily handled. Borelli[2] states that the precipitated peroxide can be ignited without loss to the dioxide, and weighed as this.

The azoimide method of Dennis[3] is of interest rather than of use. He finds that addition of potassium azoimide, N_3K, precipitates thoria quantitatively from a neutral solution, the reaction being expressed by the equation:

$$Th(NO_3)_4 + 4N_3K + 2H_2O = 4KNO_3 + ThO_2 + 4N_3H$$

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[1] *Compt. rend.* 1898, **126**, 340.

[2] Abstract in *J. Soc. Chem. Ind.* 1909, **28**, 625.

[3] *Zeitsch. anorg. Chem.* 1897, **13**, 412.

Cerium, however, if present, is always precipitated with the thorium, and cannot be removed by re-precipitation; this fact, together with the cost of the reagent and the difficulty of obtaining it pure, renders the method quite useless for mineral analysis.

Numberless experiments have been made with organic acids in the hope that an easy method of separation might be found, but though some useful results have been obtained, precipitation has always to be effected in neutral solution, so that all such processes involve the tedious preliminary work of which an outline has been given above. Metzger[1] finds that a quantitative separation of thorium can be effected from a solution in 40 per cent. alcohol by use of fumaric acid; a second precipitation is needed to secure the complete removal of the cerium elements. Neish[2] uses meta-nitrobenzoic acid, which precipitates the thorium salt from a boiling solution; cerium earths, if present, are carried down in small quantities, and are removed by dissolving the precipitate in dilute nitric acid, adding a further quantity of the organic acid, and treating carefully with ammonia to almost complete neutralisation. The compound obtained by this second precipitation is the pure thorium salt. More recently, Smith and James[3] have shown that sebacic acid gives a quantitative precipitation of the thorium salt, from boiling neutral solution, as a voluminous granular precipitate, readily filtered and washed; sebacic acid is very sparingly soluble in cold water, but dissolves readily at 100°, and since, in virtue of this property, it can be readily recovered after use, the authors suggest it as a suitable reagent for the technical separation of thorium from monazite. In all cases where thorium is precipitated as an organic salt in quantitative analysis, the precipitate is dried and ignited, and the residue weighed as the pure dioxide.

An interesting method has been worked out by Giles.[4] If pure moist lead carbonate be stirred into a neutral solution of rare earth compounds, thoria is completely precipitated.

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[1] *J. Amer. Chem. Soc.* 1902, **24**, 275 and 901.

[2] *Ibid.* 1904, **26**, 780.

[3] *Ibid.* 1912, **34**, 281.

[4] *Chem. News*, 1905, **92**, 1 and 30.

Only the tetravalent elements are separated by this method, so that if ceric compounds are present, they must first be reduced by means of sulphuretted hydrogen or sulphur dioxide; zirconium, if present, must afterwards be separated from the thorium. One precipitation is said to ensure almost complete separation from the trivalent elements. The precipitate is collected, washed, and dissolved in hydrochloric acid; after filtering, if necessary, the solution is saturated with sulphuretted hydrogen, to ensure complete removal of the lead, and thorium hydroxide is then precipitated by ammonia. The drawback to this method lies probably in the fact that it is necessary to use absolutely pure lead carbonate, a substance which, as the author's elaborate process of purification seems to show, could not be obtained very cheaply on a large scale.

An account has recently been published[1] of a volumetric method for the estimation of thorium. The mixed oxides are dissolved in concentrated acetic acid, and the solution titrated with a standard solution of ammonium molybdate. This reagent effects complete precipitation of thorium, but does not react with compounds of the cerium elements; excess of the molybdate is shown by a solution of diphenyl carbazide, $CO(NH{\cdot}NH{\cdot}C_6H_5)_2$, used as an external indicator. The carbazide, which is obtained by the action of phenyl hydrazine on urea, has the property of producing definite, though evanescent, colourations with compounds of many of the metallic elements; a drop of the working solution, brought into contact with a drop of the carbazide solution, shows a deep rose colouration when excess of ammonium molybdate is present.[2]

The iodate process of Meyer and Speter[3] has the great advantage that it is carried out in a strongly acid solution, so that here the tedious purification from phosphoric acid is no longer necessary. After decomposition of the mineral with sulphuric acid, the sulphates are extracted with water, and a suitable quantity of nitric acid added; the solution is then

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[1] Metzger and Zons, *J. Ind. Eng. Chem.* 1912, 4, 493.

[2] *Vide* Skinner and Ruhemann, *Trans. Chem. Soc.* 1888, 53, 554; also Cazeneuve, *Compt. rend.* 1900, 131, 346.

[3] *Chem. Zeitg.* 1910, 34, 306. See also *Zeitsch. anorg. Chem.* 1911, 71, 65.

treated with a nitric acid solution of potassium iodate, and the thorium iodate which separates is dissolved in concentrated nitric acid, and re-precipitated to remove traces of the cerium elements. The iodate, after washing, is dissolved in hydrochloric acid, and reduced by sulphur dioxide; the hydroxide is then precipitated by ammonia. Since zirconium is also thrown down under these conditions, the hydroxide is dissolved in hydrochloric acid; pure thorium oxalate is precipitated from this solution by oxalic acid, and is ignited and weighed as oxide, in the usual manner. Since ceric iodate is also insoluble in dilute nitric acid, it is necessary to reduce any ceric compound which may be present before the iodate treatment by the usual methods.

Another method which can be carried out in acid solution is based on the insolubility of the hypophosphite, $ThP_2O_6,11H_2O$, in dilute acids.[1] To the boiling acid solution, an aqueous solution of sodium hypophosphate, $Na_2H_2P_2O_6,6H_2O$, is added drop by drop. The precipitate, which contains any titanium and zirconium present in the original solution, is best treated with a mixture of sulphuric and fuming nitric acids; the phosphates produced by the oxidation are freed from nitric acid by evaporation, dissolved in water, with addition of sulphuric acid, and thorium precipitated as the oxalate, which is then ignited as usual. This method has been suggested for the technical separation of thorium from monazite (*vide* p. 278). Since the precipitations by means of sodium hypophosphate and potassium iodate can be carried out with solutions obtained directly from the product of the action of sulphuric acid on the mineral, these two methods are probably more suitable for the rapid and accurate estimation of thorium for technical purposes than any of the others mentioned.

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[1] Wirth, *Zeitsch. angew. Chem.* 1912, **25**, 1678; see also Koss, *Chem. Zeitg.* 1912, **36**, 686, and Rosenheim, *ibid.* p. 821.

CHAPTER XIX

THE MANUFACTURE OF MANTLES FROM COTTON AND RAMIE

The fabric chosen for the manufacture of the original Welsbach mantles was a specially selected cotton, woven from threads of a specified thickness. The oxide skeleton left after burning off the impregnated fabric, however, showed many serious defects. Gradual shrinkage occurred during use, so that the mantle was gradually withdrawn from the hottest zone of the flame ; the contraction also resulted in crumpling, which caused the fragile fabric to fall to pieces. The light-giving power showed a gradual but continuous diminution, so that after a hundred hours, the decrease sometimes amounted to thirty per cent. of the original intensity. Lastly, owing to the fragility due to the torsion introduced by the twisting together of so many short fibres in the spinning of the fabric, the life of these mantles was very short, and their susceptibility to shock very great.

With the introduction of ramie, many of these defects disappeared. Mantles made from this fibre do not shrink continuously, nor to any considerable extent, so that crumpling does not occur ; the decrease in light-giving power is very much less than with the cotton mantles, the life is much longer, and the resistance to shock very much greater. Microscopic examination of the fibres, and of the ash left after burning off, shows that these differences are traceable to differences in the mechanical structure of the two fabrics. The cotton thread is spun from a very large number of very short fibres, which are twisted together, whereas the separate fibres of ramie are of much greater length, and the torsion in the thread correspondingly less. In the case of artificial silk, continuous filaments are spun into threads, and this simple fact accounts for the very much greater durability and elasticity of mantles made from this fabric.

The introduction of ramie for the manufacture of mantles effected no great alterations in the processes employed in the case of cotton ; the treatment of artificial silk, however, requires a profoundly modified method, and in consequence the preparation of this fabric and the manufacture of mantles from it, are considered separately in another chapter. Though the manufacture of artificial silk was first commenced in France, it is in Germany that its adaptation to the incandescent mantle industry has been successfully effected. Its adoption, however, has not yet become general, and by far the greatest number of mantles are to-day made from ramie. In the United States, where the early working of the monazite deposits gave a great impetus to the industry, the manufacturers still cling largely to the older methods, so that even now quite a considerable number of mantles are made from cotton.

In the present chapter, a short account will be given of the methods employed in the manufacture of mantles from ramie and cotton. The general methods of preparation of cotton fabrics are well known. Ramie is prepared from the tschuma plant, which is found in India, China, and other parts of Asia. The fibre is obtained from the inner side of the bark ; this is dried, pressed into bales, and exported. After removal of gum and resin, by heating with sodium hydroxide solution under pressure, the fibre is bleached, dried and cleaned, and then combed and spun in the usual manner.[1]

Washing.—The influence of even small quantities of impurities on the intensity of the light emitted by a mantle is remarkably great, and the manufacture requires a degree of care and attention far beyond that needed in ordinary technical processes. Washing of the fabric in particular

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[1] For the preparation and technical uses of Ramie, or Rhea, as it was formerly called, *vide* Cross, 'The Industrial Uses of Cellulose,' in the *Cantor Lectures of the Society of Arts*, 1897, vi, p. 20.

must be very thorough and careful, if a mantle of reasonable quality is required. If the mineral content of the fabric, *i.e.* the ash left on incineration, amount to more than 0·03 per cent. of the total weight, the quality of the mantle is seriously affected. Particularly is this the case if even the smallest traces of iron come in contact with the fabric; on this account wooden implements must be used as far as possible in the washing house, and all iron parts must be carefully protected so that no water can drip from them on to the material.

The fabric is used in the form of a long cylindrical tube usually of about twice the diameter required for the base of the finished mantle. Before the mineral impurities can be removed, this must be entirely freed from grease. It is therefore washed thoroughly with a warm solution of sodium carbonate, which removes all the hydrolysable fats. If paraffin or other non-hydrolysable grease is present, the alkaline wash must be followed by a soap wash. The fabric is now cleansed from alkali and soap by running water, and mineral impurities are removed by treatment with dilute hydrochloric acid (1–3 per cent.) at a temperature of 50°–60°C.; it is finally washed free from acid with distilled water. So susceptible is the mantle to traces of impurity that the use of ordinary tap water, or even of a distilled water which has become contaminated to the smallest degree, for this final washing, will considerably lower its efficiency.

A centrifugal machine removes most of the water, and the drying is completed by passage over wooden rollers, through a small chamber, of which the air is kept at 30°–40°C. The dried fabric is now cut into lengths ready for the next process.

Impregnation.—The composition of the 'Lighting Fluid,' as the solution of salts used for impregnation is technically termed, varies slightly according to the nature of the mantle required, and the conditions of washing. It is of the greatest importance that the ratio of thoria to ceria should be constant and definite; the usual proportions are chosen so that the ratio of the oxides is 99 : 1. Fig. 11 shows at a glance to what a remarkable extent small variations in the percentage of ceria affect the luminosity of the finished product.[1] The thorium nitrate is made up with distilled water to a solution of 25–35 per cent. strength, and the calculated quantity of a standard solution of cerium nitrate is added. It is usual to add to the mixture a small quantity of another nitrate, which on ignition will leave an oxide of which the function is to strengthen the skeleton of ash. Beryllium, zirconium, magnesium, or aluminium nitrate is usually employed, in quantity calculated to leave an amount of oxide constituting about 0·5 per cent.

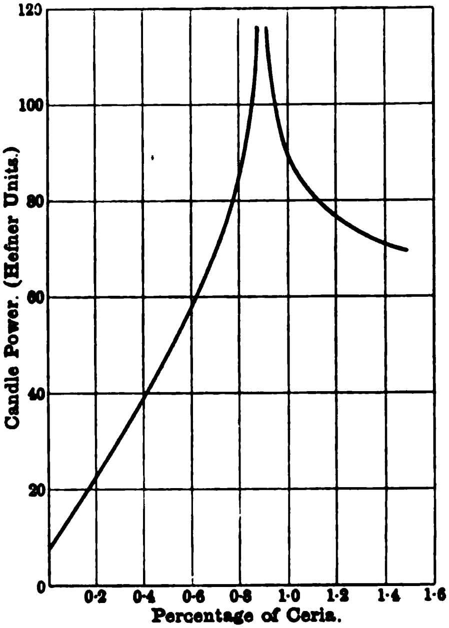

FIG. 11

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[1] Numberless theories have been advanced to account for the extraordinarily high light-emitting power of this particular mixture of thoria and ceria. An account of these would be beyond the province of the present work; the reader who desires to pursue the subject should consult the interesting work of Dr. H. W. Fischer, *Der Auerstrumpf*, Ahren's *Sammlung*, 1906, vol. xi. *Vide* also Lévy, *L'Éclairage à l'incandescence par le gaz*, Paris, 1910, Ch. II; and Foix, *Thèse présentée à la Faculté des Sciences de Paris*, Paris, Gauthier-Villars, 1910.

The diagram is after Drossbach, *J. Gasbel.* 1898, 352.

of the total oxides; for ramie fabrics, beryllium nitrate is generally chosen.

After having been immersed for two to five minutes in the solution, the separate lengths are freed from excess of the lighting fluid by means of a small wringing machine. The pressure between the rollers must be regulated very exactly, since on the amount of solution taken up by the fabric will depend the mass of the oxide skeleton. The weight of oxides left after ignition should be 0·5–0·6 gm. for a 'normal' upright mantle of 9·5 cm. length, corresponding to 1·0–1·2 gms. of the nitrates, or, for a 30 per cent. solution, to 3·3–4·0 gms. of solution. The weight of the fabric before impregnation is approximately 5 gms. for cotton, 3 gms. for ramie, and 1·5 gms. for artificial silk. A cotton mantle-fabric, therefore, must be allowed to retain rather less, a ramie fabric rather more, than its own weight of solution, whilst an artificial silk fabric must take up 2–2½ times its own weight of the fluid. The weight of the oxide ash left from these quantities has been found by experience to be most suitable; if the mass is greater than this, the light-emission is diminished without a compensating gain in strength; if it is less, the light-emission is indeed greater, but the mantle becomes too fragile.

The impregnated fabric-lengths, after passing through the wringing machine, are drawn singly on to glass forms which are arranged on stands, and freed from moisture in a drying room by hot air, a temperature of about 30°C. being maintained. Three to four hours are required, under these conditions; if the drying be too rapid, considerable shrinkage occurs, and the mantles obtained are then extremely fragile.

The Mantle Head.—The normal upright mantle is supported from a central rod of compressed magnesia—fused quartz has recently been suggested[1]—by means of an asbestos thread. The thread in the older patterns was supported by simply doubling over the fabric at the end which was to become the head; more generally, however, a strip of tulle or gauze is sewn to the head end before the impregnation. In order to

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[1] *Vide D. R. P.* 244959, March, 1912.

strengthen the head, it is treated before 'finishing' with a hardening or 'fixing' fluid, which usually consists of a mixture of magnesium and aluminium nitrates in aqueous solution; the following may be cited as a typical mixture: Aluminium nitrate, 300 parts; magnesium nitrate, 300 parts; chromium nitrate, 3 parts; borax, 5 parts; distilled water, 1500 parts. In order to secure that this fluid is applied to the head only, a little organic colouring matter is generally added, so that it may be clearly seen. The solution is soaked on to the head from mechanically held felt pads, which are kept at a convenient degree of saturation with the fluid by means of an ingenious compressed-air device. The mantle is then rapidly dried in a hot-air chamber.

After the fixing and drying processes, the head is 'finished.' The ordinary upright mantle is sewn together, at the end which has been treated, with carefully selected asbestos threads, an opening of some ten millimetres being left, and the asbestos is threaded diametrically across this opening—these diametrical threads support the mantle on its rod during use. These operations were formerly done by hand, when mantles of good quality were required, but machine treatment is gradually coming into extended use. Several mantles now on the market are supported at the head by metal rings, made from thin sheets of iron which have been plated with aluminium. In petroleum lamps, the mantle is usually supported from both sides by means of asbestos threads.

In the case of fabrics from which 'inverted' mantles are to be made, fixing is carried out as usual at one end, to a depth of about 1·5 cm. After drying, a strip of about 0·5 cm. width is bent over and sewn down, and through this double band an asbestos thread is drawn, by which the mantle is secured to a magnesia ring. The lower end is drawn together in the shape of a hemisphere, by means of threads drawn through the meshes of the fabric; an opening of 6–8 mm. is sometimes left, but in the more modern patterns the end is drawn almost completely together, and after cutting is pressed out on a wooden shaper by a wooden mallet.

The product is now ready for burning off; if it is to be marked, it is stamped at this stage with a solution of didymium nitrate and methylene blue; the former being only faintly coloured, the organic dye is added to give a definite impression. On ignition, the nitrate is converted into the oxide, which is deeply coloured, and, of course, permanent.

Burning off and Shaping.—For the production of mantles of the best quality, these processes are usually carried out by skilled operators, each mantle being treated separately. Very frequently, however, mechanical arrangements are employed. The great objection to machine treatment of such a product lies in the fact that it must be identical for every mantle; whereas it is exceedingly difficult to ensure that the original fabric, and the processes of washing, impregnating, wringing, and drying have been absolutely uniform. The operation of shaping and hardening is a very delicate one, and on the care with which it is carried out, the quality of the mantle finally depends. Until quite recently, only the cheaper kinds of mantles were machine-treated; but as the uniformity of the fabric becomes more assured, and the earlier operations more exact, employment of machines at this stage will undoubtedly increase.

The prepared fabric is shaped on a suitable form, and removed by a holder, which supports it from the asbestos thread; a flame is then applied to the head. The burning-off proceeds readily, once started; when the upper half has been incinerated, the flame is removed. The weight of the unburnt portion prevents too rapid contraction taking place at first; when the flame is removed, the glow spreads slowly downwards, and the shrinking is thus kept as uniform as possible. The operation must be carried out under a ventilating hood. The organic material of the fabric is completely oxidised, and the nitrates are converted into oxides, which retain the exact shape of the original fibres. The skeleton now undergoes the process of shaping and hardening, for which a 'radial' blowpipe flame is used. The burnt-off product is placed over this; the gas is supplied at an initial pressure of only a few inches of water, which is increased towards the end of the operation. The process commences at the head, the mantle being slowly lifted and rotated so that it is shaped and hardened along the whole length. By this means the oxide skeleton is not only suitably shaped, but is rendered considerably more elastic and resistant. For inverted mantles, of course, specially shaped burners are required. The eyes of the operators must be protected from the glare by shades of green glass. Recently the processes of burning-off and hardening have been carried out by means of the same burner.

Where machines are employed, the prepared fabrics are burnt off on wire shapers, usually in rows of ten ; mechanical arrangements for continuous ignition and motion and, in the hardening, for continuous elevation of the ash-skeleton, are in use, but the finished mantles maintain a uniform good quality only when the structure of the fabric and the earlier processes have been absolutely uniform.

Collodinisation.—The burnt-off mantle is now ready for use, but is far too fragile for transport. A method has therefore to be found by which the finished product can be protected for a time without detriment to its use for illumination. Mantles of artificial silk, particularly those for use in high-pressure lamps, are sometimes sent out without having undergone the final processes of burning off and shaping, which, in this case, must be carried out on the consumer's burner. ‘ Inverted ’ mantles also were formerly sent out after impregnation and drying. In this condition, of course, the mantles are readily packed and transported, and there is the additional advantage that the duty on the unburnt product is very much less than that on the finished mantle.

One of the earliest of Auer's patents (*vide supra*, p. 271) protected the process of collodinisation, which is now extensively employed. The oxide skeleton is dipped into a solution of collodion (the mixed lower nitro-derivatives of cellulose, or cellulose nitrates) in a mixture of alcohol and ether, to which, to prevent shrinkage on drying, a little camphor is added. On account of the inflammability of the mixture, the ethyl alcohol and ether are occasionally replaced by a mixture of methyl alcohol and acetone, but with this less volatile mixture, drying of course is slower. After dipping, the solvents are removed in a current of air, leaving the mantle coated with an exceedingly thin film of collodion, which increases enormously its power of resisting shock and vibration. This film is not removed until the mantle is placed on the consumer's burner, when on the application of a match it ignites instantly and burns away, leaving the oxide skeleton in the condition to which it was brought in the final stage of hardening and shaping in the factory. The process is now used for almost all kinds of mantles, having been successfully applied in Germany in recent years to those made from artificial silk. The addition of small quantities of various inorganic salts, *e.g.* nitrates of zirconium, magnesium, platinum, thorium, etc., to the collodion solution, has been proposed; these salts make the collodinised product extremely resistant, but have a very harmful effect on the oxide ash when the collodion has been burnt off.

The collodinised mantles are cut to length on a trimming machine, and are then ready for packing.

The present chapter may be concluded with a bare mention of a few disconnected details, selected from the great mass of proposals, suggestions, and developments which have sprung up round the incandescent mantle industry.[1]

With regard to the composition of mantles, numerous proposals have been made. It is stated that thoria with 0·25 per cent. of uranic oxide, UO_3, gives a light almost equal to that of the Auer mantle. Zirconia with 0·40 per cent. of vanadium, in the form of the pentoxide, is said to give a splendid white light; the vanadium oxide slowly volatilises, but addition of an equivalent proportion of silica is said to prevent this. Langhans claims to have obtained a product equal in light-giving power to the Auer mantle, by using as impregnating fluid a solution of colloidal silica, obtained by the addition of nitric acid to a solution of sodium silicate, to which suitable quantities of rare earth nitrates are added. Bodies obtained by the use of very similar solutions give

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[1] For a complete account of the mechanical developments, the reader is referred to the monograph 'Beleuchtung und Lichtmessung,' by Dr. Börnstein, in Dammer's *Chemische Technologie der Neuzeit*, Stuttgart, 1910–11, ii. 243–266.

skeletons which are coming into extended employment for gas radiators. The 'Sunlight' mantles use a mixture of thoria (50 per cent.), alumina (40 per cent.), and chromium sesquioxide (10 per cent.).

A direction of development in which some success has been attained is the introduction of self-lighting devices. The catalytic action of finely divided metals has been proposed in innumerable patents,[1] but these devices are unreliable, and it seems doubtful if chemical methods will ever be successfully applied to the problem. For the lighting of streets, shops, etc., the 'by-pass' system is employed; a tiny jet of gas burns continuously from a pin-hole nozzle, which is momentarily increased, when the main supply is turned on, to such an extent that the gas issuing from the burner is ignited.[2]

An account of the innumerable forms of lamps and burners which have been introduced in the last twenty years would fill several volumes. The theoretical grounds on which improvements in this direction are based are outlined in an able article by Dr. H. Bunte, a recognised authority on incandescent lighting, which appeared recently;[3] for an account of some of the lamps which have been successfully applied, the reader is referred to a recent French publication.[4]

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[1] *Vide, e.g. D. R. P.* 158974 and 253550; *F.* 417934.

[2] For automatic regulators for self-lighting, *vide J. Gasbel.* 1910, **53**, 490.

[3] *J. Gasbel.* 1911, **54**, 469; *vide* also Pickering, *J. Gaslighting*, 1911, **113**, 156.

[4] *L'Éclairage à l'incandescence par le gaz*, Lévy, Part I. Ch. III.

CHAPTER XX

ARTIFICIAL SILK—ITS PRODUCTION AND USE IN THE MANTLE INDUSTRY

The history of the artificial silk industry, since its foundation about the year 1890, illustrates curiously the rapidity with which isolated facts, of apparently merely academic interest, are seized upon and adapted to the needs of modern civilisation. It is during this period, especially, that the bonds between science and industry, in a dozen different directions, have been drawn so close that to-day it is in many cases impossible to differentiate the two. The pure science of to-day is the technology of to-morrow—and not always even of to-morrow, but of to-day. But we have moved even beyond this ; the industrial needs of the day are creating and extending our science at a rate which shows how relatively poor a stimulus has been the mere desire for knowledge. Such has been the history of the artificial silk industry. No sooner had Chardonnet shown that the preparation of a new fabric was not only possible but profitable,than a thousand aspects of the problem were taken up. Patents were taken out on all sides—the majority, as usual, valueless, one or two of great importance. Companies were formed, factories built, machines invented ; numberless applications were proposed, mostly again worthless, whilst patient research and innumerable experiments have carried one or two suggestions to a successful place in practice. Among these has been the adaptation of artificial silk to the manufacture of mantles, which will be outlined in the present chapter. Before taking up this question, however, a short account of the manufacture of the fabric itself must be given.

Chardonnet Process. — In the Chardonnet process, an account of which was published about 1890, continuous fibres are obtained by forcing through tiny jets a viscous solution of collodion, or nitrocellulose, as it has been misnamed, in a mixture of ethyl alcohol and ether. In the original form of the process, the solution was forced into water, which, by removing the alcohol and ether, caused an instantaneous coagulation of the surface, so that a filament was obtained which could be wound directly on to a spool. More generally, however, the jets deliver the solution into a chamber through which warm air is passed ; this is equally effective in removing the solvents and causing surface coagulation, and the filaments are woven directly into threads of ten to forty strands, according to the purpose for which the fabric is required, fifteen to twenty being used for silk from which mantles are to be made. On account of its inflammability, the thread is denitrated by means of a solution of ammonium sulphide.

The raw material for the process is cellulose, usually in the form of cotton. Treatment of this with a suitable mixture of concentrated sulphuric and nitric acids replaces some of the hydroxyl groups by the 'nitrate radicle,' NO_3, a mixture of various nitrates of cellulose being formed, in which the so-called tetra-, penta-, and hexa-nitrates predominate.[1] The product, cellulose nitrate or collodion, very closely resembles the original cellulose in appearance and structure. It is washed thoroughly to free it from traces of acid—which render it liable to explode spontaneously—and after drying, dissolved in the minimum quantity of the mixed solvents ;[2] the solution is filtered from insoluble impurities through wads of cotton, pressures of thirty to sixty atmospheres being required. This filtration purifies and thoroughly mixes the solution, so that perfect uniformity is obtained in the product. The glass jets

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[1] The cellulose esters are usually named as if they were derived from a compound $C_{12}H_{20}O_{10}$, the formula for cellulose being $(C_6H_{10}O_5)_n$. Thus the formation of the 'hexa-nitrate' would be represented—

$$C_{12}H_{20}O_{10} + 6HNO_3 = C_{12}H_{14}O_4(NO_3)_6 + 6H_2O.]$$

[2] In the Lehner process, in which collodion is also used, larger quantities of solvent are employed, so that much more dilute solutions are obtained; these require low pressures to form the thread, which is then hardened chemically.

through which the solution is now forced, under a pressure of forty to fifty atmospheres, have a diameter of 0·08 mm., but the threads obtained contract on the removal of the solvents, so that fibres of 0·01–0·02 mm. are formed.

Chardonnet probably began his work about 1885. It is interesting to observe that an Englishman, Swan, had proposed in 1883 to use a solution of collodion in acetic acid, fabrics prepared by his process being shown at the London Exhibition of 1884.[1]

The Pauly or Cuprammonium Process.[2]—It has long been known that a solution of copper hydroxide in ammonia solution —Schweitzer's reagent—will dissolve cellulose. The use of this solvent for the production of artificial silk was proposed about 1900, and the method has become a serious rival of the older Chardonnet process. The solvent is prepared on a large scale by passing air through an ammonia solution to which copper turnings have been added. After addition of the cellulose, and filtration, the solution is forced through tiny jets into a bath of dilute acid, which removes the copper and precipitates the cellulose again.

The solution of cellulose by Schweitzer's reagent is undoubtedly a chemical action. Cellulose is to be regarded as a polyhydric alcohol, with one or several atoms of hydrogen of the hydroxyl groups replaceable by metals. According to Piest (*loc. cit.*) a 'Cupramine base' is formed by the replacement of this hydrogen by copper and the amino-group, NH_2. The action of sodium hydroxide on cellulose, however, is generally regarded rather as an additive reaction, the product, 'alkali cellulose,' being usually written $C_6H_{10}O_5,NaOH$. A careful chemical investigation alone can reveal the actual nature of the compound formed; such an investigation, apart from its scientific interest, might yield results of considerable technical importance.

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[1] *Vide* Böhm, *Zeitsch. angew. Chem.* 1912, **25**, 657. There is no account of this process in the English patent literature.

[2] A full account of this and of the other processes employed in the manufacture of artificial silk will be found in the work of Piest, *Die Zellulose*, Stuttgart, 1910.

The Viscose Process.—Shortly after the introduction of the Chardonnet process, patents were taken out which protected a very cheap and simple method of dissolving cellulose,[1] which had been discovered by two well-known English authorities, Cross and Bevan. They found that mercerisation, *i.e.* the action of the sodium hydroxide on cellulose, produces a swollen, transparent mass, which very readily takes up carbon disulphide. When exposed to the action of this liquid for three or four hours, at ordinary temperatures, the mass swells further, gelatinising and becoming soluble in water. On treatment with water, a yellowish, extremely slimy solution is obtained, from which cellulose is precipitated on prolonged standing, by heating, or by oxidation. The substance is apparently a cellulose xanthate, and may be written $NaS \cdot CS \cdot O \cdot C_6H_9O_4, NaOH$.[2] On account of the extremely viscous nature of the aqueous solution, Cross and Bevan gave it the name Viscoid.

During the last few years this method of dissolving cellulose has been employed in the manufacture of artificial silk, under the name 'Viscose Process.' The product obtained is very suitable for the manufacture of incandescent mantles, and is considerably cheaper than either the Chardonnet or Pauly silk.

The Acetate Process.—Quite recently numerous experiments have been carried out with the object of finding methods for employing the cellulose esters of organic acids in the preparation of fabrics. The acetate, which is generally used, gives solutions from which fibres can be obtained which are comparable to natural silk in strength, and which have the further advantage of being non-inflammable, and far less readily affected by water than artificial fabrics obtained by the above methods. It is prepared by treating cellulose with dilute acid, by which the so-called 'hydrocellulose' is obtained; this is treated with a mixture of glacial acetic acid and acetyl chloride, and the whole, after addition of a little concentrated sulphuric

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[1] *Vide, e.g.* **Cross,** Bevan, and **Beadle,** *D. R. P.* 70999, **granted September, 1893.**

[2] *Vide* **Boltzer,** *Zeitsch, angew. Chem.* 1908, **21**, 1731.

acid, warmed to 65°–70° C. As early as 1894, Cross and Bevan[1] had patented a process for this preparation by the action of acetyl chloride in the cold on an intimate mixture of cellulose and zinc chloride.

From the solution obtained, the acetates are precipitated by water, washed and dried. The mixture of esters dissolves in chloroform, nitromethane, acetic acid, phenol, pyridine, etc., and is re-precipitated by addition of alcohol, benzene, or ligroin (petroleum ether). On account of its non-inflammable character, cellulose acetate, as the product is called, is being used instead of the nitrate in the manufacture of celluloid; it is also used for non-inflammable cinematograph films. Fibres can be obtained by forcing the solutions through jets, and removing the solvent, as in the above processes; these are spun into threads which are coming into increasing use, on account of their extremely low conducting power, for the insulation of very fine electric leads. The product is at present too expensive, however, for use in the textile industries, or for the manufacture of mantles.

A solvent which had at one time some technical importance is zinc chloride.[2] The concentrated aqueous solution of the salt will take up cellulose in considerable quantity; and the solution has been used in the preparation of carbon filaments for glow lamps.

The fabrics prepared by the processes which have been mentioned above are of great technical value. In lustre they far surpass natural silk, and they take dyes very well, but owing to the ease with which they tear, they cannot be woven alone for textiles, but are always used in 'mixed' materials. The acetate silk, which approaches the natural fibre in strength, is not much less expensive. Whilst the price of natural silk is roughly 35 francs per kilo. (approx. 13*s*. 3*d*. per lb.), the costs of production of the artificial fabrics are—Chardonnet 15 frs., Pauly 12 frs., Viscose 7 frs. per kilo. (respectively 5*s*. 8*d*., 4*s*. 6*d*., and 2*s*. 8*d*. per lb.). Artificial silk, however, has uses distinct

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[1] *E*. 9676, 1894.

[2] Gulbrandsen, *Prog. Age*, 1912, **30**, 77; Wynne and Powell, *E*. 16805, December, 1884.

from the natural fibre, and is at present a competitor with it in one or two small fields only. Thus the production of natural silk is ten times that of artificial silk (50,000,000 kilos. per annum to 5,000,000 kilos.) in spite of the difference in price.

Artificial silk is very susceptible to the action of water, which weakens it very considerably. Its resistance is said to be greatly increased by the action of formaldehyde ; the fabric is plunged into a bath containing an aqueous solution of the aldehyde, to which a little lactic acid has been added. The chemistry of the change is discussed at length by Beltzer (*loc. cit.*).

The threads of artificial silk far surpass in lightness those spun from vegetable fibres. A thread of twenty strands weighing one pound avoirdupois would be more than twenty miles long. At the same time the filaments have not the irregular tubular structure of vegetable fibres, but are solid cylinders. The fact that the filaments are continuous, so that there is relatively little torsion in threads spun from them, gives artificial silk its great advantage over the natural vegetable fibres for the manufacture of mantles. For this purpose the Pauly or Cuprammonium silk is most suitable, though Viscose silk is almost as good ; the fibre obtained by the Chardonnet process is not quite so useful in this direction.

The Manufacture of Mantles from Artificial Silk.—Whilst the fabrics made by the various processes outlined above are more expensive than the cotton and ramie formerly exclusively used in the mantle industry, they have the advantage, in addition to the fact that they produce better and more lasting mantles, that they do not need the laborious and troublesome process of washing which is so essential in the case of the vegetable fibres. From the nature of the methods used in its manufacture, artificial silk can contain no mineral residue ; hence the fabric is immediately ready for impregnation.

As early as the year 1892 Schlumberger and Sinibaldi proposed the use of Chardonnet silk for the manufacture of mantles ; but their patent, a Belgian one,[1] attracted little

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[1] *Vide* Böhm, *Zeitsch. angew. Chem.* 1912, **25**, 657. Apparently this patent was not taken up ; no account of it has been found in the published patents of the Belgian Government.

attention, although they stated clearly that the denitrated silk will readily take up the lighting fluid. Ignorance of this fact deferred the successful application of this fibre for ten years. In 1894 De Mare suggested the preparation of mantles by addition of the necessary salts to the collodion solution before squirting; in the following year Knöfler used the same process, recommending in addition the use of ammonium sulphide to denitrate the impregnated threads. These two attempts, which were found to be unworkable, owing to the difficulty of obtaining a homogeneous product before squirting, were merely efforts to compete against the Auer monopoly, resting on Welsbach's patents, which covered impregnation of any natural fibre. In Knöfler's process,[1] the salts were dissolved in alcohol and added to the collodion solution, which was then forced through jets into water, to which ammonia was added to prevent removal of the nitrates in solution; the threads were then denitrated with ammonium sulphide. The ammonia treatment of course converts the nitrates into the insoluble hydroxides, a departure which was followed in most of the numerous patents inspired by Knöfler's process.

The first indications of the method which ultimately led to success are to be found in a patent taken out by Plaisetty, in 1901.[2] The specification protects the addition of thorium and cerium hydroxides to the cuprammonium solution of cellulose, but apparently without any inkling of the results that were to follow, and more or less incidentally, he includes in this patent the impregnation of the finished fabric and the subsequent treatment with ammonia. In the following year he applied for a German patent,[3] which was granted in May, 1903, in which he definitely protects the impregnation of the finished fabric, and the ammonia treatment, the fabric being then washed and dried, and burnt off as usual.

Impregnation.—Since the filaments from which artificial silk is obtained are solid and rod-like in form, as opposed to the tubular structure of cotton and ramie filaments, it is rather surprising that the fabric should take up the lighting fluid

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[1] *E.* 11038, 1895, granted July, 1895.

[2] *E.* 20747, 1901.

[3] *D. R. P.* 141244.

in the necessary quantity (*vide* p. 295). It is found that a 50 per cent. solution of nitrates gives the best results, the impregnation requiring half an hour; a warm bath is usually employed. It is usual to add to the bath a quantity of thorium hydroxide, since the thorium nitrate of commerce generally contains nitric acid, which has a bad effect on the fabric.[1] The excess of solution is removed by means of a glass or porcelain centrifuge, not, as with cotton or ramie mantles, by use of a wringer; drying must be carried out very slowly. The fabric is not cut into lengths before impregnation, as in the case of cotton or ramie, but is immersed in the lighting fluid in long strips.

'Fixing.'—If the dried fabric, impregnated with the necessary salts, be finished and burnt off in the usual way, the oxide skeleton is extremely fragile, and soon falls to powder. The reason for this lies probably in the explosive decomposition of the nitrates, the weight of organic matter relative to the salts being very much less than in the case of ramie or cotton fabrics (*vide* p. 295). The additional ammonia bath advocated by Knöfler (*vide supra*) was therefore adopted by Plaisetty, and the nitrates in the dried impregnated fabric are converted into hydroxides by this treatment. For this process, to which the name 'Fixing' has been given by Böhm, numberless alternative proposals have been made. Plaisetty's ammonia fixing gives a mantle which, after burning off, is exceedingly elastic and strong, but it is nevertheless open to serious objections. Thus the nitrates may be to some extent dissolved out by the fixing bath before precipitation of the hydroxides has occurred; to remedy this, the impregnated fabric must be very thoroughly dried before fixing, and in this case, apart from the trouble involved, the acid of the commercial nitrates will attack the fabric unless addition of thorium hydroxide has been made to the impregnating fluid. Again, the conversion into oxides is not complete, the outer layer first formed preventing free diffusion of the alkaline fluid. Finally, since ammonium nitrate is formed in the reaction, a very thorough washing is necessary to remove this salt.

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[1] *Vide* Buhlmann, *D. R. P.* 188427, 1907; also *E.* 6828, 1907.

It would be impossible to mention all of the numberless proposals which have been put forward for fixing; nor are the great majority worthy of mention.[1] One of the most important was that of Albrecht,[2] by which hydrogen peroxide is substituted for ammonia. This reagent, as is well known, precipitates from solutions of thorium salts 'peroxide' compounds (*vide* p. 255); from the fabric impregnated with the nitrate, free nitric acid is liberated in the reaction. Since the peroxide is soluble in nitric acid, two baths are used, the fabric being allowed to remain for a short time only in the first, which becomes strongly acid, and being then transferred to the second, in which the precipitation is completed. The burning off of the product so treated proceeds quite quietly, and leaves a very hard and elastic skeleton. The method, however, has the grave disadvantage that cerium salts are not precipitated under these conditions, but escape into the solution. To remedy this, arbitrary additions of cerium nitrate are made to the fixing bath, but the percentage of cerium, and therefore the lighting power (*vide* p. 293) of mantles fixed by this method is liable to fluctuate. A modification has been introduced[3] in which various salts are added to the hydrogen peroxide fixing baths to prevent the withdrawal of the cerium salt; these are chiefly acetates of the alkali metals and allied compounds. The fabric requires washing after this treatment.

A rather similar proposal[4] substitutes for ammonia an alkaline solution of hydrogen peroxide, obtained by dissolving sodium peroxide in water. After saturation for a minute or so, the fabric is wrung out and dried, there being no necessity, according to the patent, for any subsequent washing. The same company in an earlier patent[5] suggest a fixing bath of 'an alkali or amine with an acid which can form insoluble basic double salts with the earth metals,' the said salt to be precipitated on the fibre, whilst an alkali or amine nitrate

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[1] A large number of patents are mentioned by Böhm, *J. Gasbel.* 1909, 52, 855.

[2] *D. R. P.* 188427, September, 1907; *E.* 15295, 1907.

[3] *Vide E.* 2240, 1908. Cerofirm Gesellschaft, by Brit. Cerofirm Co.

[4] *D.* 247940, June, 1912; *F.* 430417, August, 1911.

[5] *F.* 403433, September, 1909, Bruno Co.

goes into solution; acetic and benzoic acids and phenol are mentioned. Apparently this process did not give satisfactory results. The same may be said of the hypochlorite method of Visseaux.[1] Equally interesting, and doubtless equally practical is the proposal[2] to treat the dried impregnated mantle with ozone in a closed chamber, which possibly inspired the even more original suggestion[3] that the fabric be first washed in ozonised water, dried, then impregnated and dried, and finally treated with ozone. According to yet another French patent,[4] the impregnated and dried fabric is to be treated with an alcoholic solution of hydrofluoric acid, which will give a viscous insoluble mixture of thorium and cerium fluorides in the fabric, and at the same time will remove any impurities. Another patent[5] proposes the use of hydrazine and similar bases, cerium nitrate being added to the fixing solution.

Innumerable suggestions have been made for fixing by means of ammonia gas, or vapours of organic bases.[6] An English patent granted in February 1910[7] protects 'various improvements,' which consist in carrying out a preliminary treatment with steam, impregnation with the solution of nitrates, conversion of nitrates into oxides either by steam carrying ammonia, pyridine, etc., or by the action of these vapours without steam in a vacuum, all in one chamber, which can be exhausted or filled with various solutions or vapours as required.

More recently, the use of organic salts of thorium and cerium for impregnation has been proposed by Dr. F. W. Wirth;[8] in fixing the impregnated fabric with hydrogen peroxide, the cerium is not removed in solution, since the weak organic acid formed will not dissolve cerium peroxide. The same author has also suggested[9] the addition to the fixing bath of substances which absorb oxygen from the air—*e.g.* sodium hydrogen sulphite, resorcinol, tannin—to prevent removal of cerium. He has also advocated impregnation with amorphous salts,[8]

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[1] *F.* 408807, February, 1910.

[2] *F.* 414700, June, 1910.

[3] *F.* 422643, January, 1911.

[4] *F.* 426156, April, 1911.

[5] *E.* 11904, 1909.

[6] *Vide*, *e.g.* *D. R. P.* 199615 of June, 1908.

[7] *E.* 25549, 1908.

[8] *Chem. Zeitg.* 1911, **35**, 752.

[9] *Zeitsch. angew. Chem.* 1912, **25**, 922.

which will obviate the necessity for any subsequent fixing treatment, the hypophosphites and double compounds with ammonium oxalate being specified. Attempts have been made to achieve the same end by other methods. Thus Silbermann[1] has proposed a preliminary treatment with alkalies (mercerisation); the fabric is treated with concentrated sodium hydroxide solution in absence of air for half an hour, pressed through rollers, and plunged into the impregnating solution. Two years previously a patent was taken out by Drossbach[2] to protect the use of colloidal solutions of the hydroxides. To a boiling suspension of well-washed, freshly-precipitated thorium hydroxide, a solution of a small quantity of the nitrate is gradually added; after half an hour a colloidal solution is obtained, which, after the addition of the required quantity of cerium nitrate, and dilution to a suitable extent, is employed directly for impregnation. The patent states that this solution is more readily absorbed than the ordinary nitrate solution, but the statement has been questioned.

Artificial silk itself is of a colloidal nature, the solidification of the filaments of cellulose during the manufacture being rather in the nature of a coagulation than of a precipitation; it is to this fact that the fibres owe their solid, rod-like structure, and it is probably this circumstance also which determines the very intimate absorption of the hydroxides or peroxides produced by fixing. It is well known that colloidal substances under some circumstances possess the property of clinging tenaciously to foreign bodies, exhibiting the so-called phenomenon of adsorption. The strength and elasticity of the oxide skeleton, obtained when the fixed and dried fabric is subjected to the operation of burning off, are presumably to be referred to such a relation between the cellulose of the fibres and the insoluble thorium and cerium compounds, precipitated by one of the methods of fixing described.

The Final Stages. — The treatment of the fabric after impregnation and fixing differs only slightly from that used

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[1] *Chem. Zeitg.* 1911, **35**, 1037.

[2] *D. R. P.* 212842, August, 1909; *vide* also Kreidl and Heller, *E.* 17862, 1909, and *D. R. P.* 228203, 1910.

for the impregnated ramie and cotton products. The dried strips are cut into suitable lengths, and the head is drawn together with asbestos and threaded across. No tulle or gauze is required, the end being simply turned down before threading. After the ordinary strengthening process for the head (*vide* p. 296) the process of manufacture was, until recently, finished, the goods being sent out in the unburnt condition, on account of the difficulties of collodinisation. These have now been overcome, so that the mantles are burnt off and collodinised as usual. Burning off and shaping are now frequently effected in one operation by machine; the nature of the methods by which the fibre is made produces a uniform fabric, and if the earlier processes are carefully carried out, a uniform product is obtained, which is therefore suitable for machine treatment.

CHAPTER XXI

OTHER TECHNOLOGICAL USES OF THE CERIUM AND YTTRIUM ELEMENTS, ZIRCONIUM AND THORIUM

The technical uses of the members of this group of the elements we are considering, apart from the employment in the manufacture of incandescent mantles, are at present very restricted. Innumerable proposals for the employment of the compounds of cerium and the allied metals, which are obtained in such large quantities as by-products in the thorium industry, have been put forward, but the actual extent to which they are utilised is so small that only an insignificant fraction of the available quantities is annually required. In the metallic form, a limited application is found for various alloys, *e.g.* the so-called pyrophoric alloys, misch metal, and the magnesium and aluminium alloys. Various compounds of the elements, as well as some alloys, have been suggested for use in arc-lamp electrodes, and the use of the metals themselves, as well as of various salts, for the manufacture of flashlight powders, is protected by several patents. Investigations have been made to determine the value of the oxides and sulphates as catalysts in the contact process for the manufacture of sulphuric acid, and one patent states that the yield obtained is equal to that given by platinised asbestos. Cerium salts have been proposed for tanning, and in the preparation of enamels; cerium sodium sulphate is used in the catalytic oxidation of aniline to aniline black. The oxalate has a very slight use in medicine. The oxidising power of ceric salts is of some use in photography; ceric sulphate in acid solution is also said to be an efficient oxidising agent for aromatic hydrocarbons. On account of the deep colour of the higher oxide of praseodymium, didymium salts find a limited application for marking textiles.

Compounds of the yttrium group have at present no technical importance. They were formerly used to some extent for the manufacture of filaments for Nernst lamps, but with the introduction of metal filament lamps in electric lighting, the demand for Nernst lamps and consequently for the yttria oxides, has to a very great extent died away.

Zirconium and its compounds, on the other hand, promise to become of some technical importance. The metal received considerable attention in the earlier stages of experimental work on metallic filaments for electric lighting, but it has been shown that its melting-point is not sufficiently high to allow of extended use in this direction. The carbide has been proposed for the same purpose, but is even less suitable ; this compound, however, on account of its great hardness, is likely to find employment as an abrasive, and in glass-cutting. The oxide, which occurs in nature in an impure form as the mineral Baddeleyite (*q.v.*), is employed in the manufacture of 'Siloxide' glass and of enamels, as a pigment and polishing agent, and in various forms of lamps, *e.g.* the Nernst and Bleriot lamps, the Drummond light, etc. Far more important, however, is its use for fire-resistant crucibles, furnace linings and supports, etc., for which its refractory nature renders it particularly suitable. On account of its high specific gravity and non-poisonous character, it has been proposed for use in the Röntgen ray examination of the human body. Quite recently, metallic zirconium has been employed in metallurgy ; addition of small quantities, in the form of suitable alloys, is said to secure sound castings, with increased strength and resistance to acids.

THE CERIUM GROUP

Pyrophoric Alloys. — It has long been known that the metals of the cerium group possess the property, when scratched or struck, of throwing off glowing particles ; this power of emitting sparks is not lost when the metals are alloyed, so long as the percentage of foreign metal is not allowed to become too high. In a patent[1] protecting the use of various 'pyrophoric alloys,' as these spark-giving alloys are called, Auer states that the pure metals do not show this property, which only appears when foreign metals are present; he accordingly patents alloys of the cerium metals with iron, specifying particularly the alloy with 30 per cent. of the latter element. Auer's statement has been contradicted,[2] and it seems to be generally accepted that misch-metal[3] of ordinary technical purity has the property of sparking when scratched. This alloy of the cerium metals, however, is far too soft to be useful for the purpose, and the addition of some foreign element is required to obtain the strength, hardness, and brittleness necessary in the various forms of 'lighters.' Besides the addition of iron, the use of tin, lead, zinc, cadmium, silicon, etc., has been patented.[4]

Various forms of these lighting devices are manufactured;[5] in all of these the sparks produced by scratching the pyrophoric alloy with hardened steel, by means of some simple mechanical device, is caused to ignite a fragment of tinder, or a wick supplied with a suitable liquid, *e.g.* methyl alcohol, benzene, or petrol. In the numberless forms of cigarette-lighters at present before a somewhat indifferent public, the friction is obtained by means of a toothed wheel, actuated by a spring which is released when the device is opened. Many forms of gas-lighter are also on the market, but the demand for them is very small. Many attempts have been made to adapt the device to the ignition of the Davy miners' lamp, but none have been successful, since it is impossible to prevent the sparks flying through the gauze. Much work has also been spent in efforts to utilise the pyrophoric alloys for the automatic ignition of incandescent gas-lamps, but these have been equally

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[1] *E.* 16853, 1903; *D. R. P.* 154807.

[2] *Vide* Böhm, *Chem. Zeitg.* 1910, **34**, 361.

[3] The crude mixture of cerium, lanthanum, neodymium, praseodymium, samarium, etc., with small quantities of iron and other metals, obtained by reduction of the earth-compounds formed as by-products in the thorium industry, is technically known as 'misch-metal.'

[4] *F.* 439058, March, 1912.

[5] *Vide* Böhm, *Chem. Zeitg.* 1910, **34**, 377; also Kellermann, *Die Ceritmetalle und ihre pyrophoren Legierungen*, Wilhelm Knapp, Halle, 1912, pp. 94 *et seq.*

unsuccessful, so that it may be said that important technical applications of this interesting property have still to be made.

Auer prepared his alloys by addition of iron, or other heavy metal, to the fused mixture of cerium metals obtained in the electrolytic apparatus employed for the production of the latter. They can, however, be prepared by fusing together the required quantities of foreign metal and misch-metal, the latter being obtained by processes other than those of electrolysis usually employed. The rare metals were obtained by the earlier chemists in a very impure state by reduction of the halogen or double halogen compounds with sodium or potassium. More recently[1] much purer products have been obtained—especially in the case of zirconium—by the action of metallic calcium, in the form of powder, on the oxides. Another method,[2] which has been employed in the preparation of metallic filaments for lamps, consists in heating the oxides with powdered magnesium in an atmosphere of hydrogen or nitrogen; by this means, hydrides or nitrides are obtained, which on heating decompose into the gas and the metal.

The ease with which misch-metal and its alloys with iron and other elements throw off glowing particles when struck is due to the low ignition temperature of cerium, and the energy with which it combines with oxygen. When such alloys are scratched, small fragments are struck off, which are raised to the ignition temperature by the heat of friction. It is generally accepted, however, that this explanation is by no means a complete one, and the existence of a pyrophoric suboxide was suggested.[3] The theory was advanced that the pyrophoric properties of the alloys were due primarily to the formation on the surface of a film of this sub-oxide, and the partial oxidation of cerium alloys, protected by patent (*loc. cit.*), was said to cause a marked increase in the ease with which sparks could be obtained. In this connection, an experiment of Hirsch, who has thoroughly investigated the properties of metallic cerium,[4] is of interest. He found that when the element

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[1] *Vide* Kuzel and Wedekind, *E.* 23215, 1909.

[2] *Electrodon Gesellschaft, D. R. P.* 154691, September, 1904.

[3] *Vide F.* 407117, December, 1909.

[4] *Met. Chem. Eng.* 1911, **9**, 543.

is warmed in a sealed glass bottle, a black powder forms on the surface, which, when the bottle is opened, ignites spontaneously. It is probable that this black sub-oxide plays an important part in the production of sparks from the ordinary pyrophoric alloys.

Other Alloys.—On account of the great affinity of the cerium metals for oxygen, misch-metal has been suggested as a reducing agent,[1] as have also the alloys of cerium and magnesium;[2] the formation of the latter is endothermic, so that they act much more vigorously than either metal separately. The alloys of cerium with tin and aluminium have been thoroughly investigated from the stand-point of metallography, by Vogel.[3] It has recently been claimed that the addition of very small quantities of cerium to aluminium has a very marked effect, the rare earth metal acting as a purifying agent,[4] and greatly improving the properties of the aluminium. The cerium may be introduced as fluoride, either to the electrolytic bath in which the aluminium is being prepared, or to the latter metal, after preparation, in the fused state. The most favourable effect is said to be produced by 0·2 per cent. of cerium.

Applications of the Cerium Compounds.[5]—One of the earliest investigations in which cerium compounds were examined with a view to technical employment, was that of Kruis,[6] who made experiments on the comparative value of the salts of different metals as catalysts in the manufacture of aniline black. He showed that a solution of aniline with an oxidising agent (potassium chlorate or chromate) develops no colouration unless a salt of a heavy metal is present. In the case of the fabric impregnated with the solution, the only metals of which compounds were found suitable for producing a colour were copper, which was then generally used for the

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[1] *Vide, e.g.* Escales, *D. R. P.* 145820, October, 1903.

[2] Hirsch, *loc. cit.*

[3] *Zeitsch. anorg. Chem.* 1911, **72**, 319; 1912, **75**, 41.

[4] Borchers and Barth, *D. R. P.* 246484, May, 1912.

[5] An account of the various suggestions for the technical employment of the rare earth elements, by Dr. Max Speter, will be found in Dammer, *Die Chemische Technologie der Neuzeit*, Stuttgart, 1910, vol. i. pp. 500–504.

[6] *Dingl. Polyt. J.* 1874, **212**, 347.

purpose, and cerium, iron, and manganese. Of these, cerium, used in the form of the double sulphate, was found to be by far the most suitable, and moreover to have the advantage that only small quantities are required; the price was at that time too high to allow of its use, but it has since been employed.[1] Cerium compounds have also been proposed as mordants for alizarin,[2] but they do not appear ever to have come into general use.

In photography, ceric sulphate has been employed for some time for the purpose of 'reducing,' *i.e.* removing silver from over-developed negatives.[3] It is said to act very evenly and rapidly, the small quantity of free sulphuric acid required to hold the salt in solution having no bad effect. More recently, cerium salts have been proposed for use in colour photography.[4] An emulsion is obtained by adding salts of iron, uranium, or cerium to a colloidal solution of albumen in ammonia, borax solution, or sodium carbonate solution; this is spread on the paper or negative, and is said to be readily sensitive to light.

The crude mixture of cerous sulphate with basic sulphates of other elements of the cerium group, which has been patented for use as a catalyst in the contact process for the manufacture of sulphuric acid,[5] is prepared from the earth compounds obtained as by-products in the treatment of monazite. These are converted into the sulphates, and, after evaporation of the excess of sulphuric acid, heated for several hours at a low red heat (300°–600°C.). The porous mass is then broken, and is ready for use. It is stated that a nearly quantitative yield of sulphur trioxide is obtained, and that the mixture acts more efficiently than pure cerous sulphate. The reaction is said to depend on the continuous formation and decomposition of the ceric salt, thus:

$$Ce_2(SO_4)_3 + SO_2 + O_2 = 2Ce(SO_4)_2$$

$$2Ce(SO_4)_2 = Ce_2(SO_4)_3 + SO_3 + O$$

This process does not appear to have come into general use.

A general patent had been taken out in 1901, protecting

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[1] *Vide* Buhrig, *Dingl. Polyt. J.* 1879, **231**, 77; and *Abstr. Chem. Soc.* 1879, **36**, 683.

[2] *Vide* Witt, *Chem. Ind.* 1896, **19**, 156.

[3] *Vide* Lumière, *Bull. Soc. franc. Photog.* (2) 1900, **16**, 103. Also *E.* 470, 1900.

[4] Fateau, *E.* 20740, 1907.

[5] Hölbling, *D. R. P.* 142144 and *F.* 326321 of May, 1903.

the use of oxides of the rare earth elements for 'high-temperature catalysis' in the manufacture of sulphuric acid,[1] but the oxides do not seem to be very efficient.[2]

It has also been proposed to utilise the oxidising power of ceric salts in acid solution [3] for the preparation of aldehydes, quinones, etc., from aromatic hydrocarbons, for which purpose they are claimed to be more efficient than chromates. By the use of a crude cerium dioxide (60–70 per cent. CeO_2) obtained by the ignition of the by-products of the thorium industry, good yields were obtained of benzaldehyde, naphthaquinone and anthraquinone from toluene, naphthalene and anthracene respectively.

Garelli [4] has examined the action of cerium salts in tanning; he states that with neutral solutions, effects very similar to those produced by aluminium salts are obtained, but Eitner, who has also examined the question,[5] is of opinion that the cost of isolating and purifying the salts from the monazite residues renders their employment for this purpose impossible.

The fluoride, silicofluoride, and dioxide have also been proposed for the preparation of enamels,[6] but do not give satisfactory results.

Several patents protect the use of rare earth compounds for flashlight powders. For most of the mixtures covered, it is claimed that the usual defects of fumes, slow firing, etc., are absent. The usual recipes [7] are for magnesium or aluminium powder with chromates, nitrates, or similar salts of thorium, cerium, etc.; in one case [8] the rare earth metals, alloyed with barium, silicon, uranium, or titanium, are to be used with 'an oxidising agent which leaves a non-volatile residue.' None of these mixtures appears to have been successful.

Cerium compounds have also been proposed for use in arc-lamp electrodes; it is claimed that they give a very

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[1] Meister, Lucius and Brüning, *E.* 1385, 1901.

[2] *Vide* Plüddemann, Dissertation, *Beitrag zur Aufklärung des Schwefelsaurekontaktprozesses*, Berlin, 1907.

[3] Meister, Lucius and Brüning, *D. R. P.* 158609, March, 1905.

[4] *J. Soc. Chem. Ind.* 1912, 31, 830.

[5] *Ibid.* 1911, 30, 1128.

[6] Rickmann and Rappe, *D. R. P.* 99165, September, 1898; also *D. R. P.* 203773, October, 1908.

[7] *Vide, e.g. E.* 14692, 1908; *D. R. P.* 158215.

[8] *F.* 403722, October, 1909.

intense light, one patent[1] adding that the presence of cerium peroxide and a little fluorspar causes the arc to burn evenly and quietly. In another, the use of a mixture of tungstates or molybdates of the alkaline earths, with fluorides of the rare earth elements is protected;[2] the use of pyrophoric alloys, either entirely, or for the core of the electrode, has also been suggested.[3]

The Nernst Lamp.—The first efforts which were made for the employment of electricity in illumination endeavoured to utilize the heat produced, when a current traverses a very thin metallic filament, to raise the conductor to incandescence. Numerous efforts were made to adapt platinum to this purpose, but its melting-point was finally admitted to be too low; at length it was found possible to produce carbon filaments, and the well-known carbon lamps came into use. Numerous attempts were made to effect improvements;[4] one plan was to coat the carbon filament, after its production, with a skin of metallic conductor, and zirconium and thorium were among the metals proposed in this connection.[5] The first really important advance, however, was effected by Nernst, who took up the study of 'conductors of the second order,' and within a few months succeeded in adapting these to the purposes of illumination (1897–1898). The Nernst lamps gave a very intense white light with considerably less consumption of electricity than the carbon filament lamps; they enjoyed a very considerable vogue for some years, but have been almost entirely displaced by the cheaper metal filament lamps, which were occupying the attention of Auer von Welsbach at the time Nernst perfected his invention.[6]

In his first patent,[7] Nernst proposed the use of a rod of magnesia or zirconia as filament; these oxides, which belong to his class of conductors of the second order, are non-conductors at

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[1] *E.* 414707, June, 1910.

[2] *F.* 431040, August, 1911; also *E.* 21374, 1909.

[3] *E.* 8150, 1909.

[4] The reader is recommended to consult the *Jahresberichte über die Leistungen der Chemischen Technologie* of Fischer, Section 'Beleuchtung,' for the years 1898–1901 inclusive, from which some idea may be obtained of the innumerable proposals and suggestions, usually protected by patent, which were put forward at this time.

[5] *Vide, e.g. D. R. P.* 153959.

[6] *Vide E.* 1535, 13116 and 17580, 1898.

[7] *E.* 19424, 1897.

ordinary temperatures, but their resistance decreases as the temperature rises, so that at high temperatures they will conduct electricity at the ordinary voltage. The preliminary heating was at first effected by means of a Bunsen burner, but a later patent[1] of the same year protects a method of heating by means of a platinum spiral in an auxiliary circuit, which is automatically cut out when the current in the main circuit, bearing the filament, attains its required strength. In the following year[2] it was found that filaments composed of mixtures of oxides were far more suitable than the earlier magnesia or zirconia rods; yttria, thoria, and zirconia were the chief oxides used, small quantities of ceria being occasionally introduced. With these filaments, the increase of conductivity with temperature is far more rapid than with the pure oxides; the preliminary heating required, therefore, is less and the light obtained more intense. The filaments used were in the form of rods or spirals obtained by compressing the powdered oxides.

The Nernst filaments differ markedly from those of the ordinary electric glow lamp in that they are not conductors in the ordinary sense (or of the first order, as Nernst puts it) but electrolytes, the passage of the current being actually attended by an electro-chemical change in the filament.[3] The oxide is ionised; the ions of the metals travel to the cathode or negative pole, where the liberated atoms of metal instantly recombine with the oxygen of the air, whilst oxygen ions travel to the anode, from which the gas is liberated. There is thus a gradual redistribution, resulting in accumulation of oxide at the cathode with a corresponding loss at the anode, which is balanced, after some time, by diffusion, so that equilibrium is attained. In consequence of this redistribution the filament glows more brightly at the anode, where it is thinnest, than at the cathode.

INDUSTRIAL APPLICATIONS OF ZIRCONIUM

It has already been mentioned that zirconium received considerable attention as a suitable substance for the preparation of metallic filaments during the early stages of their

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[1] *E.* 23470, 1897. [2] *E.* 6135, 1898.

[3] *Vide* Nernst, *Zeitsch. Elektrochem.* 1899, 6, 41.

development. Whilst at the present time this element has been abandoned for the purpose,[1] several zirconium lamps were at one time on the market, and a brief mention of some of the work done in this direction may not be out of place.

One of the general methods for the preparation of the metallic filaments may be illustrated by a patent taken out in 1902 by Sander,[2] for the preparation of filaments of zirconium, with or without addition of zirconium carbide. The metal, or a compound which on heating will yield the metal and a volatile substance which can be removed, is prepared in a finely divided condition, and made into a paste with some organic binding material; the paste is then forced through a tiny aperture, and the resulting thread is shaped and heated to a high temperature *in vacuo* or in an inert atmosphere. If an organic substance be used to form a paste with metallic zirconium, the final process of heating results in the formation of the carbide; the same compound is also obtained by another process protected by Sander (*loc. cit.*) in which the hydride of zirconium, prepared by the reduction of the oxide by means of powdered magnesium in an atmosphere of hydrogen, is mixed with a cellulose solution, and the liquid treated as in the manufacture of artificial silk, the threads obtained being then heated to remove all organic matter as far as possible.

The carbide is also probably obtained by the process of the British Thomson-Houston Company, in which advantage is taken of the fact that zirconium oxalate is a pasty gelatinous substance, which can be forced through a die to form a thread without addition of any agglutinating agent. The oxalate, precipitated by addition of ammonium oxalate to a solution of a zirconium salt, is mixed with finely divided carbon, and the threads obtained from the pasty mass heated to a very high temperature in a furnace.[3] Zirconium oxalate is also proposed as a binding material for powdered tungsten, in the preparation of filaments from that metal.[4]

The compounds of zirconium and thorium with elements

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[1] *Vide* Baumhauer, *Zeitsch. angew. Chem.* 1910, 23, 2065.

[2] *D. R. P.* 133701, July, 1902.

[3] *E.* 5415, 1908.

[4] *E.* 10590, 1908.

of group VB, according to two German patents,[1] are suitable for the preparation of metallic filaments in much the same way. Thorium, titanium, and zirconium are also among the metals which, it is claimed, can be obtained in the pure fused state by heating in an electric arc *in vacuo*, so that filaments can be drawn directly.[2]

Metallic zirconium and its alloys have recently been employed in metallurgy. The pure metal can be obtained by the calcium reduction of Kuzel and Wedekind (*vide* p. 316); zirconia is not reduced by powdered aluminium (Goldschmidt's process), but alloys of zirconium and iron can be easily obtained by the reduction of mixtures of the two oxides by this method. Alloys can be obtained containing up to 35 per cent. of zirconium; this ferro-zircon, as it is called, has been used to some extent recently in place of ferro-titanium (*vide infra*) for the purification of steels.[3] Addition of small quantities of zirconium to steels, brass, copper, etc., is said to secure sound castings, and to increase considerably the strength and resistance to acids of the metal.

The Technical Uses of Zirconia.—Since the discovery of Baddeleyite, the natural oxide of zirconium (*vide* p. 75), which occurs in large quantities in Brazil, many proposals have been brought forward for the employment of this compound. Its application to the manufacture of glasses and enamels will be referred to in the next chapter. Patents have been taken out protecting its use for the preparation of white pigments,[4] as a toilet-powder,[5] and as a polishing powder,[6] for it is extremely stable towards chemical reagents, very voluminous, and at the same time very hard. It has long been employed for coating the lime and magnesia pencils used in the Drummond or 'lime' light; and recently it has been employed for the headlights of automobiles, in the Blériot lamp,[7] in which a rod of zirconia is heated in a blowpipe flame fed with oil vapour and oxygen.

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[1] *D. R. P.* 153958 and 154299, September, 1904.

[2] *Ibid.* 169928, April, 1906.

[3] *Vide* Weiss, *E.* 29376, 1910, and Lesmüller, *D. R. P.* 231002, February, 1911.

[4] *D. R. P.* 235495. [5] *Ibid.* 237624. [6] *Ibid.* 230757.

[7] *Ibid.* 174313, September, 1906.

By far the most important property of the oxide, from the technical point of view, is the ease with which it resists high temperatures. The natural oxide can be freed, to a very large extent, from the iron oxide which it encloses, by the prolonged action of hydrochloric acid; experiments were carried out on the material so obtained by Simonis,[1] who showed that by prolonged heating at a high temperature, the remaining impurities, chiefly ferric oxide and silica, could be volatilised, leaving the zirconia unchanged. Riecke[2] showed that whilst the oxide is very suitable for the manufacture of highly resistant crucibles, its use is restricted by the fact that it is easily reduced by carbon at high temperatures, forming the carbide.

Weiss and Lehmann have carried out exhaustive experiments on the preparation of crucibles of zirconia.[3] They worked first with mixtures of zirconia and magnesia, with phosphoric acid as a binding material; the best results were obtained with a mixture of 90 per cent. zirconia and 10 per cent. magnesia, which gave extraordinarily resistant crucibles. Prolonged heating at temperatures over 1900° C. eliminated all the phosphoric acid by volatilisation; the crucibles could then be heated in the blowpipe flame and plunged immediately into cold water without cracking or breaking, and were not affected by fused sodium hydroxide or potassium hydrogen sulphate. Crucibles were also made with the addition of potassium and sodium salts, and were found to answer very well; platinum could be melted in them to a mobile liquid. Similar crucibles are already on the market.

As early as 1904 the use of zirconia was suggested for coating muffles, retorts, and tubes which are required to withstand high temperatures.[4] In 1906 it was proposed[5] for the manufacture of crucibles in which rock-crystal (quartz) is fused for the preparation of quartz-glass, since zirconia is not attacked by molten silica. It promises to be of the greatest use in all cases where a very refractory material, stable towards the ordinary chemical reagents, is required.

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[1] *Sprechsaal*, 1908, 41 (1), 210.

[2] *Ibid.* 214.

[3] *Zeitsch. anorg. Chem.* 1910, 65, 218.

[4] Pufahl, *D. R. P.* 156756.

[5] Heraeus Co., *D. R. P.* 179570.

CHAPTER XXII

THE INDUSTRIAL APPLICATIONS OF TITANIUM AND ITS COMPOUNDS

THOUGH probably at least as plentiful in nature as most of the common metals, titanium has always, until quite recently, been regarded as one of the rare elements. Of its chemistry, very little indeed was known, and it is improbable, even now, that the pure element has been isolated. It had no technical value; indeed, its commonest ore, ilmenite or titaniferous iron ore, was sedulously avoided by manufacturers, who considered that even very small percentages of the element rendered an iron ore valueless because unsuitable for working in blast furnaces. Towards the end of the last century, one or two metallurgists had demonstrated that ilmenite, under the proper working conditions, would yield a pig iron of very good quality when smelted in the blast furnace, but it was left for the long and arduous researches of Rossi to show that the element is possessed of properties which render it very valuable for metallurgical purposes. Since the successful culmination of his work in the first few years of the present century, titanium has attained considerable importance in the treatment of special steels for rails, car wheels, crushing machinery, etc. At present, titaniferous iron ores are being worked on a large scale, and many titanium compounds are coming into use for technical purposes.

The titanium minerals of commercial importance are rutile and ilmenite (*vide* Part I. pp. 57 and 77). The former, the pure titanium dioxide, is of fairly wide distribution, but ilmenite occurs in far greater quantities, forming deposits of enormous dimensions, especially in America, as, *e.g.* in New York Co. and Quebec. Owing to its high melting-point and relatively low specific gravity, metallic titanium can only be incorporated with molten steels with the greatest difficulty, and for this reason alloys of titanium and iron, known technically as ferro-titanium, are usually employed for the treatment of steels. For the preparation of ferro-titanium, ilmenite of good quality is as suitable as rutile, and, of course, far cheaper; hence the latter is only employed for the preparation of titanium salts for use in colouring and mordanting, and for titanium compounds for arc-lamp electrodes, etc.

Various processes are employed for the manufacture of ferro-titanium from ilmenite. In cases in which a considerable percentage of carbon is not undesirable, for instance, where the alloy is required for the treatment of cast iron or of high-carbon steel, the mineral is reduced directly with carbon in an electric furnace; the ferro-titanium so obtained usually contains from six to eight per cent. of carbon. For pure iron-titanium alloys, the process worked out by Rossi[1] is used in America almost entirely. Ilmenite is charged into a bath of molten aluminium, heated electrically; the mineral is at once attacked, with formation of iron, in which the titanium dissolves as reduction proceeds. This process may also be used for reduction of rutile, if scrap iron is added to the aluminium bath, to allow of the formation of the required alloy. In Germany, the Goldschmidt or 'thermite' reaction is largely employed; powdered ilmenite is intimately mixed with the calculated quantity of aluminium powder, reduction being started as usual by means of a fuse of magnesium ribbon imbedded in a small quantity of barium peroxide.

Quite recently, the question of the separation of titanium compounds from ilmenite used for the manufacture of pig iron has attracted considerable attention. It has been already mentioned (*vide supra*) that titaniferous iron ores have been shown to be perfectly amenable to blast-furnace treatment, the old and deeply rooted idea that titanium-bearing slags are stiff and troublesome being entirely contrary to facts, when suitable conditions are observed;[2] moreover, it is shown

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[1] *Elect. chem. Ind.* 1903, **1**, 523.

[2] *Vide, e.g. Iron Age*, 1909, **84**, 1149 and 1223.

that the pig iron obtained is of unusually good quality. Rossi has suggested[1] that if sufficient carbon be added to reduce all the silica and oxides of iron, with enough lime to slag off the titanium dioxide as calcium titanate, the latter can be used as a source of titanium compounds or alloys, whilst a ferro-silicon will be obtained as pig metal; the temperature must be carefully adjusted to ensure reduction of the silica without loss of titanium dioxide. Another patent[2] proposes the reduction of the ore in an electric furnace, and the treatment of the crude ferro-titanium in a converter with a blast of air or nitrogen; the titanium nitride formed is then driven out of the metal by a blast of superheated steam—any ammonia or cyanogen formed being collected—and removed, the iron remaining being 'Bessemerised' directly in the same converter; the titanium nitride can be used as a manure, or for the manufacture of ammonia or nitric acid (*vide infra*). The removal of iron as the volatile carbonyl has also been suggested,[3] the titanium being subsequently transformed into the nitride.

Employment of the Element in Metallurgy.—It has been already mentioned that titanium itself is quite unsuitable for direct incorporation with steel. Besides the relatively low specific gravity (5·2), which would render mixing very difficult, the very high melting-point (given by Weiss and Kayser[4] as 2350°) would prevent uniform dissemination. The element is therefore generally used in the form of a ferro-titanium of low titanium content, 10–15 per cent. being the proportion usually employed. The addition should be made at the end of the Bessemer process, and after the addition of the required quantities of manganese and silicon alloys; the calculated quantity of ferro-titanium is added as the steel runs from the converter into the ladle. A suitable proportion is said to be one-half per cent. of alloy, so that the actual proportion of titanium to steel is somewhere about 1·5–1·8 lb. per ton. Six or eight minutes should be allowed after the addition, for the titaniferous slag to come to the surface.

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[1] *E*. 3582, 1901.

[2] Sinding-Larsen and Willumsen, *D. R. P.* 220544, April, 1910.

[3] Sinding-Larsen, *E*. 17632, 1910.

[4] *Zeitsch. anorg. Chem.* 1910, **65**, 345.

Although low percentage ferro-titanium is usually employed, it has been stated that high-percentage alloys, and even the element itself, are immediately taken up by steel if aluminium be added at the same time. Thus Venator[1] states that if titanium and aluminium be added together to the bath, both elements are immediately taken up, the reaction being very rapid and complete; the effects produced by the titanium are in no way influenced by the presence of the aluminium. Goldschmidt[2] proposes the use of ferro-titanium containing 24–25 per cent. of the element, with 3 per cent. of aluminium; this dissolves very readily, is very effective, and moreover, can be very easily prepared by the alumino-thermic reaction.

In some cases, where it is desired to treat a steel both with silicon and with titanium, ferro-alloys containing both of these elements may be employed. By reduction of ilmenite or rutile with carbon in an electric furnace, in presence of silica, Becket[3] obtains alloys of high titanium and silicon content, which are said to dissolve very easily in molten steels and to produce improved effects. The Titanium Alloy Manufacturing Company have also patented[4] the preparation of titanium-silicon alloys, with or without addition of iron or copper, by the reduction of a mixture of rutile and quartz.

Recently the use of ferro-titanium in the manufacture of pig iron has attracted attention. For this purpose, alloys of very low titanium-content (0·1–1·0 per cent.) are employed. Addition of very small amounts of such alloys to the molten metal before casting is said to have a marked cleansing effect,[5] resulting in much better and stronger castings.

Whilst it is very generally agreed that the addition of titanium results in the production of much stronger and more durable products, the question of the precise effect obtained is by no means definitely settled. The experimental work, whilst pointing on the whole to the superiority of titanium-treated steel, is by no means conclusive; in some cases, indeed,

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[1] *Stahl Eisen*, 1910, **30**, 650.

[2] *D. R. P.* 235461, June, 1911.

[3] *U. S. P.* 940665 and 941553 of November, 1909.

[4] *F.* 407858, January, 1910.

[5] *Vide* Slocum, *Chem. Eng.* 1911, **13**, 257.

it is conflicting. Thus the micro-photographs obtained by von Maltitz[1] and Venator[2] show that the titanium-treated steel has a far cleaner fracture and far more homogeneous structure than steels not so treated; on the other hand, the micro-photographs of Treuheit[3] show practically no improvement in structure for the titanium steel. The exhaustive tests of the first two authors, again, and the experiments of numerous railways in the use of titanium steel rails,[4] demonstrate clearly that the treatment results in improvement in strength and durability of the product; but the work of Otto[5] proves equally clearly that his products did not differ markedly, whether titanium-treated or not, and he is of opinion that the rail tests were not sufficiently prolonged or searching to be considered conclusive. It is nevertheless to be considered certain that the use of titanium does cause a marked improvement in the quality of the steels obtained, and especially in the durability of rails. The negative results obtained by some authors may be explained, firstly, on the ground that no tests are conclusive unless carried out with steel from the one bath, one half of which has been treated with titanium, and the other half not so treated; secondly, that the ferro-titanium must be incorporated with the metal, and must not be suffered to be taken up by the slag, and so lost; and thirdly, that the bath must be allowed to remain for some minutes after treatment, in order that the reaction may be complete, and the titanium-bearing slag allowed to rise to the surface. When these conditions are carefully observed, experiment shows that marked improvement in the quality of the steels produced is effected.

As to the actual nature of the effect produced, it is generally believed that titanium acts merely as a cleansing agent, freeing the metal from occluded or combined gases, and removing blow-holes, so producing a denser and more homogeneous structure, with consequent improvement in properties. The

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[1] *Stahl Eisen*, 1910, **29**, 1593.

[2] *Ibid.* 1910, **30**, 650.

[3] *Ibid.* 1910, **30**, 1192.

[4] *Vide* Dudley, *J. Ind. Eng. Chem.* 1910, **2**, 299; also *Cass. Mag.* 1911, **40**, 483.

[5] *Vide* abstract in *Stahl Eisen*, 1912, **32**, 1497.

added titanium is usually found entirely in the slag, so that it appears certain that it does not alloy, but merely purifies. It certainly acts as a powerful and rapid deoxidiser, removing the last traces of the gas which have escaped the action of the manganese, silicon, etc., with which steels are now generally treated. Many authorities, on the ground of analyses, and of the known affinity of titanium for nitrogen, believe that it very largely reduces the nitrogen-content,[1] which is so harmful; this, however, is still an open question.[2] It is stated that if excess of titanium is used, so that small quantities—0·05–0·20 per cent.—remain in the finished steel, the toughness and durability are further increased;[3] but as a rule, manufacturers prefer to work with smaller quantities, so that no free titanium remains in the product.

The preparation of alloys of titanium with almost all the commoner metals is protected by patent, but few of these are of technical importance. Small quantities of titanium are said to improve very considerably the properties of copper and its alloys, the brasses, bronzes, etc., especially in castings. The addition is usually made in the form of an appropriate titanium alloy, prepared by reduction of the mixed oxides with carbon in an electric furnace, or treatment of the mixed oxides, together with the alloying metal, with aluminium under similar conditions.[4] The titanium-silver alloys obtained in this way[5] are said to improve greatly the structure of silver, by preventing the familiar 'spitting' as the fused metal cools.

An interesting process, which has been patented by Rossi,[6] recalls the method of formation of cementation steels. He has found that if a metal be loosely covered with its alloy with titanium, in a finely powdered condition, and the whole heated, the titanium diffuses into the metal, to a depth and concentration which vary with the temperature and the time of heating. He suggests that in this way a metallic body may be toughened

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[1] *Vide* von Maltitz, *loc. cit.*

[2] *Vide* Venator, *loc. cit.*

[3] *Vide Bull. Imp. Inst.* 1911, **9**, 134.

[4] *Vide* Rossi, *U. S. P.* 986505, March, 1911; 935863, October, 1909, etc.

[5] Rossi, *U. S. P.* 1024476 and 1025426, August, 1912.

[6] *U. S. P* 986504, March, 1911.

and strengthened at any desired point, *e.g.* steel for armour-plate at the surface. Whether the process will be of any technical value or not can only be shown by experiment.

Application to Arc-lamp Electrodes.—During the last fifteen years, innumerable efforts have been made to adapt titanium and its compounds to the manufacture of arc-lamp electrodes, or pencils.[1] The spark-spectrum of titanium is very rich in lines, and in respect of light efficiency, the element is very suitable for the purpose ; the experimental difficulties, however, have been very great, and though electrodes containing titanium compounds have been on the market for some years, the problem cannot be said to have been satisfactorily solved. The best pencils contain titanium carbide, but successful attempts have been made to use the oxide. As early as 1904, Weedon[2] proposed an electrode prepared by heating 7 parts (1 mol.) of the dioxide with 1 part of carbon to 1500°–2000°C. ; the 'sub-oxide' produced was powdered, worked up into a paste with a suitable binding material, and forced through a nozzle. The sticks so obtained, after drying and baking in the usual manner, were said to give satisfactory results, but consumption is very rapid, and troublesome deposits of the dioxide are formed at the end of the electrode. The dioxide, which alone is a very bad conductor, enters directly into the composition of the so-called 'magnetite' pencils, which are best made[3] by fusing together magnetite, rutile, and chromite, in suitable proportions, with a little potassium fluoride, powdering the brittle mass, and using this to form a paste from which the pencils may be obtained as usual. These electrodes are said to give a very efficient and fairly steady arc. They have the disadvantage that tiny glowing particles are thrown off, which soon render the globes opaque ; the addition of sulphur[4] to the powder during manufacture is said greatly to diminish this inconvenience. Pencils made in a similar manner from powdered ferro-titanium[5] do not appear to have come into use.

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[1] *Vide, e.g.* Ladoff, *J. Ind. Eng. Chem.* 1909, 1, 711.

[2] *E.* 26921, 1904. [3] *E.* 2027, 1909. [4] *E.* 18965, 1909.

[5] *U. S. P.* 840634, January, 1907.

The carbide alone is a good conductor, and gives a very satisfactory light,[1] but electrodes made from this compound without additions have several disadvantages. The life is short, and the arc soon becomes flickering and unsteady. A deposit of the badly conducting dioxide gradually accumulates on the anode, and once the current has been interrupted, this deposit renders it very difficult to strike the arc again. These disadvantages are largely overcome by a series of improvements recently patented in Germany by the Allgemeine Elektrizitäts Gesellschaft of Berlin. Addition of small quantities—4·5 per cent.—of chromium carbide increases the length of life;[2] the unsteadiness and flickering are greatly diminished by incorporation of powdered coke, cryolite and fluorspar,[3] or better, of the titanofluoride of calcium or cerium,[4] whilst the addition of finely divided sulphur (or selenium or tellurium)[5] greatly reduces the disadvantage due to the throwing off of incandescent particles. The British Thomson-Houston Company patents a similar electrode,[6] in which a carbon-mixture is used instead of coke, and the electrode is manufactured with a carbon shell. For this purpose, the paste prepared from the powdered mixture may be filled into a hollow carbon rod, or the lightly baked pencil may be coated with pitch and heated to a high temperature. The use of a mixture of cerium fluoride and tungstate, with carbon and cryolite, is also said to prevent flickering.[7]

In arc lamps in which pencils containing titanium compounds are used, the anode is generally made of copper, and is placed below the cathode, the reverse being the case where carbon electrodes are employed. The copper is inactive, and contributes nothing to the light; if the anode be of suitable dimensions, it wears away very slowly, whereas the cathode, containing the titanium compound, is rapidly consumed. In lamps in which carbon electrodes are used, the light is emitted chiefly from the extremities of the electrodes, the path of the arc being comparatively non-luminous; the light has the familiar reddish-yellow colour characteristic of the earlier

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[1] Weedon, *Trans. Amer. El. chem. Soc.* 1911, 16, 217.

[2] *D. R. P.* 231231, February, 1911.

[3] *Ibid.* 233125, March, 1911.

[4] *Ibid.* 251837, October, 1912.

[5] *Ibid.* 234466, May, 1911.

[6] *E.* 6500, 1912.

[7] Guay, *U. S. P.* 1039522, September, 1912.

forms of arc lamps. Where titanium pencils are employed, however, the light is emitted almost entirely from the arc itself, the electrodes contributing very little, and is of a pure white colour, very different from that of the carbon lamp.

Attempts have been made to employ titanium in the manufacture of metal filaments for glow lamps. The metal would be very suitable for this purpose, by reason of its high melting-point and low conductivity, but the difficulty of obtaining it in the pure state, and the remarkable susceptibility of the filament to traces of impurity, have so far proved insuperable. For the sake of illustration, a proposal put forward in 1908 may be briefly referred to.[1] Pure titanium dioxide is heated in a stream of ammonia; the nitride obtained is decomposed at 1200° *in vacuo*, and after cooling, the metal is powdered and made into a paste with a solution of albumen in ammonia. The threads obtained from this in the usual manner are heated to 1200° in an electric furnace; the carbon deposited from the albumen forms the cyanide by reaction with the trace of nitride which has escaped decomposition, or which has been formed by further action of ammonia. The cyanide is volatile, and can be removed at high temperatures *in vacuo*, leaving a sintered filament of the metal. So susceptible is the filament to impurity, that the trace of carbon deposited from the vapour of the oil of the pump which diffuses into the vacuum is sufficient to render it so fragile as to be useless.[2]

Titanium Compounds in Dyeing and Colouring. — The use of titanium compounds as mordants in the dyeing of leather and textile goods has been known for a considerable time.[3] As early as 1896, a patent was taken out by Barnes [4] for the treatment of prepared animal skins by immersion in a bath of a titanium salt. Subsequent boiling or steaming causes hydrolysis, with precipitation in the skin of hydrated titanium dioxide, which forms lasting dye-lakes when the fabric is immersed

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[1] Trenzen and Pope, *E.* 14852, 1908.

[2] *Vide Bull. Imp. Inst.* 1911, 9, 134.

[3] A good account of some of the earlier work in this connection is given by Erban, *Chem. Zeitg.* 1906, 30, 145.

[4] *E.* 5712, 1896.

in the dye-bath. Whilst this treatment has been found satisfactory with some classes of leather goods,[1] more delicate kinds are liable to be injured by the mineral acid set free, and numerous patents protecting the preparation and employment of organic salts of the element have been taken out by Dreher.[2] The same investigator[3] has discovered that excellent results can be obtained in the cold by the addition of various 'Hülfsalze,' which are chiefly acetates or formates of the alkaline earth metals, chromium, or aluminium, or basic salts of the last two. Double decomposition of these with the titanium salt forms basic or highly hydrolysed salts of the latter, so that the hydrated oxide or a basic compound is formed on the fabric.

The titanium salts specified in these patents are salts of the element in the tetravalent condition, prepared from rutile by the action of strong mineral acids. As early as 1902, the technical preparation of salts of trivalent titanium for reducing purposes was patented by Spence and Spence, of Manchester.[4] The process is an electrolytic one, and is effected in a cell divided into two compartments by a porous partition, one electrode being introduced into each compartment; an electromotive force of 3–4 volts is required. A 20–25 per cent. titanium tetrachloride solution is introduced into the cathode compartment, and dilute hydrochloric acid into the anode compartment; on electrolysing, chlorine is evolved at the anode, and may be utilised as usual in the preparation of bleaching powder, etc., whilst the tetrachloride in the cathode compartment is reduced to trichloride. The solution is then concentrated at 65°–70°C. under reduced pressure, and the crystalline trichloride separated. In the preparation of the corresponding sulphate, sodium sulphate must be present in the cathode compartment, and a double salt is obtained; the process is carried out in lead-lined cells, in presence of excess of sulphuric acid. The preparation of the sesquioxide, Ti_2O_3, free from compounds of aluminium

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[1] *Vide* Dreher, *D. R. P.* 142464, June, 1903.

[2] *Vide E.* 22629 and 23188 of 1901, 14921 and 27597 of 1902, and 5211 of 1903.

[3] *Vide D. R. P.* 139059 and 139060 of February, 1903, and 139838 of March, 1903.

[4] *E.* 16238 and 18108 of 1902.

and iron, was also suggested by Dreher[1] by reduction of the acid solution of the impure or mixed salts with zinc or sodium amalgam, and approximate neutralisation; the sesquioxide differs from the dioxide in that it separates while the solution is still somewhat acid, which the hydrated oxides of iron and aluminium will not do. Dreher suggested that the strong reducing properties of the sesquioxide and its salts should make these valuable for bleaching, colour-printing, and similar purposes.

More recently[2] the reduction of titanium salts by means of aluminium powder has been suggested; in the case of the sulphate, the aluminium salt formed may be partly eliminated as alum, in the ordinary way, if desired, but it is claimed that its effect is beneficial rather than harmful. The preparation of organic double basic salts of trivalent titanium,[3] which hydrolyse very readily, suggested the use of such compounds as mordants and for reducing purposes. These salts may be prepared fairly easily[4] by adding concentrated solutions of the appropriate potassium, sodium, or ammonium salts in excess to concentrated solutions of the trichloride, in absence of air. The double salts separate, and are washed and dried; in this condition they are fairly stable, but the solutions hydrolyse at once on merely warming, with separation of the hydrated sesquioxide. On this account, and also because of the strong reducing action, these compounds are likely to prove valuable as mordants, and for other purposes.

Titanium compounds have frequently been suggested for the preparation of colouring-matters; the ferrocyanide has a fine green colour, and is used to some extent in place of arsenical pigments for the preparation of coloured wall-papers, whilst the dioxide is of some value for tinting artificial teeth, porcelain tiles, etc. Yellow and reddish-yellow pigments are produced from rutile and ilmenite by various methods. A fine covering paint is said to be obtained by a process[5] in

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[1] *E.* 1835, 1903.

[2] Spence, Craig, and Spence, *E.* 13260, 1911.

[3] Stähler and Bachran, *Ber.* 1911, 44, 2912.

[4] Kunheim and Co. and Stähler, *D. R. P.* 284251, June, 1912.

[5] Farup, *E.* 3649, 1910; *F.* 412563, May, 1910.

which ilmenite is powdered and roasted to 500° C.; the cooled product is crushed with water, and after one or two washings to remove soluble compounds, yields a very finely divided orange-yellow suspension, the precise shade of which varies with the duration and temperature of the roasting. The product is at once thrown down from the suspension, by addition of a small quantity of a salt solution, and so can easily be obtained in the solid state. In another process,[1] the pulverised ilmenite is warmed with concentrated sulphuric acid, in which it dissolves with great development of heat; the excess of acid is removed by evaporation and the mass calcined to decompose the sulphates. It is stated that different shades may be obtained by carrying out the last operation in an atmosphere of sulphur dioxide or other gas.

In connection with the colouring properties of the oxides of titanium, it is interesting to note that the blue colour of sapphires is probably due to the presence of compounds of trivalent titanium; Verneuil[2] has succeeded in preparing artificial sapphires in all respects identical with the natural stones by fusing alumina with small quantities of titanium dioxide and ferric oxide in the flame of the oxyhydrogen blowpipe, which effects the reduction.

Other Uses of Titanium Compounds.—Owing to the high price of the tin dioxide which is largely employed for the preparation of enamels and opaque glasses, innumerable suggestions have been made for the employment of the oxides of titanium and zirconium in this direction.[3] A critical examination of the question has been made by Grünwald;[4] he finds that the opacity consequent on addition of these compounds increases with the amount of clay used, within limits, and concludes that the effect is due to displacement of alumina by the oxides, with formation of silicates of titanium and zirconium, which dissolve in the melt. He states that the results obtained from the use of these oxides are not comparable with those given when stannic oxide is employed, and that therefore the former oxides are of little use for this purpose.

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[1] *E.* 10368, 1911.

[2] *Compt. rend.* 1910, **150**, 185.

[3] *Vide, e.g. D. R. P.* 189364, 218316, 115016, 207001; *F.* 438908, etc.

[4] *Sprechsaal*, 1911, **44**, 72.

These two oxides find employment to a small extent in the manufacture of 'Siloxide' quartz glass.[1] Quantities up to 1·5 per cent., added to the molten silica, reduce the difficulty of working the material. Exhaustive tests carried out by Thomas[2] indicate that the vessels made from this material are, on the whole, to be preferred to ordinary quartz glass, resisting high temperature better, and showing less tendency to become crystalline and therefore brittle when maintained for considerable times at high temperature.

Much work has been carried out during the last few years with the object of utilising titanium compounds for the 'fixation' of nitrogen.

The metal combines very vigorously with the gas at about 800° C. (*vide* p. 224), forming the nitride. If the gas, or air, be passed over a heated mixture of the dioxide with powdered coke, formation of the cyanonitride occurs at comparatively low temperatures (1100°–1300° C.) if a small quantity of an alkali salt be present,[3] the action being apparently catalytic; if excess of carbon is used, considerable quantities of the cyanide may be formed. Numerous experiments carried out by the chemists of the Badische Anilin- und Soda-Fabrik have shown that at high temperatures, the action of water and a suitable oxidising agent, or in the presence of metallic compounds, the action of steam alone, will liberate considerable quantities of ammonia from both these derivatives,[4] whilst in the presence of platinum compounds, if air be pumped in, the higher oxides of nitrogen are formed. One or two examples may be given:

(1) $Ti_2N_2 + 4NaOH + H_2O + 2CuO = 2NH_3 + Cu_2O + 2Na_2TiO_3$—autoclave at 180°C.

(2) $2Ti_2N_2 + 2H_2SO_4 + 6H_2O + O_2 = 4TiO_2 + 2(NH_4)_2SO_4$—autoclave at 120°–140°C.

(3) $Ti_2N_2 + 3H_2O = Ti_2O_3 + 2NH_3$—steam at 500°–600°C.

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[1] Wolf-Burckhardt and Borchers, *F.* 432786, October, 1911.

[2] *Chem. Zeitg.* 1912, 36, 25.

[3] *Vide* Bosch, *U. S. P.* 957842, May, 1910.

[4] *Vide, e.g. D. R. P.* 202563 and 203748 of March, 1907; 204204 and 204475 of November, 1908; *E.* 2414, 1908; *F.* 387002 of June, 1908; *U. S. P.* 957843 of May, 1910, gives a résumé of all the processes.

In the second case, the oxygen is derived from air pumped into the apparatus, and ferrous sulphate is used as a catalyst. In the third case, a metallic salt, oxide, or hydroxide is required as a catalyst.

In view of the success of the cyanamide method for the fixation of atmospheric nitrogen, these processes, though of considerable theoretical interest, do not seem likely to become of practical importance.

One or two minor uses have been suggested for titanium dioxide. Small quantities are fused with bauxite, silica, and ferric oxide in the preparation of abrasives,[1] whilst a mixture with carbon is suggested as a refractory body for linings, crucibles, etc., surface heating of this forming a layer of highly resistant carbide.[2] An interesting American patent protects the use of the dioxide for the preparation of phosphorus pentoxide from bone-ash or natural calcium phosphate.[3] The pulverised mixture of the phosphate and oxide is introduced at the upper end of an inclined rotating furnace, by means of a hopper and screw feed; fuel is fed in at the lower end, and an outlet is provided for the periodic removal of the calcium titanate, etc., formed. The silica and alumina of the impure phosphate, together with the titanium dioxide introduced, displace the phosphorus pentoxide, which, being volatile, escapes continuously through a special pipe; there is left a mixture of silicate, aluminate and titanate of calcium, which may be used as a source of titanium compounds.

Estimation of the Element.—Owing to the difficulties of the separation from the acidic oxides, silica, zirconia, and the pentoxides of columbium and tantalum, and from the basic oxides, alumina and the oxides of iron and tin, the estimation of titanium in a mineral or a steel is usually a difficult and tedious process. Gravimetric as well as volumetric methods are employed. In the former, the element is isolated and weighed in the form of the dioxide; in the latter, standard solutions of

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[1] Saunders, *U. S. P.* 954766, 954777, and 954778.
[2] Becket, *U. S. P.* 1038827, September, 1912.
[3] Peacock, *U. S. P.* 995897, June, 1911.

suitable oxidising agents are employed, advantage being taken of the ease with which the element can be transformed from the trivalent to the tetravalent condition.

The mineral or steel in which the element is to be estimated is usually fused with sodium hydrogen sulphate, which forms the sulphate. If thorium, uranium or rare earths are present, treatment in the cold with hydrofluoric acid is often more suitable; the acidic oxides are taken into solution, leaving the more positive elements in the form of the insoluble fluorides. Trautmann finds that steels or ferro-titaniums of high silicon content are attacked only very slightly by fused sodium bisulphate; he recommends[1] ignition to the oxides, evaporation with hydrofluoric acid to remove silicon as the volatile tetrafluoride, and fusion of the residue with bisulphate.

The bisulphate melt, after cooling, is leached with water, and the whole boiled under a reflux condenser for several hours; this treatment should throw down the oxides of titanium, columbium and tantalum, leaving zirconium and aluminium in the form of the sulphates in the acid solution; the addition of ammonia may be necessary to effect complete hydrolysis. The acidic oxides may also be precipitated if the solution be diluted and treated with excess of acetic acid before boiling. In both cases, a considerable quantity of iron is thrown down. The precipitated oxides are dissolved in the cold by dilute sulphuric acid to which hydrogen peroxide has been added.

For volumetric estimation, separation from iron is not generally necessary. If gravimetric methods are to be employed, separation may be effected in several ways. Titanium dioxide may be precipitated in a fairly pure condition by reducing the solution with sulphur dioxide, and boiling until the titanium sulphate has been completely hydrolysed. According to Barneby and Isham,[2] this method gives low results; these authors prefer to remove iron completely from the solution, and then effect complete hydrolysis by addition of ammonium acetate and acetic acid to the boiling solution.

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[1] *Zeitsch. angew. Chem.* 1911, **24**, 877.

[2] *J. Amer. Chem. Soc.* 1910, **32**, 957.

For this purpose, they dissolve the mixed oxides in hydrochloric acid, and remove ferric chloride by ether extraction. Bornemann and Schirmeister[1] precipitate titanium dioxide completely by means of ammonia, holding iron in solution as ferrocyanide; for this purpose, iron is completely reduced to the ferrous state by means of sodium hydrogen sulphite, and solutions of potassium cyanide and ammonia are added together to the warm liquid, which is afterwards heated nearly to the boiling-point to effect the precipitation.

Iron may also be removed by the ordinary methods, if some reagent be previously added to hold titanium in solution. For this purpose, tartaric acid and its salts are commonly used; none of the ordinary precipitants will throw down the element if this reagent be present. After addition of ammonium tartrate, iron is removed by means of ammonium sulphide. After filtering, tartaric acid may be removed by means of potassium permanganate, the manganese dioxide formed being reduced with sulphur dioxide. According to Thornton,[2] evaporation with a mixture of sulphuric and nitric acids is a more convenient method of destroying the organic acid; titanium dioxide is then thrown down by diluting and boiling in the usual way.

Bourion[3] describes a method of separating the oxides by the action of a mixture of hydrogen chloride and sulphur monochloride at a suitable temperature. The ferric chloride which is formed sublimes, leaving titanium dioxide unattacked.

For volumetric estimation of small quantities of titanium in solution, colorimetric methods are generally employed. Addition of hydrogen peroxide to such a solution gives an intense reddish-yellow colouration, which is compared with the colourations obtained with solutions containing known quantities of the element. Wells[4] finds that under suitable conditions, an accuracy of about 2 per cent. is to be expected with this method. Lehner and Crawford[5] find that in concentrated sulphuric acid solution, thymol gives a red colouration which is at least

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[1] *Metallurgie*, 1910, **7**, 723.

[2] *Amer. J. Sci.* [iv.], 1912, **34**, 214.

[3] *Compt. rend.* 1912, **154**, 1229.

[4] *Zeitsch. anorg. Chem.* 1911, **70**, 395.

[5] *J. Soc. Chem. Ind.* 1912, **31**, 956.

twenty-five times as intense as the colour given by hydrogen peroxide, and they accordingly propose thymol as a suitable reagent for the colorimetric estimation. Fenton[1] has shown that a very intense colouration is obtained when a solution of a titanium salt is treated with dihydroxymaleic acid; this reaction has been shown by Mellor[2] to be well adapted for the colorimetric estimation and for the estimation of titanium and vanadium together in a solution.

The volumetric methods for the estimation of larger quantities require complete reduction to the trivalent condition. This is best effected by means of zinc and hydrochloric acid, or, where potassium permanganate is to be used, by zinc and sulphuric acid. Precautions must be taken to ensure that reduction is complete; an apparatus suitable for rapid estimations has recently been described by Shimer and Shimer.[3] Where potassium permanganate is employed (Pisani's method), the iron must be estimated separately by means of a standard solution of titanium trichloride. Knecht and Hibbert[4] titrate directly, after reduction, with a standard solution of a ferric salt, using potassium thiocyanate as indicator; here no correction has to be applied for iron originally present in the solution. The same advantage attaches also to the method of titration by means of methylene blue,[5] a dye reduced to the colourless leuco-base by salts of trivalent titanium, but not affected by ferrous salts.

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[1] *Trans. Chem. Soc.* 1908, **93**, 1064. [2] *Abstr. Chem. Soc.* 1913, **104**, ii. 627.
[3] *J. Soc. Chem. Ind.* 1912, **31**, 955. [4] *Ber.* 1903, **36**, 1549.
[5] See Hibbert, *J. Soc. Chem. Ind.* 1909, **28**, 190.

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