A TEXT-BOOK OF

INORGANIC CHEMISTRY.

VOLUME IV.

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A TEXT-BOOK OF
INORGANIC CHEMISTRY.

EDITED BY

J. NEWTON FRIEND, D.SC., F.I.C., PH.D.,
Carnegie Gold Medallist.

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THE PERIODIC TABLE.*

Periods.		Group 0.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.		
First short period .	.	He 4·00	H 1·008 Li 6·94	Gl 9·1	B 11·0	C 12·005	N 14·01	O 16·00	F 19·0			
Second short period	.	Ne 20·2	Na 23·00	Mg 24·32	Al 27·1	Si 28·3	P 31·04	S 32·06	Cl 35·46			
First long period	Even series .	A 39·88	K 39·10	Ca 40·07	Sc 44·1	Ti 48·1	V 51·0	Cr 52·0	Mn 54·93	Fe 55·84	Co 58·97	Ni 58·68
	Odd ,, .	...	Cu 63·57	Zn 65·37	Ga 69·9	Ge 72·5	As 74·96	Se 79·2	Br 79·92			
Second long period	Even series .	Kr 82·9	Rb 85·45	Sr 87·63	Y 88·7	Zr 90·6	Cb 93·1	Mo 96·0	...	Ru 101·7	Rh 102·9	Pd 106·7
	Odd ,, .	...	Ag 107·88	Cd 112·4	In 114·8	Sn 118·7	Sb 120·2	Te 127·5	I 126·92			
Third long period	Even series .	X 130·2	Cs 132·81	Ba 137·37		...	...	...	...	...	...	...
	Odd ,, .	...	...	...		...	...	...	...			
Fourth long period	Even series .	...	...	...	The Rare Earth Metals	...	Ta 181·5	W 184·0	...	Os 190·9	Ir 193·1	Pt 195·2
	Odd ,, .	...	Au 197·2	Hg 200·6	Tl 204·0	Pb 207·20	Bi 208·0	...	...			
Fifth long period .	.	Nt 222·4	...	Ra 226·0	...	Th 232·4	...	U 238·2	... ...	...	...	...
Formulæ of oxides .	.	...	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4		
Formulæ of hydrides	.	...	RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH	..		
Volume in this series of text-books.		1	2	3	4	5	6	7	8	9		

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* The International Atomic Weights for 1917 are adopted in this Table.

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VOLUME IV.

ALUMINIUM AND ITS CONGENERS,
INCLUDING
THE RARE EARTH METALS

BY
H. F. V. LITTLE,
B.Sc. (Lond.), A.R.C.S., D.I.C.
(CHIEF CHEMIST TO THORIUM, LTD.)

With Frontispiece, 2 Plates, and 44 Illustrations in the Text.

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GENERAL INTRODUCTION TO THE SERIES.

During the past few years the civilised world has begun to realise the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches: namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the Elements of Group 0, the general principles of Inorganic Chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern Inorganic Chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasise their application to Inorganic Chemistry, with which branch of the subject this series of text-books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed in Volume I. deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of Physical Chemistry. Yet these are subjects of supreme importance to the student of Inorganic Chemistry, and are accordingly included in the Introduction.

Hydrogen and the ammonium salts are dealt with in Volume II., along with the Elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV., along with the Elements of Group III., as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II. and V. respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II. under ammonium, and in Volume IX. under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V. along with tin, since copper occurs earlier, namely in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX. under iron, and not under ammonium in Volume II. The ferrocyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicles and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross-referencing in the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:—

Hydrogen = 1·00762.
Sodium = 22·996.
Potassium = 39·100.
Silver = 107·880.
Carbon = 12·003.
Nitrogen = 14·008.

Oxygen = 16·000.
Sulphur = 32·065.
Fluorine = 19·015.
Chlorine = 35·457.
Bromine = 79·916.
Iodine = 126·920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and moreover it renders the data for the different elements strictly comparable throughout the whole series.

Our aim has not been to make the volumes absolutely exhaustive, as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined list.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs Charles Griffin & Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

March 1917.

PREFACE.

THE present volume aims at giving a tolerably complete and readable account of the inorganic chemistry of the elements of the third group of the Periodic Table, together with cerium and the tervalent rare earth elements. Where they are of particular interest or importance, however, various organic compounds of these elements have also been described, particularly in dealing with the rare earth elements.

So far as was possible without overburdening the text, the results of modern physico-chemical work have been included. It is hoped that the bibliography relating to the pure chemistry—inorganic and physico-chemical—of the elements described is practically complete and that no important references are omitted. The discussions of mineralogical, technical, and analytical chemistry are of necessity very brief, but it is hoped that the bibliographies attached to them will be of service to the reader.

The chapters dealing with the rare earth elements together constitute more than half the book, and form the most complete account of the chemistry of these elements that has yet appeared in English. No apology is needed for the somewhat lengthy discussion of the spectra of these elements. The nature of the cathodic phosphorescence spectra has been purposely discussed in considerable detail, and it is hoped that the description of Urbain's beautiful researches on this subject may assist English chemists in realising that the atmosphere of mystery and romance which they have so long associated with these elements has at last been dispelled.

In the preparation of the text, the Dictionaries of Morley and Muir, Watts, Wurtz, and Thorpe and the Handbooks of Abegg, Dammer, Fehling, Gmelin, Ladenburg, and Moissan have been freely consulted. The Abstracts published by the English and American Chemical Societies have also been of great service. A very considerable proportion of the text, however, has been prepared directly from the original memoirs. Books consulted for information on special topics are usually mentioned in footnotes; in addition to those, Browning's *Introduction to the Rarer Elements*, Böhm's *Die Darstellung der seltenen Erden*, and Truchot's *Les Terres Rares* may be mentioned. Most of the references cited have been checked by reference to the original journals, etc.

The Author desires to express his deep indebtedness to Dr A. B. Searle, the well-known authority on clays, for his kindness in critically revising the proof-sheets of Chapters IV. and V., and to thank Professor C. James, of New Hampshire College, U.S.A., Dr M. W. Travers, F.R.S., and several other gentlemen for private information on a variety of points. For the preparation of the name index the Author is indebted to Dr J. Newton Friend.

The photographs from which the plates have been prepared were kindly taken for the Author by Mr K. Hickman, the necessary facilities having been granted by Professor A. Fowler, F.R.S., of the Imperial College of Science and Technology, and the rare earths having been presented by Professor C. James.

Corrections, omissions, or criticisms will be thankfully received by the Author, who would also be grateful for reprints of original papers bearing on the subjects included in the book.

H. F. V. LITTLE.

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March 1917.

CONTENTS OF VOLUME IV.

LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science and Arts.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Annalen der Chemie.
Ann. Chim.	Annales de Chimie (1719–1815, and 1914 +).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
Ann. Chim. applicata	Annali di Chimica applicata.
Ann. Chim. Phys.	Annales de Chimie et de Physique (1816–1913).
Ann. Falsif.	Annales des Falsifications.
Ann. Min.	Annales des Mines.
Ann Phys.	Annales de Physique (1914 +).
Ann. Physik	Annalen der Physik.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Lincei	Atti della Reale Accademia Lincei.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deut. physikal. Ges.	Berichte der deutschen physikalischen Gesellschaft.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci. Petrograd	Bulletin de l'Académie Impériale des Sciences de Petrograd.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. d'Enc. p. l'Ind. nationale	Bulletin de la Société d'Encouragement pour l'Industrie nationale.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. U.S. Geol. Survey	Bulletin of the United States Geological Survey.
Centr. Min.	Centralblatt für Mineralogie, Geologie, und Palæontologie.
Chem. Ind.	Die chemische Industrie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Intern. Zeitsch. Metallographie	International Zeitschrift für Metallographie.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie, und Palæontologie.
Jahrb. Radioaktiv. Elektronik	Jahrbuch der Radioaktivität und Elektronik.
Jahresber.	Jahresbericht über die Fortschritte der Chemie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Coll. Sci. Tokyo	Journal of the College of Science, Tokyo.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physique	Journal de Physique.
J. Physical Chem.	Journal of Physical Chemistry.

ABBREVIATED TITLE.	JOURNAL.
J. prakt. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
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.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Kolloid-Zeitsch.	Kolloid-Zeitschrift.
K. Svenska Vet.-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Mém. Acad. Roy. Belg.	Mémoires de l'Académie Royale de Belgique.
Met. Chem. Eng.	Metallurgical and Chemical Engineering.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nova Acta Soc. Upsala.	Nova Acta Regiæ Societatis Scientiarum Upsaliensis.
Pharm. Zentr.-h.	Pharmaceutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Review	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie.
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. Amer. Acad.	Proceedings of the American Academy of Arts and Sciences.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam, Proceedings (English Version).
Proc. Manchester Lit. Phil. Soc.	Proceedings of the Manchester Literary and Philosophical Society.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Schweigger's J.	Schweigger's Journal für Chemie und Physik (continued as Journal für praktische Chemie).
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Wien.
South African J. Sci.	South African Journal of Science.
Tech. Papers, Bur. Stand.	Technical Papers, Bureau of Standards, Washington.
Tonind. Zeit.	Tonindustrie Zeitung.
Trans. Amer. Cer. Soc.	Transactions of the American Ceramic Society.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Eng. Cer. Soc.	Transactions of the English Ceramic Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Mng. Eng.	Transactions of the Institute of Mining Engineers.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
Wied. Annalen	Wiedemann's Annalen der Physik und Chemie.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.

A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOL. IV.

ALUMINIUM AND ITS CONGENERS, INCLUDING THE RARE EARTH METALS.

CHAPTER I.

INTRODUCTORY.

RETAINING Mendeléeff's original numbering for the series, Group III. of the Periodic Table may be represented as in the subjoined table. Boron is the so-called "typical element." Boron and aluminium are members of the short periods. The remaining elements belong to the long periods, and may be divided into the *odd* subgroup, or Subgroup III. B, viz., Ga, In, and Tl, and the *even* subgroup, or Subgroup III. A, viz., Sc, Y, La, and Ac. Aluminium exhibits a marked resemblance to the members of the odd subgroup, with which it is usually classed. Actinium will not be discussed in the present chapter.

Series.	Group III.	
1	...	
2	B	
3		Al
4	Sc	
5		Ga
6	Y	
7		In
8	La	
9		?
10	?	
11		Tl
12	Ac	

As a non-metal, boron possesses little in common with the other elements of this group, but exhibits a formal valency resemblance, since, like the others, it can function as a tervalent element. The sesqui-oxide of boron, however, appears to resemble the sesqui-oxides of aluminium, gallium, and indium in being amphoteric. Boron also resembles the metals of Subgroup III. B in forming alkyl derivatives.[1] Apart from the valency difference, there is considerable chemical similarity between boron and carbon, and even more between boron and silicon.

The metals of the even, like those of the odd, subgroup are tervalent, and hence corresponding compounds of all these elements have similar formulæ. The similarity, however, seldom extends to the water of crystallisation in the case of salts, and, except in the cases of the ethylsulphates and

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[1] Organometallic compounds of aluminium, indium (Thiel and Koelsch, *Zeitsch. anorg. Chem.*, 1910, **66**, 288), and thallium are known, but no attempts have been made to produce gallium compounds of this type.

acetylacetonates of scandium and indium,[1] compounds of the elements of the even subgroup are not known to be isomorphous with those of the elements of the odd subgroup. Thus, in the even subgroup double sulphates with the alkali sulphates are known, but they are not of the alum type, $M^{I}_2SO_4.M^{III}_2(SO_4)_3.24H_2O$, given by aluminium, gallium, indium, and possibly by thallium.

The hydroxides in Subgroup III. A are much stronger bases than those in Subgroup III. B. With the exception of thallic hydroxide, the latter are amphoteric. In Subgroup III. A the anhydrous chlorides, bromides, and iodides are only slightly volatile at a red heat; in Subgroup III. B they are readily volatile. Organometallic compounds are not known in Subgroup III. A, but they are in Subgroup III. B. In fact, in these and other characteristics, the odd and even subgroups of Group III. are very similar to the corresponding subgroups of Group II.

In various respects scandium differs considerably from yttrium and lanthanum.[2] The latter, however, exhibit a very close chemical resemblance. Moreover, they are very similar in chemical behaviour to the rare earth elements, with which they are generally classed. The general chemical characteristics of yttrium and lanthanum are therefore discussed later when dealing with the rare earth elements.[3]

A number of physical properties of the metals of Subgroup III. B are given in the accompanying table, the data for boron being also given for purposes of comparison. It will be noticed that the order of atomic weights is not the order of the melting-points, and that aluminium is anomalous in that it is paramagnetic.

	B.	Al.	Ga.	In.	Tl.
Atomic weight	11·0	27·1	69·9	114·8	204·0
Density	2·34	2·70	5·96	7·28	11·85
Atomic volume . . .	4·72	10·03	11·73	15·77	17·21
Melting-point	*c.* 2200°	658°	30·2°	155°	302°
Boiling-point	?	*c.* 1800°	?	?	1300°–1500°
Latent heat of fusion (cals. per gram)	?	70–80	19·1	?	7·2
Specific heat . . .	0·3066 (0°–100°)	0·218 (0°–100°)	0·079 (12°–23°)	0·0570 (0°–100°)	0·0326 (20°–100°)
Atomic heat	3·37	5·91	5·52	6·54	6·65
Coefficient of expansion × 10^5 .	?	2·44	?	4·59	3·14
Atomic refraction[4] . . .	5·4	9·5	14·8	17·4	21·6
Magnetic susceptibility[5] per gram × 10^6	– 0·65	+0·6	– 0·23	– 0·1	– 0·22
Molecule, in vapour . .	?	?	?	?	Tl
,, in Hg solution . .	...	Al_2	Ga	In	Tl
,, in Sn solution . .	...	Al_2	?	In_2	Tl

The line spectra of aluminium, gallium, indium, and thallium resemble one another in containing doublet series of the principal, diffuse, and sharp

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[1] Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1095; *Rec. trav. chim.*, 1914, **33**, 342.

[2] See Chapter IX.

[3] See Chapter X.

[4] Gladstone and Dale's formula; H_α line.

[5] See Owen, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 637; *Ann. Physik*, 1912, [iv.], **37**, 657.

types.[1] The sharp series are the best known of them. Each may be represented by a Hicks equation :—

$$S(m) = S\infty - 109675/(m + \mu + a/m)^2.$$

The values of the constants are as follows :—[2]

Metal.	Atomic Weight W.	$S_1\infty$.	μ.	a.	ν.	W^2/ν.
Al	27·1	48161·46	1·250525	− 0·063349	112·15	6·54
Ga	69·9	46318·16	1·292185	− 0·077314	826·10	5·91
In	114·8	44454·76	1·287479	− 0·069510	2212·38	5·96
Tl	204·0	41470·23	1·264328	− 0·070417	7792·39	5·34

Here ν denotes the doublet separation, or, in other words, the number to add to $S_1\infty$ to obtain $S_2\infty$. It is obvious that the values of the doublet separations ν are roughly proportional to the squares of the atomic weights W. They are, however, much more nearly in accordance with Runge and Precht's law[3] that the logarithms of ν are proportional to the logarithms of W. The relationship is shown graphically in fig. 1. It is of interest to note that the line spectra of scandium, yttrium, and lanthanum also contain doublet series of the sharp and diffuse types.[4]

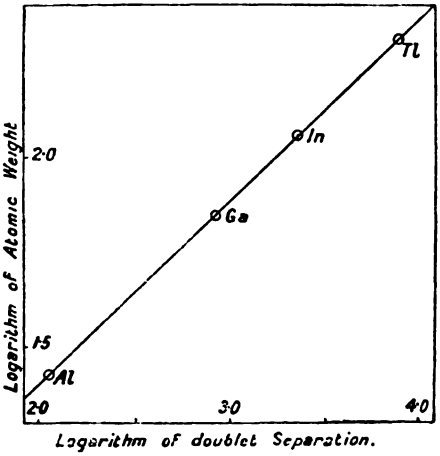

FIG. 1.—Relationship between spectra and atomic weights of Al, Ga, In, Tl.

Aluminium and gallium compounds impart no colour to the Bunsen flame; the spark spectrum of gallium is, however, very sensitive. Indium and its compounds colour the flame dark blue, thallium and its compounds a bright green; the flames show well-defined spectra.

The electrode potentials of aluminium, gallium, indium, and thallium are not known with much accuracy, but aluminium is the most electropositive of these elements. The metals aluminium, gallium, and indium pass into solution in dilute mineral acids as tervalent ions $Al^{\cdot\cdot\cdot}$, $Ga^{\cdot\cdot\cdot}$, and $In^{\cdot\cdot\cdot}$, but thallium yields the univalent ion $Tl^{\cdot}$.

The chlorides of the metals of Subgroup III. B are as follows :—

$AlCl_3$	$GaCl_3$	$InCl_3$	$TlCl_3$
	$GaCl_2$	$InCl_2$	$TlCl_2$
		$InCl$	Tl_2Cl_3
			$TlCl$

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[1] For a short account of series lines in spectra, see Vol. I. of this series.

[2] On the series lines in the spectra of Al, Ga, In, Tl, see Hicks, *Phil. Trans.*, 1912, **A**, **212**, 33 ; 1913, **A**, **213**, 323 ; Paschen and Meissner, *Ann. Physik*, 1914, [iv.], 43, 1223.

[3] See Watts, *Phil. Mag.*, 1906, [vi.], 8, 279.

[4] Hicks, *loc. cit.*

The ability of the metals to form chlorides increases with increase of atomic weight. It is interesting to observe that whereas dry hydrogen chloride reacts with heated aluminium and gallium to give $AlCl_3$ and $GaCl_3$, it yields $InCl_2$ and TlCl with indium and thallium respectively. The trichlorides are hygroscopic solids of low melting-point and volatilise at comparatively low temperatures. They are accordingly intermediate between the less volatile dichlorides of the metals of Subgroup II. B and the more volatile tetrachlorides of the elements of Subgroup IV. B. The stabilities of the trichlorides diminish in the order Al, Ga, In, Tl. Aluminium chloride is stable at a bright red heat; gallium trichloride begins to dissociate at *c.* 1000°, and indium trichloride at a rather lower temperature; while thallium trichloride dissociates at temperatures below 100°. The bromides of the metals of Subgroup III. B closely resemble the chlorides.

Each of the metals under discussion forms a sesqui-oxide. The stabilities of the sesqui-oxides diminish in the order of increasing atomic weights of the metals. Thus, hydrogen at a bright red heat has no action on alumina, but reduces gallium sesqui-oxide to the metal; the reduction of indium sesquioxide is easier to accomplish, and the reduction of thallic oxide still easier. Moreover, the last-named sesqui-oxide loses oxygen when heated, passing into thallous oxide.

The hydroxides, $M(OH)_3$, are feeble bases, practically insoluble in water. It is difficult to say definitely what is the order of their relative strengths, but gallium hydroxide is undoubtedly a weaker base than the hydroxides of aluminium and indium. With the exception of the thallic compound, the hydroxides are also feeble acids. Here, again, gallium appears to be anomalous, in that its hydroxide is a stronger acid than the hydroxides of aluminium and indium.[1]

The soluble salts of aluminium, gallium, indium, and thallium,[2] being salts derived from weak bases, are hydrolysed appreciably in aqueous solution at the ordinary temperature, and the degree of hydrolysis increases with rise of temperature. Normal salts of very weak acids, *e.g.* carbonic acid, cannot be prepared.

The sesqui-sulphides, M_2S_3, are of interest. Aluminium sulphide is completely hydrolysed by water. Gallium sulphide can be precipitated from gallium salts in acetic acid or ammoniacal solution, but only in the presence of another sulphide. Indium sulphide can be precipitated even in the presence of mineral acids provided that the concentration of acid is very small. Finally, thallic sulphide cannot be obtained by double decomposition in aqueous solution since it is readily reduced to thallous sulphide.

The double sulphates of the type $M_2^ISO_4.M_2^{III}(SO_4)_3.24H_2O$, where $M^I = Na$, K, Rb, Cs, NH_4, or Tl, and $M^{III} = Al$, Ga, In, or Tl, are known as alums, and form a group of isomorphous salts. Lithium alums are not known with certainty,[3] although from the nature of the known sodium alums it is reasonable to suppose that lithium alums might exist at temperatures below the ordinary, say 0° C. The sodium and potassium indium alums are not known. The only thallic alum known is the ammonium salt, and that has only been obtained as mixed crystals in association with the aluminium salt. Thus, as the atomic weights increase, the metals of the odd subgroup form alums with increasing difficulty.

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[1] Lecoq de Boisbaudran; see "Gallium" in Wurtz, *Dictionnaire de chimie, Supplément*, p. 859.

[2] Thallic salts are understood here.

[3] See p. 82.

In addition to the alums, double sulphates of the type $M^{I}_2So_4.M^{III}_2(SO_4)_3.8H_2O$ are known. The following have been prepared :—

$Al_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$
$Al_2(SO_4)_3.K_2SO_4.8H_2O$

$In_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$
$In_2(SO_4)_3.Na_2SO_4.8H_2O$
$In_2(SO_4)_3.K_2SO_4.8H_2O$

$Tl_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$ [1]
$Tl_2(SO_4)_3.K_2SO_4.8H_2O$ [1]
$Tl_2(SO_4)_3.Rb_2SO_4.8H_2O$

With these salts the stability increases with increase in atomic weight of the tervalent metal present. The aluminium salts, for instance, are not stable in contact with aqueous solutions. In the case of the indium ammonium salt it is known that the reversible change :—

$$In_2(SO_4)_3.(NH_4)_2SO_4.24H_2O \rightleftharpoons In_2(SO_4)_3.(NH_4)_2SO_4.8H_2O + 16H_2O$$

occurs, the transition-point being 36° C. It is therefore very probable that the sodium and potassium indium alums could be prepared at low temperatures. The octahydrates are of interest owing to the fact that several sulphates of rare earth elements form double salts of the same type.

The alums afford instances of isomorphism between compounds of aluminium, gallium, indium, and thallium. Few other cases are known. The two following isomorphous series have, however, been examined in detail :— [2]

1. The ditetragonal bipyramidal series, $R_3MX_6.2H_2O$:

$K_3TlCl_6.2H_2O$
$(NH_4)_3TlCl_6.2H_2O$
$Rb_3TlBr_6.2H_2O$

$K_3InCl_6.2H_2O$
$K_3InBr_6.2H_2O$

2. The rhombic-bipyramidal series, $R_2MX_5.H_2O$:

$Rb_2TlCl_5.H_2O$
$Rb_2InCl_5.H_2O$
$Rb_2InBr_5.H_2O$

$Cs_2TlCl_5.H_2O$
$Cs_2InCl_5.H_2O$
$Cs_2InBr_5.H_2O$

$(NH_4)_2InCl_5.H_2O$
$(NH_4)_2InBr_5.H_2O$

The isomorphism between the double chlorides and bromides of tervalent indium and thallium is valuable evidence in favour of classifying these two metals together in the same natural family.

Little is known of the compounds of bivalent gallium. The halogen compounds, however, like the halides of univalent and bivalent indium, appear to possess few of the properties of salts. Univalent thallium, on the other hand, forms a well-defined series of stable salts, while the compounds of tervalent thallium are ill-defined and unstable. In this and in other ways thallium differs from the other members of Subgroup III. B; the peculiarities of this element, however, will be discussed later.[3]

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[1] The corresponding double selenate is also known.
[2] Wallace, *Zeitsch. Kryst. Min.*, 1911, 49, 417.
[3] See Chapter VIII.

CHAPTER II.

BORON.

Symbol, B. Atomic weight, 11·0 (O = 16).

Occurrence.—Boron is widely distributed in nature, but it never occurs in the free state. It is present in minute amounts in sea-water[1] and mineral waters,[2] and is widely diffused in the vegetable kingdom;[3] the ashes of nearly all fruits contain small quantities of boron, which is accordingly found in wines. Boron has been detected in the organs and tissues of various animals.[4] It is also a constituent of certain minerals, of which *tourmaline*, *danburite*, and *axinite* may be mentioned.

Small triclinic crystals of boric acid are occasionally found in nature, being known as *sassolite*. Boric acid is also present in the jets of steam that issue from the earth in certain volcanic regions, and which are called *suffioni* in Tuscany. Salts of boric acid occur in various parts of the globe, notably in the Great Basin region of the western United States, in Chili and Peru, at Stassfurt in Germany, in Asia Minor, and in Tibet. The most important deposits are in the United States, where, after *borax* had been found in the water of Clear Lake, California, vast surface deposits of borax were found in the desert marshes of California and Nevada. In 1890, large deposits of *colemanite* were discovered, embedded in old tertiary sediments.

Mineral *borax*, $Na_2B_4O_7.10H_2O$, forms monoclinic prisms of density 1·7 and hardness 2 to 2·5. It was originally obtained from a salt lake in Tibet and sent to Europe under the name of *tinkal*.

Colemanite (or *borate spar*) is a hydrated calcium borate of the formula $Ca_2B_6O_{11},5H_2O$. In appearance it resembles calcspar; hardness, 3·5 to 4·5; density, 2·4. Two other varieties of calcium borate are also found: *priceite* (or *bechilite*) and *pandermite*. Priceite occurs in the United States in County Oregon, and is a fine, white, soft, chalky mineral. Pandermite occurs in an enormous bed of gypsum covered with several feet of clay, in Asia Minor, just south of the Sea of Marmora. It is exported from the port of Panderma. In appearance, pandermite closely resembles a fine-grained white marble.

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[1] Nöllner, *J. prakt. Chem.*, 1867, **102**, 463; Dieulafait, *Ann. Chim. Phys.*, 1877, [v.], **12**, 318; *Compt. rend.*, 1881, **93**, 224; 1882, **94**, 1352.

[2] Gooch and Whitfield, *Bull. U. S. Geol. Survey*, 1888, No. **47**; Fonzes-Diacon and Fabre, *Compt. rend.*, 1914, **158**, 1541.

[3] Jay, *Compt. rend.*, 1895, **121**, 896; Forchammer, *Phil. Trans.*, 1865, **155**, 203; Crampton, *Ber.*, 1889, **22**. 1072; Baumert, *Ber.*, 1888, **21**, 3290; Bechi, *Bull. Soc chim.*, 1890, [iii.], **3**, 122; Hotter, *Chem. Soc. Abst.*, 1890, p. 1338; Passerini, *ibid.*, 1893, ii. p. 225; von Lippmann, *Chem. Zeit.*, 1902, **26**, 465; Azzarello, *Gazzetta*, 1906, **36**, ii. 575; Dugast, *Compt. rend.*, 1910, **150**, 838; Bertainchand and Dugast, *Ann. Chim. Anal.*, 1910, **15**, 179.

[4] Jay, *loc. cit.*; Bertrand and Agulhon, *Compt. rend.*, 1912, **155**, 248; 1913, **156**, 732.

Ulexite (*boronatrocalcite*, *tiza*, or *cottonballs*) is a sodium-calcium borate, $Na_2B_4O_7.Ca_2B_6O_{11}.16H_2O$, which occurs in considerable quantities in Peru and Chili. Hardness, 1; density, 1·65. It is found as yellowish-white nodules, often encrusted with sodium sulphate and chloride.

Boracite (or *stassfurtite*), $2Mg_3B_8O_{15}.MgCl_2$, is a double borate and chloride of magnesium. It crystallises in the tetrahedral class of the regular system; hardness, 7; density, 3·0. Boracite is found at Stassfurt embedded in the *kainite* deposits.[1]

History.—Borax has been known in commerce for many centuries. The name occurs in the writings of Geber and other alchemists, but it is difficult to say whether they refer to the borax of to-day. In 1702, Homberg[2] prepared boric acid from borax, and called it *sal sedativum*. Lémery, in 1728,[3] showed that sal sedativum could be obtained by adding any mineral acid to borax; and Baron, in 1747,[4] discovered that borax was composed of sal sedativum and soda. With the establishment of Lavoisier's system of nomenclature, the name sal sedativum gave place to *boracic acid*, and the acid was looked upon as the oxide of an unknown element. This element, boron, was isolated in an impure state in 1808 by Gay-Lussac and Thenard, and by H. Davy.

Preparation.—The following methods have been proposed for the isolation of boron:—

(i.) Reduction of boron sesqui-oxide with potassium,[5] sodium,[6] magnesium,[7] or aluminium.[8] According to Wöhler and Deville, 10 parts of boron sesqui-oxide are mixed with 6 parts of sodium, covered with 5 parts of sodium chloride, and heated to redness. The magnesium process is discussed later.

(ii.) Electrolysis of fused boron sesqui-oxide[9] or borax.[10]

(iii.) Reduction of boron trifluoride by means of heated potassium.[11]

(iv.) Reduction of potassium borofluoride by means of heated potassium[12] or magnesium.[13]

(v.) Reduction of borax by heated magnesium[14] or red phosphorus.[15]

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[1] For further information concerning the occurrence of boron, see Merrill, *The Non-Metallic Minerals*, 2nd ed. (Wiley & Sons, 1910), p. 231; de Launay, *Traité de Métallogénie*, 3 vols. (Paris, 1913), vol. i. p. 621; Dupont, *J. Eng. Ind. Chem.*, 1910, **2**, 500; Wainewright, *Trans. Manchester Geol. Min. Soc.*, 1909, **31**, 60; Reichert, *Chem. Zentr.*, 1910, i. p. 197; Boeke, *Centr. Min.*, 1910, p. 531; Keyes, *Eng. Min. J.*, 1910, **88**, 826.

[2] Homberg, *Mém. Acad. Sci.*, 1702, p. 33.

[3] Lémery, *Mém. Acad. Sci.*, 1728, p. 273.

[4] Baron, *Mém. Acad. Sci. Sav. étr.*, 1750, **1**, 295, 447.

[5] Gay-Lussac and Thenard, *Gilb. Annalen*, 1808, **30**, 363; *Ann. Chim. Phys.*, 1809, **69**, 204; *Recherches physico-chimiques*, vol. i. p. 276.

[6] Wöhler and Deville, *Ann. Chim. Phys.*, 1858, [iii.], **52**, 63; *Annalen*, 1857, **101**, 113, 347; 1858, **105**, 67.

[7] Phipson, *Proc. Roy. Soc.*, 1864, **13**, 217; F. Jones, *Trans. Chem. Soc.*, 1879, **35**, 42; Winkler, *Ber.*, 1890, **23**, 772; Moissan, *vide infra*; Weintraub, *vide infra*; Ray, *Trans. Chem. Soc.*, 1914, **105**, 2162.

[8] Franck, *Chem. Zeit.*, 1898, **22**, 236; Goldschmidt, *Zeitsch. Elektrochem.*, 1898, **4**, 494; Weston and Ellis, *Trans. Faraday Soc.*, 1908, **3**, 170.

[9] H. Davy, *Phil. Trans.*, 1809, **99**, 75.

[10] Hampe, *Chem. Zeit.*, 1888, **12**, 841; Stähler and Elbert, *Ber.*, 1913, **46**, 2060; Zschille-Hartmann, *Silikat-Zeitsch.*, 1914, **2**, 34.

[11] Rawson, *Chem. News*, 1888, **58**, 283.

[12] Berzelius, *Pogg. Annalen*, 1824, **2**, 113.

[13] Geuther, *Jahresber.*, 1865, p. 126.

[14] Gattermann, *Ber.*, 1889, **22**, 195; Maisch, *Chem. Zentr.*, 1889, ii. p. 905; Ray, *vide supra*.

[15] Dragendorff, *Chem. Zentr.*, 1861, p. 865.

(vi.) Reduction of boron trichloride by means of hydrogen.[1]

(vii.) Reduction of the oxide, bromide, or nitride of boron by heating with metallic calcium.[2]

(viii.) Dissociation of magnesium boride, "boron suboxide," and boron nitride *in vacuo* at high temperatures (1500° and above).[3]

Pure boron was first obtained in 1909, by Weintraub.[3] Previous to this, Moissan claimed to have prepared boron containing not more than 2 per cent. of impurities.[4] According to Moissan, the early processes described by Guy-Lussac and Thenard, Berzelius, and Wöhler and Deville, lead to products which, after purification by heating with water and hydrochloric acid, only contain 40 to 70 per cent. of boron.

According to the method adopted in its preparation, pure boron may be obtained either in small grains having a sub-metallic appearance or in the massive form, the lumps exhibiting a conchoidal fracture. It is very probable, but not certain, that in each of these forms boron is crystalline. The so-called crystalline varieties of boron described by the earlier chemists are, however, borides of aluminium.[5]

Moissan, who considered that he had prepared nearly pure boron, described it as an amorphous, brown powder, and most of the earlier investigators described it in similar terms. The researches of Weintraub and of Ray have shown, however, that boron obtained by Moissan's method contains several per cent. of oxygen and that under certain conditions the oxygen content may reach as much as 16 per cent. In fact, the reduction of excess of either boron sesqui-oxide or borax with a suitable metallic reducing agent always leads to the production of an amorphous, brown powder containing oxygen.[6] Weintraub refers to such a product as *boron suboxide*; it is most probably a solid solution of an oxide of boron, possibly B_4O_3, in boron.[7] This so-called amorphous boron is rapidly converted into boric acid when gently warmed with 40 per cent. nitric acid. Under such treatment pure boron is hardly attacked. The small proportion of pure boron usually present in the amorphous product can therefore be readily isolated.

The practical methods for obtaining pure, or nearly pure boron, are as follows:—

1. *Reduction of Boron Trifluoride.*—The fluoride, generated in a lead or platinum apparatus to exclude silicon fluoride, and free from hydrogen fluoride, is led over sodium heated in a hard glass tube to the lowest temperature at which reduction can be effected. The product is extracted

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[1] Weintraub, *vide infra*; Pring and Fielding, *vide infra*; Besson and Fournier, *vide infra.*

[2] Moissan, *Ann. Chim. Phys.*, 1899, [vii.], **18**, 289; *cf.*, however, Stock and Holle, *Ber.*, 1908, **41**, 2095.

[3] Weintraub, *Trans. Amer. Electrochem. Soc.*, 1909, **16**, 165; *J. Ind. Eng. Chem.*, 1911, **3**, 299; 1913, **5**, 106; *U.S.A. Pat.*, 997,879; 997,880; 997,881; 997,882; 1,019,394; 1,019,569; *Eng. Pat.*, 21,667, 23,334, 25,978 (1906); 1197 (1907); 25,033 (1910); 7103 (1911).

[4] Moissan, *Compt. rend.*, 1892, **114**. 319, 392; *Ann. Chim. Phys.*, 1895, [vii.], **6**, 296; see also Binet du Jassonneix, *ibid.*, 1909, [viii.], **17**, 145.

[5] See p. 97.

[6] The product obtained by the electrolysis of fused borax also appears to be amorphous and to contain a considerable quantity of oxygen.

[7] Ray, *vide supra.*

with water and hydrochloric acid in a platinum dish, when boron is left as a brown powder.[1]

A more convenient process consists in substituting potassium borofluoride for boron trifluoride. Excess of the potassium salt is mixed with sodium in a crucible lined with magnesia, and heated to redness in a rapid stream of dry hydrogen. The boron is isolated as before.

2. *Reduction of Boron Sesqui-oxide with Magnesium and further Reduction of the "Suboxide" obtained.*—Early experimenters used for this purpose 2 parts of oxide to 1 of metal, the reaction being considered to be as follows:—

$$2B_2O_3 + 3Mg = Mg_3(BO_3)_2 + 2B.$$

Moissan increased the amount of oxide to 3 parts, thereby keeping the "amorphous boron" produced suspended in a very fluid mass of boron sesqui-oxide and away from the air. His method is as follows:—[2]

Boron sesqui-oxide (210 grams), free from sodium, calcium, and silicon compounds and recently fused and powdered, is mixed in an earthenware crucible with magnesium turnings (70 grams) free from iron and silicon. The crucible is covered and placed in a furnace already at a bright red heat. Within five minutes, a violent reaction takes place. The mass is heated for another ten minutes, then cooled and removed from the crucible. Externally the reaction product is black; internally it has a maroon colour, traversed in all directions by white crystals of magnesium borate. The black outer layers are removed and rejected. The residue is powdered and boiled with a large quantity of dilute hydrochloric acid. It is then heated with pure hydrochloric acid at the boiling-point of the latter for two hours, a procedure that is repeated six times. The solid residue is washed with water, heated with boiling 10 per cent. alcoholic potash, and again washed with water. Finally it is heated in a platinum dish for four hours with 50 per cent. hydrofluoric acid, washed with water, and dried, first on a porous plate and then in a vacuum over phosphoric anhydride. The product contains 88 to 90 per cent. boron and 2 to 4 per cent. magnesium (Weintraub), the preceding treatment having served to free it almost completely from boron sesqui-oxide, magnesium borate, boron nitride, and silica. To eliminate the remaining magnesium,[3] the boron is mixed intimately with fifty times its weight of boron sesqui-oxide, introduced between two layers of the oxide in a large earthen crucible and heated to bright redness. The product, when cold, is treated by the process already described. In this manner it is possible to obtain a brown, amorphous powder containing only 0·4 per cent. of magnesium. It is advantageous, during each heating in the furnace, to enclose the crucible in a larger one brasqued with a finely powdered mixture of rutile and carbon. An alternative method of eliminating nitrogen is to carry out the preparation in an iron vessel lined with magnesia, a rapid stream of hydrogen being passed through it.[4]

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[1] Prof. H. Brereton Baker; private communication. Rawson, *vide supra.*

[2] Moissan, *vide supra.*

[3] This magnesium is present neither as borate nor boride, but is present in solid solution either as magnesium oxide or possibly as a borite (Ray).

[4] Considerable purification may quickly be effected if, after the products of the interaction of boron sesqui-oxide and magnesium have been treated with hydrochloric acid, the residue is submitted to fractional decantation and the lighter fractions discarded (Binet du Jassonneix, *vide supra*; Weintraub, *vide supra*).

In the course of his investigations of the magnesium process, Weintraub[1] found that if a higher temperature than that used by Moissan is employed, there is no difficulty in obtaining a product free from magnesium. To obtain the higher temperature, Moissan's procedure may be used, with charges of at least one kilogram of material, or the reaction may be effected in a graphite crucible heated to 1700° in a vacuum electric furnace. The high temperature product, however, contains not 4 to 5 per cent. but 14 to 16 per cent. of oxygen, and re-fusion with a large excess of boron sesqui-oxide is without action upon it. If the ratio oxide : metal is diminished below 2 : 1, the product obtained, after the usual chemical treatment, consists mainly of magnesium boride.

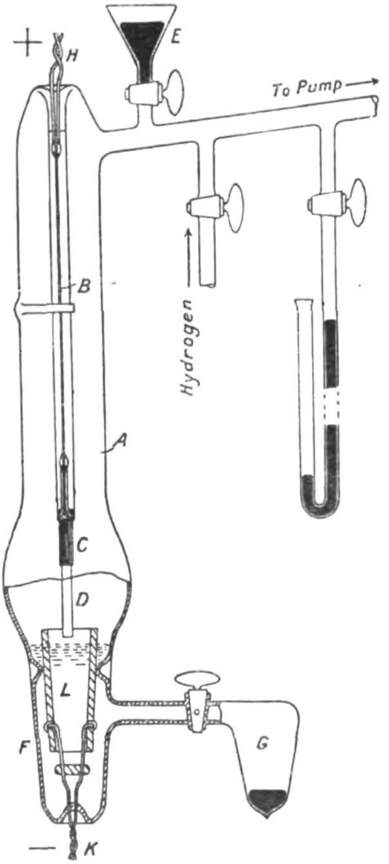

FIG. 2.—Mercury arc furnace for melting boron.

Magnesium boride, "boron suboxide," and boron nitride all dissociate when heated *in vacuo* to sufficiently high temperatures. With the boride, the change is perceptible at 1200°, and is rapid at 1500°. The suboxide and nitride, however, dissociate with more difficulty, particularly the latter. Owing to this dissociation, it is comparatively easy to obtain pure boron from the so-called "amorphous boron" or "boron suboxide," and at the same time to melt the boron. (i.) One method consists in placing the powder in a water-cooled copper cup which forms one of two copper electrodes, and passing an arc between them *in vacuo* or in hydrogen at a few millimetres pressure. Several pounds of boron may be prepared and melted at one operation in this manner, starting with boron suboxide (Weintraub). (ii.) Another method consists in using a "mercury arc furnace." In this case, Moissan's boron or boron suboxide should be compressed into rods and purified as far as possible by heating to 1200° to 1500° *in vacuo*. A boron rod D, mounted in a carbon holder C to which a lead B is attached, is placed within the cylindrical glass apparatus A (fig. 2). The apparatus may be filled with hydrogen or evacuated by means of suitable connections. The apparatus being evacuated, mercury is run in through the funnel E until the end of D is just covered. Hydrogen is then admitted up to 2·5 to 15 cms. pressure, the electrodes H and K connected to a suitable source of current, and mercury run into G until the end of D is clear of the mercury in the lower part F of the

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[1] Weintraub, *vide supra.*

apparatus. An arc is thus formed between the boron and the mercury in F, and, since at the surface of the latter great heat is developed, the end of D melts and falls off. As the rod D thus shortens, more mercury is run in from time to time from E. The bottomless alundum pot L prevents the arc from straying to the glass. In this manner, extremely pure boron may be obtained (Weintraub). (iii.) A third method, somewhat analogous to the preceding method (ii.), consists in focussing the cathode rays on the powdered material, an operation that must obviously be carried out in a nearly perfect vacuum.[1]

The preceding methods for obtaining pure boron necessitate the employment of special forms of apparatus. A fourth method is very simple to carry out, but does not give the product in the massive form. (iv.) The "suboxide" is mixed with excess of magnesium or sodium and heated to bright redness in a stream of hydrogen; in the former case magnesium boride is formed and subsequently decomposed at the high temperature employed. The product is extracted successively with water, hydrochloric acid, and warm 40 per cent. nitric acid.[2]

3. *Reduction of Boron Trichloride with Hydrogen.*—This method, also due to Weintraub, is based upon the reversible reaction

$$2BCl_3 + 3H_2 \rightleftharpoons 2B + 6HCl,$$

which has been studied by Pring and Fielding, and also by Besson and Fournier.[3] A high temperature is necessary for the production of boron by this method, and is obtained by the use of an electric arc. The preparation is effected by running one or more alternating-current arcs between water- or air-cooled copper electrodes in a mixture of boron trichloride vapour and a large excess of hydrogen; a glass or copper containing vessel may be used. The gases are mixed by passing dry hydrogen over the surface of boron trichloride contained in a vessel cooled by a freezing mixture, or by allowing the chloride to drop into a vessel (kept a little above the room temperature) through which hydrogen is passed. The boron is partly thrown off as a fine powder and partly settles on the electrodes, where it grows into small rods. These eventually melt down to beads and fall off, and the process repeats itself. The boron powder, after washing with water, contains 99 to 99·5 per cent. of boron; the fused lumps are pure boron. By any of the processes already mentioned the boron powder may be purified and melted.

Properties.—Boron is a black solid of density 2·34 and compressibility $0 \cdot 3 \times 10^{-6}$ per atmosphere at 20°.[4] In hardness it is inferior only to diamond. Its fracture is conchoidal; it shows no signs of microcrystalline structure. It is inferior to diamond in its toughness or strength. Under atmospheric pressure boron melts at about 2200°.[5] It passes into vapour at temperatures considerably below the melting-point, the vapour tension becoming noticeable at 1600°. The electrical conductivity of a piece of massive boron at ordinary temperatures is extremely small, but between room temperature and that corresponding to a dull red heat it increases to

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[1] Tiede and Birnbräuer, *Zeitsch. anorg. Chem.*, 1914, **87**, 129; Tiede, *Ber.*, 1913, **46**, 2229.

[2] Ray, *Trans. Chem. Soc.*, 1914, **105**, 2162.

[3] Pring and Fielding, *Trans. Chem. Soc.*, 1910, **95**, 1497; Besson and Fournier, *Compt. rend.*, 1910, **150**, 872; Weintraub, *loc. cit.*

[4] Richards, *J. Amer. Chem. Soc.*, 1915, **37**, 1646.

[5] Tiede and Birnbräuer, *Zeitsch. anorg. Chem.*, 1914, **87**, 129; Weintraub gives 2800°,

about two million times its initial value. For instance, a piece of boron which had a resistance of $5·62 \times 10^{6}$ ohms at 27° had a resistance of only $4·60 \times 10^{4}$ ohms at 180° C. At a dull red heat the resistance had fallen to 5 ohms. Over a short temperature interval the resistance of boron is an exponential function of the temperature. At 23° the specific resistance is about $1·7 \times 10^{6}$ ohms per cm. cube; at 0° the value is about 2×10^{6}. The specific resistance of boron is enormously decreased at ordinary temperatures by the introduction into it of small amounts of other elements, and at the same time the very large negative temperature-coefficient is diminished. Thus, a few tenths per cent. of carbon introduced into boron reduces the resistance to about one-twelfth its value at ordinary temperatures.[1]

The atomic refraction of boron in saturated compounds for the D line is 5·3 or 3·2, and for the H_{α} line 5·4 or 3·1, according as the Gladstone and Dale or the Lorenz and Lorentz formula is employed.[2]

The spark and arc spectra of boron consist simply of three lines in the ultraviolet, 3451·50, 2497·83*, and 2496·89*, the pair asterisked being more persistent than the other line.[3] Two band spectra, however, are associated with boron. The green flames due to boric acid, alkyl borates, and boron fluoride all have practically identical band spectra; the bands are headless, and the most prominent are in the green region (see fig. 3 on p. 44). They have been observed and measured by numerous scientists.[4] The same bands are observed in the arc spectra of boron and boron sesquioxide, and in the spark spectrum of a solution of boric acid in hydrochloric acid, and they are attributed to oxide of boron; they do not occur in the spark spectrum of boron itself.[5] Another series of bands, which have definite heads and degrade towards the red, is found in the spectrum of boron trichloride or methyl borate in the afterglow of active nitrogen (p. 24); these bands also occur to some extent in the arc spectrum of boron and its oxide, and are attributed to boron nitride but they do not occur in the spark spectrum of boron in nitrogen.[6]

Pure boron may be strongly heated in air without undergoing any perceptible oxidation. It is oxidised to boric acid when heated with concentrated nitric acid, but the rate of oxidation is very slow. It does not combine with either copper (Weintraub) or magnesium (Ray) at a red heat. Its other chemical properties are unknown.

Moissan's "amorphous boron" is a maroon-coloured powder of specific gravity 2·45. Its specific heat increases rapidly with rise of temperature, the

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[1] Weintraub, *vide supra*.

[2] Ghira, *Gazzetta*, 1893, **23**, i. 452, ii. 8.

[3] Crookes, *Proc. Roy. Soc.*, 1912, **A**, **86**, 36; de Gramont, *Compt. rend.*, 1908, **146**, 1260; *cf.* Hartley, *Trans. Chem. Soc.*, 1883, **43**, 390; *Proc. Roy. Soc.*, 1883, **35**, 301; Rowland, *Phil. Mag.*, 1893, [v.], **36**, 49; Kayser and Runge, *Wied. Annalen*, 1893, **48**, 126; Eder and Valenta, *Denkschr. K. Akad. Wiss. Wien*, 1893, **60**, 307; Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1897, **106**, II*a*, 494; Kayser, *Handbuch der Spectroskopie* (Leipzig, 1910), vol. v. p. 134.

[4] Lecoq de Boisbaudran, *Compt. rend.*, 1873, **76**, 833; *Spectres Lumineux* (Paris, 1874); Salet, *Ann. Chim. Phys.*, 1873, [iv.], **28**, 5; *Traité de spectroscopie* (Paris, 1888); Dieulafait, *Ann. Chim. Phys.*, 1877, [v.], **12**, 318; Ciamician, *Sitzungsber. K. Akad. Wiss. Wien*, 1880, **82**, II, 425.

[5] Lecoq de Boisbaudran, *loc. cit.*; Hagenbach and Konen, *Atlas der Emissionspektra* (Jena, 1905); Hagenbach, *Wüllner Festschrift* (Leipzig, 1905), p. 128; Kühne, *Zeitsch. Wiss. Photochem.*, 1906, **4**, 173; Auerbach, *ibid.*, 1909, **7**, 30, 41; Eder and Valenta, *Denkschr. K. Akad. Wiss. Wien*, 1893, **60**, 467; Jevons, *vide infra*.

[6] Jevons, *Proc. Roy. Soc.*, 1915, **A**, **91**, 120; *cf.* Kühne, *loc. cit.*

mean value being 0·3066 between 0° and 100°, 0·3407 between 0° and 192°, and 0·3573 between 0° and 235°.[1]

The chemical properties of "amorphous boron" have been described in detail by Moissan,[2] and are given in the following paragraphs. It must, however, be remembered that these properties refer to a substance that has been shown by Weintraub to contain 4 to 5 per cent. of oxygen. It will be noticed that several of the properties mentioned are not the properties of pure boron.

Boron unites directly with fluorine at the ordinary temperature, with chlorine at 410°, and with bromine at 700°, but is without action on iodine. With the halogen acids it reacts with greater difficulty; hydrogen fluoride attacks it at a dull red heat, hydrogen chloride at a bright red heat, the products being hydrogen and boron fluoride or chloride. Hydrogen iodide has no action on boron. When heated in oxygen, boron ignites with the production of heat and light, and it burns in air at 700°.[3] It unites readily with sulphur at 600°, producing the sesqui-sulphide, and combines with selenium at a higher temperature; it does not combine directly with tellurium. The direct combination of boron and nitrogen occurs very slowly at 900°, but rapidly at 1250°. Neither phosphorus nor arsenic vapour at 750° will combine with boron, and antimony may be fused with it without the production of any chemical change. When heated with carbon in the electric arc in an atmosphere of hydrogen, crystalline boron carbide is produced.

Boron does not unite directly with the alkali metals. On the other hand, it unites with magnesium at a dull red heat, and with iron and aluminium at a higher temperature. It also unites with silver and platinum.

Boron acts as a powerful reducing agent. It decomposes steam at a red heat, reduces iodic acid on warming, with the liberation of iodine, and at a temperature just below a dull red heat it reduces sulphur dioxide. At a dull red heat the oxides of arsenic and carbon dioxide are reduced by boron, at 800° phosphoric anhydride is reduced, and at 1200° the reduction of carbon monoxide and silica can be effected. At a bright red heat boron burns in either nitrous or nitric oxide, producing boron oxide and nitride. Concentrated sulphuric and nitric acids are readily reduced by boron, which becomes oxidised to boric acid.

A large number of oxides and salts are reduced by boron. The oxides of copper, tin, lead, antimony, and bismuth are reduced when gently warmed with boron, the mixtures becoming incandescent. At a red heat the oxides of iron and cobalt are reduced, but not the alkaline earth oxides. Silver fluoride is violently reduced by boron at ordinary temperatures, the fluorides of zinc and lead at a red heat, but not the alkali and alkaline-earth fluorides. Chlorides are less easy to reduce, but mercuric chloride can be reduced to mercury at 700°. When boron is fused with an alkali hydroxide, a violent evolution of hydrogen occurs, and an alkali borate is produced.

Reductions may be effected at the ordinary temperature with certain aqueous solutions. Thus, potassium permanganate is slowly reduced, and

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[1] Moissan and Gautier, *Ann. Chim. Phys.*, 1896, [vii.], 7, 568; *cf.* Kopp, *J. Chem. Soc.*, 1866, 19, 187; F. Weber, *Phil. Mag.*, 1875, [iv.], 161, 276; Mixter and Dana, *Annalen*, 1873, 169, 388; see also Vol. I. p. 90.

[2] Moissan, *Ann. Chim. Phys.*, 1895, [vii.], 6, 296; *Compt. rend.*, 1892, 114, 617; 1893, 117, 423; 1894, 119, 1172.

[3] The combustion is prevented by carefully drying the elements (Baker, *Phil. Trans.*, 1888, 179, 590).

precipitates of the respective metals are produced by the action of boron on aqueous solutions of silver nitrate and the chlorides of gold, platinum, and palladium.

Boron will probably receive various practical applications in the near future, owing to its remarkable electrical properties. Its volatility prevents its employment in the manufacture of electric lamp filaments. Boron is of great use in the purification of copper; if 0·03 to 0·1 per cent. be added to molten copper before it is cast, the metal is deoxidised and purified to a remarkable extent. It is cheaper, however, to use "boron suboxide" for the purpose.[1] A little boron increases the breaking stress of steel.[2]

Colloidal Boron.—Colloidal solutions of boron may be prepared from boron obtained by the action of magnesium, sodium, or potassium on boron sesqui-oxide, by extracting the products of the reaction with hydrochloric acid and washing the residue repeatedly with water until the water acquires a decided colour. Two boron hydrosols have been obtained by the magnesium method: (i.) a relatively unstable sol, and (ii.) a comparatively stable sol. The first is dark brown in colour, and may be kept in a closed vessel for not more than three or four weeks. It is immediately coagulated by electrolytes, and rapidly oxidised by dilute nitric acid or hydrogen peroxide. It cannot be purified by dialysis. The second resembles the first in appearance, but may be kept for nine weeks and purified by dialysis. Two sols have been obtained by the potassium method; they resemble those just described. Three sols have been obtained by the sodium method, and are deep blue in colour. Two are unstable, but the third is stable and may be purified by dialysis. Boron hydrosols have a high electrical resistance; the boron particles are negatively charged.[3]

Atomic Weight.—It follows from the analyses and vapour densities of numerous boron compounds that the atomic weight of boron is three times its combining weight.

The determinations of the combining weight leave much to be desired. Various attempts have been made to measure the ratio $Na_2B_4O_7.10H_2O$: $Na_2B_4O_7$, but the results of different experimenters do not agree, and the method, involving as it does the use of a hydrated salt, is a bad one. The best determinations of the combining weight are probably those due to Gautier,[4] whose values for the atomic weight of boron, derived by four methods, are as follows:—[5]

$$B_2S_3 : 3BaSO_4 :: 16·8855 : 100 \quad \therefore \quad B = 11·028$$
$$B_6C : CO_2 :: 177·258 : 100 \quad \therefore \quad B = 10·999$$
$$BBr_3 : 3AgBr :: 44·512 : 100 \quad \therefore \quad B = 11·027$$
$$BCl_3 : 3AgCl :: 27·2845 : 100 \quad \therefore \quad B = 10·955$$

The first two ratios are only based upon a few experiments, and from the nature of the analytical operations involved the results cannot be

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[1] Weintraub, *U.S. Pat.*, 1,023,604; see also *J. Ind. Eng. Chem.*, 1910, **2**, 477.

[2] Guillet, *Compt. rend.*, 1907, **144**, 1049. See also Moissan and Charpy, *Compt. rend.*, 1895, **120**, 130; Hannesen, *Zeitsch. anorg. Chem.*, 1914, **89**, 257; and Vol. IX. of this series.

[3] Ageno and Barzetti, *Atti R. Accad. Lincei*, 1910, [v.], **19**, i. 381; Gutbier, *Kolloid Zeitsch.*, 1913, **13**, 137.

[4] Gautier, *Ann. Chim. Phys.*, 1899, [vii.], **18**, 352.

[5] Clarke, *A Recalculation of the Atomic Weights*, 3rd ed. ("Smithsonian Miscellaneous Collections," vol. 54, No. 3, 1910). The antecedent data have been changed to:—Ag=107·880, Cl=35·457, Br=79·916, S=32·065, C=12·003, Ba=137·37, O=16·000, Na=22·996.

regarded as possessing much more than corroborative value. From a chemical point of view the other two ratios would be expected to yield more reliable results, but Gautier's method of determining them is open to serious criticism.

Mention should be made of Ramsay and Aston's determination of the ratio $Na_2B_4O_7 : 2NaCl$, effected by distilling anhydrous borax with hydrochloric acid and methyl alcohol.[1] The results obtained lead to the value B = 10·951. The other determinations[2] are of little importance.

The value at present adopted for the atomic weight of boron is **B = 11·0**.

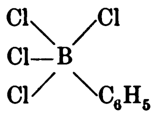
COMPOUNDS OF BORON.

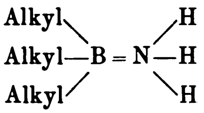
From the chemical point of view, boron is decidedly a non-metallic element. Thus, the halides are volatile compounds which are readily and irreversibly hydrolysed by water. The sulphide of boron is similarly hydrolysed by water; several hydrides are volatile. On the other hand, boron sesqui-oxide appears to be amphoteric. From the physical standpoint, boron exhibits a slight resemblance to the metallic elements; the binary systems *boron-metal*, for example, are to some extent similar to the binary systems composed of two metals.

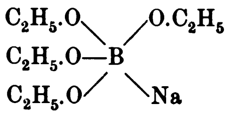
From the reactions of boron it is clear that the binary compounds of boron are very stable substances. The heats of formation (H.F.), given below, fully bear out this conclusion:—[3]

(BF_3)	H.F. = 234·9 Cals.	$[B_2O_3]$	H.F. = 272·6 Cals.
BCl_3	93·3 „	$[B_2S_3]$	82·6 „
BBr_3	43·2 „		

Boron is tervalent in its halogen derivatives, and appears to be usually tervalent in its compounds. However, it seems at times to exhibit a valency of five. Thus, Moissan has prepared boron pentasulphide; and the compounds of the formulæ $C_6H_5BCl_4$, $(CH_3)_3BNH_3$, $(C_2H_5)_3B.NH_3$, and $(C_2H_5.O)_3B.C_2H_5.ONa$ [4] may perhaps contain pentad boron and be formulated as follows:—[5]







The compound $B(CH_3)_3.NH_3$, for instance, is fairly stable; it melts at 51° and boils at 110°. The existence of certain additive products of boron

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[1] Ramsay and Aston, *Trans. Chem. Soc.*, 1893, 63, 211.

[2] Berzelius, *Pogg. Annalen*, 1826, 8, 1; Laurent, *J. prakt. Chem.*, 1849, 47, 415; Hoskyns-Abrahall, *Trans. Chem. Soc.*, 1892, 61, 650; Rimbach, *Ber.*, 1893, 26, 164; Armitage, *Proc. Chem. Soc.*, 1898, 14, 22.

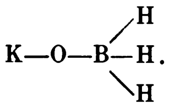
[3] Troost and Hautefeuille, *Ann. Chim. Phys.*, 1876, [v.], 9, 70; Berthelot, *Thermochimie*, vol. 2; Sabatier, *Compt. rend.*, 1891, 112, 862.

[4] Other compounds of this type are known (p. 33).

[5] Michaelis and Becker, *Ber.*, 1880, 13, 58; Gustavson, *Ber.*, 1870, 3, 426; *J. Russ. Chem. Soc.*, 1888, 20, 621; *Ber.*, 1880, 13, 58; Frankland and Duppa, *Phil. Trans.*, 1862, 152, 167; *Proc. Roy. Soc.*, 1876, 25, 165; Lorenz, *Annalen*, 1888, 247, 226; Copaux, *Compt. rend.*, 1898, 127, 719; *cf.* Frankland, *ibid.*, 1898, 127, 798.

trichloride and tribromide also suggests that boron is pentad. The same hypothesis appears necessary to account for the nature of tbe borohydrates and the lower oxides of boron.

The existence of a fairly stable hydride, B_2H_6, clearly shows that on occasion boron may be at least quadrivalent. According to Stock, boron is quadrivalent in its hydrides, and also in the hypoborates, *e.g.* $KOBH_3$, which would accordingly be written



$$\mathrm{K-O-B}\!\begin{array}{l}\diagup\mathrm{H}\\-\mathrm{H}.\\\diagdown\mathrm{H}\end{array}$$

It is of some interest in this connection to note that since boron is occasionally at least quadrivalent, its maximum valency is greater than its group number in the periodic table.

Boron Hydrides or Hydroborons.—The existence of solid hydrides of boron has been suspected by various chemists.[1] The existence of a volatile hydride was long ago anticipated from analogy with the compounds of other non-metallic elements; but neither Wöhler and Deville nor Gustavson succeeded in preparing it. In 1879, F. Jones showed that a volatile boron hydride did exist, and two years later, F. Jones and Taylor studied the hydride and assigned to it the formula BH_3.[2] Their work was confirmed in a qualitative way by Sabatier.[3] Later, Ramsay and Hatfield announced the existence of what were, in their opinion, probably two isomeric hydrides of the formula B_3H_3,[4] but Ramsay was unable subsequently to duplicate the work. No value can be placed upon the scanty experimental data which served to deduce the preceding formulæ, since the gaseous boron hydrides were undoubtedly contaminated with silicon hydride.

The hydrides prepared by Jones and Taylor, Sabatier, and Ramsay and Hatfield were obtained, mixed with a very large excess of hydrogen, by the action of dilute acids on magnesium boride, and similar gaseous mixtures can be obtained by the action of acids upon commercial iron and manganese borides.[5] From the mixed gases produced from magnesium boride and hydrochloric acid, Stock and Massenez in 1912 succeeded in isolating two distinct boron hydrides of molecular formulæ B_4H_{10} and B_6H_{12};[6] and since then Stock and others have obtained several more boron hydrides.[7] Although the compound BH_3 is not yet known, there are, according to Stock, Friederici, and Priess, at least ten boron hydrides:—

(1) B_2H_6. Obtained by heating B_4H_{10}. Colourless gas.
(2) B_4H_{10}. Obtained from magnesium boride and hydrochloric acid.
(3) A colourless liquid, very unstable, obtained like (1).
(4) B_6H_{12}. Obtained like (2).

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[1] Gattermann, *Ber.*, 1889, **22**, 195; Winkler, *Ber.*, 1890, **23**, 772; Reinitzer, *Sitzungsber. K. Akad. Wiss. Wien*, 1881, **82**, 736; *Monatsh.*, 1880, **1**, 792; Lorenz, *Annalen*, 1888, **247**, 246; J. Hoffmann, *Chem. Zeit.*, 1911, **35**, 265.

[2] Jones, *Trans. Chem. Soc.*, 1879, **35**, 41; Jones and Taylor, *ibid.*, 1881, **39**, 213.

[3] Sabatier, *Compt. rend.*, 1891, **112**, 866.

[4] Ramsay and Hatfield, *Proc. Chem. Soc.*, 1901, **17**, 152.

[5] J. Hoffmann, *Chem. Zeit.*, 1911, **35**, 265.

[6] Stock and Massenez, *Ber.*, 1912, **45**, 3539.

[7] Stock and Friederici, *Ber.*, 1913, **46**, 1959 (B_2H_6); Stock, Friederici, and Priess, *Ber.*, 1913, **46**, 3353 ($B_{10}H_{14}$); Stock, *Zeitsch. Elektrochem.*, 1913, **19**, 779.

(5) $B_{10}H_{14}$. Obtained like (1); also by heating (1).
(6) Non-volatile solid, soluble in CS_2. Obtained like (1).
(7) Non-volatile yellow solid, insoluble in CS_2. Obtained like (1), and by heating (6).
(8) Difficultly volatile liquid, obtained by heating (6).
(9) Colourless, non-volatile solid, insoluble in CS_2. Obtained by heating (1).
(10) Brown hydride or hydrides, resembling boron and poor in hydrogen content. Obtained by heating (7).

The starting-point in the preparation of the boron hydrides is crude magnesium boride, made by mixing 1 part of very finely powdered boron sesqui-oxide with 3 parts of magnesium powder and rapidly heating the mixture, 10 grams at a time, in a thin sheet-iron crucible in a stream of hydrogen. The product, quickly cooled in hydrogen, is finely powdered, sifted, and slowly dropped into 15 per cent. hydrochloric acid at 50° to 80°, a slow stream of hydrogen being passed through the apparatus. The evolved gases, dried over calcium chloride and phosphoric anhydride, are passed through U-tubes cooled in liquid air; in them the boron hydrides B_4H_{10} and B_6H_{12} solidify, together with a little carbon dioxide and silicon hydrides.

The distillation of this crude product furnishes in order the following fractions: (i.) silicon hydride, SiH_4, (ii.) carbon dioxide, (iii.) silicon hydride, Si_2H_6, (iv.) boron hydride, B_4H_{10}, (v.) boron hydride, B_6H_{12}, (vi.) residue of less volatile boron and silicon hydrides. The two hydrides B_4H_{10} and B_6H_{12} are obtained as follows:—At the temperature of liquid air the pressure above the solid is reduced to zero. Traces of hydrogen and silicon hydride are thus removed. The temperature is then raised to $-80°$, when the solid melts. The pressure is quickly lowered to a few millimetres, and the evolved gas rejected as long as it contains silicon hydride. The gas then evolved at $-80°$ and 3 mm. consists of the hydride B_4H_{10}, and, unless the room temperature is above 20°, partly condenses in the mercury pump. The residue is distilled at $-40°$ until the pressure falls to 1·5 mm., the temperature raised to 0°, and distillation continued until the pressure is only 10 mm. All the hydride B_4H_{10} has then been removed, and the residue, on further distillation, gives another hydride, B_6H_{12}, the pressure falling to less than 5 mm.

From 200 grams of magnesium boride, 100 c.c. (at N.T.P.) of pure hydride B_4H_{10} and 60 milligrams of hydride B_6H_{12} may be obtained.[1]

Tetraborodecahydride or **borobutane**, B_4H_{10}, is a colourless, very volatile liquid which boils at 16° to 17° C., and freezes at about $-112°$ C. The vapour density is 27·0 (H = 1), in accordance with the formula given. The vapour pressures at various temperatures are as follows:—

Temp. ° C. . . .	0°	6°	10°	15°	16°
Vap. press. (in mms.)	500	580	630	710	740

The hydride has a very disagreeable odour. A few bubbles when inhaled affect respiration and cause headache. It is extremely unstable, decomposing in a few hours at ordinary temperatures into a series of other hydrides. It is decomposed by electric sparks, and ignites spontaneously in air or oxygen, burning with a green flame. Nitric acid oxidises it with explosive violence.

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[1] Stock and Massenez, *loc. cit.* For a number of improvements in the preparation, see Stock, Kuss, and Priess, *Ber.*, 1914, 47, 3115.

It is slowly decomposed by water, the final result being expressed by the equation:—

$$B_4H_{10} + 12H_2O = 4H_3BO_3 + 11H_2.$$

Aqueous sodium hydroxide rapidly and completely absorbs the hydride, producing a hypoborate (p. 28), but hydrogen is slowly evolved, and the net result may be expressed thus:—

$$B_4H_{10} + 4NaOH + 4H_2O = 4NaBO_2 + 11H_2.$$

The hydride is decomposed by alcohol and reacts with ammonia, but its solution in benzene is very stable towards oxygen.[1]

Hexaborododecahydride or **borohexylene**, B_6H_{12}, is a colourless liquid, the vapour density of which is in agreement with the formula given. The vapour pressures at various temperatures are as follows:—

Temp. ° C. . .	−40°	0°	10°	24°	c. 100°
Vap. press. (mm.)	1	10	15	25	760

The hydride has a highly disagreeable odour, and ignites spontaneously in the air. It is decomposed by water and alkalies more readily than the preceding hydride:—[1]

$$B_6H_{12} + 18H_2O = 6H_3BO_3 + 15H_2$$
$$B_6H_{12} + 6NaOH + 6H_2O = 6NaBO_2 + 15H_2$$

Boron trihydride or **boro-ethane**, B_2H_6.—It has been mentioned that the compound B_4H_{10} is very unstable. When kept over mercury at the ordinary temperature it decomposes with the formation of a gaseous hydride B_2H_6 and hydrogen. The rate of decomposition is greatly augmented by ultraviolet light, but not appreciably by sunlight. The change is practically complete at 100° after one hour.

Boron trihydride is a colourless gas possessing a repulsive odour which recalls that of B_4H_{10}, and also that of hydrogen sulphide. Its vapour density corresponds with the molecular formula B_2H_6. The hydride melts at −169° and boils at −87° C. The vapour pressure of the liquid at various temperatures is as follows:—

Temp. ° C. . .	−130°	−120°	−112°	−110°	−100°	−90°	−87°
Vap. press. (in cms.)	4	10	22·4	25	40	65	76

Boron trihydride is fairly stable, but it slowly decomposes even at the ordinary temperature. When heated with a free flame, solid, but not liquid, hydrides are produced; when sparked, boron is deposited and non-volatile hydrides of unpleasant odour are produced. In the presence of air it gives rise to solids containing both boron and oxygen, and when exploded with oxygen it reacts thus:—

$$B_2H_6 + 3O_2 = B_2O_3 + 3H_2O.$$

It dissolves in carbon disulphide, and the solution decolorises bromine; it does not react with dry hydrogen chloride, but combines readily with dry ammonia.

Boron trihydride reacts with water to give boric acid and hydrogen:—

$$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2.$$

Like the hydride B_4H_{10}, it gives a hypoborate with alkali hydroxide, but some hydrogen is evolved immediately the gas and the hydroxide come into

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[1] Stock and Massenez, *loc. cit.*

contact. The hypoborate slowly decomposes, and the final result may be expressed thus :—[1]

$$B_2H_6 + 6NaOH = 2Na_3BO_3 + 6H_2.$$

Decaborotetradecahydride, $B_{10}H_{14}$.—When the hydride B_4H_{10} is heated for four or five hours to 100°, or when the hydride B_2H_6 is heated for forty-eight hours to 115° to 120°, a volatile solid hydride, $B_{10}H_{14}$, is produced.

This hydride is a colourless solid of peculiar odour resembling that of osmium tetroxide. It sublimes *in vacuo* at 60° to 80°, producing beautiful long needles of density 0·94. It melts at 99·5° to a colourless liquid that does not decompose below 200°. The molecular weight in benzene solution and the percentage composition are in harmony with the molecular formula $B_{10}H_{14}$.

The hydride is soluble in alcohol, ether, benzene, and carbon disulphide. It is not decomposed by air or water, is little affected by nitric acid, but is oxidised by potassium permanganate. It dissolves in alkalies, forming a yellow solution.

When prepared from B_1H_{10} or B_2H_6 by heating, the hydride $B_{10}H_{14}$ is accompanied by two other non-volatile solid boron hydrides, which are also produced when $B_{10}H_{14}$ is heated: (i.) a *yellow hydride*, probably $(B_5H_4)_x$, insoluble in carbon disulphide and decomposed by water; and (ii.) a *colourless hydride*, probably $B_{12}H_x$, soluble in carbon disulphide, not decomposed by water, and converted into (i.) at 150°.[2]

Borides.—The binary compounds of boron with carbon and silicon are described in this chapter as boron carbide and boron silicides. The binary compounds of boron with other, more electropositive elements, are called *borides*, and are described under the headings of the other elements.

Boron and the Fluorine Group.

Boron forms halogen compounds of the type BX_3. The fluoride,[3] chloride,[4] and bromide[5] can be prepared by the direct union of their elements,[6] but not the iodide. The chloride[7] and bromide[8] can also be prepared by heating to redness in a stream of either chlorine or bromine an intimate mixture of boron sesqui-oxide and carbon :—

$$B_2O_3 + 3C + 3X_2 = 2BX_3 + 3CO.$$

The boron halides have none of the properties of salts. At the ordinary temperature the fluoride is a gas; the liquid chloride boils at 12·5° C.; the bromide is a volatile liquid, and the iodide a solid of low melting-point. Each is rapidly decomposed by water, the change being expressed, except for the fluoride, by the (irreversible) equation :—

$$BX_3 + 3H_2O = H_3BO_3 + 3HX.$$

Besson[9] has described the **bromo-iodides** of boron, BBr_2I and $BBrI_2$. They are colourless liquids which boil at 125° and 180° respectively. A mixture

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[1] Stock and Friederici, *loc. cit.*; Stock, Friederici, and Priess, *loc. cit.*

[2] Stock, Friederici, and Priess, *loc. cit.*; Stock, *Zeitsch. Elektrochem.*, 1913, **19**, 779.

[3] Moissan, *Compt. rend.*, 1904, **139**, 364.

[4] Berzelius, *Pogg. Annalen*, 1824, **2**, 147.

[5] Wöhler and Deville, *Ann. Chim. Phys.*, 1858, [iii.], **52**, 63.

[6] These syntheses have only been effected with "amorphous boron."

[7] Dumas, *Ann. Chim. Phys.*, 1826, [ii.], **31**, 436.

[8] Poggiale, *Compt. rend.*, 1846, **22**, 127.

[9] Besson, *Compt. rend.*, 1891, **112**, 1001.

of these compounds and boron tri-iodide is obtained when hydrogen iodide acts upon boron tribromide at a high temperature.

Two **oxychlorides** of boron, BOCl and $BOCl_3$, have been described, but it is doubtful whether they really exist. The first is stated by Gustavson to be obtained as a white, gelatinous solid when boron sesqui-oxide and boron trichloride are heated together at 150° in a sealed tube.[1]

Boron trifluoride, BF_3, was originally prepared by heating a mixture of boron oxide and calcium fluoride to a white heat in an iron tube.[2] It may be prepared by heating a mixture of boron trioxide (1 pt.) and calcium fluoride (2 pts.) with concentrated sulphuric acid,[3] or better, by mixing 100 parts of potassium borofluoride with 15 to 20 parts of powdered boron sesqui-oxide and heating with concentrated sulphuric acid.[4] The gas may be collected over mercury.

Boron trifluoride is a very stable, colourless gas of suffocating odour. Its density corresponds to that required for the simple formula BF_3. When purified from hydrogen fluoride by passage over sodium fluoride, it melts at $-127°$ and boils at $-101°$.[5] The liquefaction of the fluoride was first effected by Faraday.[6] Boron trifluoride combines with its own volume of ammonia, producing a white, opaque solid, $BF_3.NH_3$, which can be sublimed without decomposition. Liquids of the composition $BF_3.2NH_3$ and $BF_3.3NH_3$ may be obtained if more ammonia is employed (J. Davy), but their individuality is doubtful. With dry phosphine at $-50°$, boron fluoride unites to form a white, unstable solid of the formula $2BF_3.PH_3$.[7] It also combines with the oxides of nitrogen.[8]

Boron trifluoride is rapidly absorbed by water, 1057 volumes being absorbed at 0° C.[9] The products of the reaction are boric acid and hydrofluoboric acid :—

$$4(BF_3) + 3H_2O + Aq. = 3HBF_4Aq. + H_3BO_3Aq. + 98{\cdot}04 \text{ Cals.}^{10}$$

Owing to the readiness with which boron trifluoride reacts with water, it has been proposed as a dehydrating agent in organic chemistry.[11]

Boron trifluoride appears to combine with hydrogen fluoride in two proportions, giving rise to $BF_3.HF$ or HBF_4 and $BF_3,3HF$. Little or nothing is known of the latter beyond the fact that it is a colourless liquid of normal vapour density.[12] The former is a well-known acid, hydrofluoboric acid.

Hydrofluoboric acid, HBF_4, was discovered by Berzelius.[13] It is obtained in aqueous solution when boron trifluoride is passed into water until the liquid reacts strongly acid, and the solution is then cooled. The boric acid simul-

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[1] Gustavson, *Ber.*, 1870, **3**, 426 ; *J. Russ. Chem. Soc.*, 1888, **20**, 621 ; R. Lorenz, *Annalen*, 1888, **247**, 226 ; Councler, *Ber.*, 1878, **11**, 1106 ; *J. prakt. Chem.*, 1878, [ii.], **18**, 399 ; Michaelis and Becker, *Ber.*, 1881, **14**, 914.

[2] Gay-Lussac and Thenard, *Ann. Chim. Phys.*, 1908, **69**, 204 ; *Recherches physico-chimiques*, vol. ii. p. 38.

[3] J. Davy, *Phil. Trans.*, 1812, **102**, 365 ; Berzelius, *Pogg. Annalen*, 1824, **2**, 113 ; Moissan, *Compt. rend.*, 1904, **139**, 711.

[4] Schiff, *Annalen Suppl.*, 1867, **5**, 172.

[5] Moissan, *loc. cit.*, and *Ann. Chim. Phys.*, 1906, [viii.], **8**, 84.

[6] Faraday, *Phil. Trans.*, 1845, **135**, 155.

[7] Besson, *Compt. rend.*, 1890, **110**, 80.

[8] Kuhlmann, *Annalen*, 1841, **39**, 319.

[9] Basarow, *Compt. rend.*, 1874, **78**, 1698.

[10] Hemmerl, *Compt. rend.*, 1880, **90**, 312.

[11] Landolph, *Compt. rend.*, 1877, **85**, 39. For its action on various organic compounds see Landolph, *ibid.*, 1878, **86**, 539, 601, 671, 1463 ; 1879, **89**, 173 ; *Ber.*, 1879, **12**, 1583.

[12] Landolph, *Compt. rend.*, 1878, **86**, 601.

[13] Berzelius, *Pogg. Annalen*, 1814, **2**, 113.

taneously formed is said to separate out as metaboric acid. An aqueous solution may also be prepared by dissolving boric acid in a cold, dilute, aqueous solution of hydrogen fluoride.

In aqueous solution, hydrofluoboric acid reacts as a monobasic complex acid, the ions of which are $H^{\cdot}$ and BF_4'. Apparently there is also a slight secondary dissociation of the ion BF_4' into BF_3 and F', the BF_3 partly hydrolysing to hydrofluoric and boric acids. The diluted acid does not attack glass; when the solution is concentrated, however, it does so, since hydrogen fluoride is produced. The acid is poisonous.

The salts of hydrofluoboric acid are called *borofluorides*. They may be prepared (i.) by neutralising the acid with metallic hydroxides, oxides, or carbonates, (ii.) by the action of the so-called fluoboric acid (p. 21) on metallic fluorides, and (iii.) by the action of a metallic fluoride and hydrofluoric acid, or an acid fluoride, on boric acid. In the last case the curious phenomenon may be observed of a mixture of two acid liquids producing an alkaline solution, *e.g.*:—

$$H_3BO_3 + 2NaHF_2 = NaBF_4 + NaOH + 2H_2O.$$

Most borofluorides are soluble in water. The insolubility of the potassium salt in 50 per cent. alcohol may be utilised for separating potassium from sodium and magnesium.[1] When heated to redness, borofluorides yield boron trifluoride and a metallic fluoride; with concentrated sulphuric acid, boron trifluoride and hydrogen fluoride are evolved. A mixture of fluoride and borate is produced by fusing a borofluoride with an alkali carbonate.[2]

Potassium borofluoride, KBF_4, may be prepared as follows:—Boric acid (1 part) and calcium fluoride (2·5 parts) are heated with boiling sulphuric acid (5·25 parts). The liquid is cooled and filtered, and a solution of a potassium salt added. Potassium borofluoride is precipitated; it is recrystallised from hot water.[3] Thus obtained, it forms anhydrous, shining, six-sided, prismatic crystals of density 2·5, and is orthorhombic ($a : b : c =$ 0·7898 : 1 : 1·2830),[4] being isomorphous with the **rubidium** salt, $RbBF_4$ ($a : b : c = 0·8067 : 1 : 1·2948$; density = 2·820).[5] When prepared from hydrofluoric acid, boric acid, and potassium carbonate, however, it forms a gelatinous mass which is converted at 100° into crystals belonging to the cubic system and showing the faces of the octahedron and dodecahedron.[4]

The following borofluorides are also known (Berzelius):—

$LiBF_4$
$NaBF_4$
KBF_4
$RbBF_4$[6]
$CsBF_4$[6]
$(NH_4)BF_4$[7]
$Mg(BF_4)_2.xH_2O$
$Zn(BF_4)_2$
$Ca(BF_4)_2.xH_2O$
$Ba(BF_4)_2.H_2O$
$Al(BF_4)_3.xH_2O$
$Y(BF_4)_3.xH_2O$
$Pb(BF_4)_2$
$Cu(BF_4)_2$

Fluoboric acid.—When boron trifluoride in sufficiently large amount is passed into cold water, a colourless, syrupy liquid is produced. A similar liquid is obtained when as much boric acid as possible is dissolved in a cold, concentrated solution of hydrofluoric acid and the solution concentrated on

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[1] Mathers, Stewart, Housemann, and Lee, *J. Amer. Chem. Soc.*, 1915, **37**, 1515.
[2] Marignac, *Zeitsch. anal. Chem.*, 1862, **1**, 405.
[3] Stolba, *Chem. Zentr.*, 1872, p. 395; 1875, p. 403; 1876, p. 703.
[4] Montemartini (and Brugnatelli), *Atti R. Accad. Lincei*, 1894, [v.], **3**, i. 339; *Gazzetta*, 1894, **24**, i. 478; *Zeitsch. Kryst. Min.*, 1894, **26**, 198.
[5] Zambonini, *Zeitsch. Kryst. Min.*, 1905, **41**, 57.
[6] Godeffroy, *Ber.*, 1876, **9**, 1367.
[7] Stolba, *Chem. Zentr.*, 1890, i. 211.

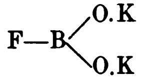
the water-bath, boiled until it evolves white fumes, and cooled over concentrated sulphuric acid.[1]

The liquid thus obtained, of density 1·584, has a composition in agreement with the formula $H_2B_2O_4.6HF$. It is decomposed by excess of water with the precipitation of boric acid, an aqueous solution of hydrofluoboric acid being produced. Berzelius regarded the liquid as a definite acid, of which he could form the alkali salts $M_2B_2O_4.6MF.H_2O$ by neutralisation with alkali. This view, however, is in all probability erroneous, although the evidence against the individuality of the liquid is not as conclusive as could be desired. Distillation of the liquid is accompanied by rise of boiling-point, and the successive liquid fractions differ in density and composition, whilst initially boron trifluoride is evolved. The "salts," when recrystallised, yield first MF and subsequently a mixture of MF and $M_2B_2O_4$, while the "acid" in aqueous solution gives with silver nitrate a precipitate of silver metaborate mixed with silver oxide. According to Basarow, the liquid is merely a mixture of metaboric, hydrofluoboric, and hydrofluoric acids.[2]

Two other fluoboric acids have been stated to exist, namely, $H_4B_2O_7.3HF$ and $H_4B_2O_9.2HF$, but little is known concerning them.[3] A physico-chemical study of mixtures of boric acid, hydrofluoric acid, and potassium fluoride has been made by Abegg, Fox, and Herz, but no definite conclusions could be deduced.[4]

Although no fluoboric acids are definitely known, two compounds have been prepared which may be looked upon as salts of such acids. These are $B_2O_3.2KF$ and $KBO_2.KF$, to which the constitutions

and



have been assigned. The former is made by fusing 7 parts of boron sesquioxide with 12 parts of potassium fluoride, allowing the melt to cool slowly, and extracting soluble impurities with alcohol; the latter, by fusing the former with the requisite amount of potassium carbonate. The compounds dissolve without decomposition in a little water, but much water decomposes them.[5]

Perfluoboric acid.—This acid is not known, but several perfluoborates have been prepared. **Potassium fluohyperborate,** $K_4B_4F_4O_{11}.H_2O$, is prepared by dissolving the compound $B_2O_3 2KF$ in cold water, adding a slightly alkaline solution of hydrogen peroxide, then adding alcohol and stirring. The dry salt is a white, crystalline solid. The aqueous solution is alkaline and slowly evolves oxygen; dilute sulphuric acid added to the solution liberates hydrogen peroxide. Concentrated sulphuric acid decomposes the substance, ozonised oxygen being evolved.

The *potassium* salt, $K_2B_2F_2O_6.H_2O$ or $O_2(BF.O.OK)_2.H_2O$, and the *ammonium* salt, $(NH_4)_2B_2F_2O_6.3H_2O$, have also been obtained.[6]

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[1] Gay-Lussac and Thenard, *Ann. Chim. Phys.*, 1809, **69**, 204; see also Berzelius, *Pogg. Annalen*, 1843, **58**, 503; 1843, **59**, 644.

[2] Basarow, *Compt. rend.*, 1874, **78**, 1698; *Ber.*, 1874, **7**, 1121.

[3] Landolph, *Ber.*, 1879, **12**, 1583.

[4] Abegg, Fox, and Herz, *Zeitsch. anorg. Chem.*, 1903, **35**, 129.

[5] Schiff and Sestini, *Annalen*, 1885, **228**, 83.

[6] Melikoff and Lordkipanidze, *Ber.*, 1899, **32**, 3349, 3510; see also Petrenko, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 37.

Boron subchloride (?).—When a mixture of boron trichloride vapour and hydrogen at the ordinary temperature is subjected to the action of the silent electric discharge, a pale yellow, transparent substance is produced which contains fewer than three atoms of chlorine per atom of boron. It is rapidly decomposed by water, hydrogen being evolved and a solution obtained which possesses marked reducing properties.[1]

Boron trichloride, BCl_3, is best prepared by either of the two methods already mentioned (p. 19). For the synthesis, impure boron (prepared by heating the oxide with magnesium and boiling the resulting mass with hydrochloric acid) is employed. It is heated to dull redness in a stream of dry hydrogen, allowed to cool in the gas, and, after displacing the hydrogen with chlorine, heated in chlorine to redness. The product is strongly cooled and protected from moisture, shaken with mercury or silver powder to remove chlorine, and fractionally distilled to eliminate hydrogen chloride and silicon chloride.[2] Boron trichloride is also produced when boron sesqui-oxide is heated for some days at 150° with phosphorus pentachloride.[3]

Boron trichloride is a colourless liquid of high refractive index and normal vapour density (Wöhler and Deville). At 0° C. its density is 1·43386;[4] its coefficient of expansion is large. It melts at $-107°$ C. and boils at 12·5° C.; its vapour pressure is as follows:—[5]

° C.	mm.	° C.	mm.	° C.	mm.	° C.	mm.	° C.	mm.
-80	4	-60	18	-40	67	-20	197	0	477
-75	6	-55	26	-35	89	-15	251	5	579
-70	9	-50	37	-30	116	-10	314	10	695
-65	13	-45	51	-25	151	-5	387	12·4	753

One gram-molecule of the trichloride, when decomposed by water, produces 79·2 Cals.[6] Boron trichloride is without action on sodium below 150°, zinc below 200°, and sulphur below 250°, but it reacts with sulphur trioxide at 120°, producing sulphuryl chloride and boron sesqui-oxide (Gustavson).[7]

When boron trichloride vapour is passed into liquid ammonia, excess of which is then removed at $-23°$, 15 molecules of ammonia are fixed for each molecule of the chloride used. The products are *boron amide* and an ammonia addition-product of ammonium chloride:—

$$BCl_3 + 15NH_3 = B(NH_2)_3 + 3NH_4Cl.3NH_3.$$

If the ammonia be removed at 0°, only 6 molecules are fixed, since the dissociation pressure of $NH_4Cl.3NH_3$ exceeds 760 mm. at 0°.[8] When the reaction takes place above 0° C., *boron imide*, $B_2(NH)_3$, is produced:—

$$2B(NH_2)_3 = B_2(NH)_3 + 3NH_3.$$

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[1] H. V. A. Briscoe; private communication.

[2] Schnitzler, *Dingl. Polyt. J.*, 1874, **211**, 485; Wöhler and Deville, *loc. cit.*; Stock and Priess, *Ber.*, 1914, **47**, 3109.

[3] Gustavson, *Ber.*, 1870, **3**, 426; 1871, **4**, 975.

[4] Ghira, *Zeitsch. physikal. Chem.*, 1893, **12**, 768; *Gazzetta*, 1893, **23**, i. 452.

[5] Stock and Priess, *loc. cit.*; *cf.* Regnault, *Mém. Acad. Sci.*, 1862, [ii.], **26**, 479, 658.

[6] Troost and Hautefeuille, *Ann. Chim. Phys.*, 1876, [v.], **9**, 70.

[7] For other reactions see Troost and Hautefeuille, *Compt. rend.*, 1872, **75**, 1819; *Ann. Chim. Phys.*, 1876, [v.], **7**, 476.

[8] Joannis, *Compt. rend.*, 1902, **135**, 1106.

According to Besson,[1] boron trichloride forms a white, solid compound, $BCl_3.PH_3$, with phosphine. The following double compounds have also been described, besides various addition-compounds with organic substances: $BCl_3.NOCl$, $BCl_3.POCl_3$, $BCl_3.CNCl$, and $BCl_3.HCN$.[2]

When boron trichloride is introduced into the afterglow of active nitrogen (see Vol. VI.), a pale bluish-green glow is developed, easily distinguished from the green colour of the boric acid flame, and a white, amorphous solid that contains both boron and nitrogen (probably boron nitride) is deposited.[3]

Boron tribromide, BBr_3, is best prepared by either of the two methods already mentioned (p. 19); its preparation and purification may be carried out as described for the chloride.[4, 5]

Boron tribromide is a colourless, mobile liquid which boils at 90·5° C.[4, 5] and solidifies to a colourless mass which melts at − 46° C.[5, 6] Its density is 2·6499 at 0° C. and 2·6175 at 16·5°.[7] The vapour density is normal;[4] the vapour pressure is as follows:—[5]

° C.	mm.	° C.	mm.	° C.	mm.	° C.	mm.	° C.	mm.
50	0·7	− 20	5·5	10	32	40	130	70	390
− 40	1·5	− 10	10·5	20	54	50	193	80	540
− 30	3	0	19	30	85	60	280	90	730

Boron tribromide reacts with ammonia at 0° to form *boron imide.*

$$2BBr_3 + 27NH_3 = B_2(NH)_3 + 6NH_4Br.3NH_3.^{8}$$

With phosphine, boron tribromide forms a white, solid substance of the formula $BBr_3.PH_3$.[9] The corresponding arsenic compound $BBr_3.AsH_3$, prepared by the direct union of arsine and boron tribromide at − 100°, is a very unstable, white, amorphous solid, which, on keeping in the dark at 0°, slowly decomposes into boron tribromide, arsenic, and hydrogen.[10] The following addition-compounds are also known: $BBr_3.PBr_3$, $BBr_3.PBR_5$, $2BBr_3.PCl_3$, $2BBr_3.PCl_5$, and $2BBr_3.P_2I_4$.[11]

Boron tri-iodide, BI_3, was first prepared by Moissan in 1891. He obtained it by three different methods: (i.) by acting upon boron trichloride vapour with hydrogen iodide at a high temperature, (ii.) by the action of iodine vapour on "amorphous boron" at 700° to 800°, and (iii.) by the action of hydrogen iodide on "amorphous boron" at a red heat. The third process is the best to employ.[12] The "boron" to be used must be obtained by Wöhler and Deville's method (p. 7), washed with hydrochloric acid, and dried at 200° in a current of hydrogen. It is heated in a Bohemian glass tube in a current of hydrogen iodide (dried over calcium iodide) to a

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[1] Besson, *Compt. rend.*, 1890, **110**, 516.

[2] Geuther, *J. prakt. Chem.*, 1873, [ii.], **8**, 357; Gustavson, *Ber.*, 1871, **4**, 975; Martius, *Annalen*, 1859, **109**, 80; Gautier, *Compt. rend.*, 1866, **63**, 920.

[3] Jevons, *Proc Roy Soc.*, 1915, **A**, **91**, 120.

[4] Wöhler and Deville, *loc. cit.*

[5] Stock and Kuss, *Ber.*, 1914, **47**, 3113.

[6] H. Gautier, *Ann. Chim. Phys.*, 1899, [vii.], **18**, 374.

[7] Ghira, *loc. cit.*; Hoskyns-Abrahall, *Trans. Chem. Soc.*, 1892, **61**, 650.

[8] Joannis, *Compt. rend.*, 1904, **139**, 364; *cf.* Besson, *ibid.*, 1892, **114**, 542.

[9] Besson, *ibid.*, 1891, **113**, 78.

[10] Stock, *Ber.*, 1901, **34**, 949.

[11] Tarible, *Compt. rend.*, 1893, **116**, 1521; 1901, **132**, 83, 204.

[12] Moissan, *Compt. rend.*, 1891, **112**, 717; *cf.* Besson, *ibid.*, 1891, **112**, 1001.

temperature just below that at which the glass softens. The crystalline product is dissolved in carbon disulphide, shaken with mercury to remove iodine, and the boron iodide recovered by allowing the carbon disulphide to evaporate.

Boron tri-iodide crystallises in colourless, transparent, nacreous plates which are very hygroscopic and are easily changed by light. It melts at 43° and boils without decomposition at 210°. It is soluble in carbon disulphide, carbon tetrachloride, benzene, and other organic media.

Boron tri-iodide is not attacked by hydrogen. It is decomposed by sodium and by magnesium at a red heat, but is unaffected by silver at 500° and by sodium at 210°. The iodine burns in oxygen, is attacked by phosphorus at the ordinary temperature, and by sulphur when gently warmed.

According to Besson,[1] boron tri-iodide forms the compound $BI_3.5NH_3$ with ammonia, and also unites with phosphine.

Boron and the Oxygen Group.

Oxides of Boron.—At least four oxides of boron appear to exist, viz. B_4O_3, B_2O_2, B_4O_5, and B_2O_3. Of these, the sesqui-oxide, B_2O_3, has been long known, and is a well-defined acidic oxide. The dioxide, B_2O_2, is also acidic.

Tetraboron trioxide, B_4O_3.—When boron dioxide is prepared by method (ii.) described below, it is found that about five per cent. of the product consists of a substance insoluble in hydrochloric acid or sodium hydroxide but readily soluble in nitric acid with conversion into boric acid. This insoluble product, when dried at 100°, appears to consist of a hydrated oxide of the composition $B_4O_3.2H_2O$.[2]

Boron dioxide, B_2O_2.—This oxide may be prepared as follows. Crude magnesium boride, made as described below, is decomposed by cold water; the filtered solution is then treated by either of the following processes: (i.) the solution is evaporated to dryness *in vacuo* and the residue heated; (ii.) the solution is treated with ammonia, filtered from magnesium hydroxide, and evaporated to dryness *in vacuo* and the residue heated. In method (i.) part of the boron dioxide obtained is present in combination with magnesia (as a magnesium borite); in method (ii.) the dioxide is obtained practically free from magnesia but contaminated with about five per cent. of the lower oxide $B_4O_3.2H_2O$.

Boron dioxide is soluble in water. Its aqueous solution can be oxidised to boric acid by evaporation in air or by heating with nitric acid, but is not affected by iodine. Freezing-point measurements indicate that the molecular formula of the oxide is B_2O_2. The oxide apparently combines with water to form an acid, and the aqueous solution dissolves an amount of freshly precipitated magnesium hydroxide corresponding to the production of a *magnesium borite*, $MgO.2B_2O_2$.[2]

Tetraboron pentoxide, B_4O_5, is prepared by treating the compound $Mg_3B_2(OH)_6$ with strong ammonia for several days in an atmosphere of hydrogen, filtering, evaporating the filtrate to dryness *in vacuo*, and heating the residue. Thus prepared, it forms a pale brown solid, infusible at the

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[1] Besson, *Compt. rend.*, 1892, 114, 542.

[2] Travers, Ray, and Gupta, *J. Indian Inst. Sci.*, 1914, 1, i. 1, and private communication from Dr Travers.

softening point of Jena glass. When allowed to remain *in vacuo* in contact with water it dissolves, forming a golden-yellow solution that oxidises rapidly in the air; a small flocculent residue, apparently consisting of $B_4O_3.2H_2O$, is also obtained. It is possible that the residue is produced by the following reaction:—[1]

$$3B_4O_5 = B_4O_3 + 4B_2O_3.$$

Borohydrates.—When one part of boron sesqui-oxide is heated with $2\frac{1}{2}$ parts of magnesium powder for 45 minutes at a red heat in a rapid stream of hydrogen, the main products are magnesia and magnesium boride, Mg_3B_2:—[2]

$$6Mg + B_2O_3 = 3MgO + Mg_3B_2.$$

It appears to be essential to the success of the experiment that the mixture should gently deflagrate for about five minutes after the heating commences.

The crude mixture from the foregoing reaction evolves hydrogen when treated with water. It has been shown by Travers, Ray, and Gupta[3] that the magnesium boride is decomposed as follows:—

$$Mg_3B_2 + 6H_2O = Mg_3B_2(OH)_6 + 3H_2.$$

The product is an almost white powder, insoluble in water; it is the magnesium derivative of a compound $B_2(OH_2)_6$, which, from analogy with the carbohydrates, may be termed a **borohydrate.**

The solution obtained by treating the boride with water is found to contain small quantities of substances which exhibit the remarkable property of evolving hydrogen, with brisk effervescence, when acidified. These substances are also borohydrates or allied compounds, and, like the hydroborons obtained from the magnesium boride by the action of acids, appear to be the products of certain unknown side reactions. The amounts of these substances obtained are very small in comparison with the amount of boride required for their production.

The solution is usually yellow, owing to the presence of colloidal boron. It decomposes slowly at the ordinary temperature, hydrogen being evolved. In the presence of platinum black the rate of decomposition is greatly accelerated. The solution precipitates silver and mercury from their salts immediately; with copper salts either copper hydride or amorphous boron appears to be precipitated, according to circumstances. When acidified, the solution evolves hydrogen; the liquid thus obtained decolorises iodine.

A careful, quantitative study of the properties of the solution has led Travers, Ray, and Gupta[4] to the conclusion that the solution contains two substances of the formulæ $H_6B_2O_2$ and $H_6B_2O_3Mg$, the latter being the magnesium derivative of a compound $H_8B_2O_3$. It is suggested that in these compounds boron has a valency of five; and if, as seems highly probable, the evolution of hydrogen takes place by the elimination of pairs of hydrogen

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[1] Travers and Ray, *J. Indian Inst. Sci.*, 1914, I, x. 97.

[2] See Ray, *Trans. Chem. Soc.*, 1914, 105, 2162; Travers, Ray, and Gupta, *J. Indian Inst. Sci.*, 1914, I, i. 1.

[3] Travers, Ray, and Gupta, *loc. cit.*

[4] Travers, Ray, and Gupta, *loc. cit.*; *cf.* Travers and Ray, *Proc. Roy. Soc.*, 1912, A, 87, 163.

atoms attached to adjacent boron atoms, the properties of these compounds can be explained by assigning to them the formulæ:—

$$\begin{array}{c}H_2B-OH\\ \|\\ H_2B-OH\end{array} \quad \text{and} \quad \begin{array}{c}HB-(OH)_3\\ |\\ HBH_3\end{array}$$

The products formed on treatment with acid arise in the following manner:—

$$\text{(i.)}\quad \begin{array}{l}H_2B.OH\\ H_2\ddot{B}.OH\end{array} = \begin{array}{l}B.OH\\ \ddot{B}.OH\end{array} + 2H_2$$

$$\text{(ii.)}\quad \begin{array}{l}HB(OH)_3\\ H\dot{B}H_3\end{array} = \begin{array}{l}B(OH)_3\\ \ddot{B}H_3\end{array} + H_2$$

The compound HO.B : B.OH, which is analogous to hyponitrous acid in its structure, and the compound $BH_3 : B(OH)_3$ are oxidised by iodine to boron dioxide, B_2O_2:—

$$\text{(iii.)}\quad \begin{array}{l}B.OH\\ \ddot{B}.OH\end{array} + I_2 = \begin{array}{l}B:O\\ \dot{B}:O\end{array} + 2HI$$

$$\text{(iv.)}\quad \begin{array}{l}BH_3\\ \ddot{B}(OH)_3\end{array} + 2I_2 = \begin{array}{l}B:O\\ \dot{B}:O\end{array} + 4HI + H_2O$$

When the solution obtained by the action of water on magnesium boride is treated with ammonia, magnesium hydroxide is precipitated. In the conversion of the magnesium derivative $H_6B_2O_3Mg$ into the ammonium compound, however, intra-molecular change apparently occurs, thus:—

$$\begin{array}{l}HB(OH)_3\\ HBH_3\end{array} \longrightarrow \begin{array}{l}H_2B(OH)_2\\ H_2\dot{B}H(OH)\end{array},$$

for the new product, when acidified, evolves twice as much hydrogen as the initial:—

$$\begin{array}{l}H_2B(OH)_2\\ H_3\dot{B}H(OH)\end{array} = \begin{array}{l}B(OH)_2\\ \dot{B}H(OH)\end{array} + 2H_2,$$

yielding a product which is oxidised by iodine to boron dioxide, B_2O_2:—

$$\begin{array}{l}B(OH)_2\\ \dot{B}H(OH)\end{array} + I_2 = \begin{array}{l}B:O\\ \dot{B}:O\end{array} + 2HI + H_2O.$$

The magnesium derivative $Mg_3B_2(OH)_6$, already mentioned, undergoes decomposition when treated with strong ammonia in an atmosphere of hydrogen. Travers and Ray,[1] who have investigated the reaction, conclude that the soluble product of the change is a di-ammonium derivative of the compound—

$$BH_2(OH)_2.BH(OH) : BH(OH).BH_2(OH)_2.$$

When acidified, this compound loses hydrogen, thus:—

$$\begin{array}{l}BH_2(OH)_2.BH(OH) : BH(OH).BH_2(OH)_2\\ \qquad = 2H_2 + BH(OH)_2 : B(OH) : B(OH) : BH(OH)_2,\end{array}$$

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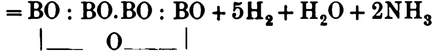
[1] Travers and Ray, *J. Indian Inst. Sci.*, 1914, I, x. 97.

and the new product loses more hydrogen when treated with iodine :—

$$BH(OH)_2 : B(OH) : B(OH) : BH(OH)_2 + I_2$$
$$= 2HI + B(OH)_2.B(OH).B(OH).B(OH)_2.$$

By evaporating the ammoniacal solution *in vacuo* and heating the residue, the oxide B_4O_5 is obtained (p. 25), thus :—

$$BP_2(OH)_2.BH(OH).BH(OH).BH_2(OH_2) + 2NH_3$$



$$= \underbrace{BO : BO.BO : BO}_{O} + 5H_2 + H_2O + 2NH_3$$

Hypoborates.—Stock and Kuss[1] have shown that when either of the hydrides B_2H_6 or B_4H_{10} dissolves in aqueous alkali hydroxide, the initial product is an alkali compound of the type $MO.BH_3$, which they term an alkali **hypoborate** ; *e.g.* :—

$$B_2H_6 + 2KOH = 2KOBH_3 + H_2$$
$$B_4H_{10} + 4KOH = 4KOBH_3 + H_2.$$

Solutions of the alkali hypoborates are fairly stable at 0°, particularly when excess of alkali is present, and may be exposed to air. When boiled, however, decomposition takes place rapidly :—

$$2KOBH_3 + 2H_2O = 2KBO_2 + 5H_2.$$

Potassium hypoborate, $KOBH_3$, may be isolated by dissolving potassium hydroxide in one and a half times its weight of water and treating it with an excess of B_4H_{10} at 0° ; the solid hypoborate is then obtained in colourless, glistening, octahedral crystals which may be dried in a high vacuum.

The compound is stable when dry. It is deliquescent, and its aqueous solution slowly decomposes at the ordinary temperature. Acids, even acetic acid, immediately decompose it. The aqueous solution is a powerful reducing agent, and gives precipitates with solutions of most salts, but insoluble hypoborates are never obtained. With copper sulphate, a precipitate of copper hydride, CuH_2, is obtained ; with nickel sulphate a very remarkable change takes place, nickel boride, Ni_2B, being precipitated.

When potassium hypoborate is heated to 500°, potassium, hydrogen, and water are expelled. The water is evolved first, and is completely expelled at 200° ; potassium begins to distil from the residue at 400°. .The reaction may be expressed thus :—

$$5KOBH_3 = K_3B_5O_3 + 2K + 2H_2O + 11H.$$

The residue, $K_3B_5O_3$, is soluble in water, giving an alkaline solution the properties of which resemble those of a solution obtained by heating boric oxide with magnesium and extracting the product with water.

Sodium hypoborate, $NaOBH_3$, resembles the potassium compound. The *barium* and *magnesium* hypoborates are only known in aqueous solution.

Boron sesqui-oxide, boron trioxide, or **boric anhydride,** B_2O_3, the best-defined of the oxides of boron at present known, is formed when boron burns in air or oxygen, and is prepared by heating boric acid to redness in a platinum dish, water being eliminated and boron sesqui-oxide left behind.

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[1] Stock and Kuss, *Ber.*, 1914, 47, 810.

Boron sesqui-oxide is an amorphous, colourless, glassy solid, which has no definite melting-point, but which is decidedly liquid at 557°.[1] It vaporises rapidly *in vacuo* at a bright red heat.[2] Its density is 1·877 at 0°, 1·848 at 12°, and 1·699 at 80°, the coefficient of cubical expansion being 0·001308.[3] Between 16° and 98° its specific heat is 0·2374.[4] It is a very bad conductor of electricity.[5]

Boron sesqui-oxide is a very stable compound, but it can be reduced to boron by sodium, potassium, aluminium, and magnesium, as has been already mentioned (p. 7). It is attacked by hydrofluoric acid and reacts with heated metallic fluorides, boron fluoride and crystalline metallic oxides being produced.[6] Being only slightly volatile at a red heat, boron sesqui-oxide is capable of decomposing nitrates, sulphates, etc., borates and volatile acids (or their decomposition products) being produced.[7]

Boron sesqui-oxide is the anhydride of boric acid, into which it passes when dissolved in water. The oxide is very hygroscopic.

Boron sesqui-oxide combines with a number of other anhydrides to form what may be regarded as mixed anhydrides. The compound $B_2O_3.P_2O_5$, sometimes called **borophosphoric acid** or **boron phosphate**, was first prepared by Vogel[8] by adding crystalline boric acid to a boiling solution of phosphoric acid. According to Mylius and Meusser,[9] when these two acids are heated together at 80° to 100° the product has the composition $B_2O_3.P_2O_5.2H_2O$ or $(BO)H_2PO_4$. Boric and phosphoric acids also condense together in sulphuric acid, acetic acid, or acetic anhydride as solvent, producing borophosphoric acid. This substance is a white powder, which, although readily hydrolysed by water when freshly prepared, is quite inert after it has been dried at 400°. At a red heat, it becomes distinctly crystalline. The *mixed anhydrides* $SO_3.B_2O_3$ and $2SO_3B_2O_3$ may be prepared by heating sulphuric and boric anhydrides together in sealed tubes at 115°–120° and 230° respectively, a mixture of both being obtained at intermediate temperatures.[10] They are colourless, amorphous, hygroscopic solids which, when strongly heated, dissociate into sulphur and boron trioxides, and which are readily hydrolysed by water to sulphuric and boric acids. The compound $(2B_2O_3.3SO_3.3H_2O$ or $BHSO_4)_3$ is produced by the interaction of boric and sulphuric acids; other compounds of the type $xB_2O_3.ySO_3.zH_2O$ have been described, but their existence has not been confirmed.[11]

The existence of the preceding compounds is generally held to show that boron sesqui-oxide may act as a feeble base, in which case boron sesqui-oxide must be classed among the amphoteric oxides.[12]

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[1] Carnelley, *Trans. Chem. Soc.*, 1878, **33**, 278.

[2] Tiede and Birnbräuer, *Zeitsch. anorg. Chem.*, 1914, **87**, 129.

[3] Ditte, *Ann. Chim. Phys.*, 1878, [v.], **13**, 67.

[4] Regnault, *ibid.*, 1841, [iii.], **1**, 129.

[5] Lapschin and Tichanowitsch, *Phil. Mag.*, 1861, [iv.], **22**, 308; Bowgoin, *Compt. rend.*, 1868, **67**, 798.

[6] Deville and Caron, *Compt. rend.*, 1858, **46**, 764.

[7] See Tate, *Quart. J. Chem. Soc.*, 1859, **12**, 160.

[8] Vogel, *Zeitsch. für Chem.*, 1870, p. 125; Gustavson, *Ber.*, 1871, **4**, 975; Meyer, *ibid.*, 1889, **22**, 2919.

[9] Mylius and Meusser, *Ber.*, 1904, **37**, 397.

[10] Pictet and Karl, *Bull. Soc. chim.*, 1908, [iv.], **3**, 1114.

[11] D'Arcy, *Trans. Chem. Soc.*, 1889, **55**, 155; *cf.* Merz, *J. prakt. Chem.*, 1866, **99**, 181; Schultz-Sellack, *Ber.*, 1871, **4**, 15; Gustavson. *ibid.*, 1873, **6**, 10.

[12] See Georgievič, *J. prakt. Chem.*, 1888, [ii.], **38**, 118.

Boric Acids.—Numerous boric acids are theoretically capable of being produced by the union of boron sesqui-oxide and water in different proportions, and the existence of various boric acids seems necessary in order to account for the types of borates known. At the present time, however, the existence in the solid state of only two boric acids, **orthoboric acid,** H_3BO_3 (*i.e.* $B_2O_3.3H_2O$), and **metaboric acid,** HBO_2 (*i.e.* $B_2O_3.H_2O$), can be definitely affirmed. The latter is formed by heating the former to 100°–140°,[1] and in aqueous solution it passes into the former, as is shown by molecular weight determinations. The existence of **pyroboric acid,** $H_2B_4O_7$, has been assumed by various chemists, but cannot be regarded as proved.[2]

Orthoboric acid, boric acid, or **boracic acid,** H_3BO_3.—This acid was first prepared by Homberg in 1702 (see p. 7). It may be readily prepared in the laboratory by treating a solution of borax (3 pts.) in hot water (12 pts.) with sulphuric acid (1 pt.). On cooling, orthoboric acid crystallises out. It is recrystallised from hot water, dried, fused to expel traces of sulphuric acid, and again dissolved in hot water and recrystallised.

Orthoboric acid is prepared on a commercial scale. Originally, all the orthoboric acid on the European markets came from Italy, and a large quantity of the acid is still derived from that country. It occurs in the *suffioni*, or jets of steam which issue from volcanic vents near Monte Rotondo, Lago Zolforeo, Sasso, and Larderello, in Tuscany. Many borings have also been made in order to produce artificial suffioni. The suffioni are surrounded by brickwork basins, several of which are generally built on the side of a hill. Water from any convenient source is run into the uppermost basin and subjected to the action of the suffioni within it for a day. It is then run into the next lower basin, and so on, until the water contains about 2 per cent. of boric acid. Next it is made to flow in a thin stream over a large sheet of corrugated lead, 2 metres wide and 125 metres long, placed on a slight incline and heated from below by the vapours from suffioni too poor in boric acid to be utilised for the extraction of the acid. Water may be evaporated in this way at the rate of 20,000 litres per day. The liquid that runs from the end of the lead sheet is further concentrated in leaden pans until the boric acid commences to crystallise out, the gypsum that is invariably deposited during the evaporation being removed from time to time. Crude Tuscan boric acid contains 74 to 80 per cent. of boric acid, 8 to 14 per cent. of ammonium and magnesium sulphates, 4·5 to 7 per cent. of water, together with small quantities of gypsum, clay, sand, sulphur, organic matter, etc.[3]

The origin of the boric acid in the suffioni is not at present understood. It has been conjectured that the boric acid arises from a reaction between boron sulphide and water; on the other hand, it has been supposed to be produced from boron nitride. According to Nasini, its source is the included tourmaline in the surrounding granite rocks, which yields boric acid when

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[1] Holt, *Mem. Manchester Phil. Soc.*, 1911, **55**, No. 10; *cf.* Merz, *J. prakt. Chem.*, 1866, **99**, 177; Ebelmen and Bouqet, *Ann. Chim. Phys.*, 1846, [iii.], **17**, 63; Schaffgotsch, *Pogg. Annalen*, 1859, **107**, 427; Bloxam, *Quart. J. Chem. Soc.*, 1859, **12**, 177.

[2] See the preceding references, and Nasini and Ageno, *Zeitsch. physikal. Chem.*, 1909, **67**, 482.

[3] Payen, *Ann. Chim. Phys.*, 1841, [iii.], **1**, 247; Wittstein, *Repert. für Pharm.*, 1840, **72**, 175; Wohl, *Dingl. polyt. J.*, 1866, **182**, 173; Erdmann, *J. prakt. Chem.*, 1838, **13**, 72.

heated in superheated steam.[1] The gases issuing from the suffioni are radio-active, as also is the granitic rock from which they issue.[2]

Boric acid is prepared on a commercial scale from the various naturally occurring borates already described (p. 6). For this purpose they are sometimes dissolved in hot hydrochloric acid, and the boric acid, which crystallises out on cooling, recrystallised from water. Numerous other methods have been proposed. In one process, ulexite is ground to an impalpable powder, suspended in boiling water, and decomposed by passing sulphur dioxide into the liquid. In another, boracite is decomposed with the equivalent amount of sodium bisulphate (a by-product of the nitric acid manufacturing process), the boric acid crystallised out, and mother-liquor worked up for the sodium sulphate it contains.[3] The American deposits of colemanite are converted mainly into borax.[4]

Orthoboric acid crystallises from water in white, six-sided laminæ which have a pearly lustre and are unctuous to the touch. The crystals are triclinic ($a : b : c = 1·7329 : 1 : 0·9228$, $\alpha = 92° 30'$, $\beta = 104° 25'$, $\gamma = 89° 49'$).[5] According to Carnelley, orthoboric acid melts at 184° to 186°.[6] The density at 15° is given by Stolba[7] as 1·434; Ditte[8] gives the following values:—

Temp. ° C.	0°	12°	14°	60°	80°
Density	1·5463	1·5172	1·5128	1·4165	1·3828

The specific heat is 0·3535.[9]

Orthoboric acid is sparingly soluble in cold water, but the solubility rapidly increases with rise of temperature. The percentages of orthoboric acid in its saturated aqueous solutions at various temperatures are as follows:—[10]

Temp. ° C. .	0°	10°	20°	30°	40°	50°	60°	70°	80°	100°
Grams. H_3BO_3 in 100 grams of solution	2·59	3·39	4·75	6·29	8·02	10·35	12·90	15·76	19·11	28·34

According to Herz and Knoch,[11] a saturated solution of orthoboric acid contains 0·620 gram-molecules of acid per litre at 13°, 0·7915 at 20°, and 0·8999 at 25°. The cryohydric point is $-0·76°$, at which temperature the saturated solution contains 2·27 per cent. of orthoboric acid. The boiling-point of a

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[1] Nasini, *Atti R. Accad. Lincei*, 1908, [v.], **17**, ii. 43; *cf.* D'Achiardi, *ibid.*, 1908, [v.], **17**, ii. 238, and the early papers of Bolley, *Annalen*, 1848, **68**, 122; Warrington, *Chem. Gazette*, 1854, **7**, 419; Wöhler and Deville, *Annalen*, 1858, **105**, 69; Popp, *Annalen Suppl.*, 1872, **8**, 1; Dieulafait, *Ann. Chim. Phys.*, 1877, [v.], **12**, 318; *Compt. rend.*, 1885, **100**, 1017, 1240.

[2] Nasini, Anderlini, and Levi, *Atti R. Accad. Lincei*, 1905, [v.], **14**, ii. 70.

[3] Heidlberg, *Chem. Zeit.*, 1907, **31**, Rep. 48.

[4] For further details and other methods, see Bigot, *J. Soc. Chem. Ind.*, 1899, **18**, 830; Chenal Douilhet & Co., *D.R.P.*, 110,421 (1899); Moore, *Eng. Pat.*, 20,384 (1899); Marquardt and Schulz, *Zeitsch. angew. Chem.*, 1895, **8**, 385; and Thorpe, *A Dictionary of Applied Chemistry* (Longmans & Co., 1912–13), 2nd ed., vol. i. p. 501.

[5] Haushofer, *Zeitsch. Kryst. Min.*, 1884, **9**, 77; *cf.* Miller, *Pogg. Annalen*, 1831, **23**, 558; Kenngott, *Sitzungsber. K. Akad. Wiss. Wien*, 1854, **12**, 26.

[6] Carnelley, *Trans. Chem. Soc.*, 1878, **33**, 275.

[7] Stolba, *J. prakt. Chem.*, 1863, **90**, 457.

[8] Ditte, *Ann. Chem. Phys.*, 1878, [v.], **13**, 67.

[9] Ditte, *loc. cit.*, and *Compt. rend.*, 1877, **85**, 1069.

[10] Interpolated from the results of Nasini and Ageno, *Zeitsch. physikal. Chem.*, 1909, **69**, 482; *Gazzetta*, 1911, **41**, i. 131; *cf.* Brandes and Firnhaber, *Arch. Pharm.*, 1824, **7**, 50; Ditte, *Compt. rend.*, 1877, **85**, 1069; *Ann. Chim. Phys.*, 1878, [v.], **13**, 67.

[11] Herz and Knoch, *Zeitsch. anorg. Chem.*, 1904, **41**, 315.

saturated solution of orthoboric acid is 103·12°.[1] The heat of solution of orthoboric acid in water is − 5·395 Cals.[2] A saturated solution of orthoboric acid has a density of 1·014 at 8°, and 1·0248 at 15° (Stolba).

The solubility of orthoboric acid in water is increased by the presence of potassium or rubidium chloride, but diminished by the presence of hydrogen, lithium, or sodium chlorides.[3] The acid is very slightly soluble in ether, more soluble in alcohols and essential oils.[4] One hundred grams of glycerol dissolve the following amounts of orthoboric acid :—[5]

Temp. ° C. .	0°	20°	40°	60°	80°	100°
Grams H_3BO_3	20	28	38	50	61	73

The partition-coefficient of boric acid between water and ether is 34·2 at 16° ; between isobutyl alcohol and water 2·74, and between amyl alcohol and water 3·37 at 15°, 3·34 at 25°, and 3·31 at 35°.[6]

Orthoboric acid is volatile in steam. The vapour given off from a saturated boiling aqueous solution of the acid contains 0·039 per cent. of acid.[7] The acid may also be volatilised from its alcoholic solutions.[8]

The salts of boric acid are called **borates**. Very few orthoborates are known, but numerous meta- and pyro-borates have been prepared. Further, salts of such hypothetical acids as $H_4B_2O_5$, $H_6B_8O_{15}$, etc., are known. Anhydrous borates may be prepared by fusing boron sesqui-oxide with metallic oxides. When an excess of boron sesqui-oxide is present, it is found that in some cases a homogeneous liquid mass is obtained which solidifies to a homogeneous glass ; in other cases it separates on cooling into conjugate liquid phases ; while in others it is not possible to obtain a homogeneous liquid melt, the mass separating into two non-miscible phases of metallic borate and boron sesqui-oxide respectively.[9]

The borates, with the exception of the alkali borates, are practically insoluble in water. The most important borate is sodium pyroborate or borax. The important borates are described under the headings of the various metals.[10]

Although the metallic orthoborates cannot be obtained by precipitation,

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[1] Nasini and Ageno, *loc. cit.*, and *Atti R. Accad. Lincei*, 1912, [v.], **21**, ii. 125.

[2] Thomsen, *Thermochemische Untersuchungen* (Leipzig, 1883), vol. iii. p. 196 ; *cf.* Ditte, *loc. cit.*

[3] Herz, *Zeitsch. anorg. Chem.*, 1910, **66**, 358.

[4] Rose, *Pogg. Annalen*, 1850, **80**, 262.

[5] Hooper, *Pharm. J.*, 1882, [iii.], **13**, 258 ; see also Herz and Knoch, *loc. cit.*

[6] Abegg, Fox, and Herz, *Zeitsch. anorg. Chem.*, 1903, **35**, 129 ; Auerbach, *ibid.*, 1904, **34**, 353 ; B. Müller and Abegg, *Zeitsch. physikal. Chem.*, 1907, **57**, 513.

[7] Nasini and Ageno, *loc. cit.*; Skirrow, *Zeitsch. physikal. Chem.*, 1901, **30**, 84.

[8] See Firth and Myers, *Trans. Chem. Soc.*, 1914, **105**, 2887.

[9] Geurtler, *Zeitsch. anorg. Chem.*, 1904, **40**, 225, 268, 337 ; *cf.* Holt, *Proc. Roy. Soc.*, 1902, **74**, 285 ; Burgess and Holt, *Proc. Chem. Soc.*, 1903, **19**, 221 ; *Proc. Roy. Soc.*, 1904, **74**, 285. For speculations on the constitution of borates, see Zulkowski, *Chem. Zentr.*, 1900, [v.], **7**, 1041 ; Ditte, *Compt. rend.*, 1873, **77**, 788 ; Le Chatelier, *ibid.*, 1891, **113**, 1034.

[10] Numerous borates are described in the following early papers, but the compositions of many of them are doubtful : Berzelius, *Pogg. Annalen*, 1824, **2**, 113 ; 1827, **9**, 433 ; 1834, **33**, 98 ; 1835, **34**, 561 ; H. Rose, *ibid.*, 1827, **9**, 176 ; 1830, **19**, 153 ; 1852, **86**, 561 ; 1852, **87**, 1, 470, 587 ; 1853, **88**, 299, 482 ; 1853, **89**, 473 ; 1854, **91**, 452 ; Wöhler, *ibid.*, 1833, **28**, 525 ; Rammelsberg, *ibid.*, 1840, **49**, 445 ; Ebelmen, *Ann. Chim. Phys.*, 1851, [iii.], **33**, 34 ; Laurent, *ibid.*, 1838, [ii.], **67**, 215 ; Bolley, *Annalen*, 1848, **68**, 122 ; Herepath, *Phil. Mag.*, 1849, [iii.], **34**, 375 ; Tissier, *Compt. rend.*, 1854, **39**, 192 ; 1857, **45**, 411 ; C. L. Bloxam, *Quart. J. Chem. Soc.*, 1859, **12**, 177 ; 1861, **14**, 143 ; Ditte, *Compt. rend.*, 1873, **77**, 783, 892 ; *Ann. Chim. Phys.*, 1883, [v.], **30**, 248.

and have only in a few cases been prepared in other ways, the **tri-alkyl esters** of boric acid, $B(OR)_3$, where R is an alkyl group C_nH_{2n+1}, are readily prepared by the interaction of boron trichloride and alcohols, *e.g.* :—

$$BCl_3 + 3C_2H_5.OH = B(OC_2H_5)_3 + 3HCl.$$

They are colourless liquids of low boiling-point and normal vapour density, and are readily hydrolysed by water.[1] They combine with the metallic derivatives of the alcohols, forming crystalline compounds in which boron is presumably a pentad. The following are known :—[2]

$LiB(OMe)_4$
$NaB(OMe)_4$
$KB(OMe)_4$
$Ca[B(OMe)_4]_2$
$NaB(OEt)_4$
$KB(OEt)_4$
$TlB(OEt)_4$
$NaB(OPr^a)_4$

In aqueous solution, orthoboric acid is a very weak acid. It turns litmus a wine-red, turmeric a reddish-brown, and has no effect on methylorange (p. 44). The aqueous solution is a very poor conductor of electricity, so that the acid is ionised only to a very slight extent. The molecular weight of the acid in solution is, in fact, that corresponding to the molecular formula H_3BO_3.[3] That there is only one molecular species present to any appreciable extent is shown by the fact that the partition-coefficients previously given (p. 32) are independent of the actual concentration of boric acid in the aqueous phase. In solution, orthoboric acid behaves as a monobasic acid. The ionisation of the acid follows Ostwald's dilution law for binary electrolytes (Vol. I. p. 224), and the dissociation must therefore be represented as $H_3BO_3 \rightleftharpoons H^{\cdot} + H_2BO_3'$. The ionic mobility of the anion at 18° is 28.[4] The affinity constant (k) of orthoboric acid varies with the temperature as follows :—[5]

Temp. ° C.	15°	25°	37°	40°
$k \times 10^{10}$	5·48	6·62	8·10	8·49

Hence boric acid is weaker than either carbonic or hydrosulphuric acid. Owing, however, to the superior volatility of these acids, a concentrated, boiling solution of boric acid can decompose certain metallic carbonates and sulphides.[6]

Both metaboric acid and pyroboric acid (orthoboric acid dehydrated till it corresponds to the formula, $H_2B_4O_7$), when dissolved in water, are converted into orthoboric acid, since their aqueous solutions are identical with solutions

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[1] Ebelmen, *Ann. Chim. Phys.*, 1846, [iii.], **16**, 129; Ebelmen and Bouqet, *ibid.*, 1846, [iii.], **17**, 54; Bowman, *Phil. Mag.*, 1846, [iii.], **29**, 546; Rose, *Pogg. Annalen*, 1856, **98**, 245; Schiff, *Annalen Suppl.*, 1867, **5**, 154; *Annalen*, 1877, **189**, 162; Councler, *Ber.*, 1876, **9**, 485; 1877, **10**, 1655; 1878, **11**, 1106; *J. prakt. Chem.*, 1878, [ii.], **18**, 371; Ghira, *Gazzetta*, 1893, **23**, i. 452, ii. 8; Copaux, *Compt. rend.*, 1898, **127**, 719; Wohl and Neuberg, *Ber.*, 1899, **32**, 3488; Fenton and Miss Gostling, *Trans. Chem. Soc.*, 1898, **73**, 554; Cohn, *Pharm. Zentr.-h.*, 1911, **52**, 479.

[2] Copaux, *loc. cit.*; Cambi, *Atti R. Accad. Lincei*, 1914, [v.], **23**, i. 244.

[3] Kahlenberg and Schreiner, *Zeitsch. physikal. Chem.*, 1896, **20**, 547; Holt, *Mem. Man. Phil. Soc.*, 1911, **55**, No. 10; Nasini and Ageno, *loc. cit.*

[4] Abegg and Cox, *Zeitsch. physikal. Chem.*, 1903, **46**, 1; Walker and Cormack, *Trans. Chem. Soc.*, 1900, **77**, 5.

[5] Lundén, *J. Chim. phys.*, 1907, **5**, 580; *cf.* Walker and Cormack, *Trans. Chem. Soc.*, 1900, **77**, 5; Hantsch and Barth, *Ber.*, 1902, **35**, 216; concentration in gram molecules per litre.

[6] Tissier, *Compt. rend.*, 1854, **39**, 192; 1857, **45**, 411; Popp, *Annalen Suppl.*, 1872, **8**, 1.

of orthoboric acid of the same boron content. Moreover, aqueous solutions of alkali meta- and pyro-borates are in every respect identical with aqueous solutions prepared from the requisite quantities of orthoboric acid and alkali hydroxide. In conformity with the view already outlined that boric acid in solution is a monobasic acid, it reacts in aqueous solution with one equivalent of alkali. This has been shown both by freezing-point measurements[1] and by thermochemical considerations.[2] Accordingly, the ions in alkali borate solutions are essentially M and H_2BO_3' or BO_2', and such solutions, by double decomposition with metallic salts, precipitate sparingly soluble *metaborates*. There must, however, be an appreciable concentration of hydroxyl ions in an alkali borate solution, since, boric acid being exceedingly weak and the alkali hydroxides very strong, the salts produced by their interaction must be perceptibly hydrolysed (Vol. I. p. 224). At ordinary temperatures, in fact, a decinormal solution of borax is hydrolysed to the extent of about 0·5 per cent.[3] Accordingly, in sufficiently dilute solutions, precipitated metallic metaborates are contaminated with co-precipitated metallic hydroxides (or oxides) if the hydroxides are very sparingly soluble substances.[4] Alkali borate solutions also contain complex polyborate ions, the precise nature of which is not known.[5]

Boric acid and its most important salt, borax, receive many practical applications. As a mild antiseptic, the acid is largely used as a food preservative. It is also used in the preparation of candle wicks. Boric acid and borax are employed in the preparation of enamels, pottery glazes, hat varnishes, paint driers, borosilicate glass, certain kinds of optical glass, cosmetics, tooth powders, soaps, parchment paper, glazed paper and cards, safe linings, and fireproof textile fabrics; they are also used by tanners for dressing leather, by coppersmiths and jewellers as fluxes in brazing and soldering operations, by laundresses, etc.

Complex Boric Acids.—Complex acids containing boron are formed by the action of boric acid upon numerous substances. The best defined inorganic compounds of this nature are the two **borotungstic acids**, $[6H_2O.B_2O_3.28WO_3].56H_2O$ and $[5H_2O.B_2O_3.24WO_3].61H_2O$, prepared by Copaux.[6]

The interaction of boric acid with numerous organic compounds has been studied by Magnanini,[7] who found that in aqueous or alcoholic solution, boric acid interacts with all hydroxycarboxylic acids in which at least one hydroxyl group is present in the α-position to a carbonyl group, the complex acids formed (which he did not isolate) being stronger than the organic acids from which they are produced. The other organic acids do not interact

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[1] Noyes and Whitney, *Zeitsch. physikal. Chem.*, 1894, **15**, 694.

[2] J. Thomsen, *Thermochemische Untersuchungen* (Leipzig, 1882), vol. i. p. 206; *cf.* Lundén, *J. Chim. phys.*, 1907, **5**, 599.

[3] Shields, *Zeitsch. physikal. Chem.*, 1893, **12**, 167.

[4] Abegg and Cox, *loc. cit.*; *cf.* the interaction of borax and silver nitrate, p. 44.

[5] Auerbach, *loc. cit.*; P. Müller and Abegg, *loc. cit.*

[6] Copaux, *Compt. rend.*, 1908, **147**, 973; *Ann. Chim. Phys.*, 1909, [viii.], **17**, 217. See Vol. VII. of this series. For evidence in favour of the existence of boro-molybdates, boro-arsenates, etc., see Mauro, *Ber.*, 1881, **14**, 1379; *Bull. Soc. chim.*, 1880, [ii.], **33**, 564; Rosenheim and Bertheim, *Zeitsch. anorg. Chem.*, 1903, **34**, 427; Schweizer, *Annalen*, 1850, **76**, 267; Auerbach, *Zeitsch. anorg. Chem.*, 1903, **37**, 353.

[7] Magnanini, *Atti R. Accad. Lincei*, 1890, [iv.], **6**, i. 260, 411, 457; *Gazzetta*, 1890, **20**, 428, 441, 448, 453; 1891, **21**, ii. 134, 215; 1911, **41**, ii. 425; 1914, **44**, i. 396; *Zeitsch. physikal. Chem.*, 1890, **6**, 58; 1892, **9**, 230; 1893, **11**, 281.

with boric acid in solution. A crystalline **potassium hydrogen boro-oxalate** $2K(BO)C_2O_4.3H_2O$,[1] can nevertheless be readily prepared by heating potassium metaborate with oxalic acid solution, or by heating boric acid with potassium hydrogen oxalate.

The interaction of boric acid with alcohols has been studied by Magnanini, P. Müller and Abegg, and others.[2] It has been shown by Müller and Abegg that complex acids are formed (by condensation of the alcohols with boric acid) to an appreciable extent when boric acid is dissolved in various liquid alcohols, but that the extent to which complex acid formation occurs, steadily diminishes as the alcoholic solvent is replaced by water. Complex acid formation between boric acid and both mannitol and glycerol, two polyhydric alcohols, is of considerable interest, both theoretically and practically. In each case the complex acid formed is much stronger than boric acid; and whereas mannitol is optically inactive, mannitoboric acid is decidedly dextro-rotatory. The extent to which these complex acids are formed in solution increases with the concentration of either the boric acid or the polyhydric alcohol, and diminishes with the dilution; in consequence of which the molecular conductivity of mannitoboric acid decreases with the dilution. Magnanini concluded from his experiments that mannitoboric acid was produced by the condensation of three molecules of boric acid with one of mannitol, but the subsequent isolation of the complex acid has shown that the condensation proceeds as expressed by the equation :—

$$H_3BO_3 + C_6H_{14}O_6 \rightleftharpoons C_6H_{15}O_8B + H_2O.$$

The preparation of **mannitoboric acid** is carried out by dissolving 12 grams of mannitol and 8·2 grams of boric acid in 95 cubic centimetres of absolute alcohol, and setting the solution aside for a few days in a cold place. The first few crystals formed are discarded; those subsequently deposited are pure mannitoboric acid, $C_6H_{15}O_8B$, and melt at 89·5°. The molecular weight of the acid in acetone solution is rather greater than that required for the preceding formula. The acid is largely decomposed by water, but its ammonium, silver, calcium, and barium salts are more stable.[3]

Perboric Acid and Perborates.—Perboric acid is unknown in the pure state, but it is possible that ethereal solutions have been prepared.[4] A number of metallic perborates, however, are known. They were discovered by Étard,[5] and first prepared in a pure state by Melikoff and Pissarjewsky.[6]

The best known perborates are derivatives of a perboric acid of the composition HBO_3. They are readily hydrolysed in aqueous solution, boric acid, or rather its salts, and hydrogen peroxide being produced. Accordingly, the perboric acid is considered to have the constitution $O : BO.OH$:—

$$O : BO.OH + 2H_2O = B(OH)_3 + HO.OH.$$

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[1] E. A. Werner, *Trans. Chem. Soc.*, 1904, **85**, 1449.

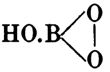
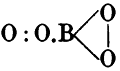
[2] P. Müller and Abegg, *Zeitsch. physikal. Chem.*, 1907, **57**, 513 ; Ageno and Valla, *Gazzetta*, 1913, **43**, ii. 163 ; Dahr, *Zeitsch. anorg. Chem.*, 1914, **86**, 196 ; Böeseken and others, *Rec. trav. chim.*, 1911, **30**, 392 ; 1915, **34**, 96, 272 ; *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 216 ; Irvine and Miss Steele, *Trans. Chem. Soc.*, 1915, **107**, 1221.

[3] Fox and Gauge, *Trans. Chem. Soc.*, 1911, **99**, 1075.

[4] Pissarjewsky, *Zeitsch. physikal. Chem.*, 1903, **43**, 170.

[5] Étard, *Compt. rend.*, 1880, **91**, 931.

[6] Melikoff and Pissarjewsky, *Ber.*, 1898, **31**, 678, 953.

This constitution, however, has been disputed on the ground that hydrated sodium or potassium perborate does not give off hydrogen peroxide when heated to 50°–60° under diminished pressure or in a current of air free from carbon dioxide; and the alternative constitution  $\mathrm{HO.B}\left\langle\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}\right.$ has been proposed by Bosshard and Zwicky.[1] The following argument, based upon the preparation and properties of KBO_4, is also given by the same chemists. The compound KBO_4, or *potassium hyperborate*, crystallises with $1H_2O$ and is fairly stable. When dried over phosphoric anhydride *in vacuo*, $4KBO_4.H_2O$ is produced, so that the original compound cannot be formulated as $KBO_3.H_2O_2$. It is rather to be considered as derived from potassium hyperoxide KO.OH, and perboric acid. Hence, two constitutions are possible, viz. KO.O.OB : O and  $\mathrm{KO:O.B}\left\langle\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}\right.$, and it is considered that the latter is much more probable than the former owing to the stability of the salt.

Sodium perborate, $NaBO_3.4H_2O$, may be prepared by adding to a saturated solution of borax an equivalent quantity of sodium hydroxide and twice the amount of hydrogen peroxide theoretically necessary; after some time the perborate commences to crystallise out :—[2]

$$Na_2B_4O_7 + 2NaOH + 4H_2O_2 = 4NaBO_3 + 5H_2O.$$

In preparing the salt on a large scale the necessary ingredients are mixed in small batches, which are then united and slowly cooled with stirring. Wooden vats and stirrers are used, and metal pipes, etc., well tinned to minimise decomposition of the hydrogen peroxide. The temperature after mixing is 25°, and the concentrations are chosen so that the perborate separates out slowly. Large and fairly stable crystals are deposited, which are centrifuged free from mother liquor and dried in a stream of pure air at a temperature not exceeding 50° C.[3]

Sodium perborate is only formed in minute quantities at the anode when aqueous sodium orthoborate, with or without excess of alkali, is electrolysed.[4]

Sodium perborate, $NaBO_3.4H_2O$, crystallises in large, transparent, monoclinic prisms, and is stable in air free from carbon dioxide.[5] The monohydrate may be obtained by careful drying, and this may be completely dehydrated *in vacuo* over phosphoric anhydride. The solubility of the salt in water, in grams per litre of solution, is as follows :—[6]

Temp. ° C.	15°	21°	26°	32°
Grams of $NaBO_3.4H_2O$	25·5	26·9	28·5	37·8

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[1] Bosshard and Zwicky, *Zeitsch. angew. Chem.*, 1912, **25**, 993.

[2] Melikoff and Pissarjewsky, *loc. cit.*; Tanatar, *Zeitsch. physikal. Chem.*, 1898, **26**, 132; 1899, **29**, 162; Jaubert, *Compt. rend.*, 1904, **139**, 796; Bruhat and Dubois, *ibid.*, 1905, **140**, 506; Jaubert and Lion, *Rev. gen. chem. pure appl.*, 1905, [vii.], **8**, 163; Christensen, *Danske Vidensk. Selsk. Forhandl.*, 1904, No. 6.

[3] Fuhrmann, *Chem. Zeit.*, 1911, **35**, 1022.

[4] See Tanatar, *Zeitsch. physikal. Chem.*, 1898, **26**, 132; *Zeitsch. anorg. Chem.*, 1901, **26**, 343; Constam and Bennett, *ibid.*, 1900, **25**, 265; 1901, **26**, 451; Bruhat and Dubois, *Compt. rend.*, 1905, **140**, 506; Pissarjewsky, *Zeitsch. anorg. Chem.*, 1902, **32**, 341; Poulenc, *Fr. Pat.*, 411,258; Beltzer, *Moniteur Scient.*, 1911, p. 10; Polack, *Trans. Faraday Soc.*, 1915, **10**, 177.

[5] Jaubert, *Compt. rend.*, 1904, **139**, 796.

[6] Jaubert and Lion, *loc. cit.*

The solubility is augmented by the addition of boric, tartaric, or citric acid, glycerol, or ammonium and magnesium sulphates in small amount.[1] The heat of solution in water is − 11·56 Cals. at 16°; in seminormal sulphuric acid it is − 8·95 Cals. at 17° C.[2]

In aqueous solution at 0° C. the hydrolysis of sodium perborate is very slight, and from conductivity measurements it follows that the molecular formula of the salt is $NaBO_3$.[3] With rise of temperature, hydrolysis proceeds further, and at 25° it is very considerable. The aqueous solution has an alkaline reaction. According to Pissarjewsky,[4] the hydrolysis proceeds in two stages, (i.) and (ii.), the third reaction (iii.) then taking place between products formed in (i.) and (ii.):—

$$\begin{aligned}
&\text{(i.)}\ NaBO_3 + 2H_2O \rightleftharpoons NaO.OH + H_3BO_3\\
&\text{(ii.)}\ NaO.OH + H_2O \rightleftharpoons NaOH + H_2O_2\\
&\text{(iii.)}\ 3NaOH + H_3BO_3 \rightleftharpoons Na_3BO_3 + 3H_2O
\end{aligned}$$

When heated above 40°, sodium perborate solution commences to evolve oxygen. The solution is an energetic oxidiser, converting ferrous salts to ferric, chromic salts to chromic acid, manganous salts to manganese dioxide, liberating chlorine from hydrochloric acid, iodine from potassium iodide, etc.[5]

Sodium perborate is used commercially under the name of "perborin" for bleaching purposes, since it may be incorporated into soaps and washing powders. "Perborin M" contains soap, alkali, and sodium perborate; "persil" contains soap, alkali carbonate and silicate, and sodium perborate; "ozonite" is similar to "persil"; and "clarax" contains borax, sodium phosphate, and sodium perborate.[6]

A *sodium perborate* of the composition $NaB_2O_4.5H_2O$ is said by Jaubert to be obtained when an intimate mixture of 248 grams of boric acid and 78 grams of sodium peroxide is slowly added to 2 litres of cold water. It cannot be recrystallised from water.[7]

Sodium hyperborate, $NaBO_4$, has not been prepared in a pure state.[8]

Potassium perborate.—The following salts have been described: (i.) $KB_2O_5.2H_2O$,[9] (ii.) $2KBO_3.KBO_4.5H_2O$ or $3KBO_3.H_2O_2.4H_2O$,[10] (iii.) $2KBO_3.H_2O$, and (iv.) $2KBO_3.H_2O_2$.[11]

Rubidium perborate, $RbBO_3.H_2O$, and **cæsium perborate,** $CsBO_3.H_2O$, are also known.[12]

Ammonium perborate, $NH_4BO_3.3H_2O$, is obtained by dissolving boric

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[1] Bruhat and Dubois, *loc. cit.*; Jaubert and Lion, *loc. cit.*

[2] Tanatar, *Zeitsch. physikal. Chem.*, 1898, **26**, 132.

[3] Constam and Bennett, *Zeitsch. anorg. Chem.*, 1900, **25**, 265.

[4] Pissarjewsky, *Zeitsch. physikal. Chem.*, 1903, **43**, 170; *cf.* Schenck, Vorländer, and Dux, *Zeitsch. angew. Chem.*, 1914, **27**, 291.

[5] For further reactions, see Jaubert, *Compt. rend.*, 1904, **139**, 796; Bruhat and Dubois, *Compt. rend.*, 1905, **140**, 506; Christensen, *Danske Vidensk. Selsk. Forhandl.*, 1904, No. 6.

[6] Matthews, *J. Ind. Eng. Chem.*, 1911, **3**, 191. For the patent literature dealing with the manufacture of alkali perborates, see *D.R.P.*. Nos. 193,559, 204,279, 237,096, 237,608; *D.R.P. Amn.*, 49,641; *Fr. Pat.*, Nos. 384,967, 411,258, 425,958; *U.S. Pat.*, Nos. 996,773, 999,497; *Eng. Pat.*, 1626 (1911); *cf.* Bosshard and Zwicky, *Zeitsch. angew. Chem.*, 1912, **25**, 938.

[7] Jaubert, *Compt. rend.*, 1904, **139**, 796.

[8] Melikoff and Pissarjewsky, *Ber.*, 1898, **31**, 678, 953.

[9] Bruhat and Dubois, *Compt. rend.*, 1905, **140**, 506.

[10] Christensen, *Danske Vidensk. Selsk. Forhandl.*, 1904, No. 6.

[11] Von Girzewald and Wolokilin, *Ber.*, 1909, **42**, 865.

[12] Christensen. *loc. cit.*

acid in 2·5 per cent. hydrogen peroxide, adding ammonia, and precipitating with alcohol. When dried for twenty-four hours over sulphuric acid, the salt $2NH_4BO_3.H_2O$ is obtained, and this may be dehydrated over phosphoric anhydride.[1]

The salt $NH_4.BO_3.NH_4.BO_4.2H_2O$ has been described by Petrenko.[2]

Barium perborate, $Ba(BO_3)_2.7H_2O$,[3] and **uranyl perborate,** UO_2BO_3,[4] are also known.

Boron sesquisulphide (boron trisulphide), B_2S_3, is produced when boron is heated to bright redness in sulphur vapour,[5] or when boron is heated to redness in a current of hydrogen sulphide.[6] It may also be prepared by heating to redness in a current of carbon disulphide vapour an intimate mixture of boron sesqui-oxide and carbon.[7] Other reactions which lead to the formation of the sulphide are the action of sulphur upon boron tri-iodide and the action of carbon disulphide and various other sulphides on boron (Moissan). The pure sesquisulphide is best prepared by heating pure boron in a stream of hydrogen sulphide largely diluted with hydrogen,[8] and a cheap method for its preparation consists in heating commercial iron boride or manganese boride to 300°–400° in hydrogen sulphide and washing away admixed sulphur from the product with carbon disulphide.[9] Only part of the boron in these borides can be removed as the sulphide.

The properties of boron sesquisulphide have been studied mainly by Moissan.[10] It forms fine, white needles, of density 1·55, which melt at 310° and volatilise without decomposition when heated in a current of hydrogen. It is unacted upon at a red heat by hydrogen, nitrogen, phosphorus, carbon, and silicon. It inflames in chlorine in the cold, in bromine vapour when warmed, and in oxygen when heated to dull redness; in each case both the boron and sulphur are converted into chloride, bromide, or oxide. At a dull red heat, boron sesquisulphide is violently decomposed by potassium, sodium, magnesium, and aluminium, but iron, zinc, copper, mercury, and silver are without action upon it. It is decomposed by carbon dioxide above 300° as follows:—[11]

$$B_2S_3 + 3CO_2 = B_2O_3 + 3CO + 3S.$$

It is violently decomposed by water at ordinary temperatures, boric acid and hydrogen sulphide being produced and much heat evolved:—[12]

$$[B_2S_3] + 6H_2O + aq. = 2H_3BO_3aq. + 3(H_2S) + 57{\cdot}8 \text{ Cals.}$$

Boron sesquisulphide is slightly soluble in phosphorus trichloride, from which it crystallises in needles. It forms the addition-compounds $B_2S_3.BCl_3$

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[1] Melikoff and Pissarjewsky, *Ber.*, 1898, **31**, 678,953; Constam and Bennett, *Zeitsch. anorg. Chem.*, 1900, **25**, 265; Tanatar, *Zeitsch. physikal. Chem.*, 1898, **26**, 132; Bruhat and Dubois, *Compt. rend.*, 1905, **140**, 506.

[2] Petrenko, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 37.

[3] Melikoff and Pissarjewsky, *loc. cit.*

[4] Bruhat and Dubois, *Compt. rend.*, 1905, **140**, 506.

[5] Berzelius, *Pogg. Annalen*, 1824, **2**, 145.

[6] Wöhler and Deville, *Ann. Chim. Phys.*, 1858, [iii.], **52**, 90.

[7] Frémy, *Ann. Chim. Phys.*, 1853, [iii.], **38**, 312.

[8] H. Gautier, *Ann. Chim. Phys.*, 1899, [vii.], **18**, 363.

[9] J. Hoffman, *Zeitsch. angew. Chem.*, 1906, **19**, 1362, 2133; *Zeitsch. anorg. Chem.*, 1908, **59**, 127.

[10] Moissan, *Compt. rend.*, 1892, **115**, 203.

[11] Costeanu, *Compt. rend.*, 1913, **157**, 934; *Ann. Chim.*, 1914, [x.], **2**, 189.

[12] Sabatier, *Compt. rend.*, 1891, **112**, 862.

and $B_2S_3.BBr_3$,[1] and according to Moissan, combines with the chlorides of phosphorus, arsenic, and antimony. When dissolved in hot carbon disulphide, saturated with hydrogen sulphide, the solvent evaporated *in vacuo* and the residue recrystallised from either carbon disulphide or benzene, white crystals of $B_2S_3.H_2S$ or **thiometaboric acid** are obtained.[2] This substance, which smells of hydrogen sulphide and is rapidly decomposed by water, has a molecular weight corresponding to the formula $H_2B_2S_4$ in benzene solutions; unlike boron sesquisulphide, it is extremely soluble in both benzene and carbon disulphide. Heated in a sealed tube, it begins to melt at 120° and forms a clear, transparent liquid at 140°; when heated in air, it readily dissociates into boron sesquisulphide and hydrogen sulphide. Thiometaboric acid dissolves in liquid ammonia; when excess of solvent is removed at ordinary temperatures, yellow crystals of $B_2S_3.6NH_3$ separate out.[1]

Boron pentasulphide, B_2S_5.—When sulphur reacts upon boron tri-iodide without the intervention of a solvent, boron sesquisulphide is produced, but when the reaction occurs in carbon disulphide solution, crystals of boron pentasulphide are said to separate from the liquid.[3] The substance dissociates into sesquisulphide and sulphur when heated *in vacuo*. It has not been obtained with less than 10 to 15 per cent. of admixed iodine.

Boron selenide, B_2Se_3, may be prepared by heating boron in selenium vapour or hydrogen selenide.[4] It is also produced if iron or manganese boride be used instead of boron itself.[5] The selenide is a yellow solid which does not appear to be volatile at a red heat. It is decomposed by water in a similar manner to the sulphide.

Boron and the Nitrogen Group.

Boron nitride, BN.—Boron unites directly with nitrogen at a red heat to form a nitride (Wöhler and Deville; Moissan). Boron nitride was discovered by Balmain[6] in 1842 by fusing boron sesqui-oxide with potassium cyanide, but its true nature was determined and the compound prepared in a nearly pure state by Wöhler in 1850.[7] His method consisted in heating an intimate mixture of anhydrous borax (1 pt.) and ammonium chloride (2 pts.) to bright redness in a platinum crucible, boiling the powdered product with very dilute hydrochloric acid as long as boric acid could be extracted, washing and drying the residue. Another method of preparation consists in heating a mixture of boron sesqui-oxide (4 pts.) and carbon (1 pt.) to whiteness in a current of nitrogen.[8] The nitride is produced when boron is heated to redness in ammonia, and may be more readily prepared by heating either boron sesqui-oxide or anhydrous borax in the same gas.[9] Numerous other methods have been proposed, as, for example, heating boron sesqui-oxide or borax with potassium ferrocyanide, potassium cyanide, mercuric cyanide, or urea.[10]

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[1] Stock and Blix, *Ber.*, 1901, **34**, 3039; 1903, **36**, 319.

[2] Stock and Poppenberg, *Ber.*, 1901, **34**, 399.

[3] Moissan, *Compt. rend.*, 1892, **115**, 271.

[4] Sabatier, *Compt. rend.*, 1891, **112**, 1000.

[5] J. Hoffmann. *Chem. Zeit.*, 1911, **35**, 713.

[6] Balmain, *Phil. Mag.*, 1842, [iii.], **21**, 170; 1843, [iii.], **22**, 467; 1844, [iii.], **24**, 191.

[7] Wöhler, *Annalen*, 1850, **74**, 70.

[8] Wöhler and Deville, *Ann. Chim. Phys.*, 1858, [iii.], **52**, 63.

[9] See Ehrich and Graetz, *D.R.P.*. 282,701 (1913); Podszus, *D.R.P.*, 282,748 (1913).

[10] Darmstadt, *Annalen*, 1869, **151**, 255; Martius, *ibid.*, 1859, **109**, 80; Rose, *Pogg. Annalen*, 1850, **80**, 265; Gustavson, *Ber.*, 1870, **3**, 426.

As a convenient method of preparation, Moeser and Eidmann[1] recommend passing ammonia over a strongly heated and previously fused mixture of boron sesqui-oxide and calcium phosphate. The product, when washed with dilute hydrochloric acid, is nearly pure boron nitride. To obtain the nitride in a state of purity, boron tribromide should be slowly dropped into liquid ammonia, the excess of solvent removed by evaporation, and the solid residue gradually heated to 750°.[2] The imide of boron initially formed (p. 24) becomes converted into nitride :—

$$B_2(NH)_3 = 2BN + NH_3.$$

The method given by Wöhler and Deville for the preparation of boron nitride has been studied by Stähler and Elbert, with respect to its utilisation for the fixation of atmospheric nitrogen. When a mixture of boron sesqui-oxide and carbon is heated in nitrogen, the yield of boron nitrogen varies with the temperature and the pressure of the nitrogen. At a pressure of one atmosphere, the best yield, 26 to 28 per cent. of nitride, is obtained at 1500° to 1700°; but at a pressure of 70 kilos per square centimetre, a yield of more than 85 per cent. is obtained at 1600°. When, however, boron sesqui-oxide is replaced by borocalcite, CaB_4O_7, a nearly theoretical yield of boron nitride, according to the equation

$$CaB_4O_7 + 8C + 3N_2 \rightleftharpoons 4BN + CaCN_2 + 7CO,$$

is obtained, even at one atmosphere pressure, by heating first to 1850° and subsequently lowering the temperature to 1400°; increasing the pressure of the nitrogen has practically no effect on the yield.[3]

Boron nitride is a light, white, amorphous solid, soft, like talc, to the touch. It can be compressed, wet or dry, into blocks of considerable rigidity. It is infusible at the melting-point of tungsten, but above 1500° it commences to dissociate *in vacuo* into boron and nitrogen.[4] At 1220°, however, the dissociation pressure does not exceed 9·4 mm.[5] At high temperatures it is the best insulator known.[6] Heated in a flame it exhibits a greenish-white fluorescence.

Boron nitride is a very stable compound. It is very slowly decomposed by boiling water, aqueous potash, hydrochloric and nitric acids, but decomposes more readily when heated in steam or at 200° in a sealed tube with water, hydrochloric or sulphuric acid :—

$$BN + 3H_2O = H_3BO_3 + NH_3.$$

Heated with fused potassium hydroxide, ammonia and potassium borate are produced; with fused potassium carbonate the products are potassium cyanate, cyanide, and borate. It is little affected by heating with oxygen, iodine, hydrogen, carbon dioxide, or carbon disulphide. In an alcohol flame fed with oxygen it burns to boron sesqui-oxide, and at high temperatures it is decomposed by chlorine. It is slowly dissolved by hydrofluoric acid, ammonium borofluoride being produced. The oxides of copper, cadmium,

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[1] Moeser and Eidmann, *Ber.*, 1902, **35**, 535.

[2] Stock and Blix, *Ber.*, 1901, **34**, 3039; Stock and Holle, *ibid.*, 1908, **41**, 2095.

[3] Stähler and Elbert, *Ber.*, 1913, **46**, 2060.

[4] See *Eng. Pat.*, 25,978 (1906).

[5] Slade and Higson, *Rep. Brit. Assoc.*, 1913, p. 451.

[6] Weintraub, *J. Ind. Eng. Chem.*, 1913, **5**, 106.

mercury, arsenic, antimony, and bismuth are reduced when heated with boron nitride, the products being metal, metallic borate, and nitrous oxide; sulphates are reduced to sulphides; but the oxides of zinc and iron are not reduced.[1]

Boron nitride prepared by heating boron imide at 125° to 130° for a long time is, according to Stock and Blix, much more reactive than the nitride prepared at high temperatures, and they suggest that the latter is a polymer of the former.

Boron amide, $B(NH_2)_3$.—The preparation of this compound has been already described (p. 23). It has not yet been prepared in a state of purity; the accompanying ammonium salt can be removed partly, but not entirely, by washing with liquid ammonia.

Boron imide, $B_2(NH)_3$, is best prepared by heating the compound $B_2S_3.6NH_3$ at 115° to 120° in a rapid stream of ammonia for some days:—[2]

$$B_2S_3.6NH_3 = B_2(NH)_3 + 3NH_4.SH.$$

Other methods of formation have been already mentioned (pp. 23, 24).

Boron imide is a light, white powder, insoluble in alcohol, ether, carbon disulphide, and liquid ammonia. It begins to decompose at 125° to 130° with the evolution of ammonia, and at a slightly higher temperature is completely resolved into boron nitride and ammonia. When boiled with water, boron imide is decomposed into ammonia and boric acid.

Boron imide is a feebly basic compound, and when added to liquid hydrogen chloride it forms a white hydrochloride, $B_2(NH)_3.3HCl$, insoluble in organic media, and decomposed by heat or water.

Boron phosphide, BP, is prepared by heating boron phospho-iodide to 450°-500° in a current of hydrogen. The iodine can also be removed from the phospho-iodide by heating with mercury or silver.[3] Another method of preparation consists in heating the compound $BBr_3.PH_3$ to 300°, when hydrogen bromide is eliminated.[4]

Boron phosphide is a light, amorphous, maroon-coloured powder, insoluble in the usual inorganic and organic solvents. It burns in chlorine in the cold and in bromine when warmed; at 200° it burns brilliantly in oxygen, and it also reacts with heated sulphur. It is not affected by iodine, nitrogen, phosphorus, or arsenic even at a red heat. It is attacked by numerous metals at a red heat, and is easily oxidised by concentrated nitric acid or fused alkali nitrates.

When heated in hydrogen at 1000°, a brown **boron subphosphide,** B_5P_3, is produced which is much less reactive than the phosphide.

Boron phospho-iodides.—The compound BPI_2 is prepared by acting upon boron tri-iodide with phosphorus in carbon disulphide solution, and, in a carbon dioxide atmosphere, washing away the iodide of phosphorus simultaneously produced with a further quantity of carbon disulphide.[5] It is a dark red solid which melts *in vacuo* at 190° to 200° and sublimes at higher temperatures. Chlorine, oxygen, and many metals attack it vigorously, and water immediately decomposes it, among the products being hydriodic,

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[1] Wöhler and Deville, *loc. cit.*; Darmstadt, *loc. cit.*; Moeser and Eidmann, *loc. cit.*

[2] Stock and Blix, *Ber.*, 1901, 34, 3039.

[3] Moissan, *Compt. rend.*, 1891, 113, 726, 787.

[4] Besson, *ibid.*, 1891, 113, 78, 772.

[5] Moissan, *Compt. rend.*, 1891, 113, 624.

phosphorous, and boric acids. When heated to 160° in hydrogen it is reduced to the compound BPI, which sublimes *in vacuo*, forming orange-yellow crystals, and closely resembles the other phospho-iodide in properties.

BORON AND THE CARBON GROUP.

Boron carbide, B_6C.—This compound was isolated in small quantities by Joly in 1883[1] from among the products of the interaction, in a carbon crucible, of boron sesqui-oxide and aluminium. Later it was prepared in quantity by Moissan,[2] by heating to 3000° in the electric furnace a mixture of sugar carbon and amorphous boron contained in a carbon crucible. A cheaper method of preparation consists in employing boron sesqui-oxide and petroleum coke as starting materials, the former being fed through a hollow graphite electrode on to a layer of the latter contained in a graphite crucible which forms the other electrode.[3] The product is purified from graphite by many treatments with boiling nitric acid and potassium chlorate, followed by treatment with boiling sulphuric acid.

Boron carbide forms brilliant black crystals, of density 2·51, and melts at 2350°.[4] The carbide conducts electricity. It is extremely hard (harder than silicon carbide) and can be used in diamond polishing. It is not affected by mineral acids at the boiling temperature, sulphur at 500°, nitrogen, phosphorus, bromine, or iodine at a bright red heat. It is slowly attacked by oxygen at 1000°, and by chlorine at a somewhat lower temperature. When fused with potassium hydroxide it is decomposed with the evolution of carbon monoxide.

The so-called carbide[5] BC is a mixture of the preceding carbide and graphite (Tucker and Bliss).

Boron thiocyanate, $B(CNS)_3$, is produced by shaking silver thiocyanate with a solution of boron tribromide in benzene, and separates from benzene in short, glistening, rhombic crystals. From ether it crystallises in thin plates. The thiocyanate is rapidly hydrolysed by water, and its action upon aniline indicates that it possesses the structure of a thiocyanate rather than that of a thiocarbimide.[6]

Boron Alkyls, $B(C_nH_{2n+1})_3$.—Although at present a hydride of the molecular formula BH_3 is unknown, the boron trialkyls have been known for many years. They are prepared by the action of zinc alkyls on trialkyl esters of orthoboric acid.[7] **Boron trimethyl,** $B(CH_3)_3$, is a gas at ordinary temperatures; **boron triethyl,** $B(C_2H_5)_3$, is a volatile liquid. Both are readily combustible, burning with a green flame, and they combine readily with ammonia. The vapour densities correspond with the above formulæ.

Boron Silicides, B_2Si and B_6Si.—These compounds are produced when a mixture of crystalline silicon (5 pts.) and amorphous boron (1 pt.), packed in a refractory earthenware tube, is heated for 40 to 60 seconds by means of an electric current of 600 ampères at 45 volts. The outer portions of the

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[1] Joly, *Compt. rend.*, 1883, **97**, 456.
[2] Moissan, *ibid.*, 1894, **118**, 556.
[3] Tucker and Bliss, *J. Amer. Chem. Soc.*, 1906, **28**, 605; Tucker, *D.R.P.*, 206,177; *cf.* Tiede and Birnbräuer, *Zeitsch. anorg. Chem.*, 1914, **87**, 129.
[4] Pring and Fielding, *Trans. Chem. Soc.*, 1909, **95**, 1497.
[5] Mühlhäuser, *Zeitsch. anorg. Chem.*, 1893, **5**, 92.
[6] Cocksedge, *Trans. Chem. Soc.*, 1908, **93**, 2177.
[7] Frankland and Duppa, *Phil. Trans.*, 1862, **152**, 167; *Proc. Roy. Soc.*, 1376, **25**, 165.

product and those portions which were in proximity to the carbon electrodes are discarded, and the remainder treated with a cold mixture of nitric and hydrofluoric acids to eliminate free silicon. The residue is purified by heating for half an hour with commercial potassium hydroxide, which is just melted but not dehydrated. After washing with water, dilute nitric acid, and boiling water, and drying at 130°, a mixture of the two silicides is obtained.

The silicide B_3Si is left when the mixture is heated with an excess of boiling nitric acid, the other compound being completely decomposed. It forms black, rhombic plates which are transparent and yellow or brown in very thin layers. The density is 2·52. It easily scratches quartz and ruby, but is softer than boron carbide. Fluorine, chlorine, and bromine attack it in increasing order of difficulty, and it is only superficially oxidised by air or oxygen at a red heat. It is rapidly oxidised by fused anhydrous potassium hydroxide, less rapidly by fused alkali carbonates, and not at all by fused alkali nitrates. Boiling concentrated sulphuric acid slowly oxidises it.

The silicide B_6Si is isolated from a mixture of the silicides, in which it is more abundant than the other, by heating with fused anhydrous potassium hydroxide. It forms thick, opaque crystals of density 2·47. In chemical properties it resembles the other silicide, except in its behaviour towards fused potassium hydroxide and boiling nitric acid.[1]

DETECTION AND ESTIMATION OF BORON.[2]

Boric acid, or a borate moistened with concentrated sulphuric acid, imparts a green colour to the flame. The material to be tested should be introduced 2 centimetres above the top of the Bunsen burner, and should not be brought closer than 2 millimetres to the visible edge of the flame, in order that other substances may be prevented from tinging the flame green. The coloration is best seen tangentially to the flame, and a hydrogen flame is preferable to the ordinary gas flame.[3] The flame of a burning alcoholic solution of an alkyl borate is also coloured green (C. Geoffrey, 1732). To utilise this fact in qualitative analysis, the material under examination is mixed with concentrated sulphuric acid and alcohol (preferably methyl alcohol), the alcohol ignited, and the mixture stirred.[4] This test is not reliable in the presence of chlorides, phosphates, molybdates, barium, copper, thallium, and tellurium, and moreover, it fails to detect boron in many minerals. Glycerol may be used instead of alcohol; in this case the substance is heated with a little sulphuric acid until excess of the latter has been driven off, the residue moistened with glycerol and a light applied.[5] A more delicate and very characteristic test consists in heating the substance with calcium fluoride and concentrated sulphuric acid and leading the evolved gases into the Bunsen flame. A mere trace of boron trifluoride will tinge

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[1] Moissan and Stock, *Compt. rend.*, 1900, **131**, 139; *Ann. Chim. Phys.*, 1900, [vii.], **20**, 433.

[2] A very full account of the analytical chemistry of boron, and copious references to the literature, will be found in Mellor, *A Treatise on Quantitative Inorganic Analysis* (Griffin & Co., 1913).

[3] Dieulafait, *Ann. Chim. Phys.*, 1877, [v.], **12**, 318. See also Bornträger, *Zeitsch. anal. Chem.*, 1900, **39**, 92.

[4] Dieulafait, *loc. cit.*; Gilm, *Ber.*, 1878, **11**, 712; Lenher and Wells, *vide infra.*

[5] Iles, *Chem. News*, 1877, **35**, 204.

the flame a vivid green.[1] The green flame of boric acid, an alkyl borate, or boron fluoride gives a beautiful band spectrum in which three prominent bands are easily recognised, the maxima being situated at λ 5480, λ 5190, and λ 4930 (fig. 3).[2]

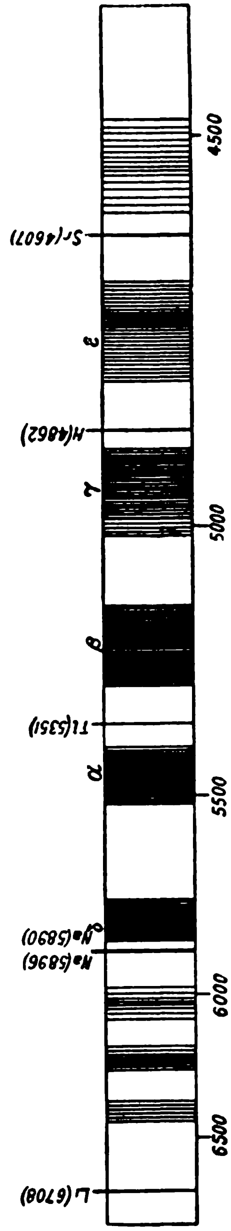

Fig. 3.—Band Spectrum of Boric Acid.

Silver nitrate gives a white precipitate of silver metaborate with a concentrated solution of borax, and a brown precipitate of silver oxide with a dilute solution.

The colour of turmeric paper, when dipped into a solution of boric acid (or of a borate acidified with hydrochloric acid) and then dried at 100°, is changed to a characteristic reddish brown (H. Rose), or, with mere traces of boric acid, pink. In using this delicate test for boric acid it must be remembered that zirconic, tantalic, columbic, and molybdic acids produce a similar coloration. The test is rendered more delicate by the presence of oxalic acid;[3] the reddish-brown colour changes to a greenish- or bluish-black when sodium hydroxide is added.[4] Boric acid turns tincture of mimosa flowers yellow, and this is in turn changed to a brick-red colour when sodium carbonate is added.[5]

Boric acid is neutral to litmus and methyl orange, and hence the metal present in an alkali borate may be titrated with acid as if it were present as alkali hydroxide.[6]

Boric acid may be easily and accurately titrated as a monobasic acid, thus:—

$$H_3BO_3 + NaOH = NaBO_2 + 2H_2O,$$

in the presence of excess of glycerol (30 per cent. by volume) or manitol (0·1 gram per cubic centimetre of solution). The latter is the more convenient to use; owing to the slight acidity of commercial glycerol, it is necessary to carry out a blank experiment when that substance is employed.

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[1] Arfvedson's test. See Ross, *Chem. News*, 1883, **47**, 186; Kämmerer, *Zeitsch. anal. Chem.*, 1873, **12**, 375; Chapman, *Chem. News*, 1877, **35**, 36; C. le Neve Foster, *ibid.*, 1877, **35**, 127; Spindler, *Chem. Zeit.*, 1905, **29**, 566, 582; Castellana, *Atti R. Accad. Lincei*, 1905, [v.], **14**, i. 465; *Gazzetta*, 1906, **36**, i. 232; Lenher and Wells, *J. Amer. Chem. Soc.*, 1899, **21**, 417.

[2] See p. 12 for references.

[3] Cassal and Gerraus, *Chem. News*, 1903, **87**, 27.

[4] For the turmeric paper test, see Kulisch, *Zeitsch. angew. Chem.*, 1894, **7**, 147; Lenher and Wells, *loc. cit.*; W. H. Low, *vide infra*; Bertrand and Agulhon, *vide infra*; Jay, *vide infra*; Price and Ingersoll, *Bull. U.S. Dept. Agric.* (*Chem.*), 1912, **137**, 115; Halphen, *Ann. Falsif.*, 1915, **8**, 1.

[5] Robin, *Compt. rend.*, 1904, **138**, 1046; *Bull. Soc. chim.*, 1913, [v.], **13**, 602.

[6] Gay Lussac, *Ann. Chim. Phys.*, 1830, **40**, 398; Joly, *Compt. rend.*, 1885, **100**, 103; Rimbach, *Ber.*, 1893, **26**, 164.

Alkali hydroxide free from carbonate should be used for the titration, and phenolphthalein must be used as indicator. Prior to the addition of the glycerol or mannitol, the solution, which should be slightly acid, is made accurately neutral to methyl orange or paranitrophenol and freed from carbon dioxide by boiling for a few minutes, a reflux condenser being employed to prevent loss of boric acid, (or better, the solution being boiled under diminished pressure).[1] Mannitol or glycerol is then added and the titration of the boric acid carried out. Mineral borates soluble in hydrochloric acid may be readily analysed by the method here outlined.[2] Boric acid may be titrated with alkali hydroxide without adding either glycerol or mannitol, if tropæolin.O (*i.e.* sodium para-benzene-azo-resorcinol-sulphonate) is used as indicator.[3]

Boron is determined in minerals (*e.g.* tourmaline) by fusing with an excess of fusion mixture, acidifying with hydrochloric acid, and titrating the boric acid produced by the procedure already outlined. It is, however, first necessary to separate the boric acid from the other substances present. This is effected most conveniently by adding a large excess of anhydrous calcium chloride, a little pure methyl alcohol, and heating to boiling while a stream of methyl alcohol vapour is blown through the liquid. The boron is volatilised as trimethyl borate, and, together with an excess of alcohol, is condensed in a suitable receiver. A decided excess of sodium hydroxide is then added to the distillate and the alcohol distilled from the liquid, when an aqueous solution of sodium borate remains.[4]

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[1] An alternative procedure consists in eliminating carbon dioxide from the slightly acid (hydrochloric) solution, adding a slight excess of potassium iodide-iodate mixture, and bleaching the liberated iodine with sodium thiosulphate. In this case metals which are precipitated as hydroxides by the iodide-iodate mixture must be absent.

[2] R. T. Thomson, *J. Soc. Chem. Ind.*, 1893, **12**, 432; Schaak, *ibid.*, 1904, **23**, 699; Hönig and Spitz, *Zeitsch. angew. Chem.*, 1896, **9**, 549; L. C. Jones, *Amer. J. Sci.*, 1899, [iv.], **7**, 147; **8**, 127; Copaux, *Compt. rend.*, 1898, **127**, 756; Stock, *ibid*,, 1900, **130**, 516; Copaux and Boiteau, *Bull. Soc. chim.*, 1909, [iv.], **5**, 217; Sargent, *J. Amer. Chem. Soc.*, 1899, **21**, 858; W. H. Low, *ibid.*, 1906, **28**, 807; Wherry and Chapin, *ibid.*, 1908, **30**, 1687; Lindgren, *ibid.*, 1915, **37**, 1137; Mandelbaum, *Zeitsch. anorg. Chem.*, 1909, **62**, 364; H. Biltz and Marcus, *ibid.*, 1912, **77**, 131; Binet du Jassonneix, *Ann. Chim. Phys.*, 1909, [viii.], **17**, 145. There is an extensive literature dealing with the estimation of boric acid in foods: see, *e.g.*, R. T. Thomson, *Analyst*, 1896, **21**, 64; Cribb and Arnaud, *ibid.*, 1906, **31**, 147; Shrewsbury, *ibid.*, 1907, **32**, 5; Richardson and Walton, *ibid.*, 1913, **38**, 140; Manning and Lang, *J. Soc. Chem. Ind.*, 1907, **26**, 803; Allen and Tankard, *Pharm. J.*, 1904, [iv.], **19**, 242; W, H. Low, *loc. cit.* For the detection of traces of borax in organic matter, see Bertrand and Agulhon, *Bull. Soc. chim.*, 1910, [iv.], **7**, 90,125; *Compt. rend.*, 1913. **157**, 1433; Jay and Dupasquier, *ibid.*, 1895, **121**, 260; Jay, *ibid.*, 1914, **158**, 357; Filippi, *Ann. chim. applicata*, 1914, **1**, 564.

[3] Prideaux, *Zeitsch. anorg. Chem.*, 1913, **83**, 362.

[4] Wherry and Chapin, *loc. cit.*; Stock, *loc. cit.*; Copaux and Boiteau, *loc. cit.*; Sargent, *loc. cit.*; W. H. Low, *loc. cit.*; Mandelbaum, *loc. cit.*; Binet du Jassonneix, *loc. cit.* The separation of boron as trimethyl borate was first developed into a quantitative method by Gooch (*Amer. Chem. J.*, 1887, **9**, 23) and Rosenbladt (*Zeitsch. anal. Chem.*, 1887, **26**, 21). The gravimetric estimation of boron is difficult and tedious, and offers no advantages over the volumetric estimation. The only reliable method is to hydrolyse the methyl borate, separated by the distillation process, with a known excess of pure lime, carefully evaporate, ignite, and determine the increase in weight of the lime, which is due to boron sesqui-oxide. This is Gooch's method; the lime may be replaced by sodium tungstate according to Gooch and L. C. Jones (*Amer. J. Sci.*, 1899, [iv.], **7**, 34). The distillation of the methyl borate must be so effected as to prevent the formation of dimethyl sulphate or methyl chloride. For details, see Gooch, *loc. cit.*; Gooch and L. C. Jones, *loc. cit.*; Moissan, *Compt. rend.*, 1893, **116**, 1087; Penfield, *Amer. J. Sci.*, 1887, **34**, 222; Arndt, *Chem. Zeit.*, 1909, **33**, 725. For the estimation of boron as *boron phosphate*, see Mylius and Meusser, *Ber.*, 1904, **37**, 397; as *potassium borofluoride* (the old method of estimation), see Stromeyer, *Annalen*, 1856, **100**, 82; Thaddéeff, *Zeitsch. anal. Chem.*, 1897, **36**, 468;

Perborates, when shaken with potassium dichromate solution and ether, give rise to the blue colour of perchromic acid.[1] They may be analysed for available oxygen by titration with potassium permanganate in acid solution and by other methods.[2]

ADDENDUM.

Boroethane, B_2H_6.—The action of chlorine and bromine on this hydride of boron has been studied by Stock, Kuss, and Priess (*Ber.*, 1914, **47**, 3115). Chlorine causes explosions at ordinary temperatures, but bromine reacts slowly, even in the light; at 100°, however, the change is complete in a few hours. One half of the halogen used up is recovered as halogen hydride, *i.e.* the reaction is one of *substitution*, and boroethane behaves as a saturated compound. The maximum valency of boron towards hydrogen is accordingly four.

Excess of halogen leads to the production of the unimolecular halides, BX_3, and not to B_2X_6. In order to trace the mechanism of these changes, the action of the halogens on excess of the boron hydride was studied and the following conclusions reached. The initial products are such products as $B_2H_4X_2$ and $B_2H_3X_3$, which speedily decompose, without the elimination of halogen hydride, yielding B_2H_5X and B_2H_6 on the one hand, and BX_3 on the other. Thus, of the various halogenated derivatives theoretically possible, a mixture of the extremes is produced. No evidence of the existence of BHX_2, BH_2X, B_2HX_5, and $B_2H_2X_4$ could be obtained.

The *monochloride*, B_2H_5Cl, is a spontaneously inflammable gas. The *monobromide*, B_2H_5Br, is a colourless gas with an irritating odour. It melts at 104° and boils at *c.* 10° C. The vapour pressure is as follows:—

Temp. ° C.	- 80°	- 70°	- 60°	- 50°	- 40°	- 30°	- 20°	- 10°	- 5°
Vap. press. in mms.	3	9	16	30	53	95	162	255	335

It burns with a pale green flame and fumes in the air owing to its reaction with water:—

$$B_2H_5Br + 3H_2O = B_2O_3 + HBr + 5H_2.$$

It immediately reacts with potassium hydroxide to form the hypoborate $KOBH_3$. It does not react with sodium, however, to any extent, so that the hydride B_4H_{10} cannot be thus produced.

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as *boric acid*, by extraction with ether, see Partheil and Rose, *Arch. Pharm.*, 1904, **242**, 477. For a bibliography and a critical examination of various processes that have been recommended from time to time, see Sargent, *loc. cit.*; *cf.* Reischle, *Zeitsch. anorg. Chem.*, 1893, **4**, 111.

[1] Lenz and Richter, *Zeitsch. anal. Chem.*, 1911, **50**, 537; Riesenfeld and Mau, *Ber.*, 1911, **44**, 3589; Bosshard and Zwicky, *Zeitsch. angew. Chem.*, 1912, **25**, 938, 993.

[2] For which, see Farrar, *J. Soc. Dyers*, 1910, **26**, 81; Rupp and Mielck, *Arch. Pharm.*, 1907, **245**, 5; Lenz and Richter, *loc. cit.*; Litterscheid and Guggiari, *Chem. Zeit.*, 1913, **37**, 690.

CHAPTER III.

ALUMINIUM.

Symbol, Al. Atomic weight, 27·1 ($O = 16$).

Occurrence.—Aluminium is the most abundant and the most widely distributed of all the metals (Vol. I. Chap. I.), but it is never found in the free state. Among the more simple minerals in which aluminium occurs are the following:—

Corundum	Al_2O_3	Gahnite	$ZnAl_2O_4$
Diaspore	$Al_2O_3.H_2O$	Cryolite	Na_3AlF_6
Hydrargillite	$Al_2O_3.3H_2O$	Websterite	$Al_2O_3.SO_3.9H_2O$
Chrysoberyl	$BeAl_2O_4$	Alunogen	$Al_2(SO_4)_3.18H_2O$
Spinel	$MgAl_2O_4$	Alunite	$Al_2(SO_4)_3.4Al(OH)_3.K_2SO_4$

Bauxite is a hydrated oxide of aluminium containing more or less ferric oxide; *turquoise*, a hydrated aluminium phosphate.

Aluminium is an essential constituent of innumerable *silicates*, which form the basis of most *rocks* and *clays*. Of the silicates, *orthoclase*, $KAlSi_3O_8$, is the most important, as it forms the chief constituent of granite, syenite, gneiss, etc. By the weathering of orthoclase, the mineral *kaolin*, $Al_2Si_2O_7.2H_2O$, is produced. Other important silicates, such as the *garnets*, *micas*, *topaz*, *tourmaline*, etc., are mentioned later (p. 92).

Aluminium is only found in small quantity in most plants, but the ashes of certain cryptogams, *e.g. lycopodium*, contain large quantities of aluminium.[1]

Aluminium is contained in the atmosphere of the sun.

History.—The term "alumen" was applied by the Romans to all bodies of an astringent taste, and among them alum was included. Alum was well known to Geber and the later alchemists, who erroneously classed it with the vitriols. This error was corrected by Paracelsus. The earth present in alum was for a long time supposed to be calcareous. In 1746, Pott stated that the basis of alum is an argillaceous earth, and in 1754, Marggraf showed that alumina and lime are two quite distinct earths, and that alumina is present in clay, combined with silica.

By the early years of the nineteenth century alumina was regarded as the

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[1] Yoshida, *Trans. Chem. Soc.*, 1887, **51**, 748; L'Hote, *Compt. rend.*, 1887, **104**, 853; Demarçay, *ibid.*, 1900, **130**, 91; Berthelot and André, *ibid.*, 1895, **120**, 288; Kratzmann, *Pharm. Post*, 1914, **47**, 101, 109; Langworthy and Peter, *The Occurrence of Aluminium in Vegetable, Animal Products, and Natural Waters* (Wiley & Sons, 1904); Czapek, *Biochemie der Pflanzen* (Jena, 1905), vol. ii. p. 855; H. G. Smith, *Chem. News*, 1903, **88**, 135.

oxide of an unknown metal, which H. Davy unsuccessfully endeavoured to isolate. Aluminium was isolated by Wöhler in 1827.

Preparation.—The oxide, sulphide, and halides of aluminium are very stable compounds, and the preparation of the metal by chemical processes is somewhat difficult. From thermochemical considerations, it may be deduced that the most successful methods would be those in which an aluminium halide is reduced by fusion with an alkali metal.

It is possible that aluminium was obtained by Oersted in 1842,[1] but it is generally acknowledged that the merit of having first prepared aluminium and studied its properties belong to Wöhler, who, by heating anhydrous aluminium chloride with potassium, obtained the metal first in the form of a grey powder which became brilliant when burnished, and subsequently as fused metallic globules.[2]

In 1854 both Bunsen and Deville succeeded in preparing aluminium by electrolysing the fused anhydron chloride, and in the same year Deville commenced his classic work on the manufacture of aluminium by reducing aluminium sodium chloride with metallic sodium.[3] The following year saw the introduction of another process, namely, the reduction of cryolite by fusion with sodium. This method was worked out by Percy in England and by Rose in Germany.[4] Later, Grabeau reduced anhydrous aluminium fluoride by means of sodium, and obtained aluminium of remarkable purity.[5]

At the present time the only method by which aluminium is produced on a commercial scale is an electrolytic method, developed independently and almost simultaneously in 1886 by C. M. Hall in America and P. V. Héroult in France. Alumina is dissolved in molten cryolite and electrolysed, when aluminium separates out at the cathode.[6] Attempts have been made to electrolyse aluminium sulphide dissolved in fused sodium sulphide, but they have not yet been commercially successful.[7]

The necessity for finding a solvent for the alumina arises from the fact that its melting-point is 2010° to 2050°. The melting-point of cryolite is a little below 1000°. In order to produce a more fluid bath, other fluorides are added to the cryolite, *e.g.* aluminium fluoride and calcium floride.

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[1] See Berzelius, *Jahresber.*, 1827, **6**, 118; Oersted, *Overs. K. Danske Vidensk. Selbsk. Forhandl.*, 1824–1825.

[2] Wöhler, *Pogg. Annalen*, 1827, **11**, 146; *Ann. Chim. Phys.*, 1828, **37**, 66; *Annalen*, 1836, **17**, 43; 1845, **53**, 422.

[3] Bunsen, *Pogg. Annalen*, 1854, **92**, 648; Deville, *Ann. Chim. Phys.*, 1855, [iii.], **43**, 5; 1856, [iii.], **46**, 415.

[4] Rose, *Pogg. Annalen*, 1855, **96**, 152; *Ann. Chim. Phys.*, 1855, [iii.], **45**, 369; and see also *Phil. Mag.*, 1855, [iv.], **10**, 364.

[5] Grabeau, *Zeitsch. angew. Chem.*, 1888, **1**, 708; 1889, **2**, 149.

[6] Hall, *U.S. Pat.*, 400,664; 400,665; 400,666; 400,667; 400,766; Héroult, *Fr. Pat.*, 175,711 (1886); see also *J. Ind. Eng. Chem.*, 1911, **3**, 143. The following papers may also be referred to: J. W. Richards, *Electrochem. Ind.*, 1903, **1**, 158; *Zeitsch. Elektrochem.*, 1895, **1**, 367; Haber, *ibid.*, 1902, **8**, 607; 1903, **9**, 360; Haber and Geipert, *ibid.*, 1902. **8**, 1, 26; Neumann and Olsen, *ibid.*, 1910, **16**, 230; Thompson, *Electrochem. Ind.*, 1909, **7**, 19; Richardson, *Trans. Amer. Elertrochem. Soc.*, 1911, **19**, 159; Fedotéev and Iljinsky, *Zeitsch. anorg. Chem.*, 1913, **80**, 113; Bock, *Zeitsch. angew. Chem.*, 1909, **22**, 1309; Puschin, Dischler, and Maksimenko, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1347; also such text-books as Allmand, *Applied Electrochemistry* (Arnold, 1912); Stansfield, *The Electric Furnace* (M'Graw-Hill Book Co., 1914); Dony-Hénault, Gall, and Guye, *Principes et applications de l'electrochimie* (Paris and Liège, 1914); J. W. Richards, *Aluminium* (Sampson Low, Marston & Co., 3rd ed., 1896); Minet, *L'aluminium* (Paris); Thorpe, *Dictionary of Applied Chemistry* (Longmans & Co., 1911), vol. i.

[7] Bucherer, *D.R.P.*, 63,995 (1892); Gin, *D.R.P.*, 148,627 (1902).

The equilibrium diagrams for the systems (i.) *alumina—cryolite*, (ii.) *alumina—fluorspar*, (iii.) *cryolite—fluorspar*, (iv.) *cryolite—alumina—fluorspar*, and (v.) *aluminium fluoride—sodium fluoride* have been partly or wholly determined. The first three systems have been studied by Pascal and Jouniaux,[1] whose results are shown graphically in figs. 4 and 5. In each system, two series of mixed crystals are formed, and the "liquidus" curve consists of two branches meeting at a eutectic point. The ternary system as worked out by the same experimenters is shown graphically in figs. 6 and 7, which represent the "liquidus" and "solidus" respectively. The isothermals are given for a series of temperatures separated by intervals of 50°. The ternary eutectic point is 868° and corresponds to a mixture of the following composition: cryolite, 59·3 per cent.; fluorspar, 23·0 per cent.; alumina, 17·7 per cent. In actual practice, according to Pascal and Jouniaux, alumina is added so as to constitute 10 to 25 per cent. of the alumina-cryolite mixture, and fluorspar is added up to 36 per cent. of the weight of the cryolite present. The working compositions are therefore included in the trapezium bounded by the lines F*b*, F*c*, *bc*, and A*a*. This trapezium includes the eutectic mixture, and no mixture in it has a melting-point higher than 980°. The temperature limits adopted in practice are given by Pascal and Jouniaux as 875° to 950°.

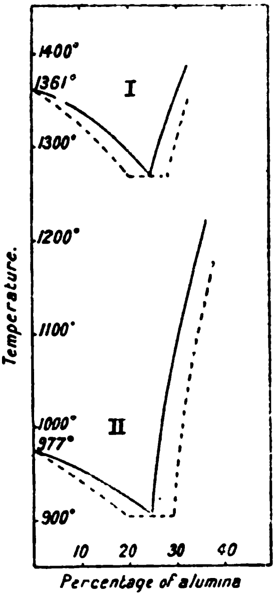

FIG. 4.—Equilibrium diagrams for the systems I. alumina—cryolite, II. alumina—fluorspar.

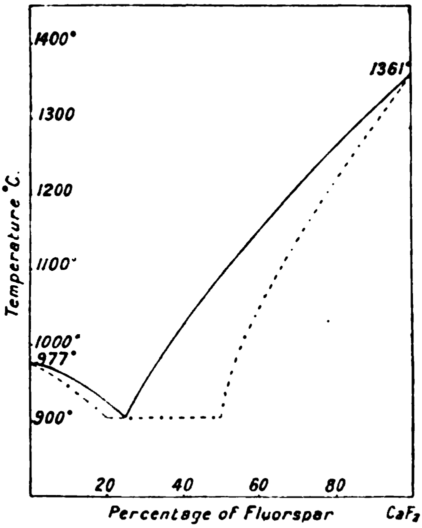

FIG. 5.—Equilibrium diagram for the system cryolite—fluorspar.

The system *aluminium fluoride—sodium fluoride* has been studied by

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[1] Pascal and Jouniaux, *Bull. Soc. chim.*, 1913, [iv.], **13**, 439; *Rev. Métallurgie*, 1914, **11**, 1069; *cf.* Pyne, *Trans. Amer. Electrochem. Soc.*, 1906, **10**, 63; Moldenhauer, *Metallurgie*, 1909, **6**, 14; Lorenz, Jabs, and Eitel, *Zeitsch. anorg. Chem.*, 1913, **83**, 39.

Fedotéev and Iljinsky,[1] whose results are shown graphically in fig. 8. The branches AB, BCD, and DE correspond to the solid phases NaF, $3NaF.AlF_3$, and $5NaF.3AlF_3$ respectively, and the latter compound breaks up at 725° into $3NaF.AlF_3$ and AlF_3. It will be seen that the addition of aluminium fluoride to cryolite produces a readily fusible mixture. Fedotéev and Iljinsky recommend that the solvent for alumina should be prepared by adding sufficient aluminium fluoride to cryolite to give the mixture the composition G (fig. 8); that the temperature should be maintained at 900°, and that the quantity of alumina added should not exceed 7·5 per cent. of the weight of the solvent. If pure cryolite be used as solvent, Fedotéev and Iljinsky recommend that not more than 10 per cent. of alumina be added.

It is essential that the molten metal shall be liberated at the cathode in a medium of lower specific gravity than the metal itself. At the ordinary temperature, aluminium is less dense than cryolite; fortunately, however, the reverse is true at high temperatures, as will be seen from the results tabulated below and represented diagrammatically in fig. 9 :—[2]

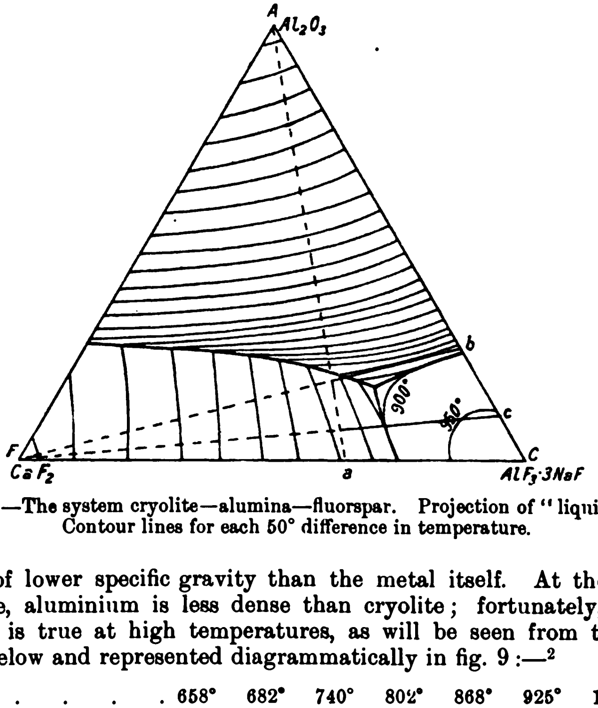

Fig. 6.—The system cryolite—alumina—fluorspar. Projection of "liquidus." Contour lines for each 50° difference in temperature.

Temperature	658°	682°	740°	802°	868°	925°	1000°	
Density of Al (liquid) . .	2·46	2·45	2·43	2·41	2·39	2·37	2·35	
Temperature	972°	975°	978°	979°	995°	1003°	1018°	1032°
Density of cryolite (liquid) .	2·185	2·197	2·203	2·197	2·220	2·209	2·196	2·189
Temperature	1039°	1048°	1061°	1069°	1075°	1070°	1083°	
Density of cryolite (liquid) .	2·177	2·167	2·154	2·139	2·129	2·113	2·102	

It will be seen that molten cryolite, like water, has a point of maximum density, the density then being 2·22 and the temperature 995°. The density of cryolite is diminished by the addition of silica and increased by the addition of calcium fluoride (see fig. 9); the influence of alumina on the

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[1] Fedotéev and Iljinsky, *loc. cit.*; see also Lorenz, Jabs, and Eitel, *Zeitsch. anorg. Chem.*, 1913, **83**, 39, 328.

[2] Pascal and Jouniaux, *Bull. Soc. chim.*, 1914, [iv.], **15**, 312.

density is rather complex, but unless a large quantity (over 20 per cent.) is added, the density is diminished (see fig. 9). The densities of the commercially important ternary mixtures of cryolite, alumina, and fluorspar at 950° are shown graphically in fig. 10; it will be seen that they are less than 2·40, and in actual practice the presence of a little silica in the cryolite makes them all a little lower than the values given in the diagram.

The Hall and Héroult processes only differ slightly in the nature of the plant employed, and perhaps to some extent in the composition of the electrolyte adopted. Each Hall cell consists of a rectangular cast-iron box, 6′ × 3′ × 3′, thickly lined with carbon. This lining forms the cathode. The actual depth of electrolyte in the bath is 6 inches. As anode, a large number of carbon rods are used, which dip into the electrolyte and end about 1 inch above the level of the aluminium at the bottom. It is therefore clear why the density of the bath must be such as to allow the aluminium, as it is produced, to sink rapidly to the bottom; otherwise, besides oxidation of the metal taking place, short circuiting will occur. About 15 to 20 parts of alumina[1] are added for each 100 parts of solvent. The electrolyte is roughly covered with a layer of carbon, on the top of which alumina is placed. As electrolysis proceeds, this alumina is stirred into the bath and at intervals the separated aluminium is tapped off from the bottom.

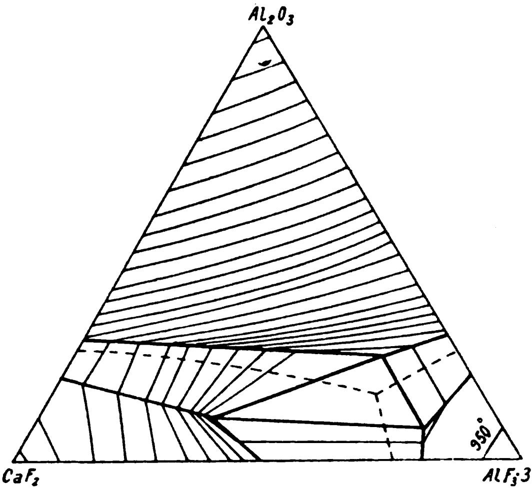

Fig. 7.—The system cryolite—alumina—fluorspar. Projection of "solidus." Contour lines for each 50° difference of temperature.

The current consumed by each cell is 10,000 ampères at 5·5 volts, the current density being 100 amp./dcm.[2] at the cathode, and about 500 amp./dcm.[2] at the anode. The current efficiency does not exceed 70 per cent., largely owing to the formation of a "metal mist" of aluminium particles which diffuse to the surface and become oxidised. The least potential difference capable of producing continuous electrolysis is 2·1 to 2·2 volts, which value does not differ greatly from the approximate figure calculated from the

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[1] Prepared as described later (p. 79).

[2] Clacher, *Met. Chem. Eng.*, 1911, 9, 137.

heat of formation of alumina. The potential differences required for the electrolysis of aluminium chloride, aluminium fluoride, sodium fluoride, and calcium fluoride are approximately 2·3, 4·0, 4·7, and 4·7 volts respectively.

The cost of the carbon anodes, which are eaten away by the liberated oxygen with the formation mainly of carbon monoxide, is a very serious item. The anode rods must be evenly hard, very slightly porous, and leave very little ash when burnt. They are usually made from petroleum coke.[1] Water-power is always employed in the production of the necessary electric current. The world's supply of aluminium is produced mainly by the Aluminium Company of America, at Niagara, Massena, and Shawingian Falls, the Société Electrométallurgique Française, at Froges, La Plaz, and St Michael, and the British Aluminium Company, at Kinlochleven in Scotland. The world's output of aluminium was about 8000 tons per annum from 1900–1905; since then it has steadily increased, and was about 30,000 tons in 1909.[2]

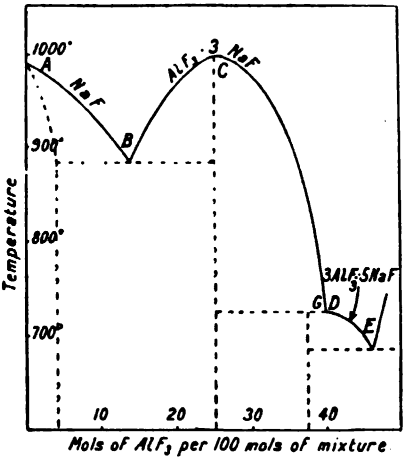

FIG. 8.—Equilibrium diagram for the system sodium fluoride—aluminium fluoride.

Aluminium produced by electrolysis contains 99 per cent. or more of aluminium, the chief impurities being iron and silicon. A little carbon is also present, and in a sample examined spectroscopically by Hartley and Ramage,[3] traces of sodium, potassium, calcium, copper, silver, manganese, lead, gallium, and indium were detected. It is extremely difficult to purify the aluminium after it has once been produced, and hence it is necessary to employ pure materials in its preparation. It is for this reason that the carbon anodes must be practically free from ash. The alumina is usually prepared from bauxite by a method described later (p. 79). The cryolite is not specially purified, but any foreign metals present are removed after it has been submitted to the action of the current for a short time.

Pure aluminium is best prepared by reducing pure, redistilled aluminium tribromide with a slight deficiency of sodium. The tribromide is mixed with sodium and potassium chlorides and heated with metallic sodium in a crucible lined with a mixture of alumina and sodium aluminate.[4]

Properties.—Aluminium is a tin-white metal which may be highly polished. The commercial metal is extremely sonorous,[5] malleable, and ductile. It is best worked at 100° to 150°; at 600° it is easily broken, and at a slightly higher temperature it may be powdered in a mortar.[6]

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[1] Clacher, *Met. Chem. Eng.*, 1911, **9**, 137.

[2] Thorpe, *A Dictionary of Applied Chemistry* (Longmans & Co., 2nd ed., 1911–1913), vol. i. p. 106.

[3] Hartley and Ramage, *Trans. Chem. Soc.*, 1897, **71**, 547.

[4] Mallet, *Phil. Trans.*, 1880, **171**, 1022; *Chem. News*, 1882, **46**, 178.

[5] The pure metal is not sonorous (Mallet, cited by Baskerville, *J. Ind. Eng. Chem.*, 1914, **6**, 183).

[6] Granger, *Bull. Soc. chim.*, 1902, [iii.], **27**, 789.

Aluminium has a crystalline structure when slowly cooled. Apparently the crystals are regular octahedra.[1] After being worked, the metal is devoid of structure. Cast aluminium is about as hard as silver, and becomes harder when hammered.[2]

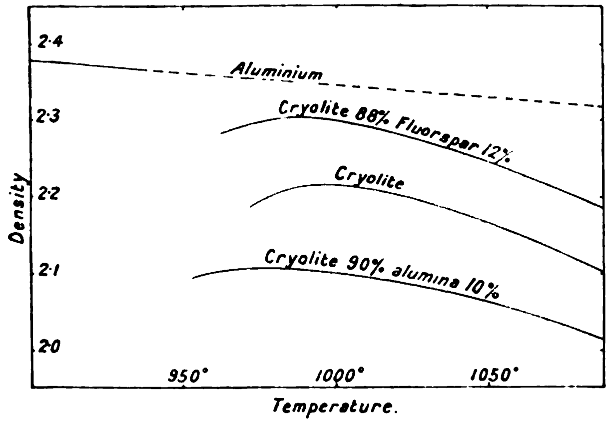

FIG. 9.—Densities of aluminium, etc., at high temperatures.

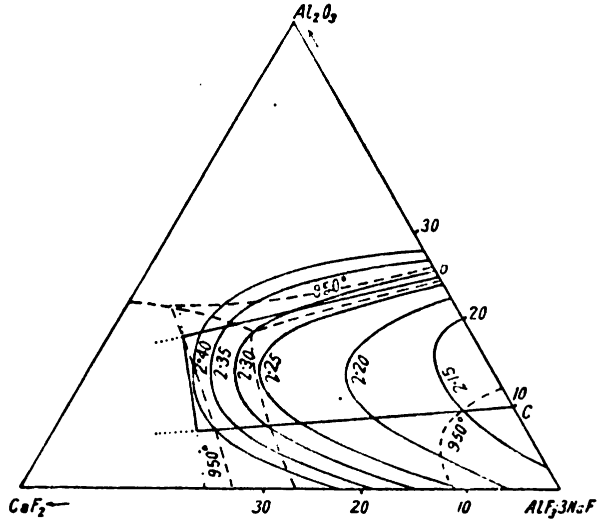

FIG. 10.—Densities of mixtures of cryolite, fluorspar, and alumina at 950°.

The density of aluminium varies with the treatment to which it has been subjected. The density of the cast metal (containing 0·36 per cent.

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[1] Deville, *Ann. Chim. Phys.*, 1855, [iii.], 43, 11.

[2] For the manufacture of aluminium foil and powder, see Guillet, *Rev. Métallurgie*, 1912, 9, 147.

impurities) is 2·703 at 18° C.; that of the worked metal may be less than 2·703, but it increases on annealing and may reach the value 2·7085 at 18°.[1] Mallet[2] gives the density of pure aluminium as 2·583 at 4° C. The mean coefficient of expansion between 0° and 100° is $2·432 \times 10^{-5}$ for hard-drawn metal and $2·454 \times 10^{-5}$ for the annealed metal.[3]

The value of Young's modulus for aluminium is about $6·91 \times 10^{3}$ (in kilos. per sq. mm.) at 20°, the rigidity being about $2·7 \times 10^{3}$ (in kilos. per sq. mm.); both these values diminish considerably with rise of temperature.[4] The compressibility is $1·49 \times 10^{-6}$ per atmosphere.[5] The tensile strength is affected by the form, method of casting, and subsequent treatment, the ultimate strength being (in tons per sq. inch) 7 in castings, 11 in sheet aluminium, and from 13 to 29 in aluminium wire.

The thermal conductivity of aluminium is 0·3435 at 0° and 0·3619 at 100° (absolute units), according to the measurements of Lorenz,[6] while Jaeger and Disselhorst[7] give 0·4804 and 0·4923 as the corresponding figures for aluminium containing 0·4 per cent. of copper and 0·5 per cent. of iron. Aluminium is therefore a slightly better heat conductor than zinc. The electrical conductivity is $35·6 \times 10^{4}$ reciprocal ohms per cm. cube at 0°, according to Sturm; while the conductivity at 0° and temperature-coefficient of the resistance (between 0° and 100°) are given by Broniewski as $40·1 \times 10^{4}$ and $4·25 \times 10^{-3}$ respectively for annealed aluminium, and $38·5 \times 10^{4}$ and $4·10 \times 10^{-3}$ for the chilled metal.[8]

Aluminium melts at 658 ± 1°,[9] boils at 1800°,[10] and expands at 4·8 per cent. on fusion.[11] Owing to the formation of a protective film of oxide, it is possible to heat a piece of aluminium wire above the melting-point without destroying its shape.[12] Being a metal of low atomic weight, aluminium has a high specific heat, which, moreover, has a large temperature-coefficient. According to E. H. Griffiths and E. Griffiths, the specific heat is 0·2096 at 0° and 0·2252 at 100°.[13] Intermediate values are given by the expression $s = 0·20957(1 + 9·161 \times 10^{-4}t - 1·7 \times 10^{-6}t^{2})$, and hence the mean specific heat is 0·2180 between 0° and 100°, and 0·2196 between 20° and 100°. For the latter value, Schmitz found 0·2191.[14] Bontscheff has experimented over a

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[1] Brislee, *Trans. Faraday Soc.*, 1912, **7**, 221; 1913, **9**, 162; Lowry and Parker, *Trans. Chem. Soc.*, 1915, **107**, 1005.

[2] Mallet, *Chem. News*, 1882, **46**, 178.

[3] Brislee, *loc. cit.*, and *Chem. News*, 1912, **105**, 3; *cf.* Fizeau, *Compt. rend.*, 1869, **68**, 1125; Le Chatelier, *ibid.*, 1889, **108**, 1096.

[4] Brislee, *Trans. Faraday Soc.*, 1913, **9**, 155; Voigt, *Wied. Annalen*, 1893, **48**, 674; G. S. Meyer, *ibid.*, 1896, **59**, 668; Schaefer, *Ann. Physik*, 1901, **5**, 220; 1902, **9**, 665, 1124; Pionchon, *Compt. rend.*, 1892, **115**, 162; Slotte, *Acta Soc. Sci. Fennicæ, Helsingfors*, 1899, **26**; 1900, **29**.

[5] Richards (and others), *J. Amer. Chem. Soc.*, 1909, **31**, 154; 1915, **37**, 164.

[6] L. Lorenz, *Wied. Annalen*, 1881, **13**, 422, 582.

[7] Jaeger and Disselhorst, *Wiss. Abh. phys.-tech. Reichsanstalt*, 1900, **3**, 269.

[8] Sturm, *Inaugural Dissertation* (Rostock, 1904); Broniewski, *Ann. Chim. Phys.*, 1912, [viii.], **25**, 5; *cf.* J. W. Richards, *Chem. News*, 1897, **75**, 217.

[9] Day, Sosman, and Allen, *Amer. J. Sci.*, 1910, [iv.], **29**, 93; Burgess, *J. Washington Acad. Sci.*, 1911, **1**, 16; *Chem. News*, 1911, **104**, 165.

[10] Greenwood, *Proc. Roy. Soc.*, 1909, **A**, **82**, 396; 1910, **A**, **83**, 483.

[11] Toepler, *Wied. Annalen*, 1894, **53**, 343.

[12] Matignon, *Bull. Soc. chim.*, 1909, [iv.], **5**, 91; *Moniteur Sci.*, 1900, [iv.], **14**, 357; von Bolton, *Zeitsch. Elektrochem.*, 1908, **14**, 766.

[13] E. H. Griffiths and E. Griffiths, *Phil. Trans.*, 1913, **A**, **213**, 119.

[14] Schmitz, *Proc. Roy. Soc.*, 1903, **72**, 177.

wide temperature interval and gives the following values for the specific heat :—[1]

Temp. °C. .	$-100°$	0°	100°	300°	500°	650°
Specific heat .	0·1893	0·2089	0·2226	0·2434	0·2739	0·3200

The results may be expressed by the formula :—

$$s = 0{\cdot}20890 + 1{\cdot}6187t \times 10^{-4} - 2{\cdot}9425t^2 \times 10^{-7} + 4{\cdot}6183t^3 \times 10^{-10}.$$

At $-193{\cdot}9°$ the specific heat of aluminium is only 0·086, and at $-253{\cdot}9$ it has fallen to 0·0024; at these extremely low temperatures the specific heat is proportional to the cube of the absolute temperature.[2] The atomic heat of aluminium at ordinary temperatures is rather lower than might be anticipated, since, adopting the mean specific heat between 20° and 100°, the atomic heat is only 5·95.[3] Griffiths and E. Griffiths give the following as the most probable values of the atomic heat of aluminium at various temperatures :—[4]

Temp. (abs.) .	32·4°	80°	120°	200°	250°	300°	340°	380°
Atomic heat .	0·25	2·27	3·74	5·14	5·54	5·81	5·98	6·13

The latent heat of fusion of aluminium is 70 to 80 cals. per gram.[5]

Aluminium is paramagnetic, the magnetic susceptibility at ordinary temperature being $+1{\cdot}8 \times 10^{-6}$ c.g.s. electromagnetic units per unit volume.[6] The atomic refraction of aluminium in its compounds is 9·5 (for the H_α line; Gladstone and Dale's formula).[7]

The electrode potential of aluminium is not known with any accuracy, the value $\epsilon_H = -1{\cdot}03$ to 1·28 volts being uncertain and probably numerically too great. In the potential series aluminium probably occupies the following position :—

Alkali and alk. earth metals, Mg, Mn, Al, Zn, Cr, Cd, Fe, etc.[8]

When aluminium is used as anode in passing a current through an aqueous solution, and the voltage does not exceed some 25 volts, the current that passes quickly falls to almost zero. This seems to be due to the formation of a layer of aluminium hydroxide on the anode. The critical voltage, above which an appreciable current can be made to flow, varies with the

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[1] Bontscheff, *Inaugural Dissertation* (Zurich, 1899); also in Laemmel, *Ann. Physik*, 1905, [iv.], **16**, 551.

[2] Nernst and Schwers, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, p. 355.

[3] For other work on the specific heat of aluminium, see Pionchon, *Compt. rend.*, 1892, **175**, 162; Tilden, *Phil. Trans.*, 1900, **A**, **194**, 233; 1903, **A**, **201**, 37; *Trans. Chem. Soc.*, 1905, **18**, 551; Trowbridge, *Science*, 1898, **8**, 6; Behn, *Wied. Annalen*, 1898, **66**, 237; Schübel, *Zeitsch. anorg. Chem.*, 1914, **87**, 81; and Vol. I., Chap. II.

[4] E. H. Griffiths and E. Griffiths, *Phil. Trans.*, 1914, **A**, **214**, 319.

[5] Pionchon, *loc. cit.*; Laschtschenko, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 311; *cf.* J. W. Richards, *Aluminium* (Baird & Co., 3rd ed., 1896), p. 80.

[6] Wills, *Phil. Mag.*, 1898, [v.], **45**, 432; Koenigsberger, *Wied. Annalen*, 1898, **66**, 698; Honda, *Ann. Physik*, 1910; [iv.], **32**, 1027; Owen, *ibid.*, 1912, **37**, 657: *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 637.

[7] Gladstone, *Proc. Roy. Soc.*, 1897, **60**, 140.

[8] Neumann, *Zeitsch. physikal. Chem.*, 1894, **14**, 217; Wilsmore, *ibid.*, 1900, **35**, 318; Burgess and Hambüchen, *Electrochem. Ind.*, 1903, **1**, 165; van Deventer and Lummel, *Chem. Weekblad.*, 1907, **4**, 771; 1908, **5**, 359; van Laar, *ibid.*, 1908, **5**, 124.

temperature and the nature of the electrolyte. This property of aluminium is utilised at times for obtaining a direct from an alternating current.[1]

The *arc* and *spark* spectra of aluminium[2] are fairly simple. The most *intense* lines in these spectra, *i.e.* the "hauptlinien," are (Exner and Haschek) the following:—

arc: 2568·08, 2575·20, 2652·56, 2660·50, **3082·30**, **3092·89**, **3944·20**, **3961·71**
spark: 2816·41, 3082·30, 3092·89, **3944·22**, **3961·74**, 4529·70, 5696·71.

The most *persistent* lines in the spark spectrum of aluminium, *i.e.* the "ultimate" lines, which should be looked for when seeking the traces of aluminium, are (Exner and Haschek's wave-lengths) 3961·74,* 3944·22,* 3092·82, 3082·30, 2816·41, those asterisked being the most sensitive.[3]

The arc spectrum of aluminium contains a number of very characteristic bands due to aluminium oxide, which disappear when the arc is surrounded by an atmosphere of hydrogen.

Aluminium always contains a little occluded gas, which may be extracted by fusing the metal *in vacuo*.[4]

Aluminium readily combines with the halogens. A compact piece of the metal is only superficially oxidised when heated in air or oxygen, but in thin foil it burns brilliantly when heated in oxygen. Aluminium powder begins to oxidise rapidly at 400°, and readily burns if strongly heated at one point, aluminium oxide and a little nitride being produced.[5] Aluminium rapidly oxidises if the surface is amalgamated with mercury, an arborescent growth of alumina quickly forming all over the metal.[6] At high temperatures finely divided aluminium readily unites with sulphur, selenium, phosphorus, and arsenic; it also combines with antimony, but with more difficulty.[7] Aluminium combines directly with nitrogen, producing a nitride; it also combines with carbon, silicon, and boron.

Owing to the extremely large heat of formation of aluminium oxide, aluminium is able to reduce many oxides, with the evolution of much heat, Thus, aluminium powder burns readily when heated in the oxides of sulphur,

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[1] W. W. Taylor and Inglis, *Phil. Mag.*, 1903, [vi.], **5**, 301; F. Fischer, *Zeitsch. physikal. Chem.*, 1901, **48**. 177; *Zeitsch. Elektrochem.*, 1904, **10**, 869; *Zeitsch. anorg. Chem.*, 1905, **43**, 341; Charters, *J. Physical Chem.*, 1905, **9**, 110; Baristo and Merser, *Trans. Faraday Soc.*, 1911, **7**, 1; Baristo, *ibid.*, 1912, **8**, 232; Schultze, *Zeitsch. Elektrochem.*, 1914, **20**, 307, 592.

[2] Kayser, *Handbuch der Spektroskopie* (Leipzig, 1900–1912), vol. v. p. 94; Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Wien, 1911); Grünter, *Zeitsch. Wiss. Photochem.*, 1913, **13**, 1 (arc and spark); Eder, *ibid.*, 1913, **13**, 20; 1914, **14**, 137 (spark, ultraviolet); Huppers. *ibid.*, 1913, **13**, 46 (arc, below 3200); de Gramont, *Compt. rend.*, 1913, **157**, 1364 (band spectrum); Stark and others, *Ann. Physik*, 1913, [iv.], **42**, 241; **45**, 29 (canal ray spectrum); Pollok, *Sci. Proc. Roy. Dubl. Soc.*, 1912, **13**, 202 (vacuum tube spectrum); L. and E. Bloch, *Compt. rend.*, 1914, **158**, 1416 (extreme ultra-violet, spark).

[3] Pollok and Leonard, *Sci. Proc. Roy. Dubl. Soc.*, 1907, **11**, 229; de Gramont, *Compt. rend.*, 1907, **144**, 1101; 1910, **151**, 308; 1914, **159**, 5; *cf.* Hartley and Moss, *Proc. Roy. Soc.*, 1912, **A**, **87**, 38.

[4] See Guichard and Jourdain, *Compt. rend.*, 1912, **155**, 160.

[5] Kohn-Abrest, *Bull. Soc. chim.*, 1904, **31**, 232; Matignon, *Compt. rend.*, 1900, **130**, 1390.

[6] Jehn and Hinze, *Ber.*, 1874, **7**, 1498; Lebon, *Compt. rend.*, 1900, **131**, 706; Jourdain, *ibid.*, 1910, **150**, 391.

[7] Fonzes-Diacon, *ibid.*, 1900, **130**, 1314.

nitrogen, and carbon.[1] The reduction of a solid oxide is best accomplished by mixing the powdered oxide with an equivalent of granulated aluminium and starting the reaction by putting a little barium peroxide and magnesium powder mixture on the top and lighting it with a match or a piece of burning magnesium ribbon. In this way the oxides of iron, manganese, chromium, etc., can be easily reduced to metal, so much heat being generated that both the metal and the alumina produced are melted in the reaction.[2] These reductions are generally known as "thermit" reactions (*vide infra*, p. 58). In a few cases the reduction of an oxide by aluminium is an endothermic change and can only be brought about by supplying the necessary heat, *e.g.* the reduction of calcium and magnesium oxides.[3] Thermit reactions may be readily applied to the preparation of phosphides, arsenides, silicides, and borides by simultaneously reducing two oxides.[4]

At ordinary temperatures aluminium is unattacked by air-free water, but ordinary water slowly acts upon it. The rate of corrosion is greatly increased by the presence of impurities, particularly by traces of sodium, copper, or iron, and is also augmented by rise of temperature.[5] Aluminium powder slowly decomposes water at 100°, and the powder, when ignited in air and plunged into steam, continues to burn, with the evolution of hydrogen.[6] Aluminium amalgam decomposes water readily, aluminium hydroxide and hydrogen being produced.[7] To effect this reaction it is only necessary to amalgamate superficially the surface of aluminium foil by immersing it in aqueous mercuric chloride, and then wash the foil with cold water. The aluminium-mercury couple thus formed, owing to the ease with which it decomposes water, constitutes a valuable reducing agent.[8]

Aluminium is rapidly corroded by dilute hydrogen peroxide, aluminium hydroxide being formed.[9]

Aluminium dissolves readily in hydrochloric acid, dilute or concentrated, hydrogen and aluminium chloride being produced. The action of dilute sulphuric acid is very slow; the concentrated acid attacks the metal with the evolution of sulphur dioxide. Phosphoric acid, dilute or concentrated, readily attacks aluminium, hydrogen being evolved. In comparison with its action on other metals, the action of nitric acid on aluminium is extremely slow. With 5 to 20 per cent. acid at 25° to 30° the main reaction is as follows:—

$$Al + 4HNO_3 = Al(NO_3)_3 + 2H_2O + NO.$$

With a large excess of acid, nitrogen appears among the gaseous products. A little ammonium nitrate is produced. Nitric acid of density 1·15 dissolves aluminium faster than the 1·45 acid, and the rate of solution of

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[1] Mallet, *Trans. Chem. Soc.*, 1876, pt. 2, 349 ; Franck, *Bull. Soc. chim.*, 1894, [iii.], **11**, 439 ; Guntz and Masson, *ibid.*, 1897, [iii.], **17**, 209 ; Matignon, *loc. cit.*

[2] Goldschmidt, *J. Soc. Chem. Ind.*, 1898, **17**, 543 ; *Electrochem. Ind.*, 1908, **6**, 360.

[3] Weston and Ellis, *Trans. Faraday Soc.*, 1908, **4**, 130 ; 1909, **4**, 166 ; Matignon, *Compt. rend.*, 1913, **156**, 1157.

[4] Colani, *Compt. rend.*, 1905, **141**, 33 ; Matignon and Trannoy, *ibid.*, 1905, **141**, 190.

[5] Donatti, *Zeitsch. angew. Chem.*, 1895, **8**, 141 ; Bailey, *J. Soc. Chem. Ind.*, 1913, **32**, 293 ; Scala, *Atti R. Accad. Lincei*, 1913, **22**, i. 43, 95.

[6] Matignon, *Compt. rend.*, 1900, **130**, 1390.

[7] Baille and Féry, *Ann. Chim. Phys.*, 1889, [vi.], **17**, 246.

[8] Cohen and Ormandy, *Trans. Chem. Soc.*, 1890, **57**, 811 ; Wislicenus, *J. prakt. Chem.*, 1896, [ii.], **54**, 18 ; Lebon, *Compt. rend.*, 1900, **131**, 706.

[9] Droste, *Chem. Zeit.*, 1913, **37**, 1317.

the metal increases with the fineness of division, thick foil dissolving very slowly, but coarse turnings much more rapidly.[1] Organic acids attack aluminium only very slowly, but if the protecting layer of hydrogen that forms on the metal is removed (*e.g.* by operating in a vacuum) the rate of solution is greatly accelerated.[2]

Alkali hydroxides in aqueous solution rapidly dissolve aluminium, alkali aluminates and hydrogen being produced. With ammonium hydroxide, the products are aluminium hydroxide and hydrogen. Aluminium also dissolves in aqueous alkali carbonates, carbon dioxide and hydrogen being evolved. Aqueous solutions of salts, *e.g.* sodium chloride, slowly attack aluminium, but only in the presence of oxygen; the addition of a small quantity of a weak organic acid hastens the corrosion.

Colloidal aluminium.—When two aluminium rods are immersed in water, their ends being separated by only 0·1 mm., and a condensed spark discharge passed between them by means of a powerful induction coil, a colloidal solution of aluminium is obtained.[3]

Applications.—Aluminium is largely employed in the iron and steel industry, as when it is added to molten steel (a few ounces per ton) it removes the dissolved gases to a large extent, and thereby prevents the development of blowholes in castings. In America, aluminium is extensively used in the place of copper for electrical transmission. It is also employed in the production of carbon-free chromium, manganese, molybdenum, ferro-titanium, ferro-vanadium, ferro-boron, manganese-copper, manganese-titanium, chromium-manganese, etc. The metallic oxide or mixture of oxides is reduced by means of a slight deficit of granulated aluminium, the reactions being carried out in large magnesia-lined crucibles as described previously (p. 57). A mixture of powdered aluminium and granulated rolling-mill scale (Fe_3O_4), known by the registered name of *thermit*, is extensively used in welding operations. When fired in the usual way (p. 57) the iron oxide is rapidly reduced to metallic iron, and so much heat is developed that both the iron and alumina are produced in the liquid state. Tram- and railway-line sections may be joined, and broken engine-frames, driving-rods, crank shafts, etc., may be repaired by igniting a charge of thermit and allowing the molten iron to flow around the place at which a join is to be effected.[4]

The light aluminium alloys (p. 61) containing a high percentage of aluminium are largely used for constructional purposes, *e.g.* for parts of motor-cycles, motor-cars, and aeroplanes. The salts of aluminium are non-poisonous, and hence aluminium is used to a considerable extent in the manufacture of kitchen utensils, particularly for army use, and is coming into use in the construction of chemical plant.[5] Aluminium cannot be satisfactorily soldered, despite the large number of solders that have been patented for the purpose. It must be riveted or welded.

Aluminium powder enters into the composition of certain explosives.[6]

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[1] Stillman, *J. Amer. Chem. Soc.*, 1897, **19**, 715 (a complete bibliography is given here); Watson Smith, *J. Soc. Chem. Ind.*, 1904, **23**, 475; van Deventer, *Chem. Weekblad.*, 1907, **4**, 69; Hale and Foster, *J. Soc. Chem. Ind.*, 1915, **34**, 464.

[2] Ditte, *Compt. rend.*, 1898, **127**, 919; 1899, **128**, 195, 793.

[3] Zavriev, *Zeitsch. physikal. Chem.*, 1914, **87**, 507.

[4] Goldschmidt, *Stahl und Eisen*, 1898, **18**, 408; *Zeitsch. Elektrochem.*, 1898, **4**, 494; 1899, **6**, 53; *J. Soc. Chem. Ind.*, 1898, **17**, 543, 584, 649; *Electrochem. Ind.*, 1908, **6**, 360; Thorpe, *A Dictionary of Applied Chemistry* (Longmans & Co., 2nd ed., 1912–13), vol. v.

[5] Seligman, *Science Progress*, 1912, **6**, 615; Moissan, *Compt. rend.*, 1899, **128**, 895.

[6] See Bichel, *Zeitsch. angew. Chem.*, 1905, **18**, 1889.

Thus, *ammonal* contains 93–97 per cent. NH_4NO_3, 4–6 per cent. Al, and 0–1 per cent. moisture, and is a good mining explosive and high explosive for shells.[1] *Ammonal B* contains 94–96 per cent. NH_4NO_3, 2·5–3·5 per cent. Al, 2–3 per cent. wood charcoal, and 0–1 per cent moisture. Another aluminium explosive[2] contains 85·5 per cent. NH_4NO_3, 8 per cent. Al, 2·5 per cent. carbon (hydrocarbon or nitrohydrocarbon), and 4 per cent. $K_2Cr_2O_7$.[3]

Atomic and Molecular Weights.—From the analyses and molecular weights of aluminium chloride, bromide, and iodide, various double compounds that the preceding salts form with organic substances, aluminium methyl, aluminium ethyl, and aluminium acetylacetonate, it follows that the atomic weight of aluminium is approximately 27, or three times its combining weight. This conclusion is in harmony with Dulong and Petit's Law, the isomorphism of (i.) alumina, ferric and chromic oxides, (ii.) the aluminium, gallium, indium, chromium, iron, vanadium, cobalt, and rhodium alums, (iii.) the aluminium, iron, chromium, and cobalt double oxalates, etc.

The atomic weight was determined by Mallet[4] in 1880 by four distinct methods, the results of which are appended:—[5]

$$\begin{array}{rl} (NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O : Al_2O_3 :: 100 : 11{\cdot}2793 & \therefore Al = 27{\cdot}152 \\ 3Ag : AlBr_3 :: 100 : 82{\cdot}455 & \therefore Al = 27{\cdot}109 \\ 3H_2 : 2Al :: 100 : 896{\cdot}33 & \therefore Al = 27{\cdot}095 \\ 2Al : 3H_2O :: 100 : 99{\cdot}818 & \therefore Al = 27{\cdot}072 \end{array}$$

The first ratio was determined by calcining ammonium alum and measuring the loss in weight; the second, by titrating aluminium bromide against silver according to the procedure of Stas. The third was determined by dissolving aluminium in sodium hydroxide and measuring the hydrogen evolved, and the fourth was carried out like the third, the hydrogen, however, being burnt to water. Other determinations[6] are of less importance. The atomic weight of aluminium is at present taken as **Al = 27·1**.

From the freezing-point determinations made by Heycock and Neville, it appears that aluminium in dilute solution in tin has the molecular formula Al_2; but it is not certain that pure tin separates on freezing.[7] Aluminium likewise appears to be present largely as diatomic molecules in solution in mercury.[8]

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[1] Von Dahmen, *Eng. Pat.*, 16,277 (1900).

[2] See *Eng. Pat.*, 16,514 (1904).

[3] On aluminium condensers for laboratory use, see Mastbaum, *Chem. Zeit.*, 1910, **34**, 1319; for aluminium stopcocks on hydrogen sulphide apparatus, see Campbell, *J. Amer. Chem. Soc.*, 1911, **33**, 947; and on the use of aluminium dishes in quantitative analysis, see Formánek and Peč, *Chem. Zeit.*, 1909, **33**, 1282.

[4] Mallet, *Phil. Trans.*, 1880, **171**, 1003.

[5] Clarke, *A Recalculation of the Atomic Weights*, 3rd ed. ("Smithsonian Miscellaneous Collections," vol. 54, No. 3, 1910). The antecedent data have been changed to the following:—

O = 16·000, H = 1·00762, Ag = 107·880, Br = 79·916, S = 32·065, N = 14·008.

[6] Berzelius, *Pogg. Annalen*, 1826, **8**, 177; Mather, *Amer. J. Sci.*, 1835, **27**, 241; Tissier, *Compt. rend.*, 1858, **46**, 1105; Isnard, *ibid.*, 1868, **66**, 508; Dumas, *Ann. Chim. Phys.*, 1858, [iii.], **55**, 151; Terreil, *Bull. Soc. chim.*, 1879, **31**, 153; Baubigny, *Compt. rend.*, 1883, **97**, 1369; Thomsen, *Zeitsch. anorg. Chem.*, 1895, **11**, 14; 1897, **15**, 447; Kohn-Abrest, *Bull. Soc. chim.*, 1905, [iii.], **33**, 121.

[7] Heycock and Neville, *Trans. Chem. Soc.*, 1890, **51**, 376.

[8] Ramsay, *ibid.*, 1889, **55**, 521.

ALLOYS AND COMPOUNDS OF ALUMINIUM.

Aluminium forms one series of salts, in which it is tervalent. The salts are derived from the basic oxide Al_2O_3. Those derived from colourless acids are themselves colourless. The soluble salts from hydrates containing considerable water of crystallisation, and the anhydrous salts, dissolve in water with the evolution of a large amount of heat. The salts are not poisonous.

On the ionic hypothesis the salts of aluminium are dissociated in aqueous solution, giving rise to a colourless cation $Al^{\cdots}$:—

$$AlX_3 \rightleftharpoons Al^{\cdots} + 3X'.$$

The ionic mobility of the cation, $\frac{1}{3}$ $Al^{\cdots}$, is 40·4 at 18° C.[1] Despite the high position occupied by aluminium in the electromotive series (p. 55), aluminium oxide is only a weak basic oxide and aluminium hydroxide but a feeble base. Accordingly, in aqueous solution, aluminium salts are appreciably hydrolysed, and those derived from moderately strong acids give a decidedly acid reaction. A solution of 1 gram-molecule of aluminium chloride or bromide in 1000 litres of water is hydrolysed to the extent of 4 per cent. at 25°; while the percentage hydrolysis (x) of the chloride in aqueous solution at 99·7 varies with the dilution (v litres per gram-molecule), as follows :—[2]

v	32	64	128	256	512
x	8·0	13·2	19·7	28·2	41·4

Aluminium hydroxide is a stronger base than ferric hydroxide, but is weaker than beryllium hydroxide. It is possible that, owing to the transformation of aluminium hydroxide into the form of a colloidal hydrosol, the degree of hydrolysis of aluminium salts gives a somewhat exaggerated idea of the weakness of the hydroxide as a base.

Owing to the appreciable hydrolysis of aluminium salts, the soluble salts derived from volatile acids cannot be prepared in the anhydrous state by the evaporation of their aqueous solutions on the steam-bath.

Aqueous solutions of aluminium salts dissolve an appreciable amount of aluminium hydroxide.

Thermochemistry of Aluminium Compounds.[3]—The heats of formation, etc., of the more important compounds of aluminium are given in the following table, in kilogram-calories :—

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[1] A. Heydweiller, *Zeitsch. physikal. Chem.*, 1915, **89**, 281.

[2] Ley, *Zeitsch. physikal. Chem.*, 1901, **30**, 245; Kablukoff and Sachanoff, *ibid.*, 1909, **69**, 419; Povarnin, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1014; 1910, **42**, 207; Wood, *Trans. Chem. Soc.*, 1908, **93**, 417; van Pelt, *Bull. Soc. chim. Belg.*, 1914, **28**, 101; Kullgren, *Zeitsch. physikal. Chem.*, 1913, **85**, 466.

[3] J. Thomsen, *Thermochemische Untersuchungen* (Leipzig, 4 vols., 1882–1886); Berthelot, *Thermochimie* (Paris, 2 vols., 1897); *Ann. Chim. Phys.*, 1901, [vii.], **22**, 479; Baud, *ibid.*, 1904, [viii.], **1**, 8; T. W. Richards and Burgess, *J. Amer. Chem. Soc.*, 1910, **32**, 431; T. W. Richards, Rowe, and Burgess, *ibid.*, 1910, **32**, 1176; Rolla, *Gazzetta*, 1915, **45**, i. 192; Mixter, *Amer. J. Sci.*, 1915, [iv.], **39**, 295.

Compound.	Heat of Formation.	Heat of Solution.
	Cals.	Cals.
AlF_3	249·0	+31·3
$AlF_3.3{\cdot}5H_2O$	...	- 1·7
$AlCl_3$	161·4	+77·6
$AlBr_3$	122·0	+85·3
AlI_3	70·3	+89·0
Al_2O_3	380·2	...
$Al(OH)_3$	297·0	...
Al_2S_3	126·4	...
$Al_2(SO_4)_3$	879·7[1]	...
$Al_2(SO_4)_3.6H_2O$	...	+56·0
$Al_2(SO_4)_3.18H_2O$	...	+ 9·2
Al_4C_3	244·8	...
$KAl(SO_4)_2.12H_2O$	...	-10·0
$(NH_4)Al(SO_4)_2.12H_2O$	...	- 9·6

The following data refer to heats of reaction :—

$[Al_2O_3]$ cryst. + $[Na_2O]$	; + 48·0 Cals.	$2[AlCl_3]+2[KCl]$	; + 26·4 Cals.
$[Al_2O_3]$ amorp. + $[Na_2O]$	; + 55·1 ,,	$2[AlCl_3]+2[NaCl]$	; + 11·9 ,,
$[Al]+3HCl.20H_2O$	; +126·0 ,,	$2[AlCl_3]+2[NH_4Cl]$	; + 26·5 ,,
$[Al]+3HCl.200H_2O$	; +127·0 ,,	$2[AlCl_3]+3[NaCl]$	; + 15·3 ,,
$\frac{1}{3}[Al(OH)_3]+HCl$ aq.	; + 9·2 ,,	$2[AlCl_3]+3[KCl]$	; + 30·5 ,,
$\frac{1}{3}[Al(OH)_3]+HF$ aq.	; + 11·7 ,,	$2[AlCl_3]+6[NaCl]$	; + 19·5 ,,
$\frac{1}{3}[Al(OH)_3]+\frac{1}{2}H_2SO_4$ aq.	; + 10·5 ,,	$2[AlCl_3]+6[KCl]$	; + 36·6 ,,
$2[AlCl_3]+2\frac{1}{3}(NH_3)$	; +167·5 ,,	$2[AlCl_3]+2[AgCl]$	; + 5·0 ,,
$2[AlCl_3]+6(NH_3)$	; +245·2 ,,	$2[AlCl_3]+1{\cdot}5[CaCl_2]$	; + 9·3 ,,
$2[AlCl_3]+10(NH_3)$	; +268·2 ,,	$2[AlCl_3]+1{\cdot}5[SrCl_2]$	; + 8·7 ,,
$2[AlCl_3]+12(NH_3)$	; +317·9 ,,	$2[AlCl_3]+[BaCl_2]$	; + 5·3 ,,
$2[AlCl_3]+18(NH_3)$	; + 9·5 ,,	$2[AlF_3]+6[NaF]$	; + 40·7 ,,
$2[AlCl_3]+(H_2S)$	; + 9·5 ,,	$2[AlF_3]+6[KF]$	; + 88·8 ,,
$2[AlCl_3]+(SO_2)$	; + 18·3 ,,	$2[AlF_3]+7H_2O$	; + 65·0 ,,
$2[AlCl_3]+2(SO_2)$	; + 28·9 ,,		

Alloys.[2]—Aluminium readily alloys with many other metals, and a large number of intermetallic compounds have been described. In general these compounds have little tendency to form continuous series of solid solutions with one another or with aluminium, and, accordingly, almost the only alloys of aluminium of engineering value are those which consist very largely of aluminium and those which contain but a few per cent. of the element.[3]

Sodium and aluminium are not mutually soluble, beyond perhaps a very slight extent, and form no chemical compound.[4]

Copper and aluminium. A number of investigations of the system copper-aluminium have been made by the thermal method, but the results are somewhat contradictory. The compounds Al_2Cu, AlCu, and $AlCu_3$ have been stated by several observers to exist. The "liquidus" curve has six or seven branches, only one of which appears to correspond to the separation of a pure compound, viz. Al_2Cu. The other branches refer to the separation of solid

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[1] This number includes the heat of solution of the anhydrous sulphate.

[2] For a bibliography, complete to 1902, see Sack, *Zeitsch. anorg. Chem.*, 1903, **35**, 249. For further information, see Law, *Alloys* (C. Griffin & Co., Ltd., 2nd ed., 1914); Gulliver, *Alloys* (C. Griffin & Co., Ltd., 2nd ed., 1913).

[3] Law, *Trans. Faraday Soc.*, 1910, **6**, 185.

[4] Mathewson, *Zeitsch. anorg. Chem.*, 1906, **48**, 191.

solutions.[1] By a study of the electrical properties of these alloys, Broniewski has confirmed the existence of the compounds already mentioned, and in addition has indicated the existence of another compound, Al_2Cu_3.[2]

Aluminium-copper alloys containing upwards of 10 per cent. of aluminium have a fine golden-yellow colour, do not tarnish, are practically non-corrodible by sea-water, and are largely used under the name of *aluminium bronzes*. The tensile strength reaches the value 39 tons per sq. inch for the alloy with 10 per cent. of aluminium; the ductility is at a maximum with 7 per cent. of aluminium. The light copper-aluminium alloys containing upwards of 4 per cent. of copper are also of great value; by rolling and drawing, the tensile strength of the 4 per cent. alloy can be raised to 20 tons per sq. inch (Carpenter and Edwards). A few per cent. of nickel are sometimes added to these alloys rich in aluminium, to obtain good rolling alloys.

Silver and aluminium alloy containing 4 per cent. of silver has been used in the construction of balance beams; the alloy with 33 per cent. has been employed for making tablespoons, etc. Two intermetallic compounds are known, $AlAg_3$ and Al_2Ag_3. They form a continuous series of solid solutions with one another; the former gives an incomplete series of solid solutions with silver, and the latter an incomplete series with aluminium.[3]

Gold and aluminium. Five intermetallic compounds are known, Au_4Al, Au_8Al_3 or Au_5Al_2, Au_2Al, $AuAl$, and $AuAl_2$. The compounds Au_2Al and $AuAl_2$ are stable at their melting-points, and the latter has a beautiful purple colour.[4]

Magnesium and aluminium. It is difficult to study this system by the thermal method. The "liquidus" appears to consist of three branches, the middle branch corresponding to the solid phase Al_2Mg_3 or Al_3Mg_4. This middle branch, however, is extremely flat. According to Broniewski, there are two intermetallic compounds, AlMg and Al_2Mg_3, which form with one another a continuous series of solid solutions. The former gives an incomplete series of solid solutions with aluminium, and the latter an incomplete series with magnesium.[5]

Aluminium alloys containing 1–2 per cent. of magnesium and a little copper, nickel, and tin are largely used for construction purposes under the name of *magnalium*;[6] the alloy *duralumin* contains 0·5 per cent. of magnesium, a few per cent. of copper, iron, and manganese, and over 90 per cent. of aluminium.

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[1] Le Chatelier, *Bull. Soc. d'Enc. p. l'Ind. nationale*, 1895, [iv.], **10**, 569; Guillet, *Compt. rend.*, 1901, **133**, 684; 1914, **158**, 704; *Rev. Métallurgie*, 1905, **2**, 567; Campbell and Mathews, *J. Amer. Chem. Soc.*, 1902, **24**, 253; Campbell, *ibid.*, 1904, **26**, 1290; Carpenter and Edwards, *Proc. Inst. Mech. Eng.*, 1907, p. 57; Curry, *J. Physical Chem.*, 1907, **11**, 425; Curry and Woods, *ibid.*, 1907, **11**, 461; Gwyer, *Zeitsch. anorg. Chem.*, 1908, **57**, 113; Portevin and Arnou, *Compt. rend.*, 1912, **154**, 511; J. H. Andrew, *Intern. Zeitsch. Metallographie*, 1914, **6**, 30.

[2] Broniewski, *Ann. Chim. Phys.*, 1912, [viii.], **25**, 5. This paper contains a useful summary of work on aluminium alloys, and also the results of investigations of the electrical properties of alloys of aluminium with numerous other metals.

[3] Broniewski, *loc. cit.*; *cf.* Petrenko, *Zeitsch. anorg. Chem.*, 1905, **46**, 49.

[4] Heycock and Neville, *Phil. Trans.*, 1900, **A**, **194**, 201; 1914, **A**, **214**, 267; *Trans. Chem. Soc.*, 1898, **73**, 714; Roberts-Austen, *Proc. Roy. Soc.*, 1892, **50**, 367; Matthey, *ibid.*, 1892, **51**, 447; Osmond and Roberts-Austen, *Phil. Trans.*, 1896, **A**, **187**, 417.

[5] Broniewski, *loc. cit.*; Grube, *Zeitsch. anorg. Chem.*, 1905, **45**, 225; Boudouard, *Compt. rend.*, 1901, **132**, 1325; **133**, 1003; Wilm, *Métallurgie*, 1911, **8**, 225; Pécheux, *Compt. rend.*, 1904, **138**, 1501; Schirmeister, *Metall und Erz*, 1914, **11**, 522.

[6] *Eng Pat*, 1898, No. 24,878; Barnett, *J. Soc. Chem. Ind.*, 1905, **24**, 832; Klaudy, *Oesterr. Chem. Zeit.*, 1899, **2**, 636.

Zinc and aluminium. It has been generally supposed that these metals form two series of solid solutions, the "liquidus" exhibiting a eutectic point, but Rosenhain and Archbutt have shown that there are three branches to the "liquidus," a compound Al_2Zn_3 separating along the middle branch, which covers the region from 5–17 per cent. of aluminium.[1]

The alloys known as *ziskon* and *zisium* are zinc-aluminium alloys, and are used for parts of scientific instruments. The alloys containing upwards of 20 per cent. of zinc are valuable casting alloys, largely used in the motor industry. In actual practice, the amount of zinc seldom exceeds 10 per cent., and 2 per cent. of copper is added.

The *zinc-copper*-aluminium alloys containing 31–27 per cent. of zinc, 68–70 per cent. of copper, and 1–3 per cent. of aluminium, form strong alloys, known commercially as *aluminium brasses.*[2]

Cadmium and aluminium, when fused and mixed, form two conjugate phases, one of aluminium containing 2 or 3 per cent. of cadmium, the other of cadmium containing less than 1 per cent. of aluminium.[3]

Mercury forms, with sufficient aluminium, a brittle solid amalgam which readily oxidises and decomposes water, forming mercury, aluminium hydroxide, and hydrogen.[4] Aluminium is superficially amalgamated when it is immersed in mercuric chloride solution, and when so treated it rapidly decomposes water. The reaction is inhibited to a considerable extent by the presence of a little copper as impurity in the metal.[5]

Calcium and aluminium alloys have been studied, and the compound $CaAl_3$ isolated.[6, 7]

ALUMINIUM AND THE FLUORINE GROUP.

Aluminium subfluoride, AlF_2, is not known with certainty.[8]

Aluminium trifluoride, AlF_3, is not found in nature in the anhydrous state, but the hydrated fluoride occurs as the mineral *fluellite*, $AlF_3.H_2O$. It crystallises in the rhombic system (bipyramidal; $a : b : c = 0{\cdot}770 : 1 : 1{\cdot}874$); its density is 2·17.

Aluminium is completely converted into the fluoride when heated in fluorine (Moissan). The fluoride is also formed when aluminium[9] or alumina[10]

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[1] Rosenhain and Archbutt, *Phil. Trans.*, 1911, A, 211, 315; Broniewski, *loc. cit.*; Shepherd, *J. Physical Chem.*, 1905, 9, 504; Pécheux, *Compt. rend.*, 1904, 138, 1103; Smirnoff, *ibid.*, 1912, 155, 351; Gautier, *Bull. Soc. d'Enc. p. l'Ind. nationale*, 1896, [v.], 1, 1293; Heycock and Neville, *Trans. Chem. Soc.*, 1897, 71, 383.

[2] For an account of these alloys, see Carpenter and Edwards, *Intern. Zeitsch. Metallographie*, 1912, 2, 209; Levi-Malvano and Marantonio, *Gazzetta*, 1911, 41, i. 282; 1912, 42, i. 353. For *aluminium-zinc-magnesium* alloys, see Eger, *Intern. Zeitsch. Metallographie*, 1913, 4, 29.

[3] Wright, *J. Soc. Chem. Ind.*, 1892, 11, 492; 1894, 13, 1014; Campbell and Mathews, *J. Amer. Chem. Soc.*, 1902, 24, 253.

[4] Baille and Féry, *Ann. Chim. Phys.*, 1889, [vi.], 17, 246; Biernacki, *Wied. Annalen*, 1896, 59, 664; Humphreys, *Trans. Chem. Soc.*, 1896, 69, 1679.

[5] Kohn-Abrest, *Bull. Soc. chim.*, 1910, [iv.], 7, 283; 1912, [iv.], 11, 570; Kohn-Abrest and Rivera-Maltes, *Compt. rend.*, 1912, 154, 1600; Nicolardot, *Bull. Soc. chim.*, 1912, [iv.], 11, 410; see also p. 379.

[6] Donski, *Zeitsch. anorg. Chem.*, 1908, 57, 185.

[7] *Gallium-aluminium* alloys are mentioned on p. 147; *thallium-aluminium* alloys on p. 175; *cerium-aluminium* alloys on p. 147. See also the subsequent volumes of this series.

[8] Hampe, *Chem. Zeit.*, 1889, 13, 1; Blackmore, *J. Soc. Chem. Ind.*, 1897, 16, 219.

[9] Poulenc, *Ann. Chim. Phys.*, 1894, [vii.], 11, 66.

[10] Brunner, *Pogg. Annalen*, 1856, 98, 488; van Haagen & Smith, *J. Amer. Chem. Soc.*, 1911, 33, 1504.

is heated to redness in hydrogen fluoride. Deville, who made an exhaustive study of the fluoride, obtained it first by heating aluminium in silicon fluoride, and afterwards prepared it by treating alumina with hydrofluoric acid and subliming the product in hydrogen at a white heat. He also obtained the fluoride by heating a mixture of fluorspar and alumina in a stream of hydrogen fluoride, and by fusing cryolite with anhydrous aluminium sulphate.[1] The impure fluoride is best purified by sublimation at 1100°.

Anhydrous aluminium fluoride forms colourless, transparent crystals which are described as rhombohedra,[2] but, according to Poulenc, are probably triclinic. It is exceedingly refractory, being insoluble in water and unattacked by alkalies and acids, including concentrated sulphuric acid. It may be decomposed by prolonged fusion with an alkali carbonate.

When 42 grams of basic aluminium acetate, 54 grams of alumina, 100 grams of water, and 66 grams of 40 per cent. hydrofluoric acid are mixed and warmed, complete solution results, and a gelatinous, hydrated aluminium fluoride separates on standing. If the solution be somewhat diluted, crystals of the trihydrate, $AlF_3.3H_2O$, slowly separate; if only 75 grams of water are employed in the preparation, crystals of another hydrate, $2AlF_3.17H_2O$, separate. The latter hydrate effloresces in air, passing into the former. The monohydrate, $AlF_3.H_2O$, can also be obtained in sparingly soluble, silky needles, and likewise the hydrate, $2AlF_3.7H_2O$, which slowly changes to the hexahydrate, $AlF_3.6H_2O$, on standing in water.[3]

The hydrate $2AlF_3.7H_2O$ has been obtained by Baud in two forms. The first, practically insoluble in water, is obtained by dissolving aluminium hydroxide in aqueous hydrofluoric acid and evaporating the solution at 100°; the second, easily soluble in water, by concentrating a solution of aluminium hydroxide in hydrofluoric acid and adding twice its volume of alcohol. An aqueous solution of the latter form is acid to litmus. The hydrate $2AlF_3.7H_2O$ loses water at 140°, leaving the hemihydrate $2AlF_3.H_2O$, which decomposes at a bright red heat.[4]

According to Deville, the compounds $AlF_3.3HF$, $3AlF_3.2HF.5H_2O$, and $2AlF_3.HF.5H_2O$ may be prepared. Aluminium fluoride enters into the composition of a large number of *double compounds.* With each of the alkali fluorides it forms a compound of the type $AlF_3.3XF$ stable at its melting-point. The melting-points are given by Puschin and Baskov[5] as follows:—

Alkali Metal . . .	Li	Na	K	Rb	Cs
Melting-point of Salt, °C. .	800°	1020°	1035°	985°	823°

According to the same authors, compounds of the type $2AlF_3.3XF$ are also formed when X = Na, K, or Rb; but this conclusion is not justified from their experiments and is probably erroneous. In the case of the sodium aluminium fluorides, the second compound has the formula $3AlF_3.5NaF$, and has no melting-point, but dissociates at 723° into $AlF_3.3NaF$ and aluminium fluoride.[6]

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[1] Deville, *Compt. rend.*, 1856, **42**, 49; *Ann. Chim. Phys.*, 1857, [iii.], **49**, 79; 1861, [iii.], **61**, 333. For other methods, see Hautefeuille, *ibid.*, 1865, [iv.], **4**, 153; Troost and Hautefeuille, *Compt. rend.*, 1872, **75**, 1819; Friedel, *Bull. Soc. chim.*, 1874, **21**, 241; Cossa, *Gazzetta*, 1877, **7**, 212.

[2] De Schulten, *Compt. rend.*, 1911, **152**, 1261.

[3] Mazzucchelli, *Atti R. Accad. Lincei*, 1907, [v.], **16**, i. 775.

[4] Baud, *Ann. Chim. Phys.*, 1904, [viii.], **1**, 8.

[5] Puschin and Baskov, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 82; *Zeitsch. anorg. Chem.*, 1913, **81**, 347.

[6] Fedotéev and Iljinsky, *Zeitsch. anorg. Chem.*, 1913, **80**, 113.

The equilibrium diagram, as far as it has been worked out, is shown in fig. 8. Calcium and aluminium fluorides form no compound; the eutectic point is 815° to 820.°

Hydrated double fluorides of the formulæ $2AlF_3.6KF.7H_2O$, $2AlF_36NaF.7H_2O$, and $2AlF_3.4NH_4F.3H_2O$ are obtained as gelatinous precipitates when the requisite alkali fluoride solutions are added to an aqueous solution of Baud's soluble hydrate of aluminium fluoride. They are slightly soluble in water, 100 parts of which dissolve 0·385 of the potassium, 0·352 of the sodium, and 1·0 of the ammonium compound at 16° (Baud, *loc. cit.*). Berzelius has described an insoluble double fluoride $AlF_3.3NH_4F$, and Petersen and Helmolt have prepared a soluble double fluoride of the same composition.[1]

The double fluoride $3AlF_3.5NaF$ occurs in nature as the tetragonal mineral *chiolite*; the compound $AlF_3.3NaF$ is found as the mineral *cryolite*. Cryolite (*i.e.* ice-stone) occurs at Ivigtut, an Esquimaux hamlet on the south-west coast of Greenland, in one huge deposit, contaminated with siderite, zincblende, galena, etc. Density, 2·96; hardness, 2·5; melting-point, *c.* 1000°. It forms monoclinic prisms (holohedral; $a:b:c = 0{\cdot}9662:1:1{\cdot}3882$, $\beta = 90°\ 11'$)[2] and at *c.* 565° is converted into a cubic modification. At 15°, 100 parts of water dissolve 0·034 of cryolite (Baud), but the latter is appreciably soluble in aqueous solutions of aluminium salts. It is decomposed by sulphuric acid. In the purification of crude cryolite, advantage is taken of the superior density of its impurities to effect a first purification, and other impurities are then removed by means of an electromagnet. Cryolite is used as a solvent for alumina in the process of manufacturing aluminium (p. 48), in the preparation of opaque white glass, and of an enamel for steel. It was formerly used as raw material for the Danish alkali industry (see Vol. II.), and ha been powdered and used by the Esquimaux as snuff.[3]

The following double salts may be prepared by dissolving the requisite hydroxides in hydrofluoric acid and evaporating the solution:—[4]

$AlF_3.ZnF_2.7H_2O$ $2AlF_3.3CuF_2.18H_2O$
$AlF_3.2CuF_2.11H_2O$ $AlF_3.CuF_2.HF.8H_2O$

Aluminium subchloride has been said to be produced by heating aluminium trichloride with aluminium in a sealed tube,[5] but the statement is in all probability erroneous.[6]

Aluminium trichloride, $AlCl_3$, was originally made by heating an intimate mixture of alumina and carbon to redness in a stream of chlorine (Oersted's method).[7] It may be more readily prepared by heating aluminium in a wide glass tube in a rapid current of dry hydrogen chloride, or in a stream of chlorine.[8] If it is required to prepare the chloride from the oxide, a

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[1] Petersen, *J. prakt. Chem.*, 1889, [ii.], **40**, 56; Helmolt, *Zeitsch. anorg. Chem.*, 1893, **3**, 115. On the detection of sodium by precipitation as sodium aluminium fluoride, see Wilks, *Proc. Camb. Phil. Soc.*, 1909, **15**, 76.

[2] Krenner, *Zeitsch. Kryst. Min.*, 1885, **10**, 525.

[3] See Halland, *J. Ind. Eng. Chem.*, 1911, **3**, 63.

[4] Weinland and Köppen, *Zeitsch. anorg. Chem.*, 1899, **22**, 266.

[5] Friedel and Roux, *Compt. rend.*, 1885, **100**, 1191.

[6] Nilson and Pettersson, *Trans. Chem. Soc.*, 1888, **53**, 826.

[7] Wöhler, *Pogg. Annalen*, 1827, **11**, 146; Liebig, *ibid.*, 1830, **18**, 43; Bunsen, *ibid.*, 1854, **92**, 648; Deville, *Compt. rend.*, 1849, **29**, 321; *Ann. Chim. Phys.*, 1855, [iii.], **43**, 11.

[8] Stockhausen and Gattermann, *Ber.*, 1892, **25**, 3521; Nilson and Pettersson, *vide infra*; Escales, *Ber.* 1897, **30**, 1314; Gustavson, *J. prakt. Chem.*, 1901, [ii.], **63**, 110; Kohn-Abrest, *Bull. Soc. chim.*, 1909, [iv.], **5**, 768.

neater method than Oersted's is to heat the oxide in a current of chlorine and sulphur chloride:—[1]

$$4Al_2O_3 + 3S_2Cl_2 + 9Cl_2 = 8AlCl_3 + 6SO_2.$$

Instead of chlorine and sulphur chloride, carbon tetrachloride vapour[2] or carbonyl chloride[3] may be used. A simple method of preparation is said to consist in heating crude alumina or clay to redness in a current of hydrogen chloride and carbon disulphide vapour, and purifying the aluminium chloride so obtained by sublimation over iron filings.[4]

Aluminium chloride, purified by sublimation over aluminium, forms white, lustrous, six-sided plates which are said by Seubert and Pollard to possess rhombic symmetry. The slightly impure chloride is usually yellow owing to the presence of a little ferric chloride. When slowly heated, aluminium chloride sublimes completely, but when a mass of the chloride is rapidly heated it melts.

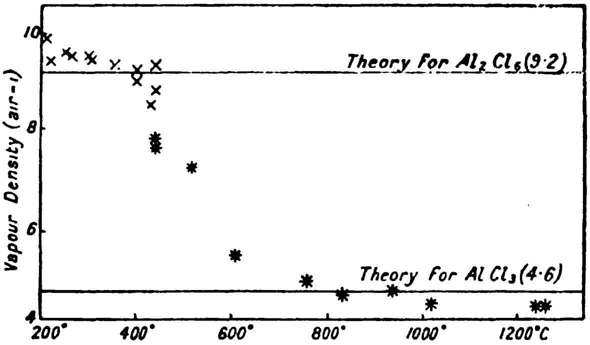

FIG. 11.—Vapour density of aluminium chloride. Results by Dumas' method shown ×, results by Victor Meyer's method shown °.

The sublimation pressure of the chloride reaches one atmosphere at 179° to 183°; the melting-point at 2·5 atmospheres pressure is 190° to 194°.[5] The critical temperature is 629·5° C.[6] The vapour density of aluminium chloride has been the subject of numerous researches. The results that have been obtained at atmospheric pressure and different temperatures (method of Dumas) are shown by crosses in fig. 11. The asterisks in the same figure

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[1] Matignon and Bourion, *Compt. rend.*, 1904, **138**, 631, 760; Bourion, *Ann. Chim. Phys.*, 1910, [viii.], **20**, 547. Alumina is not attacked by $SOCl_2$ at 200° (North and Hageman, *J. Amer. Chem. Soc.*, 1913, **35**, 352).

[2] Demarçay, *Compt. rend.*, 1887, **104**, 111; Quantin, *ibid.*, 1888, **106**, 1074; Camboulives, *ibid.*, 1910, **150**, 175, 221; L. Meyer, *Ber.*, 1887, **20**, 681.

[3] Chauvenet, *Compt. rend.*, 1911, **152**, 87.

[4] Curie, *Chem. News*, 1873, **28**, 307. For other methods of preparation, see Rose, *Pogg. Annalen*, 1848, **74**, 569; Havitsky, *Ber.*, 1873, **6**, 195; Troost and Hautefeuille, *Compt. rend.*, 1872, **75**, 1710, 1819; Weber, *Pogg. Annalen*, 1857, **101**, 465; 1858, **103**, 259; Warren, *Chem. News*, 1887, **55**, 192; Faure, *Compt. rend.*, 1888, **107**, 339; Mabery, *Ber.*, 1889, **22**, 2658.

[5] Friedel and Crafts, *Compt. rend.*, 1888, **106**, 1764; Seubert and Pollard, *Ber.*, 1891, **24**, 2575.

[6] Rotinjanz and Suchodski, *Zeitsch. physikal. Chem.*, 1914, **87**, 635.

[7] Deville and Troost, *Ann. Chim. Phys.*, 1860, [iii.], **58**, 257; Nilson and Pettersson, *Oefvers. K. Svenska Vet.-Akad. Forhandl.*, 1887, No. 8; *Zeitsch. physikal. Chem.*, 1887, **1**, 459; *Ann. Chim. Phys.*, 1890, [vi.], **19**, 145; Friedel and Crafts, *loc. cit.*; Friedel, *Ann. Chim. Phys.*, 1890, [vi.], **19**, 171.

represent the values obtained by the method of Victor Meyer, in which the partial pressure of the aluminium chloride was less than one atmosphere, but had no definite value throughout a series of experiments. The theoretical value for Al_2Cl_6 is 9·2 (air = 1), and for $AlCl_3$, 4·6. It will be seen that from 200° to 400° the molecular formula is Al_2Cl_6; above 400° the dissociation $Al_2Cl_6 \rightleftharpoons 2AlCl_3$ becomes marked; and at and above 800° the dissociation is complete. The specific heat of aluminium chloride is 0·188.[1]

Aluminium chloride dissolves in alcohol and many organic liquids. In pyridine, ether, and in nitrobenzene the molecular weight corresponds with the simple formula $AlCl_3$.[2]

Aluminium chloride is extremely deliquescent and fumes in the air. It dissolves readily in water with the evolution of much heat (p. 61). An aqueous solution of aluminium chloride is readily obtained by dissolving aluminium or its hydroxide in aqueous hydrochloric acid. A solution containing 40 parts of aluminium chloride to 100 of water has a density of 1·3415 at 15°.[3] The aqueous solution has an acid reaction and on prolonged boiling loses hydrochloric acid and becomes turbid. According to Baud, a number of definite basic chlorides exist.[4]

The hexahydrate, $AlCl_3.6H_2O$, separates out when an aqueous solution of aluminium chloride is either slowly evaporated[5] or saturated with hydrogen chloride. The hydrate forms deliquescent rhombohedral crystals ($a : c = 1 : 0·5356$) of prismatic habit and does not lose water in a sulphuric acid desiccator.[6] Dilute solutions, cooled to − 8°, are said to deposit the ennea-hydrate $AlCl_3.9H_2O$.[7]

Aluminium chloride enters into the composition of a large number of double compounds, many of which have been studied by Baud.[8] The following compounds with metallic chlorides are known :—

$2AlCl_3.2NH_4Cl$
$2AlCl_3.2KCl$
$2AlCl_3.2NaCl$
$2AlCl_3.3NaCl$
$2AlCl_3.3KCl$
$2AlCl_3.6NaCl$
$2AlCl_3.6KCl$
$2AlCl_3.2AgCl$
$2AlCl_3.BaCl_2$
$2AlCl_3.1\frac{1}{2}SrCl_2$
$2AlCl_3.1\frac{1}{2}CaCl_2$
$2AlCl_3.1\frac{1}{2}ZnCl_2$

The compound $AlCl_3.NaCl$ was formerly manufactured for use in the preparation of aluminium. It is not so hygroscopic as aluminium chloride, melts at 185°, and volatilises at a red heat. The compounds $AlCl_3.KCl$ and $AlCl_3.NH_4Cl$ are similar.

The compound $AlCl_3.SCl_4$ has been prepared by Ruff and Plato, double compounds with selenium and tellurium tetrachlorides by Weber, and with phosphorus pentachloride and oxychloride by Casselmann.[9]

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[1] Baud, *Ann. Chim. Phys.*, 1904, [viii.], **1**, 8.

[2] Werner and Schmujlow, *Zeitsch. anorg. Chem.*, 1897, **15**, 24 ; Beckmann, *Zeitsch. physikal. Chem.*, 1903, **46**, 860 ; Kohler, *Amer. Chem. J.*, 1900, **24**, 385, respectively.

[3] Gerlach, *Zeitsch. anal. Chem.*, 1869, **8**, 250.

[4] Baud, *loc. cit.* See also Liechti and Suida, *J. Soc. Chem. Ind.*, 1883, **2**, 539 ; Tommasi, *Bull. Soc. chim.*, 1882, **37**, 443 ; Hautefeuille and Perrey, *Compt. rend.*, 1885, **100**, 1219 ; Schlumberger, *Bull. Soc. chim.*, 1895, [iii.], **13**, 48.

[5] Bonsdorff, *Pogg. Annalen*, 1833, **27**, 279.

[6] Dennis and Gill, *Zeitsch. anorg. Chem.*, 1895, **9**, 339.

[7] Lubarski, *Zeitsch. anorg. Chem.*, 1898, **18**, 387.

[8] Baud, *Ann. Chim. Phys.*, 1904, [viii.], **1**, 8 ; see also p. 61.

[9] Ruff and Plato, *Ber.*, 1901, **34**, 1749 ; Weber, *Pogg. Annalen*, 1858, **104**, 421 ; Casselmann, *Annalen*, 1856, **98**, 220.

Anhydrous aluminium chloride rapidly absorbs dry ammonia. At low temperatures the compound $AlCl_3.9NH_3$ is formed, the dissociation-point of which is −14·6°. It passes into the compound $AlCl_3.6NH_3$, which is the product formed at the ordinary temperature and pressure. At 150° this passes into $AlCl_3.5NH_3$; at 275° this becomes $AlCl_3.3NH_3$; and when this last compound is distilled in hydrogen, a compound of the remarkable composition $6AlCl_3.7NH_3$ is produced which may be repeatedly distilled in hydrogen without decomposition.[1] The compounds $AlCl_3.XCl.6NH_3$ (where $X = NH_4$, Na, or K) are also known.[1] Aluminium chloride also combines with phosphine.

The compound $AlCl_3.H_2S$ can only be obtained by the use of liquid hydrogen sulphide. It dissociates at −45° into hydrogen sulphide and the compound $2AlCl_3.H_2S$, which is stable at the ordinary temperature and pressure. The compound $AlCl_3.SO_2$, prepared by subliming aluminium chloride in a current of sulphur dioxide, dissociates at 80°, giving rise to the compound $2AlCl_3.SO_2$, which can be distilled at 200°.[2]

With carbonyl chloride three compounds are formed, $2AlCl_3.5COCl_2$, melting at −2°, $2AlCl_3.3COCl_2$, and $4AlCl_3.COCl_2$. The last two compounds are said to occur in commercial aluminium chloride.[3]

The behaviour of the preceding double compounds towards water is such as would be expected from the behaviour of the constituent compounds.

Aluminium chloride combines with many organic compounds, such as acid chlorides, ketones, esters, nitro-compounds, and tertiary amines. Examples of such compounds are $AlCl_3.(C_2H_5)_2O$, $AlCl_3.C_6H_5.CO_2.C_2H_5$, $AlCl_3.NO_2.C_6H_4.CH_3$, $Al_2Cl_6.2C_6H_5NO_2$, the last compound having a molecular weight in carbon disulphide solution corresponding to the formula here given.[4] In organic chemistry, anhydrous aluminium chloride is a very valuable catalytic agent, as, for example, in the well-known Friedel and Crafts' syntheses.[5]

Aluminium tribromide, $AlBr_3$, is most readily prepared by adding aluminium carefully, in small quantities at a time, to bromine, the reaction being extremely vigorous.[6] Other methods of preparation are to pass bromine vapour over heated aluminium or an intimate mixture of alumina and carbon heated to redness.[7] The product should be rectified over metallic aluminium.

Aluminium tribromide forms colourless, transparent rhombohedra of density 2·54. It melts at 93° and boils at 263·3° under 747 mm. pressure (Mallet); its critical temperature is 772° C.[8] At 444° and 1 atmosphere the vapour density is 18·62, the formula Al_2Br_6 corresponding to the value 18·42.[9] The specific heat of aluminium bromide (22° to 76°) is 0·08912, and the latent heat of fusion 10·47 cals. per gram.; as a cryoscopic solvent the molecular depression of the freezing-point is 262.[10] The bromide is a non-electrolyte, but dissolves numerous halogen salts with the production of conducting solutions.[11] Aluminium bromide dissolves in alcohol

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[1] Baud, *loc. cit.*; *cf.* Stillman and Yoder, *Amer. Chem. J.*, 1895, **17**, 748.

[2] Baud, *loc. cit.*

[3] Baud, *Compt. rend.*, 1905, **140**, 1688.

[4] Kohler, *Amer. Chem. J.*, 1900, **24**, 385.

[5] Friedel and Crafts, *Compt. rend.*, 1877, **84**, 1392, 1450; **85**, 74, 672.

[6] Mallet, *Phil. Trans.*, 1880, **171**, 1003.

[7] Deville and Troost, *Ann. Chim. Phys.*, 1860, [iii.], **58**, 257; Gustavson, *J. prakt. Chem.* 1901, [ii.], **63**, 110; Kablukoff, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 485.

[8] Rotinjanz and Suchodski, *Zeitsch. physikal. Chem.*, 1914, **87**, 635.

[9] Deville and Troost, *loc. cit.*

[10] Kablukoff, *loc. cit.*; Isbekoff, *Zeitsch. anorg. Chem.*, 1913, **84**, 24.

[11] Isbekoff and Plotnikoff, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 18.

and many organic liquids. The molecular weight corresponds to the double formula Al_2Br_6 in carbon disulphide[1] and in bromine,[2] but in nitrobenzene it corresponds to the single formula $AlBr_3$.[1] From a solution of aluminium bromide in ethyl bromide, aluminium can be deposited by electrolysis, but the deposited metal readily attacks the solvent, butane being produced.[3]

Aluminium bromide is decomposed when heated in oxygen. It is extremely deliquescent and dissolves in water with the evolution of much heat. The aqueous solution, which may be prepared from aluminium or its hydroxide and hydrobromic acid, reacts acid and becomes basic when boiled. The hexahydrate $AlBr_3.6H_2O$ can be prepared by methods corresponding to those given for the hexahydrate of aluminium chloride (p. 67); a dilute aqueous solution when cooled is said to deposit the hydrate $2AlBr_3.15H_2O$.[4]

Aluminium bromide forms double salts with the alkali bromides, of which $AlBr_3.KBr$ and $AlBr_3.NaBr$ have been described.[5] With the tribromides of antimony and bismuth it forms solid solutions.[6] It combines with hydrogen sulphide, forming a white, crystalline compound, $AlBr_3.H_2S$, which melts at 84°;[7] and with phosphorus oxychloride, forming a compound of the molecular formula $Al_2Br_6.2POCl_3$ in carbon disulphide solution.[1] The compounds $AlBr_3.2Br_2.CS_2$ and $2AlBr_3.2Br_2.CS_2$ have also been described.[8] Like the chloride, it combines with many organic compounds. The following are the molecular formulæ, in carbon disulphide solution, of a few such compounds:—[1]

$Al_2Br_6.2C_6H_5SO_2Cl$, $Al_2Br_6.2(C_6H_5)_2CO$, $Al_2Br_6.2C_6H_5COCl$, $Al_2Br_6.2C_6H_5NO_2$.

Aluminium iodide, AlI_3, may be prepared by heating aluminium with iodine in a sealed tube, by passing iodine vapour over heated aluminium, or by adding aluminium to iodine dissolved in carbon disulphide.[9] It separates from carbon disulphide in colourless crystals of density 2·63, melts at 125°, and boils at 350°; its critical temperature is 955°.[10] At 444° the vapour density is 27·0 (air = 1), the formula Al_2I_6 requiring 28·2 (Deville and Troost). The vapour forms an exclusive mixture with air. The molecular formula is Al_2I_6 in molten iodine,[11] and in carbon disulphide solution.

Aluminium iodide is very soluble in liquid ammonia, from which the compound $AlI_3.20NH_3$ (?) may be crystallised at − 33° C. At 8–13° C. the crystals lose ammonia and leave the compound $AlI_3.6NH_3$.[12] The liquid ammonia solution reacts with potassium amide to form a soluble *aluminium ammonobasic iodide*, $Al(NH_2)_3.AlI_3$, which crystallises with six molecules of ammonia at the ordinary temperature and about twenty at low temperatures. This compound reacts with more potassium amide to produce an insoluble *ammonobasic iodide*, $Al(NH_2)_3.Al(NH_2)_2I.NH_3$, which loses two molecules of ammonia at 160° C.[12]

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[1] Kohler, *Amer. Chem. J.*, 1900, **24**, 385.

[2] Beckmann, *Zeitsch. anorg. Chem.*, 1906, **51**, 96.

[3] Plotnikoff, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 466; Patten, *J. Physical Chem.*, 1904, **8**, 548.

[4] Panfilloff, *J. Russ. Phys. Chem. Soc.*, 1895, **27**, 77.

[5] Weber, *Pogg. Annalen*, 1857, **101**, 465; 1858, **103**, 259.

[6] Isbekoff, *loc. cit.*

[7] Plotnikoff, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1162.

[8] Helle and Urech, *Ber.*, 1882, **15**, 273; Plotnikoff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 429.

[9] Weber, *loc. cit.*; Deville and Troost, *Ann. Chim. Phys.*, 1860, [iii.], **58**, 257; Gustavson, *Annalen*, 1874, **172**, 173.

[10] Rotinjanz and Suchodski, *Zeitsch. physikal. Chem.*, 1914, **87**, 635.

[11] Beckmann, *Zeitsch. anorg. Chem.*, 1912, **77**, 200, 275.

[12] Franklin, *J. Amer. Chem. Soc.*, 1915, **37**, 847.

Aluminium iodide is very soluble in water; an aqueous solution can be readily prepared from aluminium or its hydroxide and hydriodic acid. Like the chloride and bromide, it forms a hexahydrate, $AlI_3.6H_2O$; it also forms a hydrate, $2AlI_3.15H_2O$.[1]

The double salts $AlI_3.KI$, $AlI_3.NaI$ and $AlI_3.HgI_2.8H_2O$ are known.[2]

Aluminium chlorate, $Al(ClO_3)_3.9H_2O$, prepared by mixing aluminium sulphate and barium chlorate, removing the barium sulphate, and evaporating the cold solution over sulphuric acid, is very soluble in water. From a hot solution it separates as the hexahydrate. The salt is easily decomposed by heat, and explodes when slowly heated.[3]

Aluminium perchlorate, $Al(ClO_4)_3.6H_2O$, is a colourless, crystalline salt, soluble in water. Its aqueous solution gives, with sodium perchlorate, a crystalline precipitate of aluminium sodium perchlorate, $AlNa(ClO_4)_4.12H_2O$.[4]

Aluminium bromate, $Al(BrO_3)_3.9H_2O$, is prepared like the chlorate. It melts at 62·3° and easily decomposes.[5]

Aluminium periodate, $Al(IO_4)_3.3H_2O$, crystallises in regular octahedra.[6]

ALUMINIUM AND THE OXYGEN GROUP.

Aluminium suboxide.—The existence of a suboxide of aluminium has been suspected by several chemists.[7]

Aluminium sesqui-oxide or **alumina,** Al_2O_3, is found in the crystalline form in nature as the mineral *corundum*. It crystallises in the trigonal system (ditrigonal scalenohedral; $a : c = 1 : 1·365$)[8] usually in double, six-sided pyramids and rhombohedra, with the basal plane. It is therefore isomorphous with ferric and chromic oxides. Hardness, 9; density, 3·9–4·1; lustre, vitreous. The dull and opaque varieties, or "common corundum," occur in India, China, Siberia, and the United States,[9] and are largely used as abrading agents. The transparent varieties are highly valued as gem-stones. Clear, colourless stones are known as *white sapphire*; blue stones as *sapphire*; red stones as *oriental ruby*;[10] yellow stones as *oriental topaz* or *yellow sapphire*; purple stones as *oriental amethyst*; and the rare, green stones as *oriental emerald*. These coloured varieties of corundum are pleochroic. Sapphires are found in Ceylon, Burma, Siam, and parts of India, and in the gold-bearing drifts of Victoria and New South Wales. Oriental rubies occur in Ceylon and also at Mogok, Upper Burma.[11]

Impure granular or crystalline corundum, associated with magnetite, tourmaline, garnet, etc., occurs in nature as *emery*. It is obtained from

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[1] Panfilloff, *J. Russ. Phys. Chem. Soc.*, 1895, **27**, 77.

[2] Weber, *loc. cit.*; Duboin, *Compt. rend.*, 1908, **146**, 1027.

[3] Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 468.

[4] Weinland and Ensgraber, *Zeitsch. anorg. Chem.*, 1913, **84**, 368.

[5] Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 133.

[6] Eakle, *Zeitsch. Kryst. Min.*, 1896, **26**, 558.

[7] Pionchon, *Compt. rend.*, 1893, **117**, 328; Kohn-Abrest, *Bull. Soc. chim.*, 1904, [iii.], **31**, 232; *Compt. rend.*, 1905, **141**, 323; Duboin, *ibid.*, 1901, **132**, 826.

[8] Melczer, *Zeitsch. Kryst. Min.*, 1902, **35**, 561.

[9] Jenks, *Quart. J. Geol. Soc.*, 1874, **30**, 303; Judd and Hidden, *Min. Mag.*, 1899, **12**, 139; J. H. Pratt, *Bull. U.S. Geol. Survey*, 1906, No. 269.

[10] Various other red stones are technically termed ruby, *e.g.* spinel, garnet; hence the qualification "oriental" applied to corundum rubies.

[11] C. W. Brown and Judd, *Phil. Trans.*, 1896, **A**, **187**, 151; Judd, *Min. Mag.*, 1895, **11**, 56; Louis, *ibid.*, 1894, **10**, 267.

Naxos in the Greek Archipelago, Asia Minor, and Massachusetts, and is used as an abrading agent.

Alumina is obtained as an amorphous white powder or gum-like mass by heating aluminium hydroxide or the aluminium salt of a volatile oxyacid, *e.g.* the nitrate, sulphate, etc. When molten alumina solidifies, when alumina vapour condenses to the solid state and when alumina separates from its solution in a suitable solvent, it assumes the crystalline form and characteristics of corundum.[1] Rhombohedral crystals may be obtained by heating amorphous alumina with five times its weight of aluminium sulphide in the electric furnace, and treating the product with hydrochloric acid.[2]

The crystallisation of alumina has been attempted by various chemists in the hope of preparing rubies and sapphires. The ruby owes its colour to a trace of chromic oxide. The first successful experiments on the production of rubies on a large scale were made by Frémy and Feil,[3] who fused equal parts of alumina and litharge, plus 2 or 3 per cent. of potassium dichromate, in a fireclay crucible at a bright red heat. The product consisted of a layer of lead silicate and a vitreous layer in which crystals of ruby were embedded. Later, by replacing the litharge by barium fluoride and heating in a glass furnace, Frémy and Verneuil obtained beautiful rubies, which had arisen by the action of the furnace gases on aluminium fluoride vapour.[4] Loyer obtained rubies by heating sodium aluminate (100 pts.) and potassium dichromate (1 pt.) to bright redness in chlorine.[5]

At the present time, rubies are manufactured by a process devised by Verneuil.[6] The material used is powdered alumina containing a little chromic oxide (2·5 per cent.), produced by precipitating with ammonia a solution of pure ammonium alum to which a little chrome alum has been added, and igniting the mixed hydroxides. The powder is fed through the oxygen tube of an inverted oxy-coal-gas blowpipe, falls as a molten drop on to the end of a small alumina rod, and crystallises as ruby. As the process is continued, the ruby grows upwards as a pear-shaped drop or "boule." These "boules" have a density of 4·01; although externally smooth, they have a crystalline structure and differ from natural stones only in one respect, viz., they contain microscopic air-bubbles and fine-curved internal streaks. The streaks in a natural stone are straight.[7]

Sapphires are manufactured from alumina to which 1·5 per cent. of magnetic iron oxide and 0·5 per cent. of titanium oxide has been added, the mixture being fused and crystallised in an oxy-hydrogen reducing flame.[8] The introduction of cobalt oxide into alumina can only be effected in the presence of a third oxide such as lime. The stones obtained are blue, but

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[1] A second form of alumina is sometimes obtained when molten alumina is slowly cooled, particularly in the presence of a little magnesia. It is hexagonal, density 3·30. See Rankin and Merwin, *J. Amer. Chem. Soc.*, 1916, **38**, 570.

[2] Houdard, *Compt. rend.*, 1907, **144**, 1349.

[3] Frémy and Feil, *Compt. rend.*, 1877, **85**, 1029; *Phil. Mag.*, 1878, [v.], **5**, 47.

[4] Frémy and Verneuil, *Compt. rend.*, 1887, **104**, 737, 738; 1888, **106**, 565; 1890, **111**, 667; Descloizeaux, *ibid.*, 1888, **106**, 567.

[5] Loyer, *Bull. Soc. chim.*, 1897, [iii.], **17**, 345.

[6] Verneuil, *Ann. Chim. Phys.*, 1904, [viii.], **3**, 20.

[7] For early work on the ruby, see Gaudin, *Compt. rend.*, 1837, **4**, 999; 1857, **44**, 716; 1869, **69**, 1343; Ebelmen, *Ann. Chim. Phys.*, 1851, [iii.], **33**, 34; Deville and Caron, *ibid.*, 1865, [iv.], **5**, 104; Hautefeuille, *ibid.*, 1865, [iv.], **4**, 153; Debray, *Compt. rend.*, 1861, **52**, 985; De Senarmont, *ibid.*, 1851, **32**, 762; Deville, *ibid.*, 1855, **40**, 771. See also Friedel, *Bull. Soc. chim.*, 1886, [ii.], **46**, 242.

[8] Verneuil, *Compt. rend.*, 1910, **150**, 185.

they are amorphous, and have not the tint of sapphire.[1] The analyses of three natural sapphires gave the following results :—[2]

Locality . . .	Australia.	India.	Montana.
Fe_2O_3	0·920	0·72	0·560
TiO_2	0·031	0·04	0·058
SiO_2	trace	nil	0·100
Al_2O_3 (diff.)	...	...	...

It has been shown that synthetic and natural sapphires have identical properties.[3]

About ten million carats of rubies and six million carats of sapphires were manufactured in 1913, and the demand is increasing.[4]

Amorphous alumina is a white powder, insoluble in water. The density increases with the temperature at which it has been ignited, as follows :—[5]

Temperature ° C. . .	600°	700°	800°	900°	1200°
Density . . .	2·82	2·83	3·39	3·53	3·92

When slowly heated it undergoes an exothermic change at 850°,[6] and melts at 2010° to 2050°.[7] In the electric furnace it melts and boils, and the vapour condenses to the crystalline form.[8] The specific heat of ignited alumina increases with the temperature, as is shown by the following mean values :—[9]

Temp. interval ° C.	15°–100°	15°–195°	15°–315°	15°–420°	15°–510°
Specific heat .	0·2003	0·2195	0·2311	0·2400	0·2464

Alumina that has been dried at a low temperature is very hygroscopic and forms an excellent drying agent.[10]

Alumina is soluble in mineral acids unless it has been strongly heated (above 850°), when it becomes extremely refractory. Calcined alumina must be brought into solution by fusion with potassium hydrogen sulphate or alkali hydroxide.

Alumina is unaffected by hydrogen or chlorine at a red heat, but is converted by fluorine into aluminium fluoride and oxygen. At a red heat it is converted into the sulphide by carbon disulphide. Alumina is reduced by carbon to the metal at temperatures above 2000°,[11] *i.e.* at temperatures above which aluminium carbide is unstable.[12] It was shown by Moissan that carbon reduces alumina vapour.[13]

Alumina is used in the manufacture of aluminium; for this purpose it is prepared by igniting the hydroxide, prepared from bauxite as described later

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[1] Paris, *Compt. rend.*, 1908, **147**, 933 ; Verneuil, *ibid.*, 1908, **147**, 1059.

[2] Verneuil, *Compt. rend.*, 1910, **151**, 1063.

[3] Moses, *Amer. J. Sci.*, 1910, [iv.], **30**, 271.

[4] For a review of the subject of synthetic stones, see Levin, *J. Ind. Eng. Chem.*, 1913, **5**, 495.

[5] Mellor and Holdcroft, *Trans. Eng. Ceramic. Soc.*, 1911, **9**, 94.

[6] Le Chatelier, *Compt. rend.*, 1887, **104**, 1517 ; *Bull. Soc. chim.*, 1887, [iii.], **47**, 300.

[7] Kanolt, *J. Washington Acad. Sci.*, 1912, **2**, 337 ; 1913, **3**, 315 ; Ruff and Goecke, *Zeitsch. angew. Chem.*, 1911, **24**, 1459 ; Ruff, Serferheld, and Suda, *Zeitsch. anorg. Chem.*, 1913, **82**, 373 ; Tiede and Birnbräuer, *ibid.*, 1914, **87**, 129.

[8] Moissan, *Compt. rend.*, 1892, **115**, 1034.

[9] Tilden, *Trans. Chem. Soc.*, 1905, **87**, 551.

[10] Johnson, *J. Amer. Chem. Soc.*, 1912, **34**, 911.

[11] Hutton and Petavel, *Proc. Roy. Soc.*, 1907, **A**, **79**, 155.

[12] Askenasy and Lebedeff, *Zeitsch. Elektrochem.*, 1910, **16**, 559.

[13] Moissan, *Compt. rend.*, 1894, **119**, 935 ; *Bull. Soc. chim.*, 1895, [iii.], **13**, 803.

(p. 79). It has been proposed to prepare it from aluminium nitride, manufactured by Serpek's method (p. 88). Another proposal, which may possibly develop into a successful commercial method, is to obtain the alumina from sodium aluminate, itself manufactured from china-clay.[1]

The porous *alundum* laboratory utensils are composed mainly of alumina. Calcined bauxite is fused in a water-cooled electric arc furnace. The impurities in the bauxite are to a certain extent reduced and segregate at the bottom of the fused mass as an impure ferrosilicon. The cooled product consists essentially of a large mass of crystalline alumina. It is crushed, mixed with a ceramic binding material (ball-clay and felspar), moulded, dried, and fired in a porcelain kiln.[2]

Aluminium peroxide.—When excess of 30 per cent. hydrogen peroxide is added to a solution of aluminium hydroxide in 50 per cent. potassium hydroxide, a white, amorphous precipitate is obtained, of the composition $Al_2O_3.Al_2O_4.10H_2O$, which reacts as a true peroxide. Possibly an initial product Al_2O_4 is formed and partly decomposed by the water.[3]

Aluminium hydroxides; aluminates.—Two hydrated oxides of aluminium are found in nature in the crystalline state, namely, **diaspore,** $Al_2O_3.H_2O$, which occurs in orthorhombic crystals (holohedral; $a : b : c = 0·9372 : 1 : 1·6038$) of density 3·30–3·45, and **hydrargillite** (or *gibbsite*), $Al_2O_3.3H_2O$, which occurs in fibrous, monoclinic crystals (holohedral; $a : b : c = 1·7089 : 1 : 1·9184$, $\beta = 85° 29'$) of density 2·42. The most important naturally occurring hydrated oxide of aluminium, however, is **bauxite,** a white, yellowish, red, or brown clay-like, amorphous material originally found at Les Beaux near Arles in the south of France. Bauxite varies widely in composition, and consists of amorphous, colloidal, hydrated alumina (with perhaps a little diaspore and hydrargillite) associated with varying amounts of ferric hydroxide, clay, quartz, sand, etc. It is therefore better regarded as a rock than as a mineral.[4] Formerly, bauxite was regarded as a mineral of the formula $Al_2O_3.2H_2O$, but most bauxites more nearly approach the ratio $Al_2O_3 : H_2O$ than $Al_2O_3 : 2H_2O$.[5] Bauxite is a very valuable source of aluminium; it occurs mainly in the department Var (France), in County Antrim (Ireland), and in the states of Alabama, Georgia, and Arkansas (America).

When excess of ammonium hydroxide is added to an aqueous solution of an aluminium salt, a precipitate is obtained, white, opaque, and amorphous at 100°, transparent and gelatinous at ordinary temperatures. The precipitate has a pronounced tendency to pass into colloidal solution when washed with water. Air-dried in hot weather, its composition[6] corresponds to the formula $Al_2O_3.3H_2O$ or $Al(OH)_3$; dried at 100°, or at the ordinary

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[1] Cowles, *J. Ind. Eng. Chem.*, 1913, **5**, 331.

[2] C. B. Jacobs, *U.S. Pat.*, 659,926; Higgins, *U.S. Pat.*, 775,654; Williamson and Boeck, *J. Ind. Eng. Chem.*, 1912, **4**, 672. See also the following references: *Electrochem. Ind.*, 1903, **1**, 15; 1905, **3**, 30, 406; *Electrochem. and Metall. Ind.*, 1909, **7**, 223; *Min. Ind.*, 1911, **20**, 31.

[3] Terni, *Atti R. Accad. Lincei*, 1912, [v.], **21**, ii. 104.

[4] Bauer, *Jahrb. Min.*, 1898, ii. 163; Holland, *Geol. Mag.*, 1903, 59; Dittler and Doelter, *Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 282; André Gautier, *Rev. gen. Chim. pure appl.*, 1910, **13**, 389.

[5] Arsandaux, *Compt. rend.*, 1909, **148**, 936, 1115; see also E. Martin, *Ann. Chim. anal.*, 1913, **18**, 297.

[6] When precipitated from aluminium sulphate, the hydroxide is contaminated with basic sulphate.

temperature over concentrated sulphuric acid, the composition is that of a dihydrate, $Al_2O_3.2H_2O$. The amorphous trihydrate is also obtained by heating an alkali aluminate with ammonium chloride, or by boiling basic aluminium carbonate with water; when an alkali aluminate solution is boiled, the trihydrate slowly separates in a crystalline form.[1] A monohydrate, $Al_2O_3.H_2O$, is said to be obtained by heating amorphous alumina with water in a closed tube to 250°.[2]

The amorphous mono- and di-hydrates are very hygroscopic substances, absorbing water with the formation of the trihydrate or normal aluminium hydroxide. At a red heat all the hydrates are converted into alumina.

A colloidal solution of aluminium hydroxide was obtained by Crum from aluminium acetate solution. This was heated to obtain a precipitate of basic acetate, and the precipitate dissolved in 200 times its weight of boiling water. The solution was then maintained at 100° for some days, when complete hydrolysis occurred. The liquid was diluted and heated to 100° until all the acetic acid had been volatilised, fresh water being added from time to time. A colourless, tasteless, neutral solution of aluminium hydroxide was thus obtained, readily coagulated by salts and a number of acids, and the gel thus obtained dissolving only in concentrated acids. The solution did not act as a mordant, and when evaporated at 100°, left a residue difficultly soluble in acids.[3] Graham obtained aluminium hydroxide in colloidal solution by dialysing a solution of aluminium chloride saturated with aluminium hydroxide. The colloidal solution so obtained acted as a mordant, and was readily coagulated by acids, bases, and salts to a gel soluble in dilute acids.[4] Colloidal aluminium hydroxide exhibits anodic cataphoresis; it is seen to be a suspension when examined in the ultra-microscope.[5]

In the absence of salts, freshly precipitated aluminium hydroxide is perceptibly soluble in ammonia, and much more so in methylamine and other organic bases.[6] It is also readily soluble in acids and alkali hydroxides. When kept under water for several months, it becomes difficultly soluble in acids and alkalies, concentrated sulphuric acid excepted.[7] The naturally occurring hydroxides are not readily attacked by acids.

Precipitated aluminium hydroxide assumes a bright red colour, not destroyed by dilute acetic acid, when boiled with water containing a drop or two of 1 per cent. alizarin solution. This test readily distinguishes it from gelatinous hydrated silica. Aluminium hydroxide also forms soluble

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[1] E. T. Allen, *Chem. News*, 1900, **82**, 75; Allen and Rogers, *Amer. Chem. J.*, 1900, **24**, 304; Carnelley and Walker, *Trans. Chem. Soc.*, 1888, **53**, 59; Bonsdorff, *Pogg. Annalen*, 1833, **27**, 275; Cossa, *Zeitsch. für Chem.*, 1870, **13**, 443; St Gilles, *Ann. Chim. Phys.*, 1856, [iii.], **46**, 58; Löwe, *Zeitsch. für Chem.*, **3**, 247; Ditte, *Compt. rend.*, 1893, **116**, 183; De Schulten, *ibid.*, 1896, **122**, 1427; *cf.* Ramsay, *Trans. Chem. Soc.*, 1877, ii. 395; Russ, *Zeitsch. anorg. Chem.*, 1904, **41**, 216; Schlumberger, *Bull. Soc. chim.*, 1895, [iii.], **13**, 41; Maumené, Villiers, *ibid.*, 1895, [iii.], **13**, 309.

[2] Mitscherlich, *J. prakt. Chem.*, 1861, **83**, 468; see also De Senarmont, *Compt. rend.*, 1851, **32**, 762.

[3] Crum, *Quart. J. Chem. Soc.*, 1854, **6**. 216: *Ann. Chim. Phys.*, 1854, [iii.], **41**, 185.

[4] Graham, *Phil. Trans.*, 1861, **151**, 183; *Ann. Chim. Phys.*, 1862, [iii.], **65**, 175. See also Schlumberger, *loc. cit.*; W. Biltz, *Ber.*, 1902, **35**, 4431; Hantzsch and Desch, *Annalen*, 1902, **323**, 30; A. Müller, *Zeitsch. anorg. Chem.*, 1905, **43**, 320; 1908, **57**, 312; Schneider, *Annalen*, 1890, **257**, 359; Kawamura, *J. Coll. Sci. Tokyo*, 1908, **25**, viii. 1; Bentley and R. P. Rose, *J. Amer. Chem. Soc.*, 1913, **35**, 1490; Rose, *Kolloid. Chem. Beihefte*, 1914, **6**, 1.

[5] Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35**, 864.

[6] Renz, *Ber.*, 1903, **36**, 2751.

[7] Tommasi, *Chem. Zentr.*, 1905, ii. 605; *Chem. Soc. Abstr.*, 1905, **88**, ii. 712.

complex substances with many organic hydroxy-compounds. Further, it enters into combination with many organic colouring matters, producing coloured, insoluble *lakes.* Upon this property depends the use of aluminium salts as mordants in dyeing.

The solubility of aluminium hydroxide in acids is due to the fact that it acts as a weak base and reacts with acids to produce aluminium salts. In the same way, the solubility of aluminium hydroxide in alkali hydroxides is attributed to the feeble acidic character of the hydroxide. It is, in fact, an amphoteric hydroxide. The minute amount of aluminium hydroxide present in aqueous solution in equilibrium with the solid phase must be supposed to dissociate in two ways :—

$$Al^{\cdots} + 3OH' \rightleftharpoons Al(OH)_3 \rightleftharpoons H^{\cdot} + H_2AlO_3' \text{ (or } AlO_2' \text{ and } H_2O).$$

The hydroxide is weaker as an acid than as a base, and the affinity constant for the acid dissociation represented above has been estimated[1] to be approximately 1×10^{-10}, *i.e.* the acid is of the same order of strength as boric acid and its alkali salts must be perceptibly hydrolysed in aqueous solution.

From solutions of aluminium hydroxide in alkali hydroxides a number of solid substances, some of them crystalline, have been isolated, which must be regarded as salts of aluminium hydroxide (aluminic acid). These salts are called **aluminates**, and are mentioned later (p. 76). The nature of the solutions obtained by dissolving aluminium hydroxide in alkali hydroxides has been the subject of much discussion. The freezing-point of a dilute solution of sodium hydroxide is not changed by dissolving aluminium hydroxide in it. This would be expected if each OH′ ion used up leads to the production of one aluminate anion, *i.e.* the result points very clearly to the presence of a meta-aluminate, $NaAlO_2$, in solution.[2] Determinations of the ratio $Al_2O_3 : Na_2O$ (or K_2O) in solutions saturated with aluminium hydroxide are not conclusive, since the above ratio is much greater when aluminium is dissolved in alkali than when aluminium hydroxide is dissolved.[3] Moreover, unless the atomic ratio Na (or K) to Al exceeds the value two, the solutions are unstable. The equivalent conductivity gradually rises, and aluminium hydroxide is slowly precipitated.[4] The change in conductivity is in harmony with the view that the salt of a monobasic acid is undergoing hydrolysis. Moreover, no change in conductivity is observed without the simultaneous deposition of aluminium hydroxide, so that the latter, when produced by hydrolysis, does not first pass into colloidal solution. These results negative the suggestion[5] that while some of the aluminium hydroxide dissolves in alkali hydroxides with the formation of alkali aluminates, most of the hydroxide merely passes into solution as a colloidal hydrosol, which, on standing, slowly reverts either to a crystalloidal form or to a colloidal hydrogel, and so

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[1] Slade, *Zeitsch. anorg. Chem.*, 1912, **77**, 457 ; Blum, *J. Amer. Chem. Soc.*, 1913, **35**, 1499 ; *cf.* Wood, *Trans. Chem. Soc.*, 1908, **93**, 417.

[2] A. A. Noyes and Whitney, *Zeitsch. physikal. Chem.*, 1894, **15**, 694.

[3] Herz, *Zeitsch. anorg. Chem.*, 1900, **25**, 155 ; Russ, *ibid.*, 1904, **41**, 216 ; Allen and Rogers, *Amer. Chem. J.*, 1900, **24**, 304 ; Herz, *Zeitsch. Elektrochem.*, 1911, **17**, 403 ; Slade, *ibid.*, 1911, **17**, 261 ; 1912, **18**, 1.

[4] Hantzsch, *Zeitsch. anorg. Chem.*, 1902, **30**, 296 ; Russ, *loc. cit.* ; Slade and Polack, *vide infra.*

[5] Mahin, Ingraham, and O. J. Stewart, *J. Amer. Chem. Soc.*, 1913, **35**, 30 ; *cf.* J. Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35**, 864 ; Blum, *ibid.*, 1913, **35**, 1499 ; 1914, **36**, 2383 ; Mahin, *ibid.*, 1914, **36**, 2381.

precipitates. A study of the variation of the hydrogen ion concentration in an aluminium chloride solution, as sodium or potassium hydroxide is gradually added to the liquid, has been made by Hildebrand and by Blum.[1] The general nature of their results may be seen by reference to fig. 12; the points A, B, C are points of inflexion on the curve, and correspond respectively to the commencement of precipitation of the hydroxide, the completion of the precipitation, and the completion of the solution of the precipitate in sodium hydroxide. It is found that *bc* is one-third of *ab* ; *i.e.* the results point clearly to the existence of aluminates $NaAlO_2$ and $KAlO_2$ in aqueous solution :—

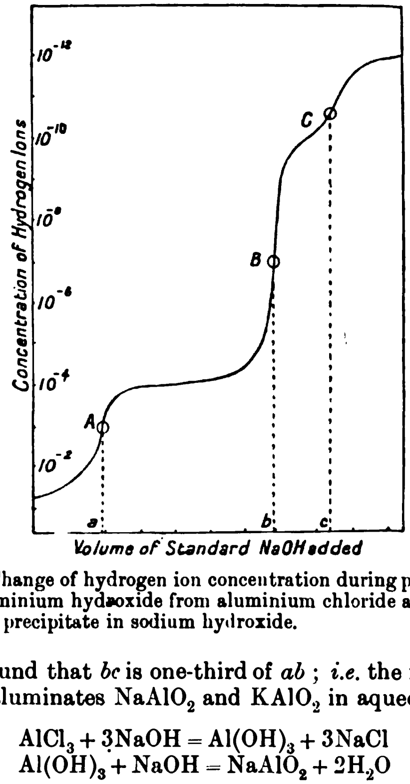

FIG. 12.—Change of hydrogen ion concentration during precipitation of aluminium hydroxide from aluminium chloride and solution of the precipitate in sodium hydroxide.

$$AlCl_3 + 3NaOH = Al(OH)_3 + 3NaCl$$
$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$$

and are opposed to the view that colloidal solution occurs to any appreciable extent. Moreover, observations with the ultra-microscope fail to indicate that the solutions are suspension-colloids.[2] The microscopic evidence, however, is not very conclusive.

The following hydrated *aluminates* have been obtained in the solid state, several of them in the crystalline form, by the interaction of aluminium with concentrated alkali hydroxides :—[3]

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[1] J. Hildebrand, *loc. cit.* ; Blum, *loc. cit.*

[2] Slade and Polack, *Trans. Faraday Soc.*, 1914, **10**, 150 ; Hildebrand, *loc. cit.*

[3] Prepared mainly by Allen and Rogers, *Amer. Chem. J.*, 1900, **24**, 304 ; see also Hawley, *J. Amer. Chem. Soc.*, 1907, **29**, 300 ; Frémy, *Ann. Chim. Phys.*, 1844, [iii.], **12**, 361 ; 1866, [iv.], **7**, 69 ; Pelouze, *ibid.*, 1851, [iii.], **33**, 13 ; Mallard, *ibid.*, 1873, [iv.], **28**, 86 ; Cavazzi, *Gazzetta*, 1885, **15**, 202 ; Beckmann, *J. prakt. Chem.*, 1882, [ii.], **26**, 385 ; Deville, *Compt. rend.*, 1862, **54**, 327 ; Gaudin, *ibid.*, 1862, **54**, 687.

$K(AlO_2).1·5H_2O$	$Ca_2Al_2O_5.7H_2O$	$Ca_3(AlO_3)_2.6H_2O$
$Na(AlO_2).2H_2O$	$Ba_2Al_2O_5.5H_2O$	$Sr_3(AlO_3)_2.6H_2O$
$LiH(AlO_2)_2.5H_2O$	$Tl_4Al_2O_5.7H_2O$	$Ba_3(AlO_3)_2.7H_2O$
$Ba(AlO_2)_2.5H_2O$	...	...
$Sr(AlO_2)_2.4H_2O$?	...	...

A number of anhydrous, crystalline alluminates occur as minerals; *e.g* :—

Magnesia spinel or *spinel ruby* . . .	$Mg(AlO_2)_2$
Magnesia iron spinel or *pleonaste* . . .	$(Mg,Fe)(AlO_2)_2$
Iron spinel or *hercynite*	$Fe(AlO_2)_2$
Zinc spinel or *gahnite*	$Zn(AlO_2)_2$

These four minerals crystallise in regular octahedra, and are isomorphous with *magnetite*, $Fe(FeO_2)_2$, and *chromite*, $Fe(CrO_2)_2$. The mineral *chrysoberyl*, or beryllium aluminate, $Be(AlO_2)_2$, is not isomorphous with the preceding, but crystallises in the orthorhombic system ($a : b : c = 0·470 ; 1 : 0·580$) and is isomorphous with *olivine*, Mg_2SiO_4. Magnesia spinel is often found in beautiful red crystals, which are used as gem-stones; such crystals contain a little chromic oxide. Beautiful yellowish-green crystals of chrysoberyl, found in Ceylon, are also used as gem-stones. The aluminates of barium, calcium, beryllium, magnesium, zinc, manganese, and cobalt were prepared in the crystalline form by Ebelmen by intensely heating alumina and the requisite oxide with boron sesqui-oxide until the latter substance, which initially acts as a solvent, had been largely volatilised.[1] The blue mass obtained in qualitative analysis when testing on charcoal for aluminium contains cobalt aluminate.

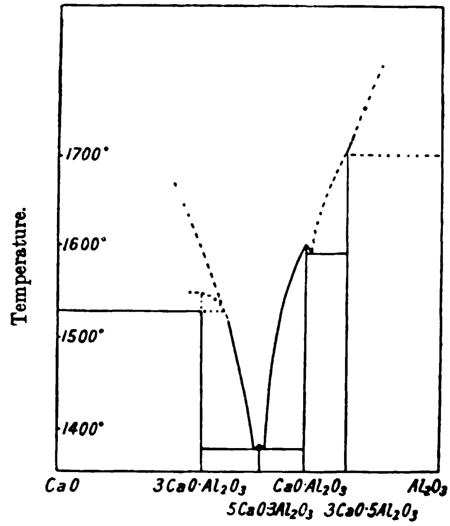

FIG. 13.—Equilibrium diagram for the system lime - alumina.

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[1] Ebelmen, *Ann. Chim. Phys.*, 1848, [iii.], **22**, 211 ; 1851, [iii.], **33**, 34 ; Deville and Caron, *ibid.*, 1865, [iv.], **5**, 104 ; Daubrée, *Compt. rend.*, 1854, **39**, 135 ; Dufau, *J. Pharm. Chim.*, 1901, [vi.], **14**, 25 ; Hedvall, *Arkiv. Kem. Min. Geol.*, 1914, **5**, No. 6 (Co) ; Jaeger and Simek, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 239, 251 (Li).

A thermal study of the system *lime - alumina* has shown that four anhydrous **calcium aluminates** can be obtained, of the formulæ $3CaO.Al_2O_3$, $CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $3CaO.5Al_2O_3$. The second and third melt at 1587° and 1387° respectively; the others have no melting-point. The third and fourth compounds are dimorphous.[1, 2] The nature of the equilibrium diagram is indicated in fig. 13. Only one **magnesium aluminate** has been obtained, namely, *spinel*, $MgO.Al_2O_3$.[1, 2]

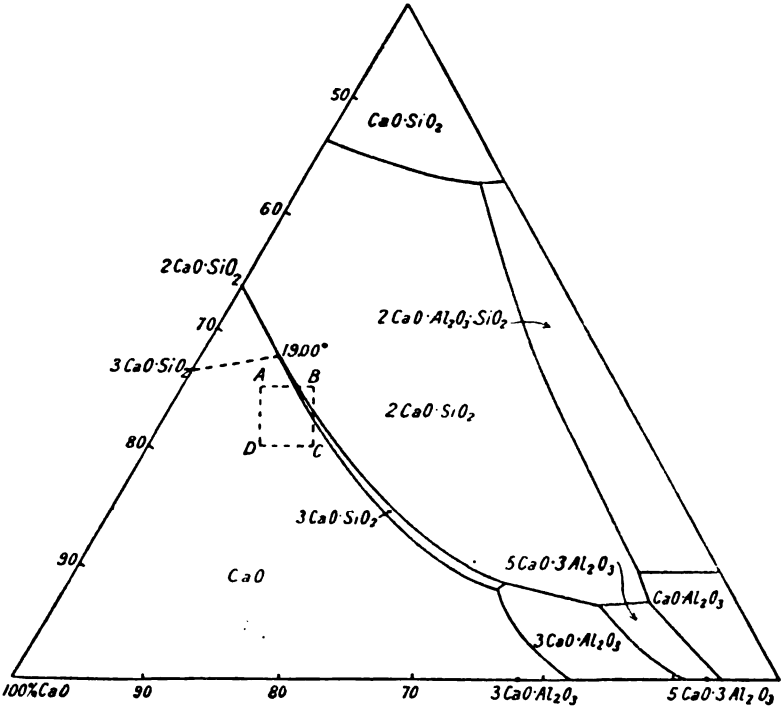

FIG. 14.—Projection of liquidus surface for the system lime - silica - alumina.

Tricalcium aluminate, $3CaO.Al_2O_3$, is an important constituent of Portland cement clinker, which consists mainly (over 90 per cent.) of silica, lime, and alumina. Its constitution has long been the subject of discussion. A complete thermal and optical study of the system *lime - silica - alumina* has been made by Rankin and Wright,[3] and the results, so far as they bear on the constitution of Portland cement, are shown in fig 14. Considering only the lime, silica, and alumina content, the variations in the composition of the commercial cement are restricted to the area ABCD. It may be deduced from the diagram by aid of the Phase Rule that a fluid mass of this composition, when slowly cooled until complete solidification has occurred, is converted

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[1] Shepherd, Rankin, and Wright, *Amer. J. Sci.*, 1915, [iv.], 28, 293.

[2] Rankin and Merwin, *J. Amer. Chem. Soc.*, 1916, 38, 568.

[3] Rankin and Wright, *Amer. J. Sci.*, 1915, [iv.], 39, 1; *cf.* Shepherd, Rankin, and Wright, *J. Ind. Eng. Chem.*, 1911, 3, 211; Rankin, *ibid.*, 1915, 7, 466.

into a mixture of tricalcium silicate, $3CaO.SiO_2$, dicalcium silicate, $2CaO.SiO_2$, and tricalcium aluminate, $3CaO.Al_2O_3$.

Portland cement clinker should therefore consist essentially of these three compounds if, in its manufacture, the heating be prolonged for a length of time sufficient for equilibrium to be established. This deduction has been verified by experiments carried out in the laboratories of the United States Bureau of Standards. Since, however, complete equilibrium is not reached in its manufacture, the cement also contains lime, CaO, and the aluminate $5CaO.3Al_2O_3$ as minor constituents. The iron oxide contained in the cement may be present as calcium ferrite or magnetite, or held in solid solution in the compounds $2CaO.SiO_2$ and $5CaO.2Al_2O_3$; the magnesia and alkalies are apparently held in solid solution in the compounds $2CaO.SiO_2$ and $3CaO.Al_2O_3$.[1]

In contact with water, the compounds $CaO.Al_2O_3$, $3CaO.Al_2O_3$, and $5CaO.3Al_2O_3$ yield an amorphous hydrate, $3CaO.Al_2O_3.xH_2O$, which in time crystallises; except with tricalcium aluminate, amorphous aluminium hydroxide is also formed. When hydrated with aqueous calcium sulphate an additional compound, *calcium "sulpho-aluminate,"* $3CaO.Al_2O_3.3CaSO_4.xH_2O$, is formed, which crystallises in long prismatic needles.[2]

Sodium aluminate is manufactured from bauxite, which is roughly powdered, calcined, and introduced into sodium hydroxide solution of specific gravity 1·45. The mixture is heated under high-pressure steam (80 lbs. per sq. inch), when the alumina passes into solution. The liquid is passed through a filter-press, and then through wood-pulp to free it from ferric hydroxide, etc. Aluminium hydroxide is prepared from this solution by stirring into it a quantity of the hydroxide previously prepared. On standing, the greater part of the aluminium separates out from the solution as aluminium hydroxide. The precipitate is washed in a filter-press, and the mother liquor concentrated and used again for attacking more bauxite. This process, due to Bayer, has largely superseded the older method of decomposing the sodium aluminate by passing carbon dioxide through the solution.

Aluminium sesqui-sulphide, Al_2S_3, was first obtained by Frémy by heating alumina to redness in a current of carbon disulphide vapour. It may be obtained by the action of hydrogen sulphide upon alumina at a red heat or by the action of sulphur on a heated mixture of alumina and carbon.[3]

Aluminium sulphide is readily prepared by heating alumina with galena in a muffle furnace, or by the direct union of its elements. The powdered elements are mixed in a fireclay crucible, heated till the sulphur fuses, and cooled. The reaction is then brought about as in a thermit reaction by means of a firing powder ignited by a piece of magnesium ribbon.[4] The sulphide is

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[1] P. H. Bates, *Concrete-Cement Age* (*Cement Mill Section*), 1913, **2**, 3; 1914, **4**, 29, 38; 1915, **7**, 1; A. A. Klein and A. J. Phillips, *Eighth Inter. Cong. Appl. Chem.*, 1912, **5**, 73; *cf.* Jänecke, *Zeitsch. anorg. Chem.*, 1911, **73**, 200; 1912, **74**, 428; **76**, 357; 1914, **89**, 355; 1915, **93**, 271; and Kühl, *Tonind.-Zeit.*, 1914, **38**, 365, who consider that a compound $8CaO.Al_2O_3.2SiO_2$ exists in the cement.

[2] A. A. Klein and A. J. Phillips, *Tech. Papers Bur. Stand.*, 1914, No. **43**; *Trans. Amer. Cer. Soc.*, 1914, **16**, 313; *J. Wash. Acad. Sci.*, 1914, **4**, 573.

[3] Gautier, *Compt. rend.*, 1906, **143**, 7; Bucherer, *Zeitsch. angew. Chem.*, 1892, **5**, 483. Early references: Frémy, *Ann. Chim. Phys.*, 1853, [iii.], **38**, 322; Sabatier, *ibid.*, 1881, [v.], **22**, 88; Vincent, *Phil. Mag.*, 1857, [iv.], **14**, 127; Spring, *Ber.*, 1883, **16**, 1011; Reichel, *J. prakt. Chem.*, 1875, [ii.], **12**, 55; Stein, *ibid.*, 1871, [ii.], **3**, 43; Knopp and Ebell, *Dingl. Poly. J.*, 1878, **229**, 69, 173.

[4] Fonzes-Diacon, *Compt. rend.*, 1900, **130**, 1314; W. Biltz and Caspari, *Zeitsch. anorg. Chem.*, 1911, **71**, 182.

purified by sublimation *in vacuo* at 1100° to 1250°, or in nitrogen at 1500° to 1600°.

According to Biltz and Caspari, aluminium sulphide crystallises in white, asbestos-like needles[1] (which are possibly hexagonal) and forms mixed crystals with alumina. It melts at 1100° ± 10° and its density at 13° is 2·02. Heated to 2100° in an inert atmosphere it loses sulphur and forms **aluminium subsulphide,** AlS; heated in air or oxygen it is converted into alumina and sulphur dioxide.

Aluminium sesqui-sulphide is rapidly and completely decomposed by water with the formation of aluminium hydroxide and hydrogen sulphide, a behaviour in accordance with the fact that it is the salt of a very weak, practically insoluble base and a very weak acid. The decomposition of the monosulphide by hydrochloric acid is represented by the equation:—

$$2AlS + 6HCl = 2AlCl_3 + 2H_2S + H_2.$$

By heating a mixture of alumina and a carbonate to redness in a current of carbon disulphide vapour, the following double sulphides have been obtained:[2] *potassium-aluminium sulphide,* $3K_2S.Al_2S_3$; *sodium-aluminium sulphide,* $3Na_2S.Al_2S_3$; and *barium-, strontium-,* and *calcium-aluminium sulphides. Aluminium-silver sulphide,* $4Ag_2S.5Al_2S_3$, melts at 1035°.[3]

Aluminium selenide, Al_2Se_3, may be prepared from its elements as described for the sulphide; or by reducing lead sulphate by means of aluminium.[4] It is a greyish-yellow solid of density 3·437, and is readily decomposed by water with the evolution of hydrogen selenide.

Aluminium telluride, Al_2Te_3, is prepared by the direct union of its elements.[5] It is a grey solid, decomposed by water with the evolution of hydrogen telluride, which, however, readily decomposes.

Aluminium sulphite.—Various basic salts have been described.[6] The acid sulphite solution has been used for purifying beet sugar.[7]

Aluminium sulphate, $Al_2(SO_4)_3$, is prepared in the anhydrous state by heating the crystalline, hydrated salt. The latter melts in its water of crystallisation, swells up, and eventually leaves a porous, white residue of anhydrous sulphate.

The anhydrous sulphate has a density of 2·713 at 17°, and its specific heat (0° to 100°) is 0·1855.[8] At a red heat it decomposes, leaving a residue of alumina; decomposition becomes appreciable at 770°.[9] It dissolves slowly in water.

A solution of aluminium sulphate is readily prepared by dissolving aluminium hydroxide in dilute sulphuric acid. The solution crystallises with difficulty, the hydrate $Al_2(SO_4)_3.18H_2O$ being deposited in thin, six-

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[1] *Cf.* Mourlot, *Compt. rend.*, 1896, **123**, 54.

[2] Jaennigen, *Chem. Zentr.*, 1895, ii. 205.

[3] Cambi, *Atti R. Accad. Lincei*, 1912, [v.], **21**, ii. 837; for other double sulphides, see Vols. VII., VIII., IX., or Houdard, *Compt. rend.*, 1907, **144**, 801, 1114.

[4] Fonzes-Diacon, *loc. cit.*

[5] Fonzes-Diacon, *loc. cit.*; Whitehead, *J. Amer. Chem. Soc.*, 1895, **17**, 849.

[6] Gougginsperg, *Annalen*, 1843, **45**, 132; Muspratt, *ibid.*, 1844, **50**, 259; Scutari and Manzoni, *Gazzetta*, 1884, **14**, 360; Seubert and Eltern, *Zeitsch. anorg. Chem.*, 1893, **4**, 44.

[7] Becker, *Dingl. poly. J.*, 1835, **257**, 300.

[8] Nilson and Pettersson, *Ber.*, 1880, **13**, 1459; *Compt. rend.*, 1880, **91**, 232; *cf.* Favre and Valson, *ibid.*, 1872, **75**, 803.

[9] Friederich, *Centr. Min.*, 1912, pp. 174, 207.

sided, nacreous plates. This hydrate has also been obtained in the form of tetrahedra.[1] At low temperatures the hydrate $Al_2(SO_4)_3.27H_2O$ separates in trigonal crystals ($a : c = 1 : 0·5408$). Other hydrates, with $16H_2O$, $12H_2O$, $10H_2O$, $9H_2O$, $6H_2O$, $3H_2O$, and $2H_2O$ have been described. The hydrates with $9H_2O$ and $10H_2O$ are said to be precipitated by alcohol, and to absorb water from a damp atmosphere, forming the hydrate with $18H_2O$. The hexahydrate results from the action of concentrated sulphuric acid on the hydrate with $18H_2O$;[2] the trihydrate forms regular tetrahedra.[3] The system *aluminium sulphate – water* has not yet been systematically investigated.[4]

The hydrate $Al_2(SO_4)_3.18H_2O$ is practically insoluble in alcohol. Its density is 1·69, and its specific heat (15° to 52°) is 0·353. As a white, fibrous efflorescence on shale and other rocks, this hydrate occurs as the mineral *alunogen.*

Aluminium sulphate is used in paper-making, as a mordant, and for the precipitation of sewage. The crude, very impure commercial preparations are manufactured by heating powdered, calcined china-clay or bauxite with sulphuric acid, the product being caused to solidify into blocks. When aluminium sulphate is required free from iron salts it is prepared from aluminium hydroxide, made as described previously (p. 79), and sulphuric acid. It is impossible to separate ferric sulphate from aluminium sulphate by crystallisation, although the two sulphates form neither a compound nor mixed crystals; but commercial aluminium sulphate may be freed from iron by crystallisation if the iron sulphate present is reduced to the ferrous state by hydrogen sulphide, sulphuric acid, etc.[5]

The *acid sulphate* $Al_2(SO_4)_3.H_2SO_4.3H_2O$ has been prepared by Baud, and also by Wirth; while Silberberger has described an *acid sulphate* of the composition $Al_2(SO_4)_3.3H_2SO_4.7H_2O$.[6] When aluminium sulphate is boiled with concentrated hydrochloric acid and the liquid cooled, crystals of *aluminium chlorosulphate,* $AlClSO_4.6H_2O$ are deposited, which are decomposed by water.[7]

About twenty different basic sulphates of aluminium have been described, but beyond the statement that the substance $Al_2O_3.2SO_3$ and one or two hydrates of it are probably definite compounds, practically nothing can be said about them.[8] A hydrated basic salt of the composition $Al_2O_3.SO_3.9H_2O$ occurs naturally as the mineral *websterite.*

Alums.—Aluminium sulphate forms double salts with the sulphates of *sodium, potassium, rubidium, cæsium, ammonium,* and *thallium* (thallous sulphate), of the type $\overset{I}{R}_2SO_4.Al_2(SO_4)_3.24H_2O$. These double salts are called **alums,** the salt $Cs_2SO_4.Al_2(SO_4)_3.24H_2O$, for example, being called cæsium

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[1] Gawalowski, *Chem Zentr.*, 1906, ii. 1236.

[2] Schmatolla, *Zeitsch. angew. Chem.*, 1903, **16**, 202.

[3] Boutzoureano, *Ann. Chim. Phys.*, 1889, [vi.], **18**, 289.

[4] See Kremann and Hüttinger, *Jahrb. K. K. Reichsanstalt*, 1908, **58**, 637.

[5] Wirth and Bakke, *Zeitsch. anorg. Chem.*, 1914, **87**, 47 ; *cf.* Wirth, *Zeitsch. angew. Chem.*, 1913, **26**, 81.

[6] Baud, *Compt. rend.*, 1903, **137**, 492 ; Wirth, *Zeitsch. anorg. Chem.*, 1913, **79**, 360 ; Silberberger, *Monatsh.*, 1904, **25**, 220.

[7] Recoura, *Compt. rend.*, 1902, **135**, 736.

[8] For $Al_2O_3.2SO_3$ and hydrates, see Spence, *D.R.P.*, 167,419 (1903); Kremann and Hüttinger, *loc. cit.* Other references are: Maus, *Pogg. Annalen*, 1827, **11**, 80 ; Rammelsberg, *ibid.*, 1838, **43**, 583 ; Bley, *Annalen*, 1854, **89**, 174 ; Böttinger, *ibid.*, 1888, **244** 224 ; Löwe, *J. prakt. Chem.*, 1860, **79**, 428 ; Marguerite, *Compt. rend.*, 1880, **90**, 1354 ; Athanasesco, *ibid.*, 1886, **103**, 271; Debray, *Bull. Soc. chim.*, 1867, [ii.], **7**, 9 ; Gadunier, *Chem. Zentr.*, 1895, ii. 1067; Pickering, *Trans. Chem. Soc.*, 1907, **91**, 1981.

aluminium alum, or simply *cæsium alum.*[1] All these salts are isomorphous with one another, usually crystallising in regular octahedra or combinations of the octahedron and cube. Further, isomorphous series of double sulphates of the same type, $R'_2SO_4.R'''_2(SO_4)_3.24H_2O$, are known, in which R' may, as before, be Na, K, Rb, Cs, NH_4, or Tl,[2] but in which R''' is not Al, but Ga, In, Cr, Fe, V, Co, Ti, Mn, or Rh. All these salts[3] crystallise in the regular system in crystals of octahedral habit, and, like the double aluminium sulphates, are also called *alums.* In naming one of these alums, both metals must be mentioned, the salt $Rb_2SO_4.Co_2(SO_4)_3.24H_2O$, for example, being called *rubidium cobalt alum*, while with an aluminium alum it is usual to mention only the univalent metal present. Finally, analogous and isomorphous double *selenates* are known, and called *selenium alums*; *e.g.*, the salt $Tl_2SeO_4.Cr_2(SeO_4)_3.24H_2O$ is called *thallium chromium selenium alum*; and *mixed alums*, in which one component salt is a sulphate and the other a selenate, have also been prepared.[4]

The alums are described in this series of text-books under the heading of the tervalent metals present. Hence only the aluminium alums are described in this chapter.

The alums are readily prepared in the crystalline form by allowing aqueous solutions of the requisite sulphates, mixed in the ratio of their molecular weights, to evaporate slowly at the ordinary temperature. The crystals which then separate almost invariably possess an octahedral habit, but in the presence of small quantities of foreign substances, the habit may undergo considerable modification.[5] Thus, it has long been known that below 45°, and in the presence of a trace of basic alum, potassium alum crystallises in cubes and not in octahedra.[6] Moreover, it is an old observation that sodium alum may separate out in monoclinic crystals;[7] but according to Surgunoff the monoclinic form ($a : b : c = 2{\cdot}510 : 1 : 0{\cdot}908$, $\beta = 109° \ 1'$) has the formula $Na_2SO_4.Al_2(SO_4)_3.22H_2O$ and separates from supersaturated solutions at temperatures above 20°.[8]

The densities of the aluminium alums at 18° to 20°, according to the careful determinations of Pettersson, are as follows:—[9]

Alum . .	Na	K	Rb	Cs	NH_4	Tl
Density . .	1·691	1·751	1·890	1·997	1·642	2·370

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[1] **Lithium alum** was said by Kratovanszky to be obtained from aqueous solution when crystallisation takes place below 11° C. (*Schweigger's J.*, 1828, **54**, 349). Its existence was denied by Rammelsberg (*Pharm. Centr.*, 1849, p. 106). Schreinemaker and de Waal (*Chem. Weekblad.*, 1906, **3**, 539) have shown that lithium alum does not exist at 30°. A study of the system $Li_2SO_4 - Al_2(SO_4)_3 - H_2O$ at 0° C. would probably prove of interest.

[2] The sulphates of hydroxylamine and numerous aliphatic amines also combine with the sulphates of aluminium, etc., to form alums.

[3] All the possible combinations are not known. In a small number of cases the attempted preparation has failed, and in other cases the combinations have not been tried.

[4] Gerichten, *Annalen*, 1873, **168**, 214.

[5] Weber, *Pogg. Annalen*, 1860, **109**, 379; Jannetaz, *Bull. Soc. chim.*, 1870, [ii.], **13**, 3; Lecoq de Boisbaudran, *Bull. Soc. chim.*, 1879, [ii.], **31**, 290; Weyberg, *Chem. Zentr.*, 1910, ii. 1026.

[6] Frémy and Pelouze; Leblanc; Kopp, *Annalen*, 1855, **94**, 122; Von Hauer, *Jahresber.*, 1865, p. 181; Loewel, *Ann. Chim. Phys.*, 1855, [iii.], **43**, 414; Persoz, *Ann. Chim. Phys.*, 1849, [iii.], **25**, 257; Polis, *Ber.*, 1880, **13**, 360.

[7] Soret, *Arch. Sci. phys. nat.*, 1884, [iii.], **11**, 62.

[8] Surgunoff, *Bull. Acad. Sci. Petrograd*, 1909, p. 1057; Soret suggested $23H_2O$.

[9] Pettersson, *Nova Acta Soc. Upsala*, 1873, [iii.], **9**, No. 4; *cf.* Spring, *Bull. Acad. roy. Belg.*, 1883, [iii.], **6**, 507.

while the refractive indices for the D-line are given by Soret[1] as follows:—

Na	K	Rb	Cs	NH_4	Tl
1·4388	1·4564	1·4566	1·4586	1·4594	1·4975

The solubilities of the alums[2] are given in the accompanying table:—[3]

Temperature ° C.	Sodium.		Potassium.		Rubidium.		Cæsium.		Ammonium.		Thallium.	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
0	...	...	3·0	5·65	0·72	1·21	0·21	0·34	2·1	3·9	3·15	4·84
5	...	...	3·5	6·62	0·86	1·48	0·25	0·40	3·5	6·9	3·80	5·86
10	36·7	103·1	4·0	7·60	1·05	1·81	0·30	0·49	5·0	9·5	4·60	7·12
15	38·7	111·3	5·0	9·59	1·28	2·20	0·35	0·57	6·3	12·7	...	...
20	40·9	121·4	5·9	11·40	1·50	2·59	0·40	0·65	7·7	15·1	6·40	10·00
25	41·3	131·8	7·23	14·14	1·80	3·12	0·50	0·81	9·2	19·2	7·60	11·95
30	45·8	146·3	8·39	16·58	2·20	3·82	0·60	0·97	10·9	22·0	9·38	14·89
40	...	...	11·70	23·83	3·25	5·69	0·85	1·38	14·9	30·9	14·40	23·57
50	...	...	17·00	36·40	4·80	8·50	1·30	2·11	20·1	44·1	22·50	38·41
60	...	...	24·75	57·35	7·40	13·36	2·00	3·27	26·7	66·7	35·36	65·19
70	...	...	40·0	110·5	12·40	23·25	3·20	5·27	...	...	...	...
80	...	...	71·0	321·3	21·60	43·25	5·40	9·01	...	...	...	...
90	...	...	109·0	2275·0	...	...	10·50	18·11	...	...	...	...
92·5	...	...	119·0	∞	...	...	...	...	...	...	...	...
95	...	...	...	...	...	...	...	...	109·7	∞	...	...
100	...	...	...	...	...	...	22·70	42·54	...	...	...	...

It will be noticed that rubidium and cæsium alums are only sparingly soluble in water. The alums are insoluble in alcohol. They melt in their water of crystallisation at the following temperatures (Locke):—

Alum . .	Na	K	Rb	Cs	NH_4	Tl
Temp. ° C. .	63°	91°	109°	122°	95°	91°

The alums are completely dehydrated at 200°; information concerning lower hydrates is not very definite.[4] The porous mass obtained by dehydrating potassium alum is called burnt alum, and dissolves slowly but completely in water. The ignition of pure ammonium alum leaves a residue of pure alumina, which is conveniently prepared in this manner.

Aqueous solutions of the alums have an acid reaction and in dilute

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[1] Soret, *Arch. Sci. phys. nat.*, 1884, [iii.], **12**, 553; see also *ibid.*, 1885, [iii.], **13**, 5; **14**, 96; 1888, **20**, 520.

[2] A = grams anhydrous salt per 100 grams water; B = grams crystalline, hydrated salt per 100 grams (extra) water. The solubility of ammonium alum is in need of redetermination.

[3] Poggiale, *Ann. Chim. Phys.*, 1843, [iii.], **8**, 467; Setterberg, *Annalen*, 1882, **211**, 104; Locke, *Amer. Chem. J.*, 1901, **26**, 166; Marino, *Gazzetta*, 1905, **35**, ii. 351; Earl of Berkeley, *Phil. Trans.*, 1904, **A**, **203**, 189; W. R. Smith, *J. Amer. Chem. Soc.*, 1909, **31**, 245; Wadmore, *Proc. Chem. Soc.*, 1905, **21**, 150; Hart and Huselton, *J. Amer. Chem. Soc.*, 1914, **36**, 2082; Seidell, *Solubilities* (Crosby, Lockwood & Son, 1907), pp. 13–15.

[4] Precht and Kraut, *Annalen*, 1875, **177**, 144; Lescœur and Mathurin, *Bull. Soc. chim.*, 1888, [ii.], **50**, 33; Maumené, *ibid.*, 1886, [ii.], **46**, 261, 807; Boissieu, *ibid.*, 1887, [ii.], **47**, 494; Naumann, *Ber.*, 1875, **8**, 1630; 1877, **10**, 457; Muller-Erzbach, *Ber.*, 1888, **21**, 2222; 1889, **22**, 3181; Lupton, *Chem. News*, 1874, **30**, 272; Favre and Valson, *Compt. rend.*, 1872, **75**, 803; Locke, *vide supra*; Earl of Berkeley, *vide supra*.

solution behave as would be expected of solutions of mixed sulphates which did not interact to any appreciable extent to produce complexes.[1]

Sodium alum, $Na_2SO_4.Al_2(SO_4)_3.24H_2O$.—The existence of this alum, occasionally denied, has been proved by Wadmore and by W. R. Smith.[2] The alum is extremely soluble in water. Several methods of preparation have been patented.[3] Sodium alum occurs as the mineral *mendozite* in South America and Japan.[4]

Potassium alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$.—This alum is an article of commerce, being used as a mordant, in the production of other aluminium mordants, in the manufacture of lake pigments, in dressing skins to produce white leather, in sizing paper, and in the production of fire-proofing materials. To a small extent it occurs naturally, and it is manufactured from aluminium sulphate (prepared from bauxite or china-clay) and potassium sulphate, from alum-rock and from alum-shale.

Natural potassium alum occurs as fibrous crystals or as an efflorescence on aluminous minerals at Whitby, Campsie, etc. At Solfatara, near Naples, and in the islands of Volcano and Milo it occurs in some quantity, and when twice recrystallised from water furnishes very good alum.

The manufacture of alum from alum-rock or *alunite* is an industry which dates from very early times. It was introduced into Europe in the thirteenth century, and several alum works were established during the fifteenth century, notably the celebrated works at La Tolfa near Civita Vecchia. In this district the manufacture of the so-called Roman alum is still an important industry, and the alum prepared there has always been highly valued on account of its purity. *Alunite* may be regarded as a double salt of potassium sulphate and a basic aluminium sulphate, $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$. It is a mineral which occurs in large quantities at La Tolfa, in Hungary, at Puy-de-Sancy and Madria in Auvergne, and in numerous other localities, having been formed by the action of volcanic gases upon felspathic trachyte. In the modern process, alunite is calcined at 500° to 1000° and the product treated with sulphuric acid. A solution is thus obtained which deposits alum when crystallised, leaving an excess of aluminium sulphate in the mother liquors. It is usual, therefore, before crystallisation, to add sufficient potassium sulphate to enable all the aluminium sulphate present to be converted into alum.

The production of alum from alum-shale, an industry of great antiquity, is at the present time only of slight commercial importance. *Alum-shale* is a kind of shale or slate containing iron pyrites disseminated throughout its mass in a very finely divided state. On prolonged exposure to the weather the pyrites undergoes oxidation and the sulphuric acid produced attacks the clay. The weathered product, when leached with water, gives a solution containing aluminium sulphate and other substances. It was known to Agricola and Libavius that this solution would not crystallise well unless an alkali had been added to it, and each of these writers describes the early practice of

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[1] Graham, *Annalen*, 1851, **77**, 56; Marignac, *Ann. Chim. Phys.*, 1874, [v.], **2**, 546; Rudorff, *Ber.*, 1888, **21**, 4; Gerlach, *Zeitsch. anal. Chem.*, 1889, **28**, 485; Jones and Mackay, *Amer. Chem. J.*, 1897, **19**, 83; Parsons and Evans, *J. Amer. Chem. Soc.*, 1910, **32**, 1378.

[2] Wadmore, *Proc. Chem. Soc.*, 1905, **21**, 150; W. R. Smith, *J. Amer. Chem. Soc.*, 1909, **31**, 245.

[3] *Eng. Pat.*, 5650 (1881); 5644 (1900); *D.R.P.*, 50,323; 141,670.

[4] Divers, *Chem. News*, 1881, **44**, 218.

adding decomposed urine to the solution to facilitate its crystallisation. Hence the alum prepared must have been mainly ammonium alum. Later, the urine was replaced by potash in the manufacture of alum. The fact that alum contains two bases, alumina and potash, was discovered by Marggraf and emphasised by Lavoisier, but was not generally accepted until 1797, when Chaptal and Vanquelin showed that potash was an essential constituent of ordinary alum, but could be replaced by ammonia, and that alum could be prepared from alunite without the addition of potash because potash was already present in the mineral. It should be mentioned that the presence of potash in alum was known to Bergman and Scheele, but they looked upon it only as an impurity.[1]

The alum-shales at Whitby have been largely worked for alum since the time of Queen Elizabeth, though not worked at the present time. The shales found in the West Riding of Yorkshire, however, are still utilised to a small extent. Unless sufficiently bituminous, the shales are mixed with fuel and slowly roasted; but some shales contain sufficient carbonaceous matter to render the addition of fuel unnecessary. The roasting lasts for ten days, and the temperature never reaches a red heat. The product, which is light red, soft, and porous, is treated with sulphuric acid (density, 1·35) at 110° in lead-lined vessels. The solution of impure aluminium sulphate thus obtained is mixed with potassium sulphate and rapidly cooled with stirring to produce small crystals of "alum meal." The meal is drained, washed with mother liquor from "block alum," dissolved to form a hot, saturated solution, and treated in leaden vessels with a little size, which precipitates a quantity of insoluble matter. The clear solution is then run into tubs fitted with movable, lead-lined staves. After several days the staves are removed and a hole is bored in each mass of "block alum" to allow the mother liquor to drain away. The "block alum" when broken up is ready for the market. When shale is employed containing much iron, it is the custom to add potassium chloride, either alone or mixed with sulphate, instead of adding potassium sulphate to the solution of aluminium sulphate. By this means contamination of the alum with isomorphous iron alum is prevented, the iron remaining behind in solution as ferric chloride.[2]

Potassium alum becomes white and opaque on the surface when exposed to the air, a change brought about by the absorption of ammonia and formation of a basic salt. When dried over sulphuric acid or heated to 61°, alum loses 18 molecules of water of crystallisation.

When an alkali is slowly added to a solution of alum, a precipitate is produced which redissolves on stirring until a certain amount of alkali has been added, after which the further addition of alkali leads to the production of a permanent precipitate. The solution which is on the point of yielding a permanent precipitate is known in commerce as *neutral alum*, and is used in dyeing, since it readily gives up alumina to the colouring matter. When heated to 40°, a precipitate is produced the composition of which may be represented by the formula $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$, *i.e.* it is identical in composition with *alunite*. The precipitate may be obtained in the crystalline form by heating the solution in a sealed tube to 230°.

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[1] Roscoe and Schorlemmer, *A Treatise on Chemistry* (Macmillan & Co., 3rd ed., 1907), vol. ii. p. 720.

[2] Further details of the manufacture of alum will be found in Thorpe, *A Dictionary of Applied Chemistry* (Longmans & Co., 2nd ed., 1912-13), vol. i., article "Aluminium."

Crystals of alum having a cubic habit are obtained by the crystallisation of an aqueous solution of the salt to which a little alkali has been added (p. 82). A study of the crystallisation of alum from hydrochloric acid solutions of different concentrations, and at various temperatures, has shown that alum crystals occasionally exhibit the faces of the pentagonal dodecahedron (210).[1]

Potassium aluminium sulphate octahydrate, $K_2SO_4.Al_2(SO_4)_3.8H_2O$, separates in slender crystals when alum is melted in its water of crystallisation and the fused mass maintained at about 86°. Analogous salts are known containing indium, thallium, and the rare earth metals in the place of aluminium.[2]

Rubidium alum,[3] $Rb_2SO_4.Al_2(SO_4)_3.24H_2O$, and **cæsium alum**,[4] $Cs_2SO_4.Al_2(SO_4)_3.24H_2O$, have been prepared by several chemists.

Ammonium alum, $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$, was formerly manufactured in England to a very large extent, but at the present time it is mainly the potassium salt that is prepared. Commercial alum is often a mixture of potassium and ammonium alums.[5]

Ammonium aluminium sulphate octahydrate, $(NH_4)_2SO_4.Al_2(SO_4)_3.8H_2O$, may be prepared like the corresponding potassium salt (Marino), or by seeding a supersaturated solution of ammonium alum with a crystal of the corresponding thallic salt, $(NH_4)_2SO_4.Tl_2(SO_4)_3.8H_2O$.[6]

Hydroxylamine alum, $(NH_3.OH)_2.SO_4.Al_2(SO_4)_3.24H_2O$, has also been prepared.[7]

Silver alum, $Ag_2SO_4.Al_2(SO_4)_3.24H_2O$, is said to be prepared by heating silver sulphate and aluminium sulphate, together with a little water, in a sealed tube, and allowing the solution to cool.[8] The existence of this alum is denied by Retgers.

Pseudo-alums.—A number of double sulphates of the type $R^{II}SO_4.Al_2(SO_4)_3.24H_2O$ have been described, namely the Fe, Zn, Mg, and Mn salts. They are called pseudo-alums, and are not isomorphous with ordinary alum. Very little is known concerning these salts, which require to be reinvestigated.[9]

Aluminium dithionate, $Al_2(S_2O_6)_3.18H_2O$, forms deliquescent plates, soluble in water and in alcohol. A double salt, $Al_2(S_2O_6)_3.(NH_4)_2S_2O_6.27H_2O$, is also known.[10]

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[1] Zemjatschensky, *Zeitsch. Kryst. Min.*, 1913, **52**, 604; see also Schubnikow, *Bull. Acad. Sci. Petrograd*, 1913, p. 817; Weber, *Pogg. Annalen*, 1860, **109**, 379; Lecoq de Boisbaudran, *Compt. rend.*, 1879, **88**, 360; L. Wulff, *Zeitsch. Kryst. Min.*, 1881, **5**, 81; N. S. Kurnakoff, *ibid.*, 1881, **5**, 591.

[2] Marino, *Gazzetta*, 1905, **35**, ii. 341.

[3] Bunsen, *Pogg. Annalen*, 1863, **119**, 1; Redtenbacher, *J. prakt. Chem.*, 1865, **94**, 442; Pettersson, *Ber.*, 1876, **9**, 1561; Tilden, *Trans. Chem. Soc.*, 1884, **45**, 266; Setterberg, *Annalen*, 1882, **211**, 100; Locke, *Amer. Chem. J.*, 1901, **26**, 166; Earl of Berkeley, *Phil. Trans.*, 1904, **A**, **203**, 189.

[4] The references cited in the preceding footnote, and Hart and Huselton, *J. Amer. Chem. Soc.*, 1914, **36**, 2082.

[5] For basic ammonium aluminium sulphates, see Maus, *Pogg. Annalen*, 1827, **11**, 81; Riffaut, *Ann. Chim. Phys.*, 1821, **16**, 359; Stolba, *J. prakt. Chem.*, 1864, **93**, 117.

[6] Piccini and Fortini, *Zeitsch. anorg. Chem.*, 1902, **31**, 451.

[7] Meyeringh, *Ber.*, 1877, **10**, 1946.

[8] Church and Northcote, *Chem. News*, 1864, **9**, 155.

[9] Klauer, *Annalen*, 1835, **14**, 261; Rammelsberg, *Pogg. Annalen*, 1838, **43**, 399; Apjohn, *ibid.*, 1838, **44**, 472; *Proc. Roy. Irish Acad.* 1839, **1**, 51.

[10] Klüss, *Annalen*, 1888, **246**, 179, 284.

Aluminium selenite, $Al_2(SeO_3)_3.7H_2O$, is produced by treating the basic selenite obtained from aluminium sulphate and sodium selenite with a dilute solution of selenious acid. It is sparingly soluble in water. Two acid selenites of the formulæ $2Al_2(SeO_3)_3.3H_2SeO_3.9H_2O$ and $Al_2(SeO_3)_3.3H_2SeO_3.2H_2O$ have also been described.[1]

Aluminium selenate, $Al_2(SeO_4)_3$, is formed by dissolving aluminium hydroxide in selenic acid and heating to expel the excess of acid. It is soluble in water, but no hydrates have been described.

Aluminium selenate forms double selenates with the selenates of sodium, potassium, rubidium, cæsium, ammonium, and thallium the formulæ of which are of the type $R^{I}_2SeO_4.Al_2(SeO_4)_3.24H_2O$, *i.e.* they are *selenium alums* (p. 82). They have been examined by various chemists.[2] The densities of the selenium alums are as follows (Pettersson):—

Alum . .	Na	K	Rb	Cs	NH_4	Tl
Density .	2·067	2·204	2·134	2·224	1·890	2·503

Aluminium chromate.—A yellow, flocculent precipitate of *basic aluminium chromate,* $Al_2O_3.CrO_3.7H_2O$, is produced by adding potassium chromate to a solution of alum.[3]

Aluminium molybdate.—A white, amorphous precipitate of the composition $5Al_2O_3.2MoO_3.xH_2O$ is obtained by adding sodium molybdate, Na_2MoO_4, to a solution of alum. The double salts $Al_2(Mo_2O_7)_3.3X_2Mo_2O_7$, where X is Na, K, or NH_4, are known and possess 22, 20, and 20 molecules of water of crystallisation respectively.[4]

Aluminium silicomolybdate, $2Al_2O_3.(SiO_2.12MoO_3)_3.93H_2O$, crystallises in yellow, regular octahedra, isomorphous with the corresponding silicotungstate.[5]

Aluminium tungstate, $Al_2W_7O_{21}.9H_2O$, is obtained as a white, flocculent precipitate by adding a solution of the corresponding sodium tungstate to an aqueous solution of an aluminium salt.[6]

Aluminium silicotungstate.—This compound is extremely soluble in water and three hydrates are known. The hydrate $2Al_2O_3(SiO_2.12WO_3)_3.93H_2O$ crystallises in regular octahedra; the hydrate with $87H_2O$ crystallises in rhombohedra ($a : c = 1 : 2·6653$); and the hydrate with $60H_2O$ forms triclinic crystals ($a : b : c = 0·8563 : 1 : 1·0658$; $\alpha = 87° 44'$, $\beta = 105° 11'$, $\gamma = 91° 48'$). The first two salts are therefore isomorphous with the corresponding gallium salts (see p. 148).[7]

Aluminium phosphotungstate, $Al_2O_3.P_2O_5.18WO_3$, has been described by Kehrmann.[8]

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[1] Nilson, *Nova Acta Soc. Upsala*, 1875, [iii.], **9**, No. 7 ; *Ber.*, 1875, **8**, 655 ; *Bull. Soc. chim.*, 1875, [ii.], **23**, 494.

[2] Weber, *Pogg. Annalen*, 1859, **108**, 615 ; Wohlwill, *Annalen*, 1860, **114**, 180; Pettersson, *Ber.*, 1876, **9**, 1563 ; *Nova Acta Soc. Upsala*, 1873, [iii.], **9**, No. 4 ; Fabre, *Compt. rend.*, 1887, **105**, 114.

[3] Fairrie, *Quart. J. Chem. Soc.*, 1852, **4**, 301 ; Elliot and Storer, *Proc. Amer. Acad.*, 1862, **5**, 192.

[4] Struve, *J. prakt. Chem.*, 1854, **61**, 459 ; Gentele, *ibid.*, 1860, **81**, 414 ; Parmentier, *Compt. rend.*, 1882, **94**, 1713.

[5] Copaux, *Ann. Chim. Phys*, 1906, [viii.], **7**, 118.

[6] Lotz, *Annalen*, 1852, **83**, 65 ; Anthon, *J. prakt. Chem.*, 1836, **8**, 399 ; 1836, **9**, 337.

[7] Wyrouboff, *Bull. Soc. franç. Min.*, 1896, **19**, 219 ; 1905, **28**, 237.

[8] Kehrmann, *Zeitsch. anorg. Chem.*, 1892, **1**, 421.

ALUMINIUM AND THE NITROGEN GROUP.

Aluminium nitride, AlN.—This compound, discovered by Mallet,[1] may be prepared by heating finely divided aluminium in nitrogen at 820° to 1000°, powdering the product, and reheating in the gas once or twice.[2] It is produced when aluminium is heated to 700° in ammonia,[3] and is manufactured by heating a mixture of alumina and carbon in a current of nitrogen:—

$$Al_2O_3 + 3C + N_2 \rightleftharpoons 2AlN + 3CO.$$

In Serpek's process, a mixture of crushed alumina or bauxite and carbon travels down an inclined rotary kiln, drops into a hopper, and is fed into another rotary kiln, a short length of which is maintained at 1500° to 1800°. Producer gas passing up to the kiln supplies the requisite nitrogen. The carbon monoxide produced is burned and the hot gases blown up the first kiln to preheat the initial charge.[4]

As usually prepared, aluminium nitride forms a grey, amorphous solid. It begins to sublime, with partial dissociation into its elements, at *c.* 1900° C.; the vapour condenses to colourless, hexagonal needles. It is decomposed by water, slowly at 0°, rapidly at 100°, aluminium hydroxide and ammonia being produced; consequently it dissolves readily in alkali hydroxides.

Aluminium phosphide, AlP, prepared from a mixture of aluminium powder and red phosphorus by the thermit reaction,[5] is a friable, yellow solid which is decomposed by water with the evolution of phosphine. The phosphides Al_3P_7, Al_5P_3, and Al_2P have been described.[6]

Aluminium arsenide, AlAs, prepared like the phosphide, is a grey, friable solid, decomposed by water with the evolution of arsine.[7]

Aluminium nitrate, $Al(NO_3)_3.9H_2O$, is prepared by dissolving aluminium in nitric acid of density 1·42 and crystallising the solution. It is dimorphous,[8] crystallising in flat, orthorhombic crystals ($a : b : c = 0{\cdot}8925 : 1 : 1{\cdot}0202$) or in monoclinic prisms ($a : b : c = 1{\cdot}1340 : 1 : 1{\cdot}9191$, $\beta = 131°\ 36'$) isomorphous with the corresponding ferric salt.[9] It melts at *c.* 70°, and at 140° is completely decomposed, amorphous aluminium hydroxide being left.[10] The aqueous solution when heated deposits basic salts.[11]

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[1] Mallet, *Trans. Chem. Soc.*, 1876, ii. 349.

[2] Fichter, *Zeitsch. anorg. Chem*, 1907, **54**, 322; *Arch. Sci. phys. nat.*, 1913, [iv.], **35**, 369; Fichter and Spengel. *Zeitsch. anorg. Chem.*, 1913, **82**, 192; Wolk, *Compt. rend.*, 1910, **151**, 318; Serpek, *ibid.*, 1910, **150**, 1520; Arons, *Chem. Zentr.*, 1899, ii. 643; J. Wolf, *Zeitsch. anorg. Chem.*, 1913, **82**, 192; 1914, **87**, 120; Russ, *Zeitsch. Elektrochem.*, 1913, **19**, 923; Fichter and Oesterheld, *ibid.*, 1915, **21**, 50.

[3] White and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, **28**, 1343; Sofianopoulos, *Bull. Soc. chim.*, 1909, [iv.], **5**, 614; see also Matignon, *Compt. rend.*, 1900, **130**, 1390; Franck and Rossel, *ibid.*, 1895, **121**, 941.

[4] See Dony-Hénault, Gall, and Guye, *Principes et applications de l'electrochimie* (Paris and Liege, 1914), p. 550; Knox, *Fixation of Atmospheric Nitrogen* (Gurney and Jackson, 1914); J. W. Richards, *Trans. Amer. Electrochem. Soc.*, 1913, **23**, 351; *J. Ind. Eng. Chem.*, 1913, **5**, 335; Tucker and Read, *Trans. Amer. Electrochem. Soc.*, 1912, **22**, 57; *Met. Chem. Eng.*, 1912, **10**, 745; Fraenkel, *Zeitsch. Elektrochem*, 1913, **19**, 362; Fraenkel, Askenasy, and Silbermann, *Chem. Zeit.*, 1913, **37**, 334.

[5] Fonzes-Diacon, *Compt. rend.*, 1900, **130**, 1314; Matignon, *ibid.*, 1900, **130**, 1390.

[6] Franck, *Chem. Zeit.*, 1898. **22**, 236.

[7] Fonzes-Diacon, *loc. cit.*

[8] Soret, *Arch Sci. phys. nat.*, 1885, [iii.], **16**, 460; Eakle, *Zeitsch. Kryst. Min.*, 1896, **26**, 558.

[9] Surgunoff, *Bull. Acad. Sci. Petrograd*, 1913, p. 407.

[10] Deville, *J. prakt. Chem.*, 1853, **60**, 9; *Ann. Chim. Phys.*, 1853, [iii.], **38**, 5.

[11] Schlumberger, *Bull. Soc. chim.*, 1895, [iii.], **13**, 48; Ordway, *Jahresber.*, 1858, p. 111.

At the ordinary temperature nitric acid of density 1·5 transforms the ennea-hydrate into the hexahydrate, $Al(NO_3)_3.6H_2O$, which is then the stable phase. The hexahydrate often separates from its solution in nitric acid of density 1·42, but it is then metastable with respect to the ennea-hydrate.[1] The transformation from hexa- to ennea-hydrate can be made to proceed in two stages, an intermediate hydrate, $2Al(NO_3)_3.15H_2O$ (or $16H_2O$?), being formed.[1, 2] Ditte[3] has described a dihydrate, $Al(NO_3)_3.2H_2O$.

Aluminium Phosphates.—The anhydrous and hydrated ortho-, meta-, and pyro-phosphates of aluminium are insoluble in water. Anhydrous **aluminium orthophosphate,** $AlPO_4$, formed by heating sodium aluminate and phosphoric acid in a sealed tube at 250°, forms colourless, hexagonal prisms of specific gravity 2·59.[4] The hydrated orthophosphate is obtained as a gelatinous precipitate by mixing sodium phosphate and neutral aluminium sulphate solutions. It is soluble in ammonia, alkali hydroxides, and mineral acids, but insoluble in acetic acid.[5]

When a solution of aluminium phosphate in an acid is precipitated with ammonia, a *basic aluminium phosphate* is obtained. Several basic aluminium phosphates occur in nature, *e.g.* the rhombic mineral *wavellite*, $3Al_2O_3.2P_2O_5.12H_2O$, and *turquoise*. Turquoise (or *calaite*) is a basic, hydrated aluminium, copper, and ferrous phosphate. It is triclinic,[6] has a sky-blue to greenish colour, and is used as a gem-stone. It occurs in Persia, Nevada, Arizona, California, and Colorado.

Basic aluminium arsenite, $Al_2O_3.As_2O_3$, and **aluminium orthoarsenate,** $AlAsO_4$, have been described.[7]

ALUMINIUM AND THE CARBON GROUP.

Aluminium carbide, Al_4C_3, is prepared by heating fragments of aluminium with sugar carbon in a carbon crucible in the electric furnace and rapidly cooling the product.[8] It may also be prepared by heating a mixture of aluminium powder and carbon for twenty minutes in a Perrot furnace or over the blowpipe; or the reaction may be started by inflaming a mixture of aluminium powder and barium peroxide on the surface. Aluminium carbide is also produced by heating aluminium with hexachlor-

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[1] Seligman and Williams, *Trans. Chem. Soc.*, 1916, **109**, 612.

[2] Salm-Horstmar, *Jahresber.*, 1850, p. 301; Jovitschitsch, *Monatsh.*, 1912, **33**, 9.

[3] Ditte, *Compt. rend.*, 1879, **89**, 643.

[4] De Schulten, *Compt. rend.*, 1881, **98**, 1583.

[5] Rammelsberg, *J. prakt. Chem.*, 1863, **89**, 116; Wittstein and Millot, *Compt. rend.*, 1876, **82**, 89; Erlenmeyer, *Annalen*, 1878, **194**, 196; Schweitzer, *Ber.*, 1870, **3**, 310; Caven and Hill, *J. Soc. Chem. Ind.*, 1897, **16**, 29. For *pyrophosphate*, see Hautefeuille and Margottet, *Compt. rend.*, 1883, **96**, 1052, 1142, 1849; Wittstein and Millot, *loc. cit.*; Rose, *Pogg. Annalen*, 1849, **76**, 16; Schwarzenberg, *Jahresber.*, 1847, p. 348. For *metaphosphate*, see Madrell, *Annalen*, 1847, **61**, 59; Margottet and Hautefeuille, *Compt. rend.*, 1888, **106**, 135; Johnson, *Ber.*, 1889, **22**, 976; Warschauer, *Zeitsch. anorg. Chem.*, 1903, **36**, 137. For *acid phosphates*, see Erlenmeyer, *loc. cit.* For *basic phosphates*, see Wittstein and Millot, *loc. cit.*; Rammelsberg, *Pogg. Annalen*, 1845, **64**, 407; Munroe, *Annalen*, 1871, **159**, 278. For *thiophosphates*, see Friedel, *Bull. Soc. chim.*, 1894, [iii.], **11**, 1057; Ferrand, *Compt. rend.*, 1896, **122**, 886.

[6] Schaller, *J. Washington Acad. Sci.*, 1911, **1**, 58.

[7] Reichard, *Ber.*, 1894, **27**, 1019; Coloriano, *Compt. rend.*, 1886, **103**, 273.

[8] Moissan, *Compt. rend.*, 1894, **119**, 16; Pring, *Trans. Chem. Soc.*, 1905, **87**, 1530; Askenasy, Jarkowsky, and Waniezek, *Zeitsch. Elektrochem.*, 1908, **14**, 811.

benzene at 225°.[1] According to Pring, the production of the carbide in the electric furnace is apparently due to the reaction:—

$$6Al + 3CO \rightleftharpoons Al_4C_3 + Al_2O_3,$$

but the elements aluminium and carbon can unite directly, the combination *in vacuo* becoming perceptible at 650° and rapid at 1400°.[2]

Aluminium carbide, purified by washing with a cold, concentrated solution of potassium hydroxide, and then with alcohol and ether, forms yellow, rhombohedral crystals[3] of density at 2·36. At temperatures between 400° and 1400° aluminium carbide is stable *in vacuo*; but above 1400° it dissociates at an appreciable rate, and at 1800° the change is rapid. Accordingly, at high temperatures alumina is reduced by carbon with the formation of much free aluminium, while at lower temperatures aluminium carbide only is produced.[4] At temperatures below 1400° aluminium carbide acts as a reducing agent on metallic oxides, *e.g.*:—

$$Al_4C_3 + 12CuO = 12Cu + 3CO_2 + 2Al_2O_3,$$

but at higher temperatures alloys are produced, the carbon only being oxidised. With metallic chlorides it yields organometallic compounds.[5]

Aluminium carbide is slowly but completely decomposed by water, aluminium hydroxide and methane being produced:—[6]

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4.$$

Aluminium carbonate.—The composition of the precipitate obtained from solutions of an aluminium salt and an alkali carbonate varies with the concentrations of the reagents, nature of the aluminium salt, temperature of precipitation, etc. The normal carbonate is never obtained, the precipitates being composed largely of aluminium hydroxide, with smaller quantities of aluminium carbonate, basic aluminium salts, and alkali carbonate.[7]

Aluminium thiocyanate, $Al(CNS)_3$, is a soluble salt, used in dyeing.[8]

When solutions of the requisite alkali thiocyanates are evaporated at the ordinary temperature, double salts of the type $M_3Al(CNS)_6.4H_2O$ (where M is K, Na, or NH_4) are obtained as colourless, deliquescent crystals.[9]

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[1] Matignon, *Ann. Chim. Phys.*, 1908, [viii.], **13**, 276; *Compt. rend.*, 1907, **145**, 676; Weston and Ellis, *Trans. Faraday Soc.*, 1908, **4**, 60; *cf.* Franck, *Bull. Soc. chim.*, 1894, [iii.], **11**, 439; Guntz and Masson, *ibid.*, 1897, [iii.], **17**, 209; Dufau, *Compt. rend.*, 1900, **131**, 541.

[2] Pring, *Trans. Chem. Soc.*, 1908, **93**, 2107.

[3] De Schulten, *Compt. rend.*, 1911, **152**, 1107.

[4] Askenasy and Lebedeff, *Zeitsch. Elektrochem.*, 1910, **16**, 559.

[5] Hilpert, Ditmar, and Grüttner, *Ber.*, 1913, **46**, 3738.

[6] Moissan, *loc. cit.*; E. Hauser, *Anal. Fis. Quim.*, 1913, **11**, 317.

[7] Bley, *J. prakt. Chem.*, 1846, **39**, 1; Rose, *Pogg. Annalen*, 1854, **91**, 452; Muspratt, *Annalen*, 1849, **72**, 120; Langlois, *Ann. Chim. Phys.*, 1856, [iii.], **48**, 502; Parkman, *Amer. J. Sci.*, 1862, [ii.], **34**, 324; Barth, *ibid.*, 1880, **202**, 372; Urbain and Reboul, *J. Pharm. Chim.*, 1879, [iv.], **30**, 340; Seubert and Eltern, *Zeitsch. anorg. Chem.*, 1893, **4**, 44; Day, *Amer. Chem. J.*, 1898, **19**, 707; Gawalowski, *Chem. Zentr.*, 1906, i. 640; Jourdain, *Compt. rend.*, 1910, **150**, 1602.

[8] Liechti and Suida, *J. Soc. Chem. Ind.*, 1883, **2**, 589; Hauff, *Ber.*, 1888, **21**, 327; Lauber and Haussmann, *Dingl. Poly. J.*, 1882, **245**, 306; G. Stein, *ibid.*, 1883, **250**, 36.

[9] Rosenheim and Cohn, *Ber.*, 1900, **33**, 1111. For *alkali aluminium ferrocyanides*, see Robinson, *Trans. Chem. Soc.*, 1909, **95**, 1353.

Aluminium oxalate, $Al_2(C_2O_4)_3.H_2O$, is precipitated when aqueous solutions of an aluminium salt and an alkali oxalate are mixed. It is soluble in oxalic acid.

When aluminium hydroxide is dissolved in hot, concentrated aqueous solutions of the alkali acid oxalates and the solutions allowed to cool, crystalline *double* or *complex oxalates* are obtained of the type $M^I_3Al(C_2O_4)_3.xH_2O$. The salts are very similar to the corresponding chromic, ferric, and cobaltic double oxalates, and salts having the same number of molecules of water of crystallisation are isomorphous. The salts $M^I_3M^{III}.(C_2O_4)_3.3H_2O$, for instance, are all monoclinic:—

		a		*b*		*c*		*β*
K.Al	salt	0·9994	:	1	:	0·3951	;	92° 51′
Rb.Al	,,	1·0188	:	1	:	0·4049	;	95° 2′
NH_4.Al	,,	0·9971	:	1	:	0·3915	;	92° 26′
Tl.Al	,,	0·9730	:	1	:	0·4128	;	93° 39′
K.Cr	,,	1·0060	:	1	:	1·3989	;	94° 0′
Rb.Cr	,,	1·0221	:	1	:	0·3963	;	92° 25′
NH_4.Cr	,,	0·9830	:	1	:	0·3870	;	95° 18′
K.Fe	,,	0·9918	:	1	:	0·3896	;	94° 15′
Rb.Fe	,,	1·0106	:	1	:	0·4004	;	95° 12′
NH_4.Fe	,,	0·9959	:	1	:	0·3932	;	92° 15′
Tl.Fe	,,	0·9601	:	1	:	0·4115	;	94° 5′
NH_4.Co	,,	1·0017	:	1	:	0·3929	;	92° 44′

The following are also isomorphous groups of salts:—[1]

$Na_3Al(C_2O_4)_3.5H_2O$
$Na_3Cr(C_2O_4)_3.5H_2O$
$Na_3Fe(C_2O_4)_3.5H_2O$
$Na_3Co(C_2O_4)_3.5H_2O$
(monoclinic)

$Li_3Al(C_2O_4)_3.6H_2O$
$Li_3Cr(C_2O_4)_3.6H_2O$
$Li_3Co(C_2O_4)_3.6H_2O$
(triclinic)
...

$Na_3(NH_4)_3Al_2(C_2O_4)_6.7H_2O$
$Na_3Rb_3Cr_2(C_2O_4)_6.7H_2O$
$Na_3(NH_4)_3Cr_2(C_2O_4)_6.7H_2O$
$Na_3(NH_4)_3Fe_2(C_2O_4)_6.7H_2O$
(monoclinic)

Aluminium alkyls.—These compounds may be prepared by heating mercury alkyls with aluminium in a sealed tube at 100°. They are colourless liquids which are decomposed by water.[2]

Aluminium methyl, $Al(CH_3)_3$, freezes at *c.* 0° and boils at 140°. **Aluminium ethyl,** $Al(C_2H_5)_3$, boils at 194°. **Aluminium propyl** boils at 248° to 252°. **Aluminium isobutyl** and **aluminium isoamyl** are also known.

At temperatures only slightly higher than their boiling-points, aluminium methyl and aluminium ethyl consist almost exclusively of double molecules $Al_2(CH_3)_6$ and $Al_2(C_2H_5)_6$. The vapour densities diminish rapidly with rise of temperature, but it is not possible to state definitely to what extent this diminution is to be attributed to the dissociation $Al_2(Alk.)_6 \rightleftharpoons 2Al(Alk.)_3$, since it appears probable that decomposition also commences. In ethylene

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[1] See Wyrouboff, *Bull. Soc. franç. Min.*, 1900, **23**, 65; Copaux, *Ann. Chim. Phys.*, 1905, [viii.], **6**, 568; Stortenbeker, *Rec. trav. chim.*, 1913, **63**, 121; Rosenheim and Cohn, *Zeitsch. anorg. Chem.*, 1896, **11**, 175; Rosenheim and Platsch, *ibid.*, 1899, **21**, 1; Löwenstein, *ibid.*, 1909, **63**, 121. Early references to aluminium oxalates are: Heese, *Compt. rend.*, 1845, **21**, 1116; Mathieu-Plessy, *ibid.*, 1883, **97**, 1033; Collin, *Ber.*, 1870, **2**, 315.

[2] Buckton and Odling, *Proc. Roy. Soc.*, 1865, **14**, 19; Cahours, *Ann. Chim. Phys.*, 1860, [iii.], **58**, 5; Hallwachs and Schufarik, *Annalen*, 1859, **109**, 206.

dibromide solution, aluminium ethyl has a molecular weight in harmony with the double formula.[1]

Aluminium acetylacetonate, $[(CH_3.CO)_2CH]_3Al$, is produced slowly by the action of aluminium hydroxide and rapidly by the action of anhydrous aluminium chloride on acetylacetone. It is best prepared by adding acetylacetone and ammonia to an aqueous solution of aluminium chloride;[2] it separates from its alcoholic solution in white monoclinic ($a : b : c = 1{\cdot}901 : 1 : 1{\cdot}361$; $\beta = 81^\circ\ 6'$)[3] crystals isomorphous with the corresponding ruthenium salt,[4] melts at 194°, and boils at 315°. At 360° the vapour density is 11·24 (air = 1), the simple formula given above corresponding to the value 11·18.[5] The molecular weight also corresponds with the simple formula in solution in benzene and carbon disulphate.[6]

Aluminium acetylacetonate separates from chloroform solution with two molecules of chloroform of crystallisation. It is insoluble in water and does not combine with ammonia.

Aluminium silicide.—Aluminium and silicon are completely miscible, but no definite compounds are known. The eutectic temperature is 578°.[7]

Aluminium silicates.—The silicate Al_2SiO_5, *i.e.* $Al_2O_3.SiO_2$, occurs in nature as three distinct minerals: **cyanite,** which crystallises in the triclinic system ($a : b : c = 0{\cdot}899 : 1 : 0{\cdot}709$, $\alpha = 90^\circ\ 5{\cdot}5'$, $\beta = 101^\circ\ 2'$, $\gamma = 105^\circ\ 44{\cdot}5'$), **andalusite,** which occurs in rhombic crystals ($a : b : c = 0{\cdot}986 : 1 : 0{\cdot}703$), and **sillimanite,** which is also rhombic ($a : b : c = 0{\cdot}9696 : 1 : 0{\cdot}7046$).[8] The only one of these forms of the silicate stable above 1300° is sillimanite.

Thermal investigation of the system silica-alumina shows the existence of only one aluminium silicate, viz. $Al_2O_3.SiO_2$, which separates from a fused mixture in crystals of sillimanite, melting at 1816° (fig. 15).[9]

Aluminium enters into the composition of numerous complex silicates, many of which are important rock-forming minerals. Only a very brief description of the more important of these can be given here.

The **felspars** are the most important of all rock-forming minerals. The chief felspars are *orthoclase* or potash felspar (monoclinic; $a : b : c = 0{\cdot}658 : 1 : 0{\cdot}555$; $\beta = 63^\circ\ 57'$) *albite* or soda felspar (triclinic; $a : b : c = 0{\cdot}6335 : 1 : 0{\cdot}5577$; $\alpha = 94^\circ\ 3'$, $\beta = 116^\circ\ 29'$, $\gamma = 88^\circ\ 9'$), *anorthite* or lime felspar (triclinic; $a : b : c = 0{\cdot}6347 : 1 : 0{\cdot}5501$; $\alpha = 93^\circ\ 13'$, $\beta = 115^\circ\ 55'$, $\gamma = 91^\circ\ 12'$), and the *plagioclases*, of which the minerals *oligoclase*, *andesite*, *labradorite*, and *bytownite* are examples. The chemical formulæ are $KAlSi_3O_8$ for orthoclase, $NaAlSi_3O_8$ for albite, and $CaAl_2Si_2O_8$ for anorthite. As originally supposed by Tschermak in 1864, the plagioclases are isomorphous mixtures of albite and anorthite.[10] Anorthite melts at 1550°.[11]

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[1] Buckton and Odling, *loc. cit.*; Quincke, *Ber.*, 1889, **22**, 551; Louïse and Roux, *Compt. rend.*, 1888, **106**, 73, 602; **107**, 600; V. Meyer, *Ber.*, 1888, **21**, 701; Ostwald, *Zeitsch. physikal. Chem.*, 1889, **3**, 47.

[2] W. Biltz, *Annalen*, 1904, **331**, 348.

[3] Jaeger, *Rec. trav. chim.*, 1914, **33**, 342.

[4] Barbieri, *Atti R. Accad. Lincei*, 1914, [v.], **23**, i., 334.

[5] Combes, *Compt. rend.*, 1887, **105**, 870; 1889, **108**, 405; *Bull. Soc. chim.*, 1889, [iii.], **1**, 345.

[6] Urbain and Debierne, *Compt. rend.*, 1899, **129**, 302; W. Biltz, *loc. cit.*

[7] Fraenkel, *Zeitsch. anorg. Chem.*, 1908, **58**, 154; C. E. Roberts, *Trans. Chem. Soc.*, 1914, **105**, 1383.

[8] Taubert, *Centr. Min.*, 1906, 372.

[9] Shepherd, Rankin, and Wright, *Amer. J. Sci.*, 1909, [iv.], **28**, 293; Ballo and Dittler, *Zeitsch. anorg. Chem.*, 1912, **76**, 39; Eitel, *ibid.*, 1914, **88**, 173.

[10] Day and E. T. Allen, *Amer. J. Sci.*, 1905, [iv.], **19**, 93; Dittler, *Centr. Min.*, 1909, 663; *Tsch. Min. Mitt.*, 1910, **29**, 273.

[11] Day and Sosman, *Amer. J. Sci.*, 1911, [iv.], **31**, 341.

Orthoclase is mined in large quantities for use in the manufacture of porcelain. Numerous attempts have been made to utilise this mineral as a commercial source of potash.[1] The Ceylon "moonstone," which is used as a gem, consists of orthoclase having a pale blue, pearly opalescence.

The **micas** are minerals of very common occurrence as constituents of rocks. Chemically, they are silicates of aluminium and either an alkali or iron and magnesium, and in addition they contain fluorine and water of constitution. They are monoclinic, but pseudohexagonal, and possess a highly perfect basal cleavage, which gives white mica or *muscovite* its commercial importance. Other micas are *biotite* or dark mica and *lepidolite* or lithia mica.

The **garnets** are a well-defined series of minerals of the general formula $R_3''R_2'''(SiO_4)_3$, where R'' is Ca, Mg, Fe, or Mn, and R''' is Al, Fe, or Cr. The following varieties are distinguished: *grossular* (Ca,Al), *pyrope* (Mg,Al), *spessartite* (Mn,Al), *almandine* (Fe,Al), *uvarovite* (Ca,Cr), and *andradite* (Ca,Fe). The garnets are cubic minerals, distinguished by their dodecahedral or icositetrahedral form, greasy lustre, strong refraction, and ready fusibility. Pyrope constitutes the common red garnet used in jewellery.

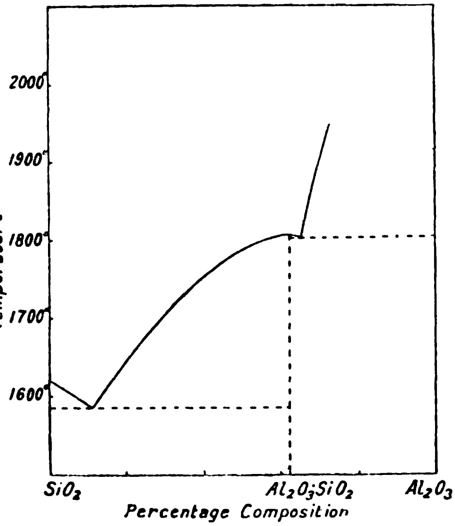

FIG. 15.—Equilibrium diagram for the system alumina - silica.

The **zeolites** are hydrated silicates of aluminium and the alkali metals (and generally of calcium as well). The following minerals are among those classed as zeolites:—

Stilbite	$CaAl_2Si_6O_{16}.6H_2O$	*Analcite*	$Na_2Al_2Si_4O_{12}.2H_2O$
Heulandite	$H_4CaAl_2Si_6O_{18}.3H_2O$	*Natrolite*	$Na_2Al_2Si_3O_{10}.2H_2O$
Chabazite	$CaAl_2Si_4O_{12}.6H_2O$	*Scolecite*	$CaAl_2Si_3O_{10}.3H_2O$

The water is very loosely held, and they intumesce before the blowpipe. With loss of water the zeolites lose their transparency, but many of them, after dehydration, can re-absorb the amount of water they originally contained, thereby regaining their transparency and original optical properties. Further, dehydrated zeolites absorb ammonia, hydrogen sulphide, alcohol, and many other vapours. The nature of these interesting minerals has therefore been the subject of numerous researches.[2]

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[1] For the literature, see Hart, *J. Ind. Eng. Chem.*, 1912, **4**, 827; also Cushman and Coggeshall, *ibid.*, 1912, **4**, 821; 1915, **7**, 145; Foote and Scholes, *ibid.*, 1912, 4, 377.

[2] Modern references are as follows: F. W. Clarke, *Proc. Washington Acad. Sci.*, 1905, **7**, 257; F. W. Clarke and Steiger, *Bull. Geol. U.S. Survey*, 1905, No. 262; Ferro, *Atti R. Accad. Lincei*, 1905, **14**, ii. 140; Zambonini, *Mem. R. Accad. Lincei*, 1905, **5**, 344; 1906, **6**, 102; *Rend. Ac., Sci. Fis. Mat. Napoli*, 1908, [iii.], **14**, 148; *Zeitsch. Kryst. Min.*, 1911, **49**, 73; Thugutt, *Centr. Min.*, 1909, 677; Grandjean, *Bull. Soc. franç. Min.*, 1910, **33**, 5.

Leucite, $KAl(SiO_3)_2$, occurs in lavas. It is pseudocubic, crystallising in icositetrahedral forms, and becomes truly cubic at 433°. **Nephelite,** $(K,Na)AlSiO_4$, a hexagonal mineral, is often found in association with leucite. The sodium-aluminium silicate, $NaAlSi_2O_8$, has been prepared artificially. It is known in two forms, the hexagonal form being called *soda-nephelite* and the triclinic form *soda-anorthite* or *carnegieite.*[1]

Spodumene, $LiAl(SiO_3)_2$, is another interesting aluminium silicate. It occurs in large quantities in South Dakota.[2] The green, transparent variety is called *hiddenite* and occurs in North Carolina. The transparent, lilac or violet-coloured variety is known as *kunzite*; it occurs in California and Madagascar and is a valuable gem-stone. Various lithium-aluminium silicates have been prepared artificially, but they do not agree in physical properties with any known lithium minerals.[3]

Topaz, $Al_2(SiO_4)F_2$, is a fluosilicate of aluminium. It is an orthorhombic mineral ($a : b : c = 0{\cdot}528 : 1 : 0{\cdot}477$), and its hardness (8), high refractive index, and variety of colour render it valuable as a gem-stone. The usual colour is pale yellow, but light brown, dark brown, and pale blue crystals are also found.

Beryl, $Al_2Be_3Si_6O_{18}$, is another beautifully crystalline aluminium mineral. It is hexagonal (hohohedral; $a : c = 1 : 0{\cdot}4989$); hardness, 7·5; density, 2·7. The pale green crystals known as *aquamarine,* and the dark green crystals known as *emerald,* are familiar as precious stones. Beryl has been synthesised by Hautefeuille and Perrey.[4]

Tourmaline is a borosilicate of aluminium, alkali metals, iron, and magnesium, containing water of constitution and a little fluorine. It may be regarded as derived from $H_9Al_3B_2(OH)_2Si_4O_{19}$ by the replacement of the nine hydrogen atoms by metals.[5] It is a trigonal mineral (ditrigonal pyramidal; $a : c = 1 : 0{\cdot}4474$); hardness, 7; density, 3·1. Tourmaline is an important rock-forming mineral; it is interesting as an excellent example of a crystal exhibiting polar symmetry and pyro-electric properties, and as a valuable material for the production of plane-polarised light. The colour of tourmaline varies greatly with its chemical composition, from colourless to red, green, brown, and black. Excellent tourmaline crystals, suitable for use as gem-stones, are found in Ceylon and also in Brazil.

Axinite, $HCa_3Al_2BS_4O_{16}$, is also an aluminium borosilicate. It is a beautifully crystalline triclinic mineral ($a : b : c = 0{\cdot}4927 : 1 : 0{\cdot}4511$; $\alpha = 82° 54'$, $\beta = 88° 9'$, $\gamma = 131° 33'$).

Sodalite, $Na_4(AlCl)Al_2(SiO_4)_3$, is a cubic mineral occurring in volcanic rocks; it crystallises in dodecahedra and usually has a blue colour. **Haüynite,** $Na_2Ca(NaSO_4Al)Al_2(SiO_4)_3$, is also a blue, cubic mineral, isomorphous with sodalite, with which it is often associated. Haüynite is of interest as being one of the very few silicates which contain sulphur.

Lapis-lazuli is a beautiful blue substance found in Persia, Afghanistan, Siberia, and Chili, and has been prized for ages as an ornamental stone. Density, 2·38 to 2·42; hardness, 5·5. It occurs embedded in limestone, from

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[1] Bowen, *Amer. J. Sci.*, 1912, [iv.], **33**, 551.

[2] Hess and Wells, *Amer. J. Sci.*, 1911, [iv.], **31**, 433.

[3] Ballo and Dittler, *Zeitsch. anorg. Chem.*, 1912, **76**, 39; Jaeger and Simek, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 239, 251.

[4] Hautefeuille and Perrey, *Ann. Chim. Phys.*, 1890, [vi.], **20**, 447.

[5] See Penfield and Foote, *Amer. J. Sci.*, 1899, [iv.], **7**, 97; Schaller, *Zeitsch. Kryst. Min.*, 1912, **51**, 321; Vernadski, *ibid.*, 1913, **53**, 273.

which it is extracted by heating the limestone and then breaking out the lapis-lazuli with a hammer. Lapis-lazuli was formerly supposed to be a simple mineral, but Brögger and Bäckström[1] have shown it to be a rock, consisting of diopside, amphibole, muscovite, calcite, pyrite, and a blue, cubic mineral to which they gave the name **lazurite**. Lazurite is a sodium-aluminium silicate containing both sulphur and chlorine, and is regarded as being closely analogous and isomorphous with sodalite and haüynite. Powdered lazurite constitutes the natural pigment *ultramarine*.

Kaolinite, $H_4Al_2Si_2O_9$, is a rare, white mineral. It crystallises in the monoclinic system ($a:b:c=0{\cdot}5748:1:0{\cdot}5997$; $\beta=96°\ 19'$); density, 2·62; hardness, 2·5. The best crystals are found near Amlwch in the island of Anglesey; they are six-sided plates or pyramids with a perfect basal cleavage. The mean refractive index is 1·563; the birefringence (0·004) is much lower than that of mica, which resembles kaolinite in appearance.[2] The water is only expelled from kaolinite at high temperatures (above 330°); hence, when the formula is written in the usual way, $Al_2O_3.2SiO_2.2H_2O$, it must be remembered that the water is "water of constitution" and not water of crystallisation. Chemically, kaolinite is best regarded as an acid.[3]

The question as to the identity or otherwise of kaolinite and the clay substance of china-clay is discussed later (p. 105).

The silicates described above are naturally occurring substances. A number of artificial aluminium silicates, however, are of considerable industrial importance and may therefore be mentioned. These are the substances prepared by Gans and known technically as **permutits**. Sodium permutit is practically an artificial zeolite of the composition $2SiO_2Al_2O_3.Na_2O.6H_2O$. It is prepared by heating together china-clay, sodium carbonate and quartz in the requisite proportions and treating the mass with water. Other substances may be added in the preparation; a mixture of 2·5 to 3 parts of china-clay, 5 to 6 of alkali carbonate, and 1·5 to 2·4 parts of borax, for instance, has been particularly specified. The permutit is of a granular or leafy, porous character.

Sodium permutit, like certain natural zeolites, is able to exchange its sodium for other metals with remarkable ease. If, for instance, a solution of calcium or magnesium chloride is allowed to percolate through a column of the permutit, a solution of sodium chloride, free from calcium or magnesium, is obtained. If now, a concentrated solution of sodium chloride is percolated through the permutit, the calcium of magnesium is expelled from it and replaced by sodium.[4] The application of sodium permutit to the softening of boiler water will therefore be obvious without further explanation.

The sodium or calcium permutits can readily be made to exchange sodium or calcium for manganese, by treatment with a manganous salt solution. When this product is acted upon by potassium permanganate solution, the latter is reduced, and a manganese-potassium permutit produced which is covered with very finely divided higher oxides of manganese. This material is a valuable oxidising agent, and, when exhausted, can readily be regenerated by allowing potassium permanganate to percolate through it; its commercial

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[1] Brögger and Bäckström, *Zeitsch. Kryst. Min.*, 1891, **18**, 209.

[2] Dick, *Min. Mag.*, 1888, **8**, 15; 1908, **15**, 124.

[3] See p. 96. On the constitution of kaolinite, see Mellor and Holdcroft, *vide infra*; Pukal, *vide infra*; Samoilov, *Bull. Acad. Sci. Petrograd*, 1914, p. 779.

[4] See G. Schulze, *Zeitsch. physikal. Chem.*, 1914, **89**, 168.

uses are for removing iron from, and oxidising the organic matter and bacteria in water. These results are easily brought about by allowing the contaminated water to flow through a layer of the permutit; in sterilising water by this means it may be necessary, in addition, first to add a little permanganate to the water.[1]

Aluminosilicic acids and aluminosilicates.—It is usual to regard the numerous known silicates, including those described in the preceding section, as the salts of various hypothetical silicic acids, or as isomorphous mixtures of such salts.[2] There are, however, good reasons for supposing that many of the compounds usually classed as aluminium silicates are no more related to the silicates than the ferrocyanides, for instance, are related to the cyanides. Numerous reasons can be adduced in favour of the view that the alumina in numerous silicates plays the rôle of an acid and not a base, and that, as was originally proposed by Vernadski, the silicates themselves are the salts of a number of complex **aluminosilicic acids,** comparable with the phosphomolybdic, silicomolybdic, and silicotungstic acids, etc.[3] For the nature of the evidence, however, the reader must be referred to the literature.

Many silicates are decomposed by the prolonged action of water and carbon dioxide, furnishing colloidal silicic acid or opal. In a similar manner, the aluminosilicates give rise to colloidal aluminosilicic acids or clays. The empirical formulæ of these acids may be tabulated as follows:—

Alumino-monosilicic acid (allophanic type)	$Al_2O_3.SiO_2.nH_2O$
Alumino-disilicic acid (kaolinic type)	$Al_2O_3.2SiO_2nH_2O$
Alumino-trisilicic acid (natrolitic type)	$Al_2O_3.3SiO_2nH_2O$
Alumino-tetrasilicic acid (pyrophyllitic type)	$Al_2O_3.4SiO_2nH_2O$
Alumino-pentasilicic acid (chabazitic type)	$Al_2O_3.5SiO_2nH_2O$
Alumino-hexasilicic acid (felspathic type)	$Al_2O_3.6SiO_2nH_2O$

The constitution of these acids at present can only be conjectured. The following groupings of important compounds are due to Mellor and Holdcroft:—[4]

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[1] See Gans, *Mitt. aus. d. K. Prüfungsanst. f. Wasserversorgung u. Abwasserbeseitigung zu Berlin*, 1907, Heft 8; *Woch. f. Brau.*, 1907, **24**, 270: *Chem. Zeit.*, 1907, **31**, 355; *J. Gasbeleucht.*, 1907, **50**, 1026; *Jahrb. K. Preuss. Geol. Landesanst. u. Bergakad., Berlin*, 1908, **26**, 179; **27**, 63; *Chem. Ind.*, 1909, **32**, 197; *Z. Ver. Deut. Zuckerind.*, 1907, p. 206; *Centr. Min.*, 1913, pp. 699, 728; 1914, pp. 273, 299, 365; Stremme, *ibid.*, 1914, p. 80, ; Wiegner, *ibid.*, 1914, p. 262; Appelius, *Chem. Rev. Fett-Harz. Ind.*, 1909, p. 300; Lührig and Becker, *Chem. Zeit.*, 1908, **32**, 514, 531; Anders, *Woch. f. Brau.*, 1911, **28**, 78; Kolb, *Chem. Zeit.*, 1911, **35**, 1393, 1410; L. H. Harrison, *Chem. World*, 1912, **1**, 238; Hamor, *J. Ind. Eng. Chem.*, 1912, **4**, 240. Also the following patents: *Eng. Pat.*, 1907, Nos. 8232, 3494; 1909, Nos. 21,184, 26,842; 1910, No. 28,353; *D.R.P.*, 1905, No. 174,097; 1908, No. 220,609; *Fr. Pat.*, 1907, No. 374,525; 1909, Nos. 405,990, 409,006; 1910, No. 423,388; 1914, No. 474,283; *U.S. Pat.*, 1909, No. 943,535; 1910, Nos. 951,641, 968,887.

[2] See Vol. V. of this series.

[3] See Wartha, *Annalen*, 1873, **170**, 338; Brauns, *Die chemische Konstitution der Silicate*, 1874, p. 6; Gorgen, *Ann. Chim. Phys.*, 1887, [vi.], **10**, 145; Vernadski, *Bull. Russ. Ges. Naturf.*, 1891, p. 1; *Zeitsch. Kryst. Min.*, 1901, **34**, 37; Zulkowski, *Chem. Ind.*, 1899, **2**, 284; Scharizer, *Zeitsch. Kryst. Min.*, 1894, **22**, 369; Ulffers, *J. prakt. Chem.*, 1907, i.], **76**, 143; Morozewicz, *Kosmos*, 1907, **32**, 496; *Zeitsch. Kryst. Min.*, 1910, **48**, 523; ukal, *Ber.*, 1910, **43**, 2107; *Sprechsaal*, 1910, **43**, 440; Mellor and Holdcroft, *Trans. Eng. eramic Soc.*, 1911, **9**, 94; 1912, **10**, 169; Mellor, *Clay and Pottery Industries* (Griffin & Co., 914); W. Asch and A. Asch, *The Silicates in Chemistry and Commerce*, trans. by Searle Constable, 1913), pp. 3–30, where a full discussion will be found.

[4] Mellor and Holdcroft, *loc. cit.*; Mellor, *opus cit.*, p. 293.

1. *Alumino-monosilicates—Allophanic Type.*

Allophane is $Al_2O_3.SiO_2.5H_2O$. Salts of this type are: *augite*, $MgO.Al_2O_3.SiO_2$; *chlorite*, $2MgO.Al_2O_3.SiO_2.2H_2O$.

2. *Alumino-disilicates—Kaolinic Type.*

Various alumino disilicic acids are:—

Rectorite	$Al_2O_3.2SiO_2.H_2O$	*Halloysite*	$Al_2O_3.2SiO_2.3H_2O$
Kaolinite	$Al_2O_3.2SiO_2.2H_2O$	*Newtonite*	$Al_2O_3.2SiO_2.5H_2O$

Among the aluminosilicates that may be looked upon as salts of the preceding acids are *nephelite*, $K_2O.Al_2O_3.2SiO_2$, and *anorthite*, $CaO.Al_2O_3.2SiO_2$.

3. *Alumino-trisilicates—Natrolitic Type.*

Salts are represented by *natrolite*, $Na_2O.Al_2O_3.3SiO_2$; *garnet*, $3CaO.Al_2O_3.3SiO_2$; *scolecite*, $CaO.Al_2O_3.3SiO_2.3H_2O$; *lepidolite*, $KLiO.Al_2O_3.3SiO_2$; etc.

4. *Alumino-tetrasilicates—Pyrophyllitic Type.*

Pyrophyllite is $Al_2O_3.4SiO_2.H_2O$. Salts are *leucite*, $K_2O.Al_2O_3.4SiO_2$; *analcite*, $Na_2O.Al_2O_3.4SiO_2.2H_2O$; *spodumene*, $Li_2O.Al_2O_3.4SiO_2$; *glaucophane*, $Na_2O.Al_2O_3.4SiO_2$; etc.

5. *Alumino-pentasilicates—Chabazitic Type.*

The group is represented by *chabazite*, $CaO.Al_2O_3.5SiO_2.7H_2O$, and *harmotine*, $BaO.Al_2O_3.5SiO_2.6H_2O$.

6. *Alumino-hexasilicates—Felspathic Type.*

This type is represented by *orthoclase*, $K_2O.Al_2O_3.6SiO_2$.

For further information concerning attempts to derive the constitutions of the aluminium silicates, the reader is referred to the literature.[1]

ALUMINIUM AND BORON.

Aluminium Borides.—Two borides are known, AlB_2 and AlB_{12}, and crystals have also been prepared containing boron, aluminium, and carbon.[2] All the substances were prepared originally by Wöhler and Deville, and regarded as allotropic forms of boron crystallising out from solution in molten aluminium. Subsequently they recognised that their *graphitic boron* was a boride of aluminium AlB_2, but looked upon the aluminium and carbon in their *adamantine boron* as accidental impurities.

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[1] The literature references are given by W. Asch and A. Asch, *opus cit.*, where a full account of the various theories of the constitution of the aluminosilicates will also be found, together with a full discussion of the *hexite-pentite* theory.

[2] The literature is as follows: Wöhler and Deville, *Ann. Chim. Phys.*, 1858, [iii.], **52**, 63; *Compt. rend.*, 1867, **64**, 19; *Annalen*, 1867, **141**, 268; Hampe, *Annalen*, 1876, **183**, 75; Joly, *Compt. rend.*, 1883, **97**, 456; Biltz, *Ber.*, 1908, **41**, 2634; 1910, **43**, 297; Kühne, *D.R.P.*, 147,871; Binet du Jassonneix, *Ann. Chim. Phys.*, 1909, [viii.], **17**, 200.

Aluminium Boride, AlB_2.—The following methods of preparation are due to Wöhler and Deville: (i.) a mixture of boron oxide and carbon is heated to redness in chlorine, and the gaseous products (boron trichloride and carbon monoxide) passed over aluminium heated to whiteness in a porcelain tube; free aluminium is removed from the product by solution in hydrochloric acid or sodium hydroxide; (ii.) potassium borofluoride (8 pts.), potassium chloride (9 pts.), sodium chloride (7 pts.), and aluminium (5 pts.) are heated together for half an hour at the melting-point of silver, and the product isolated as before. Binet du Jassonneix has produced it readily by heating to 1300°, in a stream of hydrogen, a fragment of aluminium contained in a crucible brasqued with boron.

The boride AlB_2 is a semi-metallic looking solid, which crystallises in six-sided plates belonging to the monoclinic system.[1] It is said by Wöhler and Deville, and also by Binet du Jassonneix, to be nearly black, but distinctly copper-coloured by reflected light; Joly describes it as golden-yellow in colour. The boride is unaffected by air at a red heat, dissolves slowly in hot concentrated hydrochloric acid or sodium hydroxide, and rapidly in hot nitric acid.

When prepared by the method of Binet du Jassonneix, it is accompanied by a small proportion of brown crystals of octahedral habit. These latter crystals are formed in abundance when the boride AlB_2 is heated with an excess of boron at 1400°, or when a mixture of boron and aluminium powders is heated to 1300° in hydrogen. They are heavier than the boride AlB_2 and far more resistant towards nitric acid.[2]

Aluminium Boride, AlB_{12}.—The true nature of this compound was determined by Hampe. Binet du Jassonneix has shown that it is produced, together with numerous other products, when aluminium is heated with excess of boron in a magnesia crucible in the electric furnace. It is best prepared by the method outlined by Kühne and examined in detail by H. Biltz. Boron oxide (50 grams), sulphur (75 grams), and granulated aluminium (100 grams) are mixed in a clay crucible, covered with magnesium powder, and ignited at the top to start the reaction. When cold, the crucible is broken away, the product treated with water, and the aluminium hydroxide and crystalline needles of alumina rinsed away. The lumps of residue are freed from traces of slag, at first mechanically and then by prolonged washing with water. The residue is treated with warm hydrochloric acid for several days; lighter impurities are then removed by decantation with water. The residue is boiled with hydrochloric acid, then warmed with hydrofluoric acid for some hours, and finally kept in warm, dilute hydrochloric acid for some days.

Thus prepared, the boride forms lustrous crystals, usually six-sided plates, probably belonging to the rhombic system ($a : b : c = \cdot 7130 : 1 : \cdot 7139$). The crystals appear black, but in thin layers are dark red by transmitted light. At 18° the density is $2{\cdot}554 \pm \cdot 005$; the specific heats at $-40°$, $+77°$, $+177°$, and $+233°$ are 0·1915, 0·2737, 0·3378, and 0·3663 respectively.[3] The boride is harder than corundum, but softer than diamond. According to Hampe, it is unaffected by concentrated hydrochloric acid or potassium hydroxide solution, is slowly dissolved by hot sulphuric acid, and more readily

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[1] Miller, *Proc. Roy. Soc.*, 1866, **15**, 11; *Phil. Mag.*, 1866, [iv.], **31**, 397.

[2] The boron content varies from 66·9 to 79·6 per cent.; AlB_{12} requires 83·1 per cent. Possibly they are mixed crystals of AlB_2 and AlB_{12}. Binet du Jassonneix was unable by this method to observe the formation of the characteristic black plates of AlB_{12}.

[3] Weber, *Phil. Mag.*, 1875, [iv.], **49**, 161, 276.

by hot nitric acid. It is oxidised by molten potassium hydroxide or bisulphate, but not by the nitrate, and is attacked also by heated lead chromate. It rapidly attacks heated platinum, a very fusible product being formed.

Aluminium borocarbides.—The researches of Wöhler and Deville and of Hampe were concerned mainly with the interaction of boron oxide and aluminium in either clay or graphite crucibles. Joly showed that when a graphite crucible was employed, the following products were obtained, the relative quantities varying with the conditions of the experiment: (i.) aluminium boride AlB_2; (ii.) aluminium boride AlB_{12}; (iii.) yellow crystals containing boron, aluminium, and carbon; and (iv.) boron carbide B_6C. Hampe's experiments led him to believe in the existence of a definite *borocarbide* $Al_3C_2B_{48}$. Later, Biltz obtained crystals of definite composition, corresponding to the formula $Al_3C_2B_{44}$. The method of preparation was similar to that described for the preparation of the boride AlB_{12}, except that soot (2 grams) was added to the mixture. The product, after treatment with water, concentrated hydrochloric acid, and then the warm, dilute acid for some days, consists of sparkling yellow crystals mixed with a few black crystals of AlB_{12}.

The crystals have a density at 18° of $2{\cdot}590 \pm {\cdot}006$, are harder than corundum and softer than diamond. Towards reagents they resemble the boride AlB_{12}, but are more resistant towards mineral acids.

It is difficult to believe that the formulæ given by Hampe and Biltz represent definite chemical compounds. Probably each chemist obtained products of definite composition simply because the conditions of experiment were not sufficiently varied. Crystals of quite different composition have been prepared by Binet du Jassonneix, by heating aluminium with excess of boron in a graphite crucible in an electric arc furnace. They are yellow, transparent, and occur in six-sided plates; mixed with them are crystals of boron carbide, from which they cannot be completely separated. The crystals are attacked slowly by dilute hydrochloric acid, quickly by nitric acid. After allowing for mechanically admixed boron carbide, the average composition was Al, 64 per cent.; B, 15 per cent.; C, 21 per cent.; but different preparations varied considerably in composition.[1]

Aluminium borate.—The *basic borate*, $3Al_2O_3.B_2O$, was prepared by Ebelmen by strongly heating a mixture of alumina and borax. It forms colourless, orthorhombic crystals ($a : b : c = 0{\cdot}974 : 1 : 0{\cdot}679$) of density 3·0.[2] The precipitates obtained by mixing alkali borate solutions with solutions of aluminium salts are also basic aluminium borates.[3]

Aluminium sodium perborate, $Al_2Na_2B_2O_9.5H_2O$, containing 7 to 9 per cent. of active oxygen, is prepared by mixing cold solutions of sodium aluminate (6·6 pts.) and boric acid (5 pts.) and adding 10 per cent. hydrogen peroxide solution (30 pts.). It is a colourless powder, sparingly soluble in water.[4]

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[1] It is possible that these borocarbides are mixed crystals of two or more of the following substances: AlB_2, AlB_{12}, Al_4C_3, and B_6C. The suggestion has been made by Binet du Jassonneix that his crystals are mixed crystals of aluminium boride AlB_2 and aluminium carbide Al_4C_3, but it is quite at variance with his analytical data.

[2] Ebelmen, *Ann. Chim. Phys.*, 1851, [iii.], 33, 34; Mallard, *Compt. rend.*, 1887, 105, 1260; *cf.* Troost and Hautefeuille, *ibid.*, 1872, 75, 1819; Frémy and Feil, *ibid.*, 1877, 85, 1029.

[3] Rose, *Pogg. Annalen*, 1854, 91, 452.

[4] *D.R.P.*, 235,050.

Detection and Estimation of Aluminium.

Aluminium salts give no precipitate with hydrogen sulphide in acid or neutral solution. Ammonium hydroxide, sulphide, or carbonate, precipitates aluminium as the white, gelatinous hydroxide, which, like the hydroxides of beryllium, zinc, and chromium, is soluble in cold sodium hydroxide. Alumina, when moistened with a solution of a cobalt salt and heated on charcoal, yields a bright blue, infusible mass. A test which will detect 1 part of aluminium in 10 million parts of water is to add 1 c.c. of a 0·1 per cent. solution of alizarin S to 5 c.c. of the neutral or acid solution, make just ammoniacal, boil for a few minutes, cool, and acidify with dilute acetic acid. A red colour or precipitate indicates the presence of aluminium.[1]

In quantitative analysis, aluminium is precipitated as the hydroxide,[2] washed,[3] ignited over the blowpipe, and weighed as the sesqui-oxide Al_2O_3.[4] (*a*) The precipitation is effected, best in a platinum or porcelain vessel, by adding a slight excess of freshly distilled ammonium hydroxide to a slightly acid solution of an aluminium salt, preferably in the presence of ammonium chloride. Alternative methods of precipitation are as follows. (*b*) One to three cubic centimetres of phenylhydrazine are added to the hot, very slightly acid solution, the precipitate being washed with a hot, very dilute solution of phenylhydrazine bisulphite free from excess of sulphurous acid.[5] (*c*) The dilute, neutral chloride solution is treated with excess of sodium thiosulphate and boiled until sulphur dioxide is no longer evolved.[6] (*d*) The slightly acid solution is treated with excess of a mixture of potassium iodide and potassium iodate, a moderate excess of sodium thiosulphate added, and the solution heated on the steam-bath for half an hour.[7] (*e*) The neutral solution is slightly acidified with hydrochloric acid and boiled with excess of ammonium or sodium nitrite; finally, a little ammonia is added.[8]

In methods (*b*), (*c*), (*d*), and (*e*) precipitation is due to the fact that aqueous solutions of aluminium salts are appreciably hydrolysed, and that when excess of a reagent is added which uses up the free acid present, hydrolysis proceeds to completion. The principle of method (*d*),[9] for instance, is sufficiently indicated by the following equations:—

$$\begin{aligned} 2AlCl_3 + 6H_2O &\rightleftharpoons 2Al(OH)_3 + 6HCl \\ KIO_3 + 5KI + 6HCl &= 6KCl + 3H_2O + 3I_2 \\ 6Na_2S_2O_3 + 3I_2 &= 3Na_2S_4O_6 + 6NaI \end{aligned}$$

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[1] Atack, *J. Soc. Chem. Ind.*, 1915, **34**, 936. For further information on the detection of aluminium, see A. A. Noyes, Bray, and Spear, *J. Amer. Chem. Soc.*, 1908, **30**, 481; *Chem. News*, 1908, **98**, 6, etc.; Petit, *J. Pharm. Chim.*, 1914, [vii.], **9**, 66 (detection as barium aluminate); Rathgen, *Zeitsch. anal. Chem.*, 1913, **53**, 33; and Kratzmann, *Pharm. Post*, 1914, **47**, 101, 109 (microchemical detection).

[2] For the disturbing influence of fluorides, see Veitch, *J. Amer. Chem. Soc.*, 1900, **22**, 246; Bloor, *ibid.*, 1907, **29**, 1603; Curtman and Dubin, *ibid.*, 1912, **34**, 1485; Hinrichsen, *Ber.*, 1907, **40**, 1497; *Zeitsch. anorg. Chem.*, 1908, **58**, 83; Mlle. Cavaignac, *Compt. rend.*, 1914, **158**, 948.

[3] See Daudt, *J. Ind. Eng. Chem.*, 1915, **7**, 847.

[4] For full details, see Blum, *J. Amer. Chem. Soc.*, 1916, **38**, 1282.

[5] Hess and Campbell, *J. Amer. Chem. Soc.*, 1899, **21**, 776; Allen, *ibid.*, 1903, **25**, 421.

[6] Chancel, *Compt. rend.*, 1858, **46**, 987; *cf.* Hac, *Eighth Inter. Cong. Appl. Chem.*, 1912, **1**, 205.

[7] Stock, *Ber.*, 1900, **33**, 548.

[8] Wynkoop, *J. Amer. Chem. Soc.*, 1897, **19**, 434; Schirm, *Chem. Zeit.*, 1909, **33**, 877; 1911, **35**, 979.

[9] Which may be used as a volumetric method (Moody, *Amer. J. Sci.*, 1905, [iv.], **20**, 181; Ivanov, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 419; Mlle. Kovscharova, *ibid.*, 1915, **47**, 616; Osipov, *ibid.*, 1915, **47**, 613).

The precipitates obtained by methods (*c*), (*d*), and (*e*) are very much easier to filter than that obtained by method (*a*).

In the presence of phosphoric acid the aluminium precipitate is partly or wholly aluminium phosphate. The precipitation of aluminium as hydroxide is prevented by the presence of organic hydroxy-compounds such as tartaric and citric acids, sucrose, etc., in the solution.

There is no difficulty in separating aluminium from the alkali metals and metals which form sulphides insoluble in acetic acid or dilute mineral acids. The separation of aluminium from magnesium and the alkaline-earth metals may be effected by methods (*a*), (*b*), (*d*), and (*e*) already given. In method (*a*) the ammonia should be free from carbonate, or it may be replaced by pure ammonium sulphide free from carbonate and sulphate. When precipitated by ammonium hydroxide or sulphide, aluminium may be associated with beryllium, iron, chromium, titanium, uranium, zinc, manganese, nickel, and cobalt, though if the hydroxide be used as precipitant, the bulk of the last four metals may be removed, the separation being often sufficiently precise for the purposes of ordinary qualitative analysis.

The preceding method (*e*) serves to separate aluminium from zinc, manganese, nickel, and cobalt, as also do the two following methods. (*f*) The cold, slightly acid solution of the chlorides or nitrates containing ammonium salts is shaken with excess of pure precipitated barium carbonate and allowed to stand for some hours. The aluminium is precipitated as hydroxide, in accordance with the principle already stated (p. 100), and needs separation from the excess of barium carbonate. (*g*) The hot, dilute, acidified chloride solution is made nearly neutral with ammonium hydroxide or carbonate, a slight excess of ammonium acetate added, and the solution boiled for one or two minutes, when the aluminium is precipitated as basic aluminium acetate. Method (*f*) is more tedious, but more accurate than (*g*).

Aluminium is readily separated from iron by precipitation with an excess of pure alkali hydroxide, in which only the hydroxide of aluminium is soluble. Alternative procedures are to precipitate the aluminium from a chloride solution by method (*c*) above, the iron present remaining in solution as a ferrous salt; to reduce the iron to the ferrous state with ammonium bisulphite and employ the phenylhydrazine method (*b*), double precipitation being advisable; or to dissolve the mixed aluminium and ferric chlorides in hydrochloric acid of density 1·12 and extract the ferric chloride with ether.[1] Aluminium is separated from chromium by adding excess of pure alkali hydroxide, oxidising the chromic hydroxide to alkali chromate by adding bromine to, or passing chlorine into the liquid, acidifying with nitric acid, and then precipitating the aluminium by the addition of ammonia.[2] A good separation of aluminium and titanium is that proposed by Gooch, in which the dilute solution, slightly acidified with sulphuric acid, is treated with sodium acetate and considerable acetic acid and boiled for five minutes. Titanium is precipitated as metatitanic acid.[3] An alternative procedure is to precipitate the titanium with the ammonium salt of nitrosophenylhydroxylamine (cupferron) in a dilute sulphuric acid solution.[4] Aluminium may be

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[1] Hanriot, *Bull. Soc. chim.*, 1893, [iii.], **7**, 161.

[2] *Cf.* Jakób, *Bull. Acad. Sci. Cracow*, 1913, A, 56; van Pelt, *Bull. Soc. chim. Belg.*, 1914, **28**, 138.

[3] Gooch, *Proc. Amer. Acad.*, 1884, **20**, 435; *Chem. News*, 1885, **52**, 55, 68.

[4] Bellucci and Grassi, *Atti R. Accad. Lincei*, 1913, [v.], **22**, i. 30; Thornton *Amer. J. Sci.*, 1914, [iv.], **37**, 407.

separated from zirconium in a similar manner.[1] It is separated from uranium by precipitation with excess of ammonium carbonate, the uranium remaining in solution.

An excellent method for the separation of aluminium from glucinum, iron, zinc, copper, mercury, and bismuth consists in dissolving the mixed chlorides in concentrated hydrochloric acid, adding rather more than an equal volume of ether, and saturating the mixture at 15° with hydrogen chloride gas. The aluminium separates as the hydrated chloride $AlCl_3.6H_2O$, which is filtered on asbestos and washed with a mixture of equal volumes of concentrated hydrochloric acid and ether saturated with hydrogen chloride.[2] Aluminium nitrate is insoluble in amyl alcohol, a property which may be utilised in separating aluminium from glucinum.[3]

Details of the various methods must be sought in the original memoirs or in text-books of quantitative analysis.[4]

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[1] Thornton and Hayden, *Amer. J. Sci.*, 1914, [iv.], **38**, 137; Ferrari, *Atti ist. Veneto scienze lettere ed arti*, 1914, **73**, 445.

[2] Gooch and Havens, *Amer. J. Sci.*, 1896, [iv.], **2**, 416; *Zeitsch. anorg. Chem.*, 1897, **13**, 435; Havens, *Amer. J. Sci.*, 1897, [iv.], **4**, 111; 1898, [iv.], **6**, 45; *Zeitsch. anorg. Chem.*, 1898, **16**, 15; 1898, **18**, 147; *cf.* Minnig, *Amer. J. Sci.*, 1915, [iv.], **39**, 197; **40**, 482.

[3] Browning and Kuzirian, *Eighth Inter. Cong. Appl. Chem.*, 1912, **1**, 87. For another method, see Wunder and Mlle. Chéladzé, *Ann. Chim. anal.*, 1911, **16**, 205.

[4] For the analysis of commercial aluminium and its alloys, see Moissan, *Compt. rend.*, 1894, **119**, 12; 1895, **121**, 851; 1897, **125**, 276; *Bull. Soc. chim.*, 1894, [iii.], **11**, 1021; 1897, [iii.], **17**, 4; Kohn-Abrest, *Compt. rend.*, 1908, **147**, 1293; Handy, *J. Amer. Chem. Soc.*, 1896, **18**, 766; Seligman and Willot, *J. Inst. Met.*, 1910, **3**, 138; Kleist, *Chem. Zeit.*, 1911, **35**, 668; von John, *ibid.*, 1913, **37**, 363; Czochralski, *Zeitsch. angew. Chem.*, 1913, **26**, 501; Belasio, *Ann. Chim. Applicata*, 1914, **1**, 101; Lunge, *Technical Methods of Chemical Analysis*, trans. by Keane (Gurney & Jackson, 1911), vol. 2, pt. 1, p. 346. For the estimation of aluminium in silicate and carbonate rocks, see Hillebrand, *The Analysis of Silicate and Carbonate Rocks* (*Bull. U.S. Geol. Survey*, 1910, No. 422); Hinrichsen, *Ber.*, 1907, **40**, 1497; Selch, *Zeitsch. anal. Chem.*, 1915, **54**, 395. Mellor, *A Treatise on Quantitative Analysis* (Griffin & Co., Ltd., 1913), and Treadwell-Hall, *Quantitative Analysis* (Wiley, 3rd Edn., 1913), may also be consulted with advantage.

On the technical analysis of aluminium salts, see Bayer, *Zeitsch. anal. Chem.*, 1885, **24**, 542; 1886, **25**, 180; *Chem. Zeit.*, 1887, **11**, 53; 1888, **12**, 1209; 1890, **14**, 736; R. Williams, *Chem. News*, 1887, **56**, 194; Beilstein and Grosset, *Chem. Soc. Abstr.*, 1890, p. 85; A. H. White, *J. Amer. Chem. Soc.*, 1902, **24**, 457; Schmatolla, *Ber.*, 1905, **38**, 985; Moody, *Zeitsch. anorg. Chem.*, 1907, **52**, 286; Craig, *J. Soc. Chem. Ind.*, 1911, **30**, 184; W. W. Scott, *J. Ind. Eng. Chem.*, 1915, **7**, 1059.

CHAPTER IV.

CLAY AND CERAMICS.

CLAYS[1] are the chief earthy deposits utilised in the manufacture of bricks, tiles, pottery, and other ceramic products. The term "clay" is one of popular origin and use, and has been incorporated into scientific terminology in a rather loose manner. Geologically, clays occur chiefly among the *sedimentary rocks*, although they are decomposition products of certain granites and some other igneous rocks. Chemically, clays are impure, complex aluminosilicic acids, the characteristics of a clay being dependent on the particular acid present, on its state of hydration, and on the impurities associated with it. Popularly, clays are recognised by the fact that either in a natural state or when mixed with a suitable quantity of water they become plastic, although different clays vary enormously in this respect, and when heated to redness they become converted into hard, stone-like products.

The raw materials from which most clays have been produced are the various felspars, particularly the alkali felspars orthoclase and microcline, and their decomposition products; these minerals were originally present in igneous rocks such as granite, pegmatite, trachyte, gneiss, etc. Some clays, however, have been derived from rocks containing little or no felspars, *e.g.* serpentine and some gabbros, by the decomposition of augite, hornblende, and other aluminosilicate minerals.

The decomposition of the various rock-forming minerals with the production of clay has in most cases been brought about by *epigenic* or surface actions, or, as is usually said, by "weathering." The rocks expand under the influence of the heat of the sun and contract again at night, minute cracks being thereby produced. The crystalline structure of the rocks aids the splitting in certain directions, and the disintegration is accelerated by plant roots forcing their way into the cracks and by rain water percolating in and freezing in cold weather. The silicates present in the rocks thus become more and more exposed to the action of surface waters. It has generally

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[1] For further information on clays the following works may be consulted: Searle, *British Clays, Shales, and Sands* (C. Griffin & Co., Ltd., 1912); Ries, *Clays, their Occurrence, Properties, and Uses* (Wiley & Sons, 2nd ed., 1909); Searle, *The Natural History of Clay* (Cambridge University Press, 1912); Searle, *The Clayworker's Handbook* (C. Griffin & Co., Ltd., 2nd ed., 1911); Merrill, *The Non-metallic Minerals* (Wiley & Sons, 2nd ed., 1910); Howe, *A Handbook to the Collection of Kaolin, China Clay, and China Stone in the Museum of Practical Geology* (London, 1914); Le Chatelier, *La silice et les silicates* (Paris, 1914); Moissan, *Traité de chimie minérale* (Paris, 1905), vol. iv., article "Céramique"; Thorpe, *A Dictionary of Applied Chemistry* (Longmans & Co., 1912–13), vols. ii. and iv.; Seger, *Gesammelte Schriften* (Berlin, 1896, and American translation, Easton, 1902); and Mellor, *Clay and Pottery Industries, being the Collected Papers from the County Pottery Laboratory, Staffordshire*, vol. i. (C. Griffin & Co., Ltd., 1914).

been supposed, following Forschammer,[1] that the carbonic acid held in solution by these waters has been the active agent in effecting the decomposition of the silicates. There is evidence, however, that the minerals have also succumbed slowly to the hydrolysing action of water upon them, many powdered, natural silicates being sufficiently soluble in water to react alkaline towards phenolphthalein.[2] In the case of orthoclase, for example, it has been suggested [3] that the initial change may be represented thus:—

$$K_2Al_2Si_6O_{16}+2H_2O\rightleftharpoons 2KOH+H_2Al_2Si_6O_{16},$$

the aluminosilicic acid then undergoing further decomposition, whereby the elements of silica are partly removed and the elements of water added on until, in general, the final product has the composition $H_4Al_2Si_2O_9$.[4]

Some clays are considered by eminent geologists to have been produced by *hypogenic* actions, *i.e.* actions occurring below the surface of the earth. The Cornish and some of the Zettlitz (Bohemia) china-clays have probably been produced in this manner, the decomposition of the original igneous rocks having proceeded mainly from below upwards, effected by the action of aqueous solutions of carbonic or hydrofluoric acid under pressure and at high temperatures.[5]

Clays which are found overlying or in close association with the rocks from which they have been derived are called *primary* or *residual* clays.[6] The chief primary clays are the china-clays or kaolins, which are only feebly plastic. Clays which have been carried away from their place of origin and deposited elsewhere are known as *secondary* or *transported* clays. They are "the washings and sweepings of the hills, which Nature has accumulated as her rubbish-heaps in convenient places," and generally they are very plastic. Some clays, after transportation, have been subjected to great pressures in contact with water, whereby they have become hard and laminated in structure and require to be finely ground before they exhibit any plasticity. Such clays are known as *clay-shales*; as the result of metamorphic change they pass into *slates*.[7]

Composition of Kaolins.—Clays which are white and burn to a white mass are known as *kaolins*. They may be either primary or secondary clays, but all the kaolins found in the United Kingdom appear to be primary. They occur in association with the igneous rocks from which they were derived, and have to be separated by a process of washing. The bulk of Continental and many extra-European kaolins occur as secondary deposits and need no washing; they differ from English china-clay in several important respects and are usually inferior to it. While the term "kaolin" is employed to denote either a deposit of white clay, a partially decomposed clay-forming rock or the clay that may be obtained from it, separate names are desirable

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[1] Forschammer, *Pogg. Annalen*, 1835, 35, 354.

[2] F. W. Clarke, *Bull. U.S. Geol. Survey*, 1900, No. 167.

[3] Cameron and Bell, *Bull. U.S. Bureau of Soils*, 1905, No. 30.

[4] Some chemists consider the true formula to be at least six times as large. See W. and D. Asch, *The Silicates in Chemistry and Commerce*, translation by A. B. Searle (Constable, 1913), or Searle, *Cement, Concrete and Bricks* (Constable, 1913).

[5] Daubrée, *Ann. Min.*, 1841, [iii.], 20, 65; Collins, *Min. Mag.*, 1887, 7, 205; but *cf.* Hickling, *Trans. Inst. Mng. Eng.*, 1908, 36, 10, who states that "except in appearance" the product obtained by acting upon felspar with hydrofluoric acid "has not the remotest resemblance to china-clay."

[6] The term *residual clay*, however, is sometimes used in another sense.

[7] Many other kinds of shales and slates are also known,

for these materials, and in England the terms *kaolin*, *china-clay rock*,[1] and *china-clay* are respectively used for the purpose.

English china-clay is separated from the associated rock by directing a stream of water upon it. The finely divided clay is swept away and is carried by the water to a series of catch-pits or pools, in which the sand settles to the bottom. The fluid is pumped to a convenient level and is allowed to flow slowly through a series of long shallow troughs or *drags* in which the mica and other denser particles settle, leaving the clay in suspension. The finest particles, including all the clay, are then allowed to settle in a pit, after which the clear water is run off, the fine white mud is dried and then forms the china-clay of commerce. The separation into fractions is thus effected by a combination of the processes of *sedimentation*, based upon the fact that coarse particles sink in water more rapidly than fine ones, and of *elutriation*, based upon the fact that a slow stream of water flowing over a heterogeneous mass such as a clay carries away with it the small particles more readily than it does the larger ones.[2]

Hickling[3] has made a careful study of the mineralogical composition of English china-clay, with the following results. The coarse sand which first settles out consists largely of quartz, mixed with tourmaline, biotite (brown mica), and muscovite (white mica). In the succeeding finer sands the quantities of quartz and tourmaline diminish considerably while the amount of muscovite increases. The coarse muds which follow contain considerable quantities of kaolinite. In the finest muds no biotite is found, tourmaline is extremely scarce, and quartz is only present in small quantities; the bulk of the material consists of kaolinite and the remainder is composed chiefly of muscovite. No felspar is found in English china-clay. By exceptionally careful washing it is possible to increase the percentage of kaolinite to 99 per cent., but the best commercial samples only contain 90 to 95 per cent.

Most of the other kaolins appear to resemble the English china-clay in composition, although particles of felspar are found in various Continental kaolins.

Commercial china-clay is a soft, white or nearly white substance that may easily be reduced to a very fine powder. When mixed with twice its weight of water it will pass completely through a No. 200 sieve.

Only a very small portion of commercial kaolins or china-clays can be recognised as the crystalline mineral kaolinite by microscopes of ordinary power,[4] the bulk of the material which Hickling claims to be kaolinite appearing to consist of amorphous particles. The identity of this "amorphous" material with crystalline kaolinite is not conclusively proved, and the term *clayite*, proposed by Mellor,[5] is sometimes used to describe it.

The very finely divided muscovite present in commercial china-clays is

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[1] Also known as *carclazite*.

[2] It may here be pointed out that the minerals most plentiful in clays do not differ very greatly in their densities, as shown by the following data:—

Kaolinite	2·6	Felspars	2·55–2·75	Biotite	2·7–3·1
Quartz	2·65	Muscovite	2·76–3·00	Calcite	2·7

[3] Hickling, *Trans. Inst. Mng. Eng.*, 1908, **36**, 10; *J. Soc. Dyers*, 1915, **31**, 70; *cf.* S. W. Johnson and Blake, *Amer. J. Sci.*, 1867, [ii.], **43**, 351.

[4] The particles present in washed china-clay vary from 0·0005 mm. to 0·03 mm. in diameter.

[5] Mellor, *Trans. Eng. Cer. Soc.*, 1908, **8**, 23; *Collected Papers*, vol. i. p. 158. The term *clayite* was applied some years previously to a mineral of an entirely different nature discovered by H. Clay.

not the primary muscovite of the original igneous rocks,[1] but is most probably produced by the decomposition of felspar. The kaolinite, in its turn, appears to be produced from this secondary mica; the two minerals are crystallographically very similar, and, on account of their well-developed basal cleavage, occur in china-clay mainly in thin plates.[2]

The analyses of a specimen of kaolinite and a well-washed Devonshire china-clay are given in the table on p. 108. The analyses of numerous commercial china-clays are in good agreement with the view that the clays are mixtures of kaolinite, muscovite, and quartz.

Composition of Transported Clays.—The mineralogical composition of these clays is naturally more complex than that of the kaolins, since they not only contain the various mineral constituents of the primary rocks and their decomposition products, but also numerous other minerals which have become adventitiously mixed with the clays during transportation from their places of origin to their present sites.

Many transported clays are obviously heterogeneous, and, when rubbed up with water so as to form a thin "slip" or "slurry," they may be separated into dissimilar fractions by the use of sieves varying in mesh. The finest fraction may then be further separated by sedimentation or by elutriation. The fractions thus obtained, beginning with that containing the largest grains, are known respectively as gravel, fine gravel, coarse sand, fine sand, silt, fine silt, and clay; and a statement of the composition of a clay in terms of these constituents is termed its *mechanical analysis*. The following table records the mechanical analyses of samples of Berkshire loam which is used as a brick-clay and Staffordshire "blue brick" clay:—[3]

	Berkshire Loam.	Staffordshire Clay.
Fine gravel (1–3 mm. diam.)	0·3	0·8
Coarse sand (0·2–1·0 mm. diam.)	4·4	8·6
Fine sand (0·04–0·2 mm. diam.)	34·8	7·2
Silt (0·01–0·04 mm. diam.)	9·6	8·9
Fine silt (0·002–0·01 mm. diam.)	5·0	14·0
Finest silt	4·8	15·0
Clay	27·8	34·1
Soluble in hydrochloric acid	5·8	3·6
Loss on ignition	7·5	7·8
Total	100·0	100·0

The gravel, sand, and silt are found to be devoid of the properties usually associated with clay. That portion of the original clay to which the "clayey"

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[1] The primary muscovite may be recognised in the coarse muds when china-clay rock is washed.

[2] These remarks apply particularly to English china-clay, in which the kaolinite may be described as a pseudomorph after secondary muscovite.

[3] Analyses communicated by Mr A. G. Hopkins; for method of analysis, see Hall, *Trans. Chem. Soc.*, 1904, **85**, 950. Some ceramic chemists adopt other diameters but use the same names for the fractions.

properties are due, consists of particles considerably smaller than those of fine silt. When the gravel, sand, and silt have been removed from a clay, the residue is often spoken of as "clay substance"; this expression is not, however, a very happy one, and it is perhaps better to use the term "argillaceous matter" for the purpose. The argillaceous matter is never homogeneous, and in the case of the commoner clays, such as brick-clays, it may contain notable proportions of such substances as finely divided ferric oxide and calcium carbonate (chalk) unless the clay was treated with hydrochloric acid before analysis. The figures given serve to show the small proportion of "true clay" that exists in many of the commoner clay deposits.

Microscopic examination usually reveals the presence of particles of felspar or mica (or both), but in comparatively few clays has the presence of the mineral kaolinite been established with certainty.[1] Felspar, mica, and some form of silica (quartz) are so frequently present that they may be looked upon as normal constituents. Of the numerous secondary rock-forming minerals that occur in clays in small quantities perhaps the most ubiquitous is rutile[2] (TiO_2). The almost invariable occurrence of titanium in clays was noted in 1862 by Riley;[3] the amount of titanic oxide, however, seldom exceeds 2 per cent., and in many clay analyses it is (unconsciously) included with the alumina.

Of the various other mineral species present in transported clays the most important are limonite, $2Fe_2O_3.3H_2O$; hæmatite, Fe_2O_3; magnetite, Fe_3O_4; siderite, $FeCO_3$; pyrite and marcasite, FeS_2; chalk and limestone, $CaCO_3$; magnesite, $MgCO_3$; dolomite $(Ca,Mg)CO_3$; and gypsum, $CaSO_4.2H_2O$. A clay that contains more than 4 or 5 per cent. of admixed chalk is called a *malm* or *marl*; a clay rich in sand is termed a *loam*. Small amounts of soluble salts, chiefly sodium, potassium and magnesium sulphates, phosphates and chlorides occur in many clays, and carbonaceous matter is seldom absent, although clays differ widely in the amount they contain. Clays also contain hygroscopic moisture or mechanically admixed water, removable at 105°-110° C., while a further amount of water may be obtained from them at a red heat by the decomposition of the aluminosilicic acids present.

The methods used for the *ultimate chemical analysis* of a clay are those regularly employed in the analysis of silicate rocks.[4] Results are usually expressed as percentages of acidic and basic oxides. Analyses of kaolinite and a number of typical English clays are given in the table on page 108.[5] In certain cases it is necessary to determine more precisely the nature of the "loss on ignition," by estimating separately the water, carbon dioxide, carbon present as organic matter, etc. Moreover, the figure shown for "ferric oxide" is usually only a measure of the total iron present, without reference to its mineralogical source or sources and its state of oxidation.

It is difficult and often impossible to determine the quantitative, or even the qualitative, composition of a transported clay in terms of the minerals

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[1] See Hickling, *loc. cit.*, for a review of the evidence.

[2] Hussak, *Sprechsaal*, 1889, 22, 136, 154; Teall, *Min. Mag.*, 1885-7, 7, 201; Vogt, *La Céramique*, 1903, 6, 68.

[3] Riley, *Quart. J. Chem. Soc.*, 1862, 15, 311.

[4] For the analysis of clays, see especially Mellor, *A Treatise on Quantitative Inorganic Analysis* (C. Griffin & Co., Ltd., 1913).

[5] Analyses 1 and 2 by Mellor and Holdcroft (*Trans. Eng. Cer. Soc.*, 1911, 9, 94; 1912, 10, 169); analyses 3, 4, 5, and 6 communicated by Mr A. G. Hopkins. The data refer to samples dried at 110° C. The mechanical analysis of 4 and 5 is given in the table on p. 106.

present; a fundamental difficulty arises in connection with the nature of the "true clay" present. Of what mineral or minerals is it constituted? In the case of the plastic ball-clays some approach to a definite answer may be given. These clays on careful elutriation and sedimentation yield a residue which consists mainly of amorphous material and, though never entirely free from foreign mineral particles, its analysis approximates very closely to that of the crystalline mineral kaolinite. From this fact it has often been inferred that the basis of all clays is an aluminosilicic acid (or hydrated aluminium silicate) of the formula $H_4Al_2Si_2O_9$ (or $Al_2O_3.2SiO_2.2H_2O$), an inference sometimes expressed by saying that clays are composed of true clay or kaolinite associated with various other minerals. It is, however, very undesirable that the name kaolinite should be employed to denote anything but the crystalline mineral, and it is at least premature, and most probably erroneous, to conclude that only one aluminosilicic acid exists in clays. A number of minerals which are presumably aluminosilicic acids of a somewhat similar nature to kaolinite, *e.g.* allophane, collyrite, pholerite, nacrite, rectorite, halloysite, newtonite, pyrophyllite, montmorillonite, etc., are known.[2] It is not certain that all these substances (several of which are only known in the amorphous state) are distinct mineral species; several of them may possibly be mixtures containing silicic acid and aluminium hydroxide. The detection of these substances in clays is very difficult, since, with the exception of the china-

Constituent Estimated.	1	2	3	4	5	6
	Kaolinite (Glamorganshire).	China-clay (Lee Moor, Devon).	Ball-clay (Dorsetshire).	"Blue Brick" clay (Staffordshire).	Red-burning Brick-clay (Berkshire).	Fireclay (Stourbridge, Staffs.).
Silica (SiO_2)	45·04	47·10	50·51	58·96	70·37	62·88
Titanic oxide (TiO_2)	nil	0·13	0·84	0·91	trace	0·73
Alumina (Al_2O_3)	38·58	39·42	34·22	19·61	13·45	25·26
Ferric oxide (Fe_2O_3)	0·14	0·23	1·74	9·51	6·09	1·71
Magnesia (MgO)	0·01	0·24	0·02	1·45	1·35	0·04
Lime (CaO)	0·38	0·31	0·43	0·65	0·66	0·33
Potash (K_2O)	0·18	0·16	0·81	1·28	1·38	0·19
Soda (Na_2O)	0·13	0·08	1·65	1·23	1·39	0·28
Loss on ignition (H_2O, etc.) . .	15·94[1]	12·24	9·59	6·27	4·77	8·87
Total . .	100·40	99·91	99·81	99·87	99·46	100·29

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[1] This includes 14·44 per cent. H_2O and 0·80 per cent. of carbon.

[2] The literature relating to these substances is very confusing. For example, Le Chatelier gives collyrite the formula $Al_2O_3.2SiO_2.6H_2O$ and regards allophane as identical with it; others give allophane the formula $Al_2O_3.SiO_2.5H_2O$. See Doelter, *Handbuch der Mineralchemie*, vol. ii. (1914); Ries, *opus cit.*; Searle, *British Clays, Shales, and Sands* (C. Griffin & Co., Ltd., 1912). W. and D. Asch, *The Silicates in Chemistry and Commerce*, transl. by A. B. Searle (Constable, 1913); Searle, *Cement, Concrete and Bricks* (Constable, 1913).

clays and ball-clays, the "true clay" present can rarely be isolated in anything like a pure state; from the work of van Bemmelen, however, it appears that collyrite, the only member of the series that is decomposed by hydrochloric acid, is present in numerous clays.[1] Le Chatelier[2] has proposed to identify the different aluminosilicic acids by means of certain thermal changes that may be observed when they are heated, and by this method he claims[3] to have established the identity of halloysite and pholerite with the aluminosilicic acid present in china-clay.

At the present time it is usually considered that the "true clay" present in a transported clay consists of aluminosilicic acid or mixture of such acids, sometimes with free silicic acid and aluminium hydroxide.[4] Although in the case of the ball-clays (and probably numerous other clays) the "true clay" has the same composition as kaolinite, it is not correct to consider that it is an amorphous form of that mineral, or that it is identical with clayite (p. 105). It differs from the latter firstly in that its particles are much smaller and do not seem to have been shown to be crystalline, and secondly in that it is extremely plastic. Accordingly, Searle[5] distinguishes the "true clay" of ball-clays and other highly plastic transported clays by the term *pelinite.*

Attempts to determine the mineralogical composition of clays are often made, based upon the fact that the "true clay" they contain is attacked by concentrated sulphuric acid. When a clay is heated with concentrated sulphuric acid the "true clay" contained in it is decomposed with the production of aluminium sulphate and silicic acid hydrogel, and these may be removed by digesting the mass alternately with sodium hydroxide or carbonate and hydrochloric acid.[6] The loss in weight which the clay undergoes is often regarded as representing the "true clay" or "clay substance" present. The non-plastic residue is then regarded as being a mixture of felspar or mica and quartz. The silica and alumina it contains are determined and the equivalent amounts of felspar or mica and quartz are calculated.

An analysis of clay carried out according to the scheme just outlined is called (or rather miscalled) a *rational analysis.* It is based upon the assumption that only the "true clay" is rendered soluble by sulphuric acid, whereas it is known that mica is always more or less attacked, the extent varying with the nature of the mica, its state of subdivision, the concentration of the acid, and the time of heating. Felspar is also attacked, but not so readily as mica. Hence the material decomposed by the sulphuric acid

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[1] Van Bemmelen, *Zeitsch. anorg. Chem.*, 1904, **42**, 265; 1909, **62**, 221; 1910, **66**, 322.

[2] Le Chatelier, *Compt. rend.*, 1887, **104**, 1443, 1517; *Bull. Soc. franç. Min.*, 1887, **10**, 207.

[3] Le Chatelier, *La silice et les silicates* (Paris, 1914).

[4] Clays rich in free aluminium hydroxide are termed *laterite clays* or *laterites* and are particularly abundant in the tropics. It is supposed that under tropical conditions ordinary clays are slowly decomposed into free silica and alumina (see van Bemmelen, *loc. cit.*; Lacroix, *Comp. rend.*, 1914, **159**, 617; Fermor, *Geol. Mag.*, 1915, **2**, 28, 77, 123). It has been suggested that the *bauxites* (p. 73) are clays in which the laterisation is very advanced.

[5] Searle, *The Natural History of Clay* (Cambridge University Press, 1912), p. 148.

[6] According to Asch and Asch (*opus cit.*) the effect of heating true clay with sulphuric acid is not the production of aluminium sulphate and silicic acid but the formation of a remarkably stable soluble aluminosilicic anhydride and the separation of some free silica. In the pure primary clays the number of aluminosilicic acids present is limited and the composition of the soluble anhydride is consequently constant, but transported clays have usually derived their "true clay" from several sources so that it probably contains several aluminosilicic acids and the true nature of the mixed soluble anhydrides cannot then be ascertained.

is not merely the "true clay" present. Again, many of the commoner clays contain considerable quantities of chalk, siderite, and hæmatite, or notable amounts of colloidal silicid acid or organic matter, which must be determined separately and their influence on the rational analysis allowed for; hence whilst with the purer kaolins the errors may be only small, with common clays this method of analysis is of little or no value and is frequently misleading. In fact, many rational analyses of clays recorded in the literature are quite inconsistent with the ultimate analyses of the same clays.[1] Hence, as Searle[2] has pointed out, a consideration of the ultimate chemical analysis and a microscopic examination of a clay is, at present, the most satisfactory method of arriving at an approximate idea of its mineralogical composition.

Physical Properties of Clays.—Most clays are fairly soft solid bodies, particularly when moistened with water; they have a characteristic "argillaceous" odour, which is usually attributed to the presence of organic matter. The true density usually varies between 2·50 and 2·65, but as some clays are more porous than others the apparent density varies very considerably.

Freshly dug clays vary very considerably in colour, from nearly white to almost black; most commonly they are yellow, grey, or greyish-brown. The colour is due partly to the organic matter present and partly to the presence of certain minerals, usually compounds of iron (hæmatite, limonite, siderite); colour is accordingly no reliable criterion of the purity of a clay or of the colour it will become when burned in a kiln or pottery oven.

A very obvious and extremely important property of a moist clay is its *plasticity*, or ability to change its shape without rupture when submitted to pressure and to retain its new shape when the pressure is removed. Different kinds of clays vary enormously in their degrees of plasticity. No entirely satisfactory method for measuring the plasticity of clay has yet been devised.

A decidedly plastic clay has the power of remaining plastic when other finely divided but non-plastic materials, *e.g.* sand and brick-dust, are incorporated into it. In general, the more plastic a clay the greater the amount of non-plastic material which it can thus "bind," and the more finely divided the added substance the smaller is its effect in reducing the tensile strength of the clay.

Owing to its heterogeneous character a dry clay is porous, *i.e.* its apparent volume includes the volume of a considerable quantity of air; this may be roughly estimated by determining the quantity of inert liquid which it can absorb without changing its volume. If a little water is added in small quantities the clay first becomes granular and then pasty. The addition of a still further quantity of water separates the particles to such an extent that the cohesion is destroyed, the clay "runs," and a fluid clay "slip" or "slurry" is produced.

When a clay that has been kneaded into a plastic mass with water is set aside in the open, evaporation of water commences at the surface. As the surface water evaporates it is replenished from within the mass, and as long as there is any water between the clay particles the process of drying is attended by a shrinkage in the volume of the mass. A stage is eventually reached when the solid particles are in direct contact with one another,

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[1] Mellor, *Collected Papers*, 1914, vol. i. p. 109, and *A Treatise on Quantitative Inorganic Analysis*, 1913 (C. Griffin & Co., Ltd.), chap. xliv., where a critical discussion of the method of rational analysis will be found.

[2] Searle, *opus cit.*

and the removal of the remaining small amount of water is not attended by any further shrinkage. The amount of shrinkage depends upon the texture of the clay, the relative proportions of plastic and non-plastic materials it contains, the amount of water added, and several other factors, and a shrinkage in volume of 12 to 38 per cent. may be considered normal. In the preparation of various ceramic products from clays which exhibit a large air-shrinkage, sand or material of a sandy nature is often added to reduce the shrinkage, and an additional advantage is thereby gained as the increased porosity permits the mass to be dried more rapidly and minimises danger from cracking.

Many theories have been advanced to account for the plasticity of wet clay, but not one can be considered as wholly satisfactory.[1] In a general way it may be stated that each solid particle present in the clay must be surrounded by a film that is coherent and self-healing.[2] In the opinion of Le Chatelier[3] the film is composed merely of water, the coherency of the plastic mass being attributed to (i.) the lamellar structure of the clay particles, which can accordingly slip over one another readily like the various units in a pack of cards, and (ii.) the presence of minute air-bubbles in the mass, on account of which innumerable capillary menisci are produced and the lamellar particles held tightly together by the operation of surface tension.

It is an undoubted fact that very finely divided[4] kaolinite, mica, glaucophane, calcite, gypsum, and other minerals which readily cleave into plates, acquire a certain plasticity when mixed with the requisite amount of water; yet, while it is possible that Le Chatelier's explanation of plasticity may account satisfactorily for the feeble plasticity of the kaolins, it is improbable that it can be more than a minor cause of the plasticity of the highly plastic secondary clays, even if it be granted that with a smaller size of clay particle the plasticity would be augmented.

It is difficult to connect plasticity with chemical composition, as clays which yield almost identical results upon analysis may differ widely in plasticity; moreover, clays that are richest in "clay substance" are often less plastic than those which are less pure, so that although many authorities have attributed plasticity to a peculiar structure of the clay molecule, such an explanation should not be hastily accepted.[4]

There is considerable evidence for the view that most clays contain *colloid matter*,[5] and that the plasticity of a clay is closely connected with the quantity of colloid matter present. Ashley, in a discussion of this subject,[6] considers that both inorganic and organic colloids may occur in clays. The former include amorphous aluminosilicic acids, silicic acid, ferric hydroxide, and occasionally aluminium hydroxide; the latter, which have been produced from vegetable matter, are usually referred to as "humus"

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[1] The more important theories have been carefully summarised by Searle, *British Clays, Shales, and Sands* (C. Griffin & Co., Ltd., 1912).

[2] Bancroft, *J. Physical Chem.*, 1914, 18, 783.

[3] Le Chatelier, *opus cit.* (p. 109). See also S. W. Johnson and J. M. Blake, *Amer. J. Sci.*, 1867, [ii.], 43, 351.

[4] For an attempt to connect the plasticity of clay with the chemical constitution of the clay molecule, see W. and D. Asch, *opus cit.*

[5] First suggested by Way, *J. Roy. Agric. Soc.*, 1850, 11, 313, and Schloesing, *Compt. rend.*, 1874, 79, 376, 473.

[6] Ashley, *Bull. U.S. Geol. Survey*, 1909, No. 388, where numerous references to the literature may be found.

or "humic acid." It has been suggested by some that the organic colloids are the most important,[1] but this cannot be regarded as proved. On the colloid theory of plasticity, a wet, plastic mass of clay is regarded as consisting of innumerable minute solid mineral particles disseminated throughout a gelatinous, colloidal hydrogel or mixture of hydrogels, saturated with water.

A hydrogel such as precipitated silicic acid shrinks very largely in volume on drying, and when dried at a fairly low temperature forms a very hygroscopic mass which can take up a considerable amount of water without appearing wet. In these respects it closely resembles a plastic clay. Plastic clays are in various other respects similar to hydrogels, *e.g.* they adsorb substances selectively from aqueous solutions. The adsorbed substances may be either metallic salts or organic dyes of a colloidal nature.[2] The adsorption of 1 or 2 per cent. of certain organic colloids such as gallotannic acid and catechu increases the plasticity of a clay.[3] Ashley has proposed to measure the plasticity of a clay by its power to adsorb methylene blue.

The presence of reversible colloids in a plastic clay is suggested by the manner in which the viscosity of clay slips is influenced by the presence of metallic salts.[4] For instance, a plastic clay which has been worked up with water into a very viscous mass may be transformed into a mobile liquid by the addition of a little sodium hydroxide or carbonate, and reconverted into a viscous mass by the further addition of a little hydrochloric acid. The explanation is probably as follows.[5] The colloids present in clays are negatively charged when in colloidal suspension, and accordingly it is mainly the positive ions of the electrolytes added that are of influence in producing their coagulation. All clays contain soluble salts to some extent, although it may often be but a slight one, and of the ions into which they dissociate the positive, bivalent calcium ion has most effect in preventing the hydrogels present from passing into hydrosols when the clay is stirred up with water. The addition of sodium carbonate leads to the removal of the calcium ions and their replacement by univalent sodium ions which, being of lower valency, are less able to prevent the conversion of gel into sol.[6] On this view the addition of sodium carbonate little by little would be expected first to facilitate sol formation and thus diminish the viscosity until the calcium was precipitated, and then, with increasing concentration of sodium ions, to facilitate the reverse change from sol to gel and so increase the viscosity.[7] This is precisely how the viscosity is observed

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[1] See, *e.g.*, Stewart, *J. Ind. Eng. Chem.*, 1913, **5**, 421.

[2] Way, *J. Roy. Agric. Soc.*, 1850, **11**, 313; Hirsch, *Tonind. Zeit.*, 1904, **28**, 491 ; Ries, *Trans. Amer. Cer. Soc.*, 1904, **6**, 44 ; Ashley, *loc. cit.*

[3] Acheson, *Trans. Amer. Cer. Soc.*, 1904, **6**, 31.

[4] Simonis, *Sprechsaal*, 1905, **38**, 597, 881, 1625 ; 1906, **39**, 169, 1167, 1184 ; Bleininger, *Trans. Amer. Cer. Soc.*, 1908, **10**, 389 ; Mellor, Green, and Baugh, *Trans. Eng. Cer. Soc.*, 1908, **6**, 161, or Mellor, *Collected Papers*, vol. i. p. 88 ; Back, *Trans. Amer. Cer. Soc.*, 1914, **16**, 515 ; Bleininger, *J. Franklin Inst.*, 1915, **180**, 225.

[5] W. and D. Asch (*opus cit.*) consider that the addition of small quantities of alkali converts clays into strongly acid salts by replacing only one or two hydrogen atoms in a highly complex molecule. They also consider that the addition of a weak acid replaces the alkali metal by hydrogen and restores the original clay molecule. They find confirmation of their views in the differential behaviour of china-clay, which had been treated with soda, to strong and weak acids respectively.

[6] See Vol. I. p. 84.

[7] F. Foerster, *Chem. Ind.*, 1905, **28**, 733.

to vary.[1] The great value of sodium carbonate in the production of a fluid slip containing a minimum of water has been known for many years and is utilised in preparing ceramic bodies by the method of slip casting (p. 126).

W. and D. Asch claim that their theory of the molecular constitution of clays accounts for all the so-called colloidal properties in a purely chemical manner.

Action of Heat on Clays.—The simplest case is that of the action of heat on china-clay that has been washed free from all but a very small percentage of mica and quartz, *i.e.* a mixture of clayite and kaolinite, the former being in great excess. The decomposition of this mixture by heat has been carefully studied by Mellor and Holdcroft.[2] At 100° to 110° C. the hygroscopic moisture is driven off; at higher temperatures water is evolved in consequence of the breakdown of the molecule. It is not possible to state any definite temperature below which this decomposition ceases; the rate of decomposition increases with rise of temperature and is quite perceptible at 500° C., the mass losing weight at the rate of 1·2 per cent. per hour. As the temperature is increased to a little above 500°, decomposition of the clay occurs with a decided absorption of heat (about 10·8 Cals. per formula-weight in grams of clayite). The evidence is not conclusive on the matter, but Mellor and Holdcroft think it very probable that this heat absorption corresponds with the following chemical change:—

$$H_4Al_2Si_2O_9 = Al_2O_3 + 2SiO_2 + 2H_2O.$$ [3]

When the temperature reaches a little more than 800° a marked evolution of heat is observed, owing to some kind of change (polymerisation?) taking place in the alumina (*cf.* p. 72).[4] At temperatures between 1200° and 1300° the silica and alumina commence to reunite[5] at a slow but perceptible rate, for crystals of sillimanite, $Al_2O_3.SiO_2$, begin to form in the mass. At higher temperatures (above 1700°), owing to the fusion of the traces of mica and silica initially present and the silica produced from the decomposition of the clayite, the mass commences to sinter, and it becomes decidedly fluid at 1740° C.[6]

The thermal changes observed with china-clay at temperatures just above 500° and 800° are also noticed when the pure mineral kaolinite is heated;[7]

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[1] For further information on the colloidal theory of plasticity, see Ashley, *loc. cit.*; Rohland, *Die Tone* (Vienna, 1909); Rohland, *Zeitsch. anorg. Chem.*, 1902, **31**, 158; *Sprechsaal*, 1906, **39**, 129, 1371; *Biochem. Zeitsch.*, 1912, **46**, 374; *Kolloid Zeitsch.*, 1914, **14**, 193; Cushman, *J. Amer. Chem. Soc.*, 1903, **25**, 451; *Trans. Amer. Cer. Soc.*, 1904, **6**, 65; N. B. Davis, *ibid.*, 1914, **16**, 65; *Bull. Amer. Inst. Mng. Eng.*, 1915, p. 301, and special treatises on clays.

[2] Mellor and Holdcroft, *Trans. Eng. Cer. Soc.*, 1911, **9**, 94; Mellor, *Collected Papers*, 1914, vol. i. p. 272. See also Le Chatelier, *opus cit.*, and *Bull. Soc. franç. Min.*, 1887, **10**, 207; *Compt. rend.*, 1887, **104**, 1443, 1517; Samoilov, *Bull. Acad. Sci. Petrograd*, 1914, p. 779.

[3] All that is certainly known is that water is given off in the proportion indicated in the equation, and that the residue is soluble in dilute hydrochloric acid. This is incompatible with the production of free silica, and is regarded by some chemists as indicating the formation of a soluble aluminosilicic anhydride $Al_{2x}Si_yO_{3x+2y}$ which polymerises or decomposes and becomes insoluble on further heating. See W. and D. Asch, *opus cit.*

[4] Or in the aluminosilicic anhydride (*cf.* preceding footnote).

[5] Or the aluminosilicic anhydride to decompose.

[6] Kanolt, *J. Washington Acad. Sci.*, 1912, **2**, 337; *Tech. Papers, Bur. Stand.*, 1912, No. **10**.

[7] Mellor and Holdcroft, *Trans. Eng. Cer. Soc.*, 1912, **10**, 169; Mellor, *Collected Papers*, 1914, vol. i. p. 297.

this is a strong argument in favour of the view that clayite and kaolinite are the same substance in different degrees of subdivision or different physical conditions.

Little is known of the action of heat upon the other aluminosilicic acids which are thought to exist in clays,[1] but it is at least very probable that at temperatures above 500° or thereabouts they behave like kaolinite.

Ordinary clays are heterogeneous, and hence cannot be said to have melting-points in the true sense of the term. Of the variously finely divided minerals present in them, some, *e.g.* the felspars and micas, have definite melting-points, while others, *e.g.* chalk, dolomite, siderite, pyrites, gypsum, etc., when heated, undergo chemical decomposition at temperatures below the melting-points of the former,[2] with the production of substances of very high melting-point (lime, magnesia, ferrous oxide, etc.). These substances, however, are basic in chemical character, and react with silica, micas, and felspars at temperatures of about 900° to 1000°, *i.e.* considerably below the melting-points of these substances,[3] with the production of molten silicate mixtures. As the heating is continued and the temperature rises, the felspars and micas, still unchanged, commence to melt. The felspars, micas, lime, magnesia, etc., in a clay are accordingly said to be the *fluxes* present. It is a curious fact that, except in the presence of lime, ferric oxide does not appear to act as a flux but rather as an infusible material; ferrous oxide, however, is a powerful flux. Titanic oxide is an acidic oxide which, like silica, acts as a flux in refractory clays.

The *fusibility* of a clay depends upon the nature and amount of the fluxes present. Bearing in mind that ferric oxide may or may not act as a flux, the amount of fluxes present may be seen from the ultimate analysis; the sum of the alkalies, lime, magnesia, "ferric oxide," and titanic oxide is often spoken of as the amount of fluxing impurities contained in the clay. Concerning the nature of the fluxes present, it may be said that the alkalies are contained almost entirely in the micas and felspars, which minerals also account for at least part, and sometimes practically all, of the lime and magnesia present. The presence of above 5 per cent. of lime is, however, an almost certain indication that free calcium carbonate is present in the clay.

The action of heat on a natural clay is such that at a certain temperature, which may be as low as about 900° C. or several hundred degrees higher according to the nature of the clay, molten material commences to form in it. This fluid, which is very viscous, acts as a kind of "cement," binding the still unfused particles together; on cooling, the "cement" sets to an amorphous "glass," instead of crystallising, and, unless the proportion of fluxes is too small or the time of heating too short, a hard porous mass having considerable crushing strength is obtained.

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[1] See, however, Le Chatelier, *loc. cit.*

[2] *E.g.* the dissociation-pressure of calcium carbonate reaches the value of one atmosphere at 898° C. (Johnston, *J. Amer. Chem. Soc.*, 1910, **32**, 938).

[3] The melting-points of the alkali felspars albite and orthoclase are not known with much accuracy, but are rather lower than 1200° C.; Bowen gives the value 1100 ± 10° C. for albite. The melting-points of the plagioclase felspars rise steadily with increase of calcium content from *c.* 1100° C., the melting-point of albite, to 1550° C., the melting-point of anorthite (Day and Allen, *Amer. J. Sci.*, 1905, [iv.], **19**, 93; Day and Sosman, *ibid.*, 1911, [iv.], **31**, 341; Bowen, *ibid.*, 1913, [iv.], **35**, 577). See also Joly, *Proc. Roy. Irish Acad.*, 1891, [iii.], **2**, 38; Cusack, *ibid.*, 1896, [iii.], **4**, 339; Doelter, *Tsch. Min. Mitt.*, 1901, **20**, 210; 1902, **21**, 23. White mica or muscovite is not such a readily fusible flux as an alkali felspar; see R. T. Stull, *Trans. Amer. Cer. Soc.*, 1902, **4**, 255.

If the period of heating is prolonged, more and more of the fluxes enter into the fluid state. The surface tension between fluid and solid causes the solid particles to be drawn closer and closer together, and this, with the flow of fluid into the pores, diminishes the porosity of the heated clay. At the same time the fluid exerts a solvent action upon the solid particles. The entire process is spoken of as the *vitrification* of the clay. The speed at which the vitrification proceeds at a given temperature depends upon the composition of the clay and on its texture, *i.e.* the sizes of the various kinds of particles present; quartz, for instance, is more readily dissolved by the molten fluxes when very finely divided than when it is present in coarse grains. By raising the temperature, the rate of vitrification is accelerated.

When the period of heating of the clay is sufficiently prolonged at an assigned temperature, it may happen that the vitrification is carried so far that the mass is no longer capable of retaining its shape, *i.e.* it softens. The more readily a clay softens the less refractory it is said to be. The softening of the mass is determined by the ratio of the fused to the unfused material present, *i.e.* by the extent to which vitrification has proceeded, and by the viscosity of the fused material. As the vitrification is caused by slow reactions in heterogeneous systems, the temperature of softening is not a measure of the refractoriness of a clay without reference to the manner in which it is heated, for the temperature of softening will vary with the rate of rise in the temperature of the clay, with the chemical changes undergone by the clay, with the use of an oxidising or a reducing atmosphere, and with the pressure, since a viscous fluid which is incapable of flowing under its own weight may be caused to flow by subjecting it to sufficient pressure.

When a clay is heated to a temperature at which vitrification will proceed, and maintained at that temperature, it does not follow that vitrification will continue until the mass softens. If the percentage of fluxes is low, the fluxes soon become saturated with the refractory particles and form a solution which is practically infusible at the given temperature. The temperature must then be raised before the fluxes can again resume their work of dissolving the refractory particles while drawing them closer together. On the other hand, the proportion of fluxes may be such that, although the mass does not soften, vitrification continues at the given temperature until the porosity of the mass has been reduced practically to zero and a stoneware mass, impervious to water, has been produced. The clay is then said to have been completely vitrified, and clays which behave in this manner are called *vitrifiable* or *stoneware clays*.

The extent to which vitrification proceeds increases with rise of temperature, so that a clay which completely vitrifies at a given temperature may not do so at another and higher temperature without softening and losing its shape. The temperature interval between the point of incipient vitrification and the softening point is spoken of as the "range of vitrification." Since clayware loses its commercial value when it softens and loses its shape, it will be clear that the production of stoneware from vitrifiable clays is only safe with clays having a long range of vitrification; if the range is short, disastrous results may easily occur as the result of slight overheating. It has been found that calcareous clays are those which have the shortest range of vitrification. In this respect the fluxing action of lime is in marked contrast with that of magnesia.[1]

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[1] Mäckler, *Tonind. Zeit.*, 1904, **26**, 706; Hottinger, *Trans. Amer. Cer. Soc.*, 1903, **5**, 130; Barringer, *ibid.*, 1904, **6**, 86.

The *softening point* of a clay is usually determined by forming a test portion into a small triangular pyramid about five or six times as high as the length of its base, drying it, mounting it vertically in a suitable furnace, and then raising its temperature until the pyramid, or "cone" as it is usually called, bends over and its apex reaches the level of the base. According to Mellor, if the temperature is then t_2° C. and the cone commenced to bend at t_1° C., the interval t_1 to t_2 represents the softening range and the mean temperature $(t_1 \times t_2)/2$ may be taken as the softening point: throughout the heating a reducing atmosphere should be avoided, and the temperature should be raised at the (arbitrary) rate of 10° C. per minute.[1] Mellor's definitions of the softening range and softening point of a clay are not, however, commonly adopted, and ceramists almost invariably regard t_2° C. as the softening point. Although the actual softening temperature may be measured by means of a pyrometer, it is more customary to express the result by giving the number of the *Seger cone* that has the same softening point when heated alongside the clay under examination. Seger cones were originally composed of suitable mixtures of washed Zettlitz kaolin, Rörstrand felspar, Norwegian quartz, Carrara marble, and pure ferric oxide; they were numbered from 1 to 39 in the order of increasing softening points. Cramer and Hecht, by adding boric acid and lead oxide to the list of ingredients, added the more fusible cones, numbered 01, 02, 03 . . . to 022; the softening points associated with the Seger cones then ranged from 600° C. (cone 022) to 1880° C. (cone 39).[2]

The bending points of Seger cones only correspond to definite temperatures when the conditions of heating are those for which the cones were designed. Thus, while cone 10 can be observed to soften at about 1300° C. when heated in a small gas muffle, yet when its temperature is very slowly raised in a large kiln, taking about four days to reach its maximum temperature, the same cone softens below 1200° C. Again, a fireclay that softened at cone 33 when heated in a standard manner, only softened at cone 35 when heated in a rapid injector furnace.[3] For this reason Seger was always strongly opposed to the use of a temperature scale in connection with his

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[1] See Mellor, *Collected Papers*, vol. i. p. 190. The Institution of Gas Engineers defines the softening point as the temperature at which the angular edges of the test pyramid begin to lose their angularity.

[2] In 1908 it was decided to suppress cones 21 to 25, since their softening points were very close together, and to modify the compositions of a number of the other cones. The numbers by which the new Seger cones are designated, and the softening temperatures (in degrees C.) usually associated with them, are as follows (see *Sprechsaal*, 1908, p. 561):—

022	600°	012 *a*	855°	02 *a*	1060°	9	1280°	19	1520°	34	1750°
021	650	011 *a*	880	01 *a*	1080	10	1300	20	1530	35	1770
020	670	010 *a*	900	1 *a*	1100	11	1320	26	1580	36	1790
019	690	09 *a*	920	2 *a*	1120	12	1350	27	1610	37	1825
018	710	08 *a*	940	3 *a*	1140	13	1380	28	1630	38	1850
017	730	07 *a*	960	4 *a*	1160	14	1410	29	1650	39	1880
016	750	06 *a*	980	5 *a*	1180	15	1430	30	1670	40	1920
015 *a*	790	05 *a*	1000	6 *a*	1200	16	1460	31	1690	41	1960
014 *a*	815	04 *a*	1020	7	1230	17	1480	32	1710	42	2000
013 *a*	835	03 *a*	1040	8	1250	18	1500	33	1730		

[3] Mellor, *Collected Papers*, vol. i. p 379. See also Zimmer, *Trans. Amer. Cer. Soc.*, 1899, I, 23.

cones. In general, the softening temperature of a clay is raised by increasing the rate of heating and it is decreased by increasing the pressure.

It has been previously mentioned that the *colour* of a raw clay is no safe criterion of the colour that the same clay develops when heated. In general it may be said that clays free from iron burn white, those containing 2 or 3 per cent. of iron oxide burn to a buff-coloured mass, and those containing 4 to 5 per cent. or more of iron oxide yield a red product. The colour of a burned clay does not, however, depend merely upon the quantity of iron present, but is influenced by the size of the particles and the state of oxidation of the iron, the presence of other substances, and the temperature to which the clay has been heated. When all the iron present in the burned clay is in the ferric state, the tendency is for the colour to pass from white through buff to red as the amount of iron increases, the colour deepening as the temperature of firing rises. Calcareous clays only burn to a buff colour even when much iron is present, the bleaching action of the lime being greatest when its percentage is three times that of the ferric oxide; for this reason chalk is often added to brick-clays so as to produce white or buff-coloured bricks. The presence of titanic oxide is said to intensify the colouring power of the iron. When the nature of the clay and the firing conditions are such that ferrous oxide is produced in the mass, vitrification commences at a comparatively low temperature, with the production of a dark bluish-grey or black fusible aluminosilicate containing iron in the ferrous state.

In the burning of ferruginous clays it is usually desirable to convert all the iron into the ferric state before vitrification commences, in order that the clay shall burn to the desired colour and not vitrify too readily. To accomplish this it is necessary that the burning shall take place in an oxidising atmosphere; any carbonaceous matter must be completely burned out at a temperature not exceeding about 900° C., any ferric oxide which has been reduced by the carbonaceous matter must be re-oxidised, and any pyrites or siderite initially present must be roasted to ferric oxide. The complete oxidation of pyrites or siderite in a clay is a very difficult task, and clays containing pyrites seldom burn red; instead, a buff-coloured product is obtained with black spots scattered irregularly over its surface and throughout its mass. Pyrites and siderite, however, are rarely found in surface clays, owing to the fact that by weathering they are converted into limonite; they are frequently found in shales and fire-clays, particularly those associated with coal-seams.[1]

When the complete oxidation of the iron has been accomplished the colour of the surface of the burned clay may be altered, if desired, by changing the atmosphere in the kiln from an oxidising to a reducing one. The well-known vitrified Staffordshire "blue" bricks are produced in this manner.

The vitrification of clay is usually associated with a marked change in the volume of the mass; almost invariably a *shrinkage* occurs. The volume change actually observed is the net result of a number of such changes, which are due to different circumstances. As soon as the fluxes commence to melt, the liquid produced draws the unfused particles closer and closer together. The diminution in volume which results from this depends upon the extent to which vitrification is allowed to proceed, and upon the porosity

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[1] See Mellor, *Trans. Eng. Cer. Soc.*, 1907, 6, 142; 1908, 7, 112; *Collected Papers*, vol. i. p. 122, on pyritiferous clays.

of the clay just previous to the commencement of vitrification; the latter depends upon the nature of the clay and the shrinkage it has already undergone in the drying period. The volume shrinkage due to the elimination of pores is partially compensated for by certain expansions in volume. Practically all crystalline solids expand on fusion, and the fusion of such fluxes as mica and felspar is accordingly associated with an increase in volume amounting with felspar to about 6 per cent. Polymorphic change may occur in clays rich in free silica and may be associated with an increase in volume. This arises from the fact that silica exists in quite a number of polymorphic forms,[1] of which those stable above 800° C. (tridymite, christabolite, etc.) have specific volumes some 14 per cent. greater than those stable at lower temperatures. Thus, highly siliceous fire-bricks expand when fired. The processes of solution which are operative throughout the period of vitrification also influence the volume of the mass, though only to a very slight extent.

Clays vary very much with respect to the amounts of fire-shrinkage which they undergo. Excessive shrinkage leads to warping and cracking in goods manufactured from them, and should be corrected by the addition of suitable refractory materials (see p. 121).

Kinds of Clays.—Clays may be divided into two groups, *refractory clays* and *non-refractory clays*, according to whether their softening temperatures are above or below a certain arbitrary point, for which Mellor[2] proposes 1500° C., while the German ceramic chemists[3] and the Institution of Gas Engineers adopt the softening point of Seger cone 26 (about 1580° C.).

Certain refractory clays become white or cream-coloured when fired. Of these, the *china-clays* and *kaolins* are the most important; the other clays of this type are called *pipe-clays.*[4] The other refractory clays, which become grey, buff, or red in colour, are known as *fireclays.* Mellor[2] divides them into three grades: (i.) low grade, softening between 1500° and 1650°; (ii.) medium grade, softening between 1650° and 1750°; and (iii.) high grade, softening above 1750°. The Institution of Gas Engineers recognises two grades: (i.) No. 1, when no softening occurs below Seger cone 30 (1670°); and (ii.) No. 2, when softening occurs above cone 26 (1580°), but below cone 30 (1670°).

The non-refractory clays may be either (i.) calcareous or (ii.) non-calcareous, according to whether they do or do not contain more than about 5 per cent. of admixed calcium carbonate. The calcareous clays are usually termed *malms* (or *marls*), and, as already explained, when burned in an oxidising atmosphere they yield cream, buff, or red products according to the amounts of ferric oxide and lime present. The non-calcareous clays vary greatly in their properties, from the valuable *ball-clays* which burn to a white or cream colour, to the more common buff and red-

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[1] See Vol. V.

[2] Mellor, *Collected Papers*, vol. i. p. 190.

[3] Cramer, *Tonind. Zeit.*, 1902, 26, 1064.

[4] Many pipe-clays are not refractory, this term being extensively employed for any white clay which can be used for whitening belts, etc. If a pipe-clay is found to be refractory it is at once classified among the china-clays or ball-clays, as these are of greater commercial value.

The term "pipe-clay" is also applied to clays suitable for the manufacture of drain-pipes. Such clays are better considered as fireclays or ball-clays according to their nature; they are distinguished from the true pipe-clays in not being white when dry.

burning clays used in the manufacture of bricks, terra-cottas, and common pottery ware.

Calcareous clays in which the calcium carbonate is present in a finely divided state, *i.e.* as chalk, are largely used for making light-coloured bricks. Clays may be successfully used even though they contain 25 per cent. of chalk, provided that the product is only slightly vitrified. Calcareous clays are also used in the manufacture of Portland cement.[1]

China-clays and *kaolins* are used in the manufacture of china, porcelain, stoneware, fine faience, and ultramarine (see p. 135); they are also used for weighting paper.[2] Some account of their nature has already been given (p. 104), and for further information the reader must refer to special treatises. Important deposits of china-clay are found in Cornwall and Devon in England; kaolins occur at St Yrieix, near Limoges, in France, at Zettlitz in Bohemia, in various parts of the United States, etc.

Ball-clays are highly plastic transported clays which burn to a white or cream colour. They frequently contain 3 or 4 per cent., or even a larger proportion, of organic matter, and hence in the raw state they are often nearly black in colour. In England, the best deposits are found in Devonshire and Dorset. The ball-clays form the basis of most ordinary pottery. When carefully selected they are extremely fine in texture and free from grit, and do not differ very much in composition from commercial china-clay. *Pipe-clays*[3] are inferior qualities of ball-clay, containing rather more iron and alkalies and considerably more silica.

Fireclays.—The chief fireclays are the clays and shales found in association with coal seams. In the British Isles such clays are found in large quantities in Northumberland, Durham, Yorkshire, Nottinghamshire, Derbyshire, Staffordshire (near Stourbridge), Warwickshire, Shropshire, North and South Wales, South-West Scotland (near Glasgow), and County Tyrone in Ireland. The fireclays vary very much in composition, but all are relatively low in fluxes and to this fact they owe their refractoriness. The shales occur above the coal seams, the non-laminated fireclays below them (underclays). Fireclays are generally grey or greenish-grey in colour, owing to the presence of vegetable matter and iron compounds (notably pyrites, which is detrimental to the quality of goods made from the clays); they are compact, dense, and of varying degrees of hardness. By exposing them to the weather most fireclays crumble and become easier to grind. They are utilised in the manufacture of fire-bricks and other ceramic products of a refractory nature.

Brick-clays.—Although at times it has been convenient and economical to manufacture ordinary building bricks from fireclays, yet the greater part of the bricks and tiles used for constructional purposes are made from common, non-refractory, plastic clays which develop buff or red tints when fired. Common bricks may be satisfactorily made from clays so poor in "true clay" as to be scarcely worthy of being ranked as clays. Such clays, which are frequently termed *brick-earths*, are usually rich in sand. So long as the adventitious materials present in a clay are chiefly sand and chalk, and provided that the clay is reasonably plastic and will commence to vitrify at about 950° C., with a volume contraction not exceeding 25 per cent., to

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[1] See Vol. III.

[2] See Remington, Bowack, and Davidson, *J. Ind. Eng. Chem.*, 1911, 3, 550.

[3] See note 4, p. 118.

form a mass having a crushing strength of at least 85 tons per square foot, it will generally be suitable for the manufacture of common bricks.

The clays utilised in the preparation of *roofing-tiles*, *architectural* and *decorative terra-cotta*, and *coarse pottery ware* are closely allied to those used for brickmaking, but are decidedly finer in texture, particularly those used for making the terra-cottas. When suitable clays are not found locally, it is sometimes convenient to prepare them from brick-clays by removing the coarser particles by washing and sedimentation. Some fine-grained shales are also excellent materials for use in the manufacture of terra-cotta.

Fuller's earth is an earthy deposit similar in character to clay. It usually has a characteristic greenish-grey tint. Apart from its ready fusibility, it behaves like a china-clay of unusually low plasticity. Its mineralogical composition is not yet elucidated,[1] and the recognition of true fuller's earth is not at all an easy matter. In England the best deposits occur in the neighbourhood of Reigate (Surrey) and at Woburn Sands in Bedfordshire. The following data relate to the analysis of a sample from near Reigate :—[2]

Constituent .	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	K_2O.	Na_2O.	Moisture.	Loss on Ignition.
Air-dried .	54·28	0·37	14·97	6·08	0·37	3·14	2·83	0·19	0·32	12·56	5·84
Dried at 110°C.	62·09	0·42	17·12	6·97	0·42	3·59	3·24	0·22	0·36	...	6·68

Fuller's earth absorbs grease, and was originally employed for fulling or degreasing wool. Its use for this purpose has declined considerably, but it is also used for clarifying and deodorising fats, oils, and greases (particularly lard-, castor-, coconut-, and cottonseed-oils), as a diluent for ultramarine, and in the manufacture of paper, toilet powder, and certain soaps.

Ceramics. Classification of Ceramic Products.[3]—For the production of ceramic ware a material is required that shall be (i.) sufficiently plastic when moist to be formed into any desired shape, and (ii.) dense and stone-like when "fired," *i.e.* heated to a sufficiently high temperature. Accordingly, the foundation of every piece of ceramic ware is one or other of the various natural clays, or a mixture of them. For many purposes, however, it is impossible to use clay alone, and other suitable materials have to be added to it. The clay may, for instance, be so plastic that it is unable to retain its form during the process of drying, or it may become deformed or develop cracks owing to excessive shrinkage during the same process. To overcome these and other defects it is necessary to add hardening or opening materials to the clays, and thereby modify the plasticity and shrinkage of the mass. Again, in certain kinds of pottery it is essential that the fired body be impermeable to water, and it may then become necessary to add considerable quantities of suitable fusible materials or fluxes to the clay.

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[1] It appears to be composed mainly of one or two of the minerals related to clay.

[2] Analysis communicated by Mr A. G. Hopkins.

[3] The reader seeking further information on the ceramic industries is referred to the following works: Bourry, *A Treatise on Ceramic Industries*, revised translation by A. B. Searle (Scott, Greenwood & Son, 1911); Granger, *La céramique industrielle* (Gauthier-Villars, Paris, 1905); Searle, *Modern Brickmaking* (Scott, Greenwood & Son, 1911); Granger, *Fabrication et emploi des matériaux et produits réfractaires utilisés dans l'industrie* (Paris, 1910); and the works of Thorpe, Moissan, and Le Chatelier cited on p. 103. A fairly complete list of books on ceramics is given in Searle, *Clayworker's Handbook* (C. Griffin & Co., Ltd., 1911).

Accordingly, so far as the preparation of pottery bodies is concerned, the materials used may be divided into three groups, as follows:—

(i.) *Plastic Materials.*—The different varieties of clay.

(ii.) *Opening or Hardening Materials.*—These include silica in the form of sand, flint or quartz, "grog" (*i.e.* previously fired clay), and a number of other materials less frequently used.

(iii.) *Fusible Materials or Fluxes.*—Felspar, pegmatite, bone ash (*i.e.* calcium phosphate), and chalk are the fluxes most commonly employed. The felspar employed is usually Norwegian orthoclase. In England the pegmatite used is known as Cornish stone or china stone; it is a partially kaolinised granite which behaves in many respects like a mixture of felspar and quartz. The bone ash is generally prepared by calcining the bones of oxen.

The numerous products of the ceramic industry may be divided into two classes, according as the "bodies" are (i.) *permeable* or (ii.) *impermeable* to water. The bodies in class (i.) are porous, exhibit an earthy fracture, and may be scratched by steel; those in class (ii.) are hard and sonorous, exhibit a vitreous or conchoidal fracture, and cannot be scratched by steel. The bodies of class (ii.) may be divided into two subclasses, (ii. *a*) *porcelains*, which are white and translucent in pieces 2 or 3 mm. thick, and (ii. *b*) *stonewares*, which are opaque and usually coloured, if only to a slight extent.

Porous ware may either be used as such for constructional or decorative purposes, *e.g.* numerous kinds of bricks and tiles, and terra-cotta statuary, or it may be covered with a vitreous envelope known as a *glaze* or an *enamel* according as it is transparent or opaque. Porous pottery when glazed or enamelled is known as *fine earthenware* when the body is white and as *faience* when the body is coloured, although the enamelled faience is sometimes called *majolica.*[1] Unglazed porous ware may be divided into two subclasses, (i. *a*) those which lose their form or become impermeable at a temperature higher than that at which hard porcelain is fired (*c.* 1400° C.) and (i. *b*) those which do not. The former may be termed *terra-cottas*, using the word in its literal sense (baked earth), and the latter, *fireclay* or *refractory ware. Sanitary ware* is chiefly made by glazing articles made of fireclay and is, therefore, to be included under fireclay ware. When it has a vitrified body it should be included under stoneware.

Impermeable ware, like porous ware, may or may not be glazed. Stoneware is often glazed or enamelled, and most porcelains are glazed, although with the variety known as *parian* this is seldom the case.

The preceding classification of ceramic products is that proposed by Bourry and is summarised in the following table:—

I. POROUS BODY, PERMEABLE TO WATER.
  (*a*) Not glazed: *terra-cotta.*
  (*b*) Not glazed: *fireclay goods.*
  (*c*) Glazed: *fine earthenware, sanitary ware, faience, majolica.*

II. BODY IMPERMEABLE TO WATER.
  (*a*) Translucent: *porcelain.*
  (*b*) Opaque: *stoneware.*

Ceramic ware may be glazed (or enamelled) either (i.) by drying the "body" until it is in a fit state to have the glaze applied to its surface,

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[1] This distinction between the uses of the terms "faience" and "majolica" was proposed by Burt (*Trans. Amer. Cer. Soc.*, 1904, **6**, 109).

and then firing the mass, or (ii.) by firing the unglazed body, coating the "biscuit" ware thus obtained with the glaze, and re-firing. The two firings are said to be carried out in the "biscuit" oven and the "glost" oven respectively, and the second firing always occurs at a lower temperature than the first. The second procedure is nearly always adopted, but hard porcelain, some sanitary ware, and certain kinds of stoneware are prepared by the first method.

The porcelains, and particularly the hard porcelains, are of particular interest and importance to the chemist. Being covered with hard glazes that are scarcely attacked by prolonged boiling with mineral acids or aqueous solutions of alkalies, and being capable of withstanding rapid alterations of temperature, they are invaluable for the manufacture of crucibles, basins, etc. To the chemical manufacturer the coarser stoneware is of equal importance for the construction of chemical plant, *e.g.* condensers of mineral acids, evaporating pans, storage tanks, pumps, taps, etc.

i. TERRA-COTTAS.—In accordance with the classification given above, this term includes such articles as ordinary, hollow, ornamental, vitrified, and light bricks, roofing and paving tiles, blocks, drain-pipes, and common unglazed pottery ware (such as flower-pots), in addition to the architectural and decorative wares to which the term terra-cotta is usually restricted. Such goods are prepared from natural clays, or suitable mixtures of clays, with the occasional addition of chalk or sand (see p. 119). Light bricks (or terra-cotta lumber) are obtained by incorporating sawdust or chopped straw with the clay used, the vegetable matter being, of course, burnt away in the firing process. In order to reduce the tendency to crack and to facilitate drying and burning, the larger pieces of terra-cotta are usually made hollow, and in the production of very large pieces a coarse porous clay is generally used to form the bulk of the mass, a finer terra-cotta clay being then used to cover the face of it.

ii. FIRECLAY GOODS.—These are distinguished from all other ceramic products by their resistance to heat; they include bricks and blocks used for lining furnaces, muffle kilns, crucibles, retorts, etc., employed in the metallurgical, glass and ceramic industries. They are prepared from fireclays, with the addition, when necessary, of a suitable opening material such as grog (or chamotte) and silica, but as the latter reduces the refractoriness of a good fireclay it is preferable to use the former, which consists of fireclay that has been fired at a high temperature and ground to a coarse powder. The texture of the fired article may also be more readily readjusted by the use of grog than silica. On the Continent it is customary to use a large proportion of grog, often as much as two parts of it to one of raw clay, in forming the fireclay body; the maximum amount of grog permissible depends on the plasticity of the clay. In England the use of grog in the manufacture of fireclay goods is not so extensive.

The practical value of a fireclay article is not determined solely by its refractoriness, *i.e.* its ability to be intensely heated without softening. It may have to withstand sudden temperature changes, the action of flames or molten corrosive slags, etc., according to the manner in which it is used, and these points have to be considered carefully when deciding on the composition and the texture of the body. Thus, suppose firebricks are required to withstand abrupt temperature changes. It is found that the more porous the texture the less will be the tendency of the bricks to crack, and that without the addition of opening material raw fireclays do not fire to sufficiently porous bricks. Accordingly, the fireclay used is mixed with the requisite amount of grog of a suitable degree of fineness; the coarser the grog and the greater the amount used the less the tendency of the brick to crack with sudden changes in temperature. For most purposes, however, firebricks should have a close compact texture so as to possess strength and resistance to abrasion.

Fireclay goods rich in alumina (*e.g.* bauxite bricks) are prepared by opening up fireclays with bauxite (p. 73), which, to be satisfactory, must not contain more than 10 to 15 per cent. of ferric oxide.

Fireclay goods extremely rich in silica, *e.g.* silica bricks and acid linings for steel furnaces, are prepared from ganister rock, Dinas rock, or crushed silica. *Ganister* is a fine-grained siliceous grit, the composition of which approximates to nine parts of silica mixed with one of fireclay; for use as a refractory material it must be very carefully selected. *Dinas rock* occurs in Wales in the Vale of Neath; it contains 97 to 98 per cent. of silica and is practically free from clay. For making bricks 1 to 2 per cent. of lime is added to act as a flux and the wet mixture is pressed into shape. Crushed silica is used on the Continent for making silica bricks, as no natural material of the quality of Dinas rock is available.

Carbon is used as an opening and heat-conducting material in the preparation of plumbago crucibles. Either graphite or the deposits of carbon found in gas-retorts may be utilised; the proportion used varies from 25 to 50 per cent. of the body mixture. Part of the fireclay may be in the form of fine grog. Sometimes magnesia is added to the body.

iii. EARTHENWARE and FAIENCES.—For common pottery ware, architectural faiences such as glazed bricks, tiles, etc., encaustic tiles, vases, dishes, and other decorative objects, the body consists simply of a plastic clay with the addition of sand or grog if necessary. The so-called enamelled faiences, *e.g.* stove tiles and imitation Moorish, Italian, and French faiences, are prepared from clays naturally or artificially calcareous, the body usually containing from 15 to 20 per cent. of lime when fired. The domestic white or cream-coloured earthenware is prepared from a more complex body, the basis of which is ball-clay. To whiten the body china-clay is added and to open it up flint is used; as a flux felspar or Cornish stone is utilised. To eliminate the pale yellow or cream colour from the fired body a little oxide of cobalt is usually added (0·02 to 0·08 per cent.). The following table shows how the relative proportions of the ingredients of an earthenware body may be varied:—

Ball-clay .	50	47	43	31	25	25	24	21	18	per cent.
China-clay .	10	24	24	36	32	25	27	28	43	„
Flint . .	35	22	23	21	34	40	36	38	24	„
Cornish stone .	5	7	10	12	8	10	13	13	15	„

French siliceous faiences, which form admirable artistic wares, are prepared from a body containing china-clay 24, chalk 24, flint 48, and frit 4 parts, the frit being prepared from Fontainebleau sand 85, potassium carbonate 7, sodium carbonate 3, and chalk 5 parts. This body was introduced by the celebrated faience manufacturer Deck in endeavouring to reproduce Persian faiences.

iv. STONEWARE.—Fine English stoneware is prepared from a body similar in composition to that of earthenware, but the proportion of Cornish stone is increased and that of the flint decreased, as shown by the following examples:—

Ball-clay . .	10	25	25	29	45	29 per cent.
China-clay . .	15	12·5	20	14	15	... „
Flint . . .	20	12·5	10	...	...	... „
Cornish stone .	55	50	45	57	40	71 „

"Common" stoneware articles, *e.g.* paving tiles, drain-pipes, sanitary ware, and chemical stoneware, are prepared from stoneware or vitrifiable clays (*cf.* p. 115). These clays when burned form opaqùe impermeable ware, usually of a greyish, yellowish, or bluish shade. They must be selected with great care, as stoneware clays are very liable to twist and warp when heated. The number of sources of good stoneware clay is not very considerable, the best of those found in England being the upper and less pure portions of the Devonshire and Dorset ball-clays and the more fusible fireclays. Accordingly, stoneware manufacturers are frequently obliged to adapt other clays to their needs. For this purpose felspar or Cornish stone may be added to fireclay, or a refractory material may be added to a fusible non-calcareous clay containing clay or felspar.

v. PORCELAIN.—The porcelains may be divided into two groups, (*a*) the *hard porcelains* and (*b*) the *soft* or *tender porcelains*. The hard porcelains are distinguished from the soft ones by their greater resistance to heat. When glazed, they are usually made so that the very hard glaze is fired with the body in one operation.

The basis of all porcelain is china-clay or kaolin. In order to obtain a more plastic body a little ball-clay may be added. The increased plasticity, however, is only gained at the expense of the translucency of the finished ware, and ball-clay is therefore usually excluded in the preparation of hard porcelain table-ware and ornamental goods, but utilised in the manufacture of porcelain for making electrical insulators or lining ball-mills and other vessels.

In the preparation of hard porcelain the opening materials used are quartz and biscuit porcelain, and the fluxes employed are felspar, chalk, and gypsum. From the point of view of the chemical composition of the products, the hard porcelains may be divided into those rich in alumina and very suitable for chemical purposes, and those rich in silica and well adapted for the preparation of ornamental ware. The following bodies are employed in the preparation of a number of hard porcelains:—

	Kaolin.	Felspar.	Quartz.	Chalk.	Gypsum.	Biscuit Porcelain.
Sèvres porcelain . .	65	15	14	6	...	...
Berlin „ . .	75	25	...	...	...	...
Meissen „ . .	73	25	...	...	...	2
Vienna „ . .	72	12	12	...	4	...

Presumably, the kaolins used include certain amounts of quartz and felspar or mica (see p. 105). The three most important constituents of hard porcelain are kaolin, quartz, and felspar, and according to Vogt[1] their relative propor-

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[1] See article "Céramique" in Moissan, *Traité de chimie minérale* (Paris, vol. iv., 1905).

tions should be kept within the following extremes: kaolin 65 to 35; quartz, 15 to 25; and felspar, 20 to 40 per cent.

The only kind of soft porcelain of any industrial importance is that which is variously known as phosphatic porcelain, English porcelain, bone china, or simply china; this *china ware* is almost exclusively produced in England. Its special characteristic is the large proportion of bone ash (30 to 50 per cent.) which enters into the composition of the body, which is made chiefly from china-clay, Cornish stone, and bone ash. The limits of composition are very wide; the following may be cited as examples of suitable mixtures:—

China-clay	25	30	22	29	34	per cent.
Cornish stone	25	35	31	30	...	„
Felspar	...	...	...	...	19	„
Bone ash	50	35	47	41	47	„

Parian is a soft porcelain which is usually unglazed. The body consists essentially of china-clay and felspar, a very large proportion of the latter being present, and in the preparation of English parian these appear to be the only substances used, the body containing 33 to 37 per cent. of china-clay. Parian ware closely resembles fine marble.

Information concerning the other varieties of soft porcelain, *e.g.* French or fritted porcelain, new Sèvres porcelain, and Seger's porcelain, must be sought in special treatises on ceramics (see footnote on p. 120).

Preparation of Ceramic Bodies.—The various ingredients that go to form the body of a ceramic product must be reduced to a state of fine division, and thoroughly and uniformly mixed. In the cases of cheap articles, *e.g.* bricks, where a natural clay alone is required, the preparation of the bodies is comparatively simple, it being frequently sufficient to crush or remove stones and other hard foreign bodies and then pass the wet clay through a pug-mill to secure the necessary uniformity. Some clays are dried and crushed to fine powder; all shales must be crushed and ground. The greatest care in the preparation of uniformly plastic bodies is naturally required where several different ingredients have to be ground and mixed, *e.g.* in the preparation of fine earthenware, stoneware, and porcelain. In English *fine earthenware*, for instance, the china-clay, ball-clay, china stone, and flint having all been reduced to the state of fine powder suspended in water, the requisite quantities of the "slips" are run into a large vat and thoroughly agitated. The "slip" thus obtained is passed through fine sieves to remove coarse particles and run over permanent or electro-magnets in order to remove particles of iron and magnetisable iron compounds. It then passes to filter presses, where most of the water is removed by filtration through canvas, and, the plastic body being harder on the outside than on the inside, it is thoroughly beaten up or put through a pug-mill to render it uniform and free it from air-bubbles. Instead of adopting the preceding method of "slip-blending," the raw materials are sometimes ground and dried; the requisite quantities are then weighed out and mixed with water.

Shaping Ceramic Articles.—Of the various methods by which the plastic body is formed into shape, the oldest and most general is that known as "throwing on the wheel." It is used in the preparation of round articles from sufficiently plastic bodies. "Turning" on a lathe is also adopted, particularly when an article must be made very accurate in shape and size. A process known as "expression" is used in the production of drain or sewer pipes and building blocks, bricks and tiles. For this purpose, the plastic paste is forced through a die or template so that the issuing clay is of the desired section; it is then cut into suitable lengths. The better qualities of bricks and interlocking roofing tiles are largely made by pressing the stiff plastic paste in metal moulds by powerful presses, and the same process is sometimes applied to bricks and tiles which have been roughly moulded and allowed to become half dry. "Dry pressing" is used in the production of certain classes of ceramic ware, particularly tiles used for internal decoration; the body is dried, crushed to powder, damped until it adheres together loosely when squeezed, and filled into a metal mould, where a die is forced down upon it by hand or mechanical power.

The simplest method of moulding a plastic body is that used in making bricks by hand with the use of wooden moulds. More ornamental articles are formed by beating the plastic body into a thin cake or "bat" and pressing it into moulds made of plaster of Paris. Frequently a mould has to be made in sections, which are fitted together and strapped up, the joints being smoothed down so that the clay forms one piece inside the mould. The clay dries a little on standing, contracts slightly, and detaches itself from the mould, the portions of which are then removed. "Slip casting" is another method of moulding, particularly suited to feebly plastic bodies such as porcelains. The "slip," prepared of such a consistency that one pint weighs 30 to 36 ounces, is poured into the plaster mould. The plaster absorbs the water from the slip in contact with it and a coating of the body is formed on the inside of the mould. When the coating is sufficiently thick the remaining slip is poured out and the mould and its contents dried in a hot stove. By this process it is possible to form teapots, jugs, etc., in one piece, instead of having to form them in parts and join these together afterwards.

The ware having been formed, it is slowly dried in an open shed,[1] in a drying-room, warmed by waste heat from the firing kilns, or by other suitable means. With some porcelain bodies, however, the final temperature reached in drying is much higher (700° to 900°).

The ware is then ready for firing, unless it is to be fired and glazed at one operation, when it must first receive its coating of glaze.

Firing.—Ceramic bodies are usually fired in kilns or ovens.[2] Such products as bricks, tiles, drain-pipes, etc., may be exposed directly to the flames, but this is not as a rule permissible with wares of better quality, which must therefore be packed in fireclay boxes, known as saggars. The ovens are large brickwork chambers which may be likened to vertical reverberatory furnaces. The saggars are stacked in the ovens in piles or "bungs" and the flames allowed to play directly on to them.

The final temperature reached in the kiln and the duration of the heating depend largely upon the nature of the ware required. Ordinary bricks, for instance, may only require heating to about 950° C. until vitrification, produced mainly, as a rule, by the fluxing action of lime, has so far advanced that the fired product has the necessary crushing strength. Hard porcelain,

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[1] During the summer months bricks and coarse ware may be dried in the open air, if protected from the sun and wind.

[2] There are many types of kiln and oven, each suited to the production of a particular kind of ware. A description of these is out of place in the present volume, and the reader requiring further information is referred to the treatises mentioned in the footnote on p. 120.

on the other hand, must be fired at 1400° C. or thereabouts and the vitrification pushed almost to the extreme limit.

It has already been mentioned (p. 121) that fired ceramic bodies may be divided into two classes, the permeable and the impermeable. In practice, however, these classes cannot be divided rigidly. The fine English white wares, in particular, are difficult to classify, the distinction between some pieces of faience (earthenware) and some of stoneware being almost impossible to define. Thus, the term "stoneware" is frequently applied to glazed pipes, tiles, and sanitary ware, the bodies of which are decidedly porous though the articles as a whole are impermeable.

In discussing the changes that take place in ceramic bodies during the firing process, it will only be necessary to refer to fireclay goods, white ware and porcelain, the nature of the changes undergone by other bodies having been sufficiently indicated in dealing with the action of heat on clays (p. 113).

In the preparation of *firebricks* it is of great importance that the goods shall be fired long enough and at a temperature high enough to prevent any marked after-contraction when the bricks are in use. Otherwise, under favourable temperature conditions, contraction will continue at an appreciable rate and give rise to movements in the masonry of the furnace and setting. The choice of the fireclay should be influenced by the maximum temperature likely to occur in the furnace in which the bricks are to be used. Allowing a reasonable margin of safety, the most suitable softening temperature for the clay may be obtained, and an unnecessarily refractory clay should be rejected as being likely to produce bricks too open in texture and correspondingly weak mechanically. Non-vitrifiable fireclays, poor in fluxes, exhibit a maximum contraction on firing; this varies with the temperature and rate of heating. When the maximum contraction has been attained, subsequent heating at the same temperature is attended by a slight expansion and a slight disintegration of the brick[1]; subsequent heating at a higher temperature, however, produces a further contraction, which attains a maximum as before.

As fireclay goods are manufactured for the purpose of withstanding high temperatures for prolonged periods, a few words on the nature of the changes they undergo on continued heating may be added. The ultimate character assumed by a fireclay body is that of a nearly homogeneous vitreous mass, and as this condition is approached the body tends more and more to soften and lose its shape. The longer it takes to realise this state of affairs, the longer is the life of the fireclay body. With prolonged heating there is usually associated a decrease in the crushing strength of the body. This appears to be due to a number of causes, one of which is the gradual loss of alkalies by volatilisation, followed by a slight disintegration of the "cementing" matrix which binds together the solid particles of the body.[2] Another cause is the separation of crystals of sillimanite from the vitreous matrix. The rate at which this crystallisation proceeds doubtless depends upon the proximity of the temperature to the best crystallising temperature of the matrix, as explained later in connection with glazes (p. 131). The crystallisation being irregular,[3] and attended

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[1] Mellor, *Collected Papers*, 1914, vol. i. pp. 309-315.

[2] Cramer, *Tonind. Zeit.*, 1897, 21, 288; Mellor and Austin, *Trans. Eng. Cer. Soc.*, 1907, 6, 76, 129; *J. Soc. Chem. Ind.*, 1907, 26, 375, 380.

[3] Microscopic examination reveals the growth of local patches of crystals.

by a contraction in volume, local strains are set up in the body and tend to rupture it.[1]

In the firing of *hard porcelain*[2] the felspar melts to a liquid which binds together the particles of heated clay and silica. As the heating is continued the solid particles are slowly attacked and dissolved by the molten flux, the clay more readily than the free silica; at about 1300° felspar can dissolve about 20 per cent. of china-clay and 15 per cent. of silica. The translucency of the fired body may be thus explained; the body consists of a transparent glass in which particles of silica and heated china-clay are embedded, forming a kind of framework in it. Now, china-clay particles are permeated with minute capillary pores, and the particles left after the water of constitution has been expelled still retain this porous structure. When these pores are filled up by a colourless liquid, china-clay or the material left after heating it to redness is found to be fairly transparent. The translucency of porcelain is thus a result of the molten flux penetrating into the capillary pores of the heated clay at the same time as it is slowly dissolving the clay, and the translucency increases in proportion as the percentage of china-clay in the porcelain body is reduced. It is clear, however, that there must be at least a certain (minimum) proportion of clay present, to ensure that the body shall not collapse when fired owing to lack of sufficient clay-silica framework.

Patches of acicular crystals of sillimanite frequently separate out from the glassy matrix when hard porcelain is fired, and, indeed, they seem to be produced whenever mixtures rich in clay and felspar are fired at or above 1300° C.[3] The rate at which the crystals develop depends upon the temperature,[4] and their production in heated porcelain probably explains the development of brittleness in porcelain tubes which have been heated for a considerable length of time.

The slight bluish tint usually noticed in porcelain is due to the body always containing traces of iron and titanium and to the final heating and vitrification being carried out in a slightly reducing atmosphere. The blue gives place to a yellow tint when an oxidising atmosphere is used.

Owing to the large amount of flux present and the extent to which vitrification is allowed to proceed, porcelain contracts very considerably (about 15 per cent.) in the firing. In soft *parian* porcelain, where the percentage of flux is extremely large and opening material is omitted, the contraction is still greater. Since parian is fired at a much lower temperature than hard porcelain[5] it does not show well-developed crystals of sillimanite unless, as is sometimes the case, a little lead glass is added to the parian body. The introduction of the lead glass appears to accelerate the rate at which the sillimanite crystals form.

From what has already been said the nature of the changes produced when *bone china* is fired may be inferred, especially as powdered bone ash

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[1] For further information concerning the action of heat on fireclays see Mellor, *J. Soc. Chem. Ind.*, 1907, **26**, 375; Mellor and F. J. Austin, *loc. cit.*; Mellor, *Collected Papers*, vol. i. pp. 309, 316, 379.

[2] Hussak, *Sprechsaal*, 1889, **22**, 136, 154; Mellor, *Trans. Eng. Cer. Soc.*, 1906, **5**, 75; *J. Soc. Chem. Ind.*, 1907, **26**, 375; Mellor and Austin, *loc. cit.*; Heath and Mellor, *Trans. Eng. Cer. Soc.*, 1907, **7**, 80; or Mellor, *Collected Papers*, pp. 19, 43, 98, 138.

[3] W. Vernadski, *Bull. Soc. franç. Min.*, 1889, **12**, 447; 1890, **13**, 256; Hussak, *loc. cit.*; Mellor, *loc. cit.*; Heath and Mellor, *loc. cit.*

[4] See later, under Glazes, p. 131.

[5] Hard porcelain is fired at 1250°-1400° C.; parian at 1150°-1200° C.

has a porous structure similar to that of china-clay, and so assists in producing the translucency of the china. Bone china is fired at 1250°–1300° C., and when correctly fired it approximates to a homogeneous vitrified mass more closely than almost any other type of pottery. The temperature has to be regulated with extreme care, as when over-heated, the china begins to lose its shape, phosphoric oxide fumes are evolved, the body acquires a sponge-like character and "bloats." The loss of phosphorus is due to the presence of carbon or other reducing substance in the body or in the kiln at certain stages of the firing.[1]

The changes which take place when fine *stoneware* and white *earthenware* bodies are fired are similar to those which occur in the firing of hard porcelain, but vitrification is not allowed to proceed to the same extent. Less flux is therefore required and the firing temperature need not be so high. Fine stoneware has the same general structure as hard porcelain, but it is not translucent. Why the substitution of ball-clay for china-clay should destroy the translucency of porcelain is not definitely understood, but it is probable that owing to the comparative ease with which the impure clay softens, the pores become closed up before the molten flux can penetrate into them.

Glazes and Enamels.—Glazes and enamels are vitreous envelopes used to cover ceramic bodies, either for decorative purposes or for rendering them impermeable to liquids. The finely divided glaze[2] is spread over the surface of a ceramic body and the whole heated until the glaze melts and forms a thin film covering the surface continuously. The glazed body is then allowed to cool, when the molten glaze solidifies to an amorphous "glass."

A pottery glaze should be clear, brilliant, and thin, so as not to hide modelled work; it should soften more readily than the body to which it is applied, and while being sufficiently viscous when molten not to run off an upright object it should be mobile enough to flow smoothly over the whole surface; it should be very resistant to attempts to devitrify it; its coefficient of expansion should agree with that of the body in order that it may not chip off from edges or develop minute cracks (known as crazes) upon the surface; it should be unattacked by water and acid vapours, and for culinary, domestic, or sanitary purposes it should be resistant to dilute acids.

Glazes vary very much in chemical composition and in fusibility. They all contain silica, alumina, and one or more of the oxides of the alkali or alkaline earth metals as necessary constituents. Of the other basic oxides that may be present, lead oxide is the commonest, while many of the more fusible glazes contain a second acidic oxide, namely boric oxide. In ceramics the compositions of glazes are usually expressed in a conventional manner by indicating the relative numbers of formula-weights of the various oxides present in such a manner that the total number of formula-weights of the oxides of uni- and bi-valent metals is unity; the following, for instance, represents a typical earthenware glaze:—

$$\left.\begin{array}{l} 0\cdot25(\mathrm{KNa})_2\mathrm{O} \\ 0\cdot35\mathrm{CaO} \\ 0\cdot40\mathrm{PbO} \end{array}\right\} 0\cdot2\ \mathrm{Al_2O_3} \left\{\begin{array}{l} 3\cdot0\ \mathrm{SiO_2} \\ 0\cdot4\ \mathrm{B_2O_3} \end{array}\right.$$

The general glaze "formula" may be written $\mathrm{RO} : x\mathrm{R_2O_3} : y\mathrm{RO_2}$, when it is found that y is always greater and x is generally less than unity. In general, the more bases of the RO group there are present, the more fusible the

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[1] B. Moore, *Trans. Eng. Cer. Soc.*, 1905, 5, 37.

[2] Or, more accurately, a mixture of substances which react to produce the glaze when heated.

glaze; replacement of silica by boric oxide also increases the fusibility. The proportion of alumina present largely influences the properties of a glaze, particularly its viscosity and its tendency to devitrify. The use of lead in glazes has been known and practised for centuries. Lead glazes are very quick to mature and, by suitably choosing their compositions, may be adapted for use with a fairly wide range of pottery bodies. They are not suitable, however, for use with hard porcelain and once-fired stoneware, since lead oxide volatilises rapidly at the firing temperature and, moreover, the glazes mature too rapidly. The use of lead glazes is attended with certain risks, owing to the poisonous nature of lead compounds. Lead-poisoning may affect the work-people engaged in handling the glazes, or it may affect the purchaser of a lead-glazed culinary article, unless the latter will resist the action of boiling, concentrated acetic acid. The latter evil, however, has not arisen in England.

Glazes containing only the constituents already mentioned are colourless and transparent. They may be converted into white, opaque glazes or *enamels* by the addition of stannic oxide or zinc oxide in excess of that required to saturate the glaze. The opacity is due to the presence of solid oxide of zinc or tin in suspension in the glaze. Calcium phosphate is sometimes used as an opacifying agent.

In general, the glaze is produced upon the body by the interaction of a number of suitable raw materials under the influence of heat. When all the raw materials are insoluble in water it is sufficient to grind them together and apply the mixture to the body, but when some of the raw materials are soluble (*e.g.* sodium carbonate, borax) a different procedure is adopted. The soluble ingredients are mixed with suitable proportions of the others and the mixture melted into a glass or frit. The frit is cooled, powdered, and mixed with the remainder of the insoluble ingredients.

The glaze mixture may be applied to the body in various ways. It is commonly applied by "dipping," for which purpose the glaze mixture is stirred up into a "slip" with water and the article to be glazed then dipped into it. The body, owing to its porosity, absorbs a certain amount of water and a film of glaze mixture is deposited upon its surface. Other methods include pouring a suspension of the glaze mixture over the body as it is rotated, and spraying the suspension over it.

A glaze should be regarded as a supercooled, highly viscous, and more or less imperfectly mixed solution. Accordingly, although a glaze may be made up in several different ways so as to have the same ultimate composition, it does not follow that the final glazes will "mature" in the same way. The behaviour of the glaze varies with the manner in which it is compounded, the physical condition of its constituents, and the character of the body on which it is fired.[1] A glaze, being amorphous, has no real melting-point, but becomes less and less viscous as the temperature rises. Eventually, it begins to lose its shape and begins to flow like a mobile liquid. It is difficult to determine a precise temperature at which this occurs, but a small temperature range may be located fairly readily and the mean temperature spoken of as the softening temperature of the glaze. The softening temperatures of lead silicate glazes have been measured by Mellor, Latimer, and Holdcroft,[2] who found that the gradual addition of more and more silica rapidly lowers the softening-point

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[1] Mellor, *Trans. Eng. Cer. Soc.*, 1913, **11**, 1; *Collected Papers*, vol. i. p. 339.

[2] Mellor, Latimer, and Holdcroft, *Trans. Eng. Cer. Soc.*, 1909, **9**, 126; Mellor, *Collected Papers*, vol. i. p. 247.

from 877° C. (the melting-point of litharge) to 526° C. (for $PbO + 0{\cdot}21SiO_2$) and then gradually increases it until with a composition corresponding to $PbO + 2{\cdot}4SiO_2$ the softening-point is 661°. All the softening-points are much lower than the corresponding melting-points in the system litharge-silica.

A pottery glaze, being a supercooled solution, has a certain tendency to crystallise. It has been found that the rate at which a supercooled liquid crystallises increases with the degree of supercooling up to a certain point, when the further augmenting of the degree of supercooling leads to a steady diminution of the rate of crystallisation. Hence in the cooling down of a glazed pottery body there is a certain temperature at which crystallisation of the glaze, when once started, proceeds at its maximum rate. Since in general it is not desired that the glaze shall crystallise, the temperature of the body should be hurried past this "best crystallising temperature," as all the time it is in the vicinity of it the body is in a kind of danger-zone.[1] The length of time that the body is in the danger-zone depends upon the rate of cooling and also upon the rate at which the velocity of crystallisation diminishes as the temperature changes above or below the best crystallising temperature.

A pottery glaze cannot be looked upon merely as an envelope for the body, the union being much more intimate. All the time that a glaze is maturing it is attacking the surface of the body. Where the glaze and body meet there is thus formed a concentrated solution of body in glaze, and owing to the high viscosity of this solution and of the glaze they have not sufficient time to become uniformly mixed. Consequently crystals sometimes separate out from this intervening layer of solution on cooling, and cause the glaze to peel off from the body.

Although the crystallisation of a glaze is usually a defect, the production of crystalline glazes can, in certain circumstances, be utilised for the purposes of pottery decoration. For instance, the intentional crystallisation of zinc silicate from glazes may be made to produce extremely beautiful effects. "Sunstone" and "aventurine" glazes are other well-known crystalline glazes, in which the crystals which separate out are complex silicates somewhat similar to the micas.[2]

Hard porcelain glazes are rich in silica and alumina and comparatively poor in bases; the only bases present are potash, soda, lime, and magnesia. At Sèvres the hard porcelain glaze consists of pegmatite from St Yrieix; in Austria and Germany mixtures of felspar, quartz, and kaolin are used, with the addition, at times, of calcium carbonate or sulphate. The following are some of the compositions which have been published:—

Felspar	...	32·5	...	...	per cent.
Kaolin	30·0	9·5	37·5	37·0	„
Quartz	44·0	34·5	50·0	37·0	„
Chalk	...	12·0	12·5	17·5	„
Gypsum . . .	13·5	...	...	...	„
Biscuit porcelain . .	12·5	11·5	...	8·5	„

Chinese and Japanese porcelain glazes are also calcareous. The compositions of porcelain glazes fall within the limits $RO : 0{\cdot}2R_2O_3 : 3{\cdot}5RO_2$ and $RO : 1{\cdot}25R_2O_3 : 12RO_2$.

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[1] See Mellor, *Collected Papers*, vol. i. pp. 6, 47; or *Trans. Eng. Cer. Soc.*, 1905, **4**, 49; *J. Soc. Chem. Ind.*, 1907, **26**, 375; Riddle, *Trans. Amer. Cer. Soc.*, 1906, **8**, 336.

[2] On crystalline glazes see W. Burton, *J. R. Soc. Arts*, 1901, **49**, 213; 1904, **52**, 595.

In the porcelains there is a very intimate relation between body and glaze, since they are fired together and are similar in composition. This is not so much the case with *bone china* glazes, which are applied to biscuit ware, usually contain both lead and boric acid, and are very similar to the glazes applied to *fine stoneware* and *earthenware*. The following are stated by Burton to be typical glaze recipes, (*a*) for china ware, (*b*) for white earthenware, and (*c*) for granite ware:—

Glaze.

	(*a*)	(*b*)	(*c*)
Frit	45	230	360
Flint	...	60	50
Cornish stone	15	160	50
White lead	15	120	80

Frit.

	(*a*)	(*b*)	(*c*)
Borax	50	48	80
Chalk	16	38	30
Flint	40	62	80
Cornish stone	24	...	100
Felspar	33	...	40
Soda	...	26	40
China-clay	...	30	30

At the present time much *sanitary ware* is covered with an opaque white enamel.[1] The enamel is fired on the raw body, as with hard porcelain; it contains potash, lime, and zinc oxide, but neither lead oxide nor boric acid, and is rendered opaque with zinc or tin oxide.[2] Alkaline calcareous glazes (Bristol glazes) are used to cover such common stoneware as pots and jars used for holding food or chemicals. Stoneware pipes are glazed by a process known as "salting," in which the goods are heated until the requisite degree of vitrification has been reached, after which a quantity of wet salt is thrown into the furnaces. The vapour of sodium chloride is hydrolysed by the water vapour and the alkali set free reacts with the clay on the surfaces of the pipes to produce a hard, insoluble glaze. The process of salt glazing is most successful with bodies rich in silica; the ratio $SiO_2 : Al_2O_3$ may vary between 4·6 and 12·5, and in practice it is usually about 8.[3]

Common red and brown pottery ware may be glazed by coating the unfired bodies with powdered litharge, red lead, or galena, and then firing. A brilliant lead glaze is thus produced and its durability is increased if flint and ball-clay are also constituents of the glaze.

Decoration.—Colouring matters may be applied to the decoration of ceramic products in various ways, *e.g.*:—

(i.) They may be introduced into the body, which then becomes a *coloured body*. It may or may not be glazed.

(ii.) A coloured body may be used to cover another body, either for the sake of economy or for decorating the surface with paintings and with reliefs in different colours ("*barbotine*" or *slip painting*). The coloured body may afterwards be glazed if desired.

(iii.) The colour may be incorporated into the glaze, which becomes a *coloured glaze*.

(iv.) Colours may be affixed to the surface of the body and the whole then glazed (*under-glaze colouring*).

(v.) The colour may be mixed with a flux, *i.e.* made into a vitrifiable colour and applied to the surface of the glaze (*over-glaze* or *on-glaze colouring*).

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[1] This is superior to the older yet still widely adopted practice of coating the articles with a body made of white-burning clay or a mixture similar to an earthenware body and then applying the glaze to this fine coating.

[2] See Purdy, *Trans. Amer. Cer. Soc.*, 1902, 4, 61; 1903, 5, 136.

[3] See Barringer, *Trans. Amer. Cer. Soc.*, 1902, 4, 211.

Two or more of these processes may be utilised in decorating the same object.

The best examples of *coloured bodies* are to be found in coloured parians, porcelains and jaspers, mosaic tiles and tesseræ. The bodies are rich in felspar, in which the colouring matters dissolve. The percentages of certain colouring matters that may be added to the body mixtures to produce various colours are as follows:—

Pale blue: 2 per cent. of cobalt oxide and 5 per cent. of zinc oxide.
Strong blue: 5 per cent. of cobalt oxide.
Green: 2 per cent. of cobalt oxide and 4 per cent. of chromic oxide.
Blue-green: 2·5 per cent. of chromic oxide, 1·75 per cent. of cobalt oxide, and 1·25 per cent. of zinc oxide.
Bronze-green: 5 per cent. of nickel oxide.
Brown: 1 to 5 parts of ferric oxide.
Yellow: 10 parts of titanium dioxide.
Black: 7 per cent. of ferric oxide and 3 per cent. of cobalt oxide.

Coloured glazes are usually applied to white bodies. In most cases the basis of the glaze is a frit rich in lead. For use with soft porcelains and white earthenwares Salvétat proposed the following recipe for the frit:—

Red lead	2000 parts
Flint	1000 ,,
Calcium borate	500 ,,

The glaze prepared from these amounts of raw materials may be mixed with various metallic oxides to produce coloured glazes. Thus, *blue* requires 40 to 125 parts of cobalt oxide, *blue-green*, 100 to 500 of cupric oxide; *ivory* to *deep yellow*, 70 to 200 of ferric oxide; *madder* to *purplish-brown*, 70 to 125 of manganese dioxide; etc.

From terra-cotta bodies that fire to orange or red tints it is only possible to produce red, brown, and black wares by the use of coloured glazes. For other colours the bodies must either be covered with slips or decorated with enamels. On the other hand, with yellowish terra-cotta bodies there is little difficulty in producing yellow, green, and blue wares.

Coloured terra-cotta bodies may be decorated with *enamels*. With highly calcareous bodies a sodium lead silicate rendered opaque by tin dioxide is used to produce a white enamel, and this is coloured by the addition of suitable materials, *e.g.* lead antimonate for yellow, cobalt oxide for blue, cupric oxide for green, manganese dioxide for violet, etc.

Under-glaze colours are applied to pottery bodies before they are glazed. Accordingly, they must resist the action of the glaze at its softening-point and be sufficiently infusible to remain still under it; moreover, they must have such rates of expansion as to agree with both body and glaze, since otherwise the glaze will fly off in flakes. The ingredients commonly used in the preparation of under-glaze colours are as follows (Burton):—

Black: 8 of iron chromate, 3 of trimanganic tetroxide, 3 of cobalt oxide, and 1 of flint.
Dark blue: 4 of cobalt oxide, 1 of chalk, and 1 of flint.
Azure blue: 3 of cobalt oxide and 60 of ammonium alum.
Blue-green: 12 of zinc oxide, 24 of chromic oxide, 4 of cobalt oxide, 12 of chalk, and 12 of borax.
Brown: 8 of iron chromate, 4 of zinc oxide, and 2 of ferric oxide.
Reddish-brown: 6 of precipitated iron chromate, 3 of litharge, and 20 of zinc oxide.
Pink: 100 of stannic oxide, 34 of chalk, 1 of chromic oxide, and 5 of silica.
Yellow: 6 of red lead, 3 of antimony oxide, 1 of stannic oxide, and 2 of flint.

Each of the preceding colours is prepared by finely grinding and thoroughly mixing the constituents, strongly calcining the mixture, and regrinding the product.

On-glaze colours are fusible coloured glasses which, when applied to an article already glazed and then refired, become fused to the surface. The basis of an on-glaze colour is a readily fusible glass (termed a *flux*) prepared by fusing together red lead, silica, and borax in suitable proportions. The following compositions are largely used in Staffordshire (Burton):—

	1	2	3	4	5
Red lead	64·5	50·0	30·5	15·8	40·0
Silica	21·5	16·7	41·7	21·2	20·0
Borax (cryst.)	...	33·3	27·8	63·0	40·0
Flint glass	14·0	...	...	...	...

The powdered flux is mixed with suitable colouring materials, and then, in general, the mixture is fused, cooled, and re-ground to powder. The following compositions are given by Burton (fluxes as in preceding table):—

Pale yellow: 14 of potassium antimonate, 6 of zinc carbonate, and 80 of flux No. 1.
Orange: 14 of potassium antimonate, 6 of ferric oxide, and 80 of flux No. 1.
Uranium orange: 25 of yellow oxide of uranium and 75 of flux No. 1.
Pale grey: 5 of cobalt carbonate, 3 of ferric hydroxide, and 92 of flux No. 2.
Strong grey: 6 of cobalt carbonate, 13 of ferric hydroxide, 13 of zinc carbonate, and 68 of flux No. 2.
Strong black: 10 of cobalt carbonate, 10 of ferric hydroxide, and 80 of flux No. 2.
Iridium black: 25 of iridium sesqui-oxide and 75 of flux No. 2.
Uranium black: 25 of black oxide of uranium and 75 of flux No. 2.
Pale blue: 6 of cobalt carbonate, 14 of zinc oxide, and 80 of flux No. 2.
Strong blue: 13 of cobalt carbonate, 26 of zinc carbonate, and 61 of flux No. 2.
Sea-green: 20 of copper carbonate and 80 of flux No. 2.
Yellowish-brown: 10 of ferric oxide, 15 of zinc carbonate, and 75 of flux No. 2.
Red: 25 of ferric oxide and 75 of flux No. 2.[1]
Rose: 12 of Purple of Cassius, 1 of precipitated silver, and 87 of flux No. 3.[2]
Purple: 7 of Purple of Cassius, 3 of gold oxide, and 90 of flux No. 4.[2]
Bluish-green: 6 of cobalt carbonate, 19 of chromic oxide, and 75 of flux No. 5.

Both under-glaze and on-glaze colours are mixed with resinous media and applied by painting, stencilling, transferring from printed or lithographed patterns, or in a number of other ways.

Decoration with metals is often applied to pottery. Gold, platinum, and silver are used for this purpose, usually for over-glaze decoration. Gold, platinum, silver, copper, iron, or lead may also be applied to pottery in such a manner as to cover it with a very thin, iridescent, metallic film (lustre pottery).

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[1] For the production of ferric oxide red, ferrous sulphate is calcined at 400°–420° until a brilliant red oxide is obtained; the oxide is then simply mixed with the flux and not fused with it.

[2] The colours obtained from gold are carefully heated to suitable temperatures below a red heat.

CHAPTER V.

ULTRAMARINE.[1]

It has been already mentioned (p. 95) that the blue mineral lazurite, extracted from lapis-lazuli rock by powdering and washing with water, was for many years prized as a valuable pigment under the name of ultramarine. The composition of the natural substance was determined by Klaproth[2] and by Clément and Désormes,[3] and in 1828 J. B. Guimet commenced the manufacture of artificial ultramarine. The artificial product is now, and has been for some years, produced on a very large scale, the annual production ranging from ten to fifteen thousand tons.[4]

Manufacture of Ultramarine Blue.—The constituent elements of ultramarine are sodium, aluminium, silicon, sulphur, and oxygen. The pigment is prepared by a method which may be looked upon as the calcination of a mixture of an aluminosilicic acid and sodium sulphide. The raw materials are as follows:—

(i.) Clay. China-clay or high-grade pottery clays are used.

(ii.) Silica. Kieselguhr is usually employed, but occasionally finely powdered quartz is used.

(iii.) Glauber salt. The best quality of sodium sulphate, free from iron or acid, is calcined and finely powdered.

(iv.) Sodium carbonate. The best commercial soda ash is calcined and finely powdered.

(v.) Sulphur. Rod or stick sulphur practically free from non-volatile matter is used.

(vi.) Carbon. Pine charcoal is usually preferred; it is replaced at times by pitch, tar, colophony, etc.

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[1] For further information on ultramarine, see Zerr and Rübencamp, *Treatise on Colour Manufacture*, transl. by Mayer (C. Griffin & Co., Ltd., 1909); Bersch, *Mineral and Lake Pigments*, transl. by Wright (Scott, Greenwood & Son, 1901); Parry and Coste, *The Chemistry of Pigments* (Scott, Greenwood & Son, 1902); Thorpe, *Dictionary of Applied Chemistry* (Longmans & Co., 1912–1913), vol. v.; Moissan, *Traité de chimie minérale* (Paris, 1905), vol. iv.; Dammer, *Handbuch der anorganischen Chemie* (Stuttgart, 1893), vol. iii.; R. Hoffmann, *Das Ultramarin* (Frankfurt, 1873, and Brunswick, 1902); Friend, *An Introduction to the Chemistry of Paints* (Longmans & Co., 1910).

[2] Klaproth, *Ann. Chim.*, 1797, **21**, 150.

[3] Clément and Désormes, *ibid.*, 1806, **57**, 317. Other analyses are cited by Guckelberger, *Annalen*, 1882, **213**, 208.

[4] On the history of artificial ultramarine, see Loir, *Mém. Acad. Sci. Lyons*, 1878, **23**, 333; Heintze, *J. prakt. Chem.*, 1891, [ii.], **43**, 98; Moissan, *Traité de chimie minérale* (1905), vol. iv. p. 114. See also the following early memoirs: Vauquelin, *Ann. Chim.*, 1814, **89**, 88; Kuhlmann, *Ann. Chim. Phys.*, 1829, **40**, 439; J. B. Guimet, *ibid.*, 1831, **46**, 433; Mérimée, *Bull. Soc. Enc.*, 1828, **27**, 344; C. Gmelin, *Ann. Chim. Phys.*, 1828, [ii.], **37**, 409; Breunlin, *Annalen*, 1856, **97**, 295; *Ann. Chim. Phys.*, 1856, [iii.], **48**, 64.

Three chief varieties of ultramarine blue are found in commerce, viz.:—

(i.) *Glauber salt or sulphate ultramarine*, the palest variety, which possesses small covering power.

(ii.) *Soda ultramarine* poor in sulphur, a pure blue variety, darker and possessed of more covering power than (i.).

(iii.) *Soda ultramarine* rich in sulphur and silica, the darkest variety. It possesses considerable "body" and is more resistant towards alum than (i.) or (ii.).

The first step in the manufacture consists in the powdering and mixing of the ingredients. The most suitable proportions are given by Zerr and Rübencamp as follows:—

Ultramarine Blue.	Pale, or (i.).	Medium, or (ii.).	Dark, or (iii.).
China-clay	100	100	100
Soda	9	100	103
Glauber salt	120	0	0
Carbon	25	12	4
Silica (Kieselguhr) . . .	0	0	16
Sulphur	16	60	117

The second step consists in roasting the mixed materials. This is carried out either by (*a*) the direct or (*b*) the indirect process. All ultramarines rich in silica and a certain amount of the other varieties poorer in silica are made by the former method; but the greater part of the ultramarine poor in silica is prepared by the latter method, in which ultramarine green is formed as an intermediate product. Both these are dry processes; wet methods have been described and patented, but do not seem to have been adopted on a large scale.[1]

In the direct process the roasting is carried out in such a manner that air has access to the material. Charges amounting to as much as 5 tons may be treated by this process, the heating being carried out in stone troughs, 20 feet long and 10 feet wide, placed in a furnace in such a manner that they can be reached on all sides by the flames. The troughs are filled to a depth of 12 to 16 inches, covered with firebricks, and heated for about three weeks.[2] It has been proposed to hasten the preparation by adding sodium chlorate as an oxidising agent.[3]

In the indirect process the material is filled into crucibles, the lids are fixed on with a mortar of clay, the crucibles stacked in layers in a furnace and heated, slowly at first, eventually to a bright red heat. By this means air is excluded from the mass and *green ultramarine* produced. The crucibles are opened when the furnace has completely cooled down, and the green product is removed and powdered. It is then converted into blue ultramarine by roasting it with sulphur. The process is carried out in iron or fireclay retorts, either (i.) by introducing the green ultramarine, together with the

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[1] Knapp, *J. prakt. Chem.*, 1885, [ii.], **32**, 375; 1888, [ii.], **38**, 48; M'Ivor, *Eng. Pat.*, 9200 (1890); M'Ivor and Cruickshank, *Eng. Pat.*, 19,411 (1892).

[2] Numerous special furnaces have been patented: *Eng. Pat.*, 18,527 (1890); *Fr. Pat.*, 399,211; 400,103; 403,247; 407,089 (1908); 410,055 (1909); 425,585 (1910).

[3] *Fr. Pat.*, 391,779; 391,780 (1908).

requisite amount of sulphur,[1] into a red-hot retort and raking the mass over at intervals until the sulphur has burnt away, or (ii.) by heating the green ultramarine and gradually adding the sulphur, each portion of which is allowed to burn away before the next is added.

The crude ultramarine blue, however it has been prepared, is extracted with hot water to remove soluble salts, sodium sulphate being recovered from the washings. The blue is, while wet, ground to the requisite degree of fineness and separated into particles of different sizes by levigation. The various grades are then dried in sheds, on drying hearths, in special drying rooms, or by any other convenient method. Finally, the dried products are crushed and sifted. The cheaper brands of ultramarine are usually adulterated with 10–50 per cent. of gypsum or other cheap filler.[2]

According to Singer[3] ultramarine and analogous bodies may be prepared by treating zeolites or similar compounds with sulphides, hydrosulphides, polysulphides or oxysulphides of the alkali or alkaline earth metals.

Properties.—Ultramarine blue crystallises in the cubic system, isomorphous with the minerals sodalite and haüynite. The commercial article consists of a bright, azure-blue, impalpable powder, insoluble in water; minute particles remain suspended in that liquid for a long time, the whole resembling very closely an inorganic suspension colloid.[4] It withstands a red heat fairly well, but loses some of its brilliancy and turns somewhat greenish in colour. When heated with water under pressure to 200°–300° it leaves a colourless residue free from sulphur, and sodium sulphide passes into solution. It also loses its sulphur when heated with mercuric oxide.[5] It is stable towards alkalies, but is readily decomposed by dilute mineral acids with the precipitation of sulphur and the evolution of hydrogen sulphide.[6] It is accordingly very remarkable that cold, concentrated (or fuming) sulphuric acid, or a mixture of acetic anhydride and glacial acetic acid, has no action upon it.[7] Ultramarine possesses hydraulic properties and increases the binding power of cement.[8]

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[1] Seven per cent. with soda green and ten per cent. with Glauber salt green.

[2] For further details concerning the manufacture of ultramarine, see E. Guimet, *Ann. Chim. Phys.*, 1878, [v.], **13**, 102; Rawlins, *J. Soc. Chem. Ind.*, 1887, **6**, 791; Pichot and Grangier, *ibid.*, 1888, **7**, 573; Röhrig, *Chem. Zeit.*, 1883, **7**, 567; J. Wunder, *ibid.*, 1890, **14**, 1119; Jordan, *Zeitsch. angew. Chem.*, 1893, **6**, 684, and the works cited on p. 135.

[3] Singer, *D.R.P.*, No. 221,344 (1909).

[4] Ebell, *Ber.*, 1883, **16**, 2429.

[5] Chabrié and Levallois, *Compt. rend.*, 1906, **143**, 222.

[6] As a matter of fact, both sulphur dioxide and hydrogen sulphide are evolved. The latter, however, is in excess, and part of it is used up in decomposing the sulphur dioxide. In the presence of an arsenite or a cadmium salt the hydrogen sulphide may be used up in forming arsenious or cadmium sulphide, and the evolution of sulphur dioxide may then be observed. See Guckelberger, *Annalen*, 1882, **213**, 182.

According to L. Wunder (*Zeitsch. anorg. Chem.*, 1912, **77**, 209), ultramarine blue loses one-fourth of its sulphur as hydrogen sulphide when treated with dilute hydrochloric acid. This is peculiar, however, to the sample of ultramarine he used. Other samples give different results; *e.g.* sample 7 quoted in the table on p. 139 lost one-third of its sulphur as hydrogen sulphide, and two-thirds of this hydrogen sulphide was used up in decomposing the sulphur dioxide simultaneously produced (B. Campbell, private communication; see also Guckelberger, *loc. cit.*).

[7] K. A. Hofmann and Metzener, *Ber.*, 1905, **38**, 2482; L. Wunder, *Zeitsch. anorg. Chem.*, 1912, **77**, 209. When heated with concentrated sulphuric acid a white residue is ultimately obtained, the blue colour giving place successively to blue-black, greenish, black, purple, grey, greenish-grey, and white. The purple material agrees in its composition and general properties with *violet ultramarine* (B. Campbell, private communication).

[8] Rohland, *Zeitsch. angew. Chem.*, 1904, **17**, 609.

Ultramarine blue loses part of its sulphur when heated in hydrogen to 450°, but still retains its blue colour. When heated to 250° in a stream of chlorine, hydrogen chloride, and steam, it is transformed into *violet ultramarine*,[1] which is transformed into *red ultramarine* when heated to 130°–150° in a stream of hydrogen chloride.[2] Blue ultramarine may be directly transformed into the red substance by heating to 400° in nitric oxide.[3] The properties of the red and violet ultramarines have been examined by L. Wunder. Each is produced from the blue by loss of sodium and sulphur; in the conversion from blue into red, half of each of these constituents is removed. Both the red and the violet products are decomposed by hydrochloric acid with the evolution of sulphur dioxide[4] and the separation of sulphur, and both lose a further quantity of sulphur when heated in hydrogen, leaving, however, bright blue residues.

Ultramarine blue is converted into a *white* solid, with the loss of sodium and sulphur, when heated under pressure to 150° with a solution of phosphorus in carbon tetrachloride. The product loses water and sulphur dioxide when heated, the residue becoming green and then blue. With hydrochloric acid it evolves hydrogen sulphide, and when treated with sodium hypobromite it turns bright blue.[5]

When commercial ultramarine blue is heated to 120°–140° under pressure with aqueous silver nitrate for fifteen hours, it is converted into a dark yellow *silver ultramarine*, silver nitrite and nitric oxide also being produced, but not silver sulphide.[6] The silver ultramarine is produced by the replacement of sodium in the blue ultramarine by silver, the complete substitution, however, being difficult to effect. By heating silver ultramarine with molten metallic chlorides it is possible to replace the silver by numerous other metals. The preparation of mercurous, cadmium, lead, lithium, and calcium ultramarines has also been effected directly from ultramarine blue by heating under pressure with aqueous salt solutions.[7] The replacement of the sodium by the tervalent metals aluminium, chromium, and iron cannot, however, be thus effected, the ultramarine being decomposed, but L. Wunder considers that aluminium, chromium, and iron ultramarines are produced as intermediate products which are very unstable and decompose rapidly. It has been known for years that a solution of alum slowly decolorises ultramarine blue, and the change has been attributed to the hydrolysis of the salt and consequent presence of free acid in the solution. In connection with the various ultramarines of different metals, it is possibly of considerable significance that only those of the alkali metals are blue in

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[1] J. Wunder, *Ber.*, 1876, **9**, 295; *Chem. Zeit.*, 1890, **14**, 1119; 1906, **30**, 61, 78; 1911, **35**, 221; L. Wunder, *Zeitsch. anorg. Chem.*, 1912, **77**, 209; *cf.* Zettner, *Ber.*, 1875, 8, 259, 353.

[2] J. Wunder, *loc. cit.*; *cf.* Zettner, *loc. cit.*; Scheffer, *Ber.*, 1873, 6, 1450; Büchner, *Dingl. poly. J.*, 1879, **231**, 446; *Ber.*, 1874, **7**, 990; R. Hoffmann, *Annalen*, 1878, **194**, 1.

[3] L. Wunder, *loc. cit.*

[4] *Cf.* footnote 6 on p. 137.

[5] L. Wunder, *Zeitsch. anorg. Chem.*, 1912, **77**, 209; *Chem. Zeit.*, 1913, **37**, 1017. For other *white* ultramarines, see Philipp, *Ber.*, 1876, **9**, 1109; 1877, **10**, 1227; *Annalen*, 1876, **184**, 132; 1878, **191**, 1; Böttinger, *Annalen*, 1876, **182**, 311; R. Hoffmann, *ibid.*, 1878, **194**, 1.

[6] Unger, *Dingl. poly. J.*, 1874, **212**, 232; Heumann, *Ber.*, 1877, **10**, 991, 1345, 1888; 1879, **12**, 60, 784; *Annalen*, 1879, **199**, 253; 1880, **201**, 262; **203**, 174; Philipp, *loc. cit.*; de Forcrand and Ballin, *Bull. Soc. chim.*, 1878, [ii.], **30**, 112; Chabrié and Levallois, *Compt. rend.*, 1906, **143**, 222.

[7] L. Wunder, *Zeitsch. anorg. Chem.*, 1912, **77**, 209.

colour.[1] Thus, the manganese compound is grey, the silver compound is yellow, etc.

When silver ultramarine is heated under pressure with a suitable organic iodide, the silver is replaced by an organic radicle. In this manner ethyl, amyl, benzyl, and phenyl ultramarines have been prepared.[2] Their formation is not merely a question of substituting silver for an organic radicle, since part of the sulphur is also removed. The organic ultramarines do not evolve hydrogen sulphide when treated with cold hydrochloric acid. When heated with sodium chloride, however, they give rise to a blue sodium ultramarine. When heated alone, organic sulphides (*e.g.* ethylsulphide) are evolved.

Green ultramarine has been already mentioned as an intermediate product in the manufacture of the commercial blue variety. In the conversion of the green into the blue, sodium is removed but sulphur is not added on; the conversion may be effected by heating in a sealed tube with water.[3]

When ultramarine red is heated out of contact with air it loses a little in weight and is converted into a blue product; like the commercial blue, but unlike the red ultramarine, this new blue product evolves hydrogen sulphide when treated with hydrochloric acid. It differs from the commercial blue in that it is not reduced to a white product by the action of phosphorus, and is not transformed into a violet product by heating to 170°–250° in chlorine and hydrogen chloride.[4]

Uses.—Owing to its brilliancy as a body colour and high colouring power, ultramarine blue is largely used in the preparation of blue paints in calico and wall-paper printing, for colouring writing paper and printing ink, blueing mottled soap, etc. It is also of value as a whitening agent, correcting the yellow tint of paper, cotton and linen goods, whitewash, soap, starch, sugar, etc. It also finds considerable application in the manufacture of laundry "blue."

Constitution.—It has been already mentioned (p. 136) that several grades of ultramarine blue are manufactured, differing considerably in their silica and sulphur content. Numerous analyses of ultramarine blue have been published; a selection is given in the following table:—[5]

Constituent.	1	2	3	4	5	6	7
SiO_2	40·7	37·9	42·4	41·0	41·3	38·3	40·4
Al_2O_3	24·0	30·5	24·0	24·1	24·5	29·2	23·6
Fe_2O_3	...	...	...	...	...	...	1·1
S	13·6	8·9	15·4	14·0	13·3	9·3	13·6
Na	17·4	16·9	13·9	16·4	14·5	15·5	14·6
H_2O	...	...	0·7	...	...	...	...
Ca	...	...	...	...	0·4	0·7	...

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[1] De Forcrand, *Bull. Soc. chim.*, 1879, [ii.], **31**, 161; L. Wunder, *loc. cit.*

[2] De Forcrand, *Compt. rend.*, 1879, **88**, 30; *Bull. Soc. chim.*, 1879, [ii.], **31**, 161; Chabrié and Levallois, *loc. cit.*; *cf.* Singer, *D.R.P.*, No. 221,344 (1909).

[3] Philipp, *Ber.*, 1876, **9**, 1109.

[4] L. Wunder, *Zeitsch. anorg. Chem.*, 1913, **79**, 343.

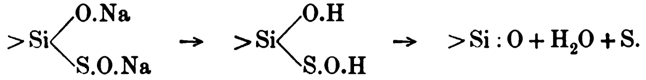
[5] Samples 1 and 2 analysed by R. Hoffmann (*Annalen*, 1878, **194**, 1); sample 3 by Parry and Coste (*The Chemistry of Pigments*, 1902); sample 4 is the mean of several analyses by Guckelberger (*Annalen*, 1882, **213**, 182); samples 5 and 6 by L. Wunder

It is clear that different samples of ultramarine blue may have widely different compositions. According to L. Wunder, the substance always contains a little "water of constitution."

Owing to the highly complex chemical constitution of the ultramarines and their derivatives, chemists are not yet agreed as to the chemical formulæ to be assigned to them. It is quite possible that the commercial ultramarines contain a number of closely related compounds in isomorphous mixture. The ultramarines are probably sodium aluminosilicates modified in some manner by the presence of sulphur in the molecules. Various suggestions as to the position of the sulphur in an ultramarine molecule have been put forward; thus, Wunder regards the sulphur liberated in the form of hydrogen sulphide by acids as being present in the grouping $>Al-S-Na$:—

$$>Al-S-Na+2HCl = >AlCl+H_2S+NaCl,$$

while groupings such as $>Si(ONa)(SONa)$ lead to deposition of sulphur when the molecule is broken up by acids:—



$$>Si\begin{matrix}\diagup O.Na\\ \diagdown S.O.Na\end{matrix} \rightarrow >Si\begin{matrix}\diagup O.H\\ \diagdown S.O.H\end{matrix} \rightarrow >Si:O+H_2O+S.$$

W. and D. Asch consider that there is an atom of oxygen between the aluminium and the sulphur, but otherwise the corresponding part of their formula is similar to that of Wunder.

For further information on the constitution of ultramarine the reader is referred to the literature.[1]

The Colour of Ultramarine.—The cause of the beautiful colour that ultramarine possesses is at present unknown.[2] Two views are advocated: first, that there is a definite chemical individual (or series of allied individuals) which constitutes the basis of ultramarine and has a blue colour, and secondly, that the colour is more or less an accidental circumstance. On the second view, it is considered that the basis of ultramarine

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(*Zeitsch. anorg. Chem.*, 1912, **77**, 209); sample 7 by B. Campbell (private communication). Numerous other analyses are quoted by Guckelberger (*loc. cit.*), Philipp (*Annalen*, 1876, **184**, 132; 1878, **191**, 1), Böttinger (*ibid.*, 1876, **182**, 311), Heumann (*ibid.*, 1879, **199**, 253; 1880, **201**, 262), Jordan (*Zeitsch. angew. Chem.*, 1893, **6**, 684), and de Forcrand (in Moissan's *Traité de chimie*, 1905, vol. iv.); see also Dammer, *Handbuch der anorganischen Chemie* (Stuttgart, 1893), vol. iii.

[1] Breunlin, *Annalen*, 1856, **97**, 295; Wilkens, *ibid.*, 1856, **99**, 21; Böckmann, *ibid.*, 1861, **118**, 212; Böttinger, *ibid.*, 1876, **182**, 311; Philipp, *ibid.*, 1877, **184**, 132; 1878, **191**, 1; Heumann, *ibid.*, 1879, **199**, 253; 1880, **201**, 262; **203**, 174; R. Hoffmann, *ibid.*, 1878, **194**, 1; Guckelberger, *ibid.*, 1882, **213**, 182; Szilasi, *ibid.*, 1889, **251**, 97; Dollfuss and Goppelsröder, *Bull. Soc. Ind. Mulh.*, 1875, **45**, 193, 196; Stein, *J. prakt. Chem.*, 1871, [ii.], **3**, 38; Plicque, *Compt. rend.*, 1877, **85**, 570; *Bull. Soc. chim.*, 1877, **28**, 518; **29**, 51; Rickmann, *Ber.*, 1878, **11**, 2013; de Forcrand, *Mém. Acad. Sci. Lyons*, 1879, **24**, 141; Silber, *Ber.*, 1880, **13**, 1854; F. W. Clarke, *Amer. Chem. J.*, 1888, **10**, 126; J. Wunder, *Chem. Zeit.*, 1890, **14**, 1119; Brögger and Bäckström, *Zeitsch. Kryst. Min.*, 1891, **18**, 209; Puchner, *Chem. Zentr.*, 1896, i. 1051; Rohland, *Zeitsch. angew. Chem.*, 1904, **17**, 609; Erdmann, *Annalen*, 1908, **362**, 133; L. Wunder, *Zeitsch. anorg. Chem.*, 1912, **77**, 209; Bock, *Zeitsch. angew. Chem.*, 1915, **28**, 147. Most of the foregoing are included in W. and D. Asch, *The Silicates in Chemistry and Commerce*, transl. by Searle (Constable, 1913).

[2] The early view that lapis-lazuli owed its blue colour to copper was disproved in 1762 by Margraff, who attributed it to iron. In 1806 Clément and Désormes showed that some specimens of lapis-lazuli were free from iron.

is a colourless, transparent solid, which holds in colloidal suspension or solid solution a small amount of another substance which gives rise to the blue colour. This second substance is generally considered to be a blue form of sulphur.[1]

The arguments used in favour of the colloidal sulphur theory are largely based on analogy, various reactions being known in which it is very probable that colloidal sulphur is produced and in which a blue colour is developed. Thus, potassium thiocyanate[2] turns blue when melted and heated to 400°, and molten sodium chloride or sulphate becomes bright blue when a little sulphur is added and the mass heated until the initial black turbidity vanishes.[3] When alkali polysulphides are added to various boiling organic solvents, blue solutions are obtained, which usually lose their colour when cooled.[4] Moreover, at very high temperatures sulphur vapour is blue in colour.[5]

It cannot be considered, however, that the colloid theory is well established. The objection based upon the fact that ultramarine retains its colour at high temperatures is perhaps not very serious, but it is difficult to see how the theory is to explain the existence of red, violet, and green ultramarines. It would necessitate all the colours being attributed to colloidal sulphur in various states of division, and the assumption that the blue colour of the commercial article is due to its temperature of formation being such as to produce the sulphur in the requisite state of fineness. Silver ultramarine, however, turns blue when heated with sodium chloride at a comparatively low temperature. Again, in the cases of the blue solutions already mentioned, where the existence of colloidal sulphur is considered probable, the blue coloration only makes its appearance in the fluid state; molten, blue potassium thiocyanate becomes white on solidification. If, however, in the manufacture of ultramarine, overheating occurs and the mass fuses, the blue colour is destroyed. Ultramarine still retains its blue colour at − 184° C.[6] A serious objection to the colloid theory is found in the fact that among the numerous substituted ultramarines, only those containing the alkali metals are blue. W. and D. Asch[7] argue in great detail for the view that the ultramarines are definite chemical compounds of a highly complex nature, and that the various colours are produced by changes in the arrangement of the various atoms within the molecule. Accordingly to L. Wunder,[8] three conditions must be fulfilled for an ultramarine to possess a blue colour: (i.) an alkali metal must be present, (ii.) part of the sulphur must be directly united to the alkali metal, and

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[1] See, *e.g.*, Knapp, *J. prakt. Chem.*, 1888, [ii.], **38**, 48; Rohland, *Zeitsch. angew. Chem.*, 1904, **17**, 609; J. Hoffmann, *Chem. Zeit.*, 1910, **34**, 821; Abegg, *Handbuch der anorganischen Chemie*, vol. iii. pt. 1, p. 126 (1906); W. Biltz, cited in Abegg, *opus cit.*; Doelter, *Handbuch der Mineralchemie* (Dresden and Leipzig), 1911, etc., vol. ii. pt. vii.; *cf.* Stein, *J. prakt. Chem.*, 1876, **14**, 387; Gentèle, *Dingl. poly. J.*, 1856, **140**, 223; **141**, 116; 1861, **160**, 453; Blackmore, *J. Soc. Chem. Ind.*, 1897, **16**, 219; E. Guimet, *Mém. Acad. Sci. Lyons*, 1878, **23**, 29.

[2] Nöllner, *Annalen*, 1858, **108**, 8; Giles, *Chem. News*, 1901, **83**, 61; Milbauer, *Zeitsch. anorg. Chem.*, 1904, **42**, 433; 1906, **49**, 46.

[3] Knapp, *loc. cit.*

[4] Paterno and Mazzucchelli, *Atti R. Accad. Lincei*, 1907, [v.], **16**, i. 465.

[5] Paterno and Mazzucchelli, *loc. cit.* For further work on blue sulphur, see Wöhler, *Annalen*, 1853, **86**, 373; N. A. Orloff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 397, 400; 1902, **34**, 52.

[6] B. Campbell (private communication).

[7] W. and D. Asch, *opus cit.*

[8] L. Wunder, *Zeitsch. anorg. Chem.*, 1913, **79**, 343; *Chem. Zeit.*, 1913, **37**, 1017.

(iii.) another part of the sulphur must be present in a lower state of oxidation (*i.e.* its valency must be less than six). Neither aluminium nor silicic acid is essential, as the former may be replaced by boron,[1] and the latter by a polyboric acid.[2]

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[1] On *boron ultramarine*, see J. Hoffmann, *Zeitsch. angew. Chem.*, 1906, **19**, 1089; 1907, **20**, 568; *Chem. Ind.*, 1911, **34**, 699.

[2] *Selenium* and *tellurium* may replace the sulphur in ultramarine; the substances thus obtained, however, are not blue; Leykauf, *Jahresber. Tech.*, 1876, p. 555; E. Guimet, *Ann. Chim. Phys.*, 1878, [v.], **13**, 102; Plicque, *Bull. Soc. chim.*, 1877, [ii.], **28**, 518; 1878, [ii.], **29**, 522; **30**, 51; Morel, *ibid.*, 1877, [ii.], **28**, 522.

CHAPTER VI.

GALLIUM.[1]

Symbol, Ga. Atomic weight, 69·9 (O = 16).

Occurrence.—Gallium is one of the rarest of the elements, occurring widely distributed in nature, but only in very minute quantities.[2] It is a frequent constituent of zinc blendes; the richest ore, the black blende from Bensberg, contains 16 milligrams of gallium per kilogram. Other blendes relatively rich in gallium are found at Pierrefitte in the Pyrenees,[3] Alston Moor in Cumberland, and Rio Tuerto in Spain.[4]

Examination of the oxy-hydrogen flame spectra of numerous minerals has shown that gallium is present in a large number of iron ores, particularly in magnetite, clay-ironstone, and black-band ore, but not in siderite. When such ores are smelted, gallium passes into the resulting metal, and Middlesbrough pig-iron, which contains 0·003 per cent. of gallium, is one of the richest sources of the element known.[5] Gallium is constantly associated with aluminium and chromium in aluminous iron ores, such as bauxite and kaolin, and accordingly occurs in commercial aluminium;[6] in one sample of the commercial metal, 0·017 per cent. of gallium was found.[7]

Gallium has been observed in pyrites and manganese ores, and in meteoric iron.[8] It also occurs in certain French mineral waters.[9] Gallium exists in the sun's atmosphere.[10]

History.—On 27th August 1875, Lecoq de Boisbaudran observed a new violet line, $\lambda 4170$, in the spark spectrum of some material he had separated from the zinc blende of Pierrefitte; further work led to the discovery of another new line, $\lambda 4031$, and established the fact that both lines belonged to

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[1] See "Gallium," by Lecoq de Boisbaudran in Wurtz, *Dictionnaire de chimie, Supplément*, pt. 2, p. 851. Gallium is identical with the element **austrium** discovered by Linnemann. See Linnemann, *Monatsh.*, 1886, **7**, 773; Pribram, *ibid.*, 1900, **21**, 148; Lecoq de Boisbaudran, *Compt. rend.*, 1886, **102**, 1436.

[2] Vernadski, *Bull. Acad. Sci. Petrograd*, 1910, p. 1129.

[3] Lecoq de Boisbaudran, *Ann. Chim. Phys.*, 1877, [v.], **10**, 136.

[4] Hartley and Ramage, *Proc. Roy. Soc.*, 1897, **60**, 35, 393; *Trans. Chem. Soc.*, 1897, **71**, 533. See also Urbain, *Compt. rend.*, 1909, **149**, 602; Angel del Campo y Cerdán, *Anal. Fis. Quim.*, 1914, **12**, 80.

[5] Hartley and Ramage, *loc. cit.*

[6] Hartley and Ramage, *Trans. Chem. Soc.*, 1897, **71**, 547.

[7] Boulanger and Bardet, *Compt. rend.*, 1913, **157**, 718.

[8] Hartley and Ramage, *Sci. Proc. Roy. Dubl. Soc.*, 1898, **8**, 703. See also the following papers dealing with the occurrence of gallium: Kirkland, *Austr. Assoc. Adv. Sci.*, 1893, p. 266; Delachanel and Mermet, *Bull. Soc. chim.*, 1876, [ii.], **25**, 197; Cornwall, *Amer. Chem. J.*, 1880, **2**, 44; Blenden and Bartlett, *J. Soc. Chem. Ind.*, 1889, **8**, 896.

[9] Bardet, *Compt. rend.*, 1913, **157**, 224.

[10] Hartley and Ramage, *Sci. Proc. Roy. Dubl. Soc.*, 1898, **7**, 1.

the spectrum of a new metallic element, to which the discoverer patriotically gave the name of **gallium** in honour of his native country.[1] The first researches on gallium[2] were conducted with only a few milligrams of material; but in 1878 Lecoq de Boisbaudran and Jungfleisch, starting with 2400 kilograms of Bensberg blende, obtained 62 grams of nearly pure gallium.[3]

The discovery of gallium marked the inauguration of the periodic classification. In putting forward that scheme for the classification of the elements, Mendeléeff was obliged to assume the existence of several elements not known at that period (1871). One of these hypothetical elements, of atomic weight about 68, he called **eka-aluminium**, and described the properties it should possess; and it was noticed very shortly after the discovery of gallium that gallium closely resembled the hypothetical eka-aluminium in its behaviour.[4] The following tabular statement will serve to illustrate how closely Mendeléeff succeeded in foretelling the properties of gallium:—[5]

Eka-aluminium.	Gallium.
Atomic weight, *c.* 68.	Atomic weight, 69·9.
Metal of density 5·9 and low melting-point; not volatile; unaffected by air; should decompose steam at a red heat and dissolve slowly in acids and alkalies.	Metal of density 5·94; melting at 30·15°; not volatile; unchanged in air; action on steam not known; dissolves slowly in acids and alkalies.
Oxide should have formula El_2O_3, density 5·5, and dissolve in acids to form salts of the type ElX_3. The hydroxide should dissolve in acids and alkalies.	Oxide, Ga_2O_3; density not known; dissolves in acids, forming salts GaX_3. The hydroxide dissolves in acids and alkalies.
There should be a tendency towards the formation of basic salts. The sulphate should form alums. The sulphide should be precipitated by H_2S or $(NH_4)_2S$. The anhydrous chloride should be more volatile than zinc chloride.	Salts readily hydrolyse and form basic salts. Alums are known. The sulphide can be precipitated by H_2S or $(NH_4)_2S$, but only under special circumstances. The anhydrous chloride is more volatile than zinc chloride.
The element will probably be discovered by spectrum analysis.	Was discovered spectroscopically.

Preparation.—Zinc blende containing gallium is dissolved in aqua regia, using a slight excess of blende, in order to leave no free nitric acid in solution, and the copper, lead, cadmium, mercury, silver, etc., present are for the most part precipitated by the introduction of strips of metallic zinc. The liquid is filtered while hydrogen is still being evolved, and the filtrate boiled for some hours with a large excess of zinc. The abundant white precipitate which forms, containing alumina, basic salts of zinc, gallium, iron, and chromium, and a little silica, is dissolved in hydrochloric acid, and the preceding processes are repeated on the solution.[6] The hydrochloric acid solution of the final precipitate is saturated with hydrogen sulphide and

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[1] Lecoq de Boisbaudran, *Compt. rend.*, 1875, **81**, 493.

[2] Lecoq de Boisbaudran, *Compt. rend.*, 1875, **81**, 1100; 1876, **82**, 168, 1036; 1876, **83**, 611, 824, 1044; *Ann. Chim. Phys.*, 1877, [v.], **10**, 100.

[3] Lecoq de Boisbaudran and Jungfleisch, *Compt. rend.*, 1878, **86**, 475.

[4] Mendeléeff, *Compt. rend.*, 1875, **81**, 969.

[5] Mendeléeff, *loc. cit.*, and *J. Russ. Chem. Soc.*, 1869, **1**, 60; 1871, **3**, 47; *Annalen Suppl.*, 1872, **8**, 133.

[6] By proceeding thus far with 10 grams of blende, concentrating the chloride solution and examining its spark spectrum, a qualitative test for gallium may be made.

filtered. From the filtrate, the zinc is precipitated as sulphide after the addition of ammonium acetate and acetic acid. This precipitate contains all the gallium (see p. 149); the precipitation is effected in fractions, the filtrate after each operation being spectroscopically examined for gallium. The washed sulphides are converted into chlorides, and the cold liquid fractionally precipitated with sodium carbonate, gallium quickly concentrating in the first fractions of the precipitate. The precipitates containing gallium are dissolved in sulphuric acid, and the solution gently heated until nearly all the excess of acid has been expelled. The residue is dissolved in cold water, the solution largely diluted, and boiled for some hours. Basic gallium sulphate separates out and is filtered and washed with hot water. The precipitate is dissolved in sulphuric acid, and any iron present is precipitated by a large excess of potassium hydroxide. From the filtered solution the gallium is precipitated by a prolonged current of carbon dioxide. The precipitate is dissolved in the minimum amount of sulphuric acid, the solution treated successively with ammonium acetate and hydrogen sulphide, and filtered. The gallium is again precipitated as a basic sulphate by boiling the largely diluted filtrate, the washed precipitate dissolved in sulphuric acid, and an excess of potassium hydroxide added. The filtered solution is then electrolysed to deposit the gallium, using a large platinum cathode. Gallium may also be deposited electrolytically from an ammoniacal solution of the sulphate. The metal, which easily separates from the electrode by bending it under water, is allowed to stand for several hours in very dilute hydrochloric acid, then in dilute potassium hydroxide at 50° to 60°, and is finally washed with water.[1]

Properties.—Gallium, the eka-aluminium of Mendeléeff, is a hard, brittle, grey metal having a greenish-blue reflex. It melts at the remarkably low temperature of 30·15° C. to a silver-white liquid which is only slightly volatile even at a red heat.[2] In the absence of the solid phase, liquid gallium possesses to an extraordinary degree the property of remaining in a superfused state. The metal crystallises with great readiness in the tetragonal (or possibly the monoclinic) system, the crystals possessing an octahedral habit and usually possessing slightly convex faces. The density of the solid is 5·96 at 24·5°; that of the liquid is 6·07 at 24·7°.[2] Gallium, therefore, like water, expands on freezing. The mean specific heat,[3] of the solid metal is 0·079 between 12° and 23°; that of the liquid is 0·0802 between 106° and 119°. The latent heat of fusion is 19·03 calories per gram of metal.[3] The specific resistance exceeds that of the alkali metals.[4] Liquid gallium is electronegative to the solid element.[5] The atomic refraction of gallium in its compounds is 14·8 (for the H_α line; Gladstone and Dale's formula).[6] Gallium is diamagnetic.[7]

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[1] For further details and alternative methods, see Lecoq de Boisbaudran, *Ann. Chim. Phys.*, 1877, [v.], 10, 129; *Compt. rend.*, 1876, 82, 1098; 83, 636; 1881, 93, 815; Wurtz, *Dictionnaire de chimie, Supplément*, pt. 2, p. 851; Lecoq de Boisbaudran and Jungfleisch, *loc. cit.*

[2] Lecoq de Boisbaudran, *Compt. rend.*, 1876, 83, 611, 1044; *Ann. Chim. Phys.*, 1877, [v.], 10, 100.

[3] Berthelot, *Compt. rend.*, 1878, 86, 786.

[4] Guntz and Broniewski, *Compt. rend.*, 1908, 147, 1474; *J. Chim. phys.*, 1909, 7, 464.

[5] Regnauld, *Compt. rend.*, 1878, 86, 1457.

[6] Gladstone, *Proc. Roy. Soc.*, 1897, 60, 140.

[7] Owen, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 637; *Ann. Physik*, 1912, [iv.], 37, 657.

The spark spectrum of gallium is characterised by two violet lines, λ4172·2 and λ4033·2, the former being the more intense.[1]

Gallium is only superficially oxidised when heated, even to redness, in air or oxygen. It does not decompose water at 100°, and under air-free water it remains bright and unaffected for a long time. It dissolves slowly in mineral acids. Solid gallium dissolves much faster in hydrochloric acid than does the liquid metal. Warm nitric acid dissolves it slowly, and the best acid solvent is aqua regia. Gallium dissolves in potassium hydroxide, with the liberation of hydrogen. It unites directly with chlorine, bromine, and iodine, in decreasing order of activity.[2]

Gallium forms two classes of compounds, of the types GaX_2 and GaX_3 (X denoting a univalent acid radicle). The latter closely resemble the compounds of aluminium. Concerning the former, which instantly reduce potassium permanganate in dilute acid solution, very little is known.

Atomic and Molecular Weights.—The vapour densities, referred to air as unity, of the two chlorides of gallium have been determined to be 4·82 (at 1000° to 1100°) and 6·13 (from 440° to 606°), corresponding to the molecular weights 140 and 178 respectively ($O_2 = 32$).[3] Since the chlorides contain 51·0 per cent. and 40·0 per cent. of gallium respectively,[4] the weights of metal in the preceding molecular weights are 71·4 and 71·2. Hence Avogadro's hypothesis leads to the approximate value 71 for the atomic weight of gallium, and to the molecular formulæ $GaCl_2$ and $GaCl_3$ for the chlorides.

The specific heat of gallium (p. 145) supports this view, since it indicates an atomic weight of about 80; and it is confirmed by the fact that gallium sulphate forms a series of double sulphates, isomorphous with ordinary alum, $Al_2(SO_4)_3.K_2SO_4.24H_2O$, which double salts, on the assumption that the approximate atomic weight of gallium is 70, must be formulated $Ga_2(SO_4)_3.R_2SO_4.24H_2O$, where R = K, Rb, Cs, NH_4, or Tl.

The preceding approximate value for the atomic weight of gallium indicates that it is three times the combining weight of the metal in its oxide and highest halogen compounds. The value at present accepted for the atomic weight, **Ga = 69·9**, results upon a single analysis of gallium ammonium alum and a single synthesis of gallium sesqui-oxide.[5]

The atomic weight of gallium was calculated by Lecoq de Boisbaudran, before sufficient material was available for an experimental determination, from considerations based upon a comparison of the wave-lengths of the spectrum lines of gallium and of other allied elements of known atomic weights. His method of calculation leads to the value Ga = 69·86.[6]

The molecule of gallium is monatomic in dilute solution in mercury.[7]

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[1] Lecoq de Boisbaudran, *Compt. rend.*, 1876, **82**, 168 ; 1887, **104**, 1584 ; 1892, **114**, 815 ; Liveing and Dewar, *Proc. Roy. Soc.*, 1879, **28**, 471 ; Kayser, *Handbuch der Spektroskopie* (Leipzig, 1900–12), vol. v. p. 460 ; Hartley and Moss, *Proc. Roy. Soc.*, 1912, **A**, **87**, 38. On series in the spectrum of gallium, see p. 3. On the high-frequency spectrum, see de Broglie, *Compt. rend.*, 1914, **159**, 304.

[2] Lecoq de Boisbaudran, *Compt. rend.*, 1876, **83**, 663, 824.

[3] Nilson and Pettersson, *Trans. Chem. Soc.*, 1888, **53**, 814.

[4] Lecoq de Boisbaudran, *Compt. rend.*, 1881, **93**, 294, 329.

[5] Lecoq de Boisbaudran, *Compt. rend.*, 1878, **86**, 941 ; see F. W. Clarke, *A Recalculation of the Atomic Weights* ("Smithsonian Miscellaneous Collections," vol. 54, No. 3), 3rd ed., 1910, p. 269.

[6] See the article "Gallium" in Wurtz, *Dictionnaire de chimie, Supplément*, pt. 2, p. 859 ; Miss Freund, *The Study of Chemical Composition* (Cambridge University Press, 1904), p. 491.

[7] Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 521.

COMPOUNDS OF GALLIUM.

Alloys.—Gallium easily alloys with aluminium, the mixtures rich in gallium being liquid at ordinary temperatures. The alloys readily decompose water, liberating hydrogen and leaving a solid residue of metallic gallium and aluminium hydroxide.[1] Gallium also alloys readily with indium.[2]

Gallium dichloride, $GaCl_2$, prepared by heating the trichloride with excess of gallium and distilling the product in carbon dioxide, forms white, transparent crystals, melting at 164° and boiling at 535°.[3] The liquid exhibits the phenomenon of superfusion to a remarkable degree, as, indeed, do all the halogen compounds of gallium. The vapour density at 1000° to 1100° is 4·82 (air = 1), the formula $GaCl_2$ corresponding to 4·86. At higher temperatures dissociation takes place, probably into GaCl and chlorine.[4]

In moist air, the dichloride deliquesces to a clear liquid. The addition of an excess of water leads to precipitation of an oxychloride, hydrogen (and perhaps gallium hydride) being evolved.[5]

Gallium trichloride, $GaCl_3$, obtained by heating gallium in chlorine or hydrogen chloride, forms long, white needles, melting at 75·5° and boiling at 215° to 220°.[6] The vapour has a density of 6·13 (air = 1) between 440° and 606°, the simple formula $GaCl_3$ corresponding to 6·08. At 1000° the vapour density indicates that dissociation has occurred, while at low temperatures the results obtained by the method of Dumas point to the existence, over the range 237° to 378°, of gaseous Ga_2Cl_6, the molecules of which gradually undergo dissociation into $GaCl_3$ with further rise of temperature.[3, 6, 7]

Molten gallium trichloride has a density of 2·36 at 80°,[8] readily absorbs gases, but evolves them on solidification. The crystalline chloride is very deliquescent and dissolves in water with the evolution of considerable heat, producing a colourless solution from which oxychlorides are slowly precipitated.[9] The aqueous solution loses hydrochloric acid when evaporated, leaving an amorphous residue which absorbs water and becomes gelatinous. An acid solution of the trichloride is obtained by dissolving gallium in aqua regia.

The **bromides** of gallium[10] closely resemble the chlorides. They are, however, less fusible and less volatile, and do not seem to have been analysed.

The **iodides** of gallium, like the bromides, require further study. Two appear to exist, a colourless tri-iodide and a yellow di-iodide.

Gallium sesqui-oxide, Ga_2O_3, which may be prepared by igniting the hydroxide or nitrate, is a white mass, infusible at a red heat. Its specific heat (0° to 100°) is 0·1062.[11] The strongly ignited oxide resembles ignited alumina in its resistance to acids and alkalies, and requires to be fused with potassium

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[1] Lecoq de Boisbaudran, *Compt. rend.*, 1878, **86**, 1204.

[2] Lecoq de Boisbaudran, *ibid.*, 1885, **100**, 701.

[3] Lecoq de Boisbaudran, *ibid.*, 1881, **93**, 294.

[4] Nilson and Pettersson, *Trans. Chem. Soc.*, 1888, **53**, 814.

[5] Lecoq de Boisbaudran, *Compt. rend.*, 1881, **93**, 294; 1882, **95**, 18.

[6] Lecoq de Boisbaudran, *ibid.*, 1881, **93**, 329.

[7] Nilson and Pettersson, *Trans. Chem. Soc.*, 1888, **53**, 814; Friedel and Crafts, *Compt. rend.*, 1888, **107**, 306.

[8] Lecoq de Boisbaudran, *Compt. rend.*, 1881, **93**, 294.

[9] Lecoq de Boisbaudran, *ibid.*, 1882, **94**, 695.

[10] Lecoq de Boisbaudran, *ibid.*, 1878, **86**, 756; with Jungfleisch, *ibid.*, 1878, **86**, 577.

[11] Nilson and Pettersson, *Compt. rend.*, 1880, **91**, 232; *Ber.*, 1880, **13**, 1459.

hydrogen sulphate in order to be brought into solution. At a red heat, hydrogen reduces the sesqui-oxide to a greyish-blue mass, probably a *suboxide* (GaO ?), which dissolves in dilute mineral acids to form solutions which instantly reduce potassium permanganate.[1] At a bright red heat, reduction to the metal can be effected. Gallium sesqui-oxide is also reduced to gallium when heated with magnesium.[2]

The oxides of samarium, Z_α (dysprosium), Z_β (terbium), and chromium act as phosphorogens when diluted with gallium sesqui-oxide and submitted to the action of cathode rays. The phosphorescence is a beautiful red when the quantity of chromium sesqui-oxide equals 0·1 per cent.[3]

Gallium hydroxide, $Ga(OH)_3$ (?), does not seem to have been analysed. It is obtained as a white precipitate, readily soluble in potassium hydroxide, by adding ammonia to a solution of a gallium salt. Tartaric acid hinders the precipitation.

Gallium sulphide, Ga_2S_3 (?), undoubtedly exists, but it has not been obtained pure, since its precipitation can only be effected in the presence of another insoluble sulphide.[4]

Gallium sulphate, $Ga_2(SO_4)_3$, is a white, crystalline salt. Its specific heat (0° to 100°) is 0·146.[5] It is very soluble in water, soluble in 60 per cent. alcohol, but insoluble in ether.[6]

Gallium ammonium alum, $Ga_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$, crystallises from a solution of mixed gallium and ammonium sulphates in combinations of the cube and regular octahedron. The aqueous solution precipitates basic salts when heated.[7]

The corresponding **potassium-, rubidium-, cæsium-,** and **thallium-gallium alums** have been prepared by Soret,[8] who gives the following values for the densities and refractive indices (μ) for the D-line at ordinary temperature:—

	NH_4.	K.	Rb.	Cs.	Tl.
density	1·777	1·895	1·962	2·113	2·477
μ	1·4684	1·4563	1·4658	1·4650	1·5067

Gallium Silicotungstate.—Gallium silicotungstate is very soluble in water. Three hydrates are known: the first, which has the formula $2Ga_2O_3.3(SiO_2.12WO_3).93H_2O$, crystallises in regular octahedra; the second has $87H_2O$ and crystallises in rhombohedra ($a:c=1:2·6346$); while the third has $60H_2O$ and crystallises in the monoclinic (?) system ($a:b:c= 0·9057:1:1·1585$; $\beta=74°\ 20'$). The first two salts therefore correspond to those of aluminium (p. 87).[9]

Gallium nitrate, $Ga(NO_3)_3.xH_2O$, is a white, deliquescent salt which is completely decomposed at 200°.[10]

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[1] Dupré, *Compt. rend.*, 1878, **86**, 720.

[2] Winkler, *Ber.*, 1890, **23**, 772.

[3] Lecoq de Boisbaudran, *Compt. rend.*, 1887, **104**, 330, 1584; **105**, 784, 1228.

[4] See p. 149, and Lecoq de Boisbaudran, *Compt. rend.*, 1881, **93**, 815.

[5] Nilson and Pettersson, *Compt. rend.*, 1880, **91**, 232; *Ber.*, 1880, **13**, 1459.

[6] Lecoq de Boisbaudran, *Ann. Chim. Phys.*, 1877, [v.], **10**, 126.

[7] Lecoq de Boisbaudran, *Compt. rend.*, 1875, **81**, 1100; 1876, **83**, 824; *Ann. Chim. Phys.*, 1877, [v.], **10**, 126.

[8] Soret, *Arch. Sci. phys. nat.*, 1885, [iii.], **14**, 96; 1888, [iii.], **20**, 520.

[9] Wyrouboff, *Bull. Soc. franç. Min.*, 1896, **19**, 219. The hydrate with $60H_2O$ is possibly triclinic; see Wyrouboff, *ibid.*, 1905, **28**, 237.

[10] Dupré, *Compt. rend.*, 1878, **86**, 720.

DETECTION AND ESTIMATION OF GALLIUM.

A solution of a pure gallium salt is not precipitated by hydrogen sulphide in acid, neutral, or alkaline solution, but, in the presence of excess of another element capable of forming an insoluble sulphide, gallium sulphide is carried down completely with the other sulphide in either acetic acid or ammoniacal solution. Arsenious sulphide is usually best to employ, but the sulphides of silver, of zinc, and particularly of manganese may be used. In solutions containing much mineral acid, gallium sulphide is not precipitated, a fact that is utilised in effecting the separation of gallium from the excess of either arsenic or silver.

Ammonium hydroxide or carbonate, and carbonates of the alkali and alkaline-earth metals, precipitate gallium as hydroxide from solutions of its salts. The precipitate dissolves appreciably in excess of the soluble precipitants, but precipitation by ammonia is practically complete if excess of ammonia is removed by boiling.

Gallium may be precipitated as ferrocyanide, but not as ferricyanide, in solutions containing 33 per cent. by volume of concentrated hydrochloric acid, the reaction being extremely delicate. It is completely precipitated as hydroxide by boiling the sulphate or chloride solution with excess of precipitated cupric hydroxide. In the presence of iron it is preferable to boil with copper to reduce ferric to ferrous salt, and then to precipitate the gallium by the addition of precipitated cuprous oxide. The detection of gallium spectroscopically in minerals has already been described (p. 144, footnote 6).

Gallium is weighed as the sesqui-oxide.[1]

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[1] Lecoq de Boisbaudran, *Ann. Chim. Phys.*, 1884, [vi.], **2**, 176, 429; *Compt. rend.*, 1881, **93**, 815; 1882, **94**, 1154, 1227, 1439, 1625; **95**, 157, 410, 503, 703, 1192, 1332; 1883, **96**, 152, 1696, 1838; **97**, 66, 142, 295, 521, 623, 730, 1463; 1884, **98**, 711, 781; **99**, 526.

CHAPTER VII.

INDIUM.

Symbol, In. Atomic weight, 114·8 (O=16).

Occurrence.—Indium is one of the rarest of the elements, occurring in minute quantities fairly widely distributed in nature.[1] It exists in most zinc blendes,[2] in some tungsten ores,[3] and in many specimens of pyrites.[4] It is a constant constituent of tin ores, and occurs in siderites,[4] associated with manganese. Indium has also been observed in some Italian galenas and in other minerals.[5]

History.—In 1863, Reich and Richter[6] observed, in the spark spectrum of a specimen of Freiberg zinc blende, two new indigo-blue lines. They attributed them to a new metallic element, which they succeeded in isolating. Subsequently, the new metal, which had been appropriately named **indium,** was studied in detail by Winkler.[7]

Preparation.—Indium is best extracted from zinc that has been prepared from blende containing indium. The zinc, which may contain 0·1 per cent. of indium, is treated with a slight deficit of dilute sulphuric or hydrochloric acid, and the solution allowed to stand in contact with the excess of zinc for several days. From the spongy residue, which contains indium, lead, copper, iron, cadmium, arsenic, and the excess of zinc, pure indium oxide is best prepared by the method due to Bayer.[8] The washed residue is dissolved in nitric acid and the solution evaporated with a slight excess of sulphuric acid. Iron and indium hydroxides are precipitated by the addition of ammonia to the filtered solution of the sulphates and the washed precipitate dissolved in hydrochloric acid. The nearly neutral solution when boiled with excess of sodium bisulphite yields basic indium sulphite as a fine, crystalline powder. The precipitate is dissolved in aqueous sulphurous acid and the filtered solution heated to boiling, when pure basic indium sulphite is obtained.[9]

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[1] Vernadski, *Bull. Acad. Sci. Petrograd*, 1910, p. 1129 ; 1911, p. 187.

[2] Reich and Richter, *vide infra* ; Kachler, *J. prakt. Chem.*, 1865, **96**, 447; Cornwall, *Chem. News*, 1873, **28**, 28 ; Urbain, *Compt. rend.*, 1909, **149**, 602 ; Angel del Campo y Cerdán, *Anal. Fis. Quim.*, 1914, **12**, 80.

[3] Hoppe-Seyler, *Annalen*, 1866, **140**, 247 ; Atkinson, *J. Amer. Chem. Soc.*, 1898, **20**, 811.

[4] Hartley and Ramage, *Trans. Chem. Soc.*, 1897, **71**, 533.

[5] De Negri, *Ber.*, 1878, **11**, 1249 ; *Gazzetta*, 1878, **8**, 120 ; Tanner, *Chem. News*, 1874, **30**, 141.

[6] Reich and Richter, *J. prakt. Chem.*, 1863, **89**, 441 ; 1863, **90**, 172 ; 1864, **92**, 480 ; Richter, *Compt. rend.*, 1867, **64**, 827.

[7] Winkler, *J. prakt. Chem.*, 1865, **94**, 1 ; **95**, 414 ; 1867, **102**, 273 ; condensed account in *Ann. Chim. Phys.*, 1868, [iv.], **13**, 490.

[8] Bayer, *Annalen*, 1871, **158**, 372 ; *J. Chem. Soc.*, 1871, **9**, 664.

[9] *Cf.* Winkler, *loc. cit.* ; Böttger, *J. prakt. Chem.*, 1866, **98**, 26 ; R. Meyer, *Annalen*, 1869, **150**, 137. For the extraction of indium from blende, see Reich and Richter, *loc. cit.* ; Winkler, *loc. cit.* ; Weselsky, *ibid.*, 1865, **94**, 443 ; Kachler and Schrötter, *ibid.*, 1865, **95**, 441 ; Stolba, *Dingl. poly. J.*, 1870, **198**, 223.

The basic sulphite is dissolved in sulphuric acid, and indium hydroxide thrown down by the addition of ammonia. The precipitate is converted into indium sesqui-oxide by ignition.

Indium oxide may be reduced to the metal by heating in hydrogen or by heating with sodium. In the latter case, the brittle alloy of indium and sodium obtained is decomposed by water and the residual indium fused with sodium carbonate.[1]

Traces of iron may be removed from indium by converting it into the trichloride, adding potassium thiocyanate to the feebly acid solution, and extracting the ferric thiocyanate with ether.[2] Pure indium trichloride is also obtained by adding pyridine to its alcoholic solution. A double compound of the chloride with pyridine is precipitated, iron and aluminium chlorides remaining in solution.[3]

Indium is easily deposited electrolytically from a solution of the chloride or sulphate, in the presence of pyridine, hydroxylamine, or formic acid,[4] and fractional electrolysis of the sulphate solution affords the best method of obtaining pure indium.[5] The deposited metal is pressed together, washed, dried at 120°, and fused in a charcoal boat in a current of hydrogen.

Properties.—Indium is a soft, ductile, silver-white metal, which melts at 155°[6] and is volatile at a red heat.[7] It crystallises, like aluminium, but unlike zinc, in the cubic system, being electrolytically deposited from its sulphate solution in regular octahedra.[8] Its density is 7·277 at 20°,[9] its coefficient of expansion, 0·0000459,[10] and its specific heat (0° to 100°) is 0·0570.[11] The atomic refraction of indium in its compounds is 17·4 (for the H_α line; Gladstone and Dale's formula).[12] Indium is diamagnetic.[13]

The flame, arc, and spark spectra of indium are characterised in the visible region by two brilliant indigo-blue lines, 4511·55 and 4101·95.[14] The most *persistent* lines in the spark spectrum of indium, and therefore the lines that should be looked for when seeking traces of the element, are (Exner and Haschek's wave-lengths) 4511·55,* 4101·95,* 3256·22,* 3039·46,* 2941·39, 2890·35, 2710·39, 2306·20, those asterisked being the most sensitive.[15]

Indium is unaffected by dry air at ordinary temperatures, but at a red

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[1] Winkler, *loc. cit.*; Böttger, *J. prakt. Chem.*, 1869, **107**, 39.

[2] Dennis and Geer, *J. Amer. Chem. Soc.*, 1904, **26**, 437; *Ber.*, 1904, **37**, 961.

[3] Renz, *Ber.*, 1904, **37**, 2110; Dennis and Geer, *loc. cit.*

[4] Dennis and Geer, *loc. cit.*

[5] Thiel, *Ber.*, 1904, **37**, 175; *Zeitsch. anorg. Chem.*, 1904, **39**, 119; **40**, 280; Mathers, *Ber.*, 1907, **40**, 1220; *J. Amer. Chem. Soc.*, 1907, **29**, 485.

[6] Thiel, *loc. cit.*

[7] Ditte, *Compt. rend.*, 1871, **72**, 858.

[8] Sachs, *Zeitsch. Kryst. Min.*, 1903, **38**, 495.

[9] Richards and Wilson, *Carnegie Institution Publications*, 1909, No. 118, p. 13; *Zeitsch. physikal. Chem.*, 1910, **72**, 129.

[10] Fizeau, *Compt. rend.*, 1869, **68**, 1125.

[11] Bunsen, *Pogg. Annalen*, 1870, **141**, 28; *Phil. Mag.*, 1871, [iv.], **41**, 161; *Ann. Chim. Phys.*, 1871, [iv.], **23**, 50.

[12] Gladstone, *Proc. Roy. Soc.*, 1897, **60**, 140.

[13] Owen, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 637; *Ann. Physik*, 1912, [iv.], **37**, 657.

[14] Kayser, *Handbuch der Spektroskopie* (Leipzig, 1900–1912), vol. v. p. 581; Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Wien, 1911); Schulemann, *Zeitsch. wiss. Photochem.*, 1912, **10**, 263 (spark). On series in the indium spectrum see p. 3.

[15] Hartley, *Phil. Trans.*, 1884, **175**, i. 325; de Gramont, *Compt. rend.*, 1907, **144**, 1101; 1910, **151**, 308; 1914, **159**, 5; Hartley and Moss, *Proc. Roy. Soc.*, 1912, **A**, **87**, 38.

heat it burns with a blue flame, producing the sesqui-oxide with the liberation of 1044·6 cals. of heat per gram of metal.[1] It unites directly with sulphur and the halogens. It is unaffected by boiling water or potassium hydroxide, but dissolves in mineral acids. The action of nitric acid is slow, and ammonia is found among the reduction products of the acid.[2] The potential differences between indium and molar, tenth-molar, and hundredth-molar solutions of indium trichloride are 0·094, 0·108, and 0·119 volts respectively at 25°, the metal being negative to the solution. The electrolytic solution-pressure of indium, 10^2 to 10^3 atmospheres, places it between iron and lead in the electromotive series.[3]

Atomic and Molecular Weights.—The early workers on indium regarded that element as a diad, and analogous to zinc. This view was based upon the facts that indium occurs naturally in association with zinc, the two metals are very similar in their analytical reactions, and no sodium- or potassium-indium sulphates could be prepared which crystallised in octahedra and could be formulated as alums on the assumption that indium was tervalent. The bivalency of indium was, however, not acceptable to Mendeléeff, who could only place indium in his periodic table on the assumption that it was a triad, of atomic weight *c.* 114. In support of the tervalency of indium, both Mendeléeff and Lothar Meyer advanced various chemical reasons;[4] and Mendeléeff and Bunsen each showed, by determinations of the specific heat of the metal, that the tervalency of indium was a necessary assumption from the point of view of Dulong and Petit's Law.[5] Subsequent work has fully substantiated this assumption. In 1873 Roessler[6] succeeded in preparing indium ammonium alum, and in 1885 Soret[7] prepared the rubidium and cæsium alums. Most convincing of all, in 1888 Nilson and Pettersson[8] prepared and determined the vapour densities of three chlorides of indium, and showed that the results were in agreement with the molecular formulæ $InCl$, $InCl_2$, and $InCl_3$, with $In=114$ approximately. This value has been confirmed by another method, which may be outlined here. The *specific opacity*[9] of an element for X-rays of a definite quality is independent

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[1] Ditte, *Compt. rend.*, 1871, **72**, 858; **73**, 108.

[2] Armstrong and Acworth, *Trans. Chem. Soc.*, 1877, ii. 84.

[3] Thiel, *loc. cit.*; measured against decinormal calomel electrode (0·620 volts). *Cf.* Erhard, *Wied. Annalen*, 1881, **14**, 504.

[4] L. Meyer, *Annalen Suppl.*, 1870, **7**, 354; Mendeléeff, *ibid.*, 1872, **8**, 183, or *Chem. News*, 1879, **40**, 231, etc.; 1880, **41**, 2, etc.

[5] Mendeléeff, *Bull. Acad. Sci. Petrograd*, 1870, p. 445; Bunsen, *Phil. Mag.*, 1871, [iv.], **41**, 161.

[6] Roessler, *J. prakt. Chem.*, 1873, [ii.], **7**, 14.

[7] Soret, *Arch. Sci. phys. nat.*, 1885, [iii.], **14**, 96.

[8] Nilson and Pettersson, *Trans. Chem. Soc.*, 1888, **53**, 814.

[9] Given unit mass of a substance (1 decigram) in the form of a right cylinder, area of base 1 sq. cm., and given that X-rays fall normally on the base and pass through the cylinder; the fraction of the rays absorbed by the cylinder measures the *specific opacity* of its material.

The *equivalent transparency* of a substance is the mass (in decigrams) of a right cylinder 1 sq. cm. in base which, when X-rays are passed through it parallel to its axis, produces the same absorption as a cylinder of paraffin wax 75 mm. high and 1 sq. cm. in cross-section.

If masses $m_1, m_2, m_3, \ldots\ldots$ of elements of equivalent transparencies $e_1, e_2, e_3, \ldots\ldots$ are present in a total mass M of substance of equivalent transparency E, then, since specific opacity is a strictly additive property,

$$\frac{M}{E}=\frac{m_1}{e_1}+\frac{m_2}{e_2}+\frac{m_3}{e_3}+\cdots\cdots$$

of its state of aggregation and of the temperature; it is also independent of whether the element is free or in combination, so that the specific opacity of a compound may be calculated from the opacities of its constituent elements. It has been found by Benoist that for X-rays of one definite quality, the specific opacity of an element increases in a regular manner with the atomic weight. This is perhaps best indicated by plotting the *equivalent transparencies*[1] of the elements (which are proportional to the reciprocals of the opacities) against the atomic weights. The points lie in a smooth curve, such as fig. 16, curve I.,[2] and the curve is somewhat similar to a hyperbola (fig. 16, curve III.), which is the graphical representation of the connection between specific heat and atomic weight (Dulong and Petit's Law). There is, however, a separate curve of transparencies for each quality of X-rays used. Thus in fig. 16, curve I. refers to rays of medium hardness, and curve II. to soft rays. Therefore, in seeking the atomic weight of an element by the X-rays method, each possible multiple of the combining weight is assumed, the elements which would immediately precede and follow it on the curve noted in each case, and the transparencies of each of these elements, and of the element under investigation, determined[3] for a particular quality of X-rays, or better, for two decidedly different qualities. The results have the great advantages over those based upon specific heats that they are not influenced by temperature or physical state and are applicable to gaseous elements.

The preceding method has been applied to the case of indium, both the free element and its acetylacetonate being used. It was found that both for the medium rays (fig. 16, curve I.) and the soft rays (curve II.) the equivalent transparency of indium is very nearly 1·10. The results point clearly to the value *c.* 114 for the atomic weight.[4]

The atomic weight of indium is therefore three times its combining weight in its highest halogen compounds and its basic oxide. Early determinations of the atomic weight of indium, made by Reich and Richter,[5] Winkler,[6] and Bunsen,[7] were made almost entirely by a faulty method—the synthesis of the sesqui-oxide—and yielded low results. Closely concordant results have since been obtained by Thiel[8] and Mathers,[9] each of whom analysed the trichloride and tribromide of indium:[10]

$InCl_3$: 3AgCl : : 51·473 : 100·000 (Thiel) In = 114·968
: : 51·442 : 100·000 (Mathers) = 114·834
$InCl_3$: 3AgBr : : 62·923 : 100·000 (Thiel) = 114·753
: : 62·932 : 100·000 (Mathers) = 114·803

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[1] See note 9 on page 152.

[2] Lithium, carbon, nitrogen, and oxygen also fall on the curve, but beyond the limit of the drawing.

[3] By experimenting with the free elements or their compounds.

[4] See Benoist, *Compt. rend.*, 1897, 124, 146; 1901, 132, 325, 545, 772; *J. de physique*, 1901, [iii.], 10, 653.

[5] Reich and Richter, *J. prakt. Chem.*, 1864, 92, 480.

[6] Winkler, *ibid.*, 1865, 94, 1; 1867, 102, 280.

[7] Bunsen, *Pogg. Annalen*, 1870, 141, 28.

[8] Thiel, *Zeitsch. anorg. Chem.*, 1904, 40, 280.

[9] Mathers, *J. Amer. Chem. Soc.*, 1907, 29, 485; *Ber.*, 1907, 40, 1220.

[10] Clarke, *A Recalculation of the Atomic Weights* ("Smithsonian Miscellaneous Collections," vol. 54, No. 3), 3rd ed., 1910, p. 269. The antecedent data have been changed to the following: Ag = 107·880, Cl = 35·457, Br = 79·916.

The most probable result, according to Clarke, is 114·86, and the international value (1916) is **In = 114·8.**

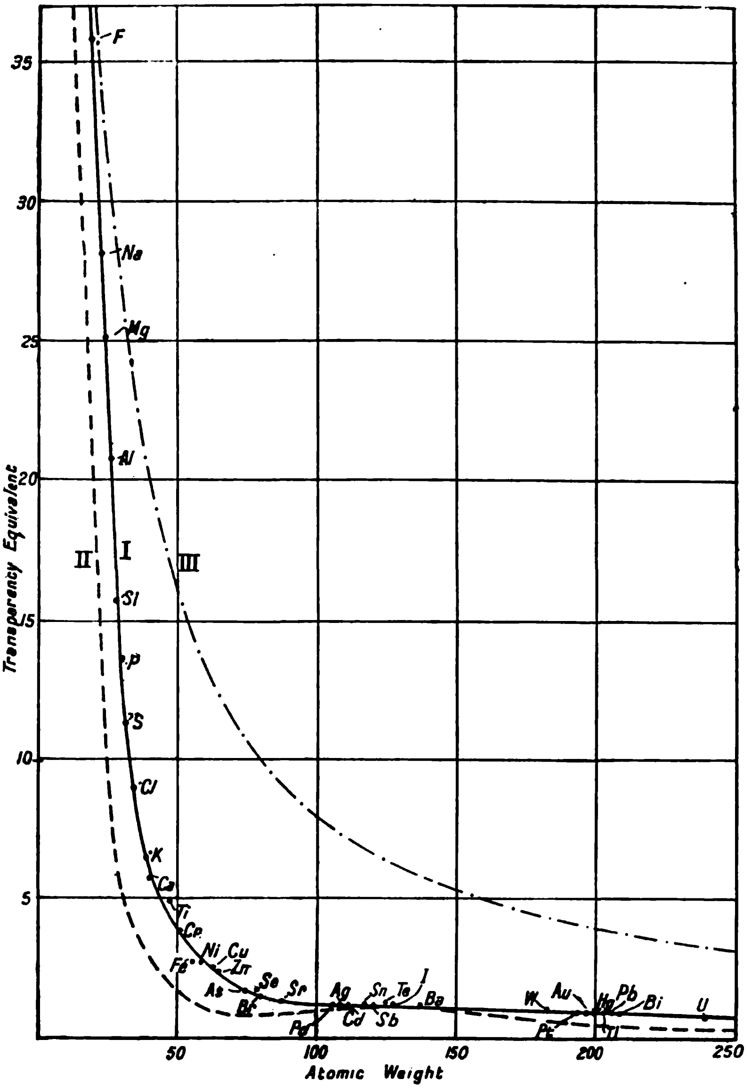

Fig. 16.—Benoist's X-ray transparency curves.

Indium readily dissolves in molten tin, and lowers the freezing-point. The "atomic fall" is 1·86°, the theoretical value for a monatomic molecule being 3·0°. Hence in dilute solution in tin, indium is mainly diatomic.[1]

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[1] Heycock and Neville, *Trans. Chem. Soc.*, 1890, 57, 385.

From the results obtained by Richards and Wilson[1] in a study of the electromotive forces of indium amalgam concentration cells, it follows that indium is essentially monatomic in solution in mercury; or more probably exists as a compound of molecular formula $InHg_x$, most likely $InHg_4$.[2] Indium is essentially monatomic in dilute solution in sodium, the "atomic fall" being 3·6° and the theoretical value for a monatomic element 4·4°.[3]

COMPOUNDS OF INDIUM.

Indium forms derivatives corresponding to the three types InX, InX_2, and InX_3 (X denoting a univalent acid radicle), but only the compounds of the last type are capable of existing in aqueous solution, in which they are appreciably hydrolysed. The solutions contain the colourless ion $In^{\cdot\cdot\cdot}$. The ions $In^{\cdot}$ and $In^{\cdot\cdot}$ appear to be unstable and to undergo change as represented by the equations

$$3In^{\cdot} = In^{\cdot\cdot\cdot} + 2In;$$

$$3In^{\cdot\cdot} = 2In^{\cdot\cdot\cdot} + In.$$

Thus the lower halogen derivatives of indium are decomposed by water, metallic indium being deposited.

The trihalides of indium appear to resemble the corresponding compounds of cadmium in their ability to form complex anions in solution, a resemblance which is not surprising since indium and cadmium occupy adjacent positions in the periodic table. The variation of the equivalent conductivity (λ) with the cube root of the concentration (m, in gram-equivalents per litre) is shown for the four salts $InCl_3$, $InBr_3$, $CdBr_2$, and $Cd(NO_3)_2$ in fig. 17. The abnormally low values for λ in solutions of moderate concentration is shown in each case except that of cadmium nitrate, and this salt does not form complex anions in solution. The low values for indium chloride are all the more remarkable since the data plotted refer to a temperature of 25°, the other data holding good for 18° C.[4]

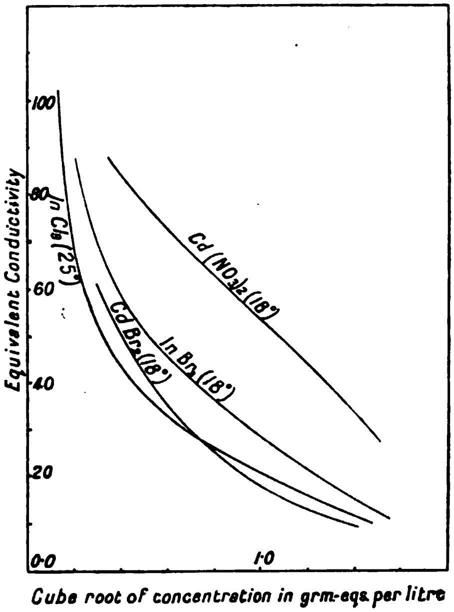

Fig. 17.—Comparison of conductivities of indium chloride and bromide solutions with those of cadmium bromide and nitrate.

Alloys.—Indium readily alloys with gallium,[5] gold,[6] lead,[7] tin,[8] and

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[1] Richards and Wilson, *loc. cit.*

[2] J. Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35**, 501.

[3] Heycock and Neville, *Trans. Chem. Soc.*, 1889, **55**, 666; 1892, **61**, 911; see also p. 171.

[4] For numerical data, see pp. 156, 157.

[5] Lecoq de Boisbaudran, *Compt. rend.*, 1885, **100**, 701.

[6] Roberts-Austen, *Phil. Trans.*, 1888, **179**, 339; 1896, **187**, 417.

[7] Kurnakoff and Puschin, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1146.

[8] Heycock and Neville, *Trans. Chem. Soc.*, 1890, **57**, 385.

sodium,[1] and easily forms an amalgam with mercury.[2] When electrolytically deposited in a platinum dish it alloys with the platinum.[3]

Indium and the Fluorine Group.

Indium Trifluoride, InF_3.—Glistening, colourless, rhombic pyramids of the trihydrate $InF_3.3H_2O$ have been obtained by Thiel,[3] and white needles of the hydrate $InF_3.9H_2O$ have been prepared by Chabrié and Bouchonnet,[4] by the action of dilute hydrofluoric acid on indium hydroxide. The hydrates are sparingly soluble in cold water, and when boiled with water are resolved into indium hydroxide and hydrofluoric acid.

The double salt *indium ammonium fluoride* is very slightly soluble in water.[5]

Indium monochloride, InCl, prepared by heating the dichloride with excess of indium and distilling the product in carbon dioxide, is a dark red solid which melts to a blood-red liquid. Its vapour density at 1100° to 1400° is about 5·3 (air = 1), corresponding to the simple formula.[6] Water decomposes it into the trichloride and metallic indium.

Indium dichloride, $InCl_2$, prepared by heating indium in a stream of dry hydrogen chloride, is a white, crystalline solid which melts to a yellow liquid. Its vapour density at 1167° to 1400° is about 6·5 (air = 1), corresponding to the simple formula.[7] Water decomposes it into the trichloride and metallic indium.

Indium trichloride, $InCl_3$, is prepared by the action of excess of chlorine upon indium, the lower chlorides, or a mixture of indium sesqui-oxide and carbon, the product being purified by distillation in a stream of carbon dioxide. It forms white, lustrous tablets, which do not volatilise appreciably at 440°. Volatilisation occurs slowly at 600.° The vapour density is 7·8, referred to air as unity, at 600° to 850°, corresponding to the molecular formula $InCl_3$; but at higher temperatures dissociation occurs.[8]

The density of the solid chloride is 4·0.[9] The chloride is very deliquescent and dissolves readily in water, in which it is slightly hydrolysed; but the solution loses very little hydrogen chloride when evaporated at 100°.

The equivalent conductivities (λ) of aqueous solutions of indium trichloride at 25° are, according to Thiel, as follows (η = conc. in gram-equivalents per c.c.; v = dilution, in litres per gram equivalent; see p. 155 and fig. 17):—

v	0·33	3·33	33·3	333	3333
1000η	3·0	0·30	0·03	0·003	0·0003
λ	10·2	30·5	50·6	101·0	225·0

Indium trichloride forms double salts with the chlorides of the alkali metals, ammonium, and platinum.[10] The salt $K_3InCl_6.2H_2O$ crystallises in the

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[1] Heycock and Neville, *ibid.*, 1889, **55**, 666.

[2] Chabrié and Rengade, *Compt. rend.*, 1901, **132**, 472; Richards and Wilson, *loc. cit.*; J. Hildebrand, *loc. cit.*

[3] Thiel, *Zeitsch. anorg. Chem.*, 1904, **40**, 280.

[4] Chabrié and Bouchonnet, *Compt. rend.*, 1905, **140**, 90.

[5] Huysse, *Zeitsch. anal. Chem.*, 1900, **39**, 9.

[6] Nilson and Pettersson, *Trans. Chem. Soc.*, 1888, **53**, 814.

[7] Nilson and Pettersson, *loc. cit.*

[8] C. and V. Meyer, *Ber.*, 1879, **12**, 609; Nilson and Pettersson, *loc. cit.*

[9] Thiel, *loc. cit.*

[10] R. E. Meyer, *Annalen*, 1869, **150**, 137; Nilson, *Ber.*, 1876, **9**, 1059, 1142.

ditetragonal, bipyramidal class of the tetragonal system; and the ammonium, rubidium, and cæsium salts of the type $X_2InCl_5.H_2O$ are isomorphous with one another, crystallising in the bipyramidal class of the rhombic system.[1] The platinum salt has the composition $2InCl_3.5PtCl_4.36H_2O$. Indium trichloride also forms an addition-product with ammonia, and with pyridine forms the *compound* $InCl_3.3C_5H_5N$, m.p. 253°.[2]

Indium oxychloride, InOCl, obtained by the action of oxygen and chlorine upon heated indium dichloride, is a white, sparingly soluble powder.[3]

Indium monobromide, InBr, and **indium dibromide,** $InBr_2$, resemble the corresponding chlorides. At 1330° the vapour of the monobromide has the normal density; but the dibromide is considerably dissociated into the monobromide and bromine.[3]

Indium tribromide, $InBr_3$, is prepared by the action of bromine vapour upon heated indium, and may be sublimed in a current of carbon dioxide. It resembles the trichloride in properties. Numerous physical properties of indium tribromide solutions have been measured by Heydweiller. The equivalent conductivities at 18° are as follows:—[4]

v	9·9701	5·0000	2·0032	0·9962	0·5003	0·2640
1000η	0·1003	0·2000	0·4992	1·0038	1·9986	3·7875
λ	53·85	46·75	37·02	28·67	19·83	11·04

The double salts $K_3InBr_6.2H_2O$, $(NH_4)_2InBr_5.H_2O$, $Rb_2InBr_5.H_2O$, and $Cs_2InBr_5.H_2O$ are isomorphous with the corresponding chlorine compounds.

The following densities (at 20°) and crystallographic constants are given by Wallace:—[5]

Tetragonal	$K_3InCl_6.2H_2O$	$a:c = 1 : 0·8173$;	density = 2·483
	$K_3InBr_6.2H_2O$		3·140
Orthorhombic	$(NH_4)_2InCl_5.H_2O$	$a:b:c = 0·9668 : 1 : 1·4005$;	density = 2·281
	$Rb_2InCl_5.H_2O$	0·9725 : 1 : 1·4085	3·089
	$Cs_2InCl_5.H_2O$	0·9841 : 1 : 1·4033	3·350
	$(NH_4)_2InBr_5.H_2O$		3·167
	$Rb_2InBr_5.H_2O$	0·9803 : 1 : 1·3951	3·409
	$Cs_2InBr_5.H_2O$	0·9734 : 1 : 1·4180	3·776

These results should be compared with those for the corresponding thallium salts (p. 181).

Indium oxybromide, InOBr, has been described.[6]

Indium mono-iodide, InI, is produced when an excess of indium is heated with iodine. Small quantities must be used, unless the reaction is carried out in an atmosphere of carbon dioxide. Indium tri-iodide is reduced to the mono-iodide by repeated distillation in hydrogen. It is a brownish-red solid, which melts at 351° and boils at *c.* 700°, and may be distilled in carbon dioxide.

Indium mono-iodide is not attacked by hot water, but dissolves in dilute

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[1] Wallace, *Zeitsch. Kryst. Min.*, 1911, **49**, 417.

[2] Renz, *Ber.*, 1904, **37**, 2110; Dennis and Geer, *ibid.*, 1904, **37**, 961.

[3] Thiel, *loc. cit.*

[4] Heydweiller, *Zeitsch. anorg. Chem.*, 1914, **88**, 103; see also p. 155 and fig. 17.

[5] Wallace, *loc. cit.*

[6] R. E. Meyer, *loc. cit.*; *cf.* Thiel, *loc. cit.*

acids with the evolution of hydrogen. It is insoluble in alcohol, ether, and chloroform. The simultaneous action of air and water leads to the production of indium hydroxide and hydriodic acid. This action is slow with cold water, and the hydroxide is obtained in colloidal solution, but with hot water the hydroxide separates in a form easily filtered.[1]

Indium di-iodide, InI_2, has not been isolated in the pure state, but thermal analysis shows that the compound exists. A mixture containing indium and iodine in the ratio $In : I_2$ melts at *c.* 212°, and the addition of either iodine or indium depresses the melting-point. The failure to obtain the di-iodide by heating the elements together in the correct ratio and distilling the product is doubtless due to dissociation of the molten di-iodide into the mono- and tri-iodides taking place to a very large extent, as the shape of the melting-point curve indicates.[2]

Indium tri-iodide, InI_3, is produced when indium is heated with an excess of iodine in an atmosphere of carbon dioxide. It is a hygroscopic, yellow solid, melting at *c.* 200° to a red liquid which can be slowly distilled in carbon dioxide at high temperatures. The tri-iodide is soluble in water, alcohol, ether, chloroform, and xylene.[3]

Indium perchlorate, $In(ClO_4)_3.8H_2O$, prepared from indium and dilute perchloric acid, forms colourless, deliquescent crystals, which melt at 80° to a turbid liquid. It is easily soluble in water and alcohol.[4]

Indium iodate, $In(IO_3)_3$, obtained from indium trichloride and potassium iodate, separates from its solution in hot dilute nitric acid as a white, crystalline powder, 1 part of which dissolves in 1500 of water at 18°, and in 150 of dilute nitric acid (1 : 5) at 80°.[4]

INDIUM AND THE OXYGEN GROUP.

Indium sesqui-oxide, In_2O_3, obtained when indium is heated in air or oxygen, is prepared by the ignition of the hydroxide, carbonate, nitrate, or sulphate. Prepared at fairly low temperatures, it forms a yellow, amorphous powder which is readily soluble in acids, producing indium salts; but when produced at high temperatures, it forms rhombohedral crystals of the colour of chlorine, and is extremely resistant towards acids. The density is 7·18; the specific heat (0° to 100°), 0·0807.[5] It is diamagnetic.[5]

Indium sesqui-oxide is reduced to indium when heated with sodium, carbon, or magnesium, or when heated in either hydrogen or ammonia;[6] and by carefully regulating the reduction in hydrogen, Winkler claims to have obtained lower oxides, including a black monoxide InO.

When heated above 850°, indium sesqui-oxide loses oxygen and becomes converted into the oxide In_3O_4, which crystallises in regular octahedra isomorphous with Fe_3O_4.[7] The loss in weight associated with this change had previously been attributed to the volatility of the sesqui-oxide.[8]

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[1] Thiel and Koelsch, *Zeitsch. anorg. Chem.*, 1910, **66**, 288.

[2] Thiel and Koelsch, *loc. cit.*

[3] R. E. Meyer, *loc. cit.*; Thiel, *loc. cit.*; Thiel and Koelsch, *loc. cit.*

[4] Mathers and Schluederberg, *J. Amer. Chem. Soc.*, 1908, **30**, 211.

[5] Nilson and Pettersson, *Compt. rend.*, 1880, **91**, 232; *Ber.*, 1880, **13**, 1459.

[6] Winkler, *J. prakt. Chem.*, 1865, **94**, 1; **95**, 414; 1867, **102**, 273; and *Ber.*, 1890, **23**, 772; Dennis and Geer, *J. Amer. Chem. Soc.*, 1904, **26**, 437; *Ber.*, 1904, **37**, 961.

[7] Thiel and Koelsch, *loc. cit.*; *cf.* Read, *Trans. Chem. Soc.*, 1894, **65**, 313.

[8] Renz, *Ber.*, 1903, **36**, 1847; 1904, **37**, 2110; Meyer, *Zeitsch. anorg. Chem.*, 1905, **47**, 281; Thiel, *ibid.*, 1906, **48**, 201.

Neither the oxide In_3O_4 nor the (metastable) In_2O_3 fuses in the oxy-hydrogen flame

From the data supplied by Ditte[1] the following results may be deduced:—

$$2[In]+3(O) = [In_2O_3]+239{\cdot}8 \text{ Cals.}$$
$$[In_2O_3]+3H_2SO_4.aq. = In_2(SO_4)_3.aq.+72{\cdot}78 \text{ Cals.}$$

Indium hydroxide, $In(OH)_3$.—Indium is slowly converted by air and moisture into indium hydroxide. The hydroxide may be prepared by adding ammonia to an aqueous solution of an indium salt and washing the precipitate. Other precipitants may be used instead of ammonia, *e.g.* potassium nitrite, hydroxylamine, and the simple aliphatic primary and secondary amines.[2] The air-dried precipitate has the composition $2In(OH)_3.3H_2O$, and loses $3H_2O$ at 100°.[3]

Freshly precipitated indium hydroxide exhibits a marked tendency to pass into the colloidal state in the absence of electrolytes. It is slightly soluble in concentrated ammonium hydroxide, and dissolves readily in alkali hydroxides. From the latter solutions it is reprecipitated on boiling or standing. When heated to redness, it leaves indium sesqui-oxide. With dilute acids it reacts to produce indium salts and water; but it possesses slight acidic properties, a **magnesium indate** being known. This substance, of the formula $MgIn_2O_4.3H_2O$, is obtained as a white precipitate when aqueous solutions of magnesium and indium chlorides are mixed and boiled.[4]

Indium monosulphide, In_2S, may be prepared by heating the tri-sulphide in a stream of hydrogen. It is volatile at a red heat and forms flat, transparent, yellowish-brown crystals.[5]

Indium disulphide, InS, is prepared by heating indium in a stream of hydrogen sulphide, and forms a soft, reddish-brown solid.[6]

Indium sesquisulphide or **trisulphide,** In_2S_3.—This compound was prepared by Winkler as a brown solid by heating either indium or its sesqui-oxide with sulphur. By igniting a mixture of sodium carbonate, indium oxide and sulphur, Winkler obtained the sesquisulphide of indium in shining, yellow crystals. Thiel has prepared the sulphide in scarlet-red shining crystals by igniting indium sesqui-oxide in a current of hydrogen sulphide. The sulphide is not volatile at a red heat, but when heated in air it is decomposed with the ultimate formation of indium sesqui-oxide.[7]

When hydrogen sulphide is passed into an aqueous solution of an indium salt, indium sesquisulphide is thrown down as a yellow precipitate, resembling cadmium sulphide in appearance. The precipitation is prevented by the presence of mineral acids except when the acidity of the solution is very slight; but acetic acid does not inhibit the precipitation. The yellow sulphide is soluble in concentrated mineral acids.

Indium sesquisulphide is obtained in colloidal solution by passing hydrogen sulphide into water in which indium hydroxide is suspended. Excess of

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[1] Ditte, *Compt. rend.*, 1871, **72**, 858; **73**, 108.

[2] Renz, *Ber.*, 1901, **34**, 2763; 1903, **36**, 2751; 1904, **37**, 2110; Bayer, *Annalen*, 1871, **158**, 372; Dennis and Geer, *Ber.*, 1904, **37**, 961; *J. Amer. Chem. Soc.*, 1904, **26**, 437.

[3] Winkler, *J. prakt. Chem.*, 1867, **102**, 273; Carnelley and Walker, *Trans. Chem. Soc.*, 1888, **53**, 74, 88.

[4] Renz, *Ber.*, 1901, **34**, 2763.

[5] Thiel, *Zeitsch. anorg. Chem.*, 1904, **40**, 280; Thiel and Koelsch, *ibid.*, 1910, **66**, 288.

[6] Thiel and Koelsch, *loc. cit.*

[7] Winkler, *J. prakt. Chem.*, 1867, **102**, 273; Thiel, *Zeitsch. anorg. Chem.*, 1904, **40**, 280.

hydrogen sulphide may be removed by boiling, but the addition of an electrolyte leads to the precipitation of the yellow sulphide.[1]

Indium sesquisulphide forms either double or complex salts with alkali sulphides. *Indium potassium sulphide*, $K_2S.In_2S_3$ or $K_2(In_2S_4)$, is obtained as insoluble, hyacinth-red, quadratic tables when indium sesqui-oxide (1 pt.), potassium carbonate (6 pts.), and sulphur (6 pts.) are fused together. By using sodium carbonate, the product obtained is soluble in water, but a white precipitate of *indium sodium sulphide*, $Na_2(In_2S_4).2H_2O$, slowly separates out.[2]

Potassium sulphide gives a white precipitate, probably of the composition $K_2(In_2S_4).xH_2O$, when added to the solution of an indium salt. In excess of potassium sulphide the precipitate dissolves. The addition of mineral acid to this solution leads to the precipitation of yellow indium sulphide, which dissolves in excess of the acid. Potassium hydrosulphide also produces a white precipitate with an indium salt, but it is insoluble in excess of the precipitant. An analogous white precipitate is produced by ammonium sulphide; it dissolves in excess of the hot, but not of the cold precipitant.[3]

Basic indium sulphite, $In_2(SO_3)_3.2In(OH)_3.5H_2O$, is obtained as an insoluble, white precipitate when a solution of an indium salt is boiled with sodium or ammonium sulphite. It dissolves in cold aqueous sulphurous acid, but separates out again as a crystalline powder when the solution is boiled. It loses $3H_2O$ at 100°, and another $5H_2O$ at 260°. At 280° sulphur dioxide begins to be evolved, and when further heated a residue of indium sesqui-oxide is ultimately obtained.[4]

Indium sulphate, $In_2(SO_4)_3$, may be prepared by dissolving indium, indium sesqui-oxide, or indium hydroxide in sulphuric acid, and carefully heating to expel water and excess of sulphuric acid. It is a white solid, very hygroscopic and extremely soluble in water, from which it is exceedingly difficult to crystallise out a hydrated sulphate. An ennea-hydrate, $In_2(SO_4)_3.9H_2O$, is said to exist, and an acid salt of the composition $In_2(SO_4)_3.H_2SO_4.8H_2O$ is described as separating from an acid solution of the sulphate when evaporated over concentrated sulphuric acid.[5]

The anhydrous sulphate has a density of 3·44 and a specific heat (between 0° and 100°) of 0·129.[6]

Various double sulphates have been prepared by mixing indium sulphate solutions with solutions of other sulphates. The **ammonium-, rubidium-, and cæsium-indium alums,** $M_2SO_4.In_2(SO_4)_3.24H_2O$ ($M = NH_4$, Rb, or Cs), can be thus prepared, the first having been discovered by Roessler and the others by Soret. Lithium, sodium, and potassium alums are not known, but **sodium indium sulphate,** $Na_2SO_4.In_2(SO_4)_3.8H_2O$, and the corresponding **potassium, ammonium,** and **thallium** salts have been prepared.

The three alums separate out in regular octahedra or combinations of the octahedron and cube. Their aqueous solutions have an acid reaction, and when heated become turbid owing to the separation of basic sulphates

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[1] Winssinger, *Bull. Soc. chim.*, 1888, [ii.], **49**, 452; Linder and Picton, *Trans. Chem. Soc.*, 1892, **61**, 134.

[2] Schneider, *J. prakt. Chem.*, 1874, [ii.], **9**, 209.

[3] Reich and Richter, *J. prakt. Chem.*, 1863, **90**, 172; 1864, **92**, 480; Winkler, *ibid.*, 1867, **102**, 273; R. E. Meyer, *Annalen*, 1869, **150**, 137.

[4] C. E. Bayer, *Annalen*, 1871, **158**, 372; *Ann. Chim. Phys.*, 1872, [iv.], **23**, 50; Thiel, *Zeitsch. anorg. Chem.*, 1904, **40**, 280.

[5] R. E. Meyer, *Annalen*, 1869, **150**, 137.

[6] Nilson and Pettersson, *Ber.*, 1880, **13**, 1459; *Compt. rend.*, 1880, **91**, 232.

or, in the case of the cæsium salt, indium hydroxide. The melting-points and solubilities of the alums in water (in grams of crystalline salt per 100 grams of water) are as follows:—[1]

		Solubilities.			
Temperature, °C.		15°	16·5°	25°	30°
Ammonium indium alum;	m.p. 36°;	...	c. 200	...	c. 400
Rubidium „ „;	m.p. 42°;	44·28	...	...	...
Cæsium „ „;	m.p. ?;	...	3·04	c. 11·7	...

In the case of the ammonium alum, the "melting-point" is known to denote the transition-point, above which the alum breaks up into the octahydrate and water (Roessler):—

$$(NH_4)_2SO_4.In_2(SO_4)_3.24H_2O \rightleftharpoons (NH_4)_2SO_4.In_2(SO_4)_3.8H_2O + 16H_2O.$$

The densities and refractive indices of the alums for the D-line at the ordinary temperature are given by Soret[2] as follows:—

	NH_4.	Rb.	Cs.
density	2·011	2·065	2·241
μ	1·4664	1·4638	1·4652

Indium sesquiselenide, In_2Se_3, is obtained by heating indium with selenium and repeatedly fusing the product with selenium. A brown precipitate of the same composition is produced by passing hydrogen selenide into indium acetate solution. The sesquiselenide is decomposed by dilute hydrochloric acid with the evolution of hydrogen selenide, and is eventually converted by nitric acid into indium selenite. When heated in hydrogen, hydrogen selenide and a dark sublimate (probably a lower selenide) are produced.[3]

Indium selenite, $In_2(SeO_3)_3.6H_2O$.—When sodium selenite is added to a solution of an aluminium salt, a basic selenite is precipitated, which is converted into the normal selenite when heated with aqueous selenious acid at 60°. The normal selenite is a white, crystalline powder, practically insoluble in water. Two acid selenites have been also described.[4]

Indium selenate, $In_2(SeO_4)_3.10H_2O$, is prepared by dissolving indium hydroxide in aqueous selenic acid and crystallising the solution. The crystals are hygroscopic and easily soluble in water. When mixed with the requisite amount of aqueous cæsium selenate, **cæsium indium selenate,** $In_2(SO_4)_3.Cs_2SO_4.24H_2O$, crystallises out in efflorescent crystals, which are described as tetragonal bipyramids and not regular octahedra as would be anticipated.[5]

Indium telluride, InTe, may be prepared by fusing together indium and tellurium in an atmosphere of nitrogen. It forms a readily fusible solid, which is insoluble in hydrochloric acid but attacked by nitric acid. A brown indium telluride is precipitated when hydrogen telluride is passed into a solution of indium acetate.[6]

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[1] Roessler, *J. prakt. Chem.*, 1873, [ii.], **7**, 14; Chabrié and Rengade, *Compt. rend.*, 1900, **131**, 1300; 1901, **132**, 472; *Bull. Soc. chim.*, 1901, [iii.], **25**, 566; Locke, *Amer. Chem. J.*, 1901, **26**, 166.

[2] Soret, *Arch. Sci. phys. nat.*, 1885, [iii.], **13**, 5; 1888, [iii.], **20**, 520.

[3] Thiel and Koelsch, *Zeitsch. anorg. Chem.*, 1910, **66**, 288.

[4] Nilson, *Nova Acta Soc. Upsala*, 1875, [iii.], **9**, No. 7; *Bull. Soc. chim.*, 1875, [ii.], **23**, 494.

[5] Mathers and Schluederberg, *J. Amer. Chem. Soc.*, 1908, **30**, 211.

[6] Thiel and Koelsch, *loc. cit.*

Indium chromate does not appear to have been analysed. **Indium molybdate,** $In_2(MoO_4)_3.2H_2O$, **indium tungstate,** and **indium uranate** are mentioned by Renz.[1]

Indium silicotungstates.—Indium silicotungstate is very soluble in water, and two hydrates may be crystallised out from the solution. The first, of the composition $2In_2O_3.3(SiO_2.12WO_3).93H_2O$, forms regular octahedra, while the second, with $63H_2O$, is triclinic ($a : b : c = 0·6025 : 1 : 0·7864$; $\alpha = 85° 10'$, $\beta = 106° 3'$, $\gamma = 90° 12'$). The *acid salt*, $In_2O_3.H_2O.2(SiO_2.12WO_3).40H_2O$, forms monoclinic crystals ($a : b : c = 0·9552 : 1 : 0·6544$; $\beta = 96° 32'$).[2]

INDIUM AND THE NITROGEN GROUP.

Indium nitrate, $2In(NO_3)_3.9H_2O$.—Indium dissolves slowly in dilute, more rapidly in concentrated nitric acid, a solution of the nitrate being produced. In the presence of nitric acid, indium nitrate readily crystallises from the solution ; but from a neutral solution it is very difficult to crystallise the salt. Indium nitrate forms colourless, deliquescent needles ; it loses one-third of its water at 100° and all of it over concentrated sulphuric acid. The nitrate is easily decomposed by heat, and its aqueous solution becomes turbid, owing to the separation of basic salt, when heated (Winkler). A double nitrate is formed with ammonium nitrate.[3]

Indium phosphide, InP, is left as a black, crystalline residue when indium mono-iodide is melted with white phosphorus and then heated to 400°. Metallic indium is only superficially attacked by phosphorus.[4]

Indium phosphate. — The precipitate obtained by adding sodium phosphate to an indium salt has not yet been examined in detail.

Indium vanadate. — Indium salts are precipitated by ammonium metavanadate.[1]

INDIUM AND THE CARBON GROUP.

Indium carbonate (?) has not yet been analysed.

Indium cyanide also does not seem to have been analysed.

The **platinocyanide,** $In_2[Pt(CN)_4]_3.2H_2O$, forms white, hygroscopic, soluble leaflets.[1]

Indium oxalate, $In_2(C_2O_4)_3.6H_2O$, is insoluble in water and ammonia.[5] Other organic salts of indium have been prepared by R. E. Meyer.[6]

Indium acetylacetonate, $[(CH_3.CO)_2CH]_3In$, is prepared by heating indium hydroxide for eight hours with a boiling alcoholic solution of acetylacetone. It crystallises from alcohol in flat, six-sided prisms and melts at 183° ; the crystals are rhombic (bipyramidal) and isomorphous with scandium and ferric acetylacetonates.[7] At 260° to 280° it partly sublimes and partly decomposes. Its molecular weight in ethylene dibromide solution is in accordance with the above simple formula.[8]

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[1] Renz, *Ber.*, 1901, **34**, 2763.

[2] Wyrouboff, *Bull. Soc. franç. Min.*, 1907, **30**, 277.

[3] Dennis and Geer, *J. Amer. Chem. Soc.*, 1904, **26**, 437.

[4] Thiel and Koelsch, *loc. cit.*

[5] Winkler, *J. prakt. Chem.*, 1867, **102**, 273 ; Böttger, *ibid.*, 1866, **98**, 26 ; Huysse, *Zeitsch. anal. Chem.*, 1900, **39**, 9.

[6] R. E. Meyer, *Annalen*, 1869, **150**, 137.

[7] Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1095 ; *Rec. trav. chim.*, 1914, **33**, 342.

[8] Chabrié and Rengade, *Compt. rend.*, 1900, **131**, 1300 ; 1901, **132**, 472.

DETECTION AND ESTIMATION OF INDIUM.

Indium salts colour the flame bluish-violet, and spectroscopic examination of the flame reveals the two dominant lines λ4511·5 and λ4102·0. To detect indium in a mineral, it may be attacked with aqua regia, the acid neutralised, and, after adding excess of sodium acetate, the solution saturated with hydrogen sulphide. The precipitated sulphides may then be treated with hydrochloric acid, and a spectroscopic test carried out.[1]

Heated in the reducing flame on charcoal with fusion mixture, indium compounds give a metallic bead and a yellow incrustation of oxide.

Indium hydroxide, freshly precipitated, is only appreciably soluble in an excess of concentrated ammonium hydroxide. It dissolves in sodium or potassium hydroxide, but is reprecipitated on boiling the solution or on standing. Indium is completely precipitated as the hydroxide by barium carbonate. Indium carbonate (?) is soluble in cold ammonium carbonate solution, but is reprecipitated on boiling the solution. Indium salts are precipitated by potassium cyanide, ferrocyanide, or chromate, but not by the dichromate. The precipitated cyanide is soluble in excess of the precipitant, but on standing or by boiling, indium hydroxide separates from the solution. Indium ferrocyanide is much more soluble in hydrochloric acid than is the corresponding gallium salt.

In neutral solutions, or solutions acidified with acetic acid, indium is completely precipitated as the yellow sulphide. In solutions containing mineral acid (except in very low concentration) the precipitation does not occur. Alkali sulphides produce more complex precipitates.

Very small quantities of indium may be detected microchemically by the formation of rubidium indium chloride.[2]

Indium is precipitated quantitatively from its salts as the hydroxide by boiling with a slight excess of ammonia. The precipitate is dried at 850° and weighed as the sesqui-oxide.[3] In place of ammonia as precipitant, dimethylamine has been suggested, and also methylamine and ethylamine or their hydrochlorides;[4] while Stock's method of precipitation (see p. 100) may be adopted.

Indium is difficult to separate from iron. The best method appears to be to deposit the indium electrolytically from its sulphate solution, dissolve the deposit, which will still retain a little iron, in nitric acid, neutralise with ammonia, add an equal volume of 50 per cent. acetic acid, and precipitate the iron by the addition of a solution of nitroso-β-naphthol in acetic acid.[5]

For the electrolytic deposition of indium, a sulphate solution containing a little free acid may be employed. Thiel uses a silvered platinum bowl as cathode; rapid deposition may be obtained with a mercury cathode and rotating anode. Good deposits on platinum cathodes are also obtained from warm cyanide or tartrate solutions, employing a rotating anode.[6]

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[1] Hoppe-Seyler, *Annalen*, 1866, **140**, 247.
[2] Kley, *Chem. Zeit.*, 1901, **25**, 563; *cf.* Huysse, *Zeitsch. anal. Chem.*, 1900, **39**, 9.
[3] Thiel and Koelsch, *Zeitsch. anorg. Chem.*, 1910, **66**, 288.
[4] Renz, *Ber.*, 1901, **34**, 2763; 1903, **36**, 2751, 4394.
[5] Mathers, *J. Amer. Chem. Soc.*, 1908, **30**, 209.
[6] Kollock and Smith, *ibid.*, 1910, **32**, 1248.

CHAPTER VIII.

THALLIUM.

Symbol, Tl. Atomic weight, 204·0 ($O = 16$).

Occurrence.—Thallium is one of the rarer elements, and only two or three minerals are known in which thallium is an essential constituent. *Crookesite*, an apparently amorphous mineral discovered by Nordenskiöld in a copper mine at Skrikerum (Sweden), has the composition Tl 17·25, Se 33·28, Cu 45·76, and Ag 3·71 per cent.[1] *Lorandite*, $TlAsS_2$, has been found as red, translucent, monoclinic crystals ($a : b : c = 1{\cdot}3291 : 1 : 1{\cdot}0780$; $\beta = 52^\circ\ 27'$) in Macedonia, associated with realgar.[2] *Vrbaite*, $TlAs_2SbS_5$, also occurs in Macedonia, associated with realgar and orpiment. It forms orthorhombic crystals ($a : b : c = 0{\cdot}5659 : 1 : 0{\cdot}4836$) which are deep red and translucent when small, and give a red streak.[3]

In small quantities thallium occurs widely distributed in nature in rocks and minerals, sometimes in association with the alkali metals, at other times with iron, zinc, lead, etc.[4] Thus it occurs in (*a*) lithia mica, (*b*) sylvine and carnallite, (*c*) alunite, (*d*) zinc blende, (*e*) pyrites, hæmatite, and marcasite, (*f*) braunite, (*g*) sphalenite, etc.[5] Thallium is also found in certain mineral waters, *e.g.* at Nauheim, and is widely diffused in the vegetable kingdom.[6]

Owing to the occurrence of traces of thallium in various minerals, it is found in small amounts in a number of commercial products, *e.g.* zinc, cadmium, platinum, bismuth, tellurium, etc.[7] It also occurs in the chamber mud and flue dust from vitriol factories where thalliferous pyrites is burnt.

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[1] Nordenskiöld, *K. Svenska Vet.-Akad. Handl.*, 1866, No. 10; *Annalen*, 1868, **145**, 127.

[2] Krenner, *Zeitsch. Kryst. Min.*, 1897, **27**, 98; Goldschmidt, *ibid.*, 1898, **30**, 272.

[3] Ježek, *ibid.*, 1912, **51**, 364; Krěhlík, *ibid.*, 1912, **51**, 379.

[4] Schramm, *Annalen*, 1883, **219**, 374; Hartley and Ramage, *Trans. Chem. Soc.*, 1897, **71**, 533; Vernadski, *Bull. Acad. Sci. Petrograd*, 1909, p. 821.

[5] (*a*) Schrötter, *Sitzungsber. K. Akad. Wiss. Wien*, 1863, **48**, 734; 1864, **50**, 268; *J. prakt. Chem.*, 1864, **91**, 45; **93**, 275; (*b*) Hammerbacher, *Annalen*, 1875, **176**, 82; (*c*) Cossa, *Gazzetta*, 1878, **8**, 235; *Ber.*, 1878, **11**, 811; (*d*) Bunsen, *Annalen*, 1865, **133**, 108; Urbain, *Compt. rend.*, 1909, **149**, 602; (*e*) Crookes, Lamy, Kuhlmann, *vide infra*; Playfair, *Chem. News*, 1879, **39**, 245; Antipoff, *J. Russ. Phys. Chem. Soc.*, 1896, **28**, i. 384; Inglestrom, *Zeitsch. Kryst. Min.*, 1895, **25**, 94; (*f*) Bischoff, *Annalen*, 1864, **129**, 375; (*g*) von Kobell, *J. prakt. Chem.*, 1871, [ii.], **3**, 176.

[6] Böttger, *Annalen*, 1863, **127**, 368; **128**, 240.

[7] Kosmann, *Chem. Zeit.*, 1886, **10**, 762; Phipson, *Compt. rend.*, 1874, **78**, 563; Warren, *Chem. News*, 1887, **55**, 241; Herepath, *ibid.*, 1863, **7**, 77; *Pharm. J.*, 1863, **4**, 302; Crookes, *Chem. News*, 1863, **7**, 109; Werther, *J. prakt. Chem.*, 1863, **88**, 180; Roepper, *Amer. J. Sci.*, 1863, [ii.], **35**, 420; Streng, *Dingl. poly. J.*, 1865, **177**, 329; Zimmermann, *Annalen*, 1886, **232**, 273.

History.—Thallium was discovered independently by Crookes in England and Lamy in France. Each of these scientists observed a new green line in the spectrum of some material he was examining, attributed it to a new element, and succeeded in isolating it. Crookes, who in March 1861 was the first to make the discovery, was engaged in extracting selenium from a deposit obtained from a sulphuric acid factory at Tilkerode in the Harz. At first he suspected that the new element was a metalloid belonging to the sulphur group, and called it **thallium** in allusion to the green colour of its spectrum line (Latin, *thallus*, a budding twig). His early work on thallium was greatly hampered by lack of material, but he eventually discovered the metallic nature of thallium, and in May 1862 was able to exhibit a few grains of the metallic element in powder form.[1] Lamy made his discovery in April 1862, when examining the lead chamber deposits from the sulphuric acid factory of M. F. Kuhlmann at Loos, where Belgian pyrites were burnt. Being more fortunate than Crookes in having considerable material at his disposal, Lamy was able very quickly to establish the metallic nature of thallium and to exhibit a lump of the metal in May 1862; and before the end of the year he was able to isolate several hundred grams of thallium and give a fairly complete account of the physical and chemical properties of the element. He showed that thallium forms more than one series of compounds, and that one series closely resembles the corresponding series of compounds of the alkali metals. Further, he found that in this series of compounds the equivalent of thallium is about 204, and (with the assistance of Regnault) showed by the application of Dulong and Petit's Law that this number also represents the atomic weight of thallium. During the same year Kuhlmann prepared a number of organic thallium salts, and de la Provostaye indicated the isomorphism of several of them with the corresponding salts of potassium.[2] During the next few years a considerable amount of work on thallium was published, notably by Crookes, Lamy, Descloizeaux, Kuhlmann, Werther, Böttger, Nicklès, Willm, and Carstanjen.[3]

At the time when thallium was discovered, the Periodic Classification had not been formulated, and it proved a difficult matter to place thallium in the classification generally accepted at that period for the metals. A number of thallous compounds were observed to resemble closely the corresponding compounds of lead in their physical properties; and even more remarkable was the resemblance between the actual elements themselves, lead and thallium. Other thallous salts, however, were observed to be isomorphous with, and to resemble quite closely, the corresponding salts of potassium. Moreover,

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[1] Crookes, *Chem. News*, 1861, **3**, 193, 303; *Phil. Mag.*, 1861, [iv.], **21**, 301.

[2] Lamy, *Soc. Impériale des Sciences de Lille*, May 16, June 20, Aug. 1, Sept. 5, Nov. 7, 1862; *Compt. rend.*, 1862, **54**, 1255; **55**, 836; *Ann. Chim. Phys.*, 1863, [iii.], **67**, 385; Regnault, *Compt. rend.*, 1862, **55**, 887; *Ann. Chim. Phys.*, 1863, [iii.], **67**, 427; Kuhlmann, *Compt. rend.*, 1862, **55**, 607; 1863, **56**, 171; *Ann. Chim. Phys.*, 1863, [iii.], **67**, 428, 431; de la Provostaye, *Compt. rend.*, 1862, **55**, 610.

[3] Crookes, *Chem. News*, 1862, **6**, 1; 1863, **7**, 109, 133, 145, 194, 218, 290; **8**, 159, 195, 219, 231, 243, 255, 279; 1864, **9**, 1, 37, 54; 1867, **15**, 204; *Phil. Mag.*, 1863, **26**, 55; *Proc. Roy. Soc.*, 1862–63, **12**, 150; Crookes and Church, *Chem. News*, 1863, **8**, 1; Lamy, *Ann. Chim. Phys.*, 1864, [iv.], **3**, 373; 1865, [iv.], **5**. 410; Lamy and Descloizeaux, *ibid.*, 1869, [iv.], **17**, 310; Kuhlmann, *Bull. Soc. chim.*, 1864, [ii.], **1**, 330; **3**, 57; Werther, *J. prakt. Chem.*, 1863, **89**, 189; 1864, **91**, 385; **92**, 128, 351; **93**, 393; Böttger, *Annalen*, 1863, **126**, 266; **127**, 368; **128**, 240, 248; Nicklès, *Compt. rend.*, 1864, **58**, 132, 537, *J. Pharm. Chim.*, 1866, [iv.], **4**, 127; Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5; Carstanjen, *J. prakt. Chem.*, 1867, **101**, 55; **102**, 65, 129.

the spectrum of thallium was extremely simple and very easy to observe, resembling in this respect the spectra of sodium, potassium, and the then newly discovered elements rubidium and cæsium. It is therefore not surprising that Dumas should have reported to the French Academy that "le thallium offre une réunion de propriétés contradictoires qui autoriserait à l'appeler le métal paradoxal, l'ornithorynque des métaux."[1]

To classify thallium with the alkali metals is clearly unsatisfactory, since the element itself is decidedly different in properties from sodium, potassium, etc., and, moreover, it forms a series of salts in which it is tervalent; to classify it with lead is worse, since the only analogies between lead and thallium salts are physical analogies between salts of univalent thallium and bivalent lead. With the publication of the Periodic Classification, Mendeléeff pointed out that thallium should really be classified with aluminium and indium, and made out a very good case for this contention.[2] Recalling the fact that when the elements are arranged in the increasing order of their atomic weights, aluminium comes between magnesium in Group II. and silicon in Group IV., while thallium comes between mercury in Group II. and lead in Group IV., the case may be stated almost exactly as it was given by Mendeléeff. Only the highest oxide of mercury shows any analogy with magnesium oxide; only the highest oxide of lead shows any analogy with silica. In the same way, only the highest oxide of thallium shows any analogy with alumina. Magnesium and mercuric oxides are basic oxides and give rise to salts of the type MX_2; aluminium and thallic oxides are more feeble bases and give rise to salts of the type MX_3; silicic and plumbic oxides are feeble acidic oxides. Thallium gives, independently of thallic oxide, a lower oxide which is a powerful base; aluminium forms no lower basic oxide. Strictly analogous is the existence of basic oxides of mercury and lead lower than mercuric and plumbic oxides, and the non-existence of lower oxides of magnesium and silicon. The higher oxides of the formulæ HgO, Tl_2O_3, PbO_2, and Bi_2O_5 are peroxides relatively to the lower oxides of the formulæ Hg_2O, Tl_2O, PbO, and Bi_2O_3, and give off oxygen when heated. The higher chloride of mercury is stable, that of thallium unstable, the tetrachloride of lead very unstable, and pentachloride of bismuth non-existent. Bismuth trichloride is decomposed by water, and lead (di)chloride when heated in steam, but thallous chloride is stable. Thallium is less volatile than mercury but more so than lead. The similarity between thallous and alkali salts is no more remarkable than that between the plumbous salts and the salts of the alkaline-earth metals, or that between bismuth salts and the salts of certain elements of Group III. (see p. 234). There is, then, no more difficulty in placing thallium in Group III. than there is in placing mercury in Group II., lead in Group IV., or bismuth in Group V.

Preparation.—The best source of thallium is thalliferous iron pyrites. All deposits of pyrites do not contain thallium in appreciable quantity. Lamy mentions the Belgian pyrites from Theux, Namur, and Philippeville and certain Spanish pyrites as being particularly rich in thallium.

Methods for extracting thallium from thalliferous pyrites have been described, but are rarely, if ever, used. Thallium is best obtained from the

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[1] Dumas, Pelouze, and Deville, Report to the French Academy, *Compt. rend.*, 1862, **55**, 866; *Ann. Chim. Phys.*, 1863, [iii.], **67**, 418.

[2] Mendeléeff, *Annalen Suppl.*, 1872, **8**, 133; or *Chem. News*, 1879, **40**, 231, etc.; 1880, **41**. 2, etc.; *cf.* Otto, *J. prakt. Chem.*, 1867, **102**, 185; Erdmann, *ibid.*, 1863, **89**, 381; Rammelsberg, *Ber.*, 1870, **3**, 276.

flue dust or chamber deposits from sulphuric acid works in which thalliferous pyrites is burnt.

Flue dust, which contains thallium, lead, arsenic, selenium, etc., is repeatedly boiled with water slightly acidified with sulphuric acid.[1] The filtered solution is concentrated and the thallium precipitated by introducing metallic zinc into the solution. Thallium is thereby precipitated in the form of needles or glittering plates. Alternative procedures are to precipitate the thallium as thallous chloride by adding a soluble chloride, or as thallous sulphide by adding sodium carbonate, filtering from precipitated impurities, adding potassium cyanide, and then saturating with hydrogen sulphide.

Lead chamber deposit[2] is neutralised with lead oxide or lime and extracted with hot water. The solution is filtered and concentrated, and the thallium precipitated as metal, chloride, or sulphide as described above.

The zinc sulphate mother liquors obtained from a white vitriol factory at Goslar in the Harz were found by Bunsen[3] to yield 0·05 per cent. of their weight of thallous chloride. The thallium in such a solution may be precipitated by means of zinc, the deposit, containing a little cadmium and copper, treated with dilute sulphuric acid to dissolve the thallium and cadmium, and the thallium precipitated as thallous iodide from the filtered solution.

The crude metallic thallium is purified[4] by converting it into thallous sulphate and treating the slightly acid solution with hydrogen sulphide to eliminate traces of mercury, silver, arsenic, antimony, and bismuth. The filtered solution is treated with ammonia to remove traces of iron and aluminium, and the filtrate concentrated until thallous sulphate crystallises out. Crude thallous chloride is slowly added to hot, concentrated sulphuric acid and the mass heated until all hydrochloric acid is expelled. The solution is, as in the preceding case, purified by successive hydrogen sulphide and ammonia treatments, and thallous sulphate then crystallised from the solution. A similar method of treatment may be applied to crude thallous sulphide. From the pure thallous sulphate, thallium is most conveniently obtained in a state of purity by electrolysis, as described by Foerster.[5] From pure thallous iodide (chloride or bromide), thallium may be prepared by fusion with potassium cyanide and sodium carbonate (Werther). Thallium may be also prepared by heating thallous oxalate in a covered crucible (Willm).

Properties.—Thallium is a bluish-white metal. It is so soft that it can be scratched with the finger-nail and cut with a knife. When freshly cut it exhibits a bright metallic lustre. The metal is extremely malleable, but has little tenacity. Its structure is crystalline, and when a bar of thallium is bent it emits a sound resembling the "cry of tin." Thallium exists in two

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[1] Crookes, *Chem. News*, 1863, **8**, 159; Böttger, *Annalen*, 1863, **126**, 266; **128**, 248; Carstanjen, *ibid.*, 1867, **101**, 55; **102**, 65, 129; Schaffner, *Dingl. poly. J.*, 1872, **205**, 55; *Sitzungsber. K. Akad. Wiss. Wien*, 1871, **63**, 176; Gunning, *Bull. Soc. chim.*, 1868, [ii.], **10**, 359; *Arch. Néerland*, 1868, **3**, 86; Nietzki, *Arch. Pharm.*, 1875, [iii.], **7**, 385; *Dingl. poly. J.*, 1876, **219**, 262: Stolba, *Chem. Soc. Abst.*, 1874, **27**, 873; Krause, *Dingl. poly. J.*, 1875, **217**, 323; Werther, *J. prakt. Chem.*, 1864, **91**, 385; **92**, 128, 351; Wöhler, *Annalen*, 1867, **142**, 263; 1872, **164**, 74; Foerster, *Zeitsch. anorg. Chem.*, 1897, **15**, 71.

[2] Lamy, *Ann. Chim. Phys.*, 1863, [iii.], **67**, 385.

[3] Bunsen, *Annalen*, 1865, **133**, 108; Schumann, *ibid.*, 1888, **249**, 340; Bartlett, *J. Soc. Chem. Ind.*, 1889, **8**, 896.

[4] On the preparation of pure thallium, see Crookes, *Phil. Trans.*, 1873, **163**, 277; *Chem. News*, 1874, **29**, 14, etc.

[5] Foerster, *Zeitsch. anorg. Chem.*, 1897, **15**, 71.

modifications which are enantiotropic; the transition-point is 226° C., and is lowered 6° for an increase of pressure of 3000 kilos. per sq. cm. Accordingly, as the temperature is raised through 226° a contraction in volume occurs, amounting to 0·000044 c.c. per gram.[1] The density of thallium is 11·85 at 20° C.,[2] the coefficient of expansion (0° to 100°) is 0·00003135,[3] and the compressibility coefficient is $2{\cdot}33 \times 10^{-6}$ per atmosphere.[4]

Thallium melts at 302° ± 1° C.,[5] the volume increasing by 3·1 per cent. during the change.[6] The latent heat of fusion is 7·2 cals. per gram.[7] *In vacuo*, thallium commences to volatilise at 174°, and boils at 818° under a pressure of 15 cm. of its own vapour.[8] It is said to boil at 1515° under normal pressure;[9] von Wartenberg, however, gives the following values for the vapour pressure of thallium:—

Temperature, °C.	634°	783°	970° C.
Vapour pressure	0·056	1·329	24·31 mm. of Hg

and estimates the boiling-point to be 1306°.[10] The mean specific heat of thallium between 20° and 100° is given as 0·0325, 0·0336, and 0·0326 by Lamy, Regnault, and Schmitz respectively; between −188° and +20° the mean value is given as 0·0300 by Schmitz and 0·0296 by Richards and Jackson.[11] The specific heat is 0·0277 at −177·3° and 0·0143 at −250·1° C.[12]

The electrical conductivity (σ) of thallium (in reciprocal ohms per cm. cube) at various temperatures is as follows:—[13]

Temperature, °C.	−180°	−80°	−40°	0°	+20°	+60°	+100°
$\sigma.10^4$	20·11	8·54	6·83	5·67	5·28	4·54	4·04

The specific refraction of thallium in its salts is (Gladstone and Dale's formula; H_α line) 0·106, and the atomic refraction is therefore 21·6.[14] Thallium and its compounds are diamagnetic (Lamy), the magnetic susceptibility of thallium at the laboratory temperature being $-2{\cdot}9 \times 10^{-6}$ c.g.s. electromagnetic units per unit volume.[15]

In appearance, hardness, elasticity, density, fusibility, specific heat, and electrical conductivity it will be noticed that thallium closely resembles lead.

The electromotive behaviour of thallium is discussed later (p. 173).

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[1] M. Werner, *Zeitsch. anorg. Chem.*, 1913, **83**, 275; *cf.* Levin, *ibid.*, 1905, **45**, 31; Williams, *ibid.*, 1906, **50**, 127.

[2] Richards and Wilson, *Carnegie Institution Publications*, Washington, 1909, No. 118; *Zeitsch. physikal. Chem.*, 1910, **72**, 129.

[3] Fizeau, *Compt. rend.*, 1869, **68**, 1125.

[4] Richards and others, *J. Amer. Chem. Soc.*, 1909, **31**, 154: 1915, **37**, 1643.

[5] Heycock and Neville, *Trans. Chem. Soc.*, 1894, **65**, 31; Petrenko, *Zeitsch. anorg. Chem.*, 1906, **50**, 133; see Burgess, *J. Washington Acad. Sci.*, 1911, **1**, 16; *Chem. News*, 1911, **104**, 165.

[6] Toepler, *Wied. Annalen*, 1894, **53**, 343; Pacher, *Nuovo Cimento*, 1895, [iv.], **2**, 143.

[7] Robertson, *Trans. Chem. Soc.*, 1902, **81**, 1233; *cf.* Heycock and Neville, *loc. cit.*

[8] Krafft and Knoche, *Ber.*, 1909, **42**, 202.

[9] Issac and Tammann, *Zeitsch. anorg. Chem.*, 1907, **55**, 58.

[10] von Wartenberg, *Zeitsch. Elektrochem.*, 1913, **19**, 482; *cf.* Krafft and Knoche, *loc. cit.*

[11] Lamy, *loc. cit.* (p. 165); Regnault, *loc. cit.* (p. 165); Schmitz, *Proc. Roy. Soc.*, 1903, **72**, 177; Richards and Jackson, *Zeitsch. physikal. Chem.*, 1910, **70**, 414.

[12] Nernst and Schwers, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, p. 355.

[13] Interpolated from the data of Dewar and Fleming, *Phil. Mag.*, 1893, [v.], **36**, 271; and Dickson, *ibid.*, 1898, [v.], **45**. 525; *cf.* de la Rive, *Compt. rend.*, 1863, **56**, 588; Matthiessen and Vogt, *Phil. Mag.*, 1863, [iv.], **26**, 542; *Pogg. Annalen*, 1863, **118**, 431.

[14] Gladstone, *Proc. Roy. Soc.*, 1897, **60**, 140; *cf.* Valson, *Compt. rend.*, 1873, **76**, 224.

[15] Honda, *Ann. Physik*, 1910, **32**, 1027; Owen, *ibid.*, 1912, [iv.], **37**, 657.

The *flame*, *arc*, and *spark* spectra of thallium are characterised in the visible region by the green ray λ 5350·7, the observation of which led to the discovery of the element by Crookes.[1] The most *intense* lines in the arc and spark spectra are the following (Exner and Haschek):—[2]

arc: 2709·33, 2767·96, **2918·42**, 2921·66, 3229·89, **3519·37**, **3529·53**, **3775·89**, **5350·70**.

spark: 3519·37, 3529·53, 3775·89, 5350·70.

The most *persistent* lines in the spark spectrum, and therefore the lines that should be looked for when seeking traces of thallium, are (Exner and Haschek's wave-lengths) 2298·25, 2530·94, 2768·00,* 3091·88, 3519·35,* 3775·89,* and 5350·69,* those asterisked being the most sensitive.[3]

Commercial thallium, when spectroscopically examined, is found to contain traces of lead, tin, copper, and aluminium.[4]

Thallium does not unite with hydrogen.[5] With each of the halogens it combines directly. When heated in oxygen, thallium is converted into thallous or thallic oxide, according to circumstances. Ozone readily attacks it at ordinary temperature, producing thallic oxide.[6] Thallium oxidises in air, slowly at the ordinary temperature, rapidly at 100°. The oxidation also occurs under water containing dissolved air, so that thallium is best preserved under air-free water or glycerol. At a red heat, thallium decomposes water. Thallium combines directly with sulphur, selenium, tellurium, phosphorus, arsenic, and antimony, but not with carbon, silicon, and boron. It is unacted upon by carbon dioxide at 300°. Thallium is insoluble in liquid ammonia.[7]

Thallium dissolves in mineral acids with the formation of thallous salts. The action is very slow with hydrochloric acid, quicker with sulphuric acid, and rapid with nitric acid. Except in the cases of nitric and concentrated sulphuric acids, hydrogen is evolved. Thallium reduces potassium permanganate at the ordinary temperature.

In accordance with its position in the electromotive series (p. 173), thallium readily displaces gold, silver, mercury, copper, and lead from aqueous solutions of their salts.

Thallium is employed in the manufacture of certain kinds of optical glass of high refractive index, since the salts of thallium are characterised by their unusually high refracting power.[8]

Atomic and Molecular Weights.—The atomic weight of thallium is equal to its combining weight in thallous salts, or three times its combining weight in thallic salts. This follows from the isomorphism of (i.) numerous

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[1] The green ray is really a triplet (Fabry and Perot, *Ann. Chim. Phys.*, 1899, [vii.], 16, 115).

[2] Kayser, *Handbuch der Spektroskopie* (Leipzig, 1900–12), vol. vi. p. 709, where a bibliography will be found; Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Wien, 1911); Huppers, *Zeitsch. wiss. Photochem.*, 1913, 13, 46 (arc).

[3] Hartley, *Phil. Trans.*, 1884, 175, i. 325; de Gramont, *Compt. rend.*, 1907, 144, 1101; 1910, 151, 308; 1914, 159, 5; Hartley and Moss, *Proc. Roy. Soc.*, 1912, A, 87, 38. For the vacuum tube spectrum of thallium, see Pollok, *Sci. Proc. Roy. Dubl. Soc.*, 1912, 13, 202.

[4] Pollok, *Sci. Proc. Roy. Dubl. Soc.*, 1909, 11, 338.

[5] Troost and Hautefeuille, *Ann. Chim. Phys.*, 1874, [v.], 2, 279.

[6] Schönbein, *J. prakt. Chem.*, 1864, 93, 35.

[7] Seely, *Chem. News*, 1871, 23, 169.

[8] Lamy, *Bull. Soc. chim.*, 1866, [ii.], 5, 164; Schrötter, *J. prakt. Chem.*, 1867, 101, 319; see also pp. 189, 190, 192, 200.

thallous, potassium, rubidium, and cæsium salts; (ii.) various double thallic halides with the corresponding indium salts (p. 5). It is, moreover, in harmony with Dulong and Petit's Law.

The atomic weight of thallium[1] has been determined with great care by Crookes,[2] who effected the synthesis of thallous nitrate. As the mean of ten extremely concordant experiments, he obtained the following result ($O = 16{\cdot}000$; $N = 14{\cdot}008$):—

$$Tl : TlNO_3 :: 100 : 130{\cdot}3910 \quad \therefore Tl = 204{\cdot}034.$$

The determinations of Lepierre[3] may be looked upon as yielding corroborative evidence in favour of Crookes's value, the results ranging from 204·021 to 204·300 for the atomic weight, and being derived from the analyses of thallous sulphate, thallous nitrate, and thallic oxide.[4] The value at present accepted for the atomic weight of thallium is **Tl = 204·0.**

According to Biltz and Meyer, thallium vapour at about 1700° is diatomic. Their results, however, are unreliable, since thallium attacks porcelain, of which their apparatus was made, and von Wartenberg has found, by using an iridium bulb in a Victor Meyer vapour density apparatus, that thallium vapour is essentially monatomic, the molecular weight being about 220.[5]

In dilute solution in mercury, the molecule of thallium is monatomic, as has been shown by the vapour-pressure determinations of Ramsay and of Tammann, and the E.M.F. measurements of Richards and Wilson.[6] Moreover, it is monatomic in dilute solution in tin, bismuth, cadmium, zinc, and sodium, as the experimental and calculated values for the depression of the freezing-point of the solvent show:—[7]

Solvent.	Depression of Freezing-point.	
	Found.	Calculated.
Tin	2·9°	3·1°
Bismuth . . .	2·0°	2·2°
Cadmium . . .	4·5°	4·6°
Zinc	5·0°	5·2°
Sodium	4·2°	4·4°

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[1] See Clarke, *A Recalculation of the Atomic Weights*, 3rd ed. ("Smithsonian Miscellaneous Collections," vol. 54, No. 3, 1910), p. 273.

[2] Crookes, *Phil. Trans.*, 1873, **163**, 277; *Chem. News*, 1874, **29**, 14, etc.

[3] Lepierre, *Bull. Soc. chim.*, 1893, [iii.], **9**, 166; 1894, [iii.], **11**, 423; *Compt. rend.*, 1893, **116**, 580.

[4] For other determinations, see Lamy, *Ann. Chim. Phys.*, 1863, [iii.], **67**, 410; Hebberling, *Annalen*, 1865, **134**, 11; Werther, *J. prakt. Chem.*, 1864, **92**, 128, 351; Wells and Penfield, *Amer. J. Sci.*, 1894, [iii.], **47**, 466.

[5] H. Biltz and V. Meyer, *Ber.*, 1889, **22**, 725; H. Biltz, *Zeitsch. physikal. Chem.*, 1896, **19**, 385; von Wartenberg, *Zeitsch. anorg. Chem.*, 1907, **56**, 320.

[6] Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 521; Tammann, *Zeitsch. physikal. Chem.*, 1889, **3**, 441; Richards and Wilson, *ibid.*, 1910, **72**, 129; *Carnegie Institution Publications*, 1909, No. 118. It is more correct to say that the molecules $TlHg_x$ exist in a dilute solution of thallium in mercury (J. Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35**, 501; J. Hildebrand and E. D. Eastman, *ibid.*, 1915, **37**, 2452; M'Phail Smith, *ibid.*, 1914, **36**, 847; Beckmann and Liesche, *Zeitsch. anorg. Chem.*, 1914, **89**, 171).

[7] Heycock and Neville, *Trans. Chem. Soc.*, 1889, **55**, 666; 1890, **57**, 376; 1892, **61**, 888; 1897, **71**, 383. The experimental numbers represent the depression produced by

COMPOUNDS OF THALLIUM.

General.—Thallium forms two series of salts: *thallous salts* (TlX^I), derived from the powerfully basic oxide *thallous oxide* (Tl_2O); and *thallic salts* (TlX_3^I), derived from the weakly basic oxide *thallic oxide* (Tl_2O_3). All the salts of thallium are poisonous, producing symptoms like those of lead poisoning.[1]

Thallous compounds and the compounds of the alkali metals have many points of similarity. The salts derived from colourless acids are generally colourless, and those which are soluble in water crystallise readily, usually as anhydrous salts. They are volatile at a red heat. Many soluble thallous salts are isomorphous with the corresponding salts of ammonium, potassium, or rubidium, a fact that was early recognised.[2] Thallous hydroxide is a strong base. It is readily soluble in water, forming a solution which readily absorbs carbon dioxide, is soapy to the touch and alkaline in reaction.

Both in appearance and in solubility, a number of sparingly soluble thallous salts (chloride, bromide, iodide, sulphide, chromate, etc.) closely resemble the corresponding salts of lead.

In aqueous solution the thallous salts are ionised to approximately the same extent as the corresponding salts of the alkali metals. The following values for the percentage dissociation at 18° are given by A. A. Noyes and Falk:—[3]

Normality.	·001	·002	·001	0·01	0·02	0·05	0·1	0·2
$TlCl$ . .	97·6	96·5	94·2	91·5	...	...	...	...
TlF . .	...	...	96·1	93·6	90·8	86·5	...	...
$TlNO_3$ . .	97·7	96·7	94·8	92·6	...	84·3	78·8	...
Tl_2SO_4 . .	94·8	92·4	88·2	83·7	78·0	69·4	62·5	56·1

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1 gram-atom of thallium in 100 gram-atoms of solvent; the calculated numbers are those derived from Van't Hoff's formula (Vol. I. p. 146) for 1 gram-molecule of solute in 100 grams of solvent, and calculated to 100 gram-atoms of solvent. For sodium, E. Griffiths' value for the latent heat of fusion of sodium, 27·5 cals. per gram, was used (Griffiths, *Proc. Roy. Soc.*, 1914. **A**, **89**, 561).

[1] Lamy, *Compt. rend.*, 1863, **57**, 442; Paulet, *ibid.*, 1863, **57**, 494; Blake, *ibid.*, 1890, **111**, 57; Curci, *Chem. Zentr.*, 1895, p. 838; 1898, p. 120.

[2] The literature on the isomorphism of thallium salts is very extensive. See de la Provostaye, *Compt. rend.*, 1862, **55**, 610; von Lang, *Phil. Mag.*, 1863, [iv.], **25**, 248; Miller, *Proc. Roy. Soc.*, 1865, **14**, 555; Werther, *J. prakt. Chem.*, 1864, **92**, 135; Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5; Lamy and Descloizeaux, *ibid.*, 1869, [iv.], **17**, 310; Roscoe, *J. Chem. Soc.*, 1866, **19**, 504; Rammelsberg, *Ber.*, 1870, **3**, 276; *Pogg. Annalen*, 1872, **146**, 592; Schroder, *Ber.*, 1874, **7**, 676; Fock, *Zeitsch. Kryst. Min.*, 1880, **4**, 583; 1882, **6**, 160; 1888, **14**, 340; 1897, **28**, 337; Wyrouboff, *Bull. Soc. franç. Min.*, 1882, **5**, 32; 1884, **7**, 139; Dufet. *Compt. rend.*, 1884, **99**, 867; Soret, *ibid.*, 1884, **99**, 990; Lepierre and Lachaud, *ibid.*, 1891, **113**, 196; Retgers, *Zeitsch. physikal. Chem.*, 1889, **4**, 623: 1891, **8**, 13; Roozeboom, *ibid.*, 1891, **8**, 513; Van Eyk, *ibid.*, 1899, **30**, 430; 1905, **51**, 721; *Proc. K. Akad. Wetensch.*, 1899, **1**, 229; Gossner, *Zeitsch. Kryst. Min.*, 1903, **38**, 110; Stortenbeker, *Rec. trav. chim.*, 1902, **21**, 87; 1905, **24**, 53; 1907, **26**, 248; Wells and Penfield, *Zeitsch. anorg. Chem.*. 1894. **6**, 312; Piccini and Fortini, *ibid.*, 1902, **31**, 451; Noyes and Hapgood, *Chem. News*, 1893, **74**, 217; Tutton, *Proc. Roy. Soc.*, 1907, **A**, **79**, 351; 1910, **A**, **83**, 211; Wallace, *Zeitsch. Kryst. Min.*, 1911, **49**, 417; Rosenbusch, *ibid.*, 1900, **33**, 99; Wallerant, *Bull. Soc. franç. Min.*, 1905, **28**, 311.

[3] A. A. Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 454.

At 18° the ionic mobility of the thallous ion is 65·55,[1] and, adopting Kohlrausch's value for its temperature-coefficient, the ionic mobility at 25° is 75·48. The corresponding value for potassium is 64·7 at 18°. The transport number for the thallous ion in dilute solution is 0·479 at 25°.[2] The equivalent conductivities at 25° of a number of thallous salts are tabulated below:—[3]

$v=$	4	8	16	32	64	128	256	512	1024
TlOH . . .	182·0	200·0	217·0	230·0	238·0	244·0	248·0	248·0	...
TlF . . .	...	...	...	115·9	120·6	123·7	126·2	128·1	130·1
TlCl . . .	...	...	...	...	...	139·6	143·1	145·1	...
$TlClO_3$ . .	...	...	...	123·6	127·8	129·8	132·1	134·2	135·4
$TlClO_4$ . .	...	...	...	129·3	134·0	137·5	139·6	141·9	143·7
$TlBrO_3$ . .	...	...	...	...	...	122·9	125·5	126·3	128·1
$TlIO_3$ . . .	...	...	...	...	...	...	...	111·5	112·0
Tl_2SO_4 . .	...	...	101·3	113·1	122·9	131·2	138·3	143·1	146·4
$Tl_2S_2O_6$ . .	...	...	...	131·7	141·9	151·7	160·2	166·7	170·6
Tl_2SeO_3 . .	...	...	...	83·0	94·9	106·1	115·2	123·7	130·8
Tl_2SeO_4 . .	...	...	...	111·2	120·7	129·0	134·7	138·6	142·2
$TlNO_3$ . .	...	...	...	128·7	133·8	137·6	104·1	142·0	142·6
TlH_2PO_4 . .	...	...	...	...	96·9	101·1	104·0	106·5	108·7
Tl_2HAsO_4 . .	...	...	70·4	74·3	78·3	81·2	82·8	84·2	85·4
Tl_2CO_3 . .	...	...	...	93·5	107·3	119·2	129·9	137·1	143·4
$Tl_2C_2O_4$ . .	...	...	...	105·0	118·0	128·5	139·0	147·7	153·5

Numerous investigations have been carried out dealing with the influence of other salts on the solubilities of thallous salts. The results may be briefly summarised as follows. For uni-univalent thallous salts the changes of solubility caused by other salts are in qualitative agreement with the deductions from the ionic theory and the law of chemical equilibrium, and quantitative agreement, though never exact, is approached most closely with the least soluble thallous salts. For unibivalent thallous salts, the solubilities are affected by salts having a common univalent ion (*i.e.* the thallous ion) in a similar manner; but the influences exerted by other salts, having bivalent ions in common with the thallous salts, are not even in approximate agreement with theoretical deductions unless it be assumed that the unibivalent salts undergo dissociation in two stages, *e.g.* $Tl_2SO_4 \rightleftharpoons Tl^{\cdot} + TlSO_4{}'$, $TlSO_4{}' \rightleftharpoons Tl^{\cdot} + SO_4{}''$, and that even in dilute solution the concentrations of the intermediate ions are considerable.[4]

Thallous hydroxide is considerably less stable than an alkali hydroxide

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[1] Bates, *J. Amer. Chem. Soc.*, 1913, **35**, 519; *cf.* Kohlrausch, *Zeitsch. physikal. Chem.*, 1905, **51**, 744.

[2] Falk, *J. Amer. Chem. Soc.*, 1910, **32**, 1555.

[3] Franke, *Zeitsch. physikal. Chem.*, 1895, **16**, 463; see also A. A. Noyes, Farrell, and Stewart, *vide infra*; Bray and Winninghoff. *vide infra*; Hunt, *J. Amer. Chem. Soc.*, 1911, **33**, 1650; Kohlrausch and Steinwehr, *Sitzungsber. K. Akad. Wiss. Berlin*, 1902, p. 581; Kohlrausch and Maltby, *ibid.*, 1899, p. 665. In the table, v = dilution, in litres per gram-equivalent.

[4] A. A. Noyes, Farrell, and Stewart, *J. Amer. Chem. Soc.*, 1911, **33**, 1650; Bray and Winninghoff, *ibid.*, 1911, **33**, 1663; Bray, *ibid.*, 1911, **33**, 1673; Harkins, *ibid.*, 1911, **33**, 1836; see also Abegg and Spencer, *Zeitsch. anorg. Chem.*, 1905, **46**, 406; A. A. Noyes, *Zeitsch. physikal. Chem.*, 1890, **6**, 241; 1892, **9**, 603; A. A. Noyes and Abbot, *ibid.*, 1895, **16**, 132.

as is indicated by its relatively small heat of formation. It is easily dehydrated (even at 100°) to thallous oxide, which has a very small heat of hydration. Further, thallium is considerably less electropositive than the alkali metals. According to the best experimental results available (1916), the following sequence of metals in the electromotive series is correct and indicates the position of thallium:—

. . . . Zn, Cd, Fe, Tl, Co, Sn, Ni, Pb . . . .

Thallium has therefore a decided tendency to assume the ionic state. The electrode potential of thallium at 25° is −0·6170 volt (normal calomel electrode being zero). For very dilute solutions, the potential of the thallium electrode varies with the concentration of thallous ion in the liquid bathing it in strict accordance with the Nernst formula; a slight deviation is noticeable when the concentration of thallium ion reaches 0·1 normal.[1] The accuracy with which the Nernst formula is capable of expressing the results is strong evidence against the hypothesis of the existence of subvalent thallium ion $\mathrm{Tl}^{\cdot}_2$, which has been supposed by Denham[2] to exist.

Thallic compounds resemble the compounds of aluminium to a certain extent. The thallic salts are in general readily soluble in water, and crystallise with considerable amounts of water of crystallisation. They are derived from a very weak base, thallic hydroxide, which is practically insoluble in water, and which in case of dehydration resembles auric hydroxide. The thallic salts are therefore considerably hydrolysed by water, and solutions of these salts are only stable in the presence of an excess of acid. A solution of thallic sulphate, for example, containing a slight excess of sulphuric acid, gives a brown precipitate of thallic hydroxide when diluted or warmed. Thallic salts are decidedly unstable, anhydrous thallic chloride, for instance, losing chlorine at temperatures below 100°, and they exhibit a great tendency to form complex salts.[3]

Thallous salts may be oxidised to thallic salts and *vice versa*, the former conversion being not so readily accomplished as the latter. The reduction of thallic to thallous salts may be readily and quantitatively effected by the ordinary reducing agents, and it therefore happens that the addition of ammonium sulphide to a solution of a thallous salt leads to the precipitation of thallous sulphide and sulphur. Further, potassium iodide gives a precipitate of thallous iodide and iodine when added to a thallic salt. Thallic salts are quantitatively reduced to thallous salts by thallium itself. Thallous salts may be oxidised by potassium permanganate, the reaction when effected in the presence of hydrochloric acid and under certain conditions being sufficiently exact to be used for the estimation of thallium. Practically complete oxidation of thallous salts can also be brought about by chlorine or bromine.

Thallous and thallic salts exhibit to a high degree the curious property of combining with each other to form what may be termed **intermediate salts,** such, for example, as the chlorides of the composition $\mathrm{Tl_2Cl_3(TlCl_3.3TlCl)}$ and

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[1] G. N. Lewis and Van Ende, *J. Amer. Chem. Soc.*, 1910, **32**, 732; *cf.* Neumann, *Zeitsch. physikal. Chem.*, 1894, **14**, 193; Spencer, *ibid.*, 1911, **76**, 360; Abegg and Spencer, *Zeitsch. anorg. Chem.*, 1905, **46**, 406; Shukoff, *Ber.*, 1905, **38**, 2691; Brislee, *Trans. Faraday Soc.*, 1909, **4**, 159.

[2] Denham, *Trans. Chem. Soc.*, 1908, **93**, 833.

[3] Abegg and Spencer, *Zeitsch. anorg. Chem.*, 1905, **44**, 379.

$TlCl_2(TlCl_3.TlCl)$. Since these salts usually resemble the thallous salts in being sparingly soluble in water, it often happens that such intermediate salts are produced during the oxidation of thallous, or the reduction of thallic salts. The *modus operandi* of these processes, however, is not definitely known.[1]

Thermochemistry of Thallium Compounds.[2]—A number of heats of formation, etc., are given in the following table:—

Compound.	Heat of Formation.	Heat of Solution.
	Cals.	Cals.
TlF	+51·4 [3]	...
$TlCl$	48·6	−10·1
$TlBr$	41·4	...
TlI	30·2	...
Tl_2O	42·2	− 3·1
$TlOH$	56·9	− 3·15
Tl_2S	21·7	...
Tl_2Se (cryst.)	17·7	...
Tl_2Te (cryst.)	12·2	...
$TlNO_3$	58·1	−10·0
Tl_2SO_4	221·0	− 8·3
$TlCl_3$	80·8	+ 8·4
$TlCl_3.4H_2O$	...	− 2·1
$TlBr_3$	56·5 [3]	...
$TlBr_3.4H_2O$	..	− 2·2
TlI_3	10·8 [3]	...
$TlClBr_2.4H_2O$	...	− 2·9

$$[Tl_2O] + H_2O = 2[TlOH] + 3\ 25 \text{ Cals.}$$
$$TlOHaq. + HCl.aq. = TlCl.aq. + 13{\cdot}74 \text{ ,,}$$
$$TlOHaq. + HNO_3.aq. = TlNO_3.aq. + 13{\cdot}70 \text{ ,,}$$
$$TlOHaq. + HF.aq. = TlF.aq. + 16{\cdot}4 \text{ ,,}$$
$$TlOHaq. + \tfrac{1}{2}H_2SO_4.aq. = \tfrac{1}{2}TlSO_4.aq. + 15{\cdot}6 \text{ ,,}$$

Alloys.[4]—Thallium readily forms alloys with many other metals. The

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[1] See V. Thomas, *Ann. Chim. Phys.*, 1907, [viii.], **11**, 204.

[2] J. Thomsen, *Pogg. Annalen*, 1871, **143**, 354, 497; *J. prakt. Chem.*, 1875, [ii.], **12**, 98; 1879, **19**, 13; 1880, **21**, 38, 449; Tommasi, *Compt. rend.*, 1884, **98**, 812; Petersen, *Zeitsch. physikal. Chem.*, 1889, **4**, 384; Fabre, *Ann. Chim. Phys.*, 1887, [vi.], **10**, 472; 1888, [vi.], **14**, 115; Thomas, *ibid.*, 1907, [viii.], **11**, 204.

[3] Including the heat of solution of the compound.

[4] With K, Carstanjen, *J. prakt. Chem.*, 1867, **102**, 65; Heycock and Neville, *Trans. Chem. Soc.*, 1889, **55**, 666; Bredig and Haber, *Ber.*, 1898, **31**, 2741; Kurnakow and Puschin, *Zeitsch. anorg. Chem.*, 1902, **30**, 86; with Na, *vide* preceding references and Tammann, *Zeitsch. physikal. Chem.*, 1889, **3**, 441; with Cu, Carstanjen, *loc. cit.*; Doerinckel, *Zeitsch. anorg. Chem.*, 1906, **48**, 185; with Ag, Heycock and Neville, *Trans. Chem. Soc.*, 1894, **65**, 31; *Phil. Trans.*, 1897, **A**, **189**, 25; Petrenko, *Zeitsch. anorg. Chem.*, 1906, **50**, 133; with Au, Heycock and Neville, *Trans. Chem. Soc.*, 1894, **65**, 31; Osmond and Roberts-Austen, *Phil. Trans.*, 1896, **A**, **187**, 417; Roberts-Austen, *ibid.*, 1888, **179**, 339; Levin, *Zeitsch. anorg. Chem.*, 1905, **45**, 31; with Ca, Donski, *ibid.*, 1908, **57**, 185; Baar, *ibid.*, 1911, **70**, 352; with Mg, Carstanjen, *loc. cit.*; Mellor, *Chem. News*, 1867, **15**, 245; Grube, *Zeitsch. anorg. Chem.*, 1905, **46**, 76; with Zn, Carstanjen, *loc. cit.*; Heycock and Neville, *Trans. Chem. Soc.*, 1897, **71**, 383; Omodei, *Jahresber.*, 1892, p. 153; von Vegesack, *Zeitsch. anorg. Chem.*, 1907, **52**, 30; with Cd, Carstanjen, *loc. cit.*; Kurnakoff and Puschin, *Zeitsch. anorg. Chem.*, 1902, **30**, 86; with Hg, Carstanjen, *loc. cit.*; Regnauld, *Compt. rend.*, 1867, **64**, 611; Humphreys, *Trans. Chem. Soc.*, 1896, **69**, 1679; Puschin, *J. Russ. Phys. Chem.*

following inter-metallic compounds have been described, containing thallium and a metal of Group I. or II. :—

NaTl, m.p. 306°	Tl_3Mg_8, m.p. 413°	$CaTl_3$, no m.p.
KTl, „ 335°	$TlMg_2$, no m.p.	CaTl, m.p. 969°
Hg_2Tl, „ 15°	Tl_2Mg_3, „	Ca_3Tl_4, no m.p.

Thallium is miscible with gold, silver, and cadmium, and with silver forms mixed crystals containing 0 to 10 per cent. of thallium. It is only partially miscible with copper and zinc, and is practically non-miscible with aluminium.

Thallium readily dissolves in mercury. A liquid amalgam containing 8·5 per cent. of thallium may be used in thermometers down to − 60°.[1]

Alloys of thallium and the metals of Groups IV. to VIII. in the Periodic Table are mentioned in the corresponding volumes of this series.

Thallium and the Fluorine Group.

THALLOUS HALIDES.—Thallous fluoride, chloride, bromide, and iodide are all known. The last three salts resemble the corresponding compounds of lead very closely in appearance and in physical properties; it has been both affirmed and denied that in the liquid state they have the properties of liquid crystals.[2] The molten chloride and bromide have not been obtained optically clear.[3]

Thallous chloride, bromide, and iodide are miscible in the liquid state, and the three systems TlCl − TlBr, TlBr − TlI, and TlCl − TlI have been studied by the thermal method. The results show that the first two systems yield continuous series of mixed crystals, the "liquidus" curves exhibiting minima, and that the last system forms an incomplete series, the "liquidus" exhibiting a transition-point.[4]

Thallous fluoride, TlF, is prepared by dissolving thallous hydroxide, carbonate, or sulphide in aqueous hydrofluoric acid, evaporating to dryness, heating to remove hydrogen fluoride, and crystallising the residue from water.[5] It may also be prepared by heating thallous oxide or carbonate to dull redness in a stream of dry hydrogen fluoride.[6] Thallium dissolves slowly in aqueous hydrofluoric acid.

Thallous fluoride is readily soluble in water, from which it crystallises in colourless, lustrous, regular octahedra. At a red heat it may be distilled in a current of hydrogen fluoride. It is insoluble in alcohol and in liquid ammonia;[7] the aqueous solution has an acid reaction.

The monohydrate, $TlF.H_2O$, is said to separate in monoclinic crystals from a solution of thallous carbonate in aqueous hydrofluoric acid;[8] and

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Soc., 1900, **32**, i. 635; Pavlovitsch, *ibid.*, 1915, **47**, 29; Kurnakoff and Puschin, *loc. cit.*; Suchini, *Zeitsch. Elektrochem.*, 1906, **12**, 726; T. W. Richards and Wilson, *Zeitsch. physikal. Chem.*, 1910, **72**, 129; J. Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35**, 501; with Al, Carstanjen, *loc. cit.*; Doerinckel, *loc. cit.*

[1] M'Intosh and Johnson, *J. Amer. Chem. Soc.*, 1912, **34**, 910.

[2] Stoltzenberg and Huth, *Zeitsch. physikal. Chem.*, 1910, **71**, 641; Tubandt and E. Lorenz, *Festschrift W. Nernst*, 1912, p. 446.

[3] R. Lorenz and Eitel, *Zeitsch. anorg. Chem.*, 1915, **91**, 61.

[4] Mönkemeyer, *Jahrb. Min. Beil.*, 1906, **22**, 1.

[5] Büchner, *J. prakt. Chem.*, 1865, **96**, 404; *Sitzungsber. K. Akad. Wiss. Wien*, 1865, [ii.], **52**, 644; Ephraim and Barteczko, *Zeitsch. anorg. Chem.*, 1909, **61**, 238.

[6] Kuhlmann, *Compt. rend.*, 1864, **58**, 1036.

[7] Gore, *Proc. Roy. Soc.*, 1873, **21**, 140.

[8] Kuhlmann, *loc. cit.*; Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5.

thallium hydrogen fluoride, TlF.HF, crystallises out in regular octahedra when a solution of thallous fluoride in concentrated aqueous hydrofluoric acid is evaporated over sulphuric acid. The acid fluoride is stable at 100°, but decomposes at higher temperatures (Büchner).

Aluminium thallous fluoride, $2AlF_3.3TlF$, and numerous other double fluorides have been prepared.[1]

Thallous chloride, TlCl, may be obtained by the action of chlorine on thallium. It is prepared by adding hydrochloric acid or a solution of a soluble chloride to a solution of a thallous salt, and forms a white, crystalline precipitate.

Thallous chloride is a white, crystalline solid of density 7·02.[2] It melts to a yellow liquid at 426° C.,[3] and boils at 708° to 731° C.[4] Its compressibility coefficient is $4{\cdot}8 \times 10^{-6}$ per atmosphere.[5] The chloride crystallises in isometric cubes and is isomorphous with potassium chloride.[6] From 830° to 1030° its vapour density is in agreement with the molecular formula TlCl;[7] and the molecular formula is also TlCl in solution in fused mercuric chloride.[8]

Thallous chloride is slightly soluble in cold, and more readily soluble in hot water. The solubility, in grams per litre, is as follows:—[9]

Temperature, °C.	0°	10°	20°	25°	30°	40°	50°	60°	80°	100°
Grams of TlCl	1·7	2·4	3·4	4·0	4·6	6·0	8·0	10·2	16·0	24·1

The chloride is less soluble in dilute solutions of hydrochloric acid and alkali chlorides than in pure water; it is insoluble in alcohol. The influence of various salts on the solubility of thallous chloride in water at 25° is shown by the following table of results, due to Bray and Winninghoff, solubilities being expressed in milli-equivalents per litre:—[10]

Conc. of Added Salt in milli-eqs. per litre.	Added Salt.						
	HCl.	KCl.	$BaCl_2$.	$TlNO_3$.	Tl_2SO_4.	KNO_3.	K_2SO_4.
0	16·07	16·07	16·07	16·07	16·07	16·07	16·07
20	...	...	...	...	10·34	17·16	17·79
25	8·66	8·69	8·98	8·80	...	...	...
50	5·83	5·90	6·18	6·24	6·77	18·26	19·42
100	3·83	3·96	4·16	4·22	4·68	19·61	21·37
200	2·53	2·68	2·82	...	...	...	...
300	...	...	...	...	...	23·13	26·00

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[1] Ephraim and Barteczko, *loc. cit.*; and subsequent volumes in this series.

[2] Lamy, *Ann. Chim. Phys.*, 1863, [iii.], **67**, 385; F. W. Clarke, *Amer. Chem. J.*, 1883, **5**, 240.

[3] Mönkemeyer, *Jahrb. Min. Beil.*, 1906, **22**, 1; Carnelley (*Trans. Chem. Soc.*, 1878, **33**, 273) gives 427°, Stoltzenberg and Huth (*Zeitsch. physikal. Chem.*, 1910, **71**, 641) give 407°, and Sandonnini (*Atti R. Accad. Lincei*, 1915, [v.], **24**, i, 616) gives 429°.

[4] Carnelley and Williams, *Trans. Chem. Soc.*, 1878, **33**, 281.

[5] Richards and Jones, *J. Amer. Chem. Soc.*, 1909, **31**, 158.

[6] Stortenbeker, *Rec. trav. chim.*, 1905, **24**, 53.

[7] Roscoe, *Proc. Roy. Soc.*, 1878, **27**, 426; *Ber.*, 1878, **11**, 1196.

[8] Beckmann, *Zeitsch. anorg. Chem.*, 1907, **55**, 175.

[9] Earl of Berkeley, *Phil. Trans.*, 1904, **A**, **203**, 208; A. A. Noyes, *Zeitsch. physikal. Chem.*, 1892, **9**, 603; Böttger, *ibid.*, 1903, **46**, 602; Kohlrausch, *ibid.*, 1903, **44**, 197; 1904, **50**, 355; Hill and Simmons, *J. Amer. Chem. Soc.*, 1909, **31**, 821.

[10] Bray and Winninghoff, *J. Amer. Chem. Soc.*, 1911, **33**, 1663.

The specific conductivity of the saturated aqueous solution is 1514×10^{-6} reciprocal ohms per cm. cube at 18°, and 2176×10^{-6} at 25° C.[1]

Fused thallous chloride is miscible with many other molten chlorides, and from a study of the freezing-point curves it has been shown that various double chlorides exist, a number of which are stable at the melting-point. The compounds at present known containing thallium and the metals of Groups I. and II. are as follows:—[2]

$2AgCl.3TlCl$
$TlCl.CaCl_2$ (m.p. 683°)
$TlCl.SrCl_2$
$TlCl.2MgCl_2$
$2TlCl.ZnCl_2$ (m.p. 352°)
$TlCl.2ZnCl_2$ (m.p. 226°)
$TlCl.CdCl_2$ (m.p. 436°)
$TlCl.HgCl_2$ (m.p. 224°)
$4TlCl.HgCl_2$

Thallous chloride forms mixed crystals with the chlorides of potassium, rubidium, zinc, and mercury. The double salt $TlCl.HgCl_2$ crystallises in needles, and was originally prepared by Carstanjen,[3] who also prepared *thallous aurichloride*, $TlAuCl_4$.

Thallous bromide, TlBr, is prepared like the corresponding chloride. It is a pale yellow solid of density 7·54,[4] and its compressibility coefficient is $5·2 \times 10^{-6}$ per atmosphere.[5] It crystallises in the isometric system in cubes, melts to a brownish-yellow liquid at 450°,[6] and boils at 800° to 814°.[7] The bromide is stable at high temperatures.[8]

The solubility of thallous bromide in water, in grams per 100 grams of water, is as follows:—[9]

Temperature, °C.	18°	20°	25°	68·5°
Grams of TlBr	0·042	0·048	0·057	0·247

The specific conductivity of the saturated aqueous solution is 192×10^{-6} reciprocal ohms per cm. cube at 18°.[10]

Thallous iodide, TlI, is prepared like the corresponding chloride and bromide, and forms a citron-yellow precipitate of density 7·07.[11] The crystalline form is orthorhombic. At 168° the yellow thallous iodide is converted into a red, cubic variety,[12] the compressibility of which is $6·8 \times 10^{-6}$

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[1] Kohlrausch, *Zeitsch. physikal. Chem.*, 1903, **44**, 197; 1904, **50**, 355; Bray and Winninghoff, *loc. cit.*

[2] Liebisch and Korreng, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, p 192; Korreng, *Jahrb. Min.*, 1914, *Beil.-Bd.*, **37**, 51; Sandonnini and Aureggi, *Atti R. Accad. Lincei*, 1911, [v.], **20**, ii, 588; Sandonnini, *ibid.*, 1913, [v.], **22**, ii. 20; 1915, [v.], **24**, i. 616.

[3] Carstanjen, *J. prakt. Chem.*, 1867, **102**, 141; Jörgensen, *ibid.*, 1873, [ii.], **6**, 82.

[4] Lamy, *Ann. Chim. Phys.*, 1863, [iii.], **67**, 385; F. W. Clarke, *Amer. Chem. J.*, 1883, **5**, 240.

[5] Richards and Jones, *J. Amer. Chem. Soc.*, 1909, **31**, 158.

[6] Mönkemeyer, *Jahrb. Min. Beil.*, 1906, **22**, 1; Carnelley (*Trans. Chem. Soc.*, 1878, **33**, 273) gives 458°, and Stoltzenberg and Huth (*Zeitschr physikal. Chem.*, 1910, **71**, 641) give 441°.

[7] Carnelley and Williams, *Trans. Chem. Soc.*, 1878, **33**, 281.

[8] Guareschi, *Atti R. Accad. Sci. Torino*, 1912–13, **48**, 735.

[9] Böttger, *loc. cit.*; Kohlrausch, *loc. cit.*; A. A. Noyes, *ibid.*, 1890, **6**, 241.

[10] Kohlrausch, *loc. cit.*

[11] Clarke, *Amer. Chem. J.*, 1883, **5**, 240.

[12] Van Eyk, *Proc. K. Akad. Wetensch. Amsterdam*, 1901, **3**, 98; Gossner, *Zeitsch. Kryst. Min.*, 1903, **38**, 110; Gernez, *Compt. rend.*, 1904, **138**, 1695.

per atmosphere,[1] and the density 7·10. The two polymorphs are interconvertible. The red form melts at 431° to a dark red liquid.[2]

The conversion of one form into the other is often extremely slow. A hot, filtered, aqueous solution of thallous iodide deposits red crystals when rapidly cooled, but a hot, saturated solution, when slowly cooled in the presence of the yellow form, deposits yellow crystals. A hot solution in aqueous potassium acetate or hydroxide deposits the metastable red modification when cooled, and the red form may also be precipitated by adding potassium iodide to a hot, concentrated solution of a thallous salt.[3] Freshly precipitated yellow thallous iodide becomes green when exposed to sunlight. The green iodide can be recrystallised from water without losing its colour, but on standing it slowly reverts to the yellow modification, the change being hastened by heating with aqueous iodine or potassium iodide.[4]

The solubility of the yellow modification in water, in grams per 100 grams of water, is as follows:—[5]

Temperature, °C.	0°	20°	40°	60°	80°	100°
Grams of TlI	0·002	0·006	0·015	0·035	0·070	0·120

The specific conductivity of the saturated aqueous solution at 18° is $22{\cdot}3 \times 10^{-6}$ reciprocal ohms per cm. cube.[6]

Thallous iodide forms mixed crystals with thallous nitrate; the "liquidus" curve for the system $TlI - TlNO_3$ consists of two parts meeting at a transition-point.[7]

THALLIC HALIDES.—**Thallic fluoride**, TlF_3, is not known, but unstable, white crystals of *thallic potassium fluoride*, $2TlF_3.KF$, have been obtained.[8]

Thallic fluochloride, $TlFCl_2.3H_2O$, is obtained in white needles by the action of chlorine on thallous fluoride dissolved in aqueous hydrofluoric acid. It becomes anhydrous when kept over phosphoric anhydride, and the anhydrous salt forms a double salt with potassium chloride, of the formula $2TlFCl_2.KCl$, and a compound with ammonia, of the formula $TlFCl_2.4NH_3$. Analogous compounds of the composition $TlFBr_2$ and $TlFBr_2.4NH_3$ are also known.[8]

Thallium oxyfluoride, TlOF, is obtained as an olive-green powder, insoluble in water, by the action of cold, aqueous hydrofluoric acid on thallic oxide.[9]

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[1] Richards and Jones, *J. Amer. Chem. Soc.*, 1909, **31**, 158.

[2] Mönkemeyer, *Jahrb. Min. Beil.*, 1906, **22**, 1; Carnelley (*Trans. Chem. Soc.*, 1878, **33**, 273) gives 439°, Stoltzenberg and Huth (*Zeitsch. physikal. Chem.*, 1910, **71**, 641) give 422°, and Van Eyk (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, **3**, 98) gives 422°.

[3] Gernez, *loc. cit.*, and *Compt. rend.*, 1904, **139**, 278; 1909, **148**, 1015; *Ann. Chim. Phys.*, 1909, [viii.], **17**, 290; Willm, *ibid.*, 1865, [iv.], **5**, 5; Hebberling, *Annalen*, 1865, **134**, 11; Werther, *J. prakt. Chem.*, 1864, **92**, 128.

[4] Knösel, *Ber.*, 1874, **7**, 576, 893.

[5] Böttger, *Zeitsch. physikal. Chem.*, 1903, **46**, 602; Kohlrausch, *ibid.*, 1903, **44**, 197; 1904, **50**, 355; Long, *Zeitsch. anal. Chem.*, 1891, **30**, 342.

[6] Kohlrausch, *loc. cit.*

[7] Van Eyk, *Proc. K. Akad. Wetensch. Amsterdam*, 1901, **3**, 98.

[8] Gewecke, *Annalen*, 1909, **366**, 217.

[9] Gewecke, *loc. cit.*; *cf.* Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5.

Thallic chloride,[1] $TlCl_3$.—Thallic chloride cannot be obtained in the pure state by the chlorination of thallous chloride except when the reaction is carried out in a sealed tube and the pressure of the chlorine is several atmospheres. Thallic chloride thus prepared is described by Thomas as consisting of white crystals, which melt at 60° to 70° (in a sealed tube).

Anhydrous thallic chloride may be obtained by dehydrating its tetrahydrate at the ordinary temperature over sulphuric acid, potash, or phosphoric anhydride, or, according to Meyer, by the decomposition *in vacuo* of the compound $TlCl_3.(C_2H_5)_2O$. The chloride thus obtained forms small, six-sided plates, and melts at 25°. It commences to lose chlorine at 40°, and the decomposition is rapid at 100°. It is extremely hygroscopic, rapidly absorbing moisture with the formation of an aqueous solution of thallic chloride; and it is soluble in alcohol, ether, and other organic solvents. With a small quantity of water, thallic chloride forms a clear solution, which is considerably hydrolysed by dilution.

When thallous chloride is suspended in water and chlorine is passed through the liquid for a sufficient length of time, a clear solution of thallic chloride is obtained. If the solution be evaporated below 60° to a syrup, and then cooled in a freezing mixture, colourless, orthorhombic (?) crystals of the tetrahydrate, $TlCl_3.4H_2O$, separate. This hydrate melts at 43° to 45°, and in dry air slowly effloresces (more rapidly at 55°) to the monohydrate, $TlCl_3.H_2O$, while according to M'Clenahan, a dihydrate, $TlCl_3.2H_2O$ also exists. The monohydrate crystallises from a saturated aqueous solution of the trichloride at ordinary temperatures.

From a solution of thallic chloride acidified with nitric acid, silver nitrate quantitatively precipitates the chlorine as silver chloride; but from a neutral solution, in addition to the precipitate of silver chloride, a brown precipitate of thallic hydroxide is obtained.

Thallic chloride combines with ammonia, producing a white, crystalline compound, $TlCl_3.3NH_3$, decomposed by water. This compound was prepared by Willm in a number of ways. According to Thomas, a compound, $TlCl_3.5NH_3$, is produced by the action of an excess of ammonia on anhydrous thallic chloride. No compound richer in ammonia is known, and the compound $TlCl_3.5NH_3$ is insoluble in liquid ammonia. Thallic chloride combines with ether, pyridine, aniline, etc.

Thallic chloride tetrahydrate readily absorbs one molecular proportion of hydrogen chloride, a liquid being produced from which, on standing over phosphoric anhydride, *hydrogen thallic chloride*, $TlCl_3.HCl.3H_2O$ or $HTlCl_4.3H_2O$, separates in deliquescent crystals.

Thallic bromide,[2] $TlBr_3$, is not known in the anhydrous state. It can be obtained in solution by the action of excess of bromine on thallous bromide suspended in water. When the solution is concentrated at 30° to 40° to a syrup, and then strongly cooled, very pale yellow crystals of the tetrahydrate, $TlBr_3.4H_2O$, are produced. Meyer has obtained the monohydrate,

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[1] Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5; Werther, *J. prakt. Chem.*, 1864, **91**, 385; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1900, **24**, 321; 1902, **32**, 72; *Ber.*, 1902, **35**, 1319; V. Thomas, *Compt. rend.*, 1902, **134**, 545; **135**, 1051; *Ann. Chim. Phys.*, 1907, [viii.], **11**, 204; Cushman, *Amer. Chem. J.*, 1900, **24**, 222; 1901, **26**, 505; M'Clenahan, *Zeitsch. anorg. Chem.*, 1904, **42**, 100; *Amer. J. Sci.*, 1904, [iv.], **18**, 104; Renz, *Ber.*, 1902, **35**, 1110.

[2] Willm, *loc. cit.*; R. J. Meyer, *loc. cit.*; Thomas, *loc. cit.*

$TlBr_3.H_2O$, by concentrating the solution *in vacuo* at the ordinary temperature. The hydrates cannot be dehydrated without loss of bromine. They absorb one molecular proportion of hydrogen bromide or hydrogen chloride. Willm has described the addition-compound, $TlBr_3.3NH_3$.

Thallic chlorobromides, $TlClBr_2.4H_2O$ and $TlCl_2Br.4H_2O$, have been prepared by Thomas by the action of bromine on thallous chloride suspended in water, and of chlorine on thallous bromide suspended in water, the solutions being concentrated to a syrupy consistency at 30° to 40°, and then strongly cooled. The hydrated salts cannot be dehydrated without loss of halogens occurring. The hydrates combine with one molecular proportion of hydrogen chloride or bromide, but the compounds formed have not been obtained in the crystalline state.[1]

Thallic iodide, TlI_3, may be prepared by digesting thallous iodide with an alcoholic solution of iodine and allowing the solution to evaporate over sulphuric acid. It forms large, dark, orthorhombic crystals ($a:b:c = 0·6828:1:1·1217$), isomorphous with rubidium and cæsium tri-iodides.[2] It might therefore be concluded that thallic iodide is a per-iodide of thallous iodide and essentially a thallous compound. According to Abegg and Maitland, it is a tautomeric substance, behaving as a thallous or as a thallic compound according to circumstances. In its sparing solubility in water and organic solvents it resembles the thallous halides, while it resembles the other thallic halides in forming complex salts with other iodides. In aqueous solution these double salts yield the stable complex ion TlI_4'.[3]

Double Salts containing Thallic Chloride, Bromide, or Iodide.—A very large number of these double salts is known.

The following compounds with the alkali metal and ammonium halides have been described:—[4]

Type $TlX_3.MX.xH_2O$.	Type $2TlX_3.3MX.xH_2O$.
$TlBr_3.NH_4Br$	$2TlCl_3.3CsCl$
$TlBr_3.NH_4Br.2H_2O$*	$2TlBr_3.3KBr.3H_2O$
$TlBr_3.NH_4Br.4H_2O$	$2TlBr_3.3CsBr$
$TlBr_3.NH_4Br.5H_2O$	$2TlI_3.3KI.3H_2O$
$TlBr_3.KBr.2H_2O$*	
$TlBr_3.RbBr.H_2O$*	
$TlBr_3.CsBr$*	
$TlI_3.NH_4I$	
$TlI_3.KI$	
$TlI_3.CsI$*	
$TlI_3.RbI.2H_2O$*	

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[1] V. Thomas, *Compt. rend.*, 1902, **135**, 545, 1051, 1208; *Ann. Chim. Phys.*, 1907, [viii.], **11**, 204.

[2] Wells and Penfield, *Amer. J. Sci.*, 1894, [iii.], **47**, 463; *Zeitsch. anorg. Chem.*, 1894, **6**, 312; *cf.* Nickès, *Compt. rend.*, 1864, **58**, 537; *J. Pharm. Chim.*, 1864, [iv.], **1**, 25.

[3] Abegg and Maitland, *Zeitsch. anorg. Chem.*, 1906, **49**, 341.

[4] Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5; Nicklès, *Compt. rend.*, 1864, **58**, 537; *J. Pharm. Chim.*, 1864, [iv.], **1**, 22; 1866, **4**, 127; Rammelsberg, *Ber.*, 1870, **3**, 360; *Pogg. Annalen*, 1872, **146**, 592; Neumann, *Annalen*, 1888, **244**, 329; Godeffroy, *Zeitsch. Oesterr. Apoth.-Ver.*, 1880, No. 9; Pratt, *Amer. J. Sci.*, 1895, [iii.], **49**, 398, 402; *Zeitsch. anorg. Chem.*, 1895, **9**, 19; Johnson, *J. Chem. Soc.*, 1878, **33**, 183; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1900, **24**, 321; Wallace, *Zeitsch. Kryst. Min.*, 1911, **49**, 417.

Type $TlX_3.2MX.xH_2O$.

$TlCl_3.2KCl.2H_2O$
$TlCl_3.2RbCl$
$TlCl_3.2RbCl.H_2O$
$TlCl_3.2CsCl$
$TlCl_3.2CsCl.H_2O$
$TlCl_3.2CsCl.2H_2O$

Type $TlX_3.3MX.xH_2O$.

$TlCl_3.3NaCl.12H_2O$
$TlCl_3.3LiCl.8H_2O$
$TlCl_3.3NH_4Cl$
$TlCl_3.3NH_4Cl.2H_2O$
$TlCl_3.3KCl.2H_2O$
$TlCl_3.3RbCl$
$TlCl_3.3RbCl.H_2O$
$TlCl_3.3RbCl.2H_2O$
$TlCl_3.3CsCl.H_2O$
$TlBr_3.3RbBr.2H_2O$

The salts of the type $TlX_3.MX.xH_2O$ appear to possess cubic symmetry, since Pratt and Wallace have shown that the asterisked salts crystallise in combinations of the cube and regular octahedron. Rammelsberg described the potassium salts of the type $2TlX_3.3MX.xH_2O$ as cubic, but according to Wallace the bromide is tetragonal ($a : c = 1 : 0·7556$) and the cæsium chloride is described by Pratt as hexagonal ($a : c = 1 : 0·8257$).

Two salts of the type $TlX_3.2MX.H_2O$ crystallise in rhombic bipyramids, isomorphous with the corresponding indium salts and with ammonium and potassium ferric chlorides, $FeCl_3.2NH_4Cl.H_2O$ and $FeCl_3.2KCl.H_2O$. The data given below are due to Wallace (compare data given on p. 157):—

$TlCl_3.2RbCl.H_2O$; $a : b : c = 0·9770 : 1 : 1·4388$; density $= 3·513$ at 20°
$TlCl_3.2CsCl.H_2O$; $a : b : c = 0·9690 : 1 : 3·4321$; density $= 3·879$ at 20°

The following salts of the type $TlX_3.3MX.2H_2O$ crystallise in tetragonal bipyramids isomorphous with the corresponding indium salts:—[1]

$TlCl_3.3KCl.2H_2O$; $a : c = 1 : 0·7941$; density $= 2·859$ at 20°
$TlCl_3.3NH_4Cl.2H_2O$; $a : c = 1 : 0·8097$; density $= 2·389$ at 20°
$TlBr_3.3RbBr.2H_2O$; $a : c = 1 : 0·8038$; density $= 4·077$ at 20°

Thallic chloride combines with the chlorides of *calcium*, *strontium*, *magnesium*, *zinc*, *copper*, and *manganese*, forming double salts of the type $2TlCl_3.MCl_2.6H_2O$.[2] *Thallic beryllium chloride*, $2TlCl_3.3BeCl_2$, and the ammonia addition-product of *thallic cupric iodide*, $2TlI_3.CuI_2.4NH_3$, have also been described.[3]

INTERMEDIATE THALLIUM HALIDES. — **Thallium sesquichloride,**[4] Tl_2Cl_3 or $3TlCl.TlCl_3$, is readily prepared by saturating a boiling solution of thallic chloride with thallous chloride and cooling, or by passing chlorine into water containing thallous chloride in suspension until no more white thallous chloride is left. In each case the product should be recrystallised from boiling water, and in the latter case the too prolonged action of chlorine should be avoided, since it converts the sparingly soluble thallium sesquichloride into very soluble thallic chloride.

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[1] Wallace, *loc. cit.*; Pratt, *loc. cit.*; compare data given on p. 157.

[2] Gewecke, *Annalen*, 1909, **366**, 217.

[3] Neumann, *Annalen*, 1888, **244**, 329 ; Jörgensen, *J. prakt. Chem.*, 1872, [ii.], **6**, 82.

[4] Lamy, *Ann. Chim. Phys.*, 1863, [iii.], **67**, 385 ; Willm, *ibid.*, 1865, [iv.], **5**, 5 ; Crookes and Church, *Chem. News*, 1863, **8**, 1 ; Werther, *J. prakt. Chem.*, 1864, **91**, 385 ; Hebberling, *Annalen*, 1865, **134**, 11; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1900, **24**, 321 ; Cushman, *Amer. Chem. J.*, 1900, **24**, 222 ; V. Thomas, *Ann. Chim. Phys.*, 1907, [viii.], **11**, 204.

Thallium sesquichloride crystallises in yellow, six-sided leaflets, of density 5·9. One litre of water at 25° dissolves 3·43 grams of the chloride.[1] The aqueous solution gives with alkali hydroxides a precipitate of thallic hydroxide, and the filtrate contains thallous salt in solution.

Thallium sesquichloride forms mixed crystals with thallous chloride, on account of which a number of other chlorides have erroneously been described by Werther.

Thallium dichloride, $TlCl_2$ or $TlCl.TlCl_3$, is the final product of the action of dry chlorine on dry thallous chloride at the ordinary temperature. The absorption of chlorine is at first rapid, but is subsequently very slow. Thallium dichloride is a pale yellow, hygroscopic solid which may be kept indefinitely in an atmosphere of dry chlorine at the ordinary temperature without any further absorption of the gas occurring. It is decomposed by water into thallic chloride and thallium sesquichloride.[2]

Thallium sesquibromide, Tl_2Br_3 or $3TlBr.TlBr_3$, is not so readily prepared as the corresponding chloride, since it is decomposed by water. The best method of preparation is to moisten 4 or 5 grams of thallous bromide with 1 or 2 c.c. of water and slowly add 0·5 c.c. of bromine. About 50 grams of water are then added, and the liquid brought to the boiling-point. The slight residue of thallous bromide is filtered off, and the filtrate caught in a vessel that is cooled by immersion in running water. Thallium sesquibromide separates out in bright red crystals. Water decomposes the bromide into thallic bromide and a solid the composition of which depends upon the relative amounts of sesquibromide and water, but which is intermediate between that of the sesquibromide and thallous bromide. Thallium sesquibromide forms orange-yellow or orange-red mixed crystals with thallous bromide.[3]

Thallium dibromide, $TlBr_2$ or $TlBr.TlBr_3$, is the final product of the action of dry bromine on dry thallous bromide, and is best prepared by heating thallous bromide with bromine in a sealed tube at 100° for six hours, opening the tube, and removing the excess of bromine by heating. The dibromide is also produced by the action of excess of a chloroform or carbon tetrachloride solution of bromine on thallous bromide, by the prolonged action of an excess of bromine dissolved in carbon disulphide on thallous bromide, and by the decomposition of the hydrates of thallic bromide.

Thallium dibromide is a dark yellow, crystalline solid readily decomposed by water.[4]

Thallium chlorobromides.[5] — The following intermediate chlorobromides have been described :—

Type TlX_2.	Type Tl_2X_3.
$Tl_3Cl_2Br_4$	$Tl_4Cl_3Br_3$
$Tl_3Cl_4Br_2$	$Tl_4Cl_4Br_2$
$TlClBr$	$Tl_4Cl_2Br_4$
Tl_2Br_3Cl	

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[1] Abegg and Spencer, *Zeitsch. anorg. Chem.*, 1905, **44**, 379.

[2] Lamy, *loc. cit.*; Thomas, *loc. cit.*

[3] Thomas, *loc. cit.*; Willm, *loc. cit.*

[4] Willm, *loc. cit.*; Thomas, *loc. cit.*, and *Compt. rend.*, 1901, **132**, 1487; 1902, **134**, 545; *Bull. Soc. chim.*, 1902, [iii.], **27**, 471, 474, 481.

[5] R. J. Meyer, *loc. cit.*; Cushman, *loc. cit.*, and *Amer. Chem. J.*, 1901, **26**, 505; Thomas, *Ann. Chim. Phys.*, 1907, [viii.], **11**, 204; *Compt. rend.*, 1900, **130**, 1316; **131**, 892, 1208; 1901, **132**, 80, 1487; **133**, 735; 1902, **134**, 545; *Bull. Soc. chim.*, 1902, [iii.], **27**, 471, 474, 481.

Type TlX_2.—(*a*) The compound $Tl_3Cl_2Br_4$ may be prepared by treating thallous chloride in solution with excess of bromine, and concentrating the solution of thallic chlorobromide $TlClBr_2$ over sulphuric acid *in vacuo*. A syrupy liquid is produced which on further concentration begins to decompose, and yellow crystals of $Tl_3Cl_2Br_4$ are deposited. Any thallic hydroxide produced is separated by decantation while there is still a little liquid left, and the crystals are then left over sulphuric acid until they are dry. The compound $Tl_3Cl_2Br_4$ forms sulphur-yellow, orthorhombic (?) prisms, and melts at 165° to a yellow liquid. It is decomposed by water with the production of impure $Tl_4Cl_3Br_3$, which may be purified by recrystallising it from hot water.

(*b*) The compound $Tl_3Cl_4Br_2$ is made by the method outlined for $Tl_3Cl_2Br_4$, but the starting materials are thallous bromide and chlorine. It resembles the preceding compound, and is decomposed by water with the production of $Tl_4Cl_3Br_3$.

(*c*) The compound TlClBr is obtained by heating thallous chloride with bromine.

(*d*) The compound Tl_2Br_3Cl was obtained by Cushman by the action of aqueous thallic bromide on the compound $Tl_4Br_3Cl_3$. It crystallises in yellow needles.

Type Tl_2X_3.—(*e*) One method for the preparation of the compound $Tl_4Cl_3Br_3$ has been given under (*a*) above. It is also said by Cushman to be produced by boiling a solution of thallic chloride with thallous bromide and cooling, or by boiling a solution of thallic bromide with thallous chloride. It is also produced when a limited quantity of bromine is added to thallous chloride suspended in cold water, the yellow solid produced dissolved in boiling water, and the filtered solution slowly cooled. The filtrate from the deposited crystals, when concentrated and cooled, deposits more of the compound $Tl_4Cl_3Br_3$, in six-sided plates, but mixed with needles of the compound $Tl_4Cl_4Br_2$.

(*f*) One method, due to Thomas, for the production of $Tl_4Cl_4Br_2$ has just been mentioned, but it is difficult to obtain the compound free from admixed $Tl_4Cl_3Br_3$. R. J. Meyer and Cushman have also described processes for the preparation of $Tl_4Cl_4Br_2$ from thallous chloride, bromine, and water.

(*g*) The preparation of $Tl_4Cl_2Br_4$ from thallous bromide, chlorine, and water has been described by R. J. Meyer.

Each of the compounds $Tl_4Cl_3Br_3$, $Tl_4Cl_2Br_4$, and $Tl_4Cl_4Br_2$ forms dark orange-yellow crystals, sparingly soluble in water. With rise of temperature the crystals rapidly become deep red in colour. The two methods given by Cushman for the preparation of $Tl_4Cl_3Br_3$ are said by that author to yield stereo-isomeric forms of the compound, but at present this cannot be regarded as proved.

Thallium sesqui-iodide, Tl_2I_3 or $3TlI.TlI_3$, has been described by Knösel.[1] The compound Tl_3I_4, or $5TlI.TlI_3$, was discovered by Strecker, and, later, prepared by Jörgensen.[2] It has been shown by Abegg and Maitland that thallous iodide passes into this compound at 25° in the presence of a solution of iodine in water or potassium iodide solution, provided that the concentration of free iodine in the liquid phase exceeds 0·0019 gram per litre, but does not exceed 0·082 gram per litre. When the concentration of free iodine exceeds the latter value, the compound Tl_3I_4 passes into thallic

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[1] Knösel, *Ber.*, 1874, 7, 576, 893.

[2] Strecker, *Annalen*, 1865, 135, 207 ; Jörgensen, *J. prakt. Chem.*, 1872, [ii.], 6, 82.

iodide. The compound Tl_3I_4 is a black solid, sparingly soluble in water and organic liquids with partial decomposition.[1]

Thallous chlorate, $TlClO_3$.—An aqueous solution of this salt is obtained by dissolving thallium in aqueous chloric acid, or by mixing equivalent quantities of barium chlorate and thallous sulphate in solution. The chlorate separates from aqueous solution in microscopic prisms of specific gravity 5·047.[2] The solubility, in grams of salt per 100 grams of water, is as follows:—

Temperature, °C.	0°	20°	50°	80°	100° C.
Grams of $TlClO_3$	2·00	3·92	12·7	33·7	57·3

One litre of the saturated solution at 20° contains 38·53 grams of thallous chlorate (Noyes and Farrell). When heated to 186°, the chlorate explodes.[3]

Thallous chlorate is monoclinic and isomorphous with potassium chlorate; and these two salts form an incomplete series of mixed crystals with one another.[4]

Thallic chlorate, $Tl(ClO_3)_3.4H_2O$, forms deliquescent, rhombic crystals.[5]

Thallous perchlorate, $TlClO_4$, may be obtained in aqueous solution by dissolving thallium in aqueous perchloric acid, or by mixing barium perchlorate and thallous sulphate. It crystallises in rhombic tablets ($a:b:c=0·7978:1:1·2898$) of density 4·844, and begins to decompose at 300°.[6] The solubility, in grams of anhydrous salt per 100 grams of water, is 10·0 at 15° and 166·6 at 100°.

Thallous perchlorate forms a complete series of mixed crystals with potassium perchlorate, with which it is isomorphous.[7]

Thallic perchlorate, $Tl(ClO_4)_3.6H_2O$, forms white, hygroscopic crystals.[8]

Thallous bromate, $TlBrO_3$, obtained by dissolving thallous oxide or carbonate in aqueous bromic acid, crystallises from aqueous solution in needles. It decomposes at 100° and detonates when heated to 150°. At 20°, 100 grams of water dissolve 0·347 of the bromate; at 40°, 0·741 gram.[9]

Thallic bromate, $Tl(BrO_3)_3.3H_2O$, forms white, hygroscopic crystals.[10]

Thallous iodate, $TlIO_3$, is obtained as a white, crystalline precipitate when a solution of an alkali iodate is added to a solution of a soluble thallous salt. It begins to decompose above 150°, with the evolution of oxygen and iodine.[11] Ditte has described a hemihydrate, $2TlIO_3.H_2O$.[12]

A saturated solution at 20° contains 0·058 gram of thallous iodate per 100 grams of water.[13]

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[1] Abegg and Maitland, *Zeitsch. anorg. Chem.*, 1905, **49**, 341.

[2] Crookes, *Chem. News*, 1863, **8**, 159; J. Muir, *Trans. Chem. Soc.*, 1876, i. 857.

[3] Gewecke, *Zeitsch. anorg. Chem.*, 1912, **75**, 272.

[4] Stortenbeker, *Rec. trav. chim.*, 1905, **24**, 53; Roozeboom, *Zeitsch. physikal. Chem.*, 1891, **8**, 513.

[5] Gewecke, *loc. cit.*

[6] Roscoe, *J. Chem. Soc.*, 1866, **19**, 504; *cf.* Carnelley and O'Shea, *Trans. Chem. Soc.*, 1884, **45**, 409.

[7] Stortenbeker, *loc. cit.*

[8] Gewecke, *lot. cit.*

[9] Böttger, *Zeitsch. physikal. Chem.*, 1903, **46**, 602; Noyes and Abbot, *ibid.*, 1895, **16**, 132.

[10] Gewecke, *loc. cit.*

[11] Rammelsberg, *Ber.*, 1870, **3**, 360.

[12] Ditte, *Ann. Chim. Phys.*, 1890, [vi.], **21**, 145

[13] Böttger, *loc. cit.*

Thallic iodate, $Tl(IO_3)_3$.—Soluble hydrates of this salt, containing $2H_2O$ and $12H_2O$, have been prepared.[1]

Thallous permanganate, $TlMnO_4$, prepared by double decomposition between barium permanganate and thallous sulphate, crystallises from aqueous solution in large, black prisms.[2]

THALLIUM AND THE OXYGEN GROUP.

Oxides and Hydroxides of Thallium.—Two basic oxides of thallium are known, *thallous oxide*, Tl_2O, and *thallic oxide*, Tl_2O_3. In addition, *thallo-thallic oxide*, $Tl_2O.Tl_2O_3$ or TlO, is known, and an oxide of the formula, Tl_3O_5 has been described.

Normal *thallous hydroxide*, TlOH or $Tl_2O.H_2O$, and *monohydrate* of *thallic oxide* or *metathallic hydroxide*, TlO.OH or $Tl_2O_3.H_2O$, are also known.

Thallous oxide, Tl_2O, is produced when thallium oxidises in air or oxygen at comparatively low temperatures. In warm air the oxidation of the metal proceeds rapidly, and at temperatures approaching dull redness thallic oxide commences to be formed in appreciable amount. Thallous oxide is best prepared by dehydrating thallous hydroxide at 100°. It is a heavy, black powder, which rapidly absorbs water, producing thallous hydroxide, and reacts with acids to produce thallous salts. It is attacked by chlorine and bromine with the production of chlorides and bromides of thallium and free oxygen. At about 300° it melts to a liquid which rapidly attacks glass. When heated to redness in hydrogen, thallous oxide is slowly reduced to metal; the reduction proceeds more readily in a stream of carbon monoxide.[3]

Thallous hydroxide, TlOH, crystallises from aqueous solution in yellow needles. A solution of the hydroxide is readily prepared by shaking an excess of thallium turnings with water in a vessel through which a stream of oxygen is passing,[4] or by double decomposition between thallous sulphate and baryta.

Thallous hydroxide is readily dissociated into thallous oxide and water:—

$$2TlOH \rightleftharpoons Tl_2O + H_2O,$$

the equilibrium pressure reaching the value 760 mm. at 139°, according to the measurements of Bahr. The hydroxide also darkens in colour *in vacuo* when exposed to light, but the nature of the chemical change is unknown.

Thallous hydroxide is readily soluble in water and alcohol. One litre of the saturated aqueous solution at $t°$ contains x grams of the hydroxide, where x and t are as follows:—[5]

$t°$	0°	20°	30°	40°	50°	60°	70°	80°	90°	100°
x	254·4	352·7	402·8	495·0	594·5	733·1	888·8	1062·6	1260·8	1505·0

Thallous hydroxide is a comparatively strong base.[6] The aqueous solution is colourless and has a strongly alkaline reaction. It precipitates metallic

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[1] Gewecke, *loc. cit.*

[2] R. J. Meyer and Best, *Zeitsch. anorg. Chem.*, 1899, **22**, 169.

[3] Lamy, *Ann. Chim. Phys.*, 1863, [iii.], **67**, 385; Flemming, *Jahresber.*, 1868, p. 250; Winkler, *Ber.*, 1890, **23**, 788; Rauter, *Annalen*, 1892, **270**, 249.

[4] Bahr, *Zeitsch. anorg. Chem.*, 1911, **71**, 79.

[5] Calculated from the data given by Bahr, *loc. cit.*

[6] Ostwald, *J. prakt. Chem.*, 1886, [ii.], **33**, 352.

hydroxide by double decomposition, readily absorbs carbon dioxide, and attacks glass and porcelain. Accordingly, unless special care is taken in its preparation, thallous hydroxide is always contaminated with a little carbonate.[1]

Thallous hydroxide is oxidised to dark brown thallic hydroxide by ozone. The reaction has been proposed as a test for ozone,[2] but is given by other oxidising agents, *e.g.* hydrogen peroxide.[3]

The *hydrate*, $TlOH.H_2O$, has been obtained, but the conditions under which it is produced are not known.[4]

Thallic oxide or **thallium sesqui-oxide,** Tl_2O_3, is produced by the action of air or oxygen upon thallium at temperatures between a dull red heat and 700°, and may be prepared by dehydrating thallic hydroxide. It is obtained in the crystalline form by fusing thallous sulphate, nitrate, or chromate with excess of potassium hydroxide at a dull red heat and extracting the mass with water,[5] or by heating thallous nitrate to 450°.[6] The crystals have a density of 9·97.

When hydrogen peroxide is added to a cold solution of a thallous salt containing excess of alkali hydroxide, brown thallic oxide is precipitated, which soon becomes crystalline and has a density of 9·65 at 21°. When precipitation is effected at 80°, the oxide obtained is black and amorphous, and has a density of 10·19 at 22°. At temperatures above 100°, the brown variety becomes black; each form contains a little water which is not completely eliminated below 500°.[7]

Thallic oxide is deposited upon the anode when a neutral solution of thallous sulphate or nitrate is electrolysed between platinum electrodes and the anodic potential difference (between electrode and electrolyte) exceeds 1·43 volts. When the potential difference at the anode exceeds 1·81 volts for thallous nitrate or 2·27 volts for thallous sulphate, thallic hydroxide is deposited.[8]

Thallic oxide melts at 725° ± 10°, begins to decompose into thallous oxide and oxygen at 800°, and decomposes rapidly at 1000°.[9] It is reduced by hydrogen and by carbon monoxide at a red heat.[10] It is insoluble in water and in alkalies; it reacts with hydrochloric acid, producing thallic and thallous chlorides and chlorine; it is scarcely affected by cold sulphuric acid, and is attacked by the hot acid with the production of thallous sulphate and oxygen.[11]

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[1] Lamy, *loc. cit.*; Carnelley and Walker, *Trans. Chem. Soc.*, 1888, **53**, 59.

[2] Schönbein, *J. prakt. Chem.*, 1867, **101**, 321; Lamy, *Bull. Soc. chim.*, 1869, [ii.], **11**, 210.

[3] Schöne, *Annalen*, 1878, **196**, 58.

[4] Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5.

[5] Lepierre and Lachaud, *Compt. rend.*, 1891, **113**, 196.

[6] V. Thomas, *ibid.*, 1904, **138**, 1697.

[7] Rabe, *Zeitsch. anorg. Chem.*, 1906, **48**, 427; 1906, **50**, 158; 1907, **55**, 130.

[8] M. Bose, *Zeitsch. anorg. Chem.*, 1905, **44**, 237; see also Crookes, *Proc. Roy. Soc.*, 1862, **12**, 150; Böttger, *Annalen*, 1863, **127**, 175; Wöhler, *ibid.*, 1868, **146**, 263, 375; Flemming, *Jahresber.*, 1868, p. 250; Heiberg, *Zeitsch. anorg. Chem.*, 1903, **35**, 347; Jonas, *Zeitsch. Elektrochem.*, 1903, **9**, 523; Lorenz, *Zeitsch. anorg. Chem.*, 1896, **12**, 439. According to Gallo and Cenni (*Atti R. Accad. Lincei*, 1908, [v.], **17**, ii. 276), the oxide deposited on the anode when thallous sulphate solution containing a trace of sulphuric acid is electrolysed has, when dried at 160° to 200°, a composition corresponding to the formula Tl_3O_5.

[9] Rabe, *loc. cit.*; *cf.* Carnelley and O'Shea, *Trans. Chem. Soc.*, 1884, **45**, 409.

[10] Werther, *J. prakt. Chem.*, 1864, **91**, 385; Flemming, *loc. cit.*; see also Winkler, *Ber.*, 1890, **23**, 788; Böttger, *Dingl. poly. J.*, 1870, **197**, 379.

[11] Lamy, *Ann. Chim. Phys.*, 1863, [iii.], **67**, 385.

Thallic hydroxide,[1] TlO.OH or $Tl_2O_3.H_2O$, is obtained by precipitating a solution of a thallic salt with a slight excess of alkali hydroxide or ammonia, washing the precipitate, and drying it at the ordinary temperature in the air.[2] It is also produced by the action of alkali hypochlorite on an alkaline solution of a thallous salt.[3]

Thallic hydroxide is a reddish-brown powder. When heated[4] to 110°–120° it is completely dehydrated to thallic oxide, and it is also dehydrated when heated in contact with the liquid from which it has been precipitated.[5] The freshly precipitated hydroxide reacts readily with acids; but, after it has been dried, solution in acids is slow, and is accompanied by partial reduction. The hydroxide is practically insoluble in water, its solubility-product[6] at 25° being only 10^{-53}.

Thallothallic oxide, TlO or $Tl_2O.Tl_2O_3$, is obtained as a bluish-black, lustrous precipitate when 3 per.cent. hydrogen peroxide is added to a solution of thallous sulphate which has been made strongly alkaline and cooled to – 15°. It should be washed with cold alcohol and then with ether. The oxide absorbs carbon dioxide, forming thallic oxide and thallous carbonate; it absorbs oxygen at the ordinary temperature, forming thallic oxide; and it is decomposed by cold water, producing thallous hydroxide and thallic oxide.[7]

Sulphides of Thallium.—When mixtures of thallium and sulphur are fused, those rich in thallium separate into two non-miscible layers of **thallous sulphide,** Tl_2S, and thallium, while those rich in sulphur form two layers consisting of **thallium pentasulphide** and sulphur. Mixtures containing more sulphur than is required for thallous sulphide and less than is required for the pentasulphide form only one liquid phase, and solid solutions appear to separate when they are cooled. The nature of these solid solutions is not known; possibly a **thallothallic sulphide,** $Tl_2S.Tl_2S_3$, also exists, but has no melting-point.[8]

Thallous sulphide, Tl_2S, is obtained as a black precipitate by passing hydrogen sulphide into, or adding ammonium sulphide to, a solution of a thallous salt. In the presence of a trace of sulphuric acid, hydrogen sulphide precipitates the sulphide from cold solutions as microscopic tetrahedra.[9] The amorphous sulphide becomes crystalline when heated for some hours to 150°–200° with excess of colourless ammonium sulphide.[10]

Thallous sulphide forms bluish-black crystals of density 8·0. It melts at 448°, and is very brittle. Heated in hydrogen, it is reduced to thallium. It

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[1] A hydroxide of the formula $Tl(OH)_3$, stable at 340°, has been described by Carnegie (*Chem. News*, 1889, 60, 113), but the formula given is based solely on an estimation of the thallium present in the substance.

[2] Lamy, *Ann. Chim. Phys.*, 1863, [iii.], 67, 385; Crookes, *J. Chem. Soc.*, 1864, 17, 112; Werther, *J. prakt. Chem.*, 1864, 91, 385; Carnelley and Walker, *Trans. Chem. Soc.*, 1888, 53, 88.

[3] Strecker, *Annalen*, 1865, 135, 207; Willm, *Ann. Chim. Phys.*, 1865, [iv.], 5, 5; see also Schönbein, *J. prakt. Chem.*, 1864, 93, 35; Weltzien, *Annalen*, 1866, 138, 129.

[4] In heating thallic oxide or hydroxide, care must be taken to prevent the access of gaseous products of combustion to the substance.

[5] R. J. Meyer, *Zeitsch. anorg. Chem.*, 1900, 24, 321.

[6] Abegg and Spencer, *Zeitsch. anorg. Chem.*, 1905, 44, 379.

[7] Rabe, *Zeitsch. anorg. Chem.*, 1908, 58, 23.

[8] Pélabon, *Compt. rend.*, 1907, 145, 118; *Ann. Chim. Phys.*, 1907, [viii.], 17, 526. Pélabon suggests the intermediate sulphide Tl_8S_7.

[9] Hebberling, *Annalen*, 1865, 134, 11.

[10] Stanek, *Zeitsch. anorg. Chem.*, 1898, 17, 117.

is readily decomposed by dilute mineral acids, but not by acetic acid, and the moist sulphide rapidly oxidises in the air. It is insoluble in ammonium sulphide, alkali hydroxides, carbonates, and cyanides.

Thallous sulphide has been obtained in colloidal solution.[1]

Thallous sulphide forms definite compounds of the formulæ $3Tl_2S.As_2S_5$ (or Tl_3AsS_4) and $2Tl_2S.SnS_2$ (or Tl_4SnS_4) with *arsenic* and *stannic* sulphides. They may be employed for the gravimetric estimation of thallium. With *arsenious*, *antimonious*, *antimonic*, and *stannous* sulphides, thallous sulphide forms series of solid solutions. They are precipitated from mixed thallous and arsenic, antimony and tin solutions by alkali sulphides.[2] Thallous sulphide also forms a double sulphide of the formula $Tl_2S.4CuS$ with *cupric* sulphide, and two series of solid solutions probably of the compound $Tl_2S.2CuS$ in $Tl_2S.4CuS$ and Tl_2S in $Tl_2S.2CuS$.[3]

Thallic sulphide, Tl_2S_3, is not precipitated from a thallic salt by hydrogen sulphide, thallous sulphide and sulphur being produced.[4] It may, however, be prepared by fusing thallium with excess of sulphur and removing excess of the latter by distillation.[5] It is a black solid, hard and brittle below 12°, soft and plastic above that temperature. It dissolves in warm dilute sulphuric acid with the evolution of hydrogen sulphide, no sulphur separating as such.

With *thallous* sulphide, thallic sulphide forms a series of solid solutions.[6] The compound *potassium thallium sulphide*, $Tl_2S_3.K_2S$, is obtained by fusing together thallous sulphate (1 pt.) with sulphur (6 pts.) and potassium carbonate (6 pts.), and washing the fused mass with water. It is a reddish-brown, crystalline solid, insoluble in water.[7]

Thallium pentasulphide, Tl_2S_5, is said by Pélabon to melt at 127°, but, if quickly cooled, to remain pasty at ordinary temperatures. When heated above the melting-point it readily loses sulphur. A crystalline pentasulphide is said to be formed by digesting thallous chloride with concentrated ammonium polysulphide solution;[8] but, according to Hawley, there is no evidence that the substance thus obtained is a definite pentasulphide, but there exists a series of solid solutions containing thallium and sulphur, in which there is more sulphur than is required for a sesquisulphide.

Thallium selenides.—According to Murakami,[9] thallium forms **thallous selenide,** Tl_2Se, melting at 368°; **thallothallic selenide,** $Tl_2Se.Tl_2Se_3$, melting at 310°; and **thallium sesquiselenide,** Tl_2Se_3, decomposing at 265°. The equilibrium diagram is complex, there being two gaps of miscibility in the liquid state. The selenides are brittle solids. Thallous

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[1] Winssinger, *Bull. Soc. chim.*, 1888, [ii.], **49**, 452.

[2] Hawley, *J. Physical Chem.*, 1906, **10**, 654; *J. Amer. Chem. Soc.*, 1907, **29**, 1011; *cf.* Gunning, *Chem. News*, 1868, **17**, 138.

[3] Bruner and Zawadski, *Bull. Acad. Sci. Cracow*, 1909, p. 312.

[4] *Cf.* Strecker, *Annalen*, 1865, **135**, 207.

[5] Carstanjen, *J. prakt. Chem.*, 1867, **102**, 65, 129.

[6] Hawley, *loc. cit.*; *cf.* Schneider, *vide infra*; Carstanjen, *J. prakt. Chem.*, 1867, **102**, 65, 159.

[7] Schneider, *J. prakt. Chem.*, 1870, [ii.], **2**, 164; 1874, [ii.], **9**, 209; **10**, 55; 1890, [ii.], **42**, 305; *Pogg. Annalen*, 1870, **139**, 661; 1875, **153**, 588; Krüss and Solereder, *Ber.*, 1886, **19**, 2736.

[8] K. A. Hofmann and Höchtlen, *Ber.*, 1903, **36**, 3090.

[9] Murakami, *Mem. Coll. Sci. Tokyo*, 1915, **1**, 153; *cf.* Pélabon, *Compt. rend.*, 1907, **145**, 118; *Ann. Chim. Phys.*, 1909, [viii.], **17**, 526; Carstanjen, *loc. cit.*; Fabre, *Ann. Chim. Phys.*, 1887, [vi.], **10**, 538; Kuhlmann, *Bull. Soc. chim.*, 1864, [ii.], **1**, 330.

selenide may be precipitated by passing hydrogen selenide into aqueous thallous carbonate. It is decomposed by acids.

Thallium tellurides.—The system thallium – tellurium has been studied by the thermal method by Pélabon and by Chikashigé. **Thallous telluride,** Tl_2Te, melts at 412°, and is almost non-miscible with thallium. The telluride Tl_3Te_2 (or Tl_5Te_3?) melts at 442°. **Thallothallic telluride,** $Tl_2Te.Tl_2Te_3$, which crystallises in long needles, is not stable in contact with a liquid phase of the same composition.[1]

Thallous sulphite, Tl_2SO_3, may be prepared by adding sulphurous acid to thallous hydroxide or by mixing solutions of thallous sulphate and sodium sulphite, when thallous sulphite is precipitated. It forms white crystals of density 6·427 at 20°, and is insoluble in alcohol. It can be recrystallised from warm water; 100 parts of water at 15° dissolve 3·34 of the salt.[2]

Thallous thiosulphate, $Tl_2S_2O_3$, is obtained as a white crystalline precipitate by adding potassium thiosulphate to a solution of a thallous salt. It can be crystallised from hot water, and begins to decompose at 130°. *Sodium thallous thiosulphate,* $2Tl_2S_2O_3.3Na_2S_2O_3.8H_2O$, is known.[3]

Thallous sulphate, Tl_2SO_4, is prepared by dissolving thallium in hot sulphuric acid, or by adding thallous hydroxide or carbonate to aqueous sulphuric acid, evaporating, and crystallising.

Thallous sulphate crystallises in rhombic prisms ($a:b:c=0·5555:1:0·7328$) of density 6·765 at 20°.[4] It is therefore isomorphous with potassium sulphate (for which $a:b:c=0·5727:1:0·7418$),[5] and these two salts form a continuous series of mixed crystals.[6] Thallous sulphate melts at 632°,[7] and at temperatures above dull redness it volatilises. The mean refractive index, 1·8708 for the D-line, is extremely high, the value for potassium sulphate being 1·4952 (Tutton).

One hundred grams of water dissolve the following amounts of thallous sulphate:—[8]

Temperature, °C.	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	99·7°
Grams of Tl_2SO_4	2·70	3·70	4·87	6·16	7·60	9·21	10·92	12·74	14·61	16·53	18·45

At a red heat hydrogen reduces thallous sulphate to a mixture of sulphide and metal, and ammonia reduces it to thallous sulphide.[9]

Numerous *double sulphates* containing thallous sulphate are known. With the sulphates of the tervalent metals *aluminium, chromium, iron, vanadium, gallium,* and *rhodium,* thallous sulphate forms **alums,** of the

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[1] Pélabon, *loc. cit.*; Chikashigé, *Zeitsch. anorg. Chem.*, 1912, **78**, 68; Fabre, *Ann. Chim. Phys.*, 1888, [vi.], **14**, 115. According to Chikashigé, thallous telluride does not exist, but this conclusion is questionable.

[2] Seubert and Elten, *Zeitsch. anorg. Chem.*, 1892, **2**, 434; 1898, **4**, 44; Röhrig, *J. prakt. Chem.*, 1888, [ii.], **37**, 217.

[3] Hebberling, *Annalen*, 1865, **134**, 11; Werther, *J. prakt. Chem.*, 1864, **92**, 130; Vortmann and Padberg, *Ber.*, 1889, **22**. 2637; Jochum, *Chem. Zentr.*, 1885, p. 642.

[4] Tutton, *Proc. Roy. Soc.*, 1907, **A**, **79**, 351.

[5] Von Lang, *Phil. Mag.*, 1863, [iv.], 25, 248; *Annalen*, 1863, 128, 76; Tutton, *loc. cit.*

[6] Stortenbeker, *Rec. trav. chim.*, 1905, **24**, 53.

[7] Carnelley and Williams, *Trans. Chem. Soc.*, 1878, **33**, 281.

[8] Earl of Berkeley, *Phil. Trans.*, 1904, **A**, **203**, 211; Seidell, *Solubilities* (Crosby Lockwood & Son, 1907), p. 338; see also Noyes, Farrell, and Stewart, *J. Amer. Chem. Soc.*, 1911, **33**, 1650.

[9] Hodgkinson and French, *Chem. News*, 1893, **66**, 223.

general formula $Tl_2SO_4.R^{\prime\prime\prime}_2(SO_4)_3.24H_2O$.[1] With the sulphates of *magnesium, zinc, iron, nickel, cobalt, copper, manganese,* and *cadmium,* thallous sulphate forms a series of isomorphous, monoclinic, double sulphates of the general formula $Tl_2SO_4.MSO_4.6H_2O$, isomorphous with the corresponding series of salts containing ammonium, potassium, rubidium, and cæsium in place of thallium.[2] The crystallographic constants, determined by Werther and by Tutton (zinc salt), are as follows:—

Salt.	a	b	c	β
$Tl_2SO_4.MgSO_4.6H_2O$	0·7422 :	1 :	0·5002	106° 24′
$Tl_2SO_4.ZnSO_4.6H_2O$	0·7413 :	1 :	0·5010	106° 16′
$Tl_2SO_4.FeSO_4.6H_2O$	0·7366 :	1 :	0·4964	105° 52′
$Tl_2SO_4.NiSO_4.6H_2O$	0·7431 :	1 :	0·4988	106° 39′
[$K_2SO_4.ZnSO_4.6H_2O$	0·7413 :	1 :	0·5044	104° 48′]

The density of the thallium-zinc salt is 3·720 at 20°; the mean refractive index for the D-line is 1·6064, while that of the potassium zinc salt is 1·4859 (Tutton).

Thallous hydrogen sulphate, $TlHSO_4$, is obtained when thallous sulphate is dissolved in sulphuric acid and brought to constant weight at 220° to 240°.[3] It may be also crystallised from a solution of thallous sulphate in moderately concentrated sulphuric acid, and exists in a monoclinic and an orthorhombic (?) form; while another modification would appear to exist, since the salt is isotrimorphous with potassium hydrogen sulphate.[4]

The *acid sulphate,* $Tl_3H(SO_4)_2$, crystallises when a solution of thallous sulphate with ten equivalents of sulphuric acid is concentrated. The crystals are trigonal ($a : c = 1 : 3·717$).[5] Another modification probably exists, since the salt is isodimorphous with the corresponding potassium salt.[6]

Thallous pyrosulphate, $Tl_2S_2O_7$, may be prepared by heating thallous sulphate with sulphur trioxide.[7]

Thallic sulphate, $Tl_2(SO_4)_3$.—Anhydrous thallic sulphate is said by Meyer and Goldschmidt to be obtained by heating acid thallic sulphate to 220°. The heptahydrate, $Tl_2(SO_4)_3.7H_2O$, has been described by Strecker,[8] but later experimenters have failed to prepare it.

Thallic sulphate is hydrolysed by water with great readiness, brown thallic hydroxide separating out.[9] From a hot solution of thallic hydroxide in moderately concentrated sulphuric acid a *basic thallic sulphate,* $Tl(OH)SO_4.2H_2O$, crystallises out, accompanied by the amorphous basic salt $Tl(OH)SO_4.H_2O$.[10]

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[1] See pp. 81, 82, 83, 148, 160; the subsequent volumes of this series; and Lamy, *Ann. Chim. Phys.*, 1863, [iii.], **67**, 385; Soret, *Arch. Sci. phys. nat.*, 1884, [iii.], **12**, 553; 1888, [iii.], **20**, 520; Soret and Duparc, *ibid.*, 1889, [iii.], **21**, 90; Spring, *Ber.*, 1883, **16**, 2723; Polis, *Ber.*, 1880, **13**, 367; Cossa, *Nuovo Cimento*, 1870, [ii.], **3**, 75; *Ber.*, 1878, **11**, 811; Stolba, *J. Chem. Soc.*, 1874, **27**, 873; Locke, *Amer. Chem. J.*, 1901, **26**, 166.

[2] Werther, *J. prakt. Chem.*, 1864, **92**, 128, 351; Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5; Lamy and Descloizeaux, *ibid.*, 1869, [iv.], **17**, 310; Tutton, *Proc. Roy. Soc.*, 1910, **A**, **83**, 211.

[3] Browning, *Amer. J. Sci.*, 1900, [iv.], **9**, 137; *Zeitsch. anorg. Chem.*, 1900, **23**, 155.

[4] Stortenbeker, *Rec. trav. chim.*, 1902, **21**, 87; 1905, **24**, 53; 1907, **26**, 248.

[5] Gossner, *Zeitsch. Kryst. Min.*, 1903, **38**, 158.

[6] Stortenbeker, *loc. cit.*

[7] R. Weber, *Ber.*, 1884, **17**, 2502, 2707.

[8] Strecker, *Annalen*, 1865, **135**, 207.

[9] See Marshall, *Proc. Roy. Soc. Edin.*, 1899, **22**, 596.

[10] Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5; Marshall, *loc. cit*

Acid thallic sulphate, $H_2SO_4.Tl_2(SO_4)_3.8H_2O$, crystallises out, according to Meyer and Goldschmidt, from a solution of thallic hydroxide in concentrated sulphuric acid.

The following double sulphates containing thallic sulphate are known :—[1]

$Rb_2SO_4.Tl_2(SO_4)_3$ (*a*, *c*)
$Na_2SO_4.Tl_2(SO_4)_3$ (*e*)
$(NH_4)_2SO_4.Tl_2(SO_4)_3$ (*a*, *c*)
$3(NH_4)_2SO_4.Tl_2(SO_4)_3$ (*a*)

$Cs_2SO_4.Tl_2(SO_4)_3.6H_2O$ (*b*)
$Cs_2SO_4.Tl_2(SO_4)_3.3H_2O$ (*b*)
$Rb_2SO_4.Tl_2(SO_4)_3.8H_2O$ (*a*, *c*, *d*)
$K_2SO_4.Tl_2(SO_4)_3.8H_2O$ (*a*, *c*, *d*)
$Na_2SO_4.Tl_2(SO_4)_3.5H_2O$ (*c*)
$Li_2SO_4.Tl_2(SO_4)_3.6H_2O$ (*c*)
$(NH_4)_2SO_4.Tl_2(SO_4)_3.8H_2O$ (*a*, *c*, *d*)

Further, Marshall has prepared the basic salt of the formula $Tl(OH)SO_4.K_2SO_4$. *Thallic ammonium sulphate*, $Tl_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$, crystallises in monoclinic prisms ($a:b:c=0{\cdot}9559:1:0{\cdot}6836$; $\beta=125° 38'$).[2]

No **alums** of thallic sulphate have yet been prepared, but Piccini and Fortini have prepared mixed crystals of ammonium alum and ammonium thallic alum.[3]

A number of **thallothallic sulphates** have been described. The simplest compound, $Tl_2SO_4.Tl_2(SO_4)_3$, separates from a sulphuric acid solution of the sulphates, mixed in the ratio of their molecular weights, in crystals which are said by Marshall to be probably orthorhombic.[4] Marshall has also prepared double sulphates of the formulæ $5Tl_2SO_4.Tl_2(SO_4)_3$ and $2Tl_2SO_4.Tl_2(SO_4)_3$, while Willm[5] has described a compound of the formula $2Tl_2SO_4.3Tl_2(SO_4)_3.22H_2O$.

By oxidising a solution of thallous sulphate with bromine and crystallising, Meyer and Goldschmidt have prepared *thallothallic bromosulphate*, $Tl_2Br_2SO_4$.

Thallous persulphate, $Tl_2S_2O_8$, prepared by double decomposition between ammonium persulphate and thallous sulphate, or by the electrolysis of thallous sulphate in a divided cell, forms monoclinic crystals isomorphous with the ammonium salt.[6] It is isomeric with thallothallic sulphate, $Tl_2SO_4.Tl_2(SO_4)_3$.

Thallous dithionate, $Tl_2S_2O_6$, is prepared in aqueous solution from barium dithionate and thallous sulphate in equivalent proportions. It crystallises in shining, monoclinic prisms ($a:b:c=0{\cdot}9292:1:0{\cdot}3986$; $\beta=96° 58'$) of density 5·573, and one gram of the salt at 18·5° dissolves in 2·39 grams of water.[7]

Potassium dithionate forms trigonal crystals, but with thallous dithionate it gives two series of mixed crystals, so that each salt is probably dimorphous.[8] Thallous dithionate is isomorphous and forms monoclinic mixed

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[1] (*a*) Marshall, *Proc. Roy. Soc. Edin.*, 1902, **24**, 305; (*b*) Locke, *Amer. Chem. J.*, 1902, **27**, 280; (*c*) R. J. Meyer and Goldschmidt, *Ber.*, 1903, **36**, 238; (*d*) Piccini and Fortini, *Zeitsch. anorg. Chem.*, 1902, **31**, 451; (*e*) Strecker, *loc. cit.*

[2] Panichi, *Gazzetta*, 1905, **35**, ii. 453.

[3] Piccini and Fortini, *Zeitsch. anorg. Chem.*, 1902, **31**, 451; Fortini, *Gazzetta*, 1905, **35**, ii. 450.

[4] *Cf.* Lepsius, *Chem. Zentr.*, 1891, i. 694.

[5] Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5; Abegg, *Anorganischen Chemie* (Leipzig, 1906), vol. iii., pt. 1, p. 446.

[6] Foster and E. Smith, *J. Amer. Chem. Soc.*, 1899, **21**, 934; Marshall, *ibid.*, 1900, **22**, 48.

[7] Klüss, *Annalen*, 1888, **246**, 179, 284; Fock, *Zeitsch. Kryst. Min.*, 1882, **6**, 160.

[8] Stortenbeker, *loc. cit.*

crystals with barium dithionate.[1] It also forms a triclinic, double salt with thallous sulphate, $3Tl_2S_2O_6.Tl_2SO_4$, and a monoclinic compound with thallous hydroxide, $Tl_2S_2O_6.TlOH.H_2O$.[2]

Thallous selenite, Tl_2SeO_3, prepared from thallous carbonate and selenious acid, forms micaceous crystals, soluble in water but insoluble in alcohol or ether. *Acid thallous selenite*, $TlHSeO_3$, is more soluble in water than the normal salt.[3]

Thallic selenite $Tl_2(SeO_3)_3$, may be obtained in white crystals by the action of selenious acid on thallic hydroxide.[4]

Thallous selenate, Tl_2SeO_4, may be prepared by neutralising selenic acid with thallous hydroxide or carbonate. It crystallises from water, in which it is not very soluble, in orthorhombic prisms ($a:b:c=0·5551:1:0·7243$) of density 6·875 at 20°, and is therefore isomorphous with potassium selenate ($a:b:c=0·5731:1:0·7319$). The mean refractive index, 1·9575 for the D-line, is very high, the value for potassium selenate being 1·5396.[5] The salt is insoluble in alcohol and ether; it melts above 400°.[6]

Thallous aluminium selenium alum, $Tl_2SeO_4.Al_2(SeO_4)_3.24H_2O$, is described on p. 87.

Of the double selenates that thallous selenate may be anticipated to form with the selenates of the bivalent metals, only the zinc salt, *thallous zinc selenate*, $Tl_2SeO_4.ZnSeO_4.6H_2O$, has been described. It forms monoclinic crystals ($a:b:c=0·7479:1:0·5022$; $\beta=105°\ 54'$) isomorphous with the corresponding double sulphates and with potassium zinc selenate ($a:b:c=0·7458:1:0·5073$; $\beta=104°\ 12'$).[7]

Thallic selenate, $Tl_2(SeO_4)_3$, has not been described, but *ammonium- and potassium-thallic selenates*, $(NH_4)_2SeO_4.Tl_2(SeO_4)_3.8H_2O$ and $K_2SeO_4.Tl_2(SeO_4)_3.8H_2O$, analogous to the double sulphates, are known.[8]

Thallous tellurate, Tl_2TeO_4, obtained from thallous oxide and telluric acid, is a white, amorphous, insoluble powder.[9]

Thallous chromate, Tl_2CrO_4, is precipitated when a solution of a thallous salt is mixed with potassium chromate. It is also produced by adding thallous hydroxide or carbonate to aqueous chromic acid, or by the action of ammonia on the dichromate. Thallous chromate is a yellow crystalline powder, very sparingly soluble in water, 100 grams of which dissolve 0·03 gram of the salt at 60° and 0·2 gram at 100°.[10] In hot, concentrated potassium hydroxide solution thallous chromate is fairly soluble, and it separates out on cooling in crystals which are apparently isomorphous with potassium chromate.[11] At a dull red heat the chromate melts, and at higher temperatures it loses oxygen.

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[1] Klüss, *loc. cit.*; Fock, *Zeitsch. Kryst. Min.*, 1888, **14**, 340; Stortenbeker, *loc. cit.*

[2] Wyrouboff, *Bull. Soc. franç. Min.*, 1884, **7**, 139; see also *ibid.*, 1882, **5**, 32.

[3] Kuhlmann, *Bull. Soc. chim.*, 1864, [ii.], **1**, 330.

[4] Marino, *Zeitsch. anorg. Chem.*, 1909, **62**, 173.

[5] Tutton, *Proc. Roy. Soc.*, 1907, **A**, **79**, 351; Kuhlmann, *loc. cit.*

[6] Glauser, *Zeitsch. anorg. Chem.*, 1910, **66**, 437.

[7] Tutton, *Proc. Roy. Soc.*, 1910, **A**, **83**, 211.

[8] Fortini, *L'Orosi*, 1902, **25**, 397.

[9] F. W. Clarke, *Amer. J. Sci.*, 1878, [iii.], **6**, 201; Dennis, Doan, and Gill, *J. Amer. Chem. Soc.*, 1896, **18**, 970.

[10] Browning and Hutchins, *Amer. J. Sci.*, 1899, [iv.], **8**, 460; *Zeitsch. anorg. Chem.*, 1900, **22**, 380.

[11] Lepierre and Lachaud, *Compt. rend.*, 1891, **113**, 196.

Thallous dichromate, $Tl_2Cr_2O_7$, is precipitated as an orange-red, crystalline powder when solutions of a soluble thallous salt and potassium dichromate are mixed (Crookes), and is also obtained by the action of sulphuric acid on the chromate (Willm).

Thallous trichromate, $Tl_2Cr_3O_{10}$, a red, crystalline, sparingly soluble salt, is obtained by the action of nitric acid on the dichromate, or of concentrated sulphuric acid on the chromate (Crookes; Willm).

Thallous chlorochromate, $CrO_2(OTl)Cl$, obtained from thallous chloride and chromic acid, forms small, prismatic crystals, decomposed by water.[1]

Thallic chromate, $Tl_2(CrO_4)_3$, has not yet been prepared, but *potassium thallic chromate,* $K_2CrO_4.Tl_2(CrO_4)_3.4H_2O$, is known as a yellow, crystalline salt, decomposed by water.[2]

Thallous molybdate, Tl_2MoO_4, is obtained as a white, sparingly soluble, crystalline solid by double decomposition, or by heating a solution of a thallous salt with molybdic acid. More complex molybdates of the formulæ $Tl_2O.11MoO_3$, $3Tl_2O.8MoO_3$, $Tl_2O.4MoO_3.H_2O$, and $5Tl_2O.12MoO_3$, have also been described.[3]

Thallous phosphomolybdate, $3Tl_2O.P_2O_5.20MoO_3$, has been described by Debray;[4] and **thallous silicomolybdate,** $2Tl_2O.SiO_2.13MoO_3.xH_2O$, by Parmentier.[5]

Thallous tungstate, Tl_2WO_4, is obtained by heating aqueous thallous carbonate with tungstic oxide, as a sparingly soluble, white, crystalline solid.[6]

Thallous phosphotungstate, $Tl_2O.P_2O_5.12WO_3.4H_2O$, has been described;[7] also **acid thallous silicotungstate,** $Tl_2O.H_2O(SiO_2.12WO_3).9H_2O$.[8]

Thallium uranates.[9]

THALLIUM AND THE NITROGEN GROUP.

Thallous azide (hydronitride, hydrazoate), TlN_3, is precipitated as a white, crystalline solid when solutions of thallous sulphate or nitrate and sodium azide are mixed. It is sparingly soluble in cold, more readily soluble in hot water, from which it separates on cooling in tetragonal needles ($a : c = 1 : 0{\cdot}5881$) isomorphous with the potassium and rubidium salts.[10] Thallous azide slowly turns brown in sunlight. It melts at 334° in an atmosphere of carbon dioxide, and is reduced to thallium when heated in hydrogen. When suddenly heated or subjected to shock, it explodes.[11]

Thallothallic azide, $TlN_3.Tl(N_3)_3$, separates in yellow, orthorhombic needles when thallic hydroxide is dissolved in aqueous hydrazoic acid and the solution evaporated in vacuum over sulphuric acid. It is very explosive.

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[1] Lepierre and Lachaud, *Compt. rend.*, 1891, **113**, 196.

[2] Hawley, *J. Amer. Chem. Soc.*, 1907, **29**, 300.

[3] Delafontaine, *Arch. Sci. phys. nat.*, 1867, **30**, 232; Flemming, *Jahresber.*, 1868, p. 250; Junius, *Zeitsch. anorg. Chem.*, 1905, **46**, 428; Wempe, *ibid.*, 1912, **78**, 298.

[4] Debray, *Compt. rend.*, 1868, **66**, 704.

[5] Parmentier, *Compt. rend.*, 1881, **92**, 1234.

[6] Flemming, *loc. cit.*; see also Schaefer, *Zeitsch. anorg. Chem.*, 1904, **38**, 142.

[7] Péchard, *Ann. Chim. Phys.*, 1891, [vi.], **22**, 187.

[8] Wyrouboff, *Bull. Soc. franç. Min.*, 1896, **19**, 219.

[9] Bolton, *Amer. Chemist*, 1872, **2**, 456.

[10] Rosenbusch, *Zeitsch. Kryst. Min.*, 1900, **33**, 99.

[11] Dennis, Doan, and Gill, *J. Amer. Chem. Soc.*, 1896, **18**, 970; Curtius and Rissom, *J. prakt. Chem.*, 1898, [ii.], **58**, 261.

Hot water decomposes the compound, thallic hydroxide being precipitated and thallous azide remaining in solution.[1]

Thallium nitride, Tl_3N, is obtained as a black precipitate when liquid ammonia solutions of thallous nitrate and potassium amide are mixed:—

$$3TlNO_3 + 3KNH_2 = Tl_3N + 3KNO_3 + 2NH_3.$$

It dissolves in a liquid ammonia solution of ammonium nitrate, re-forming thallous nitrate:—

$$Tl_3N + 3NH_4.NO_3 = 3TlNO_3 + 4NH_3,$$

and also dissolves when excess of potassium amide is added. The latter solution when evaporated at − 40° deposits yellow crystals of potassium amide and *dipotassium ammonothallite*, $TlNK_2.4NH_3$, a compound which dissociates at 20° in vacuum, leaving the *compound* $TlNK_2.2NH_3$.[2]

Thallium phosphide.—According to Lamy, thallium and phosphorus combine when heated, but no definite compound has yet been isolated.[3]

Thallium arsenide.—When thallium and arsenic in atomic proportions are heated together, a white, soft, crystalline mass is obtained, which is decomposed by cold acids, arsine being evolved.[4]

Thallium antimonide resembles the arsenide and is prepared in a similar manner.[5]

Thallous nitrite, $TlNO_2$, is prepared by mixing solutions of thallous sulphate and barium nitrite, filtering, evaporating the filtrate in vacuum, and adding alcohol. It forms orange-red crystals. The concentrated aqueous solution is yellow, but dilute solutions are nearly colourless. The dry salt has a low melting-point; it is unchanged at 140°, but at higher temperatures decomposes into thallous oxide and oxides of nitrogen, its stability being much inferior to that of the alkali nitrites.[6]

Triple nitrites containing thallium are known.[7]

Thallous nitrate, $TlNO_3$.—Thallium dissolves readily in nitric acid; and by dissolving the metal, thallous oxide, hydroxide, or carbonate in nitric acid, a solution of thallous nitrate is obtained from which the salt crystallises in the anhydrous state in orthorhombic prisms ($a : b : c = 0·5109 : 1 : 0·6507$) of density 5·55.[8] At 72·8° the rhombic substance changes into a rhombohedral form, which at 142·5° changes to a cubic modification; and this, at 205°, melts.[9] On cooling, the reverse changes take place. The transition at 72·8° is a very slow process. At temperatures above 300° decomposition of the nitrate takes place; it is rapid at 450°, crystalline thallic oxide being left, and oxygen, nitrogen, and oxides of nitrogen being evolved.[10] A little of the nitrate volatilises unchanged.

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[1] Dennis, Doan, and Gill, *loc. cit.*

[2] Franklin, *J. Physical Chem.*, 1912, **16**, 682.

[3] Willm; Carstanjen; Flemming, *Jahresber.*, 1868, p. 250.

[4] Carstanjen, *J. prakt. Chem.*, 1867, **102**, 65, 129.

[5] Carstanjen, *loc. cit.*; Omodei, *Jahresber.*, 1892, p. 158.

[6] Vogel, *Zeitsch. anorg. Chem.*, 1903, **35**, 403; Thomas, *Compt. rend.*, 1904, **138**, 1697; Ball and Abram, *Trans. Chem. Soc.*, 1913, **103**, 2132.

[7] Przibylla, *Zeitsch. anorg. Chem.*, 1898, **18**, 448; Ball and Abram, *Trans. Chem. Soc.*, 1913, **103**, 2116.

[8] Lamy, *Ann. Chim. Phys.*, 1863, [iii.], **67**, 385; Lamy and Descloizeaux, *ibid.*, 1869, [iv.], **17**, 310; Miller, *Proc. Roy. Soc.*, 1865, **14**, 555.

[9] Van Eyk, *Zeitsch. physikal. Chem.*, 1905, **51**, 721; 1899, **30**, 430; Gossner, *Zeitsch. Kryst. Min.*, 1903, **38**, 110; Retgers. *Jahrb. Min.*, 1896, ii. 183.

[10] Thomas, *Compt. rend.*, 1904, **138**, 1697.

Thallous nitrate is insoluble in alcohol. Its solubility in water is given in the following table :—[1]

t °C.	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	105°
a	3·76	5·86	8·72	12·51	17·33	23·33	31·55	41·01	52·60	66·66	80·54	85·59
b	3·91	6·22	9·55	14·3	20·9	30·4	46·2	69·5	111·0	200·0	414·0	594·0

A saturated solution in contact with excess of the salt boils at 105°.

Mixtures of molten thallous nitrate and silver, mercurous, or mercuric nitrate are useful liquids in which to effect the separation of minerals by density differences. The following melting-points and densities are due to Retgers :—[2]

Composition of salt .	$TlNO_3$	$TlAg(NO_3)_2$	$TlHg(NO_3)_2$	$Tl_2Hg(NO_2)_4$
Density of liquid .	5·3	4·8	5·3	5·0
Melting-point °C. .	205°	70°	76°	110°

When thallous nitrate is dissolved in cold nitric acid (density, 1·5) and the solution is cooled below 0° C. **acid thallous nitrate,** $TlNO_3.2HNO_3$, crystallises out. The compound melts below the ordinary temperature.[3]

With *sodium nitrate,* thallous nitrate forms neither a compound nor mixed crystals.[4]

From a study of the crystals deposited from a solution containing both *potassium nitrate* and thallous nitrate, it has been concluded that these two salts are isodimorphous.[5] The fusion curve indicates that two series of solid solutions separate out. The series containing excess of thallous salt is cubic, the other series being rhombohedral. These mixed crystals are transformed at lower temperatures into other crystalline modifications, and the various regions of stability are indicated in the diagram (fig. 18).[6]

Rubidium nitrate, and also *cæsium nitrate,* forms a continuous series of cubic mixed crystals with thallous nitrate. The cubic crystals become rhombohedral at lower temperatures, and those with a very high thallium content become orthorhombic at still lower temperatures. Cubic crystals always separate from the fused mixtures, except those very rich in rubidium, which crystallise first in rhombohedral crystals different from those already mentioned.[7]

Ammonium nitrate forms a continuous (?) series of cubic mixed crystals with thallous nitrate. These crystals separate from fused mixtures of the nitrate on cooling. Two other series of mixed crystals are stable at lower temperatures.[8]

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[1] Earl of Berkeley, *Phil. Trans.*, 1904, A, **203**; Étard, *Ann. Chim. Phys.*, 1894, [vii.], **2**, 527; Seidell, *Solubilities* (Crosby Lockwood & Son, 1907), p. 337. In table given, a = grams $TlNO_3$ per 100 grams of solution, and b = grams $TlNO_3$ per 100 grams of water.

[2] Retgers, *Jahrb. Min.*, 1893, i. 90; 1896, ii. 183; Penfield and Kreider, *Amer. J. Sci.*, 1894, [iii.], **48**, 141.

[3] H. L. Wells and Metzger, *Amer. Chem. J.*, 1901, **26**, 271; *cf.* Ditte, *Compt. rend.*, 1879, **89**, 576, 641.

[4] Van Eyk, *Zeitsch. physikal. Chem.*, 1905, **51**, 721; *Chem. News*, 1905, **91**, 295.

[5] Fock, *Zeitsch. Kryst. Min.*, 1880, **4**, 583; 1897, **28**, 337.

[6] Van Eyk, *Proc. K. Akad. Wetensch. Amsterdam*, 1899, **1**, 229; *Zeitsch. physikal. Chem.*, 1899, **30**, 430; 1905, **51**, 721; *Chem. News*, 1905, **91**, 295. See also Wallerant, *Bull. Soc. franç. Min.*, 1905, **28**, 311; Gossner, *Zeitsch. Kryst. Min.*, 1903, **38**, 110; Stortenbeker, *Zeitsch. physikal. Chem.*, 1903, **43**, 629.

[7] Wallerant, *loc. cit.*

[8] Wallerant, *loc. cit.*; *Compt. rend.*, 1905, **140**, 1045.

Silver nitrate forms no mixed crystals with thallous nitrate, but forms a *compound*, $TlNO_3.AgNO_3$, which melts at 82·8°, and only separates as the initial solid phase from fused mixtures containing 48 to 52 molecules per cent. of thallous nitrate.[1]

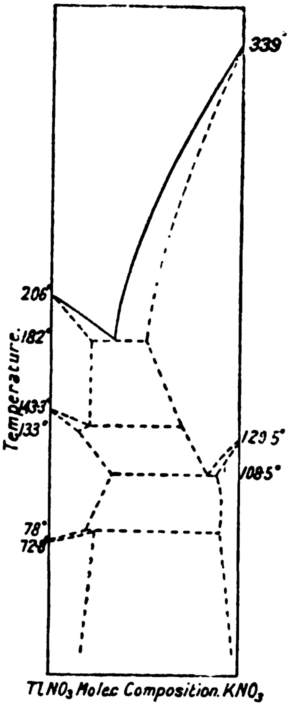

Fig. 18.—Equilibrium diagram for the system thallous nitrate—potassium nitrate.

One or two other double nitrates are known.[2]

Thallic nitrate, $Tl(NO_3)_3$, is prepared by dissolving thallic oxide in nitric acid. It separates from an acid solution in large, colourless, transparent, deliquescent crystals which contain $3H_2O$.[3] The salt is readily hydrolysed by water, and is easily decomposed by heat.

The double salt *potassium thallic nitrate*, $K_2Tl(NO_3)_5.H_2O$, readily crystallises from a solution of the mixed nitrates in nitric acid (R. J. Meyer).

Thallothallic nitrate, $Tl(NO_3)_3.2TlNO_3$, is readily obtained by dissolving thallous nitrate in warm nitric acid of density 1·50. The double salt separates in prisms, melts at 150°, and is stable in dry air.[4]

Thallous hypophosphite, TlH_2PO_2, is a sparingly soluble salt which crystallises in rhombic bipyramids ($a : b : c = 0{\cdot}786 : 1 : 0{\cdot}806$). It melts at 150°, and at higher temperatures decomposes, evolving phosphine and leaving a residue of thallous meta- and pyro-phosphates.[5]

Thallous hypophosphate, $Tl_4P_2O_6$, from thallous carbonate and hypo-phosphoric acid, is a sparingly soluble salt, which turns blue when exposed to light, and decomposes at 250° into thallium and thallium metaphosphate.

The **acid hypophosphate**, $Tl_2H_2P_2O_6$, prepared from the acid barium salt and thallous sulphate, forms monoclinic crystals, slightly soluble in cold, more readily in hot water. It melts at 200° and evolves phosphine at higher temperatures.[6]

Trithallous orthophosphate, Tl_3PO_4, is obtained by adding excess of thallous carbonate to phosphoric acid, by mixing thallous sulphate and disodium hydrogen phosphate and adding a little ammonia, or by fusing thallium metaphosphate with two molecular proportions of sodium carbonate. It crystallises in long, colourless, anhydrous needles of density 6·89, and melts at a red heat. One litre of a saturated aqueous solution contains 4·97 grams of the phosphate at 15° and 6·71 at 100°. The phosphate is insoluble

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[1] Van Eyk, *Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 480; *Zeitsch. physikal. Chem.*, 1905, **51**, 721; *Chem. News*, 1905, **91**, 295.

[2] See p. 268, and R. J. Meyer and Wendel, *Ber.*, 1903, **36**, 4055.

[3] Strecker, *Annalen*, 1865, **135**, 207; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1900, **24**, 321. Willm gave $4H_2O$ instead of $3H_2O$.

[4] Wells and Beardsley, *Amer. Chem. J.*, 1901, **26**, 275.

[5] Rammelsberg, *Ber.*, 1872, **5**, 492.

[6] Joly, *Compt. rend.*, 1894, **118**, 649; Rammelsberg, *J. prakt. Chem.*, 1892, [ii.], **45**, 156.

in alcohol, but dissolves readily in aqueous solutions of ammonium salts. The aqueous solution has an alkaline reaction.[1]

Dithallous hydrogen phosphate, $Tl_2HPO_4.H_2O$, may be prepared by neutralising a boiling solution of phosphoric acid with thallous carbonate, evaporating the liquid to a syrup, and allowing it to crystallise. The crystals are orthorhombic ($a : b : c = 0·934 : 1 : 0·657$) and isomorphous with sodium dihydrogen phosphate, $NaH_2PO_4.H_2O$.[2] The anhydrous salt has a density of 1·779.[3]

Thallous dihydrogen phosphate, TlH_2PO_4, is obtained by adding phosphoric acid to a solution of the foregoing salt and crystallising the solution. It crystallises in pearly plates or long needles, which are monoclinic ($a : b : c = 3·175 : 1 : 1·458$; $\beta = 91° 44'$) and isomorphous with di-ammonium hydrogen phosphate, $(NH_4)_2HPO_4$. The salt melts at 190°; its density is 4·723. The aqueous solution has an acid reaction.[4] According to Lamy and Descloizeaux, there exists a double salt of the formula $Tl_2HPO_4.2TlH_2PO_4$.

Thallous pyrophosphate, $Tl_4P_2O_7$, is prepared by heating dithallium hydrogen phosphate to dull redness. It dissolves in water (with the separation of some insoluble white powder), and on evaporating the solution, beautiful, lustrous monoclinic crystals ($a : b : c = 1·427 : 1 : 1·2921$; $\beta = 114° 0'$) of the anhydrous pyrophosphate separate. On standing, the mother liquor deposits monoclinic crystals ($a : b : c = 2·1022 : 1 : 1·9217$; $\beta = 114° 57'$) of the dihydrate, $Tl_4P_2O_7.2H_2O$. The density of the anhydrous salt is 6·786.[5]

An **acid pyrophosphate,** $Tl_2H_2P_2O_7$, is obtained by heating dihydrogen thallium phosphate to 240°. It is readily soluble in water, from which it crystallises in small, short prisms, melts at 270°, and is converted into the metaphosphate at a red heat.[6]

Thallous metaphosphate, $TlPO_3$, is obtained as a white solid, sparingly soluble in water, by heating dihydrogen thallium phosphate to redness. A more soluble modification is said to be formed by heating di-ammonium thallium phosphate.[7]

Thallous thiophosphate, Tl_3PS_4, prepared by heating thallous sulphide with phosphorus pentasulphide, is a yellow, crystalline solid, insoluble in water, alcohol, ether, benzene, and carbon disulphide.[8]

Thallic orthophosphate, $TlPO_4.2H_2O$, is said by Willm to be obtained by adding phosphoric acid to concentrated thallic nitrate solution, and then adding water. It is described as a white, very sparingly soluble substance, readily hydrolysed by boiling water.[9]

Thallous orthoarsenite, Tl_3AsO_3, is a yellow, crystalline solid, sparingly soluble in water, obtained by boiling a solution of thallous sulphate with potassium arsenite and a little potassium hydroxide.[10]

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[1] Crookes; Willm; Lamy, *Ann. Chim. Phys.*, 1865, [iv.], 5, 410; *Bull. Soc. chim.*, 1869, [ii.], 11, 210; Rammelsberg, *Ber.*, 1870, 3, 276; 1882, 15, 2228; *Pogg. Annalen*, 1872, 146, 592.

[2] Rammelsberg, *loc. cit.*; Lamy, *loc. cit.*; Lamy and Descloizeaux, *Ann. Chim. Phys.*, 1869, [iv.], 17, 310.

[3] Schröder, *Ber.*, 1874, 7, 676.

[4] Rammelsberg, *loc. cit.*; Lamy and Descloizeaux, *loc. cit.*

[5] Lamy, *loc. cit.*; Lamy and Descloizeaux, *loc. cit.*

[6] Lamy, *loc. cit.*; Brand, *Zeitsch. anal. Chem.*, 1889, 28, 595.

[7] Lamy, *loc. cit.*

[8] Glatzel, *Zeitsch. anorg. Chem.*, 1893, 4, 186.

[9] Willm, *Ann. Chim. Phys.*, 1865, [iv.], 5, 5; Strecker, *Annalen*, 1865, 135, 207.

[10] Stavenhagen, *J. prakt. Chem.*, 1895, [ii.], 51, 1.

Trithallous orthoarsenate, Tl_3AsO_4, is obtained as a white, crystalline precipitate by adding ammonia to an aqueous solution of thallium dihydrogen arsenate.[1]

Dithallous hydrogen arsenate, Tl_2HAsO_4, is obtained by neutralising a boiling solution of arsenic acid with thallous carbonate and cooling the solution.[1] It forms long, transparent needles, readily soluble in water. When strongly heated it gives off water, and then decomposes, leaving a black residue of thallic oxide (Lamy).

Thallous dihydrogen arsenate, TlH_2AsO_4, was prepared by Willm by boiling a solution of arsenious acid with thallic oxide, concentrating, and crystallising. It forms glittering, colourless needles and is readily soluble in water.[1]

Thallic orthoarsenate, $TlAsO_4.2H_2O$, has been described by Willm.[1]

Thallous metantimonate, $TlSbO_3.2H_2O$ has been described by Beilstein and Bläse.[2]

Thallous vanadates (see Vol. VI. of this series).

THALLIUM AND THE CARBON GROUP.

Thallous carbonate, Tl_2CO_3, is obtained by passing carbon dioxide into thallous hydroxide solution, by exposing granulated thallium to warm air for some time and then heating it with ammonium carbonate solution, or by shaking and heating barium carbonate with thallous sulphate solution. The carbonate crystallises from water in colourless, glittering, monoclinic prisms ($a : b : c = 1{\cdot}3956 : 1 : 1{\cdot}9586$; $\beta = 94° \ 47'$) of specific gravity 7·164,[3] melts at 273°,[4] and at high temperatures loses carbon dioxide. The carbonate is insoluble in alcohol; 100 grams of water dissolve the following amounts of the salt (Lamy, Crookes):—

Temperature, °C.	15·5°	18°	62°	100·8°
Grams of Tl_2CO_3	4·02	5·23	12·9	22·4

The solution has a caustic taste and an alkaline reaction.

An **acid carbonate** is not known in the pure state, in spite of various attempts to prepare it.[5] A basic carbonate has been described.[6]

Thallous cyanide, TlCN, may be obtained by adding thallous hydroxide to prussic acid, or by mixing concentrated solutions of thallous nitrate and potassium cyanide, when thallous cyanide is precipitated.[7] It is best prepared from barium cyanide and thallous sulphate. It crystallises from water, in which it is not very soluble, in glittering plates. When heated it decrepitates, melts, and decomposes.

One hundred grams of water dissolve 8·67 at 0°, 15·17 at 14°, and 29·57 grams at 31°, of thallous cyanide. The solution reacts alkaline and smells of prussic acid. The cyanide is soluble in alcohol, but very sparingly soluble

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[1] Willm, *loc. cit.*

[2] Beilstein and Bläse, *Chem. Zentr.*, 1889, 803.

[3] Lamy and Descloizeaux, *Ann. Chim. Phys.*, 1869, [iv.], **17**, 310; Miller, *Proc. Roy. Soc.*, 1865, **14**, 555.

[4] Carnelley, *Trans. Chem. Soc.*, 1878, **33**, 273.

[5] Carstanjen, *J. prakt. Chem.*, 1867, **102**, 65, 129; Giorgis, *Gazzetta*, 1894, **24**, ii. 474; *Atti R. Accad. Lincei*, 1894, [v.], **3**, ii. 104.

[6] Wyrouboff, *Bull. Soc. franç. Min.*, 1889, **12**, 536,

[7] Crookes; Kuhlmann, *Compt. rend.*, 1862, **55**, 607.

in a mixture of alcohol and ether. It dissolves in aqueous potassium cyanide, forming soluble *potassium thallium cyanide*, and forms numerous double and complex cyanides with other cyanides.[1]

Thallothallic cyanide, $TlCN.Tl(CN)_3$, is prepared by dissolving thallic oxide in aqueous prussic acid, and crystallises from the solution in colourless, orthorhombic crystals. One hundred grams of water dissolve 9·75, 15·29, and 27·31 of the salt at 0°, 12°, and 30° respectively, giving a neutral solution in which the salt is probably dissociated into the ions $Tl^{\cdot}$ and $Tl(CN)_4'$.[2] From the cold, aqueous solution, alkalies precipitate thallic hydroxide, but no precipitate is produced by ammonia. At 125° to 130° the salt melts and decomposes.[3]

Thallous cyanate, $TlCNO$, precipitated in small, glittering crystals by mixing alcoholic solutions of thallous acetate and potassium cyanate, is very soluble in water.[4]

Thallous thiocyanate, $TlCNS$, is precipitated as small, white, tetragonal crystals ($a : c = 1 : 0·5593$) when aqueous solutions of thallous nitrate and potassium thiocyanate are mixed.[5] One hundred grams of water dissolve 0·316, 0·392, and 0·732 grams of the salt at 19·94°, 25°, and 39·75° respectively.[6]

The double salt, $TlCNS.KCNS$, crystallises from a solution of thallous and potassium thiocyanates.[7] The compound, $Tl_2Pt(CNS)_6.9NH_3$, is also known.[8]

Thallous oxalate, $Tl_2C_2O_4$, prepared from thallous carbonate and oxalic acid, crystallises from boiling water, in which it is not very soluble, in small, pearly, monoclinic prisms ($a : b : c = 1·1384 : 1 : 2·2405$; $\beta = 99° 13'$) of density 6·31. One litre of a saturated aqueous solution of the salt contains 15·77 grams of the oxalate at 20°, and 18·69 at 25°.[9] **Thallium hydrogen oxalate,** $TlHC_2O_4$, also crystallises in monoclinic prisms.

Thallic oxalate, $Tl_2(C_2O_4)_3$, is precipitated when alcoholic solutions of thallic formate and oxalic acid are mixed. It is not very stable. **Thallic hydrogen oxalate,** $TlH(C_2O_4)_2.3H_2O$, is readily obtained as a white, sparingly soluble, crystalline powder, by the action of aqueous oxalic acid at 25° on thallic hydroxide or an acetic acid solution of thallic acetate. The corresponding potassium and ammonium salts may be obtained by precipitating acid solutions of thallic salts with potassium and ammonium oxalate respectively. More complex oxalates are also known, and also **thallothallic oxalate,** $Tl_2(C_2O_4)_2.3H_2O$.[10]

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[1] Fronmüller, *Ber.*, 1873, 6, 1178; 1878, 11, 91; Fischer and Benzian, *Chem. Zeit.*, 1902, 26, 49; Cunningham and F. M. Perkin, *Trans. Chem. Soc.*, 1909, 95, 1569. For *ferro-*, *ferri-*, and *cobalt-cyanides*, see Vol. IX.

[2] Goldschmidt, *Inaugural Dissertation* (Berlin, 1903).

[3] Fronmüller, *loc. cit.*

[4] Kuhlmann, *Compt. rend.*, 1862, 55, 607.

[5] Miller, *Proc. Roy. Soc.*, 1865, 14, 555; *Phil. Mag.*, 1866, [iv.], 31, 153.

[6] Böttger, *Zeitsch. physikal. Chem.*, 1903, 46, 602; A. A. Noyes, *ibid.*, 1890, 6, 249; Noyes and Abbot, *ibid.*, 1895, 16, 132.

[7] Carstanjen, *J. prakt. Chem.*, 1867, 102, 65, 129.

[8] Peters, *Zeitsch. anorg. Chem.*, 1912, 77, 137.

[9] Lamy and Descloizeaux, *Ann. Chim. Phys.*, 1869, [iv.], 17, 310; Abegg and Spencer, *Zeitsch. anorg. Chem.*, 1905, 46, 406.

[10] Rabe and Steinmetz, *Ber.*, 1902, 35, 4447; *Zeitsch. anorg. Chem.*, 1903, 37, 88; R. J. Meyer and Goldschmidt, *Ber.*, 1903, 36, 238; Abegg and Spencer, *Zeitsch. anorg. Chem.*, 1905, 44, 379; 46, 406; Abegg and Schaefer, *ibid.*, 1905, 45, 293; Strecker, *Annalen*, 1865, 135, 207.

Thallium alkyl compounds.—Thallium compounds analogous to the aluminium tri-alkyls have not yet been prepared, but numerous compounds of the type $Tl(Alkyl)_2X$ are known. They must be looked upon as binary electrolytes, which dissociate thus:—

$$Tl(Alkyl)_2X \rightleftharpoons Tl(Alkyl)_2{}^{\cdot} + X',$$

a view in accordance with the conductivities of their solutions, and with the fact that they are quite stable towards boiling aqueous ammonia and alkali hydroxides.

The thallium alkyl chlorides are readily prepared by the general reaction:—

$$TlCl_3 + 2Mg.Alkyl.Cl = Tl(Alkyl)_2Cl + 2MgCl_2,$$

the reagents being mixed in dry ethereal solution. The bromides, iodides, carbonates, etc., may then be prepared by double decomposition. The salts crystallise well, and are only sparingly soluble in water. The hydroxides are strong bases, and readily absorb carbon dioxide. The alkyl compounds thus bear a great resemblance to the thallous compounds.[1]

Thallous Alcoholates.—Anhydrous thallous oxide dissolves in absolute alcohol, producing an alcoholic solution of **thallous ethoxide**, $C_2H_5.O.Tl$. A better method of preparation consists in suspending very thin thallium foil over absolute alcohol in an apparatus through which pure, dry oxygen is slowly passed. Even at ordinary temperatures the thallium rapidly disappears. The alcoholic solution thus obtained is heated to 100° to remove excess of alcohol, and thallous ethoxide is thereby obtained as a yellow, oily liquid. The density of the liquid is 3·522 at 20°, and 3·562 at 0°, so that it is an extremely heavy liquid. The refractive index for sodium light, 1·6826 at 20°, is also very high. Thallous ethoxide is readily hydrolysed by water to thallous hydroxide and ethyl alcohol. The corresponding **amyl** derivative is an oily liquid, but the **methyl** compound is a solid the specific gravity of which is about five.[2]

Thallous acetylacetonate, $(CH_3.CO)_2CH.Tl$, prepared by heating thallous hydroxide with an alcoholic solution of acetylacetone, crystallises in flat, colourless needles, and melts with decomposition at 153°–160°.[3]

Other organic derivatives containing thallium cannot be described here, but the appended references to the literature may be of use.[4]

Thallous Silicates.—Thallous oxide or carbonate reacts with silicic acid after the manner of the corresponding sodium and potassium compounds.[5] A crystalline silicate of the composition $3Tl_2O.2SiO_2.H_2O$ has been described by Wyrouboff.[6]

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[1] R. J. Meyer and Bertheim, *Ber.*, 1904, **37**, 2051; Shukoff, *Ber.*, 1905, **38**, 2691; Hansen, *Ber.*, 1870, **3**, 9; Hartwig, *Ber.*, 1874, **7**, 298; *Annalen*, 1875, **176**, 257; Carius and Fronmüller, *Ber.*, 1874, **7**, 302.

[2] Lamy, *Ann. Chim. Phys.*, 1864, [iv.], **3**, 373; Kahlbaum, Roth, and Siedler, *Zeitsch. anorg. Chem.*, 1902, **29**, 177.

[3] Kurowski, *Ber.*, 1910, **43**, 1078; Morgan and Moss, *Trans. Chem. Soc.*, 1914, **105**, 189.

[4] Kuhlmann, *Compt. rend.*, 1862, **56**, 607; *Ann. Chim. Phys.*, 1863, [iii.], **67**, 431; *Bull. Soc. chim.*, 1864, [ii.], **1**, 330; de la Provostaye, *Compt. rend.*, 1862, **55**, 610; Crookes, *Chem. News*, 1864, **9**, 1; *J. Chem. Soc.*, 1864, **17**, 112; Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5; Lamy and Descloizeaux, *ibid.*, 1869, [iv.], **17**, 310; Lescœur, *Bull. Soc. chim.*, 1875, **24**, 516; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1900, **24**, 321; Rabe and Steinmetz, *ibid.*, 1903, **37**, 88; Hawley, *J. Amer. Chem. Soc.*, 1907, **29**, 300.

[5] Flemming, *Jahresber.*, 1868, p. 250.

[6] Wyrouboff, *Bull. Soc. franç. Min.*, 1889, **12**, 536.

Thallium enters into the composition of various kinds of optical glass of high refractive index. High refractive power is a general characteristic of thallium salts (pp. 189, 190, 192, 200).

Thallous silicofluoride, Tl_2SiF_6, is prepared from thallous carbonate and hydrofluosilicic acid, and crystallises from aqueous solution in colourless octahedra. According to Kuhlmann, the salt is volatile without decomposition, and crystallises from aqueous solution in hydrated form.[1]

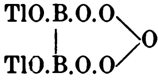
THALLIUM AND BORON.

Thallous Borates.—Thallous oxide dissolves in fused boron sesqui-oxide, and the liquid mass solidifies either to a clear glass or a crystalline solid.[2] Various borates of thallium have been described by Buchtala.[3]

Thallous tetraborate, $Tl_2B_4O_7.2H_2O$, is obtained by dissolving thallous carbonate (1 mol.) and boric acid (1–4 mols.) in water, and crystallising. It is also obtained, together with **thallous hexaborate,** $Tl_2B_6O_{10}.3H_2O$, by fusing the carbonate (1 mol.) with boric acid (6 mols.) and crystallising the product from water. If more boric acid (8 mols.) is used, a mixture of the hexaborate and **thallous decaborate,** $Tl_2B_{10}O_{16}.8H_2O$, is produced.

Thallous octaborate, $Tl_2B_8O_{13}.4H_2O$, and **thallous dodecaborate,** $Tl_2B_{12}O_{19}.7H_2O$, are prepared by dissolving thallous carbonate (1 mol.) in excess of aqueous boric acid (10 mols.). The dodecaborate also forms a pentahydrate, which is monoclinic ($a : b : c = 1{\cdot}583 : 1 : 1{\cdot}955$; $\beta = 94° 25'$).[4]

Thallous metaborate, $2TlBO_2.H_2O$, crystallises from water in colourless, wedge-shaped crystals which turn red and black on exposure to air.

Thallous perborate,[3] $Tl_2B_2O_7$, *i.e.* 

$$\begin{matrix} TlO.B.O.O \\ | \\ TlO.B.O.O \end{matrix}\Big\rangle O$$

is obtained as a white powder by adding 30 per cent. hydrogen peroxide to an aqueous solution of any of the preceding borates. It shows the usual reactions of a per-salt and explodes when rapidly heated. The aqueous solution decomposes on evaporation, thallous metaborate being produced.

DETECTION AND ESTIMATION OF THALLIUM.

The compounds of thallium impart a green colour to the Bunsen flame, and spectroscopic examination of the flame reveals the green line λ 5350·7. Thallium compounds are poisonous.

The following are the chief reactions of *thallous* salts:—(i.) Hydrogen sulphide incompletely precipitates thallium as the brown sulphide, insoluble in acetic acid. In the presence of mineral acid no precipitate is obtained. (ii.) Ammonium sulphide leads to complete precipitation of the thallium as sulphide. (iii.) Hydrochloric acid or a soluble chloride precipitates the thallium almost completely as white thallous chloride. (iv.) A soluble iodide precipitates thallium completely as yellow thallous iodide. (v.) Potassium

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[1] Kuhlmann, *Bull. Soc. chim.*, 1864, [ii.], **1**, 330; *Compt. rend.*, 1864, **58**, 1037; Werther, *J. prakt. Chem.*, 1864, **92**, 128.

[2] Guertler, *Zeitsch. anorg. Chem.*, 1904, **40**, 225.

[3] Buchtala, *J. prakt. Chem.*, 1913 [ii.], **88**, 771.

[4] Scharizer, *Zeitsch. Kryst. Min.*, 1914 **54**, 232.

chromate in neutral or ammoniacal solution precipitates thallium quantitatively as the yellow chromate. (vi.) Chloroplatinic acid precipitates thallium quantitatively as yellow thallous chloroplatinate. (vii.) Sodium cobaltinitrite precipitates thallium quantitatively as scarlet thallous cobaltinitrite.[1] (viii.) Potassium iodide and antimony trichloride lead to the precipitation of orange-red thallous antimonious iodide, $3TlI,2SbI_3$.[2]

Thallic salts give a brown precipitate of $Tl(OH)_3$ with alkali (including ammonium) hydroxides, insoluble in excess of reagent. With a soluble iodide they give thallous iodide and iodine. Alkali chloride or chromate produces no precipitate.

The detection of thallium in qualitative analysis has been studied by A. A. Noyes, Bray, and Spear, to whose work the reader is referred for details.[3]

The gravimetric estimation of thallium is somewhat difficult, since its "insoluble" salts usually have a perceptible solubility, are difficult to wash, and are distinctly volatile at high temperatures. The usual method is to precipitate as thallous iodide at 80° to 90°, wash with 80 per cent. alcohol, dry at 170°, and weigh.[4] Thallium may also be estimated as thallous chloroplatinate, 1 part of which dissolves in 15,600 of water at 15°, and in 1950 at 100°.[5] It may be precipitated and weighed as thallous chromate;[6] or by evaporation with sulphuric acid it may be converted into either thallous hydrogen sulphate at 220° to 230° or thallous sulphate at a dull red heat.[7] Thallium may also be precipitated as thallous thiostannate, Tl_4SnS_4, dried at 105°, and weighed.[8] Thallous salts may be oxidised to thallic salts with bromauric acid, and estimated by weighing the precipitated gold.[9]

The electrolytic determination of thallium is not a very accurate or convenient process, and is best effected by depositing the thallium into a mercury cathode, or, better, a dilute zinc or cadmium amalgam.[10]

Several volumetric methods for the estimation of thallium have been proposed. Thallous salts in the presence of hydrochloric acid may be oxidised to thallic salts by standard permanganate;[11] or they may be heated with potassium bromide, dilute hydrochloric acid, and an excess of standard

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[1] Cunningham and Perkin, *Trans. Chem. Soc.*, 1909, **95**, 1569; Tanatar and Petroff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 94.

[2] Ephraim, *Zeitsch. anorg. Chem.*, 1908, **58**, 353.

[3] A. A. Noyes, Bray, and Spear, *J. Amer. Chem. Soc.*, 1908, **30**, 481; *Chem. News*, 1908, **98**, 6, etc.; see also Sorby, *Chem. News*, 1869, **19**, 309; Ross, *Chem. Zentr.*, 1882, p. 54; Behrens, *Zeitsch. anal. Chem.*, 1891, **30**, 138; Chapman, *Phil. Mag.*, 1876, [v.], **2**, 397; Phipson, *Compt. rend.*, 1874, **78**, 563.

[4] Baubigny, *Compt. rend.*, 1891, **113**, 544; Werther, *Zeitsch. anal. Chem.*, 1864, **3**, 1; Long, *ibid.*, 1891, **30**, 342; Hebberling, *Annalen*, 1865, **134**, 11.

[5] Crookes, *Chem. News*, 1864, **9**, 1; Neumann, *Annalen*, 1888, **244**, 349; Cushman, *Amer. Chem. J.*, 1900, **24**, 222.

[6] Browning and Hutchins, *Amer. J. Sci.*, 1899, [iv.], 8, 460; *Chem. News*, 1899, **80**, 286.

[7] Browning, *Amer. J. Sci.*, 1900, [iv.], **9**, 137; *Zeitsch. anorg. Chem.*, 1900, **23**, 155.

[8] Hawley, *J. Amer. Chem. Soc.*, 1907, **29**, 1011.

[9] Thomas, *Compt. rend.*, 1900, **130**, 1316; *Bull. Soc. chim.*, 1902, [iii.], **27**, 470; *Ann. Chim. Phys.*, 1907, [viii.], **11**, 204.

[10] Morden, *J. Amer. Chem. Soc.*, 1909, **31**, 1045; *cf.* Neumann, *Ber.*, 1888, **21**, 356; Schucht, *Zeitsch. anal. Chem.*, 1883, **22**, 241; Heiberg, *Zeitsch. anorg. Chem.*, 1903, **35**, 347.

[11] Willm, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 5; Hawley, *J. Amer. Chem. Soc.*, 1907, **29**, 300; A. A. Noyes, *Zeitsch. physikal. Chem.*, 1892, **9**, 603.

potassium bromate, the bromine distilled into potassium iodide and the liberated iodine titrated with thiosulphate.[1] The iodine found is a measure of the oxidising power of the bromate present in excess of that required for the reaction :—

$$3TlCl + NaBrO_3 + 6HCl = 3TlCl_3 + NaBr + 3H_2O.$$

Lead is readily separated from thallium either by precipitation as the sulphide in dilute mineral acid solution, or by evaporation with sulphuric acid to remove the lead as the insoluble sulphate.[2] Silver may be separated from thallium by passing a rapid stream of chlorine through the solution. The silver is precipitated as chloride, the thallium remaining in solution as thallic chloride.[3]

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[1] Marshall, *J. Soc. Chem. Ind.*, 1900, **19**, 994. For other methods, *vide* Feit, *Zeitsch. anal. Chem.*, 1889, **28**, 314 ; Sponholz, *ibid.*, 1893, **31**, 519 ; Carnot, *Compt. rend.*, 1889, **109**, 177 ; Nietzki, *Dingl. poly. J.*, 1876, **219**, 262 ; Thomas, *Compt. rend.*, 1902, **134**, 655 ; *Ann. Chim. Phys.*, 1907, [viii.], **11**, 204 ; Browning and Palmer, *Amer. J. Sci.*, 1909, [iv.], **27**, 379 ; *Chem. News*, 1909, **99**, 304.

[2] See also Werner, *Chem. News*, 1886, **53**, 51.

[3] Spencer and Le Pla, *Trans. Chem. Soc.*, 1908, **93**, 858. For further information on the analytical chemistry of thallium, see *e.g.*, Crookes, *Select Methods of Chemical Analysis*, (Longmans & Co., 4th ed., 1905).

CHAPTER IX.

SCANDIUM.

Symbol, Sc. Atomic weight, 44·0 (O = 16).

Occurrence.—Scandium, despite its rarity, is extremely widely diffused in nature. In almost all rocks from which the mountains of the earth, or rather the chief parts of the earth's crust are formed, scandium can be detected, as the comprehensive spectroscopic researches of Eberhard[1] have shown.

The more commonly occurring minerals which contain scandium are *euxenite*[2] and *keilhauite* (p. 221) from certain localities, *mica* from Ytterby, and *cassiterite* and *wolframite* from the mountain ranges of Saxony and Bohemia, especially from Zinnwald in Saxony.[3] They are all derived from granites or certain pegmatites.[4]

It will be noticed that scandium occurs in certain rare earth minerals. However, it is by no means an invariable companion of the rare earth elements. In the course of some ten years of work on the rare earths, Urbain never met with scandium in any of his fractions,[5] and Hicks failed to detect scandium in specimens of *fergusonite*, *æschynite*, *euxenite*, and *samarskite* examined by him.[6] Scandium occurs in *gadolinite*, but only in the deposits found at Ytterby. When scandium occurs in association with the rare earth elements, the yttrium group usually predominates, and hence the occurrence of scandium in Finnish *orthite*, a cerium mineral, is of interest.[7]

The occurrence of scandium and the rare earth elements in the rare mineral *wiikite* was discovered by Crookes,[8] who isolated considerable quantities of scandia from this source. *Wiikite* is a black, amorphous mineral found with monazite in a felspar quarry at Impilaks, Lake Ladoga, Finland. Density, 4·85; hardness, 6. The mineral is feebly radioactive,

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[1] Eberhard, *Sitzungsber. K. Akad. Wiss. Berlin*, 1908, No. 38, p. 851; 1910, No. 22, p. 404; *Chem. News*, 1909, **99**, 30; 1910, **102**, 211.

[2] See p. 220; Hauser and Wirth, *Ber.*, 1909, **42**, 4445.

[3] Scandium has been found in American wolframite; Lukens, *J. Amer. Chem. Soc.*, 1913, **35**, 1470.

[4] Eberhard, *loc. cit.*; Vernadski, *Bull. Acad. Sci. Petrograd*, 1908, p. 1273.

[5] Urbain, *J. Chim. phys.*, 1906, **4**, 64; *cf.* Crookes, *Chem. News*, 1905, **91**, 61; Eberhard, *Zeitsch. anorg. Chem.*, 1905, **45**, 374.

[6] Hicks, *J. Amer. Chem. Soc.*, 1911, **33**, 1492.

[7] R. J. Meyer, *Sitzungsber. K. Akad. Wiss. Berlin*, 1911, p. 379.

[8] Crookes, *Phil. Trans.*, 1908, **A**, **209**, 15; *Proc. Roy. Soc.*, 1908, **A**, 80, 516; *Chem. News*, 1908, **98**, 274.

and when heated to redness gives off water, hydrogen, sulphide, helium, a trace of neon, etc. The wiikite examined by Crookes had approximately the following composition :—

	Per cent.		Per cent.
Ta_2O_5 and Cb_2O_5	15·91	FeO	15·52
TiO_2 and ZrO_2	23·36	UO_3	3·56
Ce_2O_3	2·55	SiO_2	16·98
Y_2O_3	7·64	H_2O and gases	5·83
Sc_2O_3	1·17	Undetermined	1·97
ThO_2	5·51		

The particular deposit of this mineral used by Crookes is now exhausted, and the other deposits do not appear to contain more than the merest traces of scandium.[1]

The only known mineral in which scandium occurs as an essential constituent is the rare mineral *thortveitite*, $(Sc,Y)_2Si_2O_7$. This is a greyish-green, translucent silicate of scandium and yttrium which has been found in pegmatite at Iveland, South Norway. Hardness, 6·5; density, 3·57. The mineral is orthorhombic ($a : b : c = 0{\cdot}7456 : 1 : 1{\cdot}4912$).[2]

Scandium has been shown spectroscopically to occur in relative abundance in the sun and stars.

History.—In 1879 Nilson was preparing ytterbia from euxenite and gadolinite by the procedure that had been given by Marignac, the discoverer of the earth (p. 225). In so doing, he made the discovery of a new earth, present in very small quantity, and characterised by its very feeble basicity (less than that of ytterbia), its very low chemical equivalent, and its spark spectrum. Only 0·3 gram of the earth was obtained, and that in an impure state. To the new element present in the earth, Nilson gave the name **scandium**. A few weeks after the announcement of the discovery, Cleve reported that he had isolated 0·8 gram of scandia from 4 kilos. of *gadolinite*, and 1·2 grams of scandia from 3 kilos. of *keilhauite*. Cleve also described a few compounds of scandium. A little later, Nilson obtained a few grams of scandia, described several scandium salts, and determined the atomic weight of the element.[3]

Scandium corresponds very closely with **ekaboron**, one of the elements predicted by Mendeléeff when he put forward the periodic classification of the elements; and its discovery, coming only four years after the discovery of eka-aluminium or gallium,[4] was a matter of great interest and assisted largely in the recognition of the merits of the periodic classification by chemists in general. The identity of ekaboron and scandium was pointed out by Cleve;[5] the following table will serve to show how closely the properties of scandium were predicted by Mendeléeff:—[6]

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[1] R. J. Meyer and Winter, *Zeitsch. anorg. Chem.*, 1910, **67**, 398; *Chem. News*, 1910, **102**, 163.

[2] Schetelig, *Mineral. Zentr.*, 1911, p. 721.

[3] Nilson, *Compt. rend.*, 1879, **88**, 645; 1880, **91**, 56, 118; *Ber.*, 1879, **12**, 550, 554; 1880, **13**, 1430, 1439; *Ofvers. af K. Svenska Vet.-Akad. Förhandl.*, 1879, No. 3; 1880, No. 6; Cleve, *Bull. Soc. chim.*, 1879, [ii.], **31**, 486; *Compt. rend.*, 1879, **89**, 419; *Chem. News*, 1879, **40**, 159; *Ofvers. af K. Svenska Vet.-Akad. Förhandl.*, 1879, No. 7.

[4] See p. 143.

[5] Cleve, *Compt. rend.*, 1879, **89**, 419; *Bull. Soc. chim.*, 1879, [ii.], **31**, 486; *Chem. News*, 1879, **40**, 159.

[6] Mendeléeff, *J. Russ. Chem. Soc.*, 1869, **1**, 60; 1871, **3**, 47; *Annalen Suppl.*, 1872, **8**, 133; trans. in *Chem. News*, 1879, **40**, 243, etc.; 1880, **41**, 2, etc.

Ekaboron.	Scandium.
Atomic weight, 44.	Atomic weight, 44.
Should give one oxide, Eb_2O_3, density, 3·5; more basic than Al_2O_3, less basic than MgO; insoluble in alkalies.	Scandium oxide, Sc_2O_3, density, 3·86, is more basic than Al_2O_3 and probably less than MgO; insoluble in alkalies.
Carbonate should be insoluble in water, and probably be precipitated as a basic salt.	Scandium carbonate, insoluble in water, readily loses carbon dioxide.
The double sulphates with alkali sulphates will probably not be alums.	Double sulphates are known, but they are not alums.
Anhydrous chloride, $EbCl_3$, should be more difficultly volatile than $AlCl_3$. In aqueous solution it should hydrolyse easier than magnesium chloride.	Scandium chloride, $ScCl_3$, begins to sublime appreciably at 850°. In aqueous solution it is decidedly hydrolysed.
Ekaboron will probably not be discovered spectroscopically.	Scandium was not detected by means of its spectrum.

Extraction of Scandia from Minerals.—The method employed by Crookes in extracting scandia from wiikite consisted in first isolating the scandia and rare earths, and then separating the scandia from this mixture by the fractional decomposition of the nitrates.[1] To obtain the mixture of scandia and rare earths, the mineral (1 pt.) was finely powdered and fused in a clay crucible with potassium hydrogen sulphate (5 pts.). The melt was cooled, powdered, and mixed with five times its weight of water, stirred for twelve hours, and then filtered through a linen filter. The filtrate was boiled with an excess of ammonia when all the earths were precipitated together with zirconia, titanic acid, ferric hydroxide, etc. The well-washed precipitate was heated with a slight excess of oxalic acid, and when cold the oxalates were filtered and washed. The oxalates were next converted into anhydrous sulphates, dissolved in cold water, filtered, and the ammonia and oxalic acid processes repeated. The oxalates were then well washed and calcined to oxides.

The extraction of scandia from *wolframite* has been very thoroughly studied by R. J. Meyer and others. Only the wolframite from Zinnwald (Z.) and Sadisof (S.) is said to be worth working up for scandium; analyses of the carefully picked mineral yield the following results:—

	WO_3.	FeO.	MnO.	$PbO+SnO_2$.	$TiO_2+Ta_2O_5$.	CaO.	Rare Earths.
(Z.)	75·41	9·34	14·00	0·18	0·50	0·55	0·15
(S.)	73·47	15·13	9·81	0·47	0·63	0·54	0·20

Rather more than half of the "rare earths" present consists of scandia.

The finely powdered wolframite is fused with about 2·3 times its weight of sodium carbonate, a little potassium nitrate being also added. The melt is boiled with water and a little alcohol, and the brown mixture of oxides left (which contains all the scandium) is washed, dissolved in hydrochloric acid, and the silica present removed in the usual manner.

The *oxide residues* from tungsten factories, if good Zinnwald wolframite has been worked up, are more convenient to use as raw material than

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[1] For an account of which, see p. 353.

wolframite itself, and contain 0·30 per cent. of rare earths. One kilogram of the oxide residues is dissolved in 3 litres of raw hydrochloric acid, the powder being introduced into the boiling acid. After drawing off the deposit of silica and boiling it with dilute hydrochloric acid, the filtrates are united.

To separate the scandium, the preceding solution is boiled, and 40 grams of sodium silicofluoride are added slowly with stirring. The boiling is continued for half an hour, when the scandium separates completely as a white, pasty precipitate of scandium fluoride (produced by decomposition of the silicofluoride). The precipitate is filtered on a Nutschen filter and boiled with very dilute hydrochloric acid. The fluoride is converted into sulphate in a platinum dish, the scandium precipitated as hydroxide with ammonia, and converted into oxalate by boiling with oxalic acid. The oxalate when washed and ignited leaves a white residue of nearly pure scandium oxide, which should weigh 3·0 to 3·3 grams.[1]

The small amount of yttrium earths present in the scandia is easily removed. The scandia is dissolved in hydrochloric acid, excess of the acid removed, and the scandium precipitated at 100° as the *basic thiosulphate.*[2] The washed precipitate is decomposed by hydrochloric acid, and the precipitation as thiosulphate repeated. The washed precipitate, now quite free from yttrium earths, is decomposed by hydrochloric acid, and the scandium in the filtered liquid precipitated as oxalate. The only impurity now remaining is thorium.[1]

It is not difficult to reduce the amount of thoria in scandia to 0·5 per cent. This may be effected in several ways, one of the most satisfactory being to pour the neutral solution of the chlorides of scandium and thorium into a large excess of 20 per cent. sodium carbonate solution, and boil the solution, when *scandium sodium carbonate* is precipitated, the bulk of the thorium remaining in solution. The final 0·5 per cent. of thoria, however, is difficult to eliminate. It cannot, for instance, be precipitated as the peroxide,[3] and, moreover, it cannot be detected in the scandia by its arc spectrum. A number of methods for its elimination are known, the first being to drop slowly a neutral solution of the scandium salt (contaminated with thorium) into a concentrated (10 to 20 per cent.) neutral solution of ammonium tartrate, and boil the clear solution so obtained with ammonia. *Scandium ammonium tartrate* is thus precipitated free from thorium, and is washed with dilute ammonium tartrate solution. The second method can only be advantageously employed on a small scale. It consists in precipitating the thorium from a nitrate solution containing much free nitric acid by the addition of an excess of potassium iodate sufficiently great to co-precipitate a portion of the scandium. The liquid is then quite free from thorium. The third method consists in pouring a neutral chloride solution of the scandium chloride into an excess of aqueous ammonium fluoride contained in a platinum dish and vigorously stirred. One gram of scandia requires 8 grams of ammonium fluoride. The liquid is evaporated at 100°, and the thorium separates out as the insoluble fluoride; any scandium ammonium fluoride that crystallises

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[1] R. J. Meyer, *Zeitsch. anorg. Chem.*, 1908, **60**, 134; *Chem. News*, 1909, **99**, 85, 97; *D.R.P.*, 202, 523 and 208, 355. The method of extracting scandia from these oxide residues is also discussed in detail by Sterba-Böhm (*Zeitsch. Elektrochem.*, 1914, **20**, 289).

[2] See p. 211.

[3] See Vol. V., and this vol., p. 320.

out may be redissolved by warming with more water, and the liquid then filtered. A fourth method, which is not, however, very convenient, is to separate the anhydrous chlorides of thorium and scandium by fractional sublimation, the former being the more volatile.[1]

Atomic Weight.—The analogy, though imperfect, between scandium compounds and the compounds of the rare earth elements, points to the tervalency of scandium, and hence, since the combining weight of scandium is 14·7, to the value 44·1 for the atomic weight. The specific heats of the oxide and sulphate may be cited in favour of this view, as the following comparison of molecular heats will show :—[2]

Al_2O_3	19·0	$Al_2(SO_4)_3$	63·6
Ga_2O_3	19·5	$Ga_2(SO_4)_3$	61·9
In_2O_3	22·2	$In_2(SO_4)_3$	66·4
Sc_2O_3	20·8	$Sc_2(SO_4)_3$	62·4
Yt_2O_3	23·3	$Yt_2(SO_4)_3$	61·6

If the formula ScO be assumed for the oxide, then the specific heat of scandium works out to the abnormally low value of 3·95 between 0° and 100°, if that of oxygen be taken as 3·0 (which is certainly not too great). The molecular weight of scandium acetylacetonate (p. 214) argues strongly for the tervalency of scandium, as also does the isomorphism of scandium ethylsulphate and acetylacetonate with the corresponding indium salts.[3] Of the multiples of the combining weight (14·7, 29·4, 44·1, 58·8, etc.) which might be taken for the atomic weight, only the value 44·1 gives scandium a position in the periodic table, and it then occupies the place of Mendeléeff's "ekaboron."

The value **Sc = 44·1** is due to Nilson; the value 45·1 obtained by Cleve is undoubtedly too high. Preliminary experiments by R. J. Meyer and Goldenberg gave the values 44·11, 44·11, 44·20, and 43·90 for the atomic weight of scandium.[4] An accurate determination of the atomic weight is, however, lacking at present. The determinations hitherto made have been effected by the "synthetic" sulphate method described later (p. 240).

COMPOUNDS OF SCANDIUM.

Scandium salts derived from colourless acids are themselves colourless and devoid of absorption spectra. They are diamagnetic, and have a sweet, astringent taste. In aqueous solution they are perceptibly hydrolysed. This will be seen from the following values for the equivalent conductivities of scandium chloride and other chlorides, the abnormal increase[5] in the conductivity of scandium chloride with dilution from $v = 32$ to $v = 1024$

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[1] R. J. Meyer and Winter, *Zeitsch. anorg. Chem.*, 1910, **67**, 398 ; *Chem. News*, 1910, **102**, 163, 175 ; R. J. Meyer and Goldenberg, *ibid.*, 1912, **106**, 13 ; R. J. Meyer and Wassjuchnow, *Zeitsch. anorg. Chem.*, 1914, **86**, 257 ; Sterba-Böhm, *loc. cit.*

[2] Nilson and Pettersson, *Compt. rend.*, 1880, **91**, 232 ; *Ber.*, 1880, **13**, 1459.

[3] Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1095 ; *Rec. trav. chim.*, 1914, **33**, 342.

[4] Cleve, *Compt. rend.*, 1879, **89**, 419 ; Nilson, *ibid.*, 1880, **91**, 56, 118 ; Meyer and Goldenberg, *loc. cit.*

[5] As compared with the chlorides of the rare earth elements.

litres being due to the high ionic mobility of the hydrogen ions of the acid set free by hydrolysis :—[1]

	Temperature, 25° C.						
$v=$	32	64	128	256	512	1024	$\lambda_{1024}-\lambda_{32}$.
$ScCl_3$	104·7	111·7	119·0	126·2	133·6	142·5	37·8
$LaCl_3$	105·8	112·1	118·0	123·4	127·3	131·5	25·7
$CeCl_3$	107·6	114·4	121·3	126·8	131·1	135·2	27·6
$AlCl_3$	99·9	106·9	114·1	123·8	131·0	138·0	38·1

The basic oxide scandia, Sc_2O_3, from which the scandium salts are derived, is decidedly stronger than alumina. It is, however, weaker than any of the rare earths of the type R_2O_3.

Scandium is often included among the rare earth elements. In doing so, however, it becomes difficult to decide whether scandia is to be regarded as an earth of the cerium or of the yttrium group. So far as basicity of oxide and solubilities of salts are concerned, scandium resembles the yttrium group; on the other hand, the solubility of its double potassium sulphate places it with the cerium group. It differs from both groups in not forming a sulphate, $Sc_2(SO_4)_3.8H_2O$,[2] and a nitrate, $Sc(NO_3)_3.6H_2O$. Further, scandium has a marked tendency to form what are probably complex as distinguished from double salts, and in this and in other respects it shows a remarkable resemblance to thorium.[3] In view of the fact that the cerium and yttrium groups of rare earth elements are distinguished by their platinocyanides (see p. 272), it is of interest to note that *scandium platinocyanide*, $Sc_2[Pt(CN)_4]_3$, forms hydrates both with $18H_2O$ and with $21H_2O$.[4]

A few salts of scandium were described by Nilson and Cleve; many others have since been prepared and described by Crookes, and by R. J. Meyer and his co-workers.[5]

SCANDIUM AND THE FLUORINE GROUP.

Scandium fluoride, ScF_3, is obtained as a white powder, difficult to filter, by heating scandia with aqueous hydrofluoric acid, or by precipitating

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[1] Meyer and Wassjuchnow, *Zeitsch. anorg. Chem.*, 1914, **86**, 271; *cf.* Meyer and Hauser, *Die chemische Analyse der seltenen Erden* (Stuttgart, 1912), p. 34.

[2] The octahydrate of the selenate, however, is known.

[3] Compare, for example, the properties of the oxalates, sulphates, double sodium sulphates, carbonates and double carbonates, and acetylacetonates.

[4] Crookes, *vide infra*; Orloff, *Chem. Zeit.*, 1912, **36**, 1407; Tschirvinski, *Zeitsch. Kryst. Min.*, 1913, **52**, 44.

[5] Nilson, *Compt. rend.*, 1879, **88**, 645; 1880, **91**, 56, 118; *Ber.*, 1879, **12**, 550, 554; 1880, **13**, 1430, 1439; Cleve, *Compt. rend.*, 1879, **89**, 419; *Bull. Soc. chim.*, 1879, [ii.], **31**, 486; *Chem. News*, 1879, **40**, 159; Crookes, *Phil. Trans.*, 1908, **A**, **209**, 15; 1910, **A**, **210**, 359; *Proc. Roy. Soc.*, 1908, **A**, **80**, 516; 1910, **A**, **84**, 79; *Chem. News*, 1908, **98**, 274, etc.; 1910, **102**, 73, etc.; R. J. Meyer and Winter, *Zeitsch. anorg. Chem.*, 1910, **67**, 398; *Chem. News*, 1910, **102**, 163; R. J. Meyer (with A. Wassjuchnow, N. Drapier, and E. Bodländer), *Zeitsch. anorg. Chem.*, 1914, **86**, 257. The last paper contains a very full account of the chemistry of scandium. References in the subsequent pages of the text to Crookes, Meyer and Winter, Meyer and Wassjuchnow, etc., refer to the papers enumerated in this footnote.

a solution of a scandium salt with hydrofluoric acid, an alkali fluoride, or fluosilicic acid. The fluoride is fusible with difficulty in the blow-pipe flame. It is very slightly soluble in hydrochloric acid, in which it resembles the thorium salt and differs from the salts of the rare earth metals (Crookes; Meyer and Wassjuchnow).

Scandium fluoride, like zirconium fluoride, is soluble in solutions of the alkali fluorides. **Scandium ammonium fluoride,** $ScF_3.3NH_4F$, is readily soluble in water, from which it crystallises in octahedra. It is decomposed by hydrochloric or dilute sulphuric acid with the precipitation of scandium fluoride or scandium ammonium sulphate. In aqueous solution it may be regarded as yielding chiefly the ions $3NH_4{}'$ and $ScF_6{}'''$, since it does not give any precipitate when boiled with ammonia. Sodium or potassium hydroxides, however, precipitate scandium hydroxide. The corresponding **potassium** and **sodium** salts, $ScF_3.3KF$ and $ScF_3.3NaF$, are known; they are less soluble in water and less "complex" than the ammonium salt (Meyer and Wassjuchnow).

Scandium chloride, $ScCl_3$, may be prepared by heating scandia in a current of disulphur dichloride vapour and chlorine. It is a white solid which begins to sublime at 800°. It is hygroscopic and dissolves in water with evolution of heat, but it is insoluble in alcohol (Meyer and Winter).

When scandium hydroxide or oxide is dissolved in hydrochloric acid and the solution concentrated, fine white needles of the hexahydrate, $ScCl_3.6H_2O$, separate out. It is deliquescent and soluble in alcohol; dried at 100° it becomes converted into $2ScCl_3.3H_2O$, and this loses hydrogen chloride when further heated (Crookes). An aqueous solution of scandium chloride reacts acid, owing to hydrolysis (p. 209).

Scandium chloride forms a very soluble double chloride with *cæsium chloride* (Meyer and Wassjuchnow). The **aurichloride,** $3ScCl_3.2AuCl_3.21H_2O$, forms readily soluble, yellow crystals, which lose water when carefully dried, and yield the hydrates with $8H_2O$ and $2H_2O$, and finally the anhydrous salt (Crookes).

Scandium bromide, $ScBr_3.6H_2O$, is prepared in the same manner as the chloride. It forms rhombic crystals which at 120° are converted into $2ScBr_3.3H_2O$ (Crookes).

Scandium perchlorate, $Sc(ClO_4)_3.xH_2O$, from scandium hydroxide and perchloric acid, crystallises as a felt-like mass of colourless, rhombic needles (Crookes).

Scandium iodate, $Sc(IO_3)_3.18H_2O$, from scandium chloride and potassium iodate, is a white, crystalline powder almost insoluble in water, but soluble in nitric acid. When dried at 250° it becomes anhydrous; at intermediate temperatures, hydrates with $15H_2O$, $13H_2O$, and $10H_2O$ may be obtained (Crookes).

SCANDIUM AND THE OXYGEN GROUP.

Scandium sesquioxide or **scandia,** Sc_2O_3, is obtained by igniting the hydroxide, carbonate, oxalate, nitrate, sulphate, etc., of scandium. It is a white powder of density 3·864, and specific heat 0·1530 (0° to 100°).[1] It is diamagnetic, the magnetic susceptibility being $-0{\cdot}05 \times 10^{-6}$ c.g.s. electromagnetic units per unit mass.[2] It dissolves slowly in cold, more readily in

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[1] Nilson and Pettersson, *Compt. rend.*, 1880, 91, 232; *Ber.*, 1880, 13, 1459.

[2] R. J. Meyer and Wuorinen, *Zeitsch. anorg. Chem.*, 1913, 80, 7.

hot dilute acids, and very readily in hot concentrated acids, scandium salts and water being produced.

Scandium hydroxide, $Sc(OH)_3$, is obtained as a white, bulky, gelatinous precipitate by adding ammonium or sodium hydroxide to a solution of a scandium salt. When dried in the air it has a composition corresponding to the above formula. The hydroxide is a rather weak base, with a marked tendency to form basic salts. It readily dissolves in acids, forming salts which have a sweet, astringent taste.

Scandium sulphide, Sc_2S_3, is a yellow solid obtained by heating scandium sulphate in hydrogen sulphide. It is stable in air, even at 100°, but is decomposed by dilute acids or boiling water with evolution of hydrogen sulphide.[1]

Scandium sulphite, $Sc_2(SO_3)_3$, is obtained as a white precipitate by mixing solutions of scandium chloride and sodium sulphite (Crookes); by passing sulphur dioxide through an aqueous suspension of scandium hydroxide, the hexahydrate $Sc_2(SO_3)_3.6H_2O$, may be obtained. It is soluble in aqueous ammonium sulphite, and by evaporating the solution in an atmosphere of sulphur dioxide, *scandium ammonium sulphite*, $Sc_2(SO_3)_3.(NH_4)_2SO_3.7H_2O$, is obtained (Meyer and Drapier).

Scandium basic thiosulphate, $Sc(OH)S_2O_3$, is obtained as a white, flaky precipitate when sodium thiosulphate is added to hot aqueous scandium chloride. Thorium and zirconium are similarly precipitated, but not the rare earth elements (Meyer and Drapier).

Scandium sulphate, $Sc_2(SO_4)_3$, is obtained by dissolving the oxide, hydroxide, or carbonate in sulphuric acid, and gently heating until water and excess of sulphuric acid are eliminated. It is a white powder of density 2·579, and specific heat 0·1639 between 0° and 100°.[2] The sulphate dissolves readily in water; at 12° there are 44·5 parts of anhydrous sulphate in 100 of the saturated solution (Crookes). Unlike the rare earth sulphates, the solubility does not diminish with rise of temperature. Scandium sulphate is not deliquescent and is insoluble in alcohol.

From a concentrated aqueous solution the hexahydrate, $Sc_2(SO_4)_3.6H_2O$, crystallises out in small globular aggregates. This hydrate effloresces in dry air and leaves the pentahydrate, $Sc_2(SO_4)_3.5H_2O$. The pentahydrate is the stable phase in contact with the solution at 25°, at which temperature 100 grams of solution contain 28·5 grams of anhydrous sulphate. The solubility alters with the addition of sulphuric acid, as shown by the following data:—[3]

Grams of H_2SO_4 per litre	0·0	24·5	49·0	121·5	243·3
Normality of H_2SO_4	0·0	0·5	1·0	4·86	9·73
Grams $Sc_2(SO_4)_3$ per 100 of solution .	28·52	29·29	19·87	8·36	1·32

When dried over sulphuric acid the pentahydrate changes into the tetrahydrate, and this at 100° becomes converted into the dihydrate. The latter may be dehydrated at 250°.

Scandium sulphate solution is only slowly and incompletely precipitated by oxalic acid and by sodium thiosulphate. Moreover, the equivalent

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[1] Wirth, *Zeitsch. anorg. Chem.*, 1914, 87, 5.

[2] Nilson and Pettersson, *loc. cit.*

[3] Wirth, *Zeitsch. anorg. Chem.*, 1914, 87, 9.

conductivity is abnormal, in that $(\lambda_{1024}-\lambda_{32})$ is much smaller than would be anticipated. This is shown by the following data :—

Temperature, 25° C.							
v =	32	64	128	256	512	1024	$\lambda_{1024}-\lambda_{32}$
$Sc_2(SO_4)_3$ . .	28·3	33·8	40·1	47·7	57·6	72·1	43·8
$Ce_2(SO_4)_3$ . .	35·1	42·0	49·9	60·2	72·7	87·1	52·0
$Al_2(SO_4)_3$ . .	51·1	60·6	71·2	83·1	95·3	107·2	56·1
$Cr_2(SO_4)_3$ . .	67·4	78·3	90·7	105·0	119·3	128·1	60·7

The explanation of these anomalous results is that scandium sulphate is really the scandium salt of a complex scandium-sulphuric acid, $H_3[Sc(SO_4)_3]$; thus, $Sc[Sc(SO_4)_3]$. In confirmation of this view it is found that whereas in migration experiments with scandium nitrate and chloride solutions nothing abnormal is observed, with scandium sulphate a considerable quantity of scandium migrates to the anode (Meyer and Bodländer).

A **basic sulphate,** $Sc_2O_3.2SO_3$, is produced when scandium sulphate is heated to dull redness (Crookes). When scandium sulphate pentahydrate is dissolved in sulphuric acid of density 1·6 **acid scandium sulphate** (or *scandium-sulphuric acid*), $Sc_2(SO_4)_3.3H_2SO_4$ (or $H_3Sc(SO_4)_3$), crystallises from the solution.[1]

Scandium potassium sulphate, $Sc_2(SO_4)_3.3K_2SO_4$ or $K_3Sc(SO_4)_3$, is obtained by adding an excess of potassium sulphate to a solution of scandium sulphate.[2] It is moderately soluble in water and dilute potassium sulphate solution, but practically insoluble in a saturated solution of potassium sulphate.[3] In this respect scandium resembles the metals of the cerite earths.

Scandium ammonium sulphate, $Sc_2(SO_4)_3.3(NH_4)_2SO_4$, resembles the potassium salt closely (Meyer and Winter). When its aqueous solution is boiled, the sparingly soluble double salt, $Sc_2(SO_4)_3.2(NH_4)_2SO_4$, separates out (Meyer and Drapier).

Scandium sodium sulphate, $Sc_2(SO_4)_3.3Na_2SO_4.10H_2O$, can only be prepared in the presence of a large excess of sulphuric acid. It is readily soluble in water and in concentrated sodium sulphate, thereby resembling thorium sodium sulphate (Meyer and Drapier).

Scandium selenite, $Sc_2(SeO_3)_3$, is an amorphous, white solid, insoluble in water. When heated with excess of aqueous selenious acid it is converted into a crystalline, insoluble **acid scandium selenite,** $Sc_2(SeO_3)_3.3H_2SeO_3$ (Nilson).

Scandium selenate, $Sc_2(SeO_4)_3$, crystallises from water in rhombic prisms of the octahydrate, $Sc_2(SeO_4)_3.8H_2O$. When dried at 100° the dihydrate is formed, and this is completely dehydrated at 400° (Crookes).

SCANDIUM AND THE NITROGEN GROUP.

Scandium nitrate, $Sc(NO_3)_3$, crystallises from a neutral aqueous solution as colourless, deliquescent, prismatic crystals of the tetrahydrate, $Sc(NO_3)_3.4H_2O$,

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[1] Wirth, *Zeitsch. anorg. Chem.*, 1914, 87, 1.

[2] Nilson, *loc. cit.*

[3] Nilson, *loc. cit.*; Crookes, *loc. cit.*

soluble in alcohol. The tetrahydrate becomes pasty and anhydrous at 100°. Basic salts of the formulæ $Sc_2O_3.2N_2O_5.3H_2O$ and $Sc_2O_3.2N_2O_5$ have also been described (Crookes).

The nitrate is readily decomposed by heat with the production of basic scandium nitrates, and finally of scandia.

SCANDIUM AND THE CARBON GROUP.

Scandium carbonate, $Sc_2(CO_3)_3.12H_2O$, is obtained as a white, bulky precipitate when a soluble carbonate is added to a scandium salt. It has the above composition when air-dried. Scandium carbonate is rather unstable, and when dried at 100° it loses a little carbon dioxide (Crookes).

Scandium carbonate dissolves in hot aqueous sodium or ammonium carbonate. When these solutions are boiled, difficultly soluble **scandium sodium carbonate,** $Sc_2(CO_3)_3.4Na_2CO_3.6H_2O$, and **scandium ammonium carbonate,** $2Sc_2(CO_3)_3.(NH_4)_2CO_3.6H_2O$, are obtained as crystalline precipitates. These double carbonates dissolve without decomposition in a large volume of cold water, but when the solutions are boiled, basic salts or hydroxide separate (R. J. Meyer and Winter).

Scandium oxalate, $Sc_2(C_2O_4)_3.5H_2O$, may be precipitated from an aqueous solution of a scandium salt by oxalic acid, and when air-dried, forms a white, crystalline powder of the above composition. It is slightly, but distinctly soluble in water. In dilute acids it is less soluble than the oxalates of the rare earth elements, as will be seen from figs. 19 and 21, and, unlike the rare earth oxalates, it is more soluble in dilute sulphuric than in hydrochloric acid. In these respects it resembles thorium oxalate. The solubility data are as follows (see fig. 19) :—[1]

Normality of Acid.	Grams of $Sc_2(C_2O_4)_3$ per 100 Grams of Saturated Solution.			
	Hydrochloric Acid.		Sulphuric Acid.	
	25°.	50°.	25°.	50°.
0·1	0·0299	0·0420	0·0385	0·0562
0·5	0·0650	0·0870	0·0997	0·1481
1·0	0·1020	0·1435	0·1663	0·2493
2·0	0·1716	0·2556	0·3176	0·4429
5·0	0·4170	0·6533	0·7761	1·1280

Boiling 10 per cent. hydrochloric acid dissolves 0·8 per cent. of its weight cf hydrated scandium oxalate; the 20 per cent. acid, 1·8 per cent. of oxalate (Meyer and Winter).

When dried over sulphuric acid, the trihydrate, $Sc_2(C_2O_4)_3.3H_2O$, is obtained; at 100° the dihydrate, and at 140° the monohydrate is produced (Crookes).

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[1] R. J. Meyer and Wassjuchnow, *Zeitsch. anorg. Chem.*, 1914, **86**, 284 ; *cf.* Wirth, *ibid.*, 1914, **87**, 11.

Scandium oxalate dissolves readily in hot ammonium oxalate solution, less readily in potassium or sodium oxalate, and on cooling, crystalline *double oxalates* of the type $Sc_2(C_2O_4)_3.3R^{I}_{2}C_2O_4.10H_2O$, or $R^{I}_{3}[Sc(C_2O_4)_3].5H_2O$, separate out.[1] Scandium oxalate has a strong tendency towards double salt formation, and when a solution of sodium or potassium oxalate is added to one of scandium nitrate, the crystalline precipitate first produced is a *double oxalate* of the type $Sc_2(C_2O_4)_3.R^{I}_{2}C_2O_4$ (Meyer and Wassjuchnow).

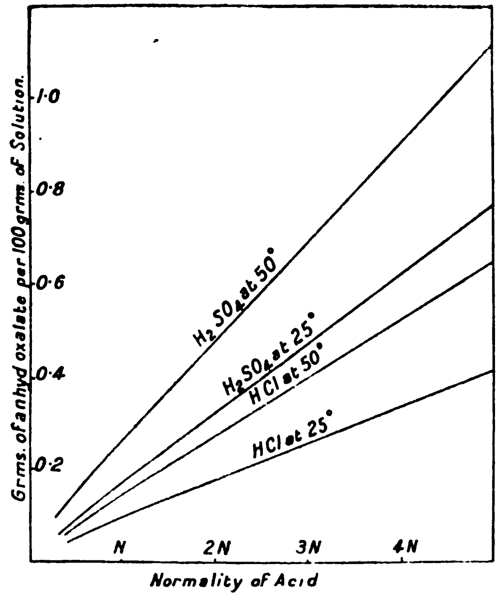

FIG. 19.—Solubility of scandium oxalate in acids.

Scandium acetylacetonate $[(CH_3.CO)_2CH]_3Sc$, is obtained by adding scandium chloride solution to acetylacetone dissolved in a slight excess of ammonia. It may be purified by crystallisation from 70 per cent. alcohol, or by dissolving it in benzene and precipitating with light petroleum. By the former method it crystallises in colourless sparkling prisms; by the latter, in needles. It is soluble in ether and chloroform, and melts at 188° C.; it crystallises in the rhombic system and is isomorphous with the indium salt.[2] Molecular weight determinations have been made by the freezing-point method in benzene, and by the boiling-point method in benzene, chloroform and carbon disulphide, and the results show clearly that the molecular formula is that given above, and not $[(CH_3.CO)_2CH]_2Sc$ or $[(CH_3.CO)_2CH]_4Sc_2$, with $Sc = 29$.[3]

Under a pressure of 8 to 10 mm., scandium acetylacetonate begins to sublime at 157°, and sublimes rapidly at 187° without decomposition. At atmospheric pressure it melts at 188°, and commences to volatilise appreciably at 190°; no decomposition occurs below 250°.[4] The acetylacetonate does not combine with ammonia. In its properties it therefore resembles thorium acetylacetonate closely, and differs appreciably from the acetylacetonates of the rare earth elements.

Scandium Salts of Organic Acids.—Many of these salts have been described by Crookes.

Scandium silicate (see p. 205).

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[1] Wirth, *Zeitsch. anorg. Chem.*, 1914, 87, 1. Meyer and Wassjuchnow (*loc. cit.*) describe the salt $Sc_2(C_2O_4)_3.4(NH_4)_2C_2O_4.7H_2O$.

[2] Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 1095; *Rec. trav. chim.*, 1914, 33, 342.

[3] Meyer and Winter, *loc. cit.*; Meyer, *Zeitsch. anorg. Chem.*, 1914, 86, 288; Morgan and Moss, *Trans. Chem. Soc.*, 1914, 105, 196.

[4] Morgan and Moss, *loc. cit.*

SCANDIUM AND BORON.

Scandium orthoborate, $ScBo_3$, prepared by fusing boric anhydride with scandia and extracting the excess of boric anhydride with water, is a white, insoluble powder (Crookes).

DETECTION AND ESTIMATION OF SCANDIUM.

Minute amounts of scandium may be detected in minerals, etc., owing to the extreme delicacy of its spark and arc spectra. When utilising the *spark spectrum* it is first necessary to decompose the substance under examination, precipitate the earths as oxalates, ignite, and dissolve the residual oxides in hydrochloric acid. Owing to the slight solubility of scandium oxalate in hydrochloric acid, the filtrate from the oxalates should be precipitated with ammonia, and the precipitate likewise tested for scandium. In examining rare earth minerals it is, moreover, necessary to concentrate the scandium into a small fraction of the rare earths. It is also necessary to carry out a preliminary chemical treatment before examining the *arc spectra* when rare earth minerals are being examined, but with other minerals and rocks it suffices to powder the substance, heat it to redness in order to drive off water and gases, and then examine the arc spectrum of the powder in the usual way, using a carbon arc. At least 0·5 gram must be used, and it must be *completely* vaporised if traces of scandium are to be detected.[1] The spectroscopic investigation should be made by the photographic method, the region from 3500 to 3700 being particularly examined (Crookes).

The most intense lines in the arc and spark spectra of scandium are as follows:—[2]

spark: 3353·89, 3558·71, 3567·88, **3572·72**, 3576·53, 3581·15, **3613·98**, **3630·90**, **3642·96**, 3651·96, **4247·00**, 4314·25, 4320·91, 4325·15, 4374·68, 4400·56, 4415·72.

arc: 3353·89, 3372·33, 3558·69, 3567·88, 3572·72, 3576·53, 3613·98, 3630·90, 3642·96, 3907·69, 3912·03, 4020·55, 4023·83, 4247·00, 4314·25, 4320·91, 4325·15, 4374·68, 4400·56, 4415·72, 6305·88.

The arc spectrum of scandium consists of two distinct sets of lines which behave very differently in solar spectra. One of these sets corresponds to the "enhanced" lines of other elements. The arc spectrum when taken in air shows very characteristic flutings due to scandium oxide. They disappear when the arc is taken in hydrogen, and at the same time the spectrum approximates to that observed with the spark discharge (Fowler).

For the quantitative estimation of scandium it is precipitated as the oxalate and weighed as the sesquioxide.

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[1] Eberhard, *Sitzungsber. K. Akad. Wiss. Berlin*, 1908, p. 851; 1910, p. 404; *Chem. News*, 1909, **99**, 30; 1910, **102**, 211.

[2] Lockyer and Baxandall, *Proc. Roy. Soc.*, 1905, **74**, 538; Fowler, *Phil. Trans.*, 1908, **A**, 209, 47; *Proc. Roy. Soc.*, 1908, **A**, **81**, 335; Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Vienna, 1911), vol. i.; Kayser, *Handbuch der Spektroskopie* (Leipzig, 1912), vol. vi. p. 444.

CHAPTER X.

THE RARE EARTH ELEMENTS.

Introductory.—"Chemists distinguish such substances by the name of pure earth, as are brittle, incombustible, infusible by the heat of furnaces, not soluble in several hundred times their weight of water, and destitute of metallic splendour. There are few earthy substances which may not be reduced by analysis to one of the five following primitive earths:—the siliceous, argillaceous, calcareous, ponderous, and magnesian earths; or otherwise, taken substantively, they are called silex, clay, lime, barytes, and magnesia."[1]

The preceding quotation will serve to show the meaning attached by chemists to the term *earth* at the time when the foundations of modern chemistry were being laid. Five earths were recognised, viz., silica, alumina, baryta, lime, and magnesia, and the existence of another (strontia) strongly suspected. Glucina or beryllia was added to the list in 1798, and a number of further additions were made within the next twenty years from that date. It will be noticed that the earths all agree in one respect, viz., they are oxides which can only be reduced with great difficulty. That the earths were oxides was suspected by Lavoisier, and Davy's classic experiments (1808) on the electrolysis of the alkalies and alkaline earths afforded the first experimental confirmation of this view. By Berzelius, Gmelin, and others the earths were usually divided into two groups, (i.) the alkaline earths (lime, strontia, baryta, and magnesia), and (ii.) the earths proper; their metallic constituents were classified, together with the alkali metals, as light metals. Moreover, silica was sometimes removed from the list of earths and placed among the acids.

For a considerable number of years it has been customary to refer to certain earths as the *rare earths*, since for many years after their discovery the only available sources of them were a number of rare minerals, found principally in Scandinavia. Originally, two such earths were recognised, ceria and yttria; these initial rare earths, however, have proved to be so extremely complex that at the present time fifteen rare earths receive official recognition, and it is probable that the existence of one or two more will be substantiated.

There is no precise limitation to the nature of the earths that are to be regarded as rare earths. In this book the term rare earths is restricted to the sesquioxides, M_2O_3, that have been recognised as components of the original "ceria" and "yttria" and to cerium sesquioxide.[2] Accordingly the earths glucina, thoria, and zirconia, and the earth-acids, viz., titanic oxide and the pentoxides of columbium and tantalum, are not discussed, although

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[1] Nicholson, *The First Principles of Chemistry*, 3rd ed., 1796, p. 99.

[2] Ceria itself is a dioxide, CeO_2.

some authors include them among the rare earths. Moreover, scandia is not included among the rare earths, but is given separate treatment (Chapter IX.).

The rare earth elements, their symbols, and atomic weights are given in the following table, in which the elements are divided into three groups for reasons that will be subsequently explained (p. 249):—

Cerium Group.			Terbium Group.			Yttrium Group.		
Lanthanum	La	139·0	Europium	Eu	152·0	Dysprosium	Dy	162·5
Cerium	Ce	140·25	Gadolinium	Gd	157·3	Holmium	Ho	163·5
Praseodymium	Pr	140·9	Terbium	Tb	159·2	Yttrium	Y	88·7
Neodymium	Nd	144·3				Erbium	Er	167·7
Samarium	Sm	150·4				Thulium	Tm	168·5
						Ytterbium	Yb	173·5
						Lutecium	Lu	175·0
						Celtium	Ct	?

From the analytical point of view, the rare earth elements resemble aluminium and chromium; from other points of view they resemble the alkaline earth metals and bismuth. Their most striking characteristic, however, is their extraordinary chemical similarity one with another, and since the rare earths are always associated together in nature, their separation from one another is a very formidable task. The difficulties encountered far surpass those met with in separating, say, calcium from strontium, or nickel from cobalt; in the separation of the rare earth elements, analytical methods similar to those ordinarily employed in analysis are restricted to the separation of cerium from the others.

In the present chapter a general account of the chemistry of the rare earth elements is given. In Chapter XI. the separation of the rare earths is discussed, and in Chapters XII., XIII., and XIV. the individual rare earth elements and their compounds are described.

Occurrence.[1]—In minute quantities, the rare earths are extremely widely disseminated in nature. This has been shown especially by experiments dealing with cathodic phosphorescence spectra.[2, 3, 4, 5] Traces of rare earths occur in many minerals, of which scheelite,[2, 5, 6] pitchblende, apatite,[2, 6] certain varieties of calcite,[2, 7] fluorspar,[3, 4, 8] cassiterite,[9] and wolframite[9] may be particularly mentioned. Rare earths have also been detected in coral,[2] bones,[2, 6] the ashes of rice and tobacco,[2, 6] etc.

The number of mineral species containing the rare earths is very large. They consist for the most part of silicates, titanates, zirconates, tantalates,

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[1] See Schilling, *Das Vorkommen der seltenen Erden im Mineralreiche* (Munich and Berlin, 1904); Brögger, *Zeitsch. Kryst. Min.*, 1890, **16**, and *Die Mineralien der südnorwegischen Granit-Pegmatitgänge*, 1906; Cahen and Wootten, *The Mineralogy of the Rarer Elements* (C. Griffin & Co., Ltd., 1912); Levy, *The Rare Earths* (Arnold, 1915), and the larger mineralogical text-books of Dana, Hintze, Doelter, etc.

[2] Crookes, *Phil. Trans.*, 1883, **174**, iii. 891; *Chem. News*, 1884, **49**, 159, 169, 181, 194, 205.

[3] Urbain and Scal, *Compt. rend.*, 1907, **144**, 30.

[4] Urbain, *Ann. Chim. Phys.*, 1909, [viii.], **18**, 356.

[5] de Rohden, *Compt. rend.*, 1914, **159**, 318; *Ann. Chim.*, 1915, [ix.], **3**, 338.

[6] Cossa, *Gazzetta*, 1879, **9**, 118; 1880, **10**, 465.

[7] Headden, *Amer. J. Sci.*, 1906, [iv.], **21**, 301.

[8] Humphreys, *Astrophys. J.*, 1904, **20**, 266.

[9] Eberhard, *Sitzungsber. K. Akad. Wiss. Berlin*, 1908, p. 851; 1910, p. 404.

and phosphates, in which the rare earths are associated with lime, thoria, glucina, oxides of iron, uranium, etc. They occur principally as included minerals in granite and pegmatite.

The minerals occur mainly in four or five localities. The Scandinavian deposits were the first known, and, although not very plentiful, are extremely rich in mineral species. In Norway, the chief localities are near Langesund Fiord, and include Arendal, Brewik, Kragerö, Hitterö, Risör, and Moss; the Swedish deposits are found at Ytterby and Bastnäs. The granites and pegmatites of the coast of Greenland are also rich in these minerals, which are almost invariably associated with *œgirite*. In North America, deposits occur in North and South Carolina, Colorado, Virginia, Idaho, Maine, and particularly at Barringer Hill, Llano Co., Texas.[1] In South America, large deposits of monazite sand occur in Brazil, particularly in the provinces of Bahia, Minas Geraes, Espirito Santo, Matto Grosso, and Goyaz. Other deposits of rare earth minerals are found in the Urals, particularly at Miask.

Among the most important rare earth minerals are *cerite*, *allanite*, *monazite*, *æschynite*, *gadolinite*, *xenotime*, *fergusonite*, *yttrotantalite*, *samarskite*, *polycrase*, and *euxenite*. The first four of these minerals are rich in ceria earths and poor in yttria earths, the reverse being true of the others.

Cerite consists essentially of a hydrated silicate of ceria, with small amounts of iron, calcium, etc. It crystallises in orthorhombic prisms ($a : b : c = 0{\cdot}999 : 1 : 0{\cdot}813$), but commonly occurs in the massive or granular form, and contains 59 to 72 per cent. of ceria.[2] The amount of yttria[2] present may reach 7 per cent. Hardness, 5·5; density, 4·86 to 4·91. The colour varies from red to brown or grey. Cerite is found embedded in gneiss at Bastnäs, associated with mica, hornblende, allanite, and chalcopyrite.

Allanite or *orthite* (varieties, *bucklandite*, *uralorthite*, *bagrationite*, *scandium-orthite*, *muromontite*, *bodenite*) is a basic orthosilicate of calcium, aluminium, iron, and cerium. It crystallises in monoclinic tables, plates, or needles ($a : b : c = 1{\cdot}551 : 1 : 1{\cdot}769$; $\beta = 64^\circ\ 59'$) of a reddish-black colour, the crystals often resembling rusty nails, and generally contains from 16 to 25 per cent. of rare earths. Hardness, 5·5 to 6; density, 3·5 to 4·2. Allanite is found in Texas, Greenland, Norway, and Sweden.

Monazite, $\mathrm{Ce(La,Di)PO_4}$, is essentially cerium (lanthanum, etc.) orthophosphate. It forms monoclinic crystals ($a : b : c = 0{\cdot}969 : 1 : 0{\cdot}926$; $\beta = 76^\circ\ 20'$) which vary in colour from hyacinth-red to brown. Hardness, 5 to 5·5; density, 5·0 to 5·2, and occasionally as high as 5·5. It generally contains 60 to 70 per cent. of ceria, and from traces to upwards of 5 per cent of yttria.

Monazite crystals, which are rather scarce, are found in granites and granitic gneisses in Norway and Greenland, in Ceylon, and in one or two other localities. Rolled grains of monazite, however, occur in abundance, being found in large deposits of sand and gravel in various localities. These *monazite sands* have been produced by the weathering of rocks which originally contained a very small percentage of monazite, and the subsequent washing away of the lighter materials produced. The monazite is associated with numerous other minerals, *e.g.* quartz, thorite, zircon, garnet, tourmaline, hornblende, augite, olivine, topaz, spinel, rutile, magnetite, titanite and cassiterite.

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[1] Hidden and Mackintosh, *Amer. J. Sci.*, 1889, [iii.], **38**, 474; 1905, [iv.], **19**, 425.

[2] By "ceria" and "yttria" throughout this section are meant "earths of the cerium group" and "earths of the yttrium group" respectively.

In North and South Carolina monazite occurs in stream beds and placer deposits, its origin being the granitic biotite-gneiss and dioritic hornblende-gneiss of the surrounding country. The gravel deposit varies from one to three feet in thickness. The Brazilian deposits occur in the provinces already mentioned (p. 218). They occur along the coast and also inland, following the course of certain water-traversed syenite rocks and gneisses. Monazite sand is also found in India in the native State of Travancore,[1] in Ceylon, in various localities in the Federated Malay States, and the protected States of Kedah and Kelantan,[2] and in various parts of Nigeria.[3]

Monazite sand is of considerable commercial importance, since all monazite contains a little *thorium*, which is employed in the manufacture of incandescent gas mantles. The commercial value of a sample of monazite sand depends, in fact, upon its thorium content.

Most of the world's supply of monazite sand has come from Brazil, where the annual production of sand containing 90 per cent. of monazite exceeds 6000 metric tons. Monazite separated from the concentrated sands found on the sea coast contains 5 to 7 per cent. of thoria; monazite from the inland deposits contains 4·0 to 5·7 per cent. of thoria.[4] Prior to its exportation, the sand and gravel is washed in sluice boxes like placer gold, and the dried sand freed from magnetite, etc., by an electromagnetic process. It is not difficult to "concentrate" the sand in this way till it contains 95 per cent. of monazite. The thoria content of the product regularly marketed varies from 5·75 to 7·1 per cent.[5] The monazite sand deposits in Carolina are poor in thoria and of little or no present commercial value, but there is a very considerable production of the sand, very rich in thoria, from Travancore.

The composition of a number of samples of monazite is given in the following table:—[6]

	Espirito Santo, Brazil.	Alcobaca, Brazil.	North Carolina.	Ratnapura, Ceylon.	Travancore.	Ekole, North Nigeria.	Ebara River, South Nigeria.	Pehang, Malay.	Kulium, State of Kedah.
ThO_2	6·06	6·50	6·49	10·29	10·22	5·00	5·50	8·38	3·53
CeO_2	62·12	61·40	31·38	27·37	31·90	30·72	31·40	25·46	64·05
La_2O_3, etc.			30·88	30·13	28·00	30·02	29·20	32·72	
Y_2O_3, etc.	0·80	0·70	...	2·14	0·46	2·74	2·00	2·80	2·40
Fe_2O_3	0·97	1·50	...	0·81	1·50	3·00	0·75	0·84	0·64
Al_2O_3	0·10	0·08	...	0·17	0·17	0·35	0·05	2·78	0·07
CaO	0·21	0·30	...	0·41	0·20	0·15	0·10	0·61	0·17
SiO_2	0·75	0·64	1·40	1·03	0·90	1·20	0·82	0·92	1·08
P_2O_5	28·50	28·46	29·28	27·67	26·82	26·29	29·92	23·92	27·87
Loss on ignition	0·38	0·64	0·20	0·20	0·46	0·25	0·44	1·28	0·52

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[1] Tipper, *Rec. Geol. Survey, India*, 1914, **44**, 186; *Ch. of Comm. J.*, 1915, **34**, 205.

[2] *Bull. Imp. Inst.*, 1906, **4**, 301; 1911, **9**, 99.

[3] See S. Johnstone, *J. Soc. Chem. Ind.*, 1914, **33**, 55.

[4] *Mineral Industry*, 1909, **18**, 537.

[5] Gottschalk, *Chem. Eng.*, 1915, **21**, 169; *Mining Engineering World*, 1915, **42**, 903.

[6] Data taken from a paper by S. Johnstone, *J. Soc. Chem. Ind.*, 1914, **33**, 55. See also Genth, *Amer. J. Sci.*, 1889, **38**, 203; Blomstrand, *J. prakt. Chem.*, 1890, [ii.], **41**, 266; *Chem. Soc. Absts.*, 1890, **58**, 111, 571; 1891, **60**, 1168; Glaser, *J. Amer. Chem. Soc.*, 1896, **18**, 782; Schilling, *Zeitsch. angew. Chem.*, 1902, **15**, 869.

The preceding results refer to monazite carefully freed from admixed minerals.[1]

Æschenite, $R_2'''Cb_4O_{13}.R_2'''(TiTh)_5O_{13}$, is a columbo-titanate of cerium; it contains a considerable quantity of thorium. It crystallises in orthorhombic prisms or tables ($a : b : c = 0{\cdot}487 : 1 : 0{\cdot}674$), which are usually black in colour. Hardness, 5 to 6; density, 4·93 to 5·17. Æschenite contains 15 to 24 per cent. of ceria, and 1 to 3 per cent. of yttria. It is found in Norway and the Urals.

Gadolinite is a basic orthosilicate of yttrium, glucinum, and iron. It forms monoclinic prisms ($a : b : c = 0{\cdot}6273 : 1 : 1{\cdot}3215$; $\beta = 89° \ 26{\cdot}5'$), and occurs in large masses, which are dark in colour and give a greenish-grey streak. Hardness, 6·5 to 7; density, 4·36 to 4·47. It contains 36 to 48 per cent. of yttria, and 5 to 16 per cent. of ceria. Gadolinite is found as crystals in granitic pegmatite in Norway and Sweden, and occurs abundantly in Llano Co., Texas.[2]

Xenotime is essentially yttrium orthophosphate, YPO_4. It forms tetragonal crystals ($a : c = 1 : 0{\cdot}6187$) resembling *zircon*. Hardness, 4 to 5; density, 4·45 to 4·56. It contains 54 to 64 per cent. of yttria, and from 8 to 11 per cent. of ceria. Xenotime occurs in gneiss, granites, syenites, and in their pegmatite veins in Norway, Sweden, Switzerland; it is also found in the monazite sands of Carolina, Georgia, and Brazil.

Fergusonite, $(Y,Ce)(Cb,Ta)O_4$, is a metatantalate and columbate of yttrium. It crystallises in tetragonal bipyramids ($a : c = 1 : 1{\cdot}464$) of brownish-black colour, and gives a pale brown streak. Hardness, 5·5 to 6; density, 5·8. It contains 30 to 46 per cent. of yttria, and upwards of 9 per cent. of ceria; also thorium and uranium in considerable quantity. Fergusonite was discovered in quartz in Greenland; it occurs in Texas, Virginia, and Carolina, associated with samarskite and gadolinite, and in Norway and Sweden, associated with euxenite.

Yttrotantalite and *samarskite* are columbo-tantalates of yttrium, iron, and calcium. Samarskite differs from yttrotantalite in being rich in uranium. Both minerals are orthorhombic and reddish-brown to black in colour. Hardness, 5 to 6; density, 5·5 to 5·9. Yttrotantalite contains 17 to 38 per cent. of yttria, and upwards of 2 per cent. of ceria; samarskite, 5 to 21 per cent. of yttria, and from 2 to 5 per cent. of ceria. Both minerals occur in granite pegmatite in various localities; samarskite occurs massive in North Carolina in large quantities.[3]

Euxenite is a columbo-titanate of yttrium, which contains uranium. It is orthorhombic ($a : b : c = 0{\cdot}364 : 1 : 0{\cdot}303$), but usually occurs in brownish-black masses which have a pitchy lustre and give a yellow to reddish-brown streak. Hardness, 6·5; density, 4·6 to 5·0. It contains 13 to 30 per cent. of yttria, and 2 to 8 per cent. of ceria. Euxenite is found in Norway and Greenland.

Polycrase is similar in composition to euxenite, with which it is iso-

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[1] For a bibliography of the literature on monazite so far as 1894, see Nitze, *Sixteenth Ann. Rep. U.S. Geol. Survey*, 1894–95, p. 667. For discussions of the constitution of monazite, see Dunnington, *Amer. Chem. J.*, 1882, **4**, 138; Penfield, *Amer. J. Sci.*, 1882, **24**, 250; 1888, **36**, 322; Rammelsberg, *Zeitsch. Kryst. Min.*, 1879, **3**, 101; Blomstrand, *loc. cit.*, and *Zeitsch. Kryst. Min.*, 1887, **6**, 160; 1892, **10**, 367; Kress and Metzger, *J. Amer. Chem. Soc.*, 1909, **31**, 640; Johnstone, *loc. cit.*

[2] Hidden and Mackintosh, *loc. cit.*; Genth, *Amer. J. Sci.*, 1889, [iii.], **38**, 198; see also *Bull. U.S. Geol. Survey*, 1908, No. **340**, 286.

[3] *Bull. U.S. Geol. Survey*, 1891, No. **74**.

morphous, but contains less columbium and more titanium. The present-day opinion is that euxenite and polycrase are members of an isomorphous series of mixed yttrium metacolumbate and metatitanate, and the name euxenite is retained for mixtures in which the ratio $Cb_2O_5 : TiO_2$ exceeds 1 : 2, while the name polycrase is given to the others. Euxenite is dimorphous, the less common crystalline form being called *priorite.* Polycrase is likewise dimorphous, the other modification being known as *blomstrandine.* Priorite and blomstrandine are isomorphous minerals. Thus the euxenite group of minerals constitutes an isodimorphous series.[1]

Among the other rare earth minerals may be mentioned *tysonite,* CeF_3; *yttrofluorite,*[2] $n\text{CaF}_2.m\text{YF}_3$; *fluocerite,* $Ce_2OF_4.4CeF_3$; *yttrocerite,* $9CaF_2.6(Ce,Y)F_3.2H_2O$; *parisite,* a fluocarbonate of cerium and calcium; *cordylite,* a fluocarbonate of cerium and barium; *bastnæsite,* $Ce_2(CO_3)_3,CeF_3$; *ancylite,* $4Ce(OH)CO_3,3SrCO_3,3H_2O$; *lanthanite,* $La_2(CO_3)_38H_2O$; *tritomite,* a fluosilicate of cerium, thorium, and calcium; *erdmannite,* a mineral resembling *allanite*; *beckelite,* $(Ce,Y)_4(SiZr)_3Ca_3O_{15}$; *hellandite, mosandrite,* and *rinkite,* cerium silicates; *tengerite,* $Y_2(CO_3)_3$; *cappelenite,* a yttrium borosilicate; *rowlandite,* $Y_4Si_3O_{12}$; *yttrialite,* $Y_2Si_2O_7$; *thalenite,* $H_2Y_4Si_4O_{15}$; *yttrocrasite,* a yttrium and thorium titanate; *keilhauite* (or *yttrotitanite*), an isomorphous mixture of titanite, $Ca(Ti,Si)_2O_5$, and $(Y,Fe,Al)_2SiO_5$; *pyrochlore,* a columbate of cerium and calcium, etc.; *koppite,* $5Ce_2Cb_2O_7.2NaF$; *risörite,*[3] a yttrium columbate, $YCbO_4$, with an isomorphous admixture of yttrium metatitanate $Y_2(TiO_3)_3$; *sipylite,*[4] $YCbO_4$; *hielmite* and *loranskite,* tantalates of yttrium; etc.

The rare earth minerals have many points of interest, which cannot be discussed in this book.[5] It may, however, be mentioned that the researches of Boltwood[6] and Strutt[7] have shown that in general the rare earth minerals are strongly *radioactive,* and that, with the exception of a few uranium minerals, scarcely any others exhibit more than a feeble radioactivity. As a rule, therefore, the rare earth minerals are rich in occluded *helium.*[8] The minerals owe their radioactivity to the presence of *thorium* or *uranium* or both. The almost invariable association of these elements with the rare earths can scarcely be fortuitous, but no explanation of it is yet known. In some cases the thorium or uranium is in excess and only small amounts of rare earths are present, *e.g. thorianite* and *pitchblende*; in other cases the reverse holds good, *e.g. monazite.* Indeed, in the cases of monazite and a number of other minerals the small amounts of uranium present were overlooked in analyses until with the development of the study of radioactivity their probable presence was inferred.

Historical.—(i.) *Early History.*—In 1794 the Finnish chemist Gadolin isolated a new earth or oxide from a black mineral (gadolinite) found at

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[1] See Brögger, *Vid.-Selsk. Skrifter, Christiania, Math.-Naturv. Kl.*, 1906, No. **6**, 1; *Abstr. Chem. Soc.*, 1907, **92**, ii., 885; Lange, *Zeitsch. Naturwiss. Halle*, 1910, **82**; *Abstr. Chem. Soc.*, 1911, **100**, ii., 499.

[2] T. Vogt, *Centr. Min.*, 1911, p. 373; *Jahrb. Min.*, 1914, II., 9.

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

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

[5] An interesting and fairly complete account of the properties of these minerals will be found in Levy, *The Rare Earths* (Arnold, 1915).

[6] B. B. Boltwood, *Amer. J. Sci.*, 1904, [iv.], **18**, 97; 1905, [iv.], **20**, 253; 1906, [iv.], **21**, 415; 1908, [iv.], **25**, 269; *Phil. Mag.*, 1905, [vi.], **9**, 599.

[7] Strutt, *Proc. Roy. Soc.*, 1904, **73**, 191; 1905, **A**, **76**, 88, 312; 1907, **A**, **80**, 56; 1908, **A**, 80, 572.

[8] On the occurrence of helium in minerals see Vol. i., pt. ii.

Ytterby, near Stockholm.[1] This discovery was confirmed in 1797 by Ekeberg,[2] who showed that Gadolin's "earth" was a mixture of the then recently discovered glucina and a new earth to which he gave the name of **yttria.** From this "yttria" Berzelius and Gahn extracted a little ceria in 1816.[3]

In 1804 another Swedish mineral, known as the "heavy stone from Bastnäs," was examined by Berzelius and Hisinger in Sweden, and by Klaproth in Germany. It was found to contain a new earth, which Klaproth[4] called *ochroite*, because it turned dark yellow when heated. The Swedish chemists called it *ceria*, *i.e.* oxide of **cerium**, and named the mineral *cerite.*[5]

In 1839 Mosander showed that "ceria" was complex, for when cerous hydroxide was suspended in potash and treated with excess of chlorine, part of it went into solution and the remainder was converted into a citron-yellow higher hydroxide. Retaining the name ceria for the earth corresponding to the yellow hydroxide, he named the earth that had passed into solution *lanthana* or oxide of **lanthanum.**[6] Subsequently he found that an approximate separation of lanthana from ceria could be made by extracting crude "ceria" with 1 per cent. nitric acid, the lanthana passing into solution. For various reasons, Mosander considered that lanthana was white, the brown colour of his preparations being due to foreign matter, and early in 1840 he obtained proof of this hypothesis, and succeeded in showing that a third earth existed in crude "ceria." This earth, which he found to be responsible for the brown colour of his ceria and lanthana and for the pale amethyst colour of his cerous and lanthanum salts, he named *didymia* or oxide of **didymium.**[7] Mosander found that the fractional crystallisation of the sulphates was the best method for separating lanthana and didymia.

The complex nature of "yttria" was suspected by Scheerer in 1842,[8] and proved by Mosander in 1843.[9] By the fractional precipitation of "yttrium" salts with ammonia, and with acid potassium oxalate, he resolved "yttria" into three oxides. The most basic oxide, which was present in largest amount, he called *yttria* or oxide of **yttrium**; of the other two, one, which was pink, he named *terbia* or oxide of **terbium**, while the other, which formed a brown peroxide, he named *erbia* or oxide of **erbium**. Their basicity decreased in the order yttria, erbia, terbia.

Mosander's cerium, lanthanum, and yttrium are to-day classed among the chemical elements. It is now known, however, that his "didymium," "erbium," and "terbium" were complex; in particular, that his peroxide-forming element "erbium" contained only a trace of an element capable of

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[1] Gadolin, *K. Svenska Vet.-Akad. Handl.*, 1794, p. 137; *Crell's Annalen*, 1796, i. 313.

[2] Ekeberg, *Crell's Annalen*, 1799, ii., 63; *K. Svenska Vet.-Akad. Handl.*, 1802, p. 68.

[3] Berzelius and Gahn, *Schweigger's J.*, 1816, **16**, 250, 404.

[4] Klaproth, *Sitzungsber. K. Akad. Wiss. Berlin*, 1804, p. 155.

[5] Berzelius and Hisinger, *Gehlen's allg. J. Chem.*, 1804, **2**, 303, 397; *Ann. Chim. Phys.*, 1804, **50**, 245; see also Vauquelin, *ibid.*, 1804, **50**, 140.

[6] The discovery was announced by Berzelius. See *Compt. rend.*, 1839, **8**, 356; *Pogg. Annalen*, 1839, **46**, 648; **47**, 207, *Annalen*, 1839, **32**, 235; *Phil. Mag.*, 1839, [iii.], **14**, 390.

[7] See *Annalen*, 1842, **44**, 125; *Pogg. Annalen*, 1842, **56**, 503. For Mosander's own account of his work see Mosander, *Phil. Mag.*, 1843, [iii.], **23**, 241; *Ann. Chim. Phys.*, 1844, [iii.], **11**, 464; *Pogg. Annalen*, 1843, **60**, 297; *Annalen*, 1843, **48**, 210. For the early methods employed in the separation of the salts of cerium, lanthanum, and didymium, see Mosander, *loc. cit.*; Marignac, *Ann. Chim. Phys.*, 1849, [iii.], **27**, 209; Watts, *Quart. J. Chem. Soc.*, 1850, **2**, 140.

[8] Scheerer, *Pogg. Annalen*, 1842, **56**, 479.

[9] Mosander, *loc. cit.*

forming a peroxide by the ignition of its hydroxide, nitrate, or oxalate. Moreover, his yttria was by no means pure.

In 1857, shortly after the invention of the spectroscope, Gladstone observed the absorption spectrum of "didymium,"[1] and in 1862 Bahr discovered the absorption spectrum of "terbium."[2] The application of the spectroscope to the investigation of the rare earths was extended by Delafontaine and others. Meanwhile, doubt was cast on the existence of Mosander's "erbium." In 1860 Berlin introduced his classic method for the fractionation of the gadolinite earths, namely, the partial decomposition of the nitrates by heat.[3] He failed to obtain the peroxide-forming earth, and unfortunately gave the name of "erbia" to Mosander's pink earth "terbia." This incorrect designation has been adopted by all subsequent workers.

The results obtained by Berlin were confirmed by Bahr and Bunsen in 1866, and by Cleve and Höglund in 1872. According to these chemists, Mosander's "peroxide of erbium" was really a trace of peroxide of "didymium."[4] The existence of Mosander's "erbium," however, was vigorously upheld by Delafontaine.[5]

In 1873 the rare earth mineral *samarskite* was found in considerable quantity in a mica mine situated in Mitchell County, North Carolina. In 1877 comparatively large amounts of this mineral became available,[6] and the chemistry of the rare earths entered upon a new phase. Almost the first result of the study of the samarskite earths was the definite establishment, by Delafontaine,[7] of the existence of Mosander's "erbia," which he was obliged to rename "terbia" as the name "erbia" was by that time in common use for Mosander's "terbia." Almost simultaneously, Marignac showed conclusively the occurrence of Mosander's "erbia" in the gadolinite earths.[8] The existence of the present-day terbia was thus placed beyond question; its isolation in a state of purity, however, was not accomplished until nearly thirty years later.[9]

Whilst engaged in the analysis of samarskite, Lawrence Smith[10] observed indications of the existence of a new rare earth, and early in 1878 he announced the discovery of **mosandrum**, a new rare earth element resembling the elements of the cerite earths.[11] The discovery was adversely criticised by Delafontaine and Marignac, who regarded "mosandrum" as identical with their "terbium,"[12] and at no time was the existence of "mosandrum" generally admitted. Eight years after the announcement of

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[1] Gladstone, *Quart. J. Chem. Soc.*, 1858, 10, 219; 1859, 11, 36.

[2] This fact is referred to in numerous early papers. Apparently, no description of the spectrum was published by Bahr until 1866 (Bahr and Bunsen, *Annalen*, 1866, 137, 1).

[3] Berlin, *Förhandl. Skand. Nat. Kjob.*, 1860, p. 448.

[4] Bahr and Bunsen, *Annalen*, 1866, 137, 1; Cleve and Höglund, *Bull. Soc. chim.*, 1872, [ii.], 18, 193, 289.

[5] Delafontaine, *Arch. Sci. phys. nat.*, 1864, 21, 97; 1865, 22, 30; 1866, 25, 105; 1874, 51, 48.

[6] See Lawrence Smith, *Amer. J. Sci.*, 1877, [iii.], 13, 359.

[7] Delafontaine, *Arch. Sci. phys. nat.*, 1877, 59, 176; 1878, 61, 273; *Ann. Chim. Phys.*, 1878, [v.], 14, 238.

[8] Marignac, *Arch. Sci. phys. nat.*, 1878, 61, 283; *Ann. Chim. Phys.*, 1878, [v.], 14, 247.

[9] Urbain, *Compt. rend.*, 1905, 141, 521.

[10] L. Smith, *Amer. J. Sci.*, 1877, [iii.], 13, 359.

[11] L. Smith, *Compt. rend.*, 1878, 87, 146, 148, 831; 1879, 89, 480; *Amer. Chem. J.*, 1883, 5, 44, 73.

[12] Delafontaine, *Compt. rend.*, 1878, 87, 600; Marignac, *ibid.*, 1878, 87, 281.

its discovery, Lecoq de Boisbaudran[1] showed the complexity of "mosandrum," and from his results it can now be stated that in addition to terbium there were present didymium (a trace), samarium, dysprosium, and probably gadolinium in the so-called element.

Shortly after the announcement of the discovery of "mosandrum," Delafontaine claimed to have isolated a new earth of the yttrium group, which he named oxide of **phillipium.**[2] The history of this so-called element may be conveniently given at this point, as subsequent work has shown "phillipium" to have been nothing but a complicated mixture. The salts of "phillipium" were said to be characterised by an absorption band λ4490, an unfortunate method of describing the element, since erbium salts have an absorption band in the same position. Soret, who pointed this out, was inclined to regard "phillipium" as identical with an element **X** which he had characterised just previously by a particular absorption spectrum.[3] Delafontaine at first admitted the possibility that "phillipium" was complex, though he thought it unlikely, but, almost immediately afterwards, he concluded that "phillipium" had no absorption spectrum, attributing the band λ4490 and others he had observed to the presence of a little of Soret's X as an impurity.[4] In 1882, however, Roscoe showed that "phillipium" was only a mixture of yttrium and the "terbium" of that period; and his conclusions were supported by Crookes.[5] The later work of Urbain[6] has confirmed the view that "phillipium" was only a mixture, though Delafontaine asserted its elementary character as late as 1897.[7]

From this point in the history it is perhaps clearer to deal separately with the cerite and gadolinite earths.

(ii.) *The Cerium Group.*—About the same time that he announced the discovery of "phillipium," Delafontaine[8] stated that in examining "didymia" extracted from samarskite, he had isolated a new earth, oxide of **decipium,** characterised by two bands in its absorption spectrum at λ4160 and λ4780. The year following, Lecoq de Boisbaudran isolated a new earth from samarskite "didymia," and called it *samaria* or oxide of **samarium.**[9] The band λ4160 was also present in the spectrum of this element, and samarium would therefore appear to be more properly called decipium but for the fact that, a year or two later, Delafontaine[10] declared his "decipia" to be a mixture of two earths, one being samaria and the other an earth the salts of which gave no absorption spectra. He reserved the name oxide of decipium for this second earth. It is almost certain that this is to be identified with the earth Y_α discovered in the meantime by Marignac. Delafontaine's designation for the earth must therefore give way to Marignac's, and so the name "decipium" disappears from the list of rare earth metals.

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[1] Lecoq de Boisbaudran, *Compt. rend.*, 1886, **102**, 617.

[2] Delafontaine, *Arch. Sci. phys. nat.*, 1878, **61**, 273 ; *Compt. rend.*, 1878, **87**, 559.

[3] Soret's element X is discussed later (p. 225).

[4] Soret, *Compt. rend.*, 1879, **89**, 521 ; Delafontaine, *ibid.*, 1880, **90**, 221 ; *Arch. Sci. phys. nat.*, 1880, [iii.], **3**, 246 ; *cf.* Cleve, *Compt. rend.*, 1879, **89**, 708.

[5] Roscoe, *Trans. Chem. Soc.*, 1882, **41**, 277 ; Crookes, *Phil. Trans.*, 1882, **174**, 910.

[6] Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184.

[7] Delafontaine, *Chem. News*, 1897, **75**, 229.

[8] Delafontaine, *Compt. rend.*, 1878, **87**, 632 ; 1880, **90**, 221 ; *Arch. Sci. phys. nat.*, 1880, [iii.], **3**, 250.

[9] Lecoq de Boisbaudran, *Compt. rend.*, 1879, **88**, 322 ; **89**, 212 ; *cf.* Delafontaine, *loc. cit.*, and *Compt. rend.*, 1878, **87**, 634 ; Soret, *ibid.*, 1879, **88**, 422.

[10] Delafontaine, *Compt. rend.*, 1881, **93**, 63.

The discovery of samarium was confirmed by a number of chemists, and in 1883 Cleve prepared numerous samarium salts and determined the atomic weight of samarium.[1]

In 1885 Auer von Welsbach made the remarkable discovery that "didymium," even when freed from "samarium," was complex, being a mixture of two elements which he named **praseodymium** and **neodymium**.[2] The salts of these two elements were found to differ strikingly in colour, being green and rose-red respectively.

In 1892 Lecoq de Boisbaudran discovered that Cleve's "samaria" was complex,[3] and that when fractionated with ammonia, the least basic fractions differed from the others in two ways: (i.) their spark spectra contained three new lines in the blue, λ4593 being the most conspicuous, and (ii.) a new band λ6110–6220 appeared in their "spectres de renversement." The new spark lines he attributed to an element which he provisionally called $\mathbf{Z}_\varepsilon$, and the band he similarly attributed to an element $\mathbf{Z}_\zeta$, expressing no opinion as to the identity or otherwise of Z_ε and Z_ζ. In 1893 he showed that Z_ζ was closely connected with an element $\mathbf{S}_\delta$, the existence of which had been previously assumed by Crookes to account for the "anomalous band" encountered in the cathodic phosphorescence spectra of the rare earths.[4]

The presence of a small amount of a new earth in "samaria" was further proved by Demarçay in 1896. Demarçay characterised his new earth by its ultraviolet spark spectrum, which was very sensitive, and provisionally called the new rare earth element **Σ**.[5] In 1900 he showed that Z_ε, Z_ζ, and Σ were probably identical, a conclusion he confirmed in 1901, when he isolated the oxide of Σ in a nearly pure state. He then established the fact that Σ is identical with Crookes' S_δ, and called the element **europium**.[6]

(iii.) *The Terbium and Yttrium Groups.*—In 1878 Marignac fractionated the gadolinite earths,[7] and Soret examined the "erbia" fractions spectroscopically.[8] As the result of his observations, Soret concluded that "erbia" was complex. Reserving the name of erbium for that rare earth element the salts of which gave rise to the most characteristic absorption bands of the old erbium spectrum, Soret designated by **X** a new element, salts of which exhibit a characteristic absorption spectrum of some ten or more bands, particularly λ6404 and λ5363. He also observed that a band, λ6840, which did not form part of the spectrum of X, did not appear to belong to the erbium spectrum either.

Pursuing the fractionation of "erbia" by Berlin's method, Marignac in 1878 made the surprising discovery that the least basic portion of "erbia" consisted of a new, colourless earth of very high chemical equivalent. This new earth he called oxide of **ytterbium**;[9] its spark spectrum was mapped by Lecoq de Boisbaudran.[10]

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[1] Cleve, *Compt. rend.*, 1883, **97**, 94.

[2] Auer von Welsbach, *Monatsh.*, 1885, **6**, 477 ; *cf. ibid.*, 1884, **5**, 1, 508. As a matter of fact, von Welsbach proposed the names **praseodidymium** and **neodidymium**, but the shorter names given in the text are generally employed.

[3] Lecoq de Boisbaudran, *Compt. rend.*, 1892, **114**, 575 ; 1893, **116**, 611, 674.

[4] The work of Crookes is discussed later (p. 294).

[5] Demarçay, *Compt. rend.*, 1896, **122**, 728 ; *cf. ibid.*, 1886, **102**, 1551 ; 1893, **117**, 163.

[6] Demarçay, *ibid.*, 1900, **130**, 1469 ; 1901, **132**, 1484.

[7] Marignac, *Arch. Sci. phys. nat.*, 1878, **61**, 283 ; *Ann. Chim. Phys.*, 1878, [v.], **14**, 247.

[8] Soret, *Arch. Sci. phys. nat.*, 1878, **63**, 89 ; *Compt. rend.*, 1878, **86**, 1062.

[9] Marignac, *Arch. Sci. phys. nat.*, 1878, **64**, 97 ; *Compt. rend.*, 1878, **87**, 578 ; see also Delafontaine, *Compt. rend.*, 1878, **87**, 933.

[10] Lecoq de Boisbaudran, *Compt. rend.*, 1879, **88**, 1342.

In the following year Nilson,[1] who had prepared large quantities of "erbia," repeated and confirmed Marignac's work, but, in addition, he isolated still another earth from "erbia." It was colourless and less basic than ytterbia, and received the name of *scandia* or oxide of **scandium.**[2] The same year Cleve[3] fractionated "erbia" freed from scandia and "ytterbia," using Berlin's method, and from the results of Thalen's spectroscopic study of the fractions, concluded that "erbia" was composed of three earths, which he called the oxides of **holmium, erbium,** and **thulium** in descending order of basicity. Each earth was characterised by the absorption spectrum of its salts, and Soret and Cleve quickly noted that holmium and Soret's X were identical, and that thulium was responsible for the somewhat anomalous band λ6840 in the spectrum of old "erbium."[4]

The elementary nature of "holmium" was disproved in 1886 by Lecoq de Boisbaudran, who showed that its absorption spectrum characterised not one, but two elements. Reserving the name of holmium for the element giving rise to the characteristic bands λ6404 and λ5363 of Soret's X, he called the other element, which was defined by the absorption bands λ7530 and λ4515, **dysprosium.**[5]

It has been already mentioned (p. 223) that Marignac confirmed the presence of "terbia" in the yttrium earths from gadolinite. "Terbia" is more abundant in samarskite than in gadolinite, and in 1880 Marignac fractionated the samarskite earths by means of the double potassium sulphates. He found[6] that "terbia" in samarskite is accompanied by two new earths, which in properties approached the cerite rather than the gadolinite earths. The two new elements he provisionally named $\mathbf{Y}_{\alpha}$ and $\mathbf{Y}_{\beta}$. It was considered highly probable by Marignac himself that Y_{α} was identical with Lecoq de Boisbaudran's samarium, discovered in the preceding year, and this opinion was confirmed by Soret.[7] The fact that Y_{β} was a new element was confirmed by Lecoq de Boisbaudran, and in 1886 Marignac named it **gadolinium.**[8] Subsequently, Lecoq de Boisbaudran found that Marignac's "gadolinia" contained about 10 per cent. of impurities, purified the material, and determined the atomic weight and spark spectrum of gadolinium.[9]

By the year 1886, then, Mosander's yttrium, erbium, and terbium had given place to the following list of elements:—Yttrium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and scandium. In addition to these elements, three other provisional elements, $\mathbf{Z}_{\alpha}$, $\mathbf{Z}_{\beta}$, and $\mathbf{Z}_{\gamma}$, had been announced by Lecoq de Boisbaudran as being present in "terbia,"[10] and the nature of "mosandrum," "decipium," and "phillipium" was still in doubt. Moreover, in 1886, Crookes propounded his celebrated theory of **meta-elements** as an interpretation of the results of several years

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[1] Nilson, *Compt. rend*, 1879, **88**, 645; *Ber.*, 1879, **12**, 551.

[2] See Chapter IX.

[3] Cleve, *Compt. rend.*, 1879, **89**, 478; *Chem. News*, 1879, **40**, 125.

[4] Soret, *Compt. rend.*, 1879, **89**, 521; Cleve, *ibid.*, 1879, **89**, 708; Lecoq de Boisbaudran, *ibid.*, 1879, **89**, 516.

[5] Lecoq de Boisbaudran, *Compt. rend.*, 1886, **102**, 1003, 1005.

[6] Marignac, *Arch. Sci. phys. nat.*, 1880, [iii.], **3**, 413; *Compt. rend.*, 1880, **90**, 899; *Ann. Chim. Phys.*, 1880, [v.], **20**, 535.

[7] Soret, *Compt. rend.*, 1880, **91**, 378; *Arch. Sci. phys. nat.*, 1880, [iii.], **4**, 261.

[8] Announced by Lecoq de Boisbaudran to the French Academy; *Compt. rend.*, 1886, **102**, 02.

[9] Lecoq de Boisbaudran, *ibid.*, 1889, **108**, 165; 1890, **111**, 393, 409, 472.

[10] See p. 227.

of research on the cathodic phosphorescence spectra of the rare earths.[1] At that time, therefore, the chemistry of the rare earth elements appeared to be of the most amazing complexity, and the confusion was increased when in 1887 Krüss and Nilson put forward a "one band—one element" theory of the absorption spectra of the rare earths.[2]

At the present time the chemistry of the rare earths is in a much more satisfactory state. The theories of Crookes and of Krüss and Nilson have been abandoned, and quite a number of rare earths which in 1886 were only recognised as distinct bodies from spectroscopic observations have now been isolated in a state of purity. Thus, pure gadolinia and terbia were isolated in 1905 by Urbain,[3] and the isolation of pure dysprosia was effected by the same chemist in 1906.[4] Practically pure holmia was isolated in 1911 by Holmberg,[5] and thulia by James in the same year.[6] Pure erbia, however, has not yet been prepared, though nearly pure preparations have been obtained by Urbain, James, and K. A. Hofmann; lastly, "ytterbia" has proved to be complex.

The complexity of "ytterbia" was discovered independently by Auer von Welsbach and Urbain. The former chemist announced his discovery in 1905, and termed the component elements of "ytterbium" **aldebaranium** and **cassiopëium.** The latter, who in 1907 published preliminary measurements of atomic weights and spectra, named the component elements **neoytterbium** and **lutecium.**[7] The International Committee on Atomic Weights has adopted the names *ytterbium* and *lutecium* respectively.

In 1911 Urbain[8] announced that the lutecium obtained from gadolinite is accompanied by a small amount of still another rare earth element, which he named **celtium.**

The previously mentioned elements Z_α, Z_β, and Z_γ were discovered spectroscopically by Lecoq de Boisbaudran. $\mathbf{Z}_\alpha$ was characterised by the bands $\lambda 5730$ and $\lambda 4765$, and $\mathbf{Z}_\beta$ by the bands $\lambda 6205$, $\lambda 5858$, $\lambda 5432$, and $\lambda 4870$ in its "spectre de renversement";[9] $\mathbf{Z}_\gamma$ was defined by the lines $\lambda 5835$, $\lambda 5750$, $\lambda 5700$, $\lambda 5269$, and $\lambda 5259$ in its spark spectrum.[10] In 1886 Lecoq de Boisbaudran also concluded that a fourth unknown element, $\mathbf{Z}_\delta$, was present in "terbia" and characterised it by the absorption band $\lambda 4880$, but this deduction was not published until 1895.[11]

In 1900 Demarçay[12] announced four more "spectroscopic" elements,

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[1] See later, p. 295.

[2] See later, p. 287.

[3] Urbain, *Compt. rend.*, 1905, **140**, 583 (Gd); 1905, **141** 521 (Tb).

[4] Urbain, *ibid.*, 1906, **142**, 785.

[5] Holmberg, *Arkiv Kem. Min. Geol.*, 1911, **4**, Nos. 2 and 10.

[6] James, *J. Amer. Chem. Soc.*, 1911, **33**, 1332.

[7] Auer von Welsbach, *Anzeiger K. Akad. Wiss. Wien*, 1905, No. 10; *Annalen*, 1907, **351**, 464; *Monatsh.*, 1906, **27**, 935; 1908, **29**, 181; *Sitzungsber. K. Akad. Wiss. Wien*, 1906, **115**, II. B, 737; 1907, **116**, II. B, 1425; Urbain, *Compt. rend.*, 1907, **145**, 759. See also Urbain, *Chem. Zeit.*, 1908, **32**, 730; *Zeitsch. anorg. Chem.*, 1910, **68**, 232; Auer von Welsbach, *Sitzungsber. K. Akad. Wiss. Wien*, 1909, **118**, II. B, 507; *Monatsh.*, 1909, **30**, 695; Wenzel, *Zeitsch. anorg. Chem.*, 1909, **64**, 119.

[8] Urbain, *Compt. rend.*, 1911, **152**, 141.

[9] Lecoq de Boisbaudran, *Compt. rend.*, 1885, **100**, 1437; **101**, 552, 588; 1886, **102**, 395, 483, 899, 1536; **103**, 113, 627; 1887, **105**, 258, 301, 343, 784; 1890, **110**, 24, 67; **111**, 474; 1893, **116**, 611.

[10] Lecoq de Boisbaudran, *Compt. rend.*, 1886, **102**, 153.

[11] Lecoq de Boisbaudran, *Compt. rend.*, 1895, **121**, 709.

[12] Demarçay, *Compt. rend.*, 1900, **131**, 387.

Γ, Δ, Ω, and Θ, each being characterised by its ultraviolet spark spectrum. According to Demarçay, Γ was possibly identical with true terbium, Δ was probably Z_γ, Ω (defined by the lines 3967·9 and 3930·9) came between holmium and erbium in his fractions, and Θ (defined by the lines 4008·2 and 3906·5) between erbium and ytterbium.

Of the eight elements, Z_α, Z_β, Z_γ, Z_δ, Γ, Δ, Ω, and Θ, only two, namely Ω and Θ, still await isolation or identification with other elements, for Urbain has shown conclusively that Z_β, Z_δ, and Γ are identical with terbium,[1] and that Z_α, Z_γ, and Δ are identical with dysprosium.[2]

(iv.) *Summary.*—The history of the discovery of the elements of the rare earths is summarised in the accompanying table:—[3]

Date.	Element.	Material in which it was discovered.	Discoverer.	Remarks.
1794	Yttrium	Gadolinite	Gadolin	
1804	Cerium	Cerite	Berzelius and Hisinger; Klaproth	
1839	Lanthanum	Ceria	Mosander	
1842	Didymium	,,	,,	
1843	Terbium	Yttria	,,	Called erbium from 1860 onwards
1843	Erbium	,,	,,	Called terbium from 1877 onwards
1878	Mosandrum	Samarskite	Lawrence Smith	A mixture
1878	Phillipium	Yttria earths	Delafontaine	,,
1878	Decipium	Samarskite	,,	,,
1878	Ytterbium	Erbia	Marignac	
1878	X	,,	Soret	Cleve's holmium
1879	Scandium	Ytterbia	Nilson	
1879	Samarium	Didymia	Lecoq de Boisbaudran	
1879	Thulium	Erbia	Cleve	Isolated in 1911
1879	Holmium	,,	,,	,,
1880	Y_a	Samarskite	Marignac	Named gadolinium in 1886
1885	Neodymium	Didymia	Auer von Welsbach	
1885	Praseodymium	,,	,,	
1885	Z_α	Terbia earths	Lecoq de Boisbaudran	Dysprosium
1885	Z_β	,,	,,	Terbium
1886	Z_γ	,,	,,	Dysprosium
1886	Z_δ	,,	,,	Terbium
1886	Dysprosium	Holmia	,,	Isolated in 1906
1886	Meta-elements	...	Crookes	See p. 295
1887	,,	...	Krüss and Nilson	See p. 287
1892	Z_ϵ	Samaria	Lecoq de Boisbaudran	Europium
1892	Z_ζ	,,	,,	,,
1894	Demonium	Yttria earths	Rowland	Dysprosium. See p. 430
1896	Σ	,,	Demarçay	Europium. Isolated in 1900
1896	Lucium	Yttria from monazite	Barrière	A mixture. See p. 368
1896	Kosmium	...	Kosmann	,, ,,

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[1] Urbain, *Compt. rend.*, 1905, **141**, 521; *J. Chim. phys.*, 1906, **4**, 334; Lecoq de Boisbaudran, *Compt. rend.*, 1904, **139**, 1015.

[2] Urbain, *Compt. rend.*, 1906, **142**, 785; *J. Chim. phys.*, 1906, **4**, 356.

[3] See Baskerville, *Chem. News*, 1904, **89**, 150.

Date.	Element.	Material in which it was discovered.	Discoverer.	Remarks.
1896	Neokosmium	...	Kosmann	A mixture. See p. 363
1897	Glaukodymium	Didymia	Chroustschoff[1]	Nature unknown
1899	Victorium (monium)	Yttria earths	Crookes	Disproved by Urbain. See p. 301
1900	Γ	Terbia earths	Demarçay	Terbium
...	Δ	,,	,,	Dysprosium
...	Ω	Yttria earths	,,	Unknown
...	Θ	,,	,,	,,
1905	Incognitum	,,	Crookes	Terbium. See p. 303
1905	Ionium	,,	,,	,, See p. 303
1905–1907	Neoytterbium (aldebaranium)	Ytterbia	Auer von Welsbach; Urbain	
1905–1907	Lutecium (cassiopëium)	,,	,,	
1911	Celtium	Lutecia	Urbain	

THE RARE EARTH METALS.

Preparation.—Few of the rare earth metals have been isolated in a state of purity. The following methods have been used:—

(i.) *Reduction of the anhydrous chloride* by heating it with sodium or potassium.[2] Most experimenters have found it very difficult to obtain even a moderate yield of metal by this process. The metal is very liable to be produced in a large number of fine globules, difficult to remove from the alkali chloride produced; further, the metal is liable to contain sodium or potassium.

(ii.) *Reduction of the anhydrous fluoride* by heating it with calcium or aluminium. This method does not appear to have furnished the pure metals, but cerium-calcium and cerium-aluminium alloys have been thus obtained.[3]

(iii.) *Reduction of the oxide* by heating it with magnesium,[4] aluminium,[5] calcium, carbon, or silicon.[6] Pure rare earth metals have not been obtained by any of these means. When magnesium, aluminium, or calcium is employed, alloys are usually obtained, while with aluminium there is evidence of the production of suboxides of the rare earth elements. When reductions

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[1] Chroustschoff, *J. Russ. Phys. Chem. Soc.*, 1897, **29**, 206.

[2] Mosander, *Pogg. Annalen*, 1826, **11**, 406; 1839, **46**, 648; **47**, 207; 1843, **56**, 504; *Annalen*, 1839, **32**, 235; 1843, **48**, 210; *Phil. Mag.*, 1843, **23**, 241 (Ce, La, "Di"); Beringer, *Annalen*, 1842, **42**, 134 (Ce); Berzelius, *Lehrbuch* (1826, vol. 2), p. 416; Wöhler, *Pogg. Annalen*, 1828, **13**, 580 (Y); *Annalen*, 1867, **144**, 251 (Ce); Popp, *Annalen*, 1864, **131**, 179 (Y); Marignac, *Ann. Chim. Phys.*, 1853, [iii.], **38**, 148 ("Di"); Cleve and Höglund, *Bull. Soc. chim.*, 1873, [ii.], **18**, 193 (Y); Cleve, *ibid.*, 1874, [ii.], **21**, 344 (Y); Matignon, *Ann. Chim. Phys.*, 1906, [viii.], **8**, 282 (Nd); Hunter, *Eighth Inter. Cong. Appl. Chem.*, 1912, **2**, 125 (Nd).

[3] Moldenhauer, *Chem. Zeit.*, 1914, **38**, 147.

[4] Winkler, *Ber.*, 1890, **23**, 772; 1891, **24**, 873 (La, Y, Ce); Matignon, *Compt. rend.*, 1900, **131**, 837.

[5] Matignon, *loc. cit.*; Schiffer, *Inaugural Dissertation* (München, Tech. Hochschule); Moldenhauer, *loc. cit.*; Hirsch, *J. Ind. Eng. Chem.*, 1911, **3**, 880; 1912, **4**, 65; *Trans. Amer. Electrochem. Soc.*, 1911, **20**, 57.

[6] Hirsch, *loc. cit.*

with carbon or silicon are carried out, the products are carbides and silicides of the rare earth elements.

(iv.) *Electrolysis of the molten, anhydrous chlorides*, with or without the addition of the chlorides of sodium, potassium, calcium, or barium.[1] The chloride may be melted in an iron crucible and electrolysed, using carbon electrodes. In carrying out the process, by means of which considerable quantities of the rare earth metals of the cerium group have been obtained, numerous practical difficulties arise, so that it is not possible usefully to abstract the description of the experimental procedure. The reader is therefore referred to the original memoirs of Hirsch and of Muthmann and his co-workers.[2]

(v.) *Electrolysis of the molten fluoride*, or better, a solution of the oxide in the fluoride.[3] According to Muthmann and Scheidmandel, this process is superior to the previous method, but Hirsch holds the opposite view.

The rare earth metals obtained by electrolysis may be purified by melting them under a layer of barium chloride in a magnesia crucible.

Properties.[4]—The rare earth elements are lustrous metals. Lanthanum has the whiteness of tin, cerium that of iron; neodymium has a yellow tinge, and praseodymium is decidedly yellow; samarium is pale grey in colour. With the exception of lanthanum, they retain their lustre in dry air. When compared with lead, tin, and zinc, the order of increasing hardness is as follows: Pb, Sn, Ce, La, Zn, Nd, Pr, Sm. Cerium can easily be cut with a knife; samarium is as hard as steel. The densities and melting-points are given by Muthmann and Weiss as follows:—

	La.	Ce.	Pr.	Nd.	Sm.
Melting-point, °C.	810°	623°	940°	840°	...
Density at 20° C.	6·155	7·042	6·475	6·956	7·7–7·8

Hirsch gives the values 635° and 6·92 (at 25°) for cerium.

The rare earth metals burn in air or oxygen very readily, with the evolution of much heat and light (p. 257). Cerium, for example, begins to burn at 160° in air. They also combine with hydrogen, nitrogen, chlorine, and bromine when heated in those gases, and react with iodine, sulphur, phosphorus, etc. They are, in fact, highly reactive elements. In dilute mineral acids they readily dissolve, and, except with nitric acid, hydrogen is evolved. They are also attacked by water, very slowly at ordinary temperatures, but more rapidly at 100°.

Numerous cerium alloys and a few alloys of the other rare earth metals have been prepared; one of these may be mentioned here, viz. the alloy known as **mischmetall.** Owing to the large amount of heat evolved when any of the rare earth metals is burnt in air, these metals form excellent

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[1] Erk, *Zeitsch. für Chem.*, 1870, [ii.], **7**, 100; *Jahresber.*, 1870, p. 319 (Ce); Cleve and Höglund, *Bull. Soc. chim.*, 1873, [ii.], **18**, 193, 289 (Y); Frey, *Annalen*, 1874, **183**, 367 (Ce); and particularly the following: Hillebrand and Norton, *Pogg. Annalen*, 1875, **155**, 633; **156**, 466 (Ce, La, "Di"); Muthmann, Hofer, and Weiss, *Annalen*, 1902, **320**, 231 (Ce, Nd); Muthmann and Kraft, *Annalen*, 1902, **325**, 261 (Ce, La); Muthmann and Weiss, *ibid.*, 1904, **331**, 1 (Ce, La, Nd, Pr, Sm); Hirsch, *loc. cit.* (Ce); Borchers and Stockem, *D.R.P.*, No. 172,529.

[2] Full details will also be found in Kellermann, *Die Ceritmetalle und ihre pyrophoren Legierungen* (Knapp, Halle, 1912).

[3] Muthmann and Scheidmandel, *Annalen*, 1907, **355**, 116; Hirsch, *loc. cit.*

[4] Hillebrand and Norton, *loc. cit.*; Muthmann and others, *loc. cit.*: Hirsch, *loc. cit.*

reducing agents for preparing other elements from their oxides. It is obvious that a mixture of rare earth metals would do equally well for this purpose; hence the preparation of mischmetall, which consists essentially of cerium, lanthanum, praseodymium, and neodymium, and is prepared from the residual salts of these metals left over after the thorium and sufficient cerium and "didymium" for the gas-mantle industry have been extracted from monazite sand. Mischmetall reduces the oxides of numerous elements, *e.g.* iron, cobalt, nickel, manganese, chromium, molybdenum, vanadium, columbium, tantalum, silicon, boron, tin, lead, titanium, and zirconium, and has been of considerable service in the preparation of a number of rare elements.[1]

VALENCY, ATOMIC WEIGHTS, AND CLASSIFICATION OF THE RARE EARTH ELEMENTS.

Theoretical.[2] *Historical Résumé.*—In 1810 the rare earths had only been separated into "ceria" and "yttria," and Berzelius, in constructing his first atomic weight table, regarded yttria as YO_2, ceria as CeO_3, and the lower oxide (cerous oxide) as CeO_2. In 1826 he first admitted the existence of sesquioxides, and in the changes necessitated in his atomic weights and formulæ the three preceding formulæ were involved and became YO, Ce_2O_3, and CeO respectively.

By the year 1842 the rare earths had been separated into ceria, lanthana, "didymia," yttria, "erbia," and "terbia"; except for the fact that Mosander's "erbia" was denied existence by various chemists, their number remained unaltered until 1878, and prior to 1870 their formulæ were all written in the form MO, ceria being excepted. These formulæ were chosen because the rare earths were strong bases like lime, strontia, and baryta, and on Gmelin's system of atomic weights (the one most commonly adopted) these substances were written CaO, SrO, BaO. Ceria, however, was discovered to be Ce_3O_4 if cerous oxide is CeO, and not Ce_2O_3 as had previously been supposed; and for some years it was supposed that ceria was a compound of two oxides CeO and CeO_2 (Ce_3O_4 being $2CeO.CeO_2$), the oxide CeO_2 being the one from which ceric salts were derived. The latter assumption was not difficult to make, for pure ceric salts had not been prepared and analysed.

The evolution of the modern system of atomic weights in 1858 did not affect the formulæ of the compounds of the rare earth elements, for the necessary experimental data were not then available. The proposal to change the accepted atomic weights and formula was made in 1870 by Mendeléeff,[3] who considered that the following formulæ should replace those that were then in use:—

ceria	CeO_2;	lanthana	LaO_2;	yttria	Y_2O_3
cerous oxide	Ce_2O_3;	didymia	Di_2O_3;	erbia	Er_2O_3.

Valuable support was soon forthcoming for Mendeléeff's views. In 1872 Cleve agreed that the tervalency of yttrium and erbium was very probable, and pointed out the fact that the formulæ of their compounds were thus

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[1] See Weiss and Aichel, *Annalen*, 1904, 337, 370.

[2] Throughout this section, ceric compounds are disregarded, except where the contrary is expressly stated.

[3] Mendeléeff, *Annalen Suppl.*, 1872, 8, 133; translation in *Chem. News*, 1879, 40, 231, etc.; 1880, 41, 2, etc.; see also Mendeléeff, *Bull. Acad. Sci. Petrograd*, 1870, p. 445.

simplified. Two years later, he definitely accepted the tervalency of yttrium, erbium, "didymium," and cerium (in the cerous salts), but differed from Mendeléeff in regarding lanthanum also as a triad.[1] In 1876 Hillebrand showed that the specific heats of lanthanum, cerium, and "didymium" were in harmony with Cleve's view,[2] and Rammelsberg,[3] who had previously objected to Mendeléeff's proposals,[4] accepted those of Cleve.

From that time onward the tervalency of the rare earth elements has been generally accepted; occasionally, however, a dissentient voice has been heard. Thus, Cossa[5] argued for the bivalency, and Winkler[6] for the quadrivalency of these elements. Winkler, however, abandoned his views after they had been criticised by Brauner;[7] and it has remained for only two chemists —Wyrouboff, and his frequent collaborator, Verneuil—consistently to uphold the bivalency of the rare earth elements.[8] These two French chemists decline to accept the *physical* evidence of specific heats and isomorphism, the latter on fairly good grounds,[9] and utterly reject any considerations based upon the Periodic Classification, which they regard as a metaphysical conception. Instead, they demand *chemical* proofs, and consider from that point of view that they can establish a very close relationship between the rare earth elements and the bivalent metals. Into the nature of these chemical relationships, however, it is hardly necessary to enter, for, whatever value may attach to them, Urbain has shown that similar relationships may be recalled which connect the rare earth elements at least as well with bismuth.[10]

The evidence bearing on the valency of the rare earth elements will now be considered in some detail.

(i.) *Dulong and Petit's Law.*—The only specific heat data for the elements themselves are given in the following table:—

Element.	Specific Heat.	Temp. Range.	Combining Weight.	Combining Weight × Specific Heat.
Cerium . . .	0·0448[11]	0°–100°	46·8	2·09 = 6·4/3 approx.
,, . . .	0·050[12]	?	46·8	2·34 = 6·4/3 ,,
,, . . .	0·0511[13]	20°–100°	46·8	2·39 = 6·4/3 ,,
Lanthanum . .	0·0449[11]	0°–100°	46·3	2·08 = 6·4/3 ,,
"Didymium" .	0·0456[11]	0°–100°	47 7	2·18 = 6·4/3 ,,

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[1] Cleve and Höglund, *Bull. Soc. chim.*, 1872, [ii.], **18**, 193, 289; Cleve, *ibid.*, 1874, [ii.], **21**, 196, 246, 344; Jolin, *ibid.*, 1874, [ii.], **21**, 533.

[2] Hillebrand, *Pogg. Annalen*, 1876, **158**, 71.

[3] Rammelsberg, *Ber.*, 1876, **9**, 1580.

[4] Rammelsberg, *Ber.*, 1873, **6**, 84. See also Delafontaine, *Arch. Sci. phys. nat.*, 1874, **51**, 45, and Mendeléeff, *Annalen*, 1873, **168**, 45.

[5] See p. 234.

[6] Winkler, *Ber.*, 1891, **24**, 873.

[7] Brauner, *Ber.*, 1891, **24**, 1328; Winkler, *Ber.*, 1891, **24**, 1966.

[8] See particularly Wyrouboff, *Bull. Soc. franç. Min.*, 1896, **19**, 219; 1905, **28**, 201; Wyrouboff and Verneuil, *Bull. Soc. chim.*, 1899, [iii.], **21**, 118; *Ann. Chim. Phys.*, 1905, [viii.], **6**, 465–482.

[9] See p. 235.

[10] Urbain, *J. Chim. phys.*, 1906, **4**, 107.

[11] Hillebrand, *Pogg. Annalen*, 1876, **158**, 71.

[12] Mendeléeff, *Bull. Acad. Sci. Petrograd*, 1870, p. 445.

[13] Hirsch, *J. Ind. Eng. Chem.*, 1911, **3**, 880; 1912, **4**, 65.

It will be seen that the results argue very strongly for the tervalency of the elements.

The extension of Dulong and Petit's Law to compounds, usually called Kopp's Law, may also be utilised. The mean specific heats between 0° and 100° of a number of the rare earths and their sulphates were measured by Nilson and Pettersson, from whose memoir the following figures are taken :—[1]

Compound.	Specific Heat.	Molecular Heat.	Compound.	Specific Heat.	Molecular Heat.
Al_2O_3	0·1879	19·32	$Al_2(SO_4)_3$	0·1855	63·59
Sc_2O_3	0·1530	20·81	$Sc_2(SO_4)_3$	0·1639	62·42
Ga_2O_3	0·1062	19·54	$Ga_2(SO_4)_3$	0·1460	61·90
Y_2O_3	0·1026 [2]	23·29	$Y_2(SO_4)_3$	0·1319	61·60
In_2O_3	0·0807	22·17	$In_2(SO_4)_3$	0·1290	66·41
Er_2O_3	0·0650	24·70	$Er_2(SO_4)_3$	0·1040	64·48
"Yb_2O_3"	0·0646	25·45	"$Yb_2(SO_4)_3$"	0·1039	65·87
La_2O_3	0·0749	24·42	$La_2(SO_4)_3$	0·1182	66·90
"Di_2O_3"	0·0810	27·62	"$Di_2(SO_4)_3$"	0·1187	68·96
			$Ce_2(SO_4)_3$	0·1168	66·23
			$Fe_2(SO_4)_3$	0·1656	66·24
			$Cr_2(SO_4)_3$	0·1718	67·41

The tervalency of the rare earth elements mentioned in the preceding table is thus seen to be in harmony with Kopp's Law, when the molecular heats of the oxides and sulphates of the tervalent elements aluminium, scandium, gallium, indium, iron, and chromium are compared with the similar data for the compounds of the rare earth elements.[3] The evidence, however, is not very strong. From measurements of the specific heats of cerous and "didymium" tungstates Cossa concluded that the rare earth elements are diads.[4]

(ii.) *Transparency to X-rays.* — Benoist's method, as described under Indium (see pp. 152–4), has been applied to cerium, and the results obtained show that the atomic weight of the element is three times the chemical equivalent of cerium in cerous salts.[5]

(iii.) *X-ray Spectra.*—The X-ray spectra of the elements are discussed later in this volume (see pp. 312, 363), where it is shown that the atomic numbers of the rare earth elements (yttrium excepted) lie between those of barium and tantalum. Since, in general, the order of increasing atomic numbers is the same as that of increasing atomic weights, it follows that the atomic weights of the rare earth elements lie between those of barium and tantalum, a clear indication that the rare earth elements are tervalent.

(iv.) *The Law of Isomorphism.* — It very frequently happens that corresponding compounds of the rare earth elements are isomorphous. The actual cases need not, however, be cited here, as full details are given later

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[1] Nilson and Pettersson, *Compt. rend.*, 1880, **91**, 232 ; *Ber.*, 1880, **13**, 1459.

[2] *Cf.* Tanatar and Voljansky, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 96.

[3] It may be remarked that the atomic heats of the elements aluminium and gallium are decidedly below the normal value 6·4. The values for scandium and yttrium are not known.

[4] Cossa, *vide infra* ; Cossa and Zechini, *vide infra*.

[5] Benoist and Copaux, *Compt. rend.*, 1914, **158**, 689.

in this chapter, when the rare earth salts are described in some detail (see pp. 250–282).

The conclusion that may be drawn from the preceding fact is very important. *The ratio* **atomic weight : combining weight** *is the same for all the rare earth elements*, the combining weights being deduced from the compositions of the basic oxides. The determination of this ratio by utilising the law of isomorphism cannot, however, be effected unless cases of isomorphism between compounds of the rare earth elements and of other elements of known atomic weight can be discovered. A number of such cases are actually known, and the conclusions to which they lead are conflicting; in part the results indicate that the rare earth elements are diads, and in part they point to their being triads.

(*a*) Cerous and "didymium" tungstates and molybdates are isomorphous, and form mixed crystals with calcium tungstate, $CaWO_4$, and lead molybdate, $PbMoO_4$.[1]

(*b*) Calcium and strontium silicotungstates are isomorphous and form mixed crystals with the silicotungstates of lanthanum, cerium, and "didymium."[2]

(*c*) Lanthanum, cerium, and "didymium" silicotungstates are also isomorphous with the thorium salt.[3]

(*d*) In certain minerals, *e.g. parisite*, *cordylite*, *yttrocerite*, and *yttrofluorite*, the fluorides of calcium, barium, and the rare earth elements are present in isomorphous mixture.[4]

(*e*) Bismuth nitrate forms a stable pentahydrate, $Bi(NO_3)_3.5H_2O$, and a labile hexahydrate, $Bi(NO_3)_3.6H_2O$; lanthanum and "didymium" nitrates form stable hexahydrates, $M(NO_3)_3.6H_2O$, and labile pentahydrates, $M(NO_3)_3.5H_2O$, if the metals are regarded as tervalent, and these salts are isodimorphous with bismuth nitrate, two series of mixed crystals being formed with the La-Bi and two with the "Di"-Bi mixtures. Two series of mixed crystals are also formed with the yttrium-bismuth mixtures.[5]

Bismuth nitrate, $Bi(NO_3)_3.5H_2O$, is isomorphous with the nitrates of the metals of the terbium and yttrium groups obtained by crystallising from fairly concentrated nitric acid (density 1·3). These hydrates are of the type $M^{III}(NO_3)_3.5H_2O$ if the rare earths are tervalent. The gadolinium, terbium, dysprosium, and holmium salts form mixed crystals with the bismuth salt, which also induces the crystallisation of neoytterbium and lutecium nitrates.[6]

The hydrates of bismuth sulphate are isomorphous with various hydrates of the rare earth sulphates, and the following mixed crystals have been prepared, but only containing a few per cent. of the rare earth salts:—[7]

$(Bi,La)_2(SO_4)_3.9H_2O$ $(Bi,\text{"Di"})_2(SO_4)_3.8H_2O$
$(Bi,La)_2(SO_4)_3.5H_2O$ $(Bi,Y)_2(SO_4)_3.8H_2O$

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[1] Cossa, *Gazzetta*, 1879, 9, 118; 1880, 10, 467; *Compt. rend.*, 1884, 98, 990; 1886, 102, 1315; Cossa and Zecchini, *Gazzetta*, 1880, 10, 225; Didier, *Compt. rend.*, 1886, 102, 823; Högbom, *Bull. Soc. chim.*, 1884, [ii.], 42, 2.

[2] Wyrouboff, *Bull. Soc. franç. Min.*, 1896, 19, 219; 1905, 28, 201.

[3] Wyrouboff, *loc. cit.*

[4] T. Vogt, *Jahrb. Min.*, 1914, II., 9.

[5] Bodman, *Bihang K. Svenska Vet.-Akad. Handl.*, 1900, 26, II., No. 3; *Zeitsch. anorg. Chem.*, 1901, 27, 254; *Zeitsch. Kryst. Min.*, 1900, 32, 613; 1902, 36, 192; *Ber.*, 1898, 31, 1237.

[6] Urbain, *Compt. rend.*, 1904, 139, 736; 1909, 149, 37; *J. Chim. phys.*, 1906, 4, 342; Blumenfeld and Urbain, *Compt. rend.*, 1914, 159, 323.

[7] Bodman, *loc. cit.*

Lanthanum ammonium nitrate, which is $La(NO_3)_3.2(NH_4)NO_3.4H_2O$, on the assumption that lanthanum is tervalent, forms mixed crystals with bismuth ammonium nitrate, $Bi(NO_3)_3.2(NH_4)NO_3.4H_2O$.[1]

Bismuth nitrate forms double salts with the nitrates of magnesium, zinc, nickel, cobalt, and manganese. They are of the type $2Bi(NO_3)_3.3M^{II}(NO_3)_2.24H_2O$, hexagonal, and isomorphous with one another. The nitrates of lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium also form double nitrates with the diad elements already mentioned. They are of the type $2M^{III}(NO_3)_3.3M^{II}(NO_3)_2.24H_2O$, if the rare earth elements are triads. These salts are hexagonal and strictly isomorphous with the bismuth salts; the latter readily form mixed crystals with the salts of gadolinium, europium, and samarium.[2]

Summing up the crystallographic evidence, it may be said that while the evidence given in paragraphs (*a*), (*b*), and (*d*) above is in favour of the view that the rare earth elements are diads, that given in (*c*) suggests that they are tetrads, and that given in (*e*) strongly suggests that they are triads. The evidence derived from the study of the silicotungstates cannot be considered at all conclusive. It may obviously be used to support the view that thorium is a diad, a view contrary to all the other evidence bearing on the valency of thorium;[3] and it may be added that it also leads to the untenable conclusion that lithium is a diad.[4] In fact, with such a large molecule as that of a silicotungstate, the nature of the metal present would appear to exert only a minor influence on the crystalline structure. The cases of the molybdates and tungstates, however, cannot be ruled aside in a similar manner, but in view of the strong evidence in favour of the tervalency of the rare earth elements afforded by their isomorphism with bismuth, it is possible that the cases of the molybdates and tungstates are to be ranked with the other "unusual" cases of isomorphism that have been pointed out by Barker.[5] The safest plan, nevertheless, is to ignore the evidence based upon considerations of isomorphism.

(v.) *Molecular Weight Measurements.*—No compounds of the rare earth elements are known that volatilise without decomposition at temperatures suitable for vapour density determinations. Molecular weights have accordingly to be measured in solution.

(*a*) The anhydrous chlorides of lanthanum, cerium, praseodymium, neodymium, and yttrium have been studied in alcoholic solution by the boiling-point method. The molecular weights are in accordance with the simple formulæ $M^{III}Cl_3$, the metals being tervalent.[6]

(*b*) The chlorides of neodymium, samarium, and "ytterbium" have been examined in aqueous solution by the freezing-point method. Here, owing to ionisation, it is necessary to express comparative results. For solu-

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[1] Urbain and Lacombe; cited by Urbain, *J. Chim. phys.*, 1906, 4, 105.

[2] Urbain and Lacombe, *Compt. rend.*, 1903, **137**, 568, 792, 820; Urbain, *J. Chim. phys.*, 1906, 4, 105.

[3] See Vol. V. of this series.

[4] See Wyrouboff, *loc. cit.*

[5] Barker, *Trans. Chem. Soc.*, 1912, **101**, 2484.

[6] Muthmann, *Ber.*, 1898, **31**, 1829 (Ce); Brauner, *Proc. Chem. Soc.*, 1901, **17**, 65; *Chem. Zentr.*, 1900, ii. 524 (Pr); Matignon, *Ann. Chim. Phys.* 1906, [viii.], 8, 273 (Nd), 435 (Y); W. Biltz, *Annalen*, 1904, **331**, 334 (La "Di"). In alcoholic solution the rare earth chlorides are undoubtedly combined with the solvent (see p. 255).

tions which freeze at − 1° C. the following "molecular depressions" have been found :—[1]

$NdCl_3$	68	$AlCl_3$	64·5
$SmCl_3$	65·6	$CrCl_3$	65
$YbCl_3$	66	$Al(NO_3)_3$	65·4

The foregoing results are calculated on the assumption that the rare earth metals are tervalent, and the assumption is seen to be very satisfactory. The alternative view that they are diads is much less satisfactory.

(*c*) Various acetylacetonates of the rare earth metals have been examined in organic media. The results are in harmony with the view that the acetylacetonates have the double molecular weight, *i.e.* $[M^{III}\{(CH_3.CO)_2CH\}_3]_2$, in moderately concentrated solution, and that the double molecules break down with dilution. The following cases have been examined :—[2]

Ce compd. in carbon tetrachloride; "Di" compd. in carbon tetrachloride.
Pr „ „ „ disulphide; Sm „ „ „ disulphide.
Nd „ „ ethyl sulphide.

(*d*) The equivalent conductivities of aqueous solutions of various salts of the rare earth elements have been measured. The following results have been obtained at 25° :—[3]

$LaCl_3$[4]	$\lambda_{1024} - \lambda_{32} = 25·7$;	YCl_3[4]	$\lambda_{1059} - \lambda_{33} = 24·7$
$CeCl_3$[5]	$\lambda_{1006} - \lambda_{33} = 28·5$;	$La(NO_3)_3$[6]	$\lambda_{1024} - \lambda_{32} = 28·0$
$PrCl_3$[5]	$\lambda_{1002} - \lambda_{31·3} = 30·4$;	$La_2(SO_4)_3$[5]	$\lambda_{1024} - \lambda_{34} = 51·6$
$NdCl_3$[5]	$\lambda_{987} - \lambda_{29·3} = 30·4$;	$Ce_2(SO_4)_3$[5]	$\lambda_{1056} - \lambda_{33} = 55·2$
$SmCl_3$[5]	$\lambda_{1043} - \lambda_{31·4} = 28·7$;	$Sm_2(SO_4)_3$[5]	$\lambda_{1003} - \lambda_{31·4} = 58·1$

According to Brauner and Švagr, the value of $\lambda_{1024} - \lambda_{32}$ at 25° for each of the sulphates of lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, yttrium, erbium, and "ytterbium" is 56 approximately.[7]

In accordance with Ostwald's Rule[8] the value of $\lambda_{1024} - \lambda_{32}$ should be about 30 for the chlorides and nitrates and about 60 for the sulphates if the rare earth elements are tervalent, the corresponding values for bivalent metals being 20 and 40 respectively. It is evident that the experimental evidence is, on the whole, decidedly favourable to the tervalency of the metals.[9]

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[1] Matignon, *Ann. Chim. Phys.*, 1906, [viii.], **8**, 274 (Nd), 403 (Sm), 443 (Yb); other data due to Raoult, *ibid.*, 1885, [vi.], **4**, 411.

[2] W. Biltz, *Annalen*, 1904, **331**, 334.

[3] The formulæ are written on the assumption that the rare earth elements are tervalent, but the numerical data, being equivalent conductivities, are independent of this assumption. The dilution *v* is expressed in litres per gram-equivalent, as usual.

[4] Ley, *Zeitsch. physikal. Chem.*, 1899, **30**, 193.

[5] Aufrecht, *Inaugural Dissertation* (Berlin, 1904); see Abegg, *Handbuch der anorganischen Chemie* (Leipzig, 1906), vol. 3, pt. 1.

[6] Muthmann, *Ber.*, 1898, **31**, 1829.

[7] Brauner and Švagr, cited in Abegg, *opus cit.*, p. 170. For other conductivity measurements, see Jones and Allen, *Amer. Chem. J.*, 1896, **18**, 321; Jones and Reese, *ibid.*, 1898, **20**, 606; Noyes and Johnston, *J. Amer. Chem. Soc.*, 1909, **31**, 987.

[8] See Vol. I. p. 150.

[9] That the rare earth elements are tervalent is also shown by the behaviour of their salts in coagulating arsenious sulphide hydrosol (Freundlich and Schucht, *Zeitsch. physikal. Chem.*, 1912, **80**, 564).

(vi.) *Composition of Salts.*—The assumption that the rare earth elements are triads often leads to formulæ considerably simpler than those necessitated by the assumption that they are diads. This was pointed out by Cleve and Höglund in discussing the compounds of yttrium and "erbium."[1] The following alternative formulæ of a number of yttrium salts may be cited:—

Diad.	Triad.
$YSO_4.\frac{8}{3}H_2O$ or $3YSO_4.8H_2O$	$Y_2(SO_4)_3.8H_2O$
$Y_3Na_2(SO_4)_4.2H_2O$ or $3YSO_4.Na_2SO_4.2H_2O$	$Y_2(SO_4)_3.Na_2SO_4.2H_2O$
$Y_3(NH_4)_4(SO_4)_4.9H_2O$ or $3YSO_4.2(NH_4)_2SO_4.9H_2O$	$Y_2(SO_4)_3.2(NH_4)_2SO_4.9H_2O$
$Y_3K_2[Fe(CN)_6]_2.4H_2O$	$YKFe(CN)_6.2H_2O$
$Y_3H_2(SeO_3)_4$ or $3YSeO_3.H_2SeO_3$	$Y_2(SeO_3)_3.H_2SeO_3$
$Y_3H_2(P_2O_7)_2.7H_2O$	$2YH(P_2O_7)_2.7H_2O$
$Y_3K_2(C_2O_4)_4.H_2O$ or $3YC_2O_4.K_2C_2O_4.H_2O$	$Y_2(C_2O_4)_3.K_2C_2O_4.H_2O$
$Y_3H_2(C_4H_4O_6)_4.6H_2O$	$YH(C_4H_4O_6)_4.6H_2O$

The manner in which Y_3 enters into the diad formulæ of the double salts is very curious and significant.

Similar results hold for the salts of each of the rare earth metals that has been studied in any detail. The compounds that cerous, neodymium, and samarium chlorides form with ammonia may be cited as further examples of the simplicity of the triad formulæ:—

Triad.	Diad.	Triad.	Diad.	Triad.	Diad.
$CeCl_3.20NH_3$	$CeCl_2.13\frac{1}{3}NH_3$	$NdCl_3.12NH_3$	$NdCl_2.8\ NH_3$	$SmCl_3.11\frac{1}{2}NH_3$	$SmCl_2.7\frac{2}{3}NH_3$
$CeCl_3.12NH_3$	$CeCl_2.\ 8\ NH_3$	$NdCl_3.11NH_3$	$NdCl_2.7\frac{1}{3}NH_3$	$SmCl_3.\ 9\frac{1}{2}NH_3$	$SmCl_2.6\frac{1}{3}NH_3$
$CeCl_3.\ 8NH_3$	$CeCl_2.\ 5\frac{1}{3}NH_3$	$NdCl_3.\ 8NH_3$	$NdCl_2.5\frac{1}{3}NH_3$	$SmCl_3.\ 8\ NH_3$	$SmCl_2.5\frac{1}{3}NH_3$
$CeCl_3.\ 4NH_3$	$CeCl_2.\ 2\frac{2}{3}NH_3$	$NdCl_3.\ 5NH_3$	$NdCl_2.3\frac{1}{3}NH_3$	$SmCl_3.\ 5\ NH_3$	$SmCl_2.3\frac{1}{3}NH_3$
$CeCl_3.\ 2NH_3$	$CeCl_2.\ 1\frac{1}{3}NH_3$	$NdCl_3.\ 4NH_3$	$NdCl_2.2\frac{2}{3}NH_3$	$SmCl_3.\ 4\ NH_3$	$SmCl_2.2\frac{2}{3}NH_3$
		$NdCl_3.\ 2NH_3$	$NdCl_2.1\frac{1}{3}NH_3$	$SmCl_3.\ 3\ NH_3$	$SmCl_2.2\ NH_3$
		$NdCl_3.\ 1NH_3$	$NdCl_2.\ \frac{2}{3}NH_3$	$SmCl_3.\ 2\ NH_3$	$SmCl_2.1\frac{1}{3}NH_3$
				$SmCl_3.\ 1\ NH_3$	$SmCl_2.\ \frac{2}{3}NH_3$

The triad formulæ are here clearly more convenient than the diad.

Further than this, the double and complex salts of the rare earth elements are often *different in type* from those of the known diad elements. Consider, for instance, the *chloroplatinates*. Those of the known uni- and bi-valent metals are normal, *i.e.* the chlorine of the platinic chloride is twice the chlorine of the metal chloride, *e.g.* $2KCl.PtCl_4$ and $MgCl_2.PtCl_4.6H_2O$. The salts of metals known to be tervalent are not, however, of the normal type, but are basic; and the salts of the rare earth elements are similar in composition to them, thus:—

$2(AlCl_3.PtCl_4).30H_2O$;	$2(CeCl_3.PtCl_4).27H_2O$
$2(FeCl_3.PtCl_4).21H_2O$;	$2(\text{"Di"}Cl_3.PtCl_4).21H_2O$
$2(CrCl_3.PtCl_4).21H_2O$;	$2(\text{"Er"}Cl_3.PtCl_4).21H_2O$
$2(LaCl_3.PtCl_4).27H_2O$;	

The indium and yttrium salts are anomalous, being $2InCl_3.5PtCl_4.36H_2O$ and $4YCl_3.5PtCl_4.52H_2O$ respectively, but neither is of the normal type. From the composition of the chloroplatinates, then, the rare earth elements must

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[1] Cleve and Höglund, *Bull. Soc. chim.*, 1872, [ii.], **18**, 193, 289. See also Cleve, *ibid.*, 1874, [ii.], **21**, 196, 246, 344; Jolin, *ibid.*, 1874, [ii.], **21**, 533.

be regarded as tervalent; and the same conclusion may be drawn from a study of the *chloroplatinites* and the *selenites*.[1]

(vii.) *The Periodic Classification.*—It has been already stated that Mendeléeff was the first to reject the idea of the bivalency of the rare earth elements, and the formulæ he proposed for the oxides of these elements have been given (see p. 231). His method of incorporating the rare earth elements into the Periodic Table was as follows:—

Sr	**Y**	Zr	Nb
Cd	In	Sn	Sb
Ba	**Di**	**Ce**	–
	–	–	–
–	**Er**	**La**	Ta

With regard to these positions, Mendeléeff was convinced of the accuracy of his views concerning cerium, the more so as he showed experimentally that cerium thereby followed Dulong and Petit's Law;[2] but although he was satisfied with the position he assigned to yttrium, he was doubtful over lanthanum, didymium, and erbium. The positions assigned to these elements by Mendeléeff in his table need not, however, be further discussed, since the "didymium" and "erbium" of 1872 are now known to be complex mixtures.

At the present time the problem is to place not five, but fifteen, rare earth elements into the Periodic Table. Inspection of that table will show that in seeking positions for the rare earth elements only two vacant places occur for elements of atomic weight less than that of barium, viz. one between strontium (87·63) and zirconium (90·6), and the other between molybdenum (96·0) and ruthenium (101·7). Between barium (137·37) and tantalum (181·0) there are many vacant places. The atomic weights of the rare earth elements are as follows, according to whether they are diads or triads:—

Element.	Diad.	Triad.	Element.	Diad.	Triad.	Element.	Diad.	Triad.
Yttrium .	59·1	88·7	Samarium .	100·3	150·4	Holmium .	109·0	163·5
Lanthanum .	92·7	139·0	Europium .	101·3	152·0	Erbium .	111·8	167·7
Cerium . .	93·5	140·3	Gadolinium .	104·9	157·3	Thulium .	112·3	168·5
Praseodymium	93·9	140·9	Terbium .	106·1	159·2	Ytterbium .	115·7	173·5
Neodymium .	96·2	144·3	Dysprosium .	108·3	162·5	Lutecium .	116·7	175·0

Assuming that the rare earth elements are diads, it is seen at once that (i.) there is no place in the Periodic Table for yttrium, (ii.) three elements

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[1] Nilson, *Ber.*, 1876, **9**, 1056 (chloroplatinates); *Ber.*, 1876, **9**, 1142; or *J. prakt. Chem.*, 1877, [ii.], **15**, 260 (chloroplatinites); *Ber.*, 1875, 8, 655; *Bull. Soc. chim.*, 1875, [ii.], **23**, 494; or *Nova Acta Soc. Upsala*, 1875, [iii.], **9**, No. 7 (selenites). See also Cleve and Höglund, *Bull. Soc. chim.*, 1872, [ii.], **18**, 193, 289; Cleve, *ibid.*, 1874, [ii.], **21**, 196, 246, 344.

[2] See p. 232.

compete for the one vacant place between molybdenum and ruthenium, (iii.) eleven other elements resemble yttrium in being without places, and (iv.) the spaces between barium and tantalum still remain unoccupied. On the other hand, assuming the elements to be triads, it is observed that (i.) yttrium occupies the vacant space between strontium and zirconium, (ii.) the space between molybdenum and ruthenium remains vacant, and (iii.) fourteen elements, the atomic weights of which lie between those of barium and tantalum, are available for filling the vacancies between the positions of those two elements.

On the assumption of the tervalency of the rare earth elements, then, it it possible to place all these elements into vacant spaces. From the chemical point of view, however, the positions that the rare earth elements then occupy are most unsatisfactory, except in the cases of yttrium, lanthanum, and cerium. Lanthanum and cerium follow directly after barium, for there are good reasons for regarding cerium as a member of Group IV. in the table. Hence, scandium, yttrium, and lanthanum must be grouped together as constituting the even subgroup of Group III.; and this view is in very fair accordance with their properties. There still remain, however, twelve more elements, and it is impossible to arrange them in positions which range from Group I. to Group VIII., to assume that each is tervalent in its salts, and still accept the truth of the Periodic Law. Clearly such assumptions are mutually contradictory. So far, therefore, as the rare earth elements are concerned, Mendeléeff's classification is defective, and cannot be legitimately utilised in arguing for or against the tervalency of the rare earth elements.

(viii.) *The Case of Cerium.*—The element cerium differs from the other rare earth elements in that it forms two basic oxides and two series of salts. Referred to unit weight of cerium, the oxygen in the lower oxide is to that in the higher oxide as 3 is to 4. From the point of view of simplicity, then, the oxides are best formulated as Ce_2O_3 and CeO_2, cerium being regarded as both triad and tetrad. If, however, cerium in cerous salts is regarded as a diad, it follows that the higher oxide is Ce_3O_4, quite a unique type of basic oxide, and that the formulæ of the ceric salts are very complicated.

There is, moreover, strong evidence in favour of the first of the two preceding views, and for classifying cerium with titanium, zirconium, and thorium as a group of tetrad elements. Since the evidence is fully discussed in a subsequent volume,[1] it is unnecessary to repeat it here; it is only necessary to point out that the fact that evidence independent of the preceding shows cerium to be tervalent in cerous salts is a strong argument in favour of the tervalency of the other rare earth elements.

(ix.) *Summary.*—The evidence bearing upon the question of the valencies and atomic weights of the rare earth elements has now been discussed, from various different points of view. Whatever the value that may be assigned to the crystallographic evidence and the appeal to the Periodic Law, the balance of evidence indicates that the rare earth elements are tervalent in their salts. This view, which is accepted by nearly all chemists, is the one adopted in this book.

Practical Methods of Atomic Weight Measurement.—The chief methods that have been employed in the determination of the atomic weights of the rare earth elements are briefly outlined in the following paragraphs.

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[1] See Vol. V. of this series.

(i.) *Sulphate Methods.*—(*a*) Synthetical. A weighed amount of the pure sesquioxide, prepared by the ignition of the pure oxalate, is dissolved in hydrochloric acid in a weighed platinum crucible, a slight excess of sulphuric acid added, and the solution evaporated as far as possible on the water-bath. The evaporation is then continued at a higher temperature until the excess of sulphuric acid has been removed and the residual anhydrous sulphate brought to constant weight at about 500°. If the weights of oxide and sulphate be a and b respectively, and the required atomic weight be X, then

$$2X + 48{\cdot}000 : 2X + 288{\cdot}195 :: a : b \qquad . \quad . \quad . \quad (I.)$$

This method, originated (in a slightly different form) by Bahr and Bunsen in 1866, has been used more than any other for determining the atomic weights of the rare earth elements.[1] Although, however, the procedure is simple, the method is certainly not the best that can be employed for the atomic weight determinations. Owing to the extremely hygroscopic nature of the anhydrous sulphates, great care must be taken to exclude moisture from the salts until they have been weighed. The chief difficulty, however, consists in obtaining the sulphates dry and neutral, since water and sulphuric acid are retained if the final temperature of heating is too low, and decomposition of the sulphates begins if the final temperature is too high. In the former case, the sulphates dissolve in water, forming clear solutions which react acid towards methyl-orange; in the latter, the sulphates do not dissolve to a clear solution. The precise final temperature to employ probably requires in each individual case a special investigation for its determination. In many cases, the boiling-point of sulphur, which is probably too low, has been chosen; Wild recommends 450°–500°, and other chemists have adopted 500°. According to Brauner, it is always necessary to dissolve the residual sulphate in water, titrate with N/10 sodium hydroxide till the solution is neutral, and apply the appropriate correction. In view of the results obtained by Jones and by Holmberg, however, it is difficult to believe that the preparation of a dry, neutral sulphate cannot be accomplished.[2]

(*b*) Analytical. In this process the octahydrated sulphate, $X_2(SO_4)_3.8H_2O$, is chosen as starting material. The sample for analysis may generally be prepared by dissolving a gram or two of oxide in hydrochloric acid, evaporating nearly to dryness, diluting to fifty cubic centimetres, adding a slight excess of sulphuric acid, and then quickly diluting with a litre of alcohol. The precipitated sulphate is well washed with alcohol, dried at 110°, dissolved in water, and crystallised at the temperature of the water-bath. The crystals are separated from the mother liquor, dried in the air, powdered in an agate mortar, and dried in a desiccator. A gram or two of the sulphate

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[1] For further details of the method, see Bahr and Bunsen, *Annalen*, 1866, 137, 1; Bailey, *Trans. Chem. Soc.*, 1887, 51, 683; Krüss, *Zeitsch. anorg. Chem.*, 1893, 3, 44; Urbain, *Ann. Chim. Phys.*, 1900, [vii.], 19, 184; Jones, *Amer. Chem. J.*, 1902, 28, 23; *Chem. News*, 1903, 88, 13; *Zeitsch. anorg. Chem.*, 1903, 36, 92; Brauner and Pavlíček, *Trans. Chem. Soc.*, 1902, 81, 1243; Brauner, *Zeitsch. anorg. Chem.*, 1903, 33, 317; Wild, *ibid.*, 1904, 38, 191; Brill, *ibid.*, 1905, 47, 464; Holmberg, *ibid.*, 1907, 53, 124; R. J. Meyer and Wuorinen, *ibid.*, 1913, 80, 7; Egan and Balke, *J. Amer. Chem. Soc.*, 1913, 35, 365.

[2] It is possible, as Meyer and Wuorinen have pointed out, that the difficulties may have usually arisen from the fact that the oxide has been ignited in platinum and contaminated with a trace of that element, and hence that the rare earth sulphate subsequently formed has been slightly contaminated with platinic sulphate; *cf.* Jones, *loc. cit.*

is weighed into a small platinum crucible, and heated to 350° till the water of crystallisation has been expelled. The loss of weight is then determined. Finally, the crucible and contents are placed in a larger crucible (which it is prevented from touching by means of a little ignited rare-earth packing) and heated almost to a white heat until the sulphate has been completely decomposed. The weight of the residual oxide is then determined.

By this method, in addition to the *oxide-sulphate* ratio (I.), values for the atomic weight may be calculated from two other ratios, viz. :—

$$X_2(SO_4)_3.8H_2O : X_2(SO_4)_3 \quad . \quad . \quad . \quad . \quad (II.)$$

and

$$X_2(SO_4)_3.8H_2O : X_2O_3 \quad . \quad . \quad . \quad . \quad (III.)$$

It should be noted that with cerium, the final residue is the dioxide. With praseodymium and terbium, the final residues are peroxides of somewhat indefinite composition. They may, however, be reduced to sesqui-oxides in a stream of hydrogen.

This method has been employed very successfully by Urbain,[1] who prefers the values deduced from ratio (III.) to the others. The *oxide-sulphate* ratio as determined by the analytical method avoids the difficulty, encountered in the synthetic method, of driving off excess of acid, but it suffers from another defect. The anhydrous sulphate obtained is extremely porous, and absorbs gases, so much so that it is impossible, for instance, to weigh anhydrous gadolinium sulphate in air with any reasonable degree of accuracy.

The foregoing method may be applied to very small quantities of material, the weighing being made on a torsion microbalance.[2]

According to Brauner, the analytical method is limited in its scope, since it is impossible to decompose completely by ignition the sulphate of lanthanum and the other sulphates derived from the strongly basic earths. The analytical method is therefore best suited to the sulphates of the elements of the terbium and erbium groups. As an illustration of the nature of the results it has afforded, the following data, referring to the atomic weight of europium, are given :—[3]

No. of Fraction.	Weight of			Atomic Weight of Eu from Ratio		
	$Eu_2(SO_4)_3.8H_2O$.	$Eu_2(SO_4)_3$	Eu_2O_3.	I	II.	III
15	1·7787	1·4303	0·8500	151·91	151·74	151·88
16	2·4785	1·9935	1·1848	151·95	152·10	151·98
17	2·4177	1·9449	1·1554	151·76	152·33	151·88
18	2·4831	1·9968	1·1870	152·04	151·80	151·98
19	2·2988	1·8488	1·0990	152·03	151·96	152·01
			Mean . .	151·94	151·98	151·94

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[1] Urbain, *J. Chim. phys.*, 1906, **4**, 52.

[2] Brill, *loc. cit.*; *cf.* Nernst and Riesenfeld, *Ber.*, 1903, **36**, 2086.

[3] Urbain and Lacombe, *Compt. rend.*, 1904, **138**, 627 ; Urbain, *J. Chim. phys.*, 1906, **4**, 118. The antecedent data are O = 16, H = 1·00762, S = 32·065. The numbers attached to the fractions have the same meanings as those on p. 349.

(ii.) *The Oxalate Method.*—This method is more suited to the rapid determination of approximate results than to the determination of exact atomic weight values. The precipitated oxalate is either air-dried or dried at 120°–130° and ground in an agate mortar to ensure its homogeneity. In one portion the percentage of rare earth oxide is determined by ignition,[1] and in another the oxalate radicle is estimated by titration with a standard solution of potassium permanganate, or by an ordinary combustion analysis. From the ratio $X_2O_3 : 3C_2O_3$ the atomic weight is easily calculated.[2] The oxalate should be prepared by precipitation with oxalic acid from a slightly acid solution; if precipitated by a soluble oxalate from a neutral or alkaline solution, the oxalates of the alkali metals and ammonium are co-precipitated to a very considerable extent.[3]

(iii.) *The Halide Methods.*—(*a*) The analysis of the pure, anhydrous chloride is an operation comparatively easy to effect, and when properly performed always yields very reliable results. The preparation of the pure, anhydrous chlorides, however, is a difficult task, so that this method has unfortunately been greatly neglected;[4] analysis of the bromides, which should give equally good results, have not yet been attempted.

(*b*) The determination of the ratio $X_2O_3 : 2XCl_3$ may be effected by dissolving the oxide, contained in a quartz flask, in hydrochloric acid, evaporating to dryness in a stream of hydrogen chloride, and dehydrating and fusing the residual chloride in a current of the same gas.[5]

(iv.) *Other Methods.*—A number of useful, rapid volumetric processes, which, however, yield only approximate results, have been described.[6] A convenient procedure is to dissolve about 0·1500 gram of the pure oxide in 50 c.c. of standard sulphuric acid (approximately seminormal), add about 8 c.c. of N/5 potassium oxalate, and heat to the boiling-point; cool and titrate the excess of sulphuric acid with sodium hydroxide, using phenolphthalein as indicator.

Experimental Results.—The experimental results which seem to be the most reliable are contained in the accompanying table, to which a fairly complete bibliography is appended. So far as the atomic weights are concerned, many of the papers referred to in the bibliography have only an historical interest.

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[1] It is difficult to effect this determination without a trace of oxide being mechanically carried away by escaping gases.

[2] Stolba, *Ber. böhm. Ges. Wiss.*, 1878; *Jahresber.*, 1878, p. 1059; 1879, p. 1044; 1882, p. 1286; Gibbs, *Proc. Amer. Acad.*, 1893, **28**, 261; *Amer. Chem. J.*, 1893, **15**, 546; Brauner, *Chem. News*, 1895, **71**, 233; Brauner and Pavlíček, *loc. cit.*; Brauner and Batěk, *Zeitsch. anorg. Chem.*, 1903, **34**, 103; Brauner, *ibid.*, 1903, **34**, 207; Browning, *Amer. J. Sci.*, 1899, [iv.], **8**, 451; Drushel, *ibid.*, 1907, [iv.], **24**, 197.

[3] Baxter and Griffin, *J. Amer. Chem. Soc.*, 1906, **28**, 1684; Baxter and Daudt, *ibid.*, 1908, **30**, 563.

[4] For determinations by this method, see Robinson, *Proc. Roy. Soc.*, 1884, **37**, 150; *Chem. News*, 1884, **50**, 251; Baxter and Chapin, *J. Amer. Chem. Soc.*, 1911, **33**, 1; Baxter and Stewart, *ibid.*, 1915, **37**, 516.

[5] Egan and Balke, *J. Amer. Chem. Soc.*, 1913, **35**, 365.

[6] See Krüss and Loose, *Zeitsch. anorg. Chem.*, 1893, **4**, 161; Wild, *ibid.*, 1904, **38**, 191; Feit and Przibylla, *ibid.*, 1905, **43**, 202; 1906, **50**, 249; Holden and James, *J. Amer. Chem. Soc.*, 1914, **36**, 638.

ATOMIC WEIGHTS OF THE RARE EARTH ELEMENTS.[1]

Date.	Authority.	Ratio Measured.	Atomic Weight.	International Value (1916).
		CERIUM.[2]		
1884	Robinson	$CeCl_3 : 3Ag$	140·14*	140·25
1885	Brauner	$Ce_2(SO_4)_3 : 2CeO_2$	140·22*	...
1897	Wyrouboff and Verneuil	$Ce_2(SO_4)_3.8H_2O : Ce_2(SO_4)_3 : 2CeO_2$	139·35	...
1903	Brauner and Batěk	$Ce_2(SO_4)_3 : 2CeO_2$	140·30*	...
1903	Brauner	$Ce_2(SO_4)_3.8H_2O : 2CeO_2$	140·26*	...
		DYSPROSIUM.[3]		
1906	Urbain and Demenitroux	$Dy_2(SO_4)_3.8H_2O : Dy_2O_3$	162·55	162·5
		ERBIUM.[4]		
1908	Hofmann and Burger	$Er_2O_3 : Er_2(SO_4)_3$	167·40	167·7
1910	Hofmann	$Er_2O_3 : Er_2(SO_4)_3$	167·68	...
		EUROPIUM.[5]		
1904	Urbain and Lacombe	$Eu_2(SO_4)_3.8H_2O : Eu_2(SC_4)_3 : Eu_2O_3$	151·98	152·0
1908	Jantsch	$Eu_2(SO_4)_3.8H_2O : Eu_2O_3$	152·05	...

[1] With one or two exceptions, the results given in the accompanying table have been computed from the data given in Clarke, *A Recalculation of the Atomic Weights* ("Smithsonian Miscellaneous Collections," vol. 54, No. 3, 1910), using the following antecedent data:—

O = 16·000; S = 32·065; H = 1·00762; Ag = 107·880; Cl = 35·457; C = 12·003.

In the few cases indicated by asterisks the weights have been reduced to vacuum standard in calculating the results.

[2] The earlier experimenters never freed their ceria completely from "didymia."

[3] Dysprosia was not isolated till 1906.

[4] Pure erbia has not yet been prepared.

[5] Europia was not isolated in the pure state till 1904.

Cerium.—Beringer, *Annalen*, 1842, **42**, 134; Hermann, *J. prakt. Chem.*, 1843, **30**, 185; Marignac, *Arch. Sci. phys. nat.*, 1848, [i.], **8**, 273; Kjerulf, *Annalen*, 1853, **87**, 12; Bunsen and Jegel, *ibid.*, 1858, **105**, 45; Rammelsberg, *Pogg. Annalen*, 1859, **108**, 44; Wolf, *Amer. J. Sci.*, 1868, [ii.], **46**, 53; Wing, *ibid.*, 1870, [ii.], **49**, 358; Bührig, *J. prakt. Chem.*, 1875, **120**, 222; Robinson, *Proc. Roy. Soc.*, 1884, **37**, 150; *Chem. News*, 1884, **50**, 251; 1886, **54**, 229; Brauner, *Trans. Chem. Soc.*, 1885, **47**, 879; Schützenberger, *Compt. rend.*, 1895, **120**, 663, 962, 1143; Brauner, *Chem. News*, 1895, **71**, 283; Wyrouboff and Verneuil, *Bull. Soc. chim.*, 1897, [iii.], **17**, 679; *Compt. rend.*, 1897, **124**, 1300: *Ann. Chim. Phys.*, 1907, [viii.], **9**, 349; Kölle, *Inaugural Dissertation* (Zurich, 1898); Brauner and Batěk, *Zeitsch. anorg. Chem.*, 1903, **34**, 103; Brauner, *ibid.*, 1903, **34**, 207.

Dysprosium.—Urbain and Demenitroux, *Compt. rend.*, 1906, **143**, 598.

Erbium.—Cleve, *K. Svenska Vet.-Akad. Handl.*, 1880, No. 7; *Compt. rend.*, 1880, **91**, 381; Brill, *Zeitsch. anorg. Chem.*, 1905, **47**, 464; Hofmann and Burger, *Ber.*, 1908, **41**, 308; Hofmann, *Ber.*, 1910, **43**, 2635.

Europium.—Urbain and Lacombe, *Compt. rend.*, 1904, **138**, 627; Urbain, *J. Chim. phys.*, 1906, **4**, 118; Jantsch, *Compt. rend.*, 1908, **146**, 473; *cf.* Demarçay, *ibid.*, 1900, **130**, 1469; 1901, **132**, 1484.

ATOMIC WEIGHTS OF THE RARE EARTH ELEMENTS—*continued.*

Date.	Authority.	Ratio Measured.	Atomic Weight.	International Value (1916).
		GADOLINIUM.[1]		
1905	Urbain	$Gd_2(SO_4)_3.8H_2O : Gd_2O_3$	157·24	157·3
		HOLMIUM.[2]		
1911	Holmberg	$Ho_2O_3 : Ho_2(SO_4)_3$	163·45	163·5
		LANTHANUM.		
1902	Jones	$La_2O_3 : La_2(SO_4)_3$	138·73*	139·0
1902	Brauner and Pavlíček	$La_2O_3 : La_2(SO_4)_3$	139·05*	...
		$La_2O_3 : 3C_2O_3$	139·08*	...
1903	Jones	$La_2O_3 : La_2(SO_4)_3$	138·76*	...
		LUTECIUM (or *cassiopeium*).[3]		
1907–8	Urbain	$Lu_2(SO_4)_3.8H_2O : Lu_2O_3$	174	175·0
1913	Auer von Welsbach	$Lu_2(SO_4)_3.8H_2O : Lu_2O_3$	175·00	...
		NEODYMIUM.		
1903	Auer von Welsbach	$Nd_2O_3 : Nd_2(SO_4)_3$	144·55	144·3
1907	Holmberg	$Nd_2O_3 : Nd_2(SO_4)_3$	144·10	...
1911	Baxter and Chapin[4]	$NdCl_3 : 3AgCl$	144·27*	...
		$NdCl_3 : 3Ag$	144·27*	...

[1] Earlier determinations are most probably affected by presence of europia in the gadolinia used.

[2] Holmia was not isolated until 1911.

[3] It is doubtful whether pure lutecia has yet been obtained.

[4] New analyses of $NdCl_3$ by Baxter, Whitcomb, Stewart, and Chapin confirm the results of Baxter and Chapin (*J. Amer. Chem. Soc.*, 1916, **38**, 302).

Gadolinium.—Marignac, *Ann. Chim. Phys.*, 1880, [v.], **20**, 535 ; Lecoq de Boisbaudran, *Compt. rend.*, 1890, **111**, 409 ; Bettendorf, *Annalen*, 1892, **270**, 376 ; Benedicks, *Zeitsch. anorg. Chem.*, 1900, **22**, 393 ; Marc, *ibid.*, 1904, **38**, 128 ; Demarçay, *Compt. rend.*, 1900, **131**, 343 ; Urbain, *ibid.*, 1905, **140**, 583 ; *J. Chim. phys.*, 1906, **4**, 326.

Holmium.—Holmberg, *Arkiv Kem. Min. Geol.*, 1911, **4**, No. 2 ; *Zeitsch. anorg. Chem.*, 1912, **71**, 226.

Lanthanum.—Mosander, *Pogg. Annalen*, 1843, **60**, 297 ; Rammelsberg, *ibid.*, 1842, **55**, 65 ; Marignac, *Arch. Sci. phys. nat.*, 1849, **11**, 21 ; *Ann. Chim. Phys.*, 1849, [iii.], **27**, 209 ; Holzmann, *J. prakt. Chem.*, 1858, **75**, 343 ; Czudnowicz, *ibid.*, 1860, **80**, 31 ; Hermann, *ibid.*, 1861, **82**, 395 ; Zschiesche, *ibid.*, 1868, **104**, 174 ; Erk, *Jenaische Zeitsch.*, 1871, **6**, 306 ; Marignac, *Arch. Sci. phys. nat.*, 1873, **46**, 215 ; *Ann. Chim. Phys.*, 1873, [iv.], **30**, 68 ; Cleve, *Bihang K. Svenska Vet.-Akad. Handl.*, 1874, **2**, No. 7 ; *Bull. Soc. chim.*, 1874, [ii.], 21, 196 ; 1883, [ii.], **39**, 151 ; Brauner, *Monatsh.*, 1882, **3**, 1, 486 ; *Trans. Chem. Soc.*, 1882, **41**, 68 ; *Ber.*, 1891, **24**, 1328, Bettendorf, *Annalen*, 1890, **256**, 159 ; Gibbs, *Proc. Amer. Acad.*, 1893, **18**, 260 ; Schützenberger, *Compt. rend.*, 1895, **120**, 1143 ; Bodman, *Bihang K. Svenska Vet.-Akad. Handl.*, 1901, **26**, II., No. 3 ; Brauner and Pavlíček, *Trans. Chem. Soc.*, 1902, **81**, 1243 ; Brauner, *Zeitsch. anorg. Chem.*, 1903, **33**, 317 ; Jones, *Amer. Chem. J.*, 1902, **28**, 23 ; *Zeitsch. anorg. Chem.*, 1903, **36**, 92 ; Brill, *ibid.*, 1905, **47**, 464 ; Feit and Przibylla, *ibid.*, 1905, **43**, 213 ; 1906, **50**, 248.

Lutecium.—Urbain, *Compt. rend.*, 1907, **145**, 759 ; 1908, **146**, 406 ; Auer von Welsbach, *Sitzungsber. K. Akad. Wiss. Wien*, 1907, **116**, II. B, 1425 ; *Monatsh.*, 1908, **29**, 181 ; 1913, **34**, 1713.

Neodymium.—Auer von Welsbach, *Monatsh.*, 1885, **6**, 477 ; *Sitzungsber. K. Akad.*

ATOMIC WEIGHTS OF THE RARE EARTH ELEMENTS—*continued.*

Date.	Authority.	Ratio Measured.	Atomic Weight.	International Value (1916).
		PRASEODYMIUM.		
1898	Jones	$Pr_2O_3 : Pr_2(SO_4)_3$	140·47	140·9
1898	von Scheele	$Pr_2O_3 : Pr_2(SO_4)_3$	140·54	...
1901	Brauner	$Pr_2O_3 : Pr_2(SO_4)_3$	140·97*	...
		$Pr_2O_3 : 3C_2O_3$	140·95*	...
1903	Auer von Welsbach	$Pr_2O_3 : Pr_2(SO_4)_3$	140·57	...
1915	Baxter and Stewart	$PrCl_3 : 3AgCl$	140·93*	...
		$PrCl_3 : 3Ag$	140·92*	...
		SAMARIUM.[1]		
1904	Urbain and Lacombe	$Sm_2(SO_4)_3 8H_2O : Sm_2(SO_4)_3 : Sm_2O_3$	150·46	150·4
		TERBIUM.[2]		
1906	Urbain	$Tb_2(SO_4)_3 8H_2O : Tb_2(SO_4)_3$	159·20	159·2
		THULIUM.[3]		
1880	Cleve	?	170·7	168·5
1905	Urbain	?	<168·5	...
		YTTERBIUM (*neoytterbium* or *aldebaranium*).		
1913	Auer von Welsbach	$Yb_2(SO_4)_3 . 8H_2O : Yb_2O_3$	173·0	173·5
1914	Blumenfeld and Urbain	$Yb_2(SO_4)_3 . 8H_2O : Yb_2O_3$	173·54	...

[1] Samaria was not obtained free from neodymia and europia until 1900.
[2] Terbia was not isolated until 1906.
[3] A reliable determination is still wanted.

Wiss. Wien, 1903, **112**, II. B, 1037; Brauner, *Proc. Chem. Soc.*, 1898, **14**, 72; 1901, **17**, 66; Abegg's *Handbuch*, vol. 3, part 1, p. 276; Boudouard, *Compt. rend.*, 1898, **126**, 900; Jones, *Amer. Chem. J.*, 1898, **20**, 345; *Zeitsch. anorg. Chem.*, 1899, **19**, 329; Brill, *ibid.*, 1905, **47**, 464; Holmberg, *ibid.*, 1907, **53**, 124; Feit and Przibylla, *ibid.*, 1906, **50**, 259; Baxter and Chapin, *J. Amer. Chem. Soc.*, 1911, **33**, 1.

Praseodymium.—Auer von Welsbach, *loc. cit.*; Brauner, *Proc. Chem. Soc.*, 1898, **14**, 70; 1901, **17**, 65; Abegg's *Handbuch*, vol. 3, part 1, p. 263; Jones, *Amer. Chem. J.*, 1898, **20**, 345; von Scheele, *Zeitsch. anorg. Chem.*, 1898, **17**, 310; Feit and Przibylla, *ibid.*, 1906, **50**, 258; Baxter and Stewart, *J. Amer. Chem. Soc.*, 1915, **37**, 516.

Samarium.—Marignac, *Arch. Sci. phys. nat.*, 1880, [iii.], **3**, 435; *Ann. Chim. Phys.*, 1880, [v.], **20**, 535; Brauner, *Trans. Chem. Soc.*, 1883, **43**, 278; Cleve, *ibid.*, 1883, **43**, 362; Bettendorf, *Annalen*, 1891, **263**, 164; Lecoq de Boisbaudran, *Compt. rend.*, 1892, **114**, 575; Demarçay, *ibid.*, 1896, **122**, 728; 1900, **130**, 1019, 1185, 1469; 1901, **132**, 1484; Muthmann and Weiss, *Annalen*, 1904, **331**, 16; Urbain and Lacombe, *Compt. rend.*, 1904, **138**, 1166; Urbain, *J. Chim. phys.*, 1906, **4**, 120; Matignon, *Compt. rend.*, 1905, **141**, 1230; Feit and Przibylla, *Zeitsch. anorg. Chem.*, 1906, **50**, 259.

Terbium.—Urbain, *Compt. rend.*, 1906, **142**, 957; *cf.* Feit, *Zeitsch. anorg. Chem.*, 1905, **43**, 280; Lecoq de Boisbaudran, *Compt. rend.*, 1886, **102**, 395, 483; 1890, **111**, 474; Potratz, *Chem. News*, 1905, **92**, 3.

Thulium.—Cleve, *Compt. rend.*, 1880, **91**, 329; Urbain, *ibid.*, 1907, **145**, 759.

Ytterbium (neoytterbium).—Blumenfeld and Urbain, *Compt. rend.*, 1914, **159**, 323. See also the references given under *lutecium.* For the "atomic weight" of old "ytterbium," see Nilson, *Compt. rend.*, 1880, **91**, 56; Astrid Cleve, *Zeitsch. anorg. Chem.*, 1902, **32**, 129; Brill, *ibid.*, 1905, **47**, 464; Brauner, Abegg's *Handbuch*, vol. 3, part 1, p. 335; G. and E. Urbain, *Compt. rend.*, 1901, **132**, 136; Feit and Przibylla, *Zeitsch. anorg. Chem.*, 1906, **50**, 261.

ATOMIC WEIGHTS OF THE RARE EARTH ELEMENTS—*continued.*

Date.	Authority.	Ratio Measured.	Atomic Weight.	International Value (1916).
		YTTRIUM.		
1882	Cleve	$Y_2O_3 : Y_2(SO_4)_3$	89·12	88·7
1895	Jones	$Y_2O_3 : Y_2(SO_4)_3$	88·97	...
1913	R. J. Meyer	$Y_2O_3 : Y_2(SO_4)_3$	88·70	...
	Wuorinen and Weinheber	$Y_2(SO_4)_3 : Y_2O_3$		
1913	Egan and Balke	$Y_2O_3 : 2YCl_3$	90·10[1]	...

[1] Preliminary results, and admittedly a little high.

Yttrium.—Berlin, *Forhandl. Skand. Nat. Kjob.*, 1860, p. 452; Popp, *Annalen*, 1864, 131, 179; Delafontaine, *ibid.*, 1865, 134, 108; *Arch. Sci. phys. nat.*, 1866, [ii.], 25, 119; Bahr and Bunsen, *Annalen*, 1866, 137, 1; Cleve and Höglund, *Bihang K. Svenska Vet.-Akad. Handl.*, 1873, No. 8; Cleve, *ibid.*, 1882, No. 9; *Bull. Soc. chim.*, 1883, [ii.], 39, 120, 287; *Compt. rend.*, 1882, 95, 1225; Jones, *Amer. Chem. J.*, 1895, 14, 154; *Chem. News*, 1895, 71, 305; Muthmann and Böhm, *Ber.*, 1900, 33, 42; G. and E. Urbain, *loc. cit.*; Brill, *loc. cit.*; Feit and Przibylla, *Zeitsch. anorg. Chem.*, 1906, 50, 262; R. J. Meyer and Wuorinen, *ibid.*, 1913, 80, 7; R. J. Meyer and Weinheber, *Ber.*, 1913, 46, 2672; Egan and Balke, *J. Amer. Chem. Soc.*, 1613, 35, 365.

It is difficult to form any precise estimates of the possible errors attaching to the atomic weight values chosen for the rare earth elements by the international committee. It is possible that the values ascribed to cerium, praseodymuim, neodymium, dysprosium, europium, gadolinium, terbium, samarium, yttrium, and ytterbium do not err by more than one- or two-tenths of a unit from the correct values, and that in three or four cases the error does not exceed one or two units in the second decimal; it is possibly premature to express the value for cerium to two places of decimals. In the case of lanthanum there is a discrepancy of nearly three-tenths of a unit between the values of Jones (138·73) and Brauner (193·05), and the evidence in favour of the lower value is at least as convincing as that for the higher. Considerable uncertainty also attaches to the values for erbium, thulium, and lutecium, while additional determinations are required to check the value ascribed to holmium. No values have yet been published for the atomic weight of celtium.[1]

Classification of the Rare Earth Elements.—In dealing with this subject it is convenient to commence by a discussion of how the elements of the rare earths fall into line with the most popular of the classifications of the elements, namely, the Periodic Classification as arranged by Mendeléeff.

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[1] The most satisfactory determinations recorded in the preceding table are undoubtedly the determinations of the atomic weights of neodymium and praseodymium by Baxter and his co-workers. For more complete discussions of the atomic weights of the rare earth elements, the reader is referred to Clarke, *A Recalculation of the Atomic Weights* ("Smithsonian Miscellaneous Collections," vol. 54, No. 3, 1910); Urbain, *Bull. Soc. chim.*, 1909, [iv.], 5, 133; and the various articles by Brauner in Abegg, *Handbuch der anorganischen Chemie*, vol. 3, pt. 1, 1906.

Let it first be supposed, then, that the Periodic Table as usually drawn up[1] is correct. Then, since it must presumably be supposed that the eighth horizontal row contains three transition-elements in the Group VIII. space, there are twenty vacant spaces between barium and tantalum, waiting to be filled by one inert gas and nineteen other elements. For these vacancies the atomic weight range is such that it includes the atomic weights of the rare earth elements, yttrium being excepted.[2] The rare earth elements must therefore be placed in these vacancies, for, on the one hand, no other places are available, and, on the other, if other places were available, those in question would still have to be filled, and it is difficult to believe that nineteen metals of suitable atomic weights still await discovery.

It requires, however, but a slight knowledge of the chemical and physical properties of the rare earth elements to realise that when these elements are placed in position in the table as indicated above, it can no longer be said that the properties of the elements are periodic functions of their atomic weights, *i.e.* the Periodic Law breaks down. Such being the case, it seems hardly worth while to attempt any detailed discussion of the precise places the rare earth elements must occupy in the table, and therefore only a few words will be said upon the subject. The best arrangement appears to be the following :—[3]

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
VII.	Ag	Cd	In	Sn	Sb	Te	I	
VIII.	Cs	Ba	**La**	**Ce**	**Pr**	**Nd**	-	
IX.	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	
X.	**Tm**	**Yb**	**Lu**	**Ct**	**Ta**	W	-	Os, Ir, Pt

This arrangement is in harmony with Moseley's work on the high frequency spectra of the elements, according to which the sequence of atomic numbers is as follows :—[4]

Ba, La, Ce, Pr, Nd, –, Sm, Eu, Gd, –, Dy, –, Er, –, –, –, –, Ta,

the blanks denoting missing elements.[5] It also agrees with the observations of Hicks,[6] (i.) that the line spectra of Cd, Eu, and Hg exhibit triplet series of the sharp and diffuse type, the triplet intervals being approximately proportional to the squares of the atomic weights, (ii.) that Gd exhibits doublet series similar to

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[1] See Frontispiece.

[2] It has been already pointed out that yttrium may readily be found a place in the table; see p. 238.

[3] Rydberg, *Lunds Univ. Arsskrift*, N.F., Afd. 2, 1913, **9**, No. 18; *J. Chim. phys.*, 1914, **12**, 585; *Rev. gen. sci.*, 1914, **25**, 734; *Phil. Mag.*, 1914, [vi.], **28**, 144; Hicks, *Phil. Mag.*, 1914, [vi.], **28**, 139. This arrangement differs considerably from that given by Brauner, *Zeitsch. Elektrochem.*, 1908, **14**, 525. Rydberg, however, prefers to reject Mendeléeff's arrangement and adopt an ingenious table in which the elements are arranged in four series, containing respectively 4, 16, 36, and 64 elements ($4p^2$, where $p = 1$, 2, 3, and 4). His table is reproduced in Hicks's paper.

[4] Moseley, *Phil. Mag.*, 1914, [vi.], **27**, 703; see also pp. 312, 363, and Vol. I. Chap. VIII.

[5] *I.e.* elements Moseley did not examine. Moseley also writes Ho in mistake for Dy.

[6] Hicks, *Phil. Trans.*, 1912, **A**, 212, 58.

those of Al, Ga, and Ti, and (iii.) that Sc, Y, La, and Yb[1] also show doublet series. It cannot, however, be reconciled with the other physical and the chemical properties of the elements, but this applies to every other similar arrangement. It should be pointed out that the arrangement given assumes that terbium and thulium are true elements, points that have been disputed, and that Marignac's "ytterbium" is composed of three elements, ytterbium, lutecium, and celtium.[2] Moreover, it is necessary to assume that Series VIII. contains no transition-elements, and that an unknown rare earth element exists, the atomic weight of which lies between the values for neodymium and samarium.

So far it has been assumed that Mendeléeff's arrangement into groups and series is correct, and it is evident that the assumption is by no means satisfactory, since of the rare earth elements only yttrium, lanthanum, and cerium can be readily fitted into the scheme. It is not surprising, therefore, that attempts have been made to improve matters by suitably modifying Mendeléeff's arrangement. Those attempts which alter that arrangement least are based on the assumption that all but one or two of the rare earth elements may be placed *en bloc* in a single place in the table.[3] The arrangement proposed by Benedicks, for instance, is as follows :—

	0.	I.	II.	III.	IV.	V.	VI	VII.	VIII.
VIII.	Xe	Cs	Ba	La	Ce, Pr, Nd, Sm, En, Gd, etc.	Ta	W	-	Os, Ir, Pt

and has the obvious disadvantage of including most of the rare earth elements in Group IV. instead of in Group III. as their valency indicates. On the other hand, to group all the rare earth elements except cerium in the Group III. position is to depart from the atomic weight sequence. Brauner's 1902 proposal was expressed in terms of an hypothesis the precise meaning of which is not very clear; indeed, it has been said that it "belongs to the realm of pure fantasy."[4] Stripped of its hypothetical garb, however, the proposal is identical with that advocated by Benedicks.

At the time when they were published, the preceding proposals could only be viewed as makeshifts, similar to the arrangements of the transition-elements in sets of three in Group VIII. Essentially the same idea, viz., that the rare earth elements form a transition group, is expressed in the arrangements of Steele and Werner, although these chemists modify the nature of Mendeléeff's table considerably.[5] Modern work on the radio-elements, however, has shown that it is often necessary to assume that several elements occupy one and the same place in the Periodic Table, an assumption analogous to the preceding. However, theoretical views concerning the structure of the atom indicate that this only arises when several elements possess the same "atomic number,"[6] and the view that the rare earth elements have the same

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[1] Old ytterbium (Yb, Lu, and Ct) (?).

[2] These questions are discussed later (pp. 358–365).

[3] Brauner, *Chem. Zentr.*, 1900, ii. 524; *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 142; *Zeitsch. anorg. Chem.*, 1902, **32**, 1; Benedicks, *ibid.*, 1904, **39**, 41; H. Biltz, *Ber.*, 1902, **35**, 562; R. J. Meyer, *Naturwissenschaften*, 1914, **2**, 781. See also Retgers, *Zeitsch. physikal. Chem.*, 1895, **16**, 651.

[4] Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [vi.], **6**, 466.

[5] Steele, *Chem. News*, 1901, **84**, 245; Werner, *Ber.*, 1905, **38**, 914; *New Ideas on Inorganic Chemistry*, trans. by Hedley (Longman & Co., 1911).

[6] See Vol. I. Chap. VIII.

"atomic number"[1] cannot be reconciled with Moseley's observations on high frequency spectra.[2]

So far, then, as a comprehensive classification, including all the known elements, is concerned, the rare earth metals offer formidable difficulties. The problem of the interclassification of the rare earth elements is not in a much better position, judged from the purely scientific standpoint.

The early division into cerite and gadolinite earths, based upon their mode of occurrence, dates from the time when but six of these earths were recognised. It divided the rare earth elements into two groups, the metals of the *cerium* and *yttrium groups* respectively. The subsequent discovery of the remarkable complexity of three of these earths was also associated with the observation that the properties which distinguished the cerite and gadolinite earths failed to effect a sharp division into two groups, and an intermediate group of *terbia earths* was recognised, particularly by Marignac and Lecoq de Boisbaudran. The importance of this group, however, as Urbain has remarked,[3] was little appreciated for a considerable number of years, an error that contributed appreciably to the remarkable confusion into which the chemistry of the rare earths was thrown throughout the period 1878 to 1900.

With the recognition of the terbia earths as an intermediate group, it is possible to divide the rare earth elements into three groups, as follows:—

Cerium Group	Terbium Group.	Yttrium Group.
Lanthanum	Europium	Dysprosium
Cerium	Gadolinium	Holmium
Praseodymium	Terbium	Yttrium
Neodymium		Erbium
Samarium		Thulium
		Ytterbium
		Lutecium
		Celtium

The yttrium group is sometimes divided into parts, the yttrium group proper (Y, Yb, Lu, Ct) and the *erbium group* (Dy, Ho, Tm, Er).

The following differences may be noticed between the properties of the compounds of these three groups:—

(i.) The platinocyanides of the cerium and terbium groups are similar in composition, but differ in crystalline form, colour, and degree of hydration from those of the yttrium group (p. 272).

(ii.) The double compounds $M(CNS)_3.3Hg(CN)_2.12H_2O$ are monoclinic in the cerium, and triclinic in the yttrium group (p. 272).

(iii.) The silicotungstates of the formula $M_4(W_{12}SiO_{40})_3.81H_2O$ and the acid silicotungstates of the formula $MH(W_{12}SiO_{40}).18H_2O$ are missing in the yttrium group, while the acid salts of the formula $2MH(W_{12}SiO_{40}).49H_2O$ are missing in the cerium group (p. 266).

(iv.) The nitrates of the metals of the cerium and terbium groups form double nitrates with the nitrates of uni- and bi-valent metals, but the nitrates of the metals of the yttrium group do not (p. 269).

Other double compounds of the nitrates may be also divided into groups.

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[1] Suggested by van den Broek, *Phil. Mag.*, 1914, [vi.], **27**, 455.

[2] The position of the rare earth elements in the Periodic Table is also discussed by Rudorf (*Zeitsch. anorg. Chem.*, 1903, **37**, 177); and by Harkins and Hall (*J. Amer. Chem. Soc.*, 1916, **38**, 169).

[3] Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184.

Thus the compounds with antipyrine appear to be of the type $M(NO_3)_3.3C_{11}H_{12}ON_2$ in the cerium and $M(NO_3)_3.4C_{11}H_{12}ON_2$ in the yttrium group.[1]

(v.) The double sulphates of potassium and the metals of the cerium group are insoluble in a cold, saturated solution of potassium sulphate; in the case of the terbium group they are sparingly soluble, and in the case of the yttrium group readily soluble (p. 261).

(vi.) The double carbonates of the alkali metals and the metals of the cerium group are decomposed by water and dilute alkali carbonates, but not by concentrated alkali carbonates; the corresponding double salts in the yttrium group are readily soluble in and not decomposed by dilute alkali carbonates (p. 271).

(vii.) The oxalates of the metals of the cerium group are only slightly soluble in hot, concentrated ammonium oxalate; those of the yttrium group are more readily soluble, and double salts may be crystallised from the solutions (p. 271).

The preceding differences are not of a very fundamental character. Moreover, differences of a similar character may be pointed out which are not in accordance with the classification into the cerium, terbium, and yttrium groups.[2]

In other natural families of elements, *e.g.* the alkali or the alkaline earth metals, progressive variation in properties usually follows the order of increasing atomic weights. The same statement cannot be so confidently affirmed in the case of the rare earth elements, for yttrium is then completely removed from the elements which chemically it most closely resembles, namely, holmium and erbium. Excluding yttrium, however, it may be stated that the solubilities of corresponding salts usually follow the order of the atomic weights of the rare earth elements (see p. 325), that the atomic weight sequence places the terbium group between the cerium and yttrium groups, and that the same arrangement brings samarium and europium, the only two rare earth elements known to form derivatives of the type MX_2, next to one another. There are, however, several indications that the atomic weight sequence is often associated not with a progressive, but with a periodic variation in properties; see, for instance, the magnetic susceptibilities of the oxides (p. 257), the melting-points of the chlorides (p. 253), and the molecular volumes of the ethylsulphates (p. 279).[3]

COMPOUNDS OF THE RARE EARTH ELEMENTS.

The great majority of these compounds are salts derived from a series of basic sesqui-oxides, M_2O_3. Three lower halides are known, viz. $SmCl_2$, SmI_2, and $EuCl_2$, in which the metals may be bivalent, but the molecular weights of the compounds are not known. Cerium forms a series of compounds in which it is quadrivalent; presumably praseodymium is also quadrivalent in the dioxide PrO_2.

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[1] Kolb, *Zeitsch. anorg. Chem.*, 1913, **83**, 143.

[2] See, *e.g.*, the compositions of the sebacates and 1 : 4 : 2-bromonitrobenzenesulphonates (p. 281).

[3] See also Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1095; *Rec. trav. chim.*, 1914, **33**, 342; R. J. Meyer, *Naturwissenschaften*, 1914, **2**, 781. A few physical properties appear to be anomalous, *e.g.* the molecular volume of cerous ethylsulphate (p. 279) and the molecular volumes of the double nitrates of neodymium and praseodymium of the type $3M''(NO_3)_2.2M'''(NO_3)_3.24H_2O$ (p. 270).

So far as the derivatives of the sesqui-oxides are concerned, the rare earth elements appear in their chemical relations to be intermediate between the alkaline earth metals and magnesium, while also bearing some resemblance to iron, aluminium, and chromium. The colours of the salts are as follows:—

Lanthanum, colourless.
Cerium (ous), colourless.
Praseodymium, green.
Neodymium, red to reddish-violet.
Samarium, topaz yellow.
Europium, pale rose.
Gadolinium, colourless.
Terbium, colourless.
Dysprosium, yellow to greenish-yellow.
Holmium, yellow to orange.
Yttrium, colourless.
Erbium, deep rose.
Thulium, green.
Ytterbium, colourless.
Lutecium, colourless.

In a general way it may be said that the salts have the properties that would be anticipated of salts derived from fairly strong bases. Of the commoner salts, the fluorides, iodates, chromates, phosphates, carbonates, and oxalates are practically insoluble in water at the ordinary temperature, and the sulphates are but sparingly soluble.[1] Corresponding salts of the rare earth elements are frequently isomorphous; numerous instances are cited in the succeeding pages.

It is often found that when corresponding salts of the rare earth elements are arranged in order of solubility, the order is identical with the order of atomic weights of the contained metals, with the exception of yttrium, which comes between holmium and erbium. This matter is discussed more fully in the next chapter (see p. 325). The order of arrangement La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Tm, Yb, Lu, Ct is sometimes conveniently spoken of as the *serial order* of the rare earth elements. With reference to the solubilities of the rare earth salts, it is interesting to note that several series of salts exhibit the rare uncommon property of being less soluble in hot than in cold water, *e.g.* the hydrated sulphates, double sulphates, and dimethylphosphates.

With regard to the formation of double salts, the rare earth compounds present several points of interest. Thus, numerous double nitrates are known, although outside the field of rare earth chemistry such salts are very uncommon. Of more interest are the double salts containing two different acid radicles, *e.g.* lanthanum oxalochloride, $La_2(C_2O_4)_3.LaCl_3.7\frac{1}{2}H_2O$, or $2La(C_2O_4)Cl.5H_2O$ as it is more conveniently written. In addition to oxalochlorides, there are known oxalonitrates, oxalobromides, oxalo-iodides, oxalosulphates, nitratosulphates, $M(NO_2).SO_4.H_2O$, and chlorocacodylates, $2M[(CH_3)_2.AsO_2]_3.MCl_3.18H_2O$.

The Rare Earth Elements and Hydrogen.

Hydrides, MH_3.—The rare earth metals combine directly with hydrogen, as Winkler and Matignon have shown.[2] The latter observed that the hydrides

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[1] For measurements of the conductivities of rare earth salts, see Muthmann, *Ber.*, 1898, 31, 1829; Ley, *Zeitsch. physikal. Chem.*, 1899, 30, 193; Rimbach and Schubert, *ibid.*, 1909, 67, 183; Aufrecht, *Inaugural Dissertation* (Berlin, 1904); Jones and Reese, *Amer. Chem. J.*, 1898, 20, 606; Jones and Allen, *ibid.*, 1896, 18, 321; A. A. Noyes and J. Johnston, *J. Amer. Chem. Soc.*, 1909, 31, 987; Holmberg, *Arkiv Kem. Min. Geol.*, 1903, 1, 1; Jantsch and Grünkraut, *Zeitsch. anorg. Chem.*, 1913, 79, 305; A. Heydweiller, *Zeitsch. physikal. Chem.*, 1915, 89, 281. For a selection of numerical results, see under the headings of the various metals.

[2] Winkler, *Ber.*, 1891, 24, 873, 1966 (La, Ce, Y); Matignon, *Compt. rend.*, 1900, 131, 891 (La, Ce, Nd, Pr, Sm).

are readily dissociated by heat. Muthmann, Kraft, and Beck have prepared various hydrides by the direct union of metal and hydrogen at 220°–270°, and find that these compounds are of the type MH_3, except the neodymium compound, which is NdH_2.[1] The hydrides are brittle, amorphous solids, the cerium and lanthanum compounds being bluish-black, the neodymium compound indigo blue, and the praseodymium compound green in colour. The atomic heat of hydrogen in cerium and praseodymium hydrides is 2·1.[2]

THE RARE EARTH ELEMENTS AND THE FLUORINE GROUP.

Fluorides, MF_3.—The anhydrous fluorides are produced by the action of fluorine on the carbides (Moissan), and by heating the oxides to redness in a current of hydrogen fluoride.[3] Hydrated fluorides may be prepared by double decomposition. According to Hirsch,[4] the best procedure consists in adding concentrated hydrofluoric acid solution to a hot solution of the chloride containing very little free hydrochloric acid. The precipitated fluoride is washed by decantation, twice with hot water and several times with 95 per cent. alcohol, and centrifuged till practically free from alcohol. The anhydrous fluoride may then be obtained by covering the product with absolute alcohol, evaporating to dryness, and heating the residue first at 100°, and finally at 200°.

The precipitated fluorides are practically insoluble in water and dilute mineral acids. In a large excess of hot, concentrated hydrochloric acid they are perceptibly soluble, the fluorides of the cerium group being more soluble than those of the yttrium group. In similar circumstances the fluorides of thorium and scandium are much less soluble.[5]

The fluorides of the rare earth elements crystallise in the cubic system and are isomorphous with fluorspar, in which mineral they frequently occur in traces (see pp. 217, 234).

Chlorides, MCl_3.—The anhydrous chlorides may be prepared in the pure state by the following methods:—

(i.) Dehydration of the hydrated salt, by heating the latter to 105°–130° in a current of pure, dry hydrogen chloride (taking care to avoid fusion of the hydrated salt) until no more water is given off, and then heating the residual monohydrate, $MCl_3.H_2O$, to 180–200° in the stream of gas as before. When water ceases to be given off, the temperature may be raised until the chloride fuses.[6]

(ii.) Conversion of the oxide (sulphate or oxalate) into chloride by heating it in a current of disulphur dichloride vapour.[7] The process is started at 250° and the temperature slowly raised to a point about 50° below the

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[1] Muthmann and Kraft, *Annalen*, 1902, **325**, 261 (La, Ce); Muthmann and Beck, *ibid.*, 1904, **331**, 58 (Nd, Pr); see also Muthmann and Baur, *Annalen*, 1902, **325**, 281 (La, Ce).

[2] Kellenberger and Kraft, *Annalen*, 1902, **325**, 279. Temperature range not stated.

[3] Van Haagen and E. F. Smith, *J. Amer. Chem. Soc.*, 1911, **33**, 1504 (La, Ce, Y).

[4] Hirsch, *J. Ind. Eng. Chem.*, 1911, **3**, 885.

[5] See under Scandium, p. 207.

[6] Matignon, *Ann. Chim. Phys.*, 1906, [viii.], **8**, 364 (general), 243 (Nd), 386 (Pr), 402 (Sm), 426 (La), 433 (Y), 440 ("Yb"): *Compt. rend.*, 1901, **133**, 289; 1905, **140**, 1637 (Nd); 1902, **134**, 427 (Pr), 1308 (Sm, Y, "Yb"); Baxter and Chapin, *J. Amer. Chem. Soc.*, 1911, **33**, 1 (Nd); Baxter and Stewart, *ibid.*, 1915, **37**, 516 (Pr); *cf.* Marignac, *Ann. Chim. Phys.*, 1853, [iii.], **38**, 148; Hermann, *J. prakt. Chem.*, 1861, **82**, 385.

[7] *Not* a mixture of sulphur chloride and chlorine, since in that case the product always contains oxychloride that cannot be converted into chloride.

melting-point of the chloride. Finally, the chloride is fused and cooled in a current of dry hydrogen chloride.[1] A rapid method of preparation, which is essentially a combination of methods (i.) and (ii.), consists in evaporating a solution of the chloride to dryness on the sand-bath and heating the solid residue in a current of dry hydrogen chloride and disulphur dichloride.

(iii.) Conversion of the oxide into chloride by heating it in a stream of carbonyl chloride[2] or a mixture of carbon monoxide and chlorine,[3] or in a stream of carbon tetrachloride vapour.[4]

(iv.) Conversion of the oxalate into chloride by heating it carefully in a stream of dry hydrogen chloride.[5] The oxide may be similarly converted into the chloride at a red heat, but it is practically impossible to carry out the conversion quantitatively.[6]

The anhydrous chlorides are formed when the metals are heated in chlorine or hydrogen chloride,[7] when the carbides are heated in chlorine,[8] and when the sulphides are heated in chlorine or hydrogen chloride,[9] but these processes are of little value as methods of preparation, except, perhaps, the sulphide method. Further, the classic method of heating a mixture of the oxide and carbon in a stream of chlorine is of no practical value, since the chlorides are non-volatile at a red heat.

The anhydrous chlorides are solids which melt at a red heat and crystallise on cooling. The densities (at 0°) and melting-points are given by Bourion as follows (melting-point of yttrium chloride by Matignon):—

	$LaCl_3$.	$CeCl_3$.	$PrCl_3$.	$NdCl_3$.	$SmCl_3$.	$GdCl_3$.	$TbCl_3$.	$DyCl_3$.	YCl_3
Density	3·79	3·92	4·07	4·14	4·27	4·52	4·35	3·67	...
M.pt. °C.	890°	848°	810°	784°	686°	628°	588°	680°	$<686°$

	$YbCl_3$.[10]	$LuCl_3$.[10]
Density	3·98	...
M.pt. °C.	880°	$>916°$

According to Matignon, the densities at 18° are as follows:—

$LaCl_3$.	$PrCl_3$.	$NdCl_3$.	$SmCl_3$.	YCl_3.
3·947	4·017	4·195	4·465	2·80

The volatility of the chlorides at a red heat is very slight, but the chlorides of the yttrium group are distinctly more volatile than those of the cerium group.

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[1] Bourion, *Ann. Chim. Phys.*, 1910, [viii.], **20**, 547 ; **21**, 49 (La, Ce, Pr. Nd, Sa, Gd, Tb, Dy, Yb, Lu); *cf.* Matignon and Bourion, *Compt. rend.*, 1904, **138**, 631 ; Matignon, *ibid.*, 1905, **140**, 1181, 1339.

[2] Chauvenet, *Compt. rend.*, 1911, **152**, 87.

[3] Didier, *Compt. rend*, 1885, **101**, 882 ; *Ann. l'Ecole Normale*, 1887, [iii.], **4**, 65 ; Duboin, *ibid.*, 1888, [iii.], **5**, 416 ; Matignon and Delépine, *Compt. rend.*, 1901, **132**, 37.

[4] Demarçay, *Compt. rend.*, 1887, **104**, 111 ; Quantin, *ibid.*, 1887, **104**, 223 ; 1888, **106**, 1074 ; L. Meyer, *Ber.*, 1887, **20**, 681 ; Matignon and Delépine, *loc. cit.*

[5] Robinson, *Proc. Roy. Soc.*, 1884, **37**, 150 ; *Chem. News*, 1884, **50**, 251 (Ce).

[6] Matignon, *Ann. Chim. Phys.*, 1906, [viii.], **8**, 364 ; Pettersson, *Zeitsch. anorg. Chem.*, 1893, **4**, 1.

[7] Hillebrand and Norton, *ibid.*, 1875, **155**, 633.

[8] Pettersson, *Ber.*, 1895, **28**, 2419 ; Moissan, *Compt. rend.*, 1896, **122**, 357 ; 1900, **131**, 595, 924 ; Moissan and Étard, *ibid.*, 1896, **122**, 573.

[9] Muthmann and Stutzel, *Ber.*, 1899, **32**, 3413.

[10] Material of doubtful purity.

The chlorides are extremely hygroscopic, and dissolve in water with the evolution of considerable heat. The following values for the heats of solution are given by Matignon :—

$LaCl_3$.	$PrCl_3$.	$NdCl_3$.	$SmCl_3$.	YCl_3.
31·3	33·5	35·4	37·4	45·3 Cals.

The aqueous solutions are neutral to methylorange. The chlorides are readily soluble in alcohol, less so in pyridine, and insoluble in ether, chloroform, acetone,[1] and the chlorides of phosphorus, arsenic, sulphur, and tin (Matignon); 100 grams of pyridine at 15° dissolve the following amounts of the anhydrous salts :—

$PrCl_3$.	$NdCl_3$.	$SmCl_3$.	YCl_3.
2·1	1·8	6·4	6·5

The chlorides are readily prepared in solution by dissolving the oxides, hydroxides, or carbonates in concentrated hydrochloric acid; by concentrating the solutions over sulphuric acid, cooling the hot, saturated solutions, or saturating the cold aqueous solutions with gaseous hydrogen chloride, crystalline, hydrated chlorides are readily prepared, usually of the type $MCl_3.6H_2O$. The hydrates thus obtained, when heated to 105°–130° in a stream of dry hydrogen chloride, are partly dehydrated, the monohydrates, $MCl_3.H_2O$, being produced; the monohydrates are completely dehydrated at 180°–200° in hydrogen chloride.[2] The hydrated salts cannot be dehydrated by simple heating in air without decomposition taking place.

Cæsium chloride combines with the rare earth chlorides, and the following crystalline salts have been obtained :—[3]

$$LACl_3.3CsCl.4H_2O\ (?\,5H_2O)$$
$$PrCl_3.3CsCl.5H_2O$$
$$NdCl_3.3CsCl.5H_2O$$
$$SmCl_3.3CsCl.5H_2O$$

Other double chlorides containing rare earth metals and the metals of Groups I. and II. are not known, with the exception of the *aurichlorides*. Double chlorides with antimony, bismuth, and tin chlorides,[4] and the chlorides of platinum,[5] have, however, been prepared. The *chloroplatinates* are of interest, since their composition affords evidence for the tervalency of the rare earth elements (see p. 237). They are readily soluble, orange-red, hygroscopic, crystalline salts, and the amount of water of crystallisation they contain is variously given as 12, 12·5, and $13H_2O$. The chloroplatinates of the metals of the cerium group are isomorphous, crystallising in tetragonal bipyramids :—[6]

$$CeCl_3.PtCl_4.12H_2O \qquad a : c = 1 : 1·1272$$
$$PrCl_3.PtCl_4.12H_2O \qquad = 1 : 1·13$$

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[1] Barnebey, *J. Amer. Chem. Soc.*, 1912, **34**, 1174.

[2] Matignon; see references on p. 252.

[3] R. J. Meyer and Wassjuchnow, *Zeitsch. anorg. Chem.*, 1914, **86**, 257.

[4] Dehnicke, *Inaugural Dissertation* (Berlin, 1904).

[5] See Vol. IX., or Nilson, *Bull. Soc. chim.*, 1877, [ii.], **27**, 206, 208; also Nilson, *ibid.*, 1877, [ii.], **27**, 210, for the chloroplatinites.

[6] Marignac, *Ann. Chim. Phys.*, 1873, [iv.], **30**, 65; Topsöe, *Bihang K. Svenska Vet.-Akad. Handl.*, 1873–5, **2**, No. 5; Söderström, *Zeitsch. Kryst. Min.*, 1902, **36**, 194 (Pr).

The rare earth chlorides also form double compounds with *mercuric cyanide*, of the type $RCl_3.3Hg(CN)_2.8H_2O$; these compounds lose $8H_2O$ over concentrated sulphuric acid or at 100°.[1]

The chlorides of the rare earth elements form compounds with alcohol, pyridine, and other organic bases. The compounds tabulated below have been obtained by Matignon:—[2]

$PrCl_3.2C_5H_5N$
$NdCl_3.3C_5H_5N$
$SmCl_3.3C_5H_5N$
$YCl_3.3C_5H_5N$

$NdCl_3.3C_2H_5.OH$
$NdCl_3.C_2H_5.OH$
$YCl_3.C_2H_5.OH$

Oxychlorides, MOCl.—These compounds may be prepared, sometimes in the crystalline form, by passing a slow current of air or steam (carried by an inert gas) over the molten, anhydrous chlorides.[3] They are also produced by heating the hydrated chlorides, or better, the oxalochlorides,[4] $M(C_2O_4)Cl.xH_2O$, to a red heat. The best method for obtaining them in the crystalline state consists in adding the oxides or sulphates to molten magnesium chloride, allowing to cool, and extracting the soluble salts with dilute acetic or hydrochloric acid.[5]

The oxychlorides are practically insoluble in cold water, dissolve very slowly in dilute acids, and are converted into oxides by prolonged heating in air. They are of considerable practical value, since their reflection-spectra (p. 291) are very well defined. For the purpose of examining these spectra the oxychlorides are readily prepared in the following manner. The oxides are dissolved in hydrochloric acid, ammonium chloride added, the solution evaporated to dryness, and the residue heated carefully.[6] It is then extracted with water and the insoluble spangles of oxychloride collected on a filter paper.[7]

Bromides, MBr_3.—These salts have not been examined so closely as the chlorides. The anhydrous bromides have been prepared by heating the anhydrous chlorides in pure, dry hydrogen bromide, taking care to avoid fusing during the operation,[8] by heating the sulphides in dry hydrogen bromide,[9] by heating the oxides in sulphur bromide vapour,[10] and by heating the oxides in a current of sulphur chloride and hydrogen bromide, the latter being in excess.[11] The bromides resemble the chlorides in properties. They are slightly soluble in acetone.[12] From aqueous solution they usually crystallise as hexahydrates $MBr_3.6H_2O$.

Iodides, MI_2.—Very little is known of these salts. Matignon has prepared the anhydrous iodides of *neodymium*, *praseodymium*, and *samarium* by

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[1] Alén, *Bull. Soc. chim.*, 1877, [ii.], **27**, 365 (La, Ce, "Df," Y, "Er").

[2] Matignon, references on p. 252; see also R. J. Meyer and Koss, *Ber.*, 1902, **35**, 2622; Jefferson, *J. Amer. Chem. Soc.*, 1902, **24**, 540; Hartwell, *ibid.*, 1903, **25**, 1128; Barbieri and Calzolari, *Atti R. Accad. Lincei*, 1911, [v.], **20**, i., 164.

[3] Matignon, references on p. 252 (Pr, Nd, Sm); Bourion, *Ann. Chim. Phys.*, 1910, [viii.], **21**, 49 (Gd, Dy).

[4] Job, *Compt. rend.*, 1898, **126**, 246.

[5] K. A. Hofmann and Höschele, *Ber.*, 1914, **47**, 238 (Pr, Nd, Sm, Er).

[6] It is advisable to add a mixture of sodium and potassium chlorides to the original solution and heat finally until the mixed chlorides fuse.

[7] Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 222.

[8] Matignon, references on p. 252 for Nd and Pr.

[9] Muthmann and Stützel, *Ber.*, 1899, **32**, 3413 (Ce).

[10] Barre, *Bull. Soc. chim.*, 1912, [iv.], **11**, 433.

[11] Bourion, *Compt. rend.*, 1907, **145**, 243 (La, Ce, Nd, Pr, Sm, Gd, Dy, Tb, "Yb")

[12] Barnebey, *J. Amer. Chem. Soc.*, 1912, **34**, 1174.

heating the anhydrous chlorides in pure, dry hydrogen iodide and avoiding fusion during the process.[1] They are extremely hygroscopic, and soluble in acetone.[2]

Bromates, $M(BrO_3)_3$.—The bromates are best prepared by covering barium bromate with water, heating on the steam-bath, and adding gradually, with continual stirring, the neutral rare earth sulphates. A slight excess of the barium bromate is necessary. When the double decomposition is complete, the barium sulphate is removed by filtration and the bromates crystallised from the solution. They form an isomorphous series of salts of the general formula $M(BrO_3)_3.9H_2O$, crystallise in hexagonal prisms, and are easily soluble in water.[3] The melting-points and solubilities at 25° (in grams of crystalline salt dissolved by 100 grams of water) of a number of bromates are as follows:—[4]

	La.	Ce.	Pr.	Nd.	Sm.	Y.
Melting-point, °C.	37·5°	49°	56·5°	66·7°	75°	74°
Grams of $M(BrO_3)_3.9H_2O$	416	...	190	146	114	168

Iodates, $M(IO_3)_3$.—The iodates are readily prepared by double decomposition. They are crystalline salts, sparingly soluble in water, but readily soluble in concentrated nitric acid. In the latter respect they differ markedly from the iodates of zirconium and thorium.[5]

THE RARE EARTH ELEMENTS AND THE OXYGEN GROUP.

Sesqui-oxides, M_2O_3.—Each of the rare earth elements forms a basic sesqui-oxide, the series of sesqui-oxides constituting the rare earths themselves. With the exception of the compounds of cerium, praseodymium, and terbium, the sesqui-oxides are stable in air even at a bright red heat, and so may be produced by the ignition of the hydroxides, carbonates, nitrates, oxalates, sulphates, and many other salts of oxyacids. The sesqui-oxides of praseodymium and terbium, however, combine with oxygen when heated, forming dark brown peroxides of somewhat indefinite composition; these peroxides may be reduced to sesqui-oxides in a stream of hydrogen at a red heat. Cerium sesqui-oxide, on the other hand, is extremely easily oxidised to cerium dioxide, which can only be reduced again with great difficulty.

When prepared by the ignition of suitable salts, the rare earths are obtained as amorphous powders; lanthana has also been obtained in the crystalline form. The appearance and chemical reactivity of a rare earth depend upon its method of formation, *i.e.* whether it has been formed from the oxalate, say, at a red heat or from the sulphate at a white heat. Practically nothing is known as to the cause of this difference; it does not even appear to be known whether the different forms have different densities. As a rule, the differences in reactivity are attributed to the fact that the various modifications are highly, but unequally, polymerised.

The sesqui-oxides are only reduced to the metallic state with considerable

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[1] Matignon, references on p. 252.

[2] Barnebey, *J. Amer. Chem Soc.*, 1912, **34**, 1174.

[3] Rammelsberg, *Pogg. Annalen*, 1842, **55**, 63; Marignac, *Ann. Min.*, 1859, [v.], **15**, 221.

[4] James, *J. Amer. Chem. Soc.*, 1908, **30**, 182; *Chem. News*, 1908, **97**, 61; James and Langelier, *J. Amer. Chem. Soc.*, 1909, **31**, 913; *Chem. News*, 1909, **100**, 85.

[5] Davis, *J. Amer. Chem. Soc.*, 1889, **11**, 26; R. J. Meyer and Speter, *Chem. Zeit.*, 1910, **34**, 306; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1911, **71**, 65.

difficulty, since their heats of formation are very high. The following values for the heats of formation (in Cals. per gram-equivalent of oxide) of lanthana, praseodymia, neodymia, ceria, and the refractory oxides magnesia and alumina, will serve to illustrate this fact:—[1]

$\frac{1}{6}La_2O_3$.	$\frac{1}{6}Pr_2O_3$.	$\frac{1}{6}Nd_2O_3$.	$\frac{1}{4}CeO_2$.	$\frac{1}{6}Al_2O_3$.	$\frac{1}{2}MgO$.
74·1	68·7	72·5	56·1	64·3	71·5

The magnetic susceptibilities of the rare earths are of considerable practical importance, since the values vary very considerably and thus afford a reliable means of following the processes of fractional crystallisation, precipitation, etc. (see p. 330). The following values have been recorded for the magnetic susceptibilities (x) per gram of sesqui-oxide at the ordinary temperature:—[2]

	La_2O_3.	Pr_2O_3.	Nd_2O_3.	Sm_2O_3.	Eu_2O_3.	Gd_2O_3.	Tb_2O_3.	Dy_2O_3.
$x \times 10^6 =$	−0·18	+ve	+33·5	+6·5	+33·5	+161	+240	+290

	Ho_2O_3.	Y_2O_3.	Er_2O_3.	Tm_2O_3.	Yb_2O_3.	Lu_2O_3.	Ct_2O_3.
$x \times 10^6 =$	+ve	−0·14	+ve	+ve	+33·6	+*c.* 8	+*c.* 2

The values for lutecia and celtia are only approximately known, ytterbia being about four or five times as paramagnetic as lutecia, which in its turn is four times as paramagnetic as celtia. The values for dysprosia, holmia, erbia, thulia, and ytterbia are known to be in descending order of magnitude. Praseodymia is not so paramagnetic as neodymia. It is of interest to note that the three elements which may definitely be assigned positions in Subgroup III. A of Mendeléeff's Table, viz. scandium, yttrium, and lanthanum, all form feebly diamagnetic oxides.

The rare earths are fairly strong basic oxides, being much stronger bases than the sesqui-oxides of Subgroup III. B. From general chemical and thermochemical[3] considerations it may be concluded that they are stronger bases than magnesia, but weaker than the alkaline earths. Thus, the strongly ignited oxides are readily soluble in mineral acids,[4] several of them combine directly with water and absorb carbon dioxide from the air, and all of them liberate ammonia from cold solutions of ammonium salts. Normal salts of numerous weak acids, *e.g.* chromic, carbonic, and acetic acids, are readily prepared. The salts derived from strong acids are only hydrolysed to a very slight extent even in dilute aqueous solution at the ordinary temperature.[5]

The determination of the relative strengths of the rare earths as bases has so far only been attempted in a qualitative manner, and the results are

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[1] Muthmann and Weiss, *Annalen*, 1904, **331**, 1.

[2] Urbain and Jantsch, *Compt. rend.*, 1908, **147**, 1286 (Nd, Sm, Eu, Gd, Tb, Dy); Urbain, *ibid.*, 1909, **149**, 37 (Tb); Blumenfeld and Urbain, *ibid.*, 1914, **159**, 323 (Yb); R. J. Meyer and Wuorinen, *Zeitsch. anorg. Chem.*, 1913, **80**, 7 (La, Y). See also S. Meyer, *Sitzungsber. K. Akad. Wiss. Wien*, 1901, **110**, IIa., 492; 1902, **111**, IIa., 38; *Monatsh.*, 1899, **20**, 369; 1908, **29**, 1017; *Ber.*, 1900, **33**, 320, 1918; *Ann. Physik*, 1900, [iv.], **1**, 664, 668; Onnes and Perrier, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **14**, 115; Onnes and Oosterhuis, *ibid.*, 1912, **15**, 322. On the magnetic dichroism of the rare earths, see Meslin, *Compt. rend.*, 1909, **148**, 1598.

[3] Matignon, *Ann. Chim. Phys.*, 1906, [viii.], **8**, 242, 364, 386, 402, 426, 433, 440; 1907, [viii.], **10**, 104.

[4] The most basic oxides are more readily soluble than the others.

[5] See Muthmann, *Ber.*, 1898, **31**, 1829; Ley, *Zeitsch. physikal. Chem.*, 1899, **30**, 193; Rimbach and Schubert, *ibid.*, 1909, **67**, 183; Denham, *Zeitsch. anorg. Chem.*, 1908, **57**, 378; Aufrecht, *Inaugural Dissertation* (Berlin, 1904).

somewhat contradictory. The strongest base is lanthana, the earths of the cerium group are stronger than those of the yttrium group, yttria itself being excepted, and the terbia earths are intermediate in strength between the ceria and yttria earths. Yttria itself is possibly as strong a base as neodymia. The rare earth elements are most probably arranged in the order of decreasing basic strength of their oxides as follows:—

La, Ce^{III}, Pr, Nd and Y, Sm, Eu, Gd, Tb, Dy, Ho, Er,
Tm, Yb, Lu, Ct, (Sc), (Ce^{IV}).

This order is usually in harmony with (i.) the order in which the nitrates decompose when heated, (ii.) the order in which the hydroxides are precipitated from the mixed salts by the gradual addition of ammonium, sodium, or potassium hydroxide, and (iii.) the relative degrees of hydrolysis of aqueous solutions of the sulphates.[1] It is in complete disagreement with the order obtained by Wöhler and Grünzweig[2] from measurements of the dissociation tensions of the anhydrous sulphates; it is difficult to believe that their results are accurate. Thermochemical data indicate that lanthana, praseodymia, neodymia, and samaria are arranged in order of diminishing basic strength in the order in which they have been named. Thus, in the reaction:—

$$[M_2O_3] + 6(HCl) = 2[MCl_3] + 3[H_2O] + q \text{ Cals.}$$

the values of q are:—[3]

Metal	La.	Pr.	Nd.	Sm.
Calories	160·6	147·8	143·1	128·4

and in the reaction:—

$$[M_2O_3] + 3[H_2SO_4] = [M_2(SO_4)_3] + 3[H_2O] + r \text{ Cals.}$$

the values of r are:—[4]

Metal	La.	Pr.	Nd.	Sm.
Calories	138·2	125·7	125·1	113·8

In connection with the order of basic strength given above, there is one curious anomaly. Fractional precipitation with ammonia indicates that samaria is a stronger base than europia, but a weaker base than gadolinia,[5] while other methods indicate that samaria is stronger than gadolinia. It may be pointed out, however, that it is only an assumption to regard the order in which the hydroxides are precipitated as the order of their relative strengths, the weakest precipitating first. In accordance with the ionic theory, the order of precipitation represents merely the order of increasing solubility-products, and this only represents the order of increasing basic strength of the hydroxides provided that the hydroxides are very largely dissociated in solution and the un-ionised portions have approximately equal solubilities.

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[1] Katz and James, *J. Amer. Chem. Soc.*, 1914, **36**, 779.
[2] Wöhler and Grünzweig, *Ber.*, 1913, **46**, 1726.
[3] Matignon, *loc. cit.*
[4] Matignon, *Compt. rend.*, 1906, **142**, 276.
[5] Lecoq de Boisbaudran, *Compt. rend.*, 1890, **111**, 393; 1892, **114**, 575; Benedicks, *Zeitsch. anorg. Chem.*, 1900, **22**, 393.

Higher Oxides.—Cerium forms a well-defined basic dioxide, CeO_2; praseodymium also forms a dioxide, PrO_2, and terbium forms a higher oxide of the approximate composition Tb_4O_7. These substances are not peroxides in the strict sense of the term, *i.e.* they are not constituted like hydrogen peroxide. They are described under the headings of the respective metals.

All the rare earth elements appear to be capable of forming true *hydrated peroxides* of the type $M_2O_5.xH_2O$, the constitutions of the compounds being expressed by the formula $(OH)_2.M.O.OH$. They may be obtained by the addition of hydrogen peroxide and ammonia to solutions of rare earth salts, and are described under the headings of the respective metals.

Hydroxides, $M(OH)_3$.—The hydroxides of the rare earth elements may be obtained as gelatinous precipitates by the addition of excess of ammonium, or an alkali hydroxide, (or ammonium sulphide) to hot, dilute solutions of the nitrates, chlorides, etc. The hydroxides are insoluble in excess of precipitant; when a deficit of the latter is added, or the precipitation carried out with cold solutions, the precipitated hydroxides are contaminated with basic salts.

The hydroxides are fairly strong bases, and absorb carbon dioxide from the air. They interact readily with acids to produce salts.

In the presence of ammonium acetate the hydroxides are only slowly and incompletely precipitated by the addition of ammonia; this property may be conveniently utilised in separating moderate amounts of iron from the rare earth elements.[1] The precipitation of the hydroxides may also be inhibited by the addition of citric acid and other organic hydroxy-acids. The case of tartaric acid is of particular interest. When sufficient of this acid has been previously added, precipitation of the hydroxides by sodium hydroxide is completely inhibited. Potassium hydroxide, on the other hand, gives precipitates of double potassium tartrates with the members of the yttrium group, but only from boiling solutions. Lastly, ammonium hydroxide gives rise to precipitates of double ammonium tartrates with the yttrium group even in cold solutions; the precipitates become crystalline when warmed.[2] Müller[3] has found the precipitation of cerous and neodymium hydroxides to be inhibited by the addition of glycerol.

Sulphides, M_2S_3.—The sulphides of the rare earth metals cannot be prepared by wet methods. The best methods of preparation consist in heating either (*a*) the oxide or (*b*) the anhydrous sulphate to redness in a current of pure, dry hydrogen sulphide.[4]

The sulphides have been obtained as coloured powders; sometimes in the crystalline state. They are comparatively stable in the air, but are slowly

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[1] Lecoq de Boisbaudran, *Compt. rend.*, 1890, **111**, 394; Sterba, *Ann. Chim. Phys.*, 1904, [viii.], **2**, 199; *cf.* the work of Delafontaine and others on colloidal basic acetates (Delafontaine, *Chem. News*, 1896, **73**, 284; W. Biltz, *Ber.*, 1904, **37**, 719; Orloff, *Chem. Zeit.*, 1907, **31**, 45).

[2] R. J. Meyer and Goldenberg, *Chem. News*, 1912, **106**, 13; Meyer and Hauser, *Die Analyse der seltenen Erden und der Erdsäuren* (Stuttgart, 1912), p. 43.

[3] Müller, *Zeitsch. anorg. Chem.*, 1905, **43**, 320.

[4] (*a*) Didier, *Compt. rend.*, 1885, **100**, 1461; **101**, 882 (La, Ce); Sterba, *Ann. Chim. Phys.*, 1904, [viii.], **2**, 193 (Ce); (*b*) Muthmann and Stützel, *Ber.*, 1899, **32**, 3413 (La, Ce, Pr, Nd); Sterba, *loc. cit.* (Ce); Erdmann and Wirth, *Annalen*, 1908, **361**, 190 (Sm, Gd). The early literature on the sulphides is as follows: Mosander, *Pogg. Annalen*, 1826, **11**, 406 (Ce); Beringer, *Annalen*, 1842, **42**, 138 (La); Lange, *J. prakt. Chem.*, 1861, **82**, 129 (Ce, La); Hermann, *J. prakt. Chem.*, 1861, **82**, 385 (La); Frerichs and Smith, *Annalen*, 1878, **191**, 331 (La, Ce); Popp, *ibid.*, 1864, **131**, 197 (Y).

hydrolysed by boiling water to the hydroxides, hydrogen sulphide being evolved. The sulphides are readily decomposed by dilute mineral acids.

Oxysulphides and *polysulphides* are known only in a few instances.

Sulphites, $M_2(SO_3)_3$.—The sulphites of the rare earth metals are practically insoluble in water, and may be obtained by double decomposition between sodium sulphite and rare earth salts.[1] They are soluble in aqueous sulphurous acid, since the hydroxides, oxides, and carbonates may be dissolved in an excess of that reagent. The solutions thus obtained deposit crystals of the normal sulphites when evaporated over sulphuric acid, or when heated.[2]

Thiosulphates, $M_2(S_2O_3)_3$.—The rare earth elements form well-defined crystalline thiosulphates, which are readily soluble in water. They are not hydrolysed with the precipitation of basic salts when their aqueous solutions are boiled,[3] in which respect they differ sharply from the corresponding salts of scandium, zirconium, and thorium, which may be completely hydrolysed.

Sulphates, $M_2(SO_4)_3$.—The anhydrous sulphates of the rare earth metals may be prepared by heating the oxides, hydroxides, carbonates, chlorides, nitrates, or oxalates with an excess of concentrated sulphuric acid, and eliminating the excess of acid and destroying acid sulphates by heating to 500°. It is a matter of great difficulty to obtain the pure, anhydrous, normal sulphates by this method (see p. 240). An alternative method of preparing the anhydrous sulphates consists in dehydrating the hydrated salts at about 400°. At temperatures higher than 500°, decomposition commences, and at a white heat the sulphates are completely decomposed, the oxides being left.

The anhydrous sulphates of the rare earth metals are hygroscopic solids which dissolve in water with the evolution of heat. In order to obtain them in concentrated solution it is necessary to add the powdered solid gradually, with stirring, to ice-cold water, avoiding any local rise in temperature. Concentrated solutions thus obtained are metastable with respect to the hydrated sulphates. Moreover, the solubilities of the hydrated salts diminish with rise of temperature very markedly.[4] Hence, when a cold, concentrated solution of a rare earth sulphate is warmed, a copious precipitate of a hydrated salt is obtained, which cannot be brought into solution by cooling unless a considerable excess of the solvent be added. The most important hydrates of the sulphates are the octahydrates, $M_2(SO_4)_3.8H_2O$, which seem to be given by the sulphates of all the rare earth metals except lanthanum.

The *densities* of the sulphates are given in the following table:—

	La.	Ce.	Pr.	Nd.	Sm.	Gd.	Y.	Er.
Anhydrous .	3·60	3·91	3·72	...	...	4·14	2·61	3·68
$5H_2O$ . .	...	3·17	3·17	...	...	...	...	...
$8H_2O$ . .	...	2·89	2·82	2·85	2·93	3·01	2·54	3·20
$9H_2O$ . .	2·83	2·84	...	...	...	...	...	...

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[1] Chavastelon, *Compt. rend.*, 1900, **130**, 781; Grossmann, *Zeitsch. anorg. Chem.*, 1905, **44**, 229 (Ce, La).

[2] Jolin, *Bull. Soc. chim.*, 1874, [ii.], **21**, 533 (Ce); Cleve, *ibid.*, 1874, [ii.], **21**, 196 (La); *Chem. News*, 1886, **53**, 81 (Sm); Cleve and Höglund, *Bull. Soc. chim.*, 1873, [ii.], **18**, 193, 289 (Y).

[3] In concentrated solutions a slight precipitation is observed in the yttrium group (Crookes, *Chem. News*, 1896, **74**, 259).

[4] See fig. 39 on p. 388.

With the exception of the cerium salt, all the octahydrates of the sulphates crystallise in monoclinic prisms, isomorphous with one another and with the corresponding selenates :—[1]

Salt.	a.	b.	c.	β.
$Pr_2(SO_4)_3.8H_2O$	2·9863	1	1·9995	118° 0′
$Nd_2(SO_4)_3.8H_2O$	2·9835	1	1·9968	118° 8·5′
$Sm_2(SO_4)_3.8H_2O$	3·0030	1	2·0022	118° 16′
$Gd_2(SO_4)_3.8H_2O$	3·0086	1	2·0068	118° 2′
$Y_2(SO_4)_3.8H_2O$	3·0284	1	2·0092	118° 25′
$Er_2(SO_4)_3.8H_2O$	3·0120	1	2·0043	118° 27′

The enneahydrates of cerium and lanthanum crystallise in the hexagonal system (bipyramidal), isomorphous with one another :—

$La_2(SO_4)_3.9H_2O$, $a : c = 1 : 0·7356$
$Ce_2(SO_4)_3.9H_2O$, $a : c = 1 : 0·7310$

The pentahydrates of cerium and praseodymium are also isomorphous with one another (monoclinic prisms) :—

$Pr_2(SO_4)_3.5H_2O$; $a : b : c = 1·4450 : 1 : 1·1157$, $\beta = 101° 16'$
$Ce_2(SO_4)_3.5H_2O$; $a : b : c = 1·4656 : 1 : 1·1264$, $\beta = 102° 40'$

The order of solubility of the hydrated sulphates in water at 25° is as follows, beginning with the least soluble :—

La, Gd, Sm, Y, Nd, Ce, Pr, Er, "Yb."

The actual solubilities at 25°, in grams of anhydrous sulphate per 100 grams of solution, are as follows :—[2]

Solid Phase.	Solubility.	Solid Phase.	Solubility.	Solid Phase.	Solubility.
$La_2(SO_4)_3.9H_2O$	2·483	$Y(SO_4)_3.8H_2O$	5·02	$Pr_2(SO_4)_3.8H_2O$	11·11
$Gd_2(SO_4)_3.8H_2O$	2·981	$Nd_2(SO_4)_3.8H_2O$	5·30	$Er_2(SO_4)_3.8H_2O$	11·94
$Sm(SO_4)_3.8H_2O$	3·426	$Ce_2(SO_4)_3.8H_2O$	7·60		

The solubilities of a number of the preceding salts in aqueous sulphuric acid have been determined at 25°. The results[3] are shown to scale in fig. 20.

Double Sulphates.—The sulphates form numerous double sulphates with the sulphates of **ammonium** and the **alkali metals.** Disregarding the water of crystallisation, they may be classified into the following types :—

$3M_2(SO_4)_3.2R_2SO_4$; $M_2(SO_4)_3.R_2SO_4$; $2M_2(SO_4)_3.3R_2SO_4$; $M_2(SO_4)_3.2R_2SO_4$; $2M_2(SO_4)_3.5R_2SO_4$; $M_2(SO_4)_3.3R_2SO_4$; $M_2(SO_4)_3.4R_2SO_4$; $2M_2(SO_4)_3.9R_2SO_4$; $M_2(SO_4)_3.5R_2SO_4$.

Only one or two systematic investigations of the double sulphates have been made.

The double *potassium* sulphates of the cerium and terbium groups are very sparingly soluble in cold water, and in a cold, saturated solution of

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[1] Data from Groth, *Chemische Krystallographie* (Leipzig, 1906–1910), vol. ii.

[2] See Wirth, *Zeitsch. anorg. Chem.*, 1912, **76**, 174 ; James and Holden, *J. Amer. Chem. Soc.*, 1913, **35**, 559 ; no data are available for rare earth sulphates other than those quoted.

[3] Wirth, *loc. cit.*

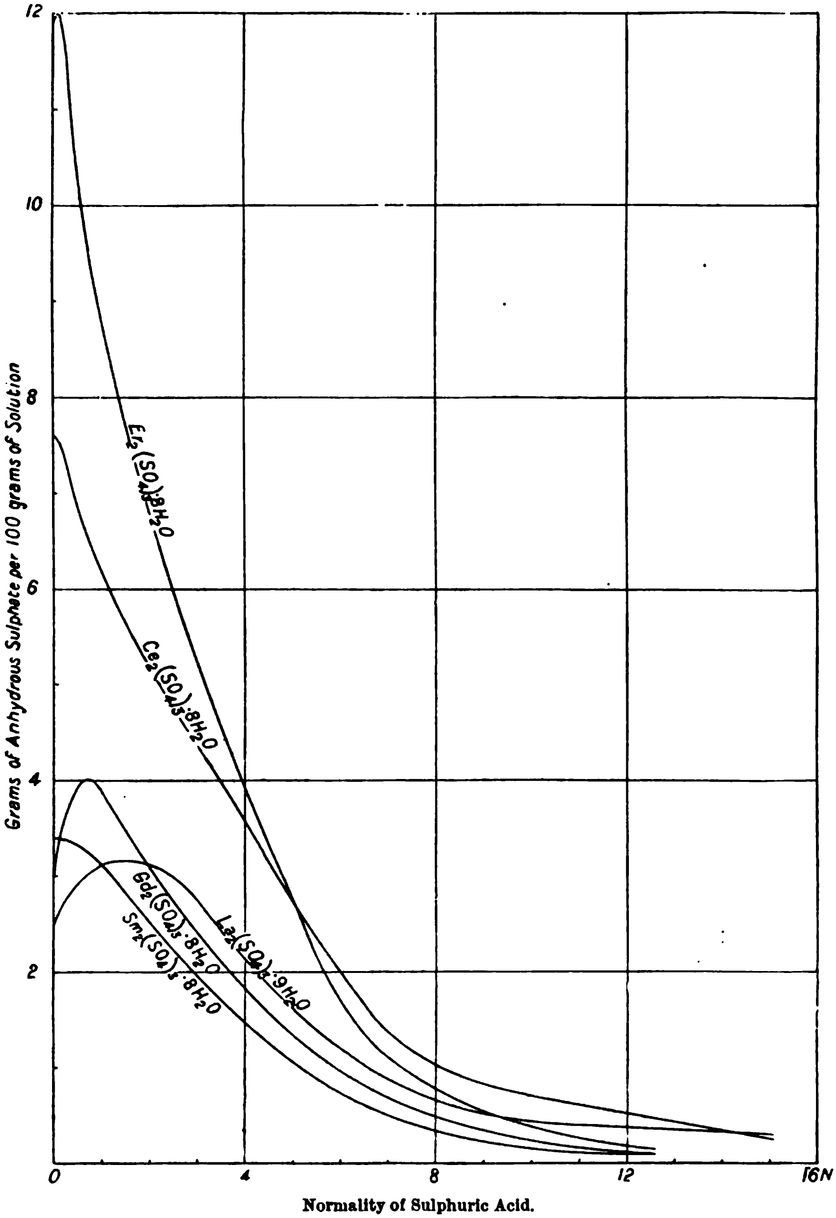

FIG. 20.—Solubilities of the sulphates of some of the rare earth elements in aqueous sulphuric acid at 25° C.

potassium sulphate they are even less soluble. In fact, the lanthanum, cerium, praseodymium, and neodymium salts are practically insoluble in the sulphate solution.[1] On the other hand, the double *potassium* sulphates of the yttrium group do not differ greatly from the simple rare earth sulphates in their solubility in water, and are readily soluble in cold, saturated potassium sulphate solution.

The double *sodium* and *ammonium* sulphates resemble the potassium salts in their solubilities, but are rather more soluble, particularly the ammonium salts (see pp. 385, 408, 423).

The double *ammonium* salts of the type $M_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$ form an isomorphous series, crystallising in monoclinic prisms:—[2]

Salt.	$a : b : c$.	β.	Density.
La	0·3509 : 1 : 0·9145 ;	97° 36′	2·516
Ce	0·3598 : 1 : 0·9340 ;	97° 15′	2·523
"Di"	0·3417 : 1 : 0·9234 ;	95° 28′	...

The double sulphates are of great practical importance. The sparingly soluble double salts may be brought into solution by heating them with concentrated nitric acid and pouring the whole into boiling water,[3] or by dissolving them in concentrated ammonium acetate solution.[4] They may be converted directly into hydroxides by heating with alkali hydroxide,[5] and into oxalates by prolonged heating with aqueous oxalic acid.[6] By heating to redness for an hour or so with four times their weight of powdered charcoal, they are almost completely reduced to sulphides, which may be dissolved in hydrochloric acid.[7]

Acid Sulphates, $M(HSO_4)_3$.—These salts may be prepared by dissolving the normal sulphates in boiling sulphuric acid and cooling the solution, when the crystalline acid salts separate out;[8] or by dissolving the normal salts in ice-cold water and adding a large excess of sulphuric acid.[9] Adhering sulphuric acid may be removed by heating *in vacuo* to 130°, but above 180° decomposition commences.

The cerous salt forms colourless, glistening needles; the yttrium salt, colourless pyramids; the lanthanum, praseodymium, neodymium, and samarium salts form colourless, green, rose-red, and golden-yellow, silky needles respectively. All the acid salts are converted into normal salts at temperatures approaching dull redness.

Basic Sulphates, $M_2O_3.SO_3$.—It is only at a white heat that a rare earth sulphate can be completely converted into the oxide. When heated to 900°,

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[1] This statement does not rigidly apply when mixtures of rare earth sulphates are dealt with; see p. 338.

[2] Morton, *Zeitsch. Kryst. Min.*, 1887, **12**, 520; Kraus, *ibid.*, 1901, **34**, 307; Wyrouboff, *Bull. Soc. franç. Min.*, 1891, **14**, 83.

[3] Hisinger and Berzelius, *Ann. Chim.*, 1803, [i.], **50**, 245; R. J. Meyer and Marckwald, *Ber.*, 1900, **33**, 3003.

[4] Urbain, *Bull. Soc. chim.*, 1896, [iii.], **15**, 338, 347; *cf.* Muthmann and Rölig, *Ber.*, 1898, **31**, 1718.

[5] Von Scheele, *Ber.*, 1899, **32**, 409.

[6] Auer von Welsbach, *Monatsh.*, 1883, **4**, 630; Muthmann and Rölig, *loc. cit.*

[7] Browning and Blumenthal, *Amer. J. Sci.*, 1911, [iv.], **32**, 164; Dennis and Rhodes, *J. Amer. Chem. Soc.*, 1915, **37**, 809.

[8] Wyrouboff, *Bull. Soc. chim.*, 1889, [iii.], **2**, 745 (Ce); Matignon, *Compt. rend.*, 1902, **134**, 657 (Pr, Nd); 1905, **141**, 1230 (Sm).

[9] Brauner and Picek, *Zeitsch. anorg. Chem.*, 1904, **38**, 322 (La, Ce, Pr, Nd, Sm, Y).

basic sulphates of the type $M_2O_3.SO_3$ are obtained (except from cerous sulphate) as amorphous powders, stable at 1000°.[1]

Selenites, $M_2(SeO_3)_3$.—The precipitates obtained by adding sodium selenite to an aqueous solution of rare earth salts are usually *basic selenites.* When a solution of selenious acid is used as precipitant, the *normal selenites* are generally precipitated. By heating the basic selenites with dilute aqueous selenious acid, the normal selenites may be obtained, and if more concentrated selenious acid be employed, *acid selenites* are formed.[2]

Selenates, $M_2(SeO_4)_3$.—The selenates may be obtained as hydrated salts by dissolving the oxides, hydroxides, or carbonates in aqueous selenic acid and crystallising from the solution. By carefully heating the hydrated salts, anhydrous selenates may be obtained. The selenates are not so well known as the sulphates. A number of octahydrates are known, and those that have been measured are isomorphous with the corresponding sulphates:—[3]

$Gd_2(SeO_4)_3.8H_2O$, $a:b:c=3{\cdot}1424:1:2{\cdot}0714$, $\beta=117°\ 50'$
"Er_2"$(SeO_4)_3.8H_2O$, $a:b:c=3{\cdot}0218:1:2{\cdot}0012$, $\beta=118°\ 45'$
$Y_2(SeO_4)_3.8H_2O$, $a:b:c=3{\cdot}1041:1:2{\cdot}0346$, $\beta=118°\ 12'$

The decahydrates of the same three elements crystallise in orthorhombic bipyramids and are isomorphous with one another; the data for two are as follows:—[4]

"Er_2"$(SeO_4)_3.10H_2O$, $a:b:c=0{\cdot}9300:1:0{\cdot}4807$
$Y(SeO_4)_3.10H_2O$, $a:b:c=0{\cdot}9358:1:0{\cdot}4829$

The *densities* of the selenates are given in the following table:—

	La.	Pr.	Sm.	Gd.	Y.
Anhydrous	...	4·30	4·08	4·18	...
$6H_2O$	3·48	...	...	...	...
$8H_2O$	...	3·08	3·33	3·32	2·91
$9H_2O$	2·66	...	...	...	...
$10H_2O$	...	...	...	3·06	2·78
$12H_2O$	...	...	3·01	...	...

In general, the *double selenates* are rather more soluble in water than the corresponding double sulphates.

Chromates, $M_2(CrO_4)_3$.—Few of these salts appear to have been analysed. The chromates are sparingly soluble in water, and so may be obtained as crystalline precipitates by double decomposition, using potassium chromate as precipitant. When a large excess of precipitant is used, double chromates may be obtained, particularly in the yttrium group. The chromates appear as a rule to have the composition $M_2(CrO_4)_3.8H_2O$ and to be isomorphous with the corresponding sulphates.

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[1] Matignon, *Compt. rend.*, 1902, **134**, 657 (Nd, Pr); 1905, **141**, 1230 (Sm); 1906, **142**, 394; Wild, *Zeitsch. anorg. Chem.*, 1905, **47**, 464 (La, Sm, Y, Er, "Yb"); L. Wöhler and Grünzweig, *Ber.*, 1913, **46**, 1726 (La, Pr, Nd, Sm, Gd, Y, Er, Yb, Lu).

[2] Nilson, *Nova Acta Soc Upsala*, 1875, [iii.], **9**, No. 7; *Ber.*, 1875, **8**, 655; *Bull. Soc. chim.*, 1875, [ii.], **23**, 494.

[3] Topsöe, *Bihang K. Svenska Vet.-Akad. Handl.*, 1874, **2**, No. 5; *Bull. Soc. chim.*, 1874, [ii.], **22**, 353; *Ber.*, 1875, **8**, 129 (Er, Y); Benedicks, *Zeitsch. anorg. Chem.*, 1900, **22**, 393 (Gd).

[4] Topsöe, *loc. cit.*

The rare earth salts are not precipitated by the addition of chromic acid or an alkali dichromate; in this respect they differ from those of zirconium, thorium, and quadrivalent cerium.

The chromates are of value for the separation of the rare earths from one another (see pp. 343, 352).

Molybdates, $M_2(MoO_4)_3$.—These salts closely resemble the corresponding tungstates in crystalline form and properties, and may be prepared by means similar to those described in the next section for the preparation of tungstates. Cerous and "didymium" molybdates have been shown by Cossa to be isomorphous with lead molybdate.[1]

A number of *complex molybdates* have been prepared containing the rare earth elements of the cerium group. They have the general formula $(NH_4)_6M_2Mo_{14}O_{48}.24H_2O$, and form a series of isomorphous salts crystallising in the triclinic system:—[2]

	a : b : c.	α.	β.	γ.
La	0·3502 : 1 : 0·3416	102° 29′	54° 18′	103° 10′
Ce	0·3523 : 1 : 0·3409	102° 22′	54° 30′	103° 4′
Pr	0·3514 : 1 : 0·3461	102° 11′	54° 15′	103° 45′
Nd	0·3492 : 1 : 0·3385	102° 15′	54° 8′	103° 29′
Sm	0·3611 : 1 : 0·3330	102° 49′	54° 45′	102° 37′

Tungstates, $M_2(WO_4)_3$.—The normal tungstates of the rare earth elements are practically insoluble in water, and may be obtained by double decomposition between sodium tungstate and a rare earth nitrate or sulphate. The precipitates are usually amorphous, but may become crystalline when heated. The amorphous tungstates may be crystallised by fusing them in an inert atmosphere and cooling, or by mixing them with an excess of sodium chloride and fusing the mixture. The tungstates crystallise in tetragonal bipyramids. It was discovered by Cossa that *cerous*, "*didymium,*" and *calcium* tungstates are isomorphous and form mixed crystals,[3] and Zambonini[4] has shown that cerous and lead tungstates are completely miscible both in the liquid and the solid states.

When a rare earth is fused with tungstic acid, sodium tungstate, and sodium chloride, and maintained at a red heat for some time, double tungstates are formed and may be isolated by washing the mass with water, in which they are insoluble. The following salts have been thus obtained in crystals which closely resemble those of the simple rare earth tungstates:—[5]

$La_4Na_6(WO_4)_9$	$Sm_4Na_6(WO_4)_9$
$La_2Na_8(WO_4)_7$	$Er_4Na_6(WO_4)_9$
$Ce_2Na_8(WO_4)_7$	$Y_2Na_8(WO_4)_7$

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[1] Frerichs and Smith, *Annalen*, 1878, **191**, 331 ($La_2(HMoO_4)_3$); Cossa, *Compt. rend.*, 1884, **98**, 990 ("Di"); 1886, **102**, 1315 (Ce); *Gazzetta*, 1886, **16**, 284 (Ce, "Di"); Cleve, *Chem. News*, 1886, **53**, 93 (Sm); Hitchcock, *J. Amer. Chem. Soc.*, 1895, **17**, 520 (La, Ce, Pr, Nd).

[2] Barbieri, *Atti R. Accad. Lincei*, 1908, [v.], **17**, i. 540; 1911, [v.], **20**, i. 18 (La, Ce, Nd, Pr, Sm); Billows, *Zeitsch. Kryst. Min.*, 1912, **50**, 500.

[3] Cossa, *Gazzetta*, 1879, **9**, 118 ("Di"); Cossa and Zecchini, *ibid.*, 1880, **10**, 225 (Ce); Cossa, *ibid.*, 1880, **10**, 467 ("Di"); 1886, **16**, 284 (Ce); Frerichs and Smith, *Annalen*, 1878, **191**, 331 (La); Hitchcock, *J. Amer. Chem. Soc.*, 1895, **17**, 520 (La, Ce, Pr, Nd).

[4] Zambonini, *Atti R. Accad. Lincei*, 1913, [v.], **22**, i. 519.

[5] Högbom, *Oefvers. Svenska Vet.-Akad. Forhandl.*, 1884, No. 5; *Bull. Soc. chim.*, 1884, [ii.], **42**, 2.

The *metatungstates* of the rare earth metals are extremely soluble in water, and may be prepared from barium metatungstate and the sulphates. The *lanthanum*, *cerium*, and "*didymium*" salts form two series of hydrates, $M_2(W_4O_{13})_3.27H_2O$ and $M_2(W_4O_{13})_3.30H_2O$, the latter crystallising below 16° in the triclinic, the former above 16° in the orthorhombic system :—

$27H_2O$.	$a:b:c$.	$30H_2O$.	$a:b:c$.	α.	β.	γ.
"Di"	0·9736 : 1 : 1·2952	La	0·9859 : 1 : 0·5786	97° 6′	93° 50′	89° 2′
		Ce	0·9838 : 1 : 0·5825	96° 43′	92° 34′	91° 30′

A *samarium* salt, $Sa_2(W_4O_{13})_3.35H_2O$, has also been described.[1]

A number of very *complex tungstates*, in which rare earth and tungstic anhydride are in the ratio $M_2O_3 : 16WO_3$, have been prepared by Rogers and E. F. Smith.[2] The formulæ of these compounds are given below :—

$2(NH_4)_2O.Ce_2O_3.16WO_3.2H_2O$
$2(NH_4)_2O.Pr_2O_3.16WO_3.16H_2O$
$4BaO.Pr_2O_3.16WO_3.7H_2O$
$6BaO.Pr_2O_3.16WO_3.9H_2O$
$4Ag_2O.Pr_2O_3.16WO_3.8H_2O$
$2(NH_4)_2O.La_2O_3.16WO_3.16H_2O$
$5BaO.La_2O_3.16WO_3.16H_2O$
$5Ag_2O.La_2O_3.16WO_3.4H_2O$
$3(NH_4)_2O.Nd_2O_3.16WO_3.20H_2O$
$6BaO.Nd_2O_3.16WO_3.17H_2O$

Silicotungstates, $M_4(W_{12}SiO_{40})_3$, *i.e.* $2M_2O_3.[12WO_3.SiO_2]_3$.—The *normal* and *acid* silicotungstates of the rare earth elements are soluble salts which crystallise well. They have been examined by Wyrouboff.[3] The following types of *normal* salts are known :—

(i.) $M_4(W_{12}SiO_{40})_3.78H_2O$, crystallising in the trigonal system (Nd, Sm, Gd, Tb, Y, "Yb" salts known). The ratio c/a (vertical to lateral crystallographic axis) is as follows :—

Salt.	Nd.	Sm.	Gd.	Tb.	Y.	"Yb."
c/a	1·6636	1·7244	1·7144	1·7043	1·7120	1·6997

(ii.) $M_4(W_{12}SiO_{40})_3.81H_2O$, crystallising in the trigonal system (La, Ce, Pr, Nd, Sm, Gd salts known) :—

Salt.	La.	Ce.	"Di."	Sm.	Gd.
c/a	2·6392	2·6820	2·6653	2·6786	2·6653

The *cerium* and "*didymium*" salts are also known in monoclinic forms :—

Ce $a:b:c = 1·7090 : 1 : 2·6558$, $\beta = 90°\ 20'$
"Di" $a:b:c = 1·7000 : 1 : 2·6325$, $\beta = 90°\ 10'$

(iii.) $M_4(W_{12}SiO_{40})_3.90H_2O$.—Only the *gadolinium* salt is known (trigonal ; $a:c = 1 : 2·6238$).

The *acid* salts also fall into three classes :—

(i.) $MH(W_{12}SiO_{40}).18H_2O$, crystallising in the triclinic system (La, Ce, Pr, Nd, Sm, Gd salts known) :—

Salt.	$a:b:c$.	α.	β.	γ.
$LaH(W_{12}SiO_{40}).18H_2O$	0·4081 : 1 : 0·4420	89° 34′	93° 8′	84° 29′
$CeH(W_{12}SiO_{40}).18H_2O$	0·3922 : 1 : 0·4195	90° 43′	92° 20′	84° 38′
"Di"$H(W_{12}SiO_{40}).18H_2O$	0·4003 : 1 : 0·4262	89° 58′	92° 48′	83° 20′
$GdH(W_{12}SiO_{40}).18H_2O$	0·4127 : 1 : 0·4393	89° 20′	92° 35′	84° 9′

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[1] Scheibler, *J. prakt. Chem.*, 1861, **83**, 273 (Ce) ; Wyrouboff, *Bull. Soc. franç. Min.*, 1892, **15**, 63 (La, Ce, "Di") ; Cleve, *Chem. News*, 1886, **53**, 93 (Sm).

[2] Rogers and Smith, *J. Amer. Chem. Soc.*, 1904, **26**, 1474.

[3] Wyrouboff, *Bull. Soc. franç. Min.*, 1896, **19**, 219 ; 1905, **28**, 201.

(ii.) $MH.(W_{12}SiO_{40}).24\frac{1}{2}H_2O$.—Monoclinic crystals (Tb, Y, Er, "Yb" salts known):—

Salt.	a : b : c.	β.
$TbH(W_{12}SiO_{40}).24\frac{1}{2}H_2O$	1·0270 : 1 : 1·4132	92° 39′
$YH(W_{12}SiO_{40}).24\frac{1}{2}H_2O$	1·0446 : 1 : 1·4835	92° 4′
"Yb"$H(W_{12}SiO_{40}).24\frac{1}{2}H_2O$	1·0356 : 1 : 1·4747	92° 5′

(iii.) $MH(W_{12}SiO_{40}).25\frac{1}{2}H_2O$.—Only the *erbium* salt is known (trigonal; $a:c = 1:1·7244$).

It is an interesting fact that the normal silicotungstates of lanthanum, cerium, and "didymium" with $81H_2O$ are isomorphous with thorium silicotungstate and the silicotungstates of calcium and strontium (see p. 234).

The Rare Earth Elements and the Nitrogen Group.

Nitrides, MN.—The fact that the rare earth metals combine directly with nitrogen to produce nitrides was discovered by Matignon. The compounds are of the type $M^{III}N$, as Muthmann, Kraft, and Beck have shown, and are readily prepared by heating the metals to 900° in nitrogen. Moissan has demonstrated the formation of nitrides when the carbides are heated to 1000° in ammonia, and Dafert and Miklauz[1] have shown that cerous nitride may be obtained in a pure condition by heating the hydride to 800°–900° in pure nitrogen.[2]

The nitrides are brittle, amorphous solids, the cerium compound being brass-yellow and the compounds of lanthanum, praseodymium, and neodymium black in colour. They are decomposed by moist air or by water, hydroxides and ammonia being produced. The atomic heat of nitrogen in the cerium and lanthanum compounds is 4·9.[3]

Nitrites, $M(NO_2)_3$.—Practically nothing is known of the rare earth nitrites. A number of *platinonitrites* and *platino-iodonitrites* have been prepared by Nilson.[4]

Nitrates, $M(NO_3)_3$.—These salts are readily obtained in solution by dissolving the sesqui-oxides, hydroxides, or carbonates in nitric acid, or by oxidising the oxalates with hot, concentrated nitric acid. They are readily soluble in water, from which the majority crystallise as hexahydrates, $M(NO_3)_3.6H_2O$. They are readily soluble in alcohol and also in acetone.[5] When heated they decompose, giving rise to basic salts and finally to the oxides.

The solubilities of a number of the hexahydrates in water at 25° are as follows (in parts of anhydrous nitrate per 100 of water):—[6]

$La(NO_3)_3.6H_2O$,	151·1;	$Y(NO_3)_3.6H_2O$,	141·6
$Nd(NO_3)_3.6H_2O$,	152·9;		

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[1] These chemists deny that cerous nitride may be prepared by heating cerium in nitrogen.

[2] Matignon, *Compt. rend.*, 1900, 131, 837 (La, Ce, Pr, Nd, Sm); Moissan, *ibid.*, 1900, 131, 595, 865 (Pr, Nd); Muthmann and Kraft, *Annalen*, 1902, 325, 261 (Ce, La); Muthmann and Beck, *ibid.*, 1904, 331, 58 (Pr, Nd); Dafert and Miklauz, *Monatsh.*, 1912, 33. 911 (Ce).

[3] Kellenberger and Kraft, *Annalen*, 1902, 325, 279. Temperature interval not stated.

[4] Nilson, *Nova Acta Soc. Upsala*, 1879, [iii.], 10, No. 16; *Ber.*, 1876, 9, 1722; 1878, 11, 879.

[5] Barnebey, *J. Amer. Chem. Soc.*, 1912, 34, 1174.

[6] James and Pratt, *J. Amer. Chem. Soc.*, 1910, 32, 873 (Y); James and Robinson, *ibid.*, 1913, 35, 754 (Nd); James and Whittemore, *ibid.*, 1912, 34, 1168 (La).

The solubilities are diminished by the addition of nitric acid, but from concentrated nitric acid (dens. 1·4) the pentahydrates, $M(NO_3)_3.5H_2O$, usually separate out. The fractional crystallisation of the nitrates is often used in separating the rare earths.

The hexahydrates crystallise in the triclinic system, as the following results[1] indicate:—

	$a:b:c.$	α	$\beta.$	$\gamma.$
$La(NO_3)_3.6H_2O$	0·8345 : 1 : 0·6215	79° 12′	101° 58′	92° 18′
$Ce(NO_3)_3.6H_2O$	0·8346 : 1 : 0·6242	78° 54′	102° 9′	92° 3′
"$Di(NO_3)_3.6H_2O$"	2·4035 : 1 : 1·8597	69° 6′	97° 30′	92° 48′
$Gd(NO_3)_3.6H_2O$	0·5571 : 1 : 0·7615	90° 6′	109° 55′	109° 48′

The nitrates of neodymium, lanthanum, and yttrium have been shown to be isodimorphous with bismuth nitrate (p. 234).

Since double nitrates are rather uncommon, it is interesting to notice that the nitrates of the rare earth metals form numerous double salts, of great practical value. The nitrates of the metals of the cerium group form double *ammonium* nitrates of the type $2(NH_4)NO_3.M(NO_3)_3.4H_2O$, crystallising in monoclinic prisms.[2]

$2(NH_4)NO_3.La(NO_3)_3.4H_2O$	$a:b:c = 1·2475 : 1 : 2·1863$;	$\beta = 112°\ 36'$
$2(NH_4)NO_3.Ce(NO_3)_3.4H_2O$	$a:b:c = 1·2321 : 1 : 2·1695$;	$\beta = 112°\ 45'$
$2(NH_4)NO_3.$"Di"$(NO_3)_3.4H_2O$	$a:b:c = 1·2449 : 1 : 2·1186$;	$\beta = 113°\ 1'$

Of the double nitrates formed with alkali nitrates, only those containing *rubidium* are of the type $2MNO_3.X(NO_3)_3.4H_2O$, and isomorphous with the ammonium salts. The following data are due to Wyrouboff:—[3]

	$a:b:c.$	$\beta.$
$2RbNO_3.Ce(NO_3)_3.4H_2O$	1·2298 : 1 : 0·9910	101° 16′
$2RbNO_3.La(NO_3)_3.4H_2O$	1·2349 : 1 : 0·9888	101°
$2RbNO_3.Nd(NO_3)_3.4H_2O$	1·2276 : 1 : 1·0153	100° 29′

The corresponding praseodymium-rubidium salt has been prepared by Jantsch and Wigdorow,[4] who have likewise prepared the *thallium* double salts

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

which they state are isomorphous with the preceding salts.

The following melting-points and densities of the preceding double nitrates have been determined, mainly by Jantsch and Wigdorow:—

	Ce.	La.	Pr.	Nd.	Ce.	La.	Pr.	Nd.
NH_4	74°	...	...	...	...	...	2·151	...
Rb	70°	86°	63·5°	47°	2·497	2·497	2·50	2·56
Tl	64·5°	72°	...	...	3·326	3·318	...	...

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[1] Taken from Groth, *Chemische Krystallographie* (Leipzig, vol. ii., 1908).

[2] Data from Groth, *opus cit.*; *cf.* Wyrouboff, *Bull. Soc. franç. Min.*, 1906, **29**, 324.

[3] Wyrouboff, *Bull. Soc. franç. Min.*, 1907, **30**, 299; the choice of axes and parametral plane is not the same as that for which the preceding data concerning ammonium salts apply.

[4] Jantsch and Wigdorow, *Zeitsch. anorg. Chem.*, 1911, **69**, 221.

The other double nitrates containing the alkali metals will be described under the headings of the rare earth metals. All the double nitrates are best crystallised from fairly concentrated nitric acid at comparatively low temperatures, *e.g.* 30° C. At temperatures above 70°, *anhydrous double salts* separate out.[1] They are of the type $2M^{III}(NO_3)_3.3M^{I}NO_3$, crystallise in the cubic system, and rotate the plane of polarised light.[2] When kept at the ordinary temperature, they become converted into other polymorphic forms having a low degree of symmetry.[3]

With the nitrates of *magnesium*, *nickel*, *cobalt*, *zinc*, and *manganese*, the nitrates of the cerium and terbium metals form double salts of the type $2M^{III}(NO_3)_3.3M^{II}(NO_3)_2.24H_2O$. These double nitrates form a comprehensive group of isomorphous salts, crystallising in the trigonal (scalenohedral) system, isomorphous with the corresponding bismuth double salts. The following values for the ratio (*c*) of the vertical to the lateral axes have been recorded :—[4]

	Mg.	Mn.	Ni.	Co.	Zn.	Fe (ous).
Ce	1·5378	1·5775	1·5667	1·5742	1·5677	...
Nd	1·5720	...	...	...	...	...
"Di"	...	...	...	...	...	1·5590
Gd	1·5786	...	...	...	...	...

The double salts melt in their water of crystallisation at the following temperatures :—[5]

	Mg.	Mn.	Ni.	Co.	Zn.
La . .	113°·5	87°·2	110°·5	111°·8	98°·0
Ce . .	111·5	83·7	108·5	98·5	92·8
Pr . .	111·2	81·0	108·0	97·0	91·5
Nd . .	109·0	77·0	105·6	95·5	88·5
Sm . .	96·2	70·2	92·2	83·2	76·5
Gd . .	77·5	...	72·5	63·2	56·5

The order of fusibility is therefore the same in each series.

The solubilities of the double nitrates in nitric acid (of density 1·325 at 16°) have been determined by Jantsch. The following data represent the solubilities in gram-molecules of salt per litre at 16° :—

	Mg.	Mn.	Ni.	Co.	Zn.
Ce . .	0·0382	0·1103	0·0460	0·0632	0·0675
La . .	0·0418	0·1192	0·0492	0·0669	0·0751
Pr . .	0·0503	0·1442	0·0568	0·0794	0·0888
Nd . .	0·0635	0·1816	0·0710	0·0923	0·1066
Sm . .	0·1583	0·3047	0·1760	0·2072	0·2179
Gd . .	0·2252	...	0·2405	0·2706	0·2801
Bi . .	0·2503	0·3742	0·2612	0·3090	0·3215

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[1] Except in the case of the sodium salts (or cæsium ? the original paper is ambiguous).

[2] Class 28 of Vol. I. p. 53.

[3] Wyrouboff, *Bull. Soc. franç. Min.*, 1907, **30**, 299 ; 1909, **32**, 365.

[4] Geipel, *Zeitsch. Kryst. Min.*, 1902, **35**, 625 ; Fock, *ibid.*, 1894, **22**, 37 ; Kraus, *ibid.*, 1901, **34**, 430 ; Groth, *Chemische Krystallographie* (Leipzig, 1906-1910), vol. ii.

[5] Jantsch, *Zeitsch. anorg. Chem.*, 1912, **76**, 303.

The densities at 0° C. and the gram-molecular volumes of the double nitrates are as follows, the data being also due to Jantsch :—

	Mg.		Mn.		Ni.		Co.		Zn.	
La	1·988	768·3	2·080	778·6	2·146	759·7	2·131	765·5	2·161	763·8
Ce	2·002	764·2	2·102	771·6	2·178	751·5	2·157	757·5	2·188	755·5
Pr	2·019	758·0	2·109	769·3	2·195	744·3	2·176	751·1	2·215	751·0
Nd	2·020	761·2	2·114	771·0	2·202	745·3	2·195	748·0	2·208	750·0
Sm	2·088	742·4	2·188	750·3	2·272	727·7	2·237	739·2	2·283	732·8
Gd	2·163	723·0	...	...	2·356	707·0	2·315	720·5	2·351	717·5

The more soluble of the preceding double nitrates are best crystallised from nitric acid.

The nitrates of the metals of the yttrium group do not appear to combine with other nitrates.[1]

Orthophosphates, MPO_4.—Few phosphates of the rare earth elements have been studied in any detail; such information as is available will be found under the headings of the various metals. Certain phosphates occur naturally, *e.g.* cerous phosphate or monazite (p. 218) and yttrium phosphate or xenotime (p. 220).

When orthophosphoric acid or an alkali orthophosphate is added to a solution of a rare earth salt a gelatinous precipitate of an orthophosphate is produced, which becomes crystalline on standing. The precipitate is soluble in excess of orthophosphoric acid, but is reprecipitated when the solution is boiled; it is also soluble in dilute mineral acids.

THE RARE EARTH ELEMENTS AND THE CARBON GROUP.

Carbides, MC_2.—The carbides of the rare earth metals are readily prepared by heating intimate mixtures of the rare earths and sugar carbon in the electric furnace :—

$$M_2O_3 + 7C = 2MC_2 + 3CO.$$

They were first prepared by Pettersson, and have been examined in detail by Moissan.[2] It will be noticed that the carbides of the rare earth elements are of the same type as calcium carbide, CaC_2, and are not analogous to aluminium carbide, Al_4C_3.

The carbides are brittle, crystalline solids, which in thin layers are transparent and yellow in colour. Their densities are as follows :—

LaC_2.	CeC_2.	PrC_2.	NdC_2.	SmC_2.	YC_2.
5·02	5·23	5·10	5·15	5·86	4·13

The carbides burn in fluorine when warmed, giving rise to fluorides and carbon. They likewise burn in chlorine, bromine, and iodine vapour at

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[1] For double compounds with organic substances, see Kolb, *Zeitsch. anorg. Chem.*, 1908, **60**, 123; 1913, **83**, 143; Barbieri and Calzolari, *Atti R. Accad. Lincei*, 1911, [v.], **20**, i. 164.

[2] Pettersson, *Ber.*, 1895, **28**, 2419 (Ce, La); Moissan, *Compt. rend.*, 1896, **122**, 357 (Ce); **123**, 148 (La); 1900, **131**, 595 (Pr, Nd), 924 (Sm); Moissan and Étard, *ibid.*, 1896, **122**, 573 (Y); Moissan, *Ann. Chim. Phys.*, 1896, [vii.], **9**, 302 (La, Ce); 1901, [vii.], **22**, 110 (Sm); Muthmann, Hofer, and Weiss, *Annalen*, 1902, **320**, 231 (Ce).

temperatures considerably below a red heat, and yield chlorides or iodides, hydrogen and carbon when heated in a stream of hydrogen chloride or iodide. At a red heat they are decomposed by hydrogen sulphide, and burn readily when heated in a stream of oxygen. They are decomposed by sulphur vapour, but only slowly; selenium at a red heat has more action than sulphur on the carbides. At 1200° they are decomposed by nitrogen (or better, ammonia), nitrides being formed. The carbides are unattacked by cold, concentrated nitric and sulphuric acids, but the latter acid oxidises them slowly when heated. They are decomposed by fusion with potassium hydroxide, carbonate, nitrate, chlorate, or permanganate.

The most interesting property of the rare earth carbides is their behaviour towards cold water, which rapidly decomposes them with the evolution of gas, the formation of a little liquid (unsaturated hydrocarbons), and the precipitation of hydroxides, $M(OH)_3$.[1] The chief constituent of the gas evolved is acetylene (68–72 per cent.); the constituents next in quantity are hydrogen (5–14 per cent.) and ethane (8–13 per cent.). Both the acetylene and the ethane are accompanied by small amounts of their homologues. Ethylene is also present (5–9 per cent.), but methane is absent. Apparently the initial reaction is:—

$$MC_2 + 3H_2O = M(OH)_3 + C_2H_2 + H_2,$$

followed by the hydrogenation of part of the acetylene to ethylene and ethane.[2]

Carbonates, $M_2(CO_3)_3$.—That the rare earths are strongly basic oxides is indicated by the fact that normal carbonates of the rare earth elements are easily prepared. They may be obtained in the crystalline form by passing a current of carbon dioxide through aqueous suspensions of the hydroxides, and as amorphous or crystalline precipitates by adding a very dilute solution of an alkali carbonate or bicarbonate to dilute solutions of rare earth salts.

The normal carbonates are insoluble in water. When the precipitated carbonates are allowed to stand in contact with concentrated alkali carbonate solutions, they are transformed into crystalline *double carbonates*. The double salts may be directly precipitated by adding a concentrated solution of a rare earth salt, drop by drop, to a cold, concentrated solution of an alkali carbonate. (i.) The double salts of the *cerium group* of metals are slightly soluble in concentrated *sodium* or *ammonium* carbonate, but readily soluble in concentrated *potassium* carbonate solution, the order of increasing solubility being *lanthanum*, *praseodymium*, *cerium*, and *neodymium*.[3] The potassium salts may therefore be prepared by adding the requisite rare earth chlorides to excess of concentrated potassium carbonate solution, warming to dissolve the precipitates, cooling, and diluting slightly; the potassium-neodymium and potassium-praseodymium salts may be obtained in glittering needles by the slow evaporation of their solutions in potassium carbonate. (ii.) The double salts of the *yttrium group* of elements are much more readily soluble in *sodium* or *ammonium* carbonate than those of the cerium group, particularly when warmed.[4] All the double carbonates are decomposed

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[1] Even in the case of cerium.

[2] Damiens, *Compt. rend.*, 1913, 157, 214; *cf.* the previous references.

[3] Hiller, *Inaugural Dissertation* (Berlin, 1904); R. J. Meyer, *Zeitsch. anorg. Chem.*, 1904, 41, 97; Arnold, *Ber.*, 1905, 35, 1173.

[4] Drossbach, *Ber.*, 1900, 33, 3506; Dennis and Dales, *J. Amer. Chem. Soc.*, 1902, 24, 400; Arnold, *loc. cit.*

by water or dilute alkali carbonates, particularly the sodium salts, and the salts of the cerium group are more readily decomposed than those of the yttrium group.

The *sodium*, *potassium*, and *ammonium* salts are of the type $R^I_2CO_3.M_2(CO_3)_3.xH_2O$, and *sodium* salts of the type $3Na_2CO_3.2M_2(CO_3)_3.xH_2O$ are also known.

Cyanides.—The simple cyanides of the rare earth metals are not known, hydroxides being precipitated when attempts are made to prepare the salts from potassium cyanide and rare earth salt solutions. The **platinocyanides**, however, are beautiful crystalline salts. Those of the metals of the cerium group are monoclinic, yellow in colour with a blue reflex, and belong to the type $Pt_3M_2(CN)_{12}.18H_2O$; those of the metals of the terbium and yttrium groups are rhombic, red in colour with a green reflex, and belong to the type $Pt_3M_2(CN)_{12}.21H_2O$:—[1]

	$a : b : c.$	β.	Density.
$La_2Pt_3(CN)_{12}.18H_2O$	... ...	...	2·626
$Ce_2Pt_3(CN)_{12}.18H_2O$	0·5806 : 1 : 0·5527	107° 33′	2·657
"Di_2"$Pt_3(CN)_{12}.18H_2O$	0·5806 : 1 : 0·5517	107° 29·5′	...

	$a : b : c.$	Density.
$Gd_2Pt_3(CN)_{12}.21H_2O$	... ...	2·563
$Y_2Pt_3(CN)_{12}.21H_2O$	0·8920 : 1 : 0·6157	2·376
"Er_2"$Pt_3(CN)_{12}.21H_2O$	0·8965 : 1 : 0·6194	...

Thiocyanates, $M(CNS)_3$.—These salts are readily soluble in water and alcohol. They form double salts with mercuric cyanide, of the type $M(CNS)_3.3Hg(CN)_2.12H_2O$. The *lanthanum* and *cerium* salts are monoclinic:—

La; $a : b : c = 2·2787 : 1 : 2·5787$, $\beta = 92° \ 37'$

Ce; $a : b : c = 2·2921 : 1 : 2·5655$, $\beta = 92° \ 39'$

but the *yttrium* and *erbium* salts are triclinic:—[2]

Y; $a : b : c = 2·2815 : 1 : 2·5836$, $\alpha = 79° \ 47'$, $\beta = 102° \ 43'$, $\gamma = 88° \ 21'$

"Er"; $a : b : c = 2·2697 : 1 : 2·5976$, $\alpha = 79° \ 41'$, $\beta = 102° \ 43'$, $\gamma = 88° \ 30'$

Formates, $(H.COO)_3M$.—The formates of the rare earth elements form well-defined crystals. They belong to the regular system, crystallising in pentagonal dodecahedra.[3] The formates of the cerium metals are sparingly soluble and those of the yttrium group fairly readily soluble in water, the formates of the terbium metals being intermediate in solubility. These solubility differences have at times been utilised for fractionating the rare earths (see p. 347).

Acetates, $(CH_3.COO)_3M$.—These salts are readily soluble in water. Basic salts do not separate out from dilute boiling aqueous solutions.

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[1] Topsöe, *Bihang K. Svenska Vet.-Akad. Handl.*, 1874, **2**, No. 5; Söderström, *Zeitsch. Kryst. Min.*, 1902, **36**, 194 (Pr); Baumhauer, *Zeitsch. Kryst. Min.*, 1907, **43**, 356 (Y); Tschirvinski, *ibid.*, 1913, **52**, 44 (Y); Boguslawski, *Ann. Physik*, 1914, [iv.], **44**, 1077 (Y).

[2] Topsöe, *Bihang K. Svenska Vet.-Akad. Handl.*, 1874, **2**, No. 5.

[3] Behrens, *Arch. Néerland.*, 1901, [ii.], **6**, 67; *Rec. trav. chim.*, 1904, **23**, 413.

Oxalates, $M_2(C_2O_4)_3$.—The oxalates are readily obtained by the addition of an aqueous solution of oxalic acid to solutions of soluble salts of the rare earth elements; they are perhaps best obtained from the nitrates.[1] The oxalates are first precipitated in the amorphous state, but on warming and shaking they rapidly become crystalline. The salts thus obtained are hydrated, 1 molecule of the oxalate being as a rule associated with 9, 10, or 11 molecules of water.

The oxalates of lanthanum, cerium, and "didymium" of the type $M_2(C_2O_4)_3.11H_2O$ are isomorphous, crystallising in the monoclinic system:—[2]

	$a:b:c$.	β.
$La_2(C_2O_4)_3.11H_2O$	1·0730 : 1 : 2·1750	92° 27′
$Ce_2(C_2O_4)_3.11H_2O$	1·1300 : 1 : 2·0098	95° 13′
"Di_2"$(C_2O_4)_3.11H_2O$	1·0693 : 1 : 2·1346	92° 47′

and the enneahydrates of lanthanum and cerium, $M_2(C_2O_4)_3.9H_2O$, are also isomorphous, crystallising in the tetragonal system.[3]

The oxalates are practically insoluble in water. The following table contains the solubility determinations that have been published, the data representing milligrams of anhydrous oxalate per litre at 19°–27° C.:—

Solid Phase.	A.	B.	C.	D.
$La_2(C_2O_4)_3.10H_2O$	0·62	0·70	0·96	1·21
$Ce_2(C_2O_4)_3.10H_2O$	0·41	0·45	0·81	0·99
$Pr_2(C_2O_4)_3.10H_2O$	0·74	...	...	...
$Nd_2(C_2O_4)_3.10H_2O$	0·49	0·31	0·59	0·73
$Sm_2(C_2O_4)_3.10H_2O$	0·54	...	...	...
$Y_2(C_2O_4)_3.9H_2O$	1·00	...	...	...
"Yb_2"$(C_2O_4)_3.10H_2O$	3·34	...	...	...

The values given under A were determined by Rimbach and Schubert[4] by the electrical conductivity method. The other values are due to Hauser and Herzfeld;[5] those given under B were determined from conductivity measurements, and those under C and D by the gravimetric and volumetric analyses of the saturated solutions. The determinations are only approximately correct, but they show the oxalates of the yttrium group to be more soluble in water than those of the cerium group.

The oxalates are slightly soluble in dilute mineral acids, the solubilities increasing with the concentration of the acid and with the temperature. The solubilities in aqueous sulphuric acid at 25° have been carefully determined for a few oxalates;[6] the results are shown graphically in fig. 21, in which,

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[1] On the precipitation of the pure oxalates, see the section on analytical chemistry (p. 368).

[2] Wyrouboff, *Bull. Soc. franç. Min.*, 1901, **24**, 105; 1902, **25**, 66.

[3] Wyrouboff, *ibid.*, 1901, **24**, 111.

[4] Rimbach and Schubert, *Zeitsch. physikal. Chem.*, 1909, **67**, 183.

[5] Cited in Meyer and Hauser, *Die Analyse der seltenen Erden und der Erdsäuren* (Stuttgart, 1912), p. 61.

[6] Hauser and Wirth, *Zeitsch. anal. Chem.*, 1908, **47**, 389; Wirth, *Zeitsch. anorg. Chem.*, 1912, **76**, 174; Meyer and Wassjuchnow, cited in Meyer and Hauser, *opus cit.* (Nd); *cf.* Brauner, *Trans. Chem. Soc.*, 1898, **73**, 951.

instead of plotting the amounts of the oxalates contained in the solutions, the equivalent qualities of the oxides have been indicated. The solubilities of scandium and thorium oxalates have also been indicated for purposes of comparison. Were it not for the position of the erbium oxalate curve, it might be concluded that the more basic the rare earth, the more soluble is the corresponding oxalate in sulphuric acid.

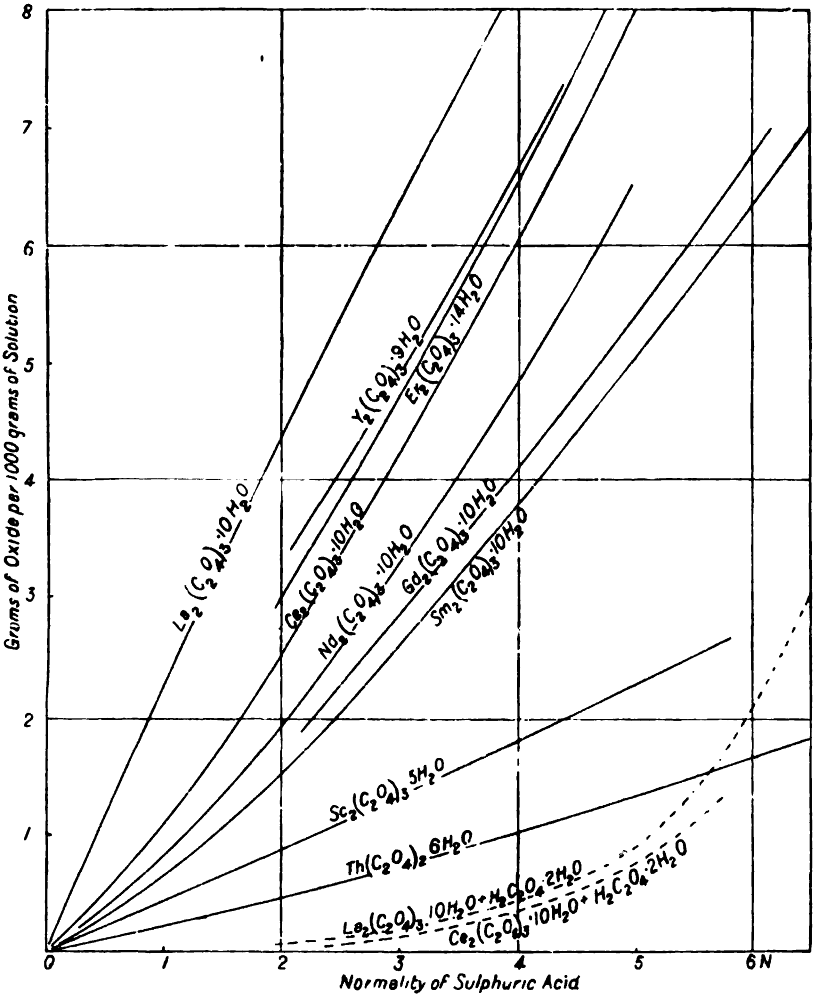

FIG. 21.—Solubilities of the oxalates of some of the rare earth elements in aqueous sulphuric acid at 25° C.

A few of the experimental results for the solubilities are contained in the following table, the data denoting grams of oxide (CeO_2 in the case of cerium) or anhydrous oxalate per 100 grams of saturated solution :—

Normality of Sulphuric Acid.	Solubility of Oxalate in Terms of		Normality of Sulphuric Acid.	Solubility of Oxalate in Terms of	
	Oxide.	Anhydrous Oxalate.		Oxide.	Anhydrous Oxalate.
	$La_2(C_2O_4)_3.10H_2O$.			$Sm_2(C_2O_4)_3.10H_2O$.	
0·10	0·0208	0·0346	0·10	0·0058	0·0094
0·50	0·0979	0·1628	0·50	0·0313	0·0507
1·00	0·2383	0·3962	1·00	0·0627	0·1016
1·50	0·3190	0·5304	1·445	0·1114	0·1804
2·00	0·4417	0·7344	2·39	0·1914	0·3099
3·20	0·7632	1·2690	4·32	0·4328	0·7008
	$Ce_2(C_2O_4)_3.10H_2O$.			$Gd_2(C_2O_4)_3.10H_2O$.	
0·10	0·0136	0·0215	2·16	0·1883	0·3005
0·50	0·0524	0·0828	3·11	0·3010	0·4803
1·00	0·1140	0·1802	4·32	0·4359	0·6956
1·445	0·1764	0·2788			
2·39	0·3083	0·4873		$Y_2(C_2O_4)_3.9H_2O$.	
3·90	0·6300	0·9957	2·16	0·352	0·6884
	$Nd_2(C_2O_4)_3.10H_2O$.		4·32	0·7236	1·4000
0·50	0·0336	0·0552		$Er_2(C_2O_4)_3.14H_2O$.	
1·00	0·0752	0·1235	2·16	0·329	0·514
2·00	0·1872	0·3074	3·11	0·493	0·771
5·00	0·6603	1·0840	4·32	0·704	1·100

When the concentration of the sulphuric acid exceeds a certain value, the stable solid phase in contact with the solution changes from the oxalate to the sulphate.[1]

The oxalates of the rare earth elements are more soluble in aqueous hydrochloric than in sulphuric acid, differing in this respect from scandium oxalate (see p. 214). This will be seen from fig. 22, where the results for cerous, neodymium, and scandium oxalates are represented graphically. The numerical data[2] are as follows, in grams of anhydrous oxalate per 100 grams of solution :—

Normality of HCl.	0·125.	0·25.	0·5.	1·0.	1·5.	2.	3.	4.	5.
$Ce_2(C_2O_4)_3.10H_2O$.	0·0151	0·0343	0·0812	0·1974	0·355	0·532	0·977	1·555	...
$Nd_2(C_2O_4)_3.10H_2O$.	...	...	0·0270	0·0732	...	0·333	...	...	1·721

From hot, concentrated hydrochloric acid, the *oxalochlorides* of the rare earth elements, $M(C_2O_4)Cl.xH_2O$, may be obtained.[3]

The oxalates of the rare earth elements are practically insoluble in aqueous oxalic acid, thereby resembling thorium and scandium oxalates, but differing from the zirconium salt. Moreover, the addition of a moderate amount of oxalic acid greatly reduces the solubilities of the oxalates in mineral acids, a fact of great practical importance. The extent by which the

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[1] See Wirth, *Zeitsch. anorg. Chem.*, 1908, **58**, 213.

[2] Taken from Meyer and Hauser, *opus cit.*

[3] Job, *Compt. rend.*, 1898, **126**, 246.

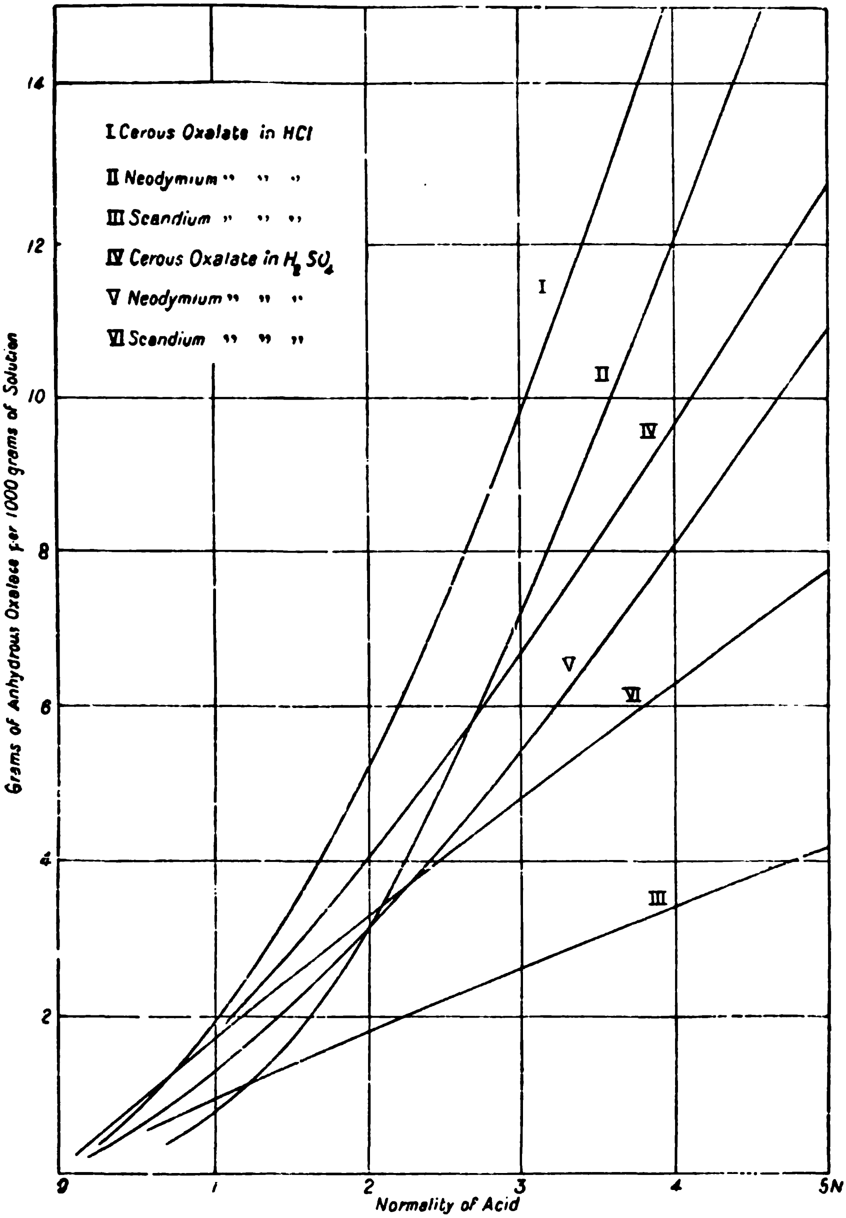

FIG. 22.—Solubilities of the oxalates of cerium, neodymium, and scandium in aqueous hydrochloric and sulphuric acids at 25° C.

solubility is diminished may be seen by comparing the results given in the following table[1] with those already quoted (solubilities in grams of anhydrous oxalate per 100 grams of solution at 25° C.) :—

Normality of		Solubility of		
H_2SO_4.	$H_2C_2O_4$.	$La_2(C_2O_4)_3.10H_2O$.	$Ce_2(C_2O_4)_3.10H_2O$.	$Sm_2(C_2O_4)_3.10H_2O$.
0·05	0·05	...	0·0030	...
0·50	0·05	0·0334	0·0105	...
0·25	0·25	0·0099	0·0046	...
0·05	0·50	0·0039	0·0025[2]	0·0009
0·25	0·50	0·0069	...	...
0·50	0·50	0·0090	0·0010[2]	0·0010
0·96	0·50	0·0138	...	0·0032
1·19	0·50	0·0203	...	0·0042
1·44	0·50	0·0293	...	0·0057
1·70	0·50	0·0369	...	0·0080

The diminution in the solubility of lanthanum and cerous oxalates in aqueous sulphuric acid, brought about by saturating the solutions with oxalic acid, is shown graphically in fig. 21 by the dotted lines, which represent the results of Wirth.

The oxalates of the cerium group are practically insoluble in dilute aqueous solutions of alkali oxalates; those of the yttrium group are perceptibly soluble. One gram of ammonium oxalate dissolved in 38 grams of water at 20° C. dissolves the oxalates in quantities equivalent to the following amounts of oxides :—[3]

Oxide.	La_2O_3.	Pr_2O_3.	Nd_2O_3.	Ce_2O_3.	Y_2O_3.	"Yb_2"O_3.	ThO_2.
Grams dissolved . .	0·00023	0·00023	0·00034	0·00042	0·00256	0·0244	0·620
Relative solubilities .	1·0	1·1	1·4	1·8	11·0	104·6	2663

It is clear that the order of increasing solubility of the oxalates is approximately the order of decreasing basic strength of the corresponding oxides. The slight solubilities of the oxalates of the rare earth elements, in comparison with the solubility of thorium oxalate, is also obvious.

Ammonium and potassium oxalates are better solvents for the oxalates of the yttrium group than sodium oxalate. The solubility of the oxalates of the rare earth elements in solutions of these salts is connected with the fact that double or complex oxalates are produced. In the yttrium group the *double ammonium oxalates* may be readily prepared by dissolving the rare earth oxalates in hot, concentrated ammonium oxalate and cooling the solutions; the salts thus obtained are of considerable value for the separation of the yttria earths. Various double oxalates are stated to be formed merely

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[1] Hauser and Wirth, *loc. cit.*

[2] These results appear to be in error.

[3] Brauner, *Trans. Chem. Soc.*, 1898, 73, 951.

by the addition of soluble salts of the rare earth elements to concentrated solutions of ammonium or an alkali oxalate (see pp. 425, 431).

In consequence of this tendency towards the formation of double oxalates, occlusion of soluble oxalate occurs to a notable extent when the oxalates of the rare earth elements are precipitated by means of soluble oxalates instead of oxalic acid. This is the case even with the oxalates of the cerium group.[1]

It has been mentioned that *oxalochlorides* may be prepared by crystallising solutions of the oxalates in hot, concentrated hydrochloric acid. These salts may also be prepared by dissolving the oxalates in concentrated solutions of the corresponding chlorides.[2] Analogous *oxalobromides* and *oxalo-iodides* are stated by Job to exist. The oxalates are about as soluble in dilute nitric as in dilute hydrochloric acid, and may be crystallised unchanged from the solution, but when heated with concentrated nitric acid decomposition ensues and *oxalonitrates* are produced.[3] On further heating with boiling, concentrated nitric acid, the oxalonitrates are readily oxidised to nitrates. The conversion of oxalate into nitrate in this manner proceeds very readily in the case of the cerium salt, the presence of which also has a very marked catalytic effect in increasing the rates of oxidation of the other oxalates.[4] Oxalonitrates may in certain cases be produced by dissolving the oxalates in concentrated solutions of the corresponding nitrates (see, *e.g.*, p. 420). It is probable that *oxalosulphates* may also be prepared.

When heated, the oxalates first lose their water of crystallisation, but it is almost impossible to obtain the pure, anhydrous oxalates, decomposition commencing before the last traces of water are expelled. In decomposing, the oxalates first evolve carbon monoxide, leaving behind the carbonates, and the latter then lose carbon dioxide and leave the oxides. When thus heated to redness in air, cerous oxalate leaves a residue of ceria, CeO_2, praseodymium and terbium oxalates leave peroxides of the (approximate) composition M_4O_7, and the other oxalates leave the sesqui-oxides, M_2O_3, as residues.

The oxalates of the rare earth elements are extremely important substances from the practical point of view. At times they may be conveniently prepared by heating the precipitated hydroxides, carbonates, or double alkali sulphates with aqueous oxalic acid. It is often necessary to transform the oxalates into soluble salts. The conversion into nitrates by heating with nitric acid has been mentioned. The oxalates may be transformed into anhydrous sulphates by heating with concentrated sulphuric acid. By heating with concentrated alkali hydroxide (preferably potassium hydroxide) they may be converted into the hydroxides, which may then be dissolved in a suitable acid. The transformation from oxalate to another salt may often be readily carried out by first igniting the oxalate to oxide and then dissolving the latter in an acid, unless a mixture of oxides is obtained containing more than 45–50 per cent. of ceria.[5]

Ethylsulphates, $M(C_2H_5.SO_4)_3.9H_2O$.—The ethylsulphates of the rare earth metals are beautifully crystalline salts. They may be prepared by two

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[1] Baxter and Griffin, *J. Amer. Chem. Soc.*, 1906, **28**, 1684; Baxter and Daudt, *ibid.*, 1908, **30**, 563. See also p. 368.

[2] Matignon, *Ann. Chim. Phys.*, 1906, [viii.], **8**, 243.

[3] Brauner, *Trans. Chem. Soc.*, 1898, **73**, 951; R. J. Meyer and Marckwald, *Ber.*, 1900, **33**, 3003.

[4] Barbieri and Volpino, *Atti R. Accad. Lincei*, 1907 [v.], **16**, i. 399.

[5] For the necessary procedure in such a case, see p. 332.

methods: (i.) double decomposition between barium ethylsulphate and the rare earth sulphates, rigorously exempt from free acid, and crystallisation of the liquid at as low a temperature as possible after removing the barium sulphate;[1] and (ii.) double decomposition between alcoholic solutions of sodium ethylsulphate and the rare earth chlorides, sodium chloride being precipitated.[2]

The ethylsulphates form a strictly isomorphous series of salts, crystallising from water as the hydrated salts $M(C_2H_5.SO_4)_3.9H_2O$, which belong to the bipyramidal class of the hexagonal system. Twelve of them have been carefully examined by Jaeger, to whom the following data are due:—

Salt of	Density at 25°.	Molec. Volume.	Axial Ratios *a* : *c*.	Salt of	Density at 25°.	Molec. Volume.	Axial Ratios *a* : *c*.
La	1·845	366·6	1 : 0·5073	Gd[4]	1·919	362·0	1 : 0·5050
Ce	1·930	351·1	1 : 0·5075	Dy	1·942	360·4	1 : 0·5050
Pr[3]	1·876	361·4	1 : 0·5058	Y	1·764	354·9	1 : 0·5035
Nd[3]	1·883	362·1	1 : 0·5068	Er	1·907	369·8	1 : 0·5053
Sm	1·904	361·3	1 : 0·5072	Tm	2·001	352·8	1 : 0·5044
Eu	1·909	361·2	1 : 0·5058	Yb	2·019	351·4	1 : 0·5079

According to Jaeger, in no case does the axial ratio $a : c$ differ from the mean value $1 : 0·5062 \pm 0·0012$ by more than can be attributed to experimental error. Scandium ethylsulphate, moreover, is not isomorphous with the preceding salts.[5]

The ethylsulphates are extremely useful salts to use for the fractional crystallisation of the earths of the yttrium group.

Acetylacetonates,[6] $M(CH_3.CO.CH.CO.CH_3)_3$.—These substances may be prepared by shaking the hydroxides with a dilute alcoholic solution of acetylacetone, or, more simply, by adding a slightly ammoniacal solution of acetylacetone to a neutral solution of the chloride or nitrate. They are sparingly soluble in water, but may be crystallised from aqueous alcohol or organic solvents such as benzene, chloroform, etc.

The melting-points of the acetylacetonates are not very definite. W. Biltz gives the following values:—

La.	Ce^{III}.	Pr.	Nd.	Sm.
185°	131–2°	146°	144–6°	146–7°

The cerous compound forms a trihydrate, m.p. 145° C. The acetylacetonates cannot be sublimed without decomposition taking place. In this respect, and

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[1] Urbain, *Bull. Soc. chim.*, 1898, [iii.], **19**, 376; *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184; *J. Chim. phys.*, 1906, **4**, 56.

[2] James, *J. Amer. Chem. Soc.*, 1912, **34**, 767.

[3] *Cf.* Morton, *Zeitsch. Kryst. Min.*, 1887, **12**, 517.

[4] *Cf.* Benedicks, *Zeitsch. anorg. Chem.*, 1900, **22**, 413.

[5] Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1095; *Rec. trav. chim.*, 1914, **33**, 342.

[6] Urbain, *Bull. Soc. chim.*, 1897, [iii.], **17**, 98; *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184; Urbain and Budischovsky, *Compt. rend.*. 1897, **124**, 618; Hantzsch and Desch, *Annalen*, 1902, **323**, 1 (La); W. Biltz, *ibid.*, 1904, **331**, 334 (La, Ce, Pr, Nd, Sm); W. Biltz and Clinch, *Zeitsch. anorg. Chem.*, 1904, **40**, 218; James, *J. Amer. Chem. Soc.*, 1911, **33**, 1332 (Tm); G. T. Morgan and H. W. Moss, *Trans. Chem. Soc.*, 1914, **105**, 189 (Y).

in crystalline form,[1] they differ from the *scandium* compound. In solution they exist mainly as double molecules, $M_2(CH_3.CO.CH.CO.CH_3)_6$.[2] The acetylacetonates form crystalline, addition compounds with ammonia, substituted ammonias, and pyridine.

Other Organic Salts.—In the hope of finding suitable compounds for effecting the fractionation of the rare earths, numerous organic salts of rare earth elements have been prepared.[3]

The **malonates** are sparingly soluble crystalline salts, prepared from the hydroxides of the meta and malonic acid. The following have been described :—

$La_2[CH_2(COO)_2].5H_2O$
$Ce_2[CH_2(COO)_2].5H_2O$
$Pr_2[CH_2(COO)_2].6H_2O$
$Nd_2[CH_2(COO)_2].5H_2O$
$Sm_2[CH_2(COO)_2].6H_2O$
$Gd_2[CH_2(COO)_2].8H_2O$
$Y_2[CH_2(COO)_2].5H_2O$
$Er_2[CH_2(COO)_2].10H_2O$

In the cerium group the salts form monoclinic plates; in the yttrium group they crystallise in rhombic needles.[4]

The **glycollates,** like the malonates, are sparingly soluble crystalline salts. In the cerium group the salts are anhydrous. The following solubilities, in grams of salt per litre of solution at 18°, are due to Jantsch and Grünkraut :—[5]

$La[CH_2(OH)COO]_3$	3·328	$Sm[CH_2(OH).COO]$	6·373
$Ce[CH_2(OH)COO]_3$	3·563	$Gd[CH_2(OH).COO].2H_2O$	14·147
$Pr[CH_2(OH)COO]_3$	3·578	$Y[CH_2(OH).COO].2H_2O$	2·447
$Nd[CH_2(OH)COO]_3$	4·609		

The **cacodylates**[6] are of interest, since those of the cerium group are readily soluble and those of the yttrium group practically insoluble in cold water. The solubilities at 25°, in grams of salt dissolved by 100 grams of water, are as follows :—

$La[(CH_3)_2AsO_2]_3.xH_2O$	v. sol.;	$Sm[(CH_3)_2AsO_2].8H_2O$	1·60
$Ce[(CH_3)_2AsO_2]_3.xH_2O$	v. sol.;	$Y[(CH_3)_2AsO_2].9H_2O$	insol.
$Pr[(CH_3)_2AsO_2]_3.8H_2O$	8·43;	$Tm[(CH_3)_2AsO_2].8H_2O$	insol.
$Nd[(CH_3)_2AsO_2]_3.8H_2O$	5·13;		

The cacodylates form double salts with the rare earth chlorides, nitrates, etc.; they are crystalline and sparingly soluble in water. The lanthanum, cerium, and neodymium salts of the type $2M[(CH_3)_2AsO_2]_3.MCl_3.18H_2O$ have been analysed.

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[1] Jaeger, *loc. cit.*

[2] See p. 236.

[3] A list will be found under the heading of each of the rare earth elements; see Chaps. XII., XIII., and XIV.

[4] Erdmann and Wirth, *Annalen*, 1908, **361**, 190 (La, Ce, Pr, Nd, Sm, Gd, Y, Er); Rimbach and Kilian, *ibid.*, 1909, **368**, 110 (Ce); Holmberg, *Zeitsch. anorg. Chem.*, 1907, **53**, 83 (La, Ce, Y).

[5] Jantsch and Grünkraut, *Zeitsch. anorg. Chem.*, 1912, **79**, 305. See also Rimbach and Kilian, *Annalen*, 1909, **368**, 110 (Ce); James, Hoben, and Robinson, *J. Amer. Chem. Soc.*, 1912, **34**, 276 (Sm); Pratt and James, *ibid.*, 1911, **33**, 1330 (Y).

[6] Whittemore and James, *J. Amer. Chem. Soc.*, 1913, **35**, 127.

The **sebacates** are of interest owing to the fact that they are of value in quantitative analysis. The following have been described:—[1]

$La_2[C_8H_{16}(COO)_2]_3.2H_2O$
$Pr_2[C_8H_{16}(COO)_2]_3.2H_2O$
$Nd_2[C_8H_{16}(COO)_2]_3.3H_2O$
$Sm_2[C_8H_{16}(COO)_2]_3.4H_2O$
$Y_2[C_8H_{16}(COO)_2]_3.4H_2O$

The **dimethylphosphates,** $M[(CH_3)_2PO_4]_3$, are of considerable practical value. In the cerium group they are readily soluble and in the yttrium group sparingly soluble in water, and all the salts are less soluble in hot water than in cold. With the exception of the lanthanum and cerium salts, they are anhydrous. In the cerium group the salts crystallise in hexagonal plates or prisms, but in the terbium and yttrium groups they crystallise in long needles. The solubilities, in grams of anhydrous salt per 100 grams of water at 25° and 95°, are as follows:—[2]

Salt of	25°.	95°.	Salt of	25°.	95°.	Salt of	25°.	95°.
La	103·7	...	Nd	56·1	22·3	Y	2·8	0·55
Ce	79·6	65	Sm	35·2	10·8	Er	1·78	...
Pr	64·1	...	Gd	23·0	6·7	Yb	1·2	0·25

The **m-nitrobenzenesulphonates,** $M[C_6H_4(NO_2)SO_3]_3$, are of value for the separation of the cerium group. They are readily soluble in water and crystallise readily. Two isomorphous series are known: (i.) the hexahydrates of the La, Ce, Pr, and Nd salts, and (ii.) the heptahydrates of the Sm, Gd, and Y salts. The solubilities at 15°, in grams of anhydrous salt per 100 grams of water, are as follows:—[3]

La.	Ce.	Pr.	Nd.	Sm.	Gd.	Y.
16·0	25·5	33·9	46·1	50·9	43·8	48·3

The **1 : 4 : 2 - bromonitrobenzenesulphonates** are well-defined crystalline salts, crystallising with 8, 10, or $12H_2O$. The following have been prepared:—

$La(C_6H_3Br.NO_2.SO_3)_3.8H_2O$
$Ce(C_6H_3Br.NO_2.SO_3)_3.8H_2O$
$Pr(C_6H_3Br.NO_2.SO_3)_3.8H_2O$
$Nd(C_6H_3Br.NO_2.SO_3)_3.8H_2O$
$Sm(C_6H_3Br.NO_2.SO_3)_3.10H_2O$
$Eu(C_6H_3Br.NO_2.SO_3)_3.10H_2O$
$Gd(C_6H_3Br.NO_2.SO_3)_3.10H_2O$
$Y(C_6H_3Br.NO_2.SO_3)_3.10H_2O$
$Er(C_6H_3Br.NO_2.SO_3)_3.12H_2O$
$Tm(C_6H_3Br.NO_2.SO_3)_3.12H_2O$
$Yb(C_6H_3Br.NO_2.SO_3)_3.12H_2O$

The solubilities at 25° (expressed as grams of anhydrous salt in 100 grams of saturated solution) are as follows:—[4]

La salt	4·77	Sm salt	7·27	Er salt	6·06
Ce „	5·56	Eu „	6·31	Tm „	6·38
Pr „	5·73	Gd „	5·94	Yb „	7·29
Nd „	6·76	Y „	5·74		

The **p-dichlorobenzenesulphonates** and **p-dibromobenzenesulphonates** of a number of rare earth elements have been examined

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[1] Whittemore and James, *loc. cit.*

[2] J. C. Morgan and James, *J. Amer. Chem. Soc.*, 1914, 36, 10.

[3] Holmberg, *Zeitsch. anorg. Chem.*, 1907, 53, 83.

[4] Katz and James, *J. Amer. Chem. Soc.*, 1913, 35, 872. See also fig. 35 on p. 326.

crystallographically by Armstrong and Rodd.[1] The dibromo salts of the cerium group form hydrates with $9H_2O$ and with $18H_2O$ (Sm salt not known). The enneahydrates form a series of isomorphous, orthorhombic salts :—

	$a : b : c$.
$La(C_6H_3Br_2.SO_3)_3.9H_2O$	1·3965 : 1 : 0·8753
$Ce(C_6H_3Br_2.SO_3)_3.9H_2O$	1·4106 : 1 : 0·8873
$Pr(C_6H_3Br_2.SO_3)_3.9H_2O$	1·3964 : 1 : 0·8798
$Nd(C_6H_3Br_2.SO_3)_3.9H_2O$	1·3990 : 1 : 0·8789

Gadolinium, however, forms a monoclinic heptahydrate, $Gd(C_6H_3Br_2.SO_3)_3.7H_2O$ ($a : b : c = 1·2595 : 1 : 0·6031$; $\beta = 89°\ 16'$) and a monoclinic dodecahydrate, $Gd(C_6H_3Br_2.SO_3)_3.12H_2O$. The latter is isomorphous with the praseodymium and neodymium salts of p-dichlorobenzene-sulphonic acid :—

	$a : b : c$.	β.
$Pr(C_6H_3Cl_2.SO_3)_3.12H_2O$	0·5887 : 1 : 0·3819 ;	76° 26′
$Nd(C_6H_3Cl_2.SO_3)_3.12H_2O$	0·5872 : 1 : 0·3810 ;	76° 34′
$Gd(C_6H_3Br_2.SO_3)_3.12H_2O$	0·5952 : 1 : 0·3817 ;	76° 48′

Further, lanthanum and praseodymium form isomorphous, triclinic pentadecahydrates, $La(C_6H_3Cl_2.SO_3)_3.15H_2O$ ($a : b : c = 1·6193 : 1 : 1·6028$; $\alpha = 76°\ 26'$, $\beta = 113°\ 48'$, $\gamma = 68°\ 6'$) and $Pr(C_6H_3Cl_2.SO_3)_3.15H_2O$.

Various **tartrates,**[2] **citrates,**[2] **malates,**[3] etc., have also been examined.

THE RARE EARTH ELEMENTS AND BORON.

Metaborates, $M(BO_2)_3$.—When the oxalate of a rare earth element is added to excess of molten boron sesqui-oxide, the mass obtained separates into two layers (conjugate phases), the upper one consisting almost entirely of boron sesqui-oxide. The lower layer solidifies to a glassy mass, which devitrifies when heated for some hours over a Bunsen burner. From it a little boric anhydride can then be extracted with boiling water, leaving as residue a crystalline metaborate, $M^{III}(BO_2)_3$. Even in the case of cerium, the product is said to be of this type, if the cerous oxalate is added to the molten oxide in an atmosphere of carbon dioxide, and it is also stated that cerous metaborate is obtained when ceric oxide is substituted for cerous oxalate.[4]

SPECTRA OF THE RARE EARTH ELEMENTS AND THEIR COMPOUNDS.[5]

The various types of rare earth spectra may be classified as follows :—

A. **Absorption spectra.**—These include the following :—

(*a*) Absorption spectra by transmission.
(*b*) Absorption spectra by reflection.

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[1] H. E. Armstrong and Rodd, *Proc. Roy. Soc.*, 1912, **A**, **87**, 204 ; Rodd, *ibid.*, 1914, **A**, **89**, 292.

[2] Holmberg, *loc. cit.*

[3] Jautsch, *Chem. Zeit.*, 1914, **38**, 794.

[4] Guertler, *Zeitsch. anorg. Chem.*, 1904, **40**, 225 (La, Ce, "Di," Sm, Gd); *cf.* Nordenskiöld, *Pogg. Annalen*, 1861, **114**, 612 ; Holm, *Inaugural Dissertation* (Munich, 1902).

[5] The most comprehensive treatise on Spectroscopy is Kayser, *Handbuch der Spektroskopie* (Hirzel, Leipzig, 6 vols., 1900–1910). Of the smaller text-books, Baly, *Spectroscopy* (Longmans, 2nd ed., 1912), and Urbain, *Introduction à l'étude de la spectrochimie* (Hermann et Fils, Paris, 1911), may be mentioned ; the latter gives a very clear account of the theoretical side of the subject.

B. **Emission spectra.**—These include the following:—

- (i.) *Band spectra.*
  - (*a*) Flame spectra.
  - (*b*) Reversion spectra (*spectres de renversement*).
  - (*c*) Cathodic phosphorescence spectra.
- (ii.) *Line spectra.*
  - (*a*) Spark spectra.
  - (*b*) Arc spectra.
  - (*c*) X-ray or high frequency spectra.

The above order of arrangement is adopted in the following account.

ABSORPTION SPECTRA BY TRANSMISSION AND REFLECTION.

General.—The salts (derived from colourless acids) of the following rare earth elements are coloured, and in solution exhibit well-defined absorption spectra in the visible region: praseodymium, neodymium, samarium, europium, dysprosium, holmium, erbium, and thulium. In addition, the salts of terbium exhibit a single band in the visible region of the spectrum. Absorption bands are not limited merely to the visible part of the spectrum, but may also occur in the infra-red and ultra-violet regions. The absorption spectrum of gadolinium, for instance, lies wholly in the ultra-violet.

The absorption spectra of the rare earth compounds differ markedly from other absorption spectra in the large number of bands they exhibit, and in the great intensity and the remarkable narrowness of many of the bands. Of the visible absorption spectra, only those of europium and terbium are weak. The presence of the absorbing rare earth elements is therefore easily detected. Further, when the absorption spectrum of a rare earth element appears only faintly, the element is known to be present only in very small concentration.

The literature relating to the absorption spectra of the compounds of the rare earth elements is fairly extensive. It may be recalled that the first observations on these spectra were made by Bahr in 1852, and that their study was pursued by Gladstone, Delafontaine, and others. At a period when the discovery of samarskite had led to renewed interest in the rare earths, the work of Soret upon their absorption spectra was of great importance.[1] From the historical point of view, the work of Krüss and Nilson[2] is also of interest. Of the more modern work, that of Forsling,[3] and particularly that of H. C. Jones and his co-workers,[4] may be mentioned.

The absorption spectra of solids may be examined in the ordinary manner applicable to liquids if thin, transparent, crystal slices are available; other-

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[1] Soret, *Compt. rend.*, 1878, 86, 1062; 1879, 88, 422, 1077; 89, 521; 1880, 91, 378; *Arch. Sci. phys. nat.*, 1878, [ii.], 63, 41, 89; 1880, [iii.], 4, 261.

[2] See p. 287.

[3] Forsling, *Bihang K. Svenska Vet.-Akad. Handl.*, 1892, 18, I., No. 4; 1893, 18, I., No. 10; 1898, 23, I., No. 5; 1899, 24, I., No. 7; 1902, 28, II., No. 1.

[4] Jones and Anderson, *Proc. Amer. Phil. Soc.*, 1908, 47, 276; *Amer. Chem. J.*, 1909, 41, 276; Jones and Strong, *Proc. Amer. Phil. Soc.*, 1909, 48, 194; *Amer. Chem. J.*, 1910, 43, 37, 97; 1911, 45, 1; 1912, 47, 27, 126; Jones and Guy, *ibid.*, 1913, 49, 1; 50, 257; *Physikal. Zeitsch.*, 1912, 13, 649; Jones and Anderson, *Carnegie Institution Publications*, 1909, No. 110; Jones and Strong, *ibid.*, 1910, No. 130; 1911, No. 160; Jones and others, *ibid.*, 1915, No. 210.

wise it is necessary to examine the light they reflect for absorption bands. Observations upon the absorption spectra of the rare earths are usually made with salt solutions, generally with aqueous solutions.

Absorption spectra are often described by stating for each band the limits between which absorption is observed in the spectrum. This, however, necessitates a full description of the experimental details to be of real value, since the width of a band is increased when either the concentration of the solution or the depth of solution through which absorption takes place is increased. Moreover, the edges of the bands are often hazy and difficult to define with accuracy. A better method of description is to state for each band the wave-length corresponding to the position of maximum absorption, *i.e.* what is known as the "head" of the band. This is not necessarily at the middle of the band; moreover, a broad band may show two or more maxima. The position of the "head" of a band is, in general, practically independent of the concentration of the solution.

The absorption is said to follow *Beer's Law* when the increase in the intensity of absorption at any point in the spectrum due to increase of concentration of the absorbing solution, may be exactly nullified by a diminution in thickness of the absorbing solution in the same ratio. For moderately dilute solutions (aqueous or otherwise) of rare earth compounds, the absorption is described with considerable accuracy by Beer's Law, as H. C. Jones and his co-workers have shown.

When the absorption spectrum of a rare earth compound in solution is observed at different dilutions through the same thickness of solution, it is observed that certain broad bands seen in concentrated solution become resolved into a number of narrower bands as the dilution is continued. Eventually, as dilution proceeds, the bands disappear, but the dilution at which one band disappears is not necessarily the same as that at which any other band ceases to be visible. Some bands can only be observed in moderately concentrated solution, while others are still visible in extremely dilute solution. It must therefore be borne in mind when consulting complete lists of absorption bands that all the bands enumerated cannot be seen at one and the same time, for in solutions sufficiently concentrated to exhibit the weak bands others will have coalesced, producing a smaller number of broader bands (see figs. 24 and 25 on pp. 288 and 290).

When the absorption spectra of various compounds of the same rare earth element are examined in the absence of any solvent, it is found that they are decidedly different from one another, although a certain "family likeness" may be apparent. It was discovered by Bunsen that the relative intensities of the bands in the spectrum of "didymium" sulphate octahydrate vary according to direction in which light passes through the crystal. This arises from the fact that the crystal is doubly refracting and absorbs the ordinary and extraordinary rays unequally, *i.e.* the crystal is pleochroic. H. Becquerel has studied this phenomenon in great detail for various salts of "didymium," and also for various transparent minerals, such as scheelite, apatite, parisite, xenotime, monazite, etc., which contain "didymium" either in traces or in quantity. The bands differ only in relative intensities, not in actual position.[1]

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[1] Bunsen, *Pogg. Annalen*, 1866, **128**, 100 ; *Phil. Mag.*, 1866, [iv.], **32**, 177 ; H. Becquerel, *Compt. rend.*, 1886, **102**, 106 ; **103**, 198 ; 1887, **104**, 165, 777, 1691 ; *Ann. Chim. Phys.*, 1888, [vi.], **14**, 170, 257 ; G. H. Bailey, *Brit. Assoc. Rep.*, 1887, p. 654 ; 1890, p. 778 ; Dufet, *Bull. Soc. franç. Min.*, 1901, **24**, 373.

The absorption spectra of crystals of rare earth compounds are extremely rich in intense, narrow bands. As the temperature is lowered below the ordinary, the bands become even more narrow and intense.[1] In the immediate vicinity of the absorption bands, the crystals exhibit the phenomenon of anomalous magnetic rotatory dispersion; aqueous solutions of rare earth salts exhibit the same phenomenon.[2]

The absorption spectrum of a solid rare earth compound differs considerably from the spectrum of its aqueous solution.[3] The absorption spectra of the aqueous solutions of salts of a rare earth element differ from one another, but there is a greater "family likeness" between these spectra than between the spectra of the solid salts themselves. In fact, the dilute aqueous solutions exhibit absorption spectra which are often practically identical. One or two bands observed with one salt may not be seen with another salt, and variations (usually not very pronounced) in the relative intensities of corresponding bands may occur. Moreover, the wave-lengths of the "heads" of corresponding bands usually differ only by very small amounts.[4] The differences in the spectra become more pronounced, however, in concentrated solutions. In terms of the ionic theory, the results have been interpreted as indicating that absorption spectra of dilute solutions are spectra of ions, but that the absorption spectra of concentrated solutions are the spectra of both ions and molecules.[5] This simple explanation, however, is inadequate. For instance, several cases are known in which the spectra are strikingly different, instead of being practically identical as the ionic explanation requires them to be,[6] and not infrequently the "heads" of corresponding absorption bands differ appreciably in position.[7] Moreover, the ionic interpretation cannot be reconciled with the repeated observation that Beer's Law holds for moderately dilute solutions, since it leads to the conclusion that the ions of the rare earth elements produce the same absorption spectra as the molecules of their salts.[8]

Solutions of one and the same rare earth compound in different solvents exhibit different absorption spectra. Sometimes the differences are very striking; in other cases, the differences may be slight. For example, the absorption spectrum of neodymium chloride in glycerol bears a considerable resemblance to the spectrum of the same substance in water, the "glycerol

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[1] See J. Becquerel, *Phil. Mag.*, 1908, [vi.], **16**, 153.

[2] J. Becquerel, *loc. cit.*; R. W. Wood, *Phil. Mag.*, 1908, [vi.], **15**, 270; Elias, *Physikal. Zeitsch.*, 1906, **7**, 931.

[3] Bahr and Bunsen, *Annalen*, 1866, **137**, 1; Bunsen, *Pogg. Annalen*, 1866, **128**, 100; *Phil. Mag.*, 1866, [iv.], **32**, 177. See also G. H. Bailey, *loc. cit.*, and *Ber.*, 1887, **20**, 2769, 3325; 1888, **21**, 1520; H. Becquerel, *loc. cit.*; Bettendorf, *Annalen*, 1890, **256**, 159; 1891, **263**, 164.

[4] Bahr and Bunsen, *loc. cit.*; Bunsen, *loc. cit.*; Bailey, *loc. cit.*; Becquerel, *loc. cit.*

[5] See Liveing, *Trans. Camb. Phil. Soc.*, 1900, **18**, 298; Purvis, *Proc. Camb. Phil. Soc.*, 1903, **12**, 202, 206; Aufrecht, *Inaugural Dissertation* (Berlin, 1904); Langlet, *Zeitsch. Physikal. Chem.*, 1906, **56**, 624; Ball, *Proc. Roy. Soc.*, 1912, **A**, **87**, 121.

[6] Muthmann and Stützel, *Ber.*, 1899, **32**, 2653; Muthmann and Heramhof, *Annalen*, 1907, **355**, 165; Waegner, *Ber.*, 1903, **36**, 3055. Remarkable differences are observed, for instance, between the spectra of the aqueous solutions of the chlorides of Nd and Pr and the spectra of the aqueous solutions of the corresponding double potassium carbonates.

[7] *E.g.* aqueous solutions of neodymium chloride and acetate. The bands in the spectrum of the latter substance are less intense, wider, and nearer the red end of the spectrum than those of the former (Jones and Strong, *loc. cit.*).

[8] See Rudorf, *Ahren's Sammlung*, 1904, No. 9; *Jahresber. Elektronik*, 1907, **3**, 423; *Zeitsch. wiss. Photochem.*, 1907, **5**, 24; Sheppard, *Photochemistry* (Longmans & Co., 1914), p. 153.

bands" being, however, rather closer to the red end of the spectrum than the corresponding "water bands." On the other hand, the spectrum of neodymium chloride in ethyl alcohol is strikingly different from the preceding spectra.[1]

The absorption spectrum of a rare earth salt dissolved in a mixture of two solvents shows the absorption bands of the two spectra that may be observed by using the solvents separately.[2] The relative intensities of these two component spectra vary with the composition of the mixed solvent; in some cases several bands are observed which cannot be attributed to either of the component spectra. These facts argue strongly in favour of the view that chemical combination occurs between the dissolved salt and the solvents, as has been pointed out by H. C. Jones.[3]

In connection with the influence of the medium upon the absorption spectra, it is important to note that the spectra of rare earth salt solutions are considerably modified by the addition of a mineral acid, the bands (or some of the bands) usually being rendered weaker and more diffuse.[4] The effect of nitric acid upon the absorption spectrum of aqueous neodymium nitrate, for instance, is very marked, the bands becoming weaker, more diffuse, and wider towards the red end of the spectrum; in this case the colour of the solution is changed in a very striking manner. The intensity of absorption of a rare earth salt is also changed, usually diminished, by the addition of another rare earth salt, whether the added salt produces absorption or not; and the various bands in the spectrum are in general unequally affected.[5]

Absorption spectra are affected by change of temperature. The nature of the change produced has been studied by Hartley, Liveing, H. C. Jones and others.[6] Rise of temperature (above the ordinary atmospheric temperature) has the effect of slightly intensifying the absorption, broadening some bands, and increasing the extent of the general absorption in the ultra-violet and infra-red; the positions of the "heads" of the bands, however, are little, if at all, affected. At temperatures much below the ordinary, the absorption bands become extremely narrow.[7] The preceding statements may require modification at times when foreign substances are present. Thus, in the presence of calcium chloride, some of the bands in the spectrum of aqueous neodymium chloride diminish in intensity with rise of temperature, and the "heads" of the bands undergo a slight displacement (Jones and Strong).

It not infrequently happens that different rare earth salts present in the same solution give rise to absorption bands in almost the same region of the

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[1] H. C. Jones and others, *loc. cit.* See also Ball, *Proc. Roy. Soc.*, 1912, **A**, **87**, 121.

[2] H. C. Jones and others, *loc. cit.*; *cf.* Miss H. Schaeffer, *Physikal. Zeitsch.*, 1906, **7**, 822.

[3] H. C. Jones and others, *loc. cit.*; H. C. Jones, *Amer. Chem. J.*, 1910, **41**, 19; *Phil. Mag.*, 1912, [vi.], **23**, 730; *Zeitsch. Elektrochem.*, 1914, **20**, 552.

[4] Bunsen, *Pogg. Annalen*, 1866, **128**, 100; *Phil. Mag.*, 1866, [iv.], **32**, 177; Lecoq de Boisbaudran and Smith, *Compt. rend.*, 1879, **88**, 1167; Soret, *ibid.*, 1880, **91**, 378; G. H. Bailey, *Brit. Assoc. Rep.*, 1890, p. 773; Liveing, *loc. cit.*; Strong, *Physikal. Zeitsch.*, 1910, **11**, 668; H. C. Jones and Strong, *Amer. Chem. J.*, 1911, **45**, 1.

[5] Brauner, *Trans. Chem. Soc.*, 1883, **43**, 278; Demarçay, *Compt. rend.*, 1898, **126** 1039; Auer von Welsbach, *Sitzungsber. K. Akad. Wiss. Wien*, 1885, **92**, II. 317; 1903, **112**, II. A, 1037; *Anzeiger K. Akad. Wiss. Wien*, 1905, No. 10, p. 122.

[6] Hartley, *Sci. Trans. Roy. Dubl. Soc.*, 1900, II. **7**, 253; Liveing, *loc. cit.*; H. C Jones and others, *loc. cit.*

[7] J. Becquerel, *Phil. Mag.*, 1906, [vi.], **16**, 153.

spectrum, the most striking case being that of the two bands situated at λ4690, one due to praseodymium and the other to neodymium. Another interesting case is that of the two neodymium bands λ4610 and λ4750 and the two samarium bands λ4630 and λ4760. When such bands partly or wholly overlap, they may appear abnormally intense. The "heads" of such bands may also at times appear to vary in position as a composite material is fractionated.

Owing to the manner in which the absorption spectra of the rare earth compounds vary with the conditions of experiment, erroneous conclusions have not infrequently been drawn from researches upon them. Thus, Krüss and Nilson[1] were led to suppose that the rare earth elements the compounds of which give rise to absorption spectra are in reality extremely complex substances, composed of numerous **meta-elements** each characterised by a single band in the absorption spectra of its compounds. This theory of "one band—one element" was supported at the time by Crookes, but adversely criticised by Bailey and by Schottländer.[2] At the present time it cannot be seriously entertained; it will be sufficient to point out that there is no logical reason for restricting the absorption bands to the visible region of the spectrum, or for restricting the theory to the rare earth elements.

Methods of Observing Absorption Spectra.—In order to observe an absorption spectrum, a suitable source of light is focussed upon the slit of the spectroscope and the absorbing medium interposed between the light source and the slit, close up to the latter. For observations in the visual region the solution may be contained in a glass test tube or, better, in a glass cell with a pair of plane, parallel ends; diffused daylight serves as a convenient source of light. In accurate work it is usually necessary to photograph the absorption spectrum. It is then necessary, if observations are to be made for a considerable distance into the ultra-violet region, to replace all glass parts in the line between slit and light source by quartz. A convenient absorption cell is shown in fig. 23; the tube A and B are joined by a broad rubber band C, and the absorbing solution poured in at D; the plates E and F which close the ends of the tubes may be made of quartz if necessary. The changes in the absorption spectrum as the thickness of the absorbing medium is varied can be easily followed by sliding the inner up and down the outer tube.

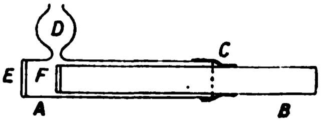

FIG. 23.—Absorption cell.

For photographic purposes the positive crater of a carbon arc serves as a convenient source of light so far as the visible spectrum (and particularly the red end) is concerned; for the violet and ultra-violet regions, however, it is of little use, and should be replaced by a Nernst lamp. Either of these sources of light gives a continuous spectrum. In order to obtain wave-length measurements, the simplest plan is generally to photograph the iron arc spectrum on the same plate, slightly overlapping the absorption spectrum. Some experimenters prefer to utilise a source of light that gives not a con-

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[1] Krüss and Nilson, *Ber.*, 1887, **20**, 1676, 2134, 3067 ; 1888, **21**, 585, 2019 ; Kiesewetter and Krüss, *Ber.*, 1882, **21**, 2310.

[2] Crookes, *Chem. News*, 1886, **54**, 27 ; Bailey, *Brit. Assoc. Rep.*, 1887, p. 654 ; 1890, p. 773 ; *Ber.*, 1887, **20**, 2769, 3325 ; 1888, **21**, 1520 ; Schottländer, *Ber.*, 1892, **25**, 378, 569.

tinuous, but a discontinuous spectrum consisting of a very large number of lines, situated close together and not differing greatly in relative intensities. A suitable light source of this nature is obtained by sparking between carbon electrodes impregnated with the oxides of molybdenum and uranium.[1]

Absorption Spectra of the Rare Earths.—The absorption spectra are briefly described in the following paragraphs.[2]

Praseodymium.—Five absorption bands characterise the visible absorption spectrum of aqueous praseodymium chloride or nitrate, the positions of the "heads" being as follows:—

5970; 5870; **4815**; **4690**; **4435**.

Of these bands, the violet band is broad and very intense, the blue bands are intense, and the yellow bands weak.[3] The absorption curve for aqueous praseodymium chloride, according to Rech, is shown in fig. 24.

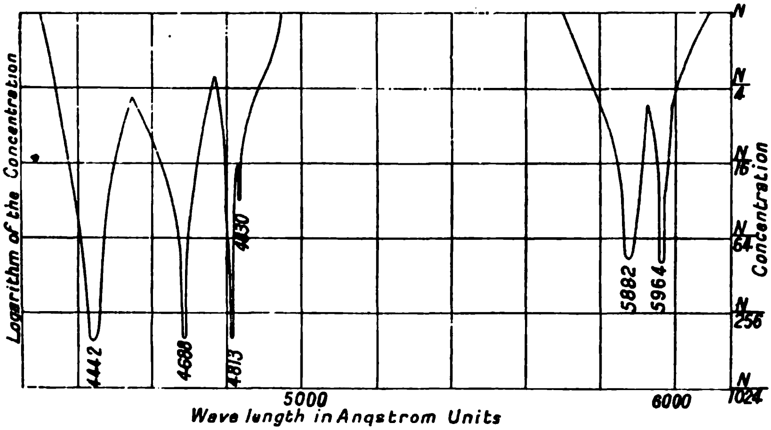

FIG. 24.—Absorption spectrum of aqueous praseodymium chloride (Rech; thickness of absorbing layer = 20 cms.).

Neodymium.—The absorption spectra of aqueous neodymium chloride and nitrate are very beautiful and extremely rich in bands. The maxima that have been observed are as follows:—

7324; 6890; 6790; 6730; 6360; 6280; 6250; 6220; 5870; 5830; **5800**; **5780**; **5750**; **5740**; 5710; 5470; 5310; 5250; **5210**; **5200**; **5120**; **5090**; 4870; 4800; 4750; 4690; 4610; 4327; 4290; **4274**; 4180; 3801; **3556**; **3540**; **3507**; **3465**; 3399; **3288**; 3231; 3144; 3067; 3047; 3030; 3015; 2998; **2983**; 2937; 2913; 2902.

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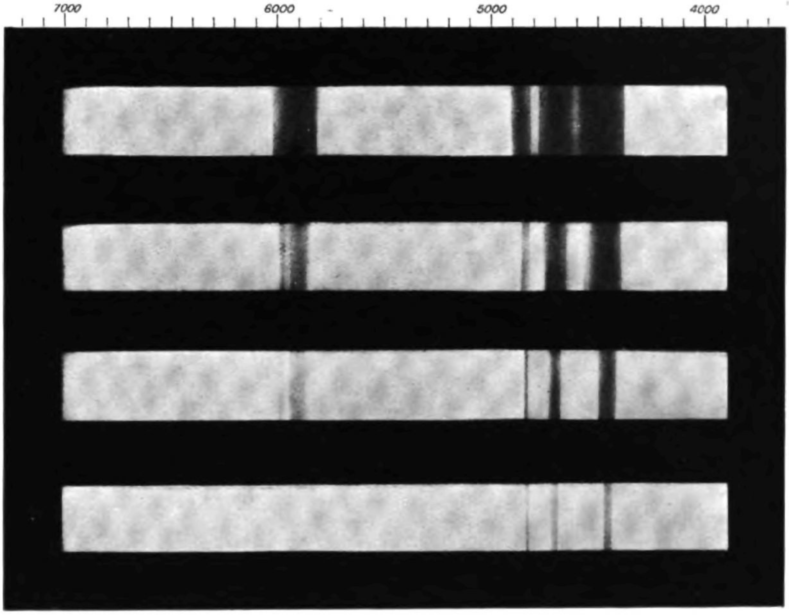
[1] For further information, see, *e.g.*, Kayser, *opus cit.* (p. 282); Jones and others, *loc. cit.*, p. 283); Rech, *Zeitsch. wiss. Photochem.*, 1905, **3**, 411.

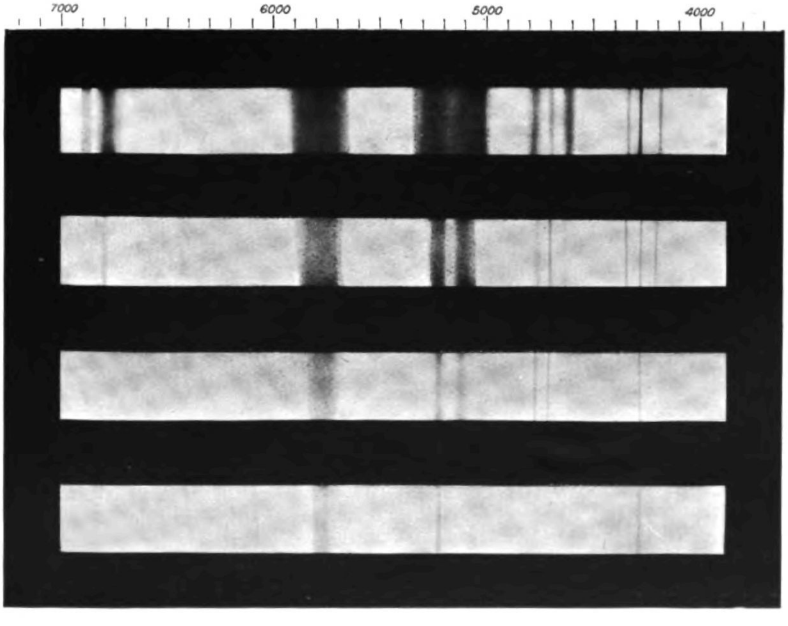
[2] It should be mentioned that measurements of the position of a maximum of absorption by different experimenters usually differ by several Angstrom units, partly owing to experimental error and partly owing to the fact that they have not all worked with the same salt.

[3] Forsling, *Bihang K. Svenska Vet.-Akad. Handl.*, 1893, **18**, I., No. 10; 1898, **23**, I., No. 5; Langlet, *ibid.*, 1901, **26**, II., No. 2; Rech, *Zeitsch. wiss. Photochem.*, 1905, **3**, 411; Aufrecht, *loc. cit.*; Schottländer, *loc. cit.*; H. C. Jones and others, *loc. cit.*; Baxter and Stewart, *J. Amer. Chem. Soc.*, 1915, **37**, 516.



PRASEODYMIUM.

Absorption spectrum of a normal solution of praseodymium nitrate; thickness of absorbing layer = 10·0, 3·3, 1·1, and 0·4 cms. respectively.



NEODYMIUM.

Absorption spectrum of a normal solution of neodymium nitrate; thickness of absorbing layer = 10·0, 3·3, 1·1, and 0·4 cms. respectively.

The two bands λ5800 and λ5470 are seen when the nitrate is examined, but do not appear in the chloride spectrum.[1] The absorption curve of aqueous neodymium chloride is shown in fig. 25, which has been drawn from the data given by Rech.

Samarium.[2]—According to Demarçay, the following are the positions of the centres (not the "heads") of the bands in the absorption spectrum of a twenty per cent. solution of samarium nitrate in strong nitric acid (thickness of solution = 13 mm.):—

5590; 5290; 4980; **4760**; **4630**; 4530; 4430; **4170**; 4070; **4020**; 3900; 3750; 3620.

Several of these bands are complex. The positions of the "heads" of the bands in the spectrum of aqueous samarium chloride are as follows, according to Forsling:—

5600; 5001; 4804–4783; 4761–4727; 4632; 4443–4383; 4177; 4157; 4083; 4077; 4035–4030; 4016–4007; 3942–3932; 3906; 3752–3742; 3738–3732; 3630–3615.

It is an unfortunate circumstance that the strongest of the samarium bands are very closely in the neighbourhood of prominent bands of neodymium and europium, since these are the two elements most difficult to remove from samarium.

Europium.—A neutral solution of the chloride exhibits the following maxima of absorption, the visible bands being narrow and rather faint:—

5913; 5882; 5790; 5337; **5251**; **5234**; **4656**; **4645**; 4000; 3950; 3853; 3836; 3800; 3760; 3746; 3663; **3615**; 3207; 3192; **3178**; **3168**; 2983.

In the nitrate solution a single band λ5913 replaces the two bands λ5913 and λ5882; the band λ5790 is much more intense and narrow than in the chloride spectrum; the unsymmetrical chloride band λ5337 gives place to a symmetrical band λ5354; a single band λ5250 replaces the two chloride bands λ5251 and λ5234; and a single band λ4660 replaces the two chloride bands λ4656 and λ4645.[3]

Gadolinium.—The only absorption bands of gadolinium are in the ultra-violet region:—[4]

3794; 3697; 3596; 3515; **3108**; **3059**; **3056**; **3052**.

Terbium.—The absorption spectrum of terbium lies in the ultra-violet with the exception of a feeble band at λ4880:—[5]

4880; 3787; 3694; 3592; 3519; 3420; 3390; **3266**; **3176**; 3029.

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[1] Forsling, *Bihang K. Svenska Vet.-Akad. Handl.*, 1892, **18**, I., No 4; 1893, **18**, I., No. 10; Demarçay, *Compt. rend.*, 1898, **126**, 1039; Rech, *Zeitsch. wiss. Photochem.*, 1905, **3**, 411; Holmberg, *Zeitsch. anorg. Chem.*, 1907, **53**, 116; Strong, *Physikal. Zeitsch.*, 1910, **11**, 668; Baxter and Chapin, *J. Amer. Chem. Soc.*, 1911, **33**, 1; Baxter and Woodward, *ibid.*, 1911, **33**, 270; H. C. Jones and others, *loc. cit.*; Stahl, *Le Radium*, 1909, **6**, 215; Garnier, *Arch. Sci. phys. nat.*, 1915, [iv.], **40**, 93, 199.

[2] Forsling, *loc. cit.*; Demarçay, *Compt. rend.*, 1900, **130**, 1185; Jones and Strong, *loc. cit.*

[3] Urbain, *J. Chim. phys.*, 1906, **4**, 242; *cf.* Demarçay, *Compt. rend.*, 1900, **130**, 1469.

[4] Urbain, *Compt. rend.*, 1905, **140**, 1233; *J. Chim. phys.*, 1906, **4**, 328; *cf.* Jones and Strong, *loc. cit.*

[5] Urbain, *Compt. rend.*, 1905, **141**, 521; *J. Chim. phys.*, 1906, **4**, 346.

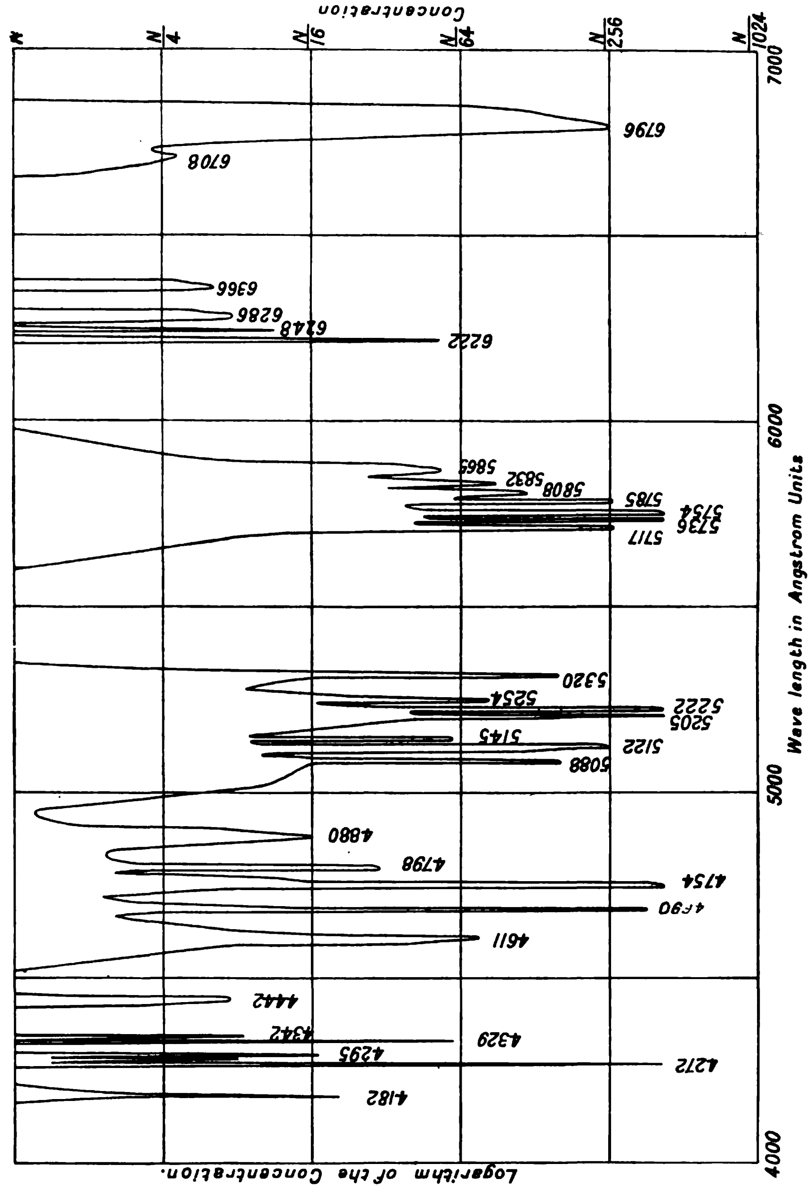
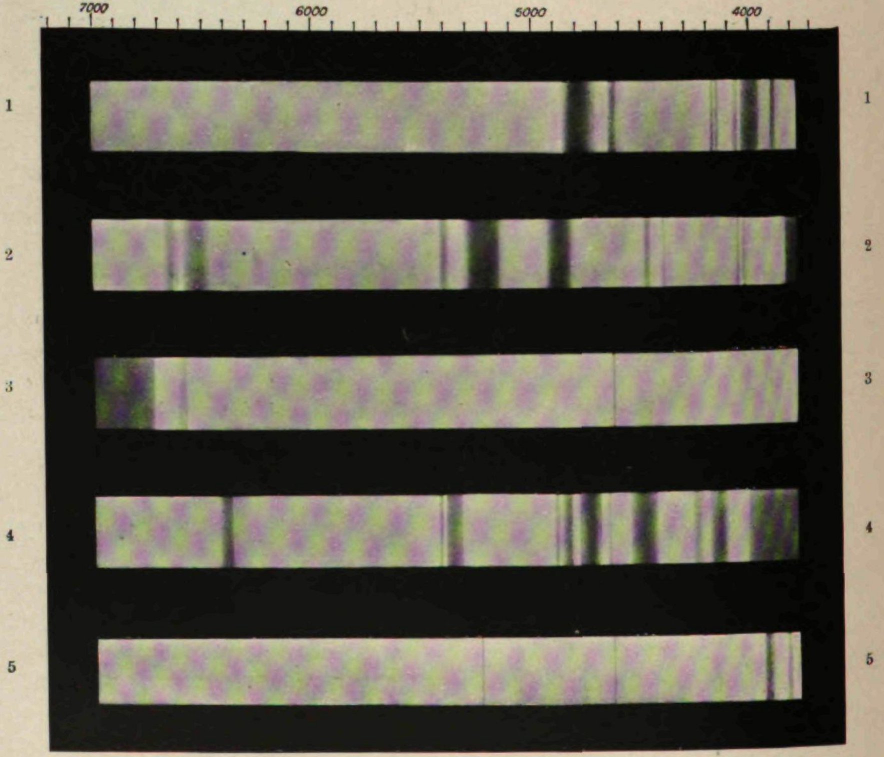


FIG. 25.—Absorption spectrum of aqueous neodymium chloride (Bech; thickness of absorbing layer = 20 cms.).



Absorption spectra of the nitrates of various rare earth elements in dilute aqueous solution.

1. Samarium.
2. Erbium.
3. Thulium.
4. Dysprosium and Holmium.
5. Europium.

there is no experimental work available from which an answer may be deduced, but from work on other substances it has been found that the spectra are different. Theoretically there should be a difference, because the reflecting power of an absorbing medium increases with the refractive index, and owing to the phenomenon of "anomalous dispersion" being exhibited in the neighbourhood of an absorption band, it follows that an absorption band in the reflection spectrum should be relatively less intense on the red side and more intense on the blue side than the corresponding band in the absorption spectrum by transmission.[1]

The reflection spectra of the rare earths were discovered by Bahr and Bunsen, and have been subsequently studied by Hartley, Crookes, Humpidge, H. Becquerel, Dennis and Chamot, Exner, Haitinger, and others.[2] Anderson[3] and Joye[4] have described convenient methods for photographing the spectra.

Examination of the reflection spectra of the oxychlorides of the rare earth metals is of considerable value for following the course of separation of these metals by fractional crystallisation, etc. Only a few milligrams of material are necessary.[5] Instead of the oxychlorides the basic nitrates may be used.

For the rapid examination of the reflection spectrum of a small quantity of a solid, the light of the carbon arc is concentrated upon it. Between the illuminated solid and the slit of the spectroscope a lens is placed to focus the light from the solid on to the slit. It is possible in this manner to observe absorption bands in the spectrum of a substance when its aqueous solution no longer appears to exhibit selective absorption.[6]

For detailed descriptions of reflection spectra the reader is referred to the original memoirs.[7]

Flame Spectra.

When the oxides, borates, or phosphates of some of the rare earth elements are heated to incandescence in a non-luminous flame, such as that of a Bunsen burner, the light emitted is found to give not a continuous spectrum, as would be anticipated, but a sharply discontinuous band spectrum. The

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[1] See R. W. Wood, *Phil. Mag.*, 1902, [vi.], **3**, 620.

[2] Bahr and Bunsen, *Annalen*, 1866, **137**, 1; Hartley, *Trans. Chem. Soc.*, 1882, **41**, 210; *Chem. News*, 1886, **53**, 179; Crookes, *Compt. rend.*, 1886. **102**, 506; Humpidge, *Chem. News*, 1886, **53**, 154; H. Becquerel, *Ann. Chim. Phys.*, 1888, [vi.], **14**, 170, 257; Haitinger, *Monatsh.*, 1891, **12**, 362; Dennis and Chamot, *J. Amer. Chem. Soc.*, 1897, **19**, 799; Exner, *Sitzungsber. K. Akad. Wiss. Wien*, 1899, **108**, IIa, 1252; Urbain, *vide infra*; Waegner, *Ber.*, 1903, **36**, 3055; *Zeitsch. anorg. Chem.*, 1904, **42**, 122; Muthmann and Heramhof, *Annalen*, 1907, **355**, 165; Anderson, *vide infra*; Hofmann and Bugge, *Ber.*, 1908, **41**, 3783; Hofmann and Kirmreuther, *vide infra*; Hofmann and Höschele, *Ber.*, 1914, **47**, 240; Schaum and Wüstenfeld, *Zeitsch. wiss. Photochem.*, 1911, **10**, 226; Joye, *vide infra*.

[3] Anderson, *Astrophys. J.*, 1907, **26**, 73.

[4] Joye, *Arch. Sci. phys. nat.*, 1913, [iv.], **36**, 41.

[5] Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 222. For the rapid preparation of the oxychlorides, see p. 255.

[6] Urbain, *loc. cit.*

[7] See Joye, *Arch. Sci. phys. nat.*, 1913, [iv.], **36**, 41 (Nd_2O_3, $Nd_2O_3.3H_2O$, $2Nd_2O_3.3H_2O$, $Nd_2O_3.H_2O$, $Nd_2(SO_4)_3$, Nd_2S_3, $NdCl_3$, $NdBr_3$, $Nd_2(CO_3)_3$, $Nd_2(C_2O_4)_3.10H_2O$, $Nd(NO_3)_3.6H_2O$): Joye, *ibid.*, 1913, [iv.], **36**, 431 (Pr_2O_3, $Pr_2O_3.3H_2O$, $PrCl_3$, Pr_2S_3, $Pr_2(SO_4)_3$, $Pr(NO_3)_3.6H_2O$, $Pr_2(C_2O_4)_3.10H_2O$); Hofmann and Kirmreuther, *Zeitsch. physikal. Chem.*, 1910, **71**, 312 (Er_2O_3, $Er_2O_3.SO_3$, $Er_2(SO_4)_3$, Er_2S_3, $ErCl_3$); Hofmann and Höschele, *Ber.*, 1914, **47**, 240 (PrOCl, NdOCl, SmOCl, ErOCl).

spectrum of neodymia was discovered by Bunsen[1] in 1864, and that of erbia by Bahr[2] in 1865. Up to the present time it has been found that, under suitable conditions, praseodymia,[3] neodymia,[4] samaria,[5] erbia,[6] and thulia[7] give rise to these emission spectra. No satisfactory explanation of their production has yet been advanced. It has been stated that the spectra are due to thin layers of glowing vapour,[8] but this is almost certainly not the case.[9]

It is not definitely known whether a pure rare earth gives rise to a flame spectrum or not. It is stated that praseodymia gives no such spectrum unless mixed with another oxide, *e.g.* alumina or magnesia, while the flame spectrum of neodymia alone is said to be very hazy. Most observations of these spectra have been made with erbia, and pure erbia has not yet been prepared.

The flame spectrum of a rare earth differs considerably from its cathodic phosphorescence spectrum, but is closely connected with its reflection spectrum. The emission bands in the flame spectrum of erbia, for instance, are in almost exactly the same positions as the absorption bands in the reflection spectrum of the same substance. The reflection spectrum varies with the temperature, and in the cases of erbia and neodymia it has been found by Anderson that the bands in the flame and reflection spectra occupy identical positions when examined at the same temperature. This result is in accordance with Kirchhoff's Law.[10]

The flame spectra of different compounds of the same rare earth element exhibit a marked resemblance to one another, without, however, being identical.[11] Moreover, it follows from what has been already stated that these emission spectra must correspond approximately with the absorption spectra of the compounds of the same rare earth element. This correspondence was noted by Bahr and Bunsen.

The flame spectra of the rare earths are of little or no practical value to the chemist.

REVERSION SPECTRA.

When the spark spectrum of a solution of a salt is examined in the usual way (p. 305), the external metallic electrode and the salt solution are

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[1] Bunsen, *Annalen*, 1864, **131**, 255; Bahr and Bunsen, *ibid.*, 1866, **137**, 1.

[2] Bahr, *Annalen*, 1865, **135**, 376; Bahr and Bunsen, *loc. cit.*

[3] Haitinger, *Monatsh.*, 1891, **12**, 362.

[4] Auer von Welsbach, *Sitzungsber. K. Akad. Wiss. Wien*, 1885, **92**, II. 317; *Monatsh.*, 1885, **6**, 477; Haitinger, *loc. cit.*; Schaum and Wüstenfeld, *Zeitsch. wiss. Photochem.*, 1911, **10**, 226; Anderson, *Astrophys. J.*, 1907, **26**, 73.

[5] Lecoq de Boisbaudran, *Compt. rend.*, 1879, **88**, 322; **89**, 212; Bettendorf, *Annalen*, 1891, **263**, 164.

[6] Bahr, *loc. cit.*; Bahr and Bunsen, *loc. cit.*; Lecoq de Boisbaudran, *Compt. rend.*, 1873, **76**, 1080; *Spectres lumineux* (Paris, 1874); Thalen, *Compt. rend.*, 1880, **91**, 326; Crookes, *ibid.*, 1886, **102**, 506; Hofmann and Bugge, *Ber.*, 1908, **41**, 3783; Hofmann and Kirmreuther, *Zeitsch. physikal. Chem.*, 1910, **71**, 312; Anderson, *loc. cit.*; Schaum and Wüstenfeld, *loc. cit.*

[7] Thalen, *Compt. rend.*, 1880, **91**, 376.

[8] Huggins, *Proc. Roy. Soc.*, 1870, **18**, 546; *Phil. Mag.*, 1870, [iv.], **40**, 302; Reynolds, *ibid.*, 1870, [iv.], **40**, 306.

[9] Anderson, *Astrophys. J.*, 1907, **26**, 73.

[10] Anderson, *loc. cit.*; see also Schaum and Wüstenfeld, *loc. cit.*, and Hofmann and Kirmreuther, *loc. cit.*

[11] Lecoq de Boisbaudran, *Compt. rend.*, 1873, **76**, 1080.

connected to the positive and negative poles respectively of the induction coil. If this arrangement is reversed, so that the solution is positive to the external electrode, the line spectrum of the metal can scarcely be seen, but with solutions of samarium, europium, terbium, and dysprosium salts, if a long spark is used, the liquid surface becomes phosphorescent immediately below the external electrode (see fig. 26). The phosphorescent light, when examined spectroscopically, is found in each case to yield a discontinuous band spectrum. These spectra are known as **reversion spectra** (*spectres de renversement*). They were discovered by Lecoq de Boisbaudran.[1]

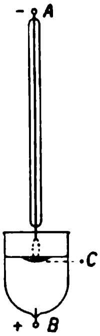

FIG. 26.—Apparatus for production of reversion spectra. C is the phosphorescent zone.

The reversion spectra bear a striking resemblance to the corresponding cathodic phosphorescence spectra. In dilute solution they are practically independent of the acid radicle present. The intensity of a reversion spectrum is approximately proportional to the concentration of the solution, and its sensitiveness is comparable with that of an absorption spectrum.[2]

Samarium chloride or nitrate solution gives a yellow phosphorescence the spectrum of which consists of three bands, the maxima being at λ6440, λ6000, λ5640.[3]

Europium (or Z_ζ) gives rise to a red phosphorescence. A dilute acid solution shows two beautiful bands, (i.) λ6160 to λ6110, maximum at λ6125, and (ii.) λ5970 to λ5920, maximum at λ5890.[4]

Terbium (or Z_β) gives rise to a beautiful green phosphorescence. The spectrum of the chloride solution shows four distinct bands, the maxima being situated at λλ6205, 5858, 5432, and 4870.[5]

Dysprosium (or Z_α) gives rise to a yellow phosphorescence the spectrum of which consists of two bands. The maxima are at λ5730 and λ4765.[6]

CATHODIC PHOSPHORESCENCE SPECTRA.

Historical.—In 1881 Crookes[7] discovered that numerous substances, when exposed to the bombardment of the cathode rays, emit a phosphor-

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[1] Lecoq de Boisbaudran, *Compt. rend.*, 1885, **100**, 1437 ; *Chem. News*, 1885, **52**, 4.

[2] The presence of certain elements, *e.g.* iron and ruthenium, inhibits the production of the reversion spectra (Lecoq de Boisbaudran, *Compt. rend.*, 1886, **103**, 113).

[3] Demarçay, *Compt. rend.*, 1900, **130**, 1185 ; *cf.* Lecoq de Boisbaudran, *ibid.*, 1892, **114**, 575 ; 1893, **116**, 611.

[4] Urbain, *J. Chim. phys.*, 1906, **4**, 247 ; Demarçay, *Compt. rend.*, 1900, **130**, 1469 ; Lecoq de Boisbaudran, *Compt. rend.*, 1892, **114**, 575 ; 1893, **116**, 611, 674.

[5] Lecoq de Boisbaudran, *Compt. rend.*, 1886, **102**, 899 ; Urbain, *J. Chim. phys.*, 1906, **4**, 348.

[6] Lecoq de Boisbaudran, *Compt. rend.*, 1886, **102**, 899 ; Urbain, *ibid.*, 1906, **142**, 785. For further information concerning reversion spectra, see the references to Lecoq de Boisbaudran cited on p. 296, and Urbain, *Ann. Chim. Phys.*, 1909, [viii.], **18**, 222.

[7] The work of Crookes on phosphorescent spectra will be found in the following memoirs or reprints : *Compt. rend.*, 1879, **88**, 283 ; 1881, **92**, 1281 ; 1885, **100**, 1380, 1495 ; 1886, **102**, 506, 646, 1464 ; *Phil. Trans.*, 1883, **174**, pt. III., 891 ; 1885, **176**, pt. II., 691 ; *Proc. Roy. Soc.*, 1881, **32**, 256 ; 1883, **35**, 262 ; 1885, **38**, 414 ; 1886, **40**, 77, 236, 502 ; 1887, **42**, 111 ; *Chem. News*, 1881, **43**, 237 ; 1883, **47**, 261 ; 1884, **49**, 159, 169, 181, 194, 205 ; 1885, **51**, 301 ; 1886, **53**, 75, 133 ; **54**, 13, 29, 38, 40, 54, 63, 76, 155 ; 1889, **60**, 27, 39, 51, 63 ; *Brit. Assoc. Reports*, 1886, p. 558 ; *Trans. Chem. Soc.*, 1888, **53**, 487 ; 1889, **55**, 250.

escent light which, analysed spectroscopically, shows in general a faint continuous spectrum with a more or less decided concentration in the region corresponding with the colour of the emitted light. Less commonly, the spectrum is discontinuous.

In studying these discontinuous spectra, Crookes was particularly interested in a bright citron band at λ5740, and endeavoured to identify the element which gave rise to it. He assumed *a priori* that the brightness of the band λ5740 would increase in proportion as the element responsible for it concentrated in his preparations. In general he decomposed his materials with sulphuric acid, evaporated off the excess of acid, and exposed the anhydrous sulphates to the cathode rays. After many experiments, the element was traced to the yttrium group of the rare earth elements. Accordingly, he prepared specimens of the yttria earths in as pure a state as was possible at that period, examined their sulphates, and identified the sought-for element with *yttrium*. In this, however, he was wrong, for, as will be seen later, the citron band is due to *dysprosium*.

A pair of orange bands, λ5970 and λ6030, also attracted attention, and an endeavour was made to trace the element X which produced them. As the result of many experiments carried out with this end in view, Crookes discovered the remarkable fact that the compounds of X are only sensibly phosphorescent when intimately mixed with certain other substances, of which the compounds of calcium are at least as good as any, and consequently he nearly always introduced calcium sulphate into his materials when studying their phosphorescence spectra. As before, he traced X to the rare earth elements, and on examining specimens of Cleve's rare earth preparations, correctly identified the element X with *samarium*.

Still another band, a red one at λ6090, attracted his attention. Sometimes it was nebulous; at other times it was clear and sharp, and almost as narrow as a spark line. In the phosphorescence spectrum of samarium sulphate it was very feeble; it did not occur in the spectrum of yttrium sulphate; but in the spectra of certain mixtures of these sulphates it stood out brilliantly. Crookes called it the *anomalous line*, and originally supposed that it corresponded to a vibration that could only be set up by the simultaneous presence of samarium and yttrium. Shortly afterwards, however, he abandoned this idea, and attributed the anomalous line to a separate element which provisionally received the designation S_δ. It will be seen subsequently that S_δ is the element *europium*.

Crookes observed that the citron band was accompanied by numerous red, green, blue, and violet bands, a number of which were extremely sharp and narrow. In 1886 he discovered that these bands varied among themselves in relative intensity when yttria was methodically fractionated, and concluded that yttrium must be an extremely complicated substance which can be split up, at least partially, into numerous simpler substances, each characterised by a phosphorescence spectrum of great simplicity, consisting for the most part of a single band. From further experiments, he drew the conclusion that samarium and Marignac's Y_a (gadolinium) are also complex substances. The simpler constituents of these "elements" he called **meta-elements** and gave provisional names, and he put forward a new theory of the nature of the chemical elements in his British Association address in 1886. Owing to the striking and original nature of these views, they created great interest.

The compositions of samarium, yttrium, and gadolinium in terms of their component meta-elements were given by Crookes in 1889 as follows:—

Meta-element.	λ.		Meta-element.	λ.		Meta-element.	λ.	
S_δ	6090	Samarium	G_β	5450	Gadolinium	G_α	4820	Yttrium
G_ϵ	5970		G_ζ	6190		G_β	5450	
G_γ	5640					G_ζ	6190	
G_θ	6390					G_δ	5740	
						G_ϵ	5970	
						G_η	6470	

It will be seen that a meta-element could enter into the composition of more than one "element."

These ideas were all opposed by Lecoq de Boisbaudran,[1] who in 1885 discovered two new rare earth elements, Z_α and Z_β, belonging to the terbia group, by means of their reversion spectra, and was struck by the resemblance between these spectra and the phosphorescence spectra attributed by Crookes to G_δ and G_β respectively. By careful fractionation, the French spectroscopist prepared pure yttria, and found it to be devoid of phosphorescence; the addition of a little Z_α and Z_β, however, produced the "yttrium" spectrum described by Crookes. He further found that whereas the atomic weight of yttrium is about 89, the values for Z_α and Z_β are about 160, and that the spark spectra of these elements show no lines that can be attributed to yttrium. Lecoq de Boisbaudran therefore concluded that pure substances are not phosphorescent, and that yttria acts merely as a diluent, in which Z_α and Z_β are able to exhibit their phosphorescence spectra, in precisely the same way as Crookes had shown lime to act as a diluent towards samarium. He further showed the correctness of this by studying numerous phosphorescent systems made up of compounds of some of the common elements. The views propounded by Lecoq de Boisbaudran were not, however, accepted by Crookes, and the Crookes—de Boisbaudran controversy served but to emphasise the difficulties of rare earth chemistry without either of the protagonists succeeding in establishing his views to the satisfaction of chemists in general. In 1900 Muthmann and Baur[2] were led to believe that Lecoq de Boisbaudran's conclusions were incorrect; in the following year, however, Baur, in association with Marc, arrived at the opposite conclusion.[3]

At the present time the controversy may be regarded as closed. The beautiful researches of Urbain and his collaborators[4] have clearly demonstrated the correctness of Lecoq de Boisbaudran's views, and the fascinating theory of the meta-elements is now seen to be nothing more than a daring

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[1] Lecoq de Boisbaudran's work on phosphorescence spectra will be found in the following papers: *Compt. rend.*, 1885, **101**, 552, 588; 1886, **102**, 153, 1536; **103**, 113, 468, 627, 629, 1064, 1107; 1887, **104**, 330, 478, 554, 824, 1584, 1680; **105**, 45, 206, 258, 261, 301, 304, 343, 347, 784, 1228; 1888, **106**, 452, 1386, 1781; **107**, 311, 468, 490; 1890, **110**, 24, 67.

[2] Muthmann and Baur, *Ber.*, 1900, **33**, 1748.

[3] Baur and Marc, *Ber.*, 1901, **34**, 2460.

[4] Urbain, *Ann. Chim. Phys.*, 1909, [viii.], **18**, 222–376; Bruninghaus, *ibid.*, 1910, [viii.], **20**, 519–546; **21**, 210–283. See also Urbain, *Compt. rend.*, 1906, **142**, 205, 1518; **143**, 229; 1907, **145**, 1335; *J. Chim. phys.*, 1906, **4**, 233; Urbain and Scal, *ibid.*, 1907, **144**, 1363.

but erroneous interpretation of experimental results. By its fall the chemistry of the rare earths lost some of its charm, but it has gained enormously in simplicity.[1]

General Laws.—Experiment shows that *pure* substances are not sensibly phosphorescent when exposed to the cathode rays; the phosphorescence exhibited by a "pure" substance is found to be attributable to the presence of traces of impurities.

The addition of a trace of a second compound B to a pure non-phosphorescent compound A frequently results in the production of an extremely phosphorescent mixture.[2] The manner in which the intensity of phosphorescence varies as the relative amounts of A and B are changed has been examined by Urbain and Bruninghaus for a large number of mixtures, and they have found that as the amount of one compound, say B, is varied from an exceedingly small percentage upwards, the intensity of the phosphorescence (the mode of excitation being the same throughout) quickly increases to a maximum and then steadily diminishes.[3] The percentage of B present in the mixture of maximum phosphorescing power depends upon the natures of both A and B, but is always of the order of 0·5 to 1·0 per cent., and mixtures with 20 per cent. and more of B are often not sensibly phosphorescent.[4]

When B is a rare earth compound, the phosphorescence spectrum is sharply *discontinuous*, often exhibiting a large number of quite narrow bands, and as the percentage of B alters, so also does the colour of the phosphorescent light. Spectroscopic observation shows, however, that the preceding "maximum law" holds good for *each band in the spectrum*. The colour changes are due to the fact that for mixtures of two given substances A and B, the luminous maxima of the bands correspond to different percentages of B; in other words, the bands vary independently. Concerning the maxima of the various bands, the general rule may be stated that the most refrangible bands are at their maxima for smaller percentages of B than is the case with the least refrangible bands. Hence, as the percentage of B changes from zero upwards, the changes observed in the colour of the phosphorescent light occur in the direction from blue to red along the spectrum.

The percentage of B corresponding to the luminous maximum is independent of the intensity of the exciting cathode rays, and also of the temperature, though the latter factor may produce sensible changes in the phosphorescence spectrum.

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[1] In addition to the memoirs already cited, the following also relate to phosphorescence spectra: Marignac, *Œuvres complètes*, 1902, vol. ii. p. 811; Bettendorf, *Annalen*, 1891, **263**, 164; 1892, **270**, 376; Marc, *Ber.*, 1906, **39**, 1392; Wiedemann and Schmidt, *Zeitsch. physikal. Chem.*, 1895, **18**, 529; Goldstein, *Sitzungsber. K. Akad. Wiss. Berlin*, 1900, p. 824; Campbell-Swinton, *Proc. Roy. Soc.*, 1899, **65**, 115; Kowalski and Garnier, *Compt. rend.*, 1907, **144**, 836.

[2] It may be stated here once for all that mere mechanical mixing is not sufficient; substances must be extremely intimately mixed by chemical processes. Thus the rare earth oxide mixtures referred to later are made by precipitating the oxalates together from solution, washing, drying, and igniting the mixture. By treatment with concentrated sulphuric acid, sulphate mixtures are obtained, etc.

[3] This law is called *la loi de l'optimum* by its discoverers.

[4] It is of interest to notice the analogy between this result and that which expresses the manner in which the light-emitting power of a mixture of thoria and ceria varies with the composition; the maximum here corresponds to 0·9 per cent. of ceria, and the light-emitting power diminishes rapidly as the percentage of ceria is decreased or increased from this value.

The preceding observations naturally suggest the question as to whether the phosphorescence spectrum observed in a binary mixture is to be attributed to B, which in the mixture of maximum phosphorescing power does not exceed 1 per cent. of the whole, or to A, or to both. Is, for example, the phosphorescence spectrum of terbia—gadolinia mixtures to be attributed to terbia, to gadolinia, or to both? It is found that mixtures of terbia and either yttria, lime, alumina, or glucina give phosphorescent spectra which, without being identical, exhibit a very strong family resemblance to one another and to the terbia—gadolinia spectrum. Moreover, the five mixtures phosphoresce most brilliantly for quantities of terbia of about 1 per cent. Gadolinia, however, when mixed with any of the other four oxides, yields a mixture which produces no visible phosphorescence. The observed phosphorescence of the system terbia—gadolinia must therefore be attributed to terbium, in just the same way as the absorption spectrum of an aqueous solution of neodymium chloride is attributed to the neodymium chloride.

Accordingly, in a system A—B which exhibits a maximum phosphorescence when the amount of B present is only of the order of 1 per cent., the phosphorescence is a specific property of B. The substance B is called the *phosphorogen* (or active matter) and A the *diluent*.

It has been mentioned that the spectra of terbium in various diluents exhibit a marked similarity, but that they are not identical. This influence of the diluent is a general phenomenon, and was observed by Crookes, particularly for the samarium spectrum. The spectra of a phosphorogen in various diluents exhibit bands in the same regions of the spectrum, but the positions of similar bands are not identical. There is very little difference, however, in passing from one diluent to another if the metallic constituents of the diluents are the same, *e.g.* the spectra of samarium are very similar when the oxide, sulphate, fluoride, and borate of samarium are diluted in the corresponding salts of calcium; but a change in diluent from, say, lime to yttria, produces a small but decided change in the positions of the bands. The nature of the spectrum of a phosphorogen also depends upon the physical state of the diluent, and hence, in the oxide systems to be described later, differs somewhat according as the preparation has been made by heating the oxalates or the sulphates.

It is beyond the scope of this book to enter into a discussion of the various theories of phosphorescence,[1] but it may be observed that phosphorogens are coloured substances, compounds of metals the salts of which are coloured and exhibit absorption spectra in solution. Good diluents, however, are colourless compounds practically devoid of electrical conductivity. These statements apply to systems which are visually phosphorescent; it is possible for a colourless substance to act the rôle of a phosphorogen, gadolinia being a case in point, but its phosphorescence spectrum lies in the ultra-violet region. It is significant that gadolinium exhibits a well-defined ultra-violet absorption spectrum. Apparently, a substance does not act both as a diluent and a phosphorogen, but does act both as an absorber and a phosphorogen in the same region of the spectrum. However, in the case of the rare earths at least, the phosphorescence and absorption bands do not coincide.

In practice, systems more complex than the binary systems hitherto discussed are encountered. Various ternary systems, in which two phosphorogens are diluted in a common diluent, have been studied by Urbain

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[1] On this point see Bruninghaus, *loc. cit.*

and Scal, and it has been found that the observed phosphorescence spectrum of such a system is made up of the spectra of the two phosphorogens, though in each component spectrum the relative intensities of the bands may differ somewhat from those observed in the spectrum of the corresponding binary system. For each spectrum the *loi de l'optimum* holds good, but each phosphorogen appears to diminish the luminosity of the spectrum of the other, and in this action the less intense phosphorescence suffers much more than the other.

The Phosphorescence Spectra of the Rare Earths.—So far as visible phosphorescences are concerned, lanthana, gadolinia, and yttria act as diluents, and praseodymia, neodymia, samaria, europia, terbia, dysprosia, and erbia act as phosphorogens, and rare earth mixtures in which a large excess of diluent is present phosphoresce brightly under the influence of the cathode rays. It is curious to notice that holmia and thulia do not appear to act as phosphorogens, although the salts of holmium and thulium exhibit well-defined absorption spectra.

The form of vacuum tube best suited to the observation of cathodic phosphorescence spectra is indicated in fig. 27. The electrodes A and C are made of aluminium. The substance under examination is placed in the lower part of the apparatus (which is joined to the upper part by a lubricated ground glass joint) with its surface slightly inclined. The upper part of the apparatus is sealed on to a mercury pump by means of a side tube not shown in the diagram. For observing the spectra, a spectroscope of not too great dispersion should be used, and the slit opened fairly widely. In photographing the spectra, an exposure of from twenty minutes to two hours is necessary, and in order to include the ultra-violet region, a special form of tube with a quartz window B should replace the bottom part of the apparatus (see the dotted portion of fig. 27).

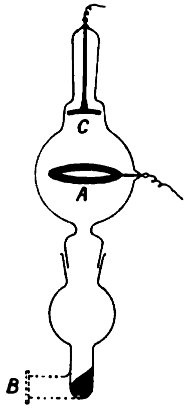

Fig. 27.—Apparatus for producing cathodic phosphorescence spectra.

Binary Systems.[1]—From the practical point of view, systems in which lanthana is the diluent are not of much interest; those with gadolinia or yttria are much more important.

Praseodymium.—When diluted in lime, praseodymia exhibits a red phosphorescence, and so also does the sulphate when diluted in calcium sulphate. The spectra are indicated in figs. 28 and 29.[2]

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[1] To prepare binary rare earth mixtures, precipitate the oxalates together, and calcine in a muffle furnace; to prepare rare earth—lime mixtures, precipitate the mixed carbonates, and ignite to oxides over a good Bunsen burner; to prepare rare earth—alumina or rare earth—glucina mixtures, strongly ignite the precipitated mixed hydroxides; etc. The diluents should be pure. Ordinary "pure" lime gives an orange phosphorescence due to traces of manganese; calcium nitrate should be fractionally crystallised from nitric acid in order to eliminate the manganese (in the tails). Ordinary alumina gives a red phosphorescence due to traces of chromium; the nitrate should be fractionally crystallised from nitric acid to remove the chromium (in the tails); etc.

[2] The relative intensities of the bands in the spectra are represented in the accompanying drawings by plotting the intensities as ordinates against a scale of wave-lengths (unit = 10 angstroms). They represent Urbain's results, and, unless otherwise stated, refer to the spectra when at their luminous maxima (about 1 per cent. of phosphorogen).

Neodymium.—The phosphorescence is not very bright. With the system Nd_2O_3—CaO, the following maxima are observed:—

5045; 4690; 4660; 4610; **4575**; 4515; 4400; **4295**; 4270; **4230**; **4220**; **4190**; **3980**; **3920**.

The system $Nd_2(SO_4)_3$—$CaSO_4$ shows only one broad band, from λ5770 to λ5010.

Samarium.—The phosphorescence produced by samarium is orange-yellow, orange, or orange-red in colour. The spectra observed when the diluents are calcium oxide, sulphate, and fluoride and gadolinium oxide and sulphate are shown in figs. 28–32.

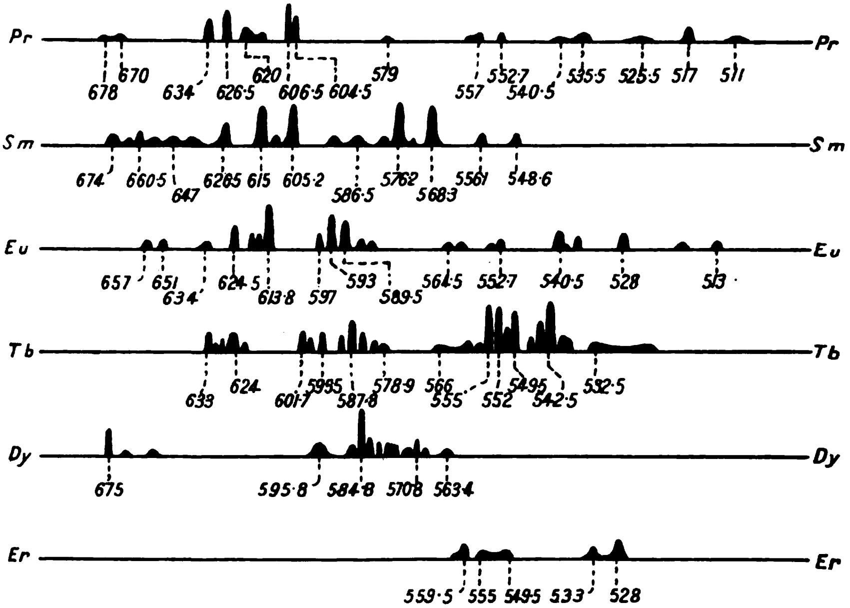

FIG. 28.—Phosphorescence spectra of the rare earths diluted with quicklime.

Europium.—The colour of the europium phosphorescence is generally orange-red or carmine-red. The spectra observed with oxide, sulphate, and fluoride of calcium and oxide and sulphate of gadolinia as diluents are shown in figs. 28–32.

The optimum mixture for Eu_2O_3—Gd_2O_3 contains only 0·42 per cent. of europia. With this system, the variations in the relative intensities of the bands with the dilution is exhibited in a most striking manner.

Europium was shown by Demarçay[1] to be identical with Crookes's Sδ. The identity has been disputed by Crookes,[2] since the position of the "anomalous band" given by Demarçay and later by Urbain does not agree

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[1] Demarçay, *Compt. rend.*, 1901, **132**, 1484.

[2] Crookes, *Chem. News*, 1901, **84**, 2; 1905, **92**, 25; *Proc. Roy. Soc.*, 1905, **A**, **76**, 411.

with the position λ6090 that he found. This discrepancy, however, is due to change of the diluent.[1]

Gadolinium.—The phosphorescence spectrum of gadolinium lies wholly in the ultra-violet region, and for the system Gd_2O_3—CaO comprises the following maxima :—

3166 ; **3159** ; 3155·5 ; **3153** ; 3150·5 ; **3147** ; 3144, **3140·5** ; 3138 ; 3136 ; **3134** ; 3130 ; 3094 ; 3088·5 ; 3085 ; 2828·3 ; 2789·5.

The gadolinium spectrum is of particular interest. In 1899 Crookes[2] observed a new phosphorescence spectrum in the ultra-violet region and

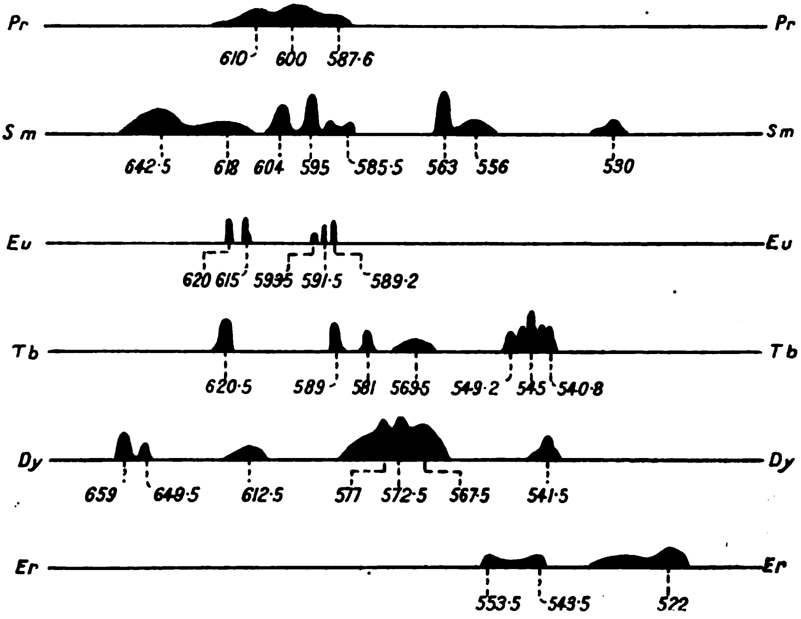

FIG. 29.—Phosphorescence spectra of rare earth sulphates diluted with calcium sulphate.

attributed it to an element **victorium.**[3] According to Crookes, "victoria" was more basic than terbia, but less so than yttria, and the atomic weight of "victorium" was equal to about 117.

In 1905 Crookes[4] concluded that Urbain's purest gadolinia contained "victorium" as an impurity. Urbain has shown, however, that the phosphorescence spectrum which defines "victorium" is really part of the gadolinium spectrum.[5] If "victorium" were present merely as impurity in gadolinium, then dilution of gadolinia with a large excess of lime should cause the "victorium" phosphorescence spectrum to vanish. Actually, it greatly intensifies the spectrum, which is shown very feebly by practically pure gadolinia. The

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[1] On this point see also Lecoq de Boisbaudran, *Compt. rend.*, 1892, **114**, 575 ; 1893, **116**, 611.

[2] Crookes, *Proc. Roy. Soc.*, 1899, **65**, 237 ; *Chem. News*, 1899, **79**, 212 ; **80**, 49.

[3] First called *monium.*

[4] Crookes, *Chem. News*, 1905, **91**, 61 ; 1906, **93**, 143.

[5] Urbain, *J. Chim. phys.*, 1906, **4**, 321 ; *Ann. Chim. Phys.*, 1909, [viii.], **18**, 301.

"victorium" spectrum, in fact, is at its maximum in the system Gd_2O_3—CaO when about 1 per cent. of gadolinia is present. According to Urbain, the method employed by Crookes in isolating "victorium" can only lead to the production of a mixture composed essentially of gadolinium and yttrium, the number of fractions being far too small to lead to the isolation of a new earth. Moreover, there is no corroborative evidence in favour of the view that a new element of atomic weight 117 can be separated anywhere between samarium and dysprosium. Most convincing of all, a mixture of 226 parts of gadolinia and 58 parts of yttria corresponds to an "atomic weight" of 118 and possesses all the properties associated by Crookes with oxide of "victorium."[1] The "victorium" spectrum observed by Crookes is, then, the spectrum of gadolinium in the system $Gd_2(SO_4)_3$—$Y_2(SO_4)_3$.

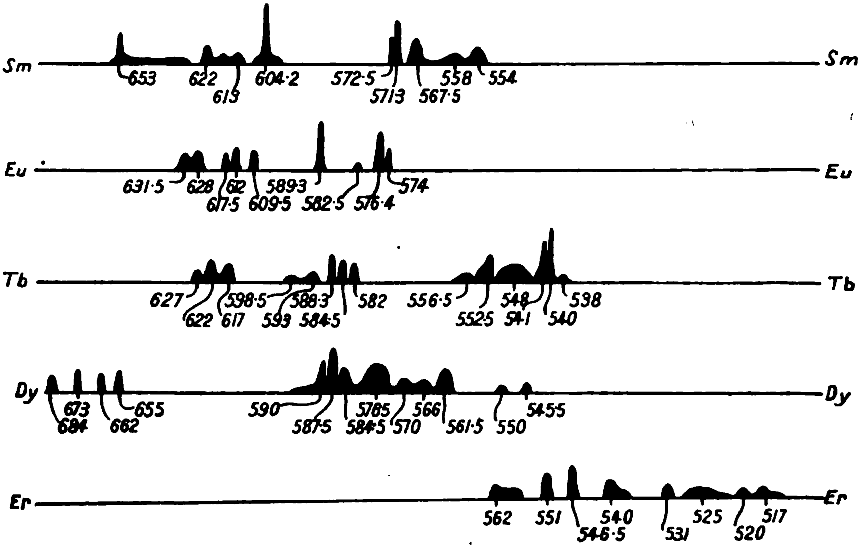

FIG. 30.—Phosphorescence spectra of the rare earth fluorides diluted with calcium fluoride.

The spectrum of gadolinium is more sensitive in calcium sulphate than in calcium oxide.

Terbium.—The phosphorescence of a system containing terbium is blue, bluish-green, or green, according to the amount of terbium present. The spectra of terbium in calcium oxide, sulphate, and fluoride and in gadolinium oxide and sulphate are shown in figs. 28–32.

The spectrum of terbium extends a considerable distance into the ultra-violet. In addition to the bands shown in the diagram, the system Tb_2O_3—CaO shows the following:—

5030; 4945; 4895; 4855; 4825; 4785–4730; 4670; 4640; 4620–4570; 4472; 4455; 4440; 4410; 4395; 4370; 4350; 4340; 4300; 4280; 4245; 4220; 4210; 4200; 4190; 4180; 4160; 4145; 4140; 4130; 4120; 3915; 3900; 3880; 3865–3840; 3820; 3805; 3795–3780; 3770; 3750; 3735; 3720.

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[1] Its pale brown colour (due to terbium) excepted.

The system $Tb_2(SO_4)_3$—$Gd_2(SO_4)_3$ shows the following additional bands :—

4995-4975; **4900-4830**; 4730; 4580; **4420**; 4370; **4355**; 4300; **4195-4065**; 3955; 3935; 3850; 3810; **3765**.

The system $Tb_2(SO_4)_3$—$CaSO_4$ shows the following bands :—

4990-4840; **4750-4675**; **4590-4510**; **4420**; **4390**; **4355**; 4320; **4255**; **4190-4080**; **3865-3765**; 3735-3685.

The system TbF_3—CaF_2 shows the following bands :—

5020-4890; 4890-4825; 4705; 4650-4550; **4435-4405**; 4390; **4380-4350**; 4310; 4270; 4245; **4220-4200**; **4190-4170**; **4135**; 3865; **3825**; 3800.

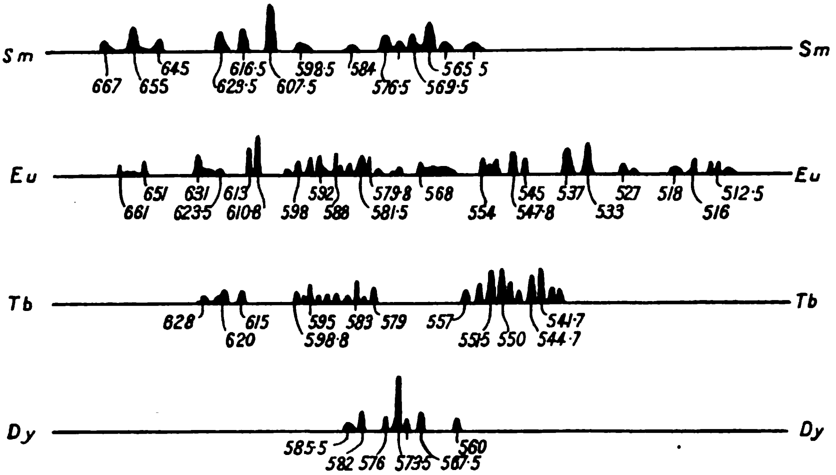

FIG. 31.—Phosphorescence spectra of the rare earths diluted with gadolinia (oxides prepared from oxalates).

The spectrum of terbium is of considerable interest. In 1905 Crookes[1] announced the discovery of two new rare earth elements, **incognitum** and **ionium**,[2] which he characterised by their ultra-violet phosphorescence spectra. The maxima were λλ3760, 3819, 3852 for "incognitum" and λλ4354, 4374, 4423 for "ionium." Reference to the figures given above will show that the "incognitum" and "ionium" spectra form part of the terbium spectrum in the system $Tb_2(SO_4)_3$—$Gd_2(SO_4)_3$. The spectra assigned by Crookes to the "meta-elements" G_ζ, G_β, and G_α also form parts of this same spectrum.

The independent variations in the intensities of the different bands in the terbium spectrum with the dilution are exhibited in a most striking manner.

Dysprosium.—The phosphorescence due to this element is pure yellow or greenish-yellow in colour. The spectra observed in calcium oxide, sulphate, and fluoride and in gadolinium oxide and sulphate as diluents are shown in figs. 28–32.

Dysprosium is the element responsible for Crookes's citron band. The

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[1] Crookes, *Chem. News*, 1905, 92, 273.

[2] Not to be confused with the radioactive element of that name.

correspondence of the band at λ5848 in the system Dy_2O_3—CaO with the citron band λ5740 has, however, been denied by Crookes.[1] The difference in wave-length is due to the fact that in his experiments the diluent was not lime but yttrium sulphate. It will be seen from the diagram (fig. 32) that when the diluent is gadolinium sulphate, the dysprosium spectrum reduces to an intense band at λ5740. Moreover, it is found that the addition of a trace of dysprosia to a sample of yttria so pure as scarcely to show the citron band causes that band to stand out with great brilliance. The spectrum of dysprosium in yttria as diluent comprises the following bands (yellow phosphorescence):—

5875; 5850; **5830**; 5790; **5757**; **5740**; **5730**; **5705**; 5670; 5640; 5587; 5540; **5495**; 5470; 5375; 5360.

Erbium.—The phosphorescences due to erbium are either green, greenish-blue, or blue. The spectra observed with calcium oxide, sulphate, and fluoride as diluents are shown in figs. 28, 29, and 30.[2]

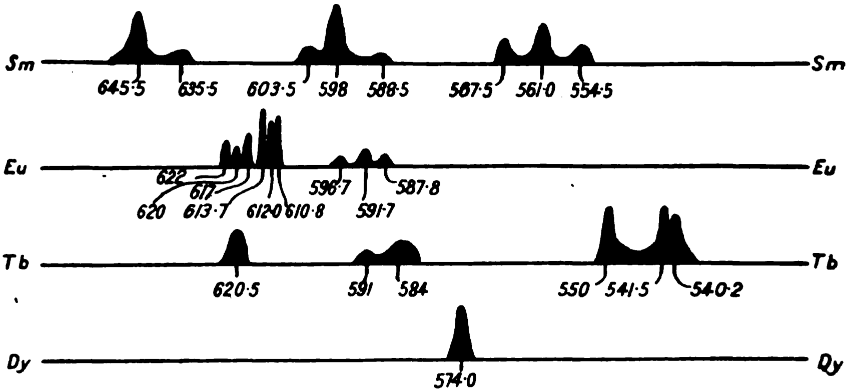

FIG. 32.—Phosphorescence spectra of rare earth sulphates diluted with gadolinium sulphate.

The following bands are exhibited by erbia diluted in yttria:—

6610; **6540**; 5730; 5680; **5642**; **5615**; 5568; **5535**; 5510; 5500; **5490**; 5475; 5460; **5390**; 5340; 5325; 5290; 5270; **5263**; 5255; 5235; **5225**; 5210; **5200**.

TERNARY SYSTEMS.—In ternary systems composed of two phosphorogens and one diluent the order of decreasing sensitiveness of the four most active phosphorogens is dysprosium, terbium, europium, and samarium, except in oxide systems. In the latter case, the order of decreasing sensitiveness is terbium, europium, dysprosium, samarium, praseodymium, and neodymium. As has been already mentioned, when two phosphorogens are simultaneously present the most sensitive spectrum is slightly, and the other considerably enfeebled.

The preceding considerations indicate that when the rare earths are

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[1] Crookes, *Chem. News*, 1906, 94, 79.

[2] The erbia used contained 30 per cent. of yttria, and the Er_2O_3—CaO system contained 1·5 per cent. of the erbia—yttria mixture.

present to a minute extent in a mineral and the latter is examined by the method of Crookes (p. 295) for its phosphorescence spectrum, the bands most readily observed will be the citron band of dysprosium, the orange bands of samarium, the green bands of terbium, and the "anomalous band" of europium. That the last named often fails to make its appearance is due to the extreme rarity of europium, which is only one-fiftieth as plentiful as dysprosium.

Utility of Phosphorescence Spectra in Analysis.—For analytical purposes it is best to dilute a small portion of the rare earth mixture to be examined with pure lime so that the mixture contains 1 per cent. of rare earths. A pure rare earth that acts only as a diluent then shows practically no phosphorescence, while a pure rare earth phosphorogen phosphoresces with its maximum power; with a rare earth mixture, on the other hand, each phosphorogen gives rise to its own phosphorescence spectrum, but not at its maximum brilliancy. The phosphorogens present may be recognised by the positions of their bands and reference to fig. 28. According to Urbain, the observations may be made with the same degree of certainty as may observations of arc or spark spectra, with the advantage that, unlike these latter spectra, "parasite" rays (*e.g.* air lines and lines of gold or platinum in the spark and carbon bands in the arc) are absent.

LINE SPECTRA.

Arc and Spark Spectra.—The line spectra of the elements as usually observed may be divided into *arc* and *spark* spectra according to the nature of the experimental procedure followed in producing them.

The *arc* spectra of the rare earth elements are most simply produced by introducing small quantities of their oxides into the positive crater of a carbon arc light and focussing the light upon the slit of the spectroscope. Since the arc spectra are very rich in lines, the most important of which lie in the ultra-violet region, the spectra must be produced by means of an instrument of high dispersion, the optical parts must be made of quartz, and the spectra must be photographed. Lines and bands due to the carbon arc itself are eliminated by taking, on the same plate, a comparison photograph of the spectrum of the arc; the wave-lengths of the lines are found by taking another comparison photograph of a known spectrum, usually the arc spectrum of iron.

The *spark* spectra of the rare earth elements are most conveniently obtained by the following method of illumination: electric sparks from an induction coil or transformer are passed between a platinum, gold, or graphite electrode and a solution of the chloride or nitrate of a rare earth metal, the solution being made negative to the other electrode. Here, again, the spectra should be photographed, since the most important lines lie in the ultra-violet region.

Numerous convenient forms of apparatus have been described, and one is shown in fig. 33.[1] A piece of glass tubing about six inches long and with a capillary bore is bent into a U-tube, as shown, and a small funnel of about 2 c.c. capacity blown at each end. A gold wire is passed through the capillary tube and made to project a little above the rim of the lower funnel; over its

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[1] For others, see Baly, *Spectroscopy* (Longmans, 2nd ed., 1912); Crookes, *Proc. Roy. Soc.*, 1903, **A**, **72**, 295; *Chem. News*, 1903, **88**, 202.

projecting end a short piece of thin-walled capillary tubing is slipped so that the end of the wire is level with the top of the tubing. The salt solution ascends the capillary and keeps the end of the gold wire well wetted. Another gold wire serves as the external, positive electrode.

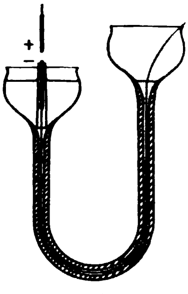

FIG. 33.—Apparatus for production of spark spectra.

In examining the spark spectrum of a rare earth element it is usual to make use of the condensed spark, by inserting an electrical condenser in parallel with the sparking apparatus. Further, in order to eliminate spectrum lines due to air, a self-induction coil is generally introduced into the secondary circuit. A powerful induction coil or transformer is necessary, in order to obtain a heavy spark discharge, for the spark spectra of the rare earth elements are not equally sensitive, and when dealing with mixtures a feeble spark only suffices to bring out lines of the most sensitive spectrum. It is a rather fortunate circumstance that the most sensitive spark spectra are those of the rare earth elements that do not give rise to absorption spectra. The sensitiveness of the yttrium spectrum, for instance, is very great.

When the spark spectrum of an aqueous solution of a salt is examined, it is found that as the solution is gradually diluted the lines weaken and die out at different rates. Given the same conditions, however, it was found by Hartley [1] that the same lines always disappear at the same dilution. Hartley's work has been continued by de Gramont [2] and by Pollok and Leonard,[3] who have given the name of *ultimate* or *residual lines* to those few lines that persist the longest when the solution is diluted. It will be obvious that when the relative degrees of persistency of the various lines in the spark spectrum of an element have been determined, the observations may be advantageously employed for purposes of quantitative analysis. The results are conveniently represented in the following manner, due to Hartley: lines seen in a 0·001 per cent. solution of the metal are denoted by ω, those seen in a 0·01 per cent. but not in a 0·001 per cent. solution by ψ, those seen in a 0·1 per cent. but not in a 0·01 per cent. solution by χ, those seen in a 1·0 per cent. but not in a 0·1 per cent. solution by ϕ, those only seen in solutions more concentrated than 1·0 per cent. by σ, and those seen in the metallic spark but not given by an aqueous salt solution by τ.

In the case of the rare earth elements, the necessary measurements have only yet been effected for cerium, lanthanum, and yttrium.[4]

With regard to the ultimate lines in the spectrum of an element it is important to note that they are not necessarily the lines towards which a photographic plate is most sensitive (*i.e.* the most intense lines). The data for cerium in the accompanying table of wave-lengths will serve to illustrate this point. In a number of cases, according to de Gramont, the ultimate lines of an element are independent of the method by which the

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[1] Hartley, *Phil. Trans.*, 1884, **175**, 325.

[2] A. de Gramont, *Compt. rend.*, 1907, **144**, 1101; **145**, 231; 1908, **146**, 1260; **147**, 239, 307; 1909, **149**, 263; 1910, **150**, 1235; **151**, 308; 1914, **159**, 5; *Ann. Chim. Phys.*, 1909, [viii.], **17**, 437.

[3] Pollok, *Sci. Proc. Roy. Dubl. Soc.*, 1907, **11**, 184, 331; Pollok and Leonard, *ibid.*, 1907–8, **11**, 217, 229, 257; Leonard, *ibid.*, 1908, **11**, 270.

[4] Pollok and Leonard, *loc. cit.* The condensed spark was used and the apparatus pictured in fig. 33 utilised.

spectrum is produced (flame, spark, arc, etc.). When, as often happens,[1] this is not the case, it is nevertheless found that the ultimate lines are always lines of great persistency in the condensed spark spectrum.

A number of regularities in the line spectra of some of the rare earth elements has been observed, but no definite series of lines have yet been detected.[2]

The accompanying table gives the wave-lengths of the most intense, and, where known, the most persistent lines in the arc and spark spectra of the rare earth elements.

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[1] Pollok, *Sci. Proc. Roy. Dubl. Soc.*, 1912, **13**, 202, 253.

[2] See Hicks, *Phil. Trans.*, 1912, **A**, **212**, 33; 1913, **A**, 213, 323 (Sc, Y, La, Gd, Yb); Popov, *Ann. Physik*, 1914, [iv.], **45**, 147 (Y); Paulson, *ibid.*, 1914, [iv.], **45**, 419 (Sc, Y), 1203 (La); *Physikal. Zeitsch.*, 1914, **15**, 892 (Y, Sc, Lu); 1915, **16**, 7 (Gd), 352 (Tm).

CHIEF ARC AND SPARK LINES IN THE SPECTRA OF THE RARE EARTH ELEMENTS.*

Spark.	Arc.	Spark.	Arc.	Spark.	Arc.
			2949·5	4150·09	4382·32
CELTIUM.[1]					
			3080·7 [2]	4165·75 [3]	4386·95
	2459·4		3118·6 [2]	*4181·25* [3]	4460·40
	2469·3		3171·4	4186·71	4479·52
	2481·6		3197·9 [2]	4296·88	4487·06
	2536·9		3326·0	4391·81	4527·51
	2677·7		3391·5	4460·38	4528·64
	2685·2 [2]		3665·6	*4527·52* [3]	4539·90
	2729·1			4562·52	4562·52
	2737·9			4572·46	4572·45
		CERIUM.			
	2765·8			4594·12	4594·11
	2834·3	*2603·72* [3]	3952·77	4628·33	4628·33
	2837·3	*3056·66* [3]	4119·99	*5079·5* [3]	5353·72
	2845·2	3801·71	4150·11	*5511·2* [3]	5512·27
	2870·2	*3940·49* [3]	4186·78		6272·28
	2885·1	4012·58	4222·78		6371·36
	2903·9	4133·98	4296·88		
	2931·7	4137·78	4337·96		

[1] Only the range λ2450 to λ3700 has been examined.

[2] The most intense arc lines of celtium.

[3] Degree of persistency equal to χ.

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* With the exception of the lines of *celtium*, the lines given in these tables in ordinary and in clarendon types represent the "hauptlinien" or most *intense* lines, and are taken from Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Vienna, 1911). Lines given in italics are among the most *persistent* but not among the most intense lines. Where they are known, the relative persistences of the spark lines are indicated in Hartley's notation (p. 306). Lines of intensity 50 or over on Exner and Haschek's scale of intensities are given in heavy type.

The wave-lengths given by Exner and Haschek are correct to within one or two units in the second decimal place. Bearing this in mind it is easy to pick out the "hauptlinien" of a rare earth element that are common to the arc and spark spectra.

SPARK SPECTRA.—The following is not a complete bibliography, but includes practically all the modern references to the spark spectra of the rare earths :—

Cerium.—Brauner, *Monatsh.*, 1882, **3**, 1; Lohse, *Publ. Astrophys. Observ. Potsdam*, 1902, **12**, 109; Pollok and Leonard, *Sci. Proc. Roy. Dubl. Soc.*, 1908, **11**, 257; Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1899, **108**, IIa, 1071, and *opus cit.*

CHIEF ARC AND SPARK LINES, ETC.—*continued.*

Spark.	Arc.	Spark.	Arc.	Spark.	Arc.
DYSPROSIUM.			3729·69	4129·90[2]	3972·16
			3830·69	4205·20[2]	4129·90
3454·50	3524·14		3896·40	4435·74	4205·20
3524·20	3524·18		3902·95	4522·75	4435·75
3531·88[1]	3531·87		3906·47	4594·28[3]	4522·76
3550·35[1]	3536·20		3932·48	6645·41	4594·27
3600·49	3538·66		3938·79		4627·47
3645·55	3538·70		3973·26		4662·10
3676·71	3550·37		3973·78		6645·44
3694·99	3944·83		3974·89		
3698·30	3968·56		4008·12		
3806·44	4000·61		4020·69		
3898·70	4000·69		4059·98	GADOLINIUM.	
3944·82[1]	4046·16		4087·80	2628·22	3082·15
3978·72[1]	4078·14		4143·11	2904·84	3100·66
4000·64	4103·50		4151·29	2955·62	3422·62
4078·15	4168·15		4419·78	3350·66	3545·94
	4187·00		4563·45	3362·41	3549·52
	4211·89		4631·10	3422·65	3585·12
	4211·89		4675·77	3545·95[4]	3646·36
	4221·30		4759·83	3549·51[4]	3671·39
	4589·53		5827·01	3565·10	3719·63
	4957·59		6221·22	3646·32	3743·68
				3664·76	3768·60
ERBIUM.				3712·89	3796·62
		EUROPIUM.		3719·62	3814·18
3372·91	3312·60			3743·60	3852·65
3499·29	3372·92	3725·08	3688·57	3768·54	3916·70
3692·80	3385·23	3819·81[2]	3725·10	3782·51	4037·49
3906·51	3499·28	3907·30	3819·80	3796·58	4050·05
4419·79	3616·75	3930·65[2]	3907·28	4130·55	4063·62
4675·80	3692·85	3972·16[2]	3930·66	4184·48	4071·51

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[1] Demarçay's element Δ. The other lines ascribed to Δ by the same authority are λλ4212·6, 4195·5, 4187·3, and 3595·0; they are presumably very persistent dysprosium lines.

[2] Demarçay's element Σ.

[3] Lecoq de Boisbaudran's element Z_ϵ. The other lines ascribed to Z_ϵ by the same authority are λλ4627·39 and 4662·08; they are presumably very persistent europium lines.

[4] An *ultimate* line, according to Demarçay.

Dysprosium.—Lecoq de Boisbaudran, *Compt. rend.*, 1886, **102**, 153, 1003, 1005; Demarçay, *ibid.*, 1900, **131**, 387; Urbain, *ibid.*, 1908, **146**, 922; Exner and Haschek, *opus cit.*

Erbium.—Thalen, *Compt. rend.*, 1880, **91**, 326; *Oefvers. K. Vet.-Akad. Förhandl.*, 1881, **6**, 13; Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1899, **108**, II*a*, 1123, and *opus cit.*

Europium.—Demarçay, *Compt. rend.*, 1896, **122**, 728; 1900, **130**, 1019, 1469; 1901, **132**, 1484; Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1902, **111**, II*a*, 42, and *opus cit.*; Crookes, *Proc. Roy. Soc.*, 1905, **74**, 550.

Gadolinium.—Lecoq de Boisbaudran, *Compt. rend.*, 1886, **102**, 902; 1889, **108**, 165; 1890, **111**, 472; Demarçay, *ibid.*, 1896, **122**, 728; 1900, **131**, 343, 995; Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1900, **109**, II*a*, 103; 1901, **110**, II*a*, 557, and *opus cit.*

Holmium.—Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1901, **110**, II*a*, 557; 1910, **119**, II*a*, 771, and *opus cit.*

Lanthanum.—Brauner, *Monatsh.*, 1882, **3**, 1; Bettendorf, *Annalen*, 1890, **256**, 159; Exner and Haschek, *opus cit.*, and *Sitzungsber. K. Akad. Wiss. Wien*, 1899, **108**, II*a*,

CHIEF ARC AND SPARK LINES, ETC.—*continued.*

Spark.	Arc.
4251·94	4073·99
4342·40	4085·73
4406·80	4098·80
4436·43	4130·59
4540·23	4184·48
	4251·90
	4262·24
	4325·83
	4327·29
	4342·35
	6114·26
Holmium.	
2936·88	3399·12
3181·60	3425·49
3399·11	3428·27
3415·01	3456·15
3416·60	3474·40
3425·47	3484·98
3428·21	3515·73
3456·15	3598·92
3484·99	3748·32
3494·90	3757·41
3515·74	3889·10
3556·95	3891·17
3598·92	4045·58
3748·35	4254·59
3757·40	
3796·91	
3810·91	
3891·18	
Lanthanum.	
2297·90 [1]	3949·27
2379·49 [2]	3988·69
2476·80 [1]	4238·55
2610·46 [1]	4333·98
2808·46 [1]	6250·14
3171·79 [2]	6262·52
3517·26	6394·46
3759·33	
3791·02	
3794·99	
3871·89	
3949·22 [2]	
3988·66 [1]	
4031·86	
4043·18	
4086·90	
4123·39	
4287·09	
4333·97 [3]	
4522·54 [1]	
4901·10 [1]	
4921·13 [1]	
5455·34 [1]	
5588·54 [1]	
Lutecium (*cassiopēium*).	
2603·41	2615·50
2615·52	2911·53
2772·70	3077·75
2895·00	3198·27
2911·59	3254·45
2963·44	3281·89
3058·08	3312·30
3077·75	3359·74
3254·45	3376·69
3397·18	3397·21
3472·62	3472·65
3507·56	3507·57
3554·58	3508·55
4184·41	3554·58
	3568·00
	3624·10
	3636·41
	3876·80
	4124·87
	4184·40
	4518·74
	5476·88
	5983·92
	5984·32
	6222·10
	6463·40
Neodymium.	
4012·42	3863·52
4031·93	3951·32
4061·26	4061·27
4156·30	4156·30
4177·50	4247·54
4303·77	4282·67

[1] Degree of persistency equal to χ.
[2] Degree of persistency equal to ψ.
[3] Cleve's "element" Diβ.

1071; Eder and Valenta, *ibid.*, 1909, **118**, II*a*, 511; Lohse, *Publ. Astrophys. Observ. Potsdam*, 1902, **12**, 109; Pollok and Leonard, *Sci. Proc. Roy. Dubl. Soc.*, 1908, **11**, 257.

Lutecium.—Urbain, *Compt. rend.*, 1907, **145**, 759; 1908, **164**, 406; Auer von Welsbach, *Sitzungsber. K. Akad. Wiss. Wien*, 1907, **116**, II*b*, 1425; 1909, **118**, II*b*, 507; Exner and Haschek, *ibid.*, 1899, **108**, II*a*, 1123, and *opus cit.*; Crookes, *vide infra*.

Neodymium.—Auer von Welsbach, *Monatsh.*, 1885, **6**, 477; *Sitzungsber. K. Akad. Wiss. Wien*, 1885, **92**, II. 317; 1903, **112**, II*a*, 1037; Exner and Haschek, *ibid.*, 1899, **108**, II*a*, 1071, and *opus cit.*

Praseodymium.—Auer von Welsbach, *loc. cit.*; Exner and Haschek, *loc. cit.*

Samarium.—Bettendorf, *Annalen*, 1891, **263**, 164; Demarçay, *Compt. rend.*, 1900, **131**, 995; Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1900, **109**, II*a*, 103; 1901, **110**, II*a*, 557, and *opus cit.*

Terbium.—Demarçay, *Compt. rend.*, 1900, **131**, 387; Urbain, *ibid.*, 1906, **142**, 957; *J. Chim. phys.*, 1906, **4**, 349; Exner and Haschek, *opus cit.*

Thulium.—Thalen, *Compt. rend.*, 1880, **91**, 376; Exner and Haschek, *opus cit.*, and *Sitzungsber. K. Akad. Wiss. Wien*, 1901, **110**, II*a*, 964; 1910, **119**, II*a*, 771; Auer von Welsbach, *ibid.*, 1911, **119**, II*a*, 193; *Monatsh.*, 1911, **32**, 373; *Zeitsch. anorg. Chem.*, 1911, **71**, 439; Crookes, *Proc. Roy. Soc.*, 1906, **A**, **78**, 154; Urbain, *Compt. rend.*, 1907, **145**, 759.

Yttrium.—Hartley, *Trans. Chem. Soc.*, 1882, **41**, 210; Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1899, **108**, II*a*, 1123, and *opus cit.*; Pollok and Leonard, *Sci. Proc. Roy. Dubl. Soc.*, 1908, **11**, 257.

CHIEF ARC AND SPARK LINES, ETC.—*continued.*

Spark.	Arc.	Spark.	Arc.	Spark.	Arc.
4446·54	4303·78	4409·01	4429·38		4544·12
4451·68	4325·87	4429·41	4496·60		4566·38
4463·12	4375·11	4496·63	4510·32		4577·88
	4385·81	4510·33			4642·41
	4400·96				4674·79
	4446·51	SAMARIUM.			
	4451·71	4319·12	3739·30	TERBIUM.[1]	
	4463·09	4391·05	4152·38	2659·01	3324·53
	4920·84	4424·52	4203·18	2891·40	3509·34
	5293·35	4434·50	4225·48	2909·35	3531·86
	5319·98	4467·49	4229·83	2913·39	3561·90
	5594·58		4236·88	3509·32[2]	3568·69
	5620·75		4256·54	3561·90[2]	3600·60
	6310·69		4319·12	3676·52[2]	3628·35
	6341·69		4329·21	3703·00[2]	3650·60
	6385·32		4334·32	3747·48	3659·02
			4347·95	3848·90	3704·10
PRASEODYMIUM.			4391·03	3874·32	3711·91
3877·38	4008·90		4420·72	3925·60	3848·90
4100·89	4100·91		4421·32	3939·71	3874·33
4118·63	4118·70		4424·55	3977·00	3899·34
4143·28	4143·33		4434·07	3892·04	3925·60
4179·60	4179·60		4434·52	4144·60	3939·75
4189·70	4189·70		4452·92	4278·67	3977·01
4206·81	4206·88		4454·84		3982·07
4223·20	4223·18		4458·70		4005·70
4225·54	4225·50		4467·50		4012·99
4241·28	4241·20		4519·80		4278·70
4305·99	4305·99		4524·08		4752·69

[1] According to Eberhard, the most persistent lines in the arc spectrum of terbium are λλ3523·82, 3676·52, 3703·00, 3704·10, 4005·70, 4278·70.

[2] Demarçay's element Γ. The other lines ascribed to Γ by that authority are λλ3523·79, 3540·42, 3568·68, and 3704·08, which are presumably very persistent terbium lines.

Ytterbium (neoytterbium).—Urbain, *Compt. rend.*, 1907, **145**, 759 ; 1908, **146**, 406 ; Auer von Welsbach, *Sitzungsber. K. Akad. Wiss. Wien*, 1907, **116**, II*b*, 1425 ; 1909, **118**, II*b*, 507 ; Exner and Haschek, *opus cit.* ; Crookes, *loc. cit.*

ARC SPECTRA.—The following is not a complete bibliography, but includes practically all the modern references to the arc spectra of the rare earths :—

General.—Exner and Haschek, *opus cit.* (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb) ; Eder and Valenta, *Sitzungsber. K. Akad. Wiss. Wien*, 1910, **119**, II*a*, 3 (Lu, Yb), 9 (Dy, Tb, Er, Gd, Ho, Y, La, Sm, Eu), 103 (Tm), 519 (Lu, Ce, La, Nd, Pr, Y).

Celtium.—Urbain, *Compt. rend.*, 1911, **152**, 141.

Cerium.—Bakowski, *Zeitsch. wiss. Photochem.*, 1908, **6**, 73 ; Cooper, *Astrophys. J.*, 1909, **29**, 329 ; Eder, *Chem. Zentr.*, 1915, i. 1046.

Dysprosium.—Eberhard, *Zeitsch. wiss. Photochem.*, 1906, **4**, 137 ; *Astrophys. J.*, 1906, **24**, 309 ; *Publ. Astrophys. Observ. Potsdam*, 1909, **20**, 3.

Erbium.—Exner and Haschek, *opus cit.* ; Eder and Valenta, *loc. cit.*

Europium.—Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1902, **111**, II*a*, 42, and *opus cit.*

Gadolinium.—Eberhard, *Zeitsch. wiss. Photochem.*, 1906, **4**, 137.

Holmium.—Eberhard, *Publ. Astrophys. Observ. Potsdam*, 1909, **20**, 3.

Lanthanum.—Rowland and Harrison, *Astrophys. J.*, 1898, **7**, 373 ; Kellner, *Inaug. Dissertation* (Bonn, 1904) ; E. Wolff, *Zeitsch. wiss. Photochem.*, 1905, **3**, 395 ; Humphreys, *Astrophys. J.*, 1907, **26**, 18 ; Eder, *Chem. Zentr.*, 1915, i. 1046.

CHIEF ARC AND SPARK LINES, ETC.—*continued.*

Thulium.

Spark.	Arc.
3131·40	3131·40
3134·01	3134·00
3151·18	3362·78
3172·98	3425·27
3236·96	3441·71
3261·75	3453·82
3362·75	3462·37
3425·25	3608·92
3462·38	3700·41
3700·40	3701·54
3701·52	3718·07
3761·50	3734·29
3762·05	3744·22
3795·50	3761·49
3848·14	3762·09
4522·76	3795·90
	3848·13
	4094·33
	4105·99
	4187·79
	4481·44

Ytterbium[1] (*neoytterbium* or *aldebaranium*).

Spark.	Arc.
2803·55	3081·26
2818·39	3107·99
2891·50	3289·50
2919·49	3464·47
3005·85	3694·35
3026·78	3988·16
3108·00	5556·67
3193·01	
3289·50	
3375·65	
3478·99	
3694·35[2]	
3988·20[2]	
4726·24	
4786·82	

Yttrium.

Spark.	Arc.
2367·30	3216·83
2414·78[3]	3242·42
2422·30[3]	3328·02
2817·14[3]	3600·92
2946·15[3]	3611·20
3216·84[3]	3621·10
3242·40[4]	3633·28
3328·03	3664·78
3549·12	3710·47
3600·90[3]	3774·52
3602·12	3788·88
3611·19[3]	3950·52
3633·28	3982·79
3664·76	4077·54
3710·44[3]	4102·57
3774·51[3]	4128·50
3788·88	4143·03
3850·51	4177·74
3982·78	4302·45
4177·68[4]	4309·79
4309·81	4348·93
4375·11[4]	4375·12
4855·06	4883·89
4883·95[3]	6191·91
4900·35[3]	6435·27
5087·61[3]	
5663·17	

Demarçay's Ω.

Spark.	Arc.
3930·9	
3967·9	

Demarçay's Θ.

Spark.	Arc.
3906·5	
4008·2	

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[1] The data given in the table for ytterbium are taken from Exner and Haschek, *opus cit.* At the present time (1916) the only spectrum measurements that have been taken with pure ytterbia are the measurements of the arc lines effected by Blumenfeld and Urbain (*Compt. rend.*, 1914, 159, 401). The most intense arc lines between λ=2300 and λ=3500 are as follows, according to these observers:—

2390·8, 2398·1, 2464·5, 2512·1, 2538·7, 2596·4, 2617·1, 2642·0, 2644·3, 2653·9, 2665·1, 2672·8, 2684·8, 2710·7, 2718·5, 2732·9, 2750·6, 2771·5, 2776·4, 2784·8, 2814·6, 2821·3, 2825·1, 2831·1, 2847·4, 2851·2, 2861·5, 2867·3, 2891·5, 2919·5, 2946·0, 2970·7, 2984·2, 2995·0, 3005·9, 3031·3, 3065·2, 3089·2, 3107·9, 3193·0, 3201·2, 3226·0, 3261·6, 3289·4, 3337·3, 3343·0, 3476·4, 3479·0, and 3496·0.

[2] The most persistent lines of ytterbium, according to de Gramont.

[3] Degree of persistency equal to χ.

[4] Degree of persistency equal to ψ.

Lutecium.—Exner and Haschek, *opus cit.* ; Eder and Valenta, *loc. cit.*

Neodymium.—Bertram, *Zeitsch. wiss. Photochem.*, 1906, 4, 16.

Praseodymium.—Bertram, *loc. cit.*

Samarium.—Rütten, *Zeitsch. wiss. Photochem.*, 1905, 3, 181.

Terbium.—Eberhard, *ibid.*, 1906, 4, 137 ; *Sitzungsber. K. Akad. Wiss. Berlin*, 1906, p. 384.

Thulium.—Exner and Haschek, *opus cit.* ; Urbain and Blumenfeld, *Compt. rend.*, 1914, 159, 323, 401.

Yttrium.—Kayser, *Abhandl. Berlin Akad.*, 1903 ; Eberhard, *Zeitsch. wiss. Photochem.*, 1909, 7, 245.

Ytterbium (neoytterbium).—Exner and Haschek, *opus cit.* ; Eder and Valenta, *loc. cit.* ; Urbain and Blumenfeld, *Compt. rend.*, 1914, 159, 323, 401.

The X-Ray or High Frequency Spectra.—X-rays are emitted by an element when the element or one of its compounds is bombarded with cathode rays. The X-rays are ether-waves of very small wave-length, *i.e.* of very high frequency, and the spectrum of the X-rays emitted by an element may be examined by a process analogous to the diffraction-grating method for the examination of ordinary spectra. For a description of the process the reader is, however, referred elsewhere, as it is beyond the scope of this book.[1]

The X-ray spectra of the elements have been examined by Moseley and others.[2] The spectra are extremely simple, consisting as a rule of four or five lines at the most. When, therefore, the necessary apparatus is available, the study of these spectra should be preferable to that of the arc or spark spectra, which are extremely complex. Preliminary wave-length measurements have been made by Moseley for the following rare earth elements: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium,[3] yttrium, and erbium.

The X-ray spectra of the rare earth elements throw a good deal of light on the question of the homogeneity of these substances. Further discussion of these spectra is therefore given in the following chapter (see p. 363).

APPLICATIONS OF THE RARE EARTHS.[4]

According to a statement by Stern[5] in 1913, the incandescent mantle industry consumes about 3300 tons of monazite sand per annum, 300 tons of thorium nitrate being produced. Very large quantities of earths of the cerium group are obtained as by-products; in fact, about 1000 tons of ceria per annum are obtained, only 3 tons of which are required by the mantle industry. The mixed rare earth oxalates or carbonates left as residues are usually known as crude cerium oxalate or carbonate, and their profitable utilisation in chemical industry is a problem that has at present received no really satisfactory solution, although many applications of them have been suggested. A number of these may be briefly discussed.

Gas Mantles and Electric Filaments.—An ordinary incandescent gas mantle contains about 0·8–1·0 per cent. of ceria, CeO_2, and a few tenths of a per cent. of glucina, GlO, and alumina, Al_2O_3, the remainder being composed of thoria, ThO_2. In mantles designed for use with high-pressure gas the percentage of ceria is increased and may reach the value 2·8 per cent.

As has been already mentioned, the annual consumption of ceria in the mantle industry is very small. To an even smaller extent "didymia" is also employed. When mantles are required to be marked they are stamped, just before the burning-off process, with a solution of "didymium" nitrate. The mark then appears on the finished mantle as a pale brown, permanent coloration.

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[1] See Kaye, *X-Rays* (Longmans & Co., 1914), and the papers cited in the next footnote.

[2] Moseley, *Phil. Mag.*, 1913, [vi.], **26**, 1024; 1914, [vi.], **27**, 703; Malmer, *ibid.*, 1914, [vi.], **28**, 787; Rydberg, *ibid.*, 1914, [vi.], **28**, 144; de Broglie, *Compt. rend.*, 1914, **159**, 304.

[3] Erroneously referred to as holmium in Moseley's paper.

[4] For further information on this topic, see Böhm, *Chem. Ind.*, 1913, **36**, 120, 153, 189, 232; *Die Verwendung der seltenen Erden* (Veit, Leipzig, 1913); Dammer, *Die chemische Technologie der Neuzeit* (Stuttgart, 1910), vol. i. p. 500; Kellermann, *Die Ceritmetalle und ihre pyrophoren Legierungen* (Knapp, Halle, 1912).

[5] Stern, *Zeitsch. angew. Chem.*, 1913, **26**, 806.

There is a small demand for yttria in connection with the manufacture of Nernst lamps. In these lamps illumination is produced by passing an electric current through a filament composed of a mixture of refractory oxides, of which yttria, thoria, and zirconia are the most suitable for the purpose.[1] As a source of yttria the gadolinite deposits found at Barringer Hill, Llano Co., Texas, are utilised.

Alloys.—The production of mischmetall, an alloy of the metals of the cerium group, has been mentioned earlier in this chapter (p. 230). Owing to the great stability of the oxides of the rare earth elements, these elements and certain of their alloys form valuable reducing agents. Mischmetall and the cerium-magnesium alloys have been especially mentioned in this connection.[2]

The ignition temperature of cerium in air is very low. Further, numerous alloys rich in cerium are hard and brittle, so that when struck with hard steel small particles of the alloys are detached and at the same time heated sufficiently to cause them to ignite. These alloys are usually called pyrophoric alloys; the preparation and uses of many of them are protected by patents. They may be prepared either from cerium or from mischmetall; the alloys containing 30 per cent. of iron (nickel or cobalt) have been particularly specified by Auer von Welsbach,[3] and alloys with tin, lead, zinc, cadmium, silicon, titanium, etc., have also been patented.[4] The alloys are used in the manufacture of automatic cigarette-lighters, gas-lighters, etc. It has also been proposed[5] to utilise them as arc-lamp electrodes, either alone or as the cores of carbons. According to Stern,[6] 200 tons of ceria are utilised annually in the production of pyrophoric alloys.[7]

According to Hirsch,[8] cerium-magnesium alloys rich in cerium form excellent flashlight powders.[9]

It has been claimed that the introduction of 0·2 per cent. of cerium into aluminium[10] greatly improves the mechanical properties of the metal.[11]

Arc-lamp Electrodes.—The incorporation of cerium compounds, particularly cerium fluoride, into the carbons used as arc-lamp electrodes is the subject of various patents.[12] It is claimed that a very intense light is thereby obtained and the arc burns evenly and quietly. One impregnating mixture proposed for the purpose contains 60 per cent. of the mixed molybdates and tungstates of the cerium group, 20 per cent. of the corresponding iron salts, and 20 per cent. of the fluorides of the cerium group.

According to Stern,[13] 300 tons of ceria are consumed annually in the form of fluoride for impregnating arc-light carbons.

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[1] See *Eng. Pat.*, 1898, No. 6135.

[2] See pp. 231, 379, and Muthmann and Beck, *Annalen*, 1904, **331**, 46; Hirsch, *J. Ind. Eng. Chem.*, 1911, **3**, 880; *Trans. Amer. Electrochem. Soc.*, 1911, **29**, 57; Weiss and Aichel, *Annalen*, 1905, **337**, 370; Kellermann, *Die Ceritmetalle und ihre pyrophoren Legierungen* (Knapp, Halle, 1912); Escales, *D.R.P.*, 145,820 (1903).

[3] Auer von Welsbach, *D.R.P.*, 154,807 (1903); *Eng. Pat.*, 16,853 (1903).

[4] See, *e.g.*, *Eng. Pat.*, 27,341 (1908); *Fr. Pat.*, 439,058 (1912).

[5] See *Eng. Pat.*, 1909, Nos. 8150 and 8151.

[6] Stern, *loc. cit.*

[7] For further information on these alloys, see Kellermann, *opus cit.*; Olsen, *Polytech. Eng.*, 1914, **14**, 24.

[8] Hirsch, *loc. cit.*

[9] *Cf. Eng. Pat.*, 14,692 (1908); *D.R.P.*, 158,215 (1908); *Fr. Pat.*, 403,722 (1909).

[10] By adding cerium fluoride to the electrolyte employed in the preparation of aluminium.

[11] Barth, *Metallurgie*, 1911, **9**, 261; Borchers and Barth, *D.R.P.*, 246,484 (1912).

[12] See, *e.g.*, *Eng. Pat.*, 21,374 (1909); *Fr. Pat.*, 414,707 (1910), 431,040 (1911).

[13] Stern, *loc. cit.*

Cerium Glass.—The incorporation of ceria into an ordinary colourless soda glass results in the production of a glass that has at the most a faint yellow tinge. It is very transparent to luminous rays, but cuts off practically all the ultra-violet and about 30 per cent. of the heat rays. By introducing other special ingredients into the cerium glass, a valuable series of glasses has been prepared by Crookes.[1] The compositions of the mixtures employed in their preparation are given in the following table (the "raw soda flux" has the composition, sand 61·00, anhydrous sodium carbonate 25·50, sodium nitrate 5·00, calcium carbonate 7·20, borax 0·75, and arsenious oxide 0·55 per cent., and the "fused soda flux" is obtained from the raw flux by fusion):—

	1	2	3	4	5	6	7	8	9	10	11	12
Raw soda flux	...	...	87·56	...	...	...	77·0	92·00	...	...	88·00	72·60
Fused soda flux	90·00	89·75	...	83·0	79·00	80·0	...	...	94·60	88·47	...	...
$Ce(NO_3)_3.6H_2O$	...	...	...	17·0	20·50	13·4	23·0	...	4·72	10·00	...	24·90
$CeBO_3$	8·13	8·18	8·00	...	...	...	...	6·30	...	...	5·00	...
$NiSO_4.7H_2O$	0·07	...	...	...	0·30	...	...	...	...	...	...	...
$CoSO_4.7H_2O$	...	...	...	...	0·05	...	...	...	0·08	0·03	...	...
$FeSO_4.7H_2O$	...	...	3·00	...	...	...	...	...	...	...	4·15	...
$CuSO_4.5H_2O$	...	...	...	...	...	...	...	...	...	...	...	2·10
Fe_3O_4	...	2·03	...	...	...	...	...	...	...	...	...	...
Fe_2O_3	...	...	...	...	...	...	...	1·60	...	1·50	...	...
Cr_2O_3	...	0·09	0·80	...	...	...	...	0·06	...	...	0·10	...
NiO	...	...	0·09	...	...	...	...	0·04	0·30	...	...	0·40
U_3O_8	1·80	...	...	...	0·15	6·6	...	...	...	...	2·75	...
UO_3	...	...	0·55	...	...	...	...	...	0·30	...	...	...

The next table gives the tints of these glasses, the percentages of heat rays absorbed and visible rays transmitted, and the wave-length beyond which the ultra-violet is absorbed:—

No. of Glass	Tint of Glass.	Heat Rays Absorbed.	Luminous Rays Transmitted.	Ultra-violet Absorbed.
		Per cent.	Per cent.	from
1	Pale yellow	37	78	λ3613
2	Pale greenish-yellow	63	54	3700
3	,, ,,	38	48	3680
4	Almost colourless	27	99	3650
5	Pale neutral	41	45	3700
6	Pale yellow	39	60	3685
7	Almost colourless	34	71	3610
8	Pale green	29	71	3620
9	Dark neutral	47	30	3550
10	Very pale blue	51	63	3550
11	Pale greenish-yellow	25	74	3685
12	Pale bluish-green	47	45	3680

The preceding glasses are of considerable value for the construction of spectacles. Glass 10 is fairly transparent and does not perceptibly alter the

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[1] Crookes, *Phil. Trans.*, 1914, **A**, **214**, 1; *Chem. News*, 1914, **109**, 265, 277, 289, 301.

colours of objects viewed through it; since it cuts off 51 per cent. of the heat rays, it is well adapted for making spectacles for those employed in glass works. Glasses 1, 2, 5, and 6 are good absorbers of ultra-violet rays, numbers 1, 4, 7, 8, and 11 are the most transparent to visible rays, while for glare-reducing spectacles numbers 3, 5, 9, 10, and 12 are eminently suitable.

Tanning.—It has long been known that certain aluminium, iron, and chromium salts are capable of converting hides into leather, and chrome tanning is of considerable importance. According to Garelli, salts of cerium, lanthanum, and "didymium" have tanning properties similar to those of aluminium salts, while ceric salts are particularly well adapted for the process of tanning. Parenzo agrees with Garelli's views, but Eitner is of the contrary opinion.[1]

Photographic Uses.—A solution of ceric sulphate in dilute sulphuric acid has a certain limited application in photography as a reducer of over-developed negatives, its action being even and rapid.[2] Ceric salts have also been incorporated into photographic emulsions for pigment printing. The printing paper is coated with an emulsion prepared by adding the ceric salt to a colloidal solution of albumin in aqueous ammonia, sodium carbonate, or borax. The paper, which is very sensitive to light, is exposed in the usual way and developed in a suitable solvent for the albumin, *e.g.* aqueous ammonia, sodium carbonate, or potassium oxalate.[3]

Dyeing.—Cerium compounds have been at times proposed as mordants, *e.g.* in dyeing with alizarin. They do not, however, appear to be used.[4]

Rare Earth Catalysts.—The crude mixture of basic sulphates of the cerium group has been proposed as a suitable catalytic agent for use in the contact process for manufacturing sulphuric acid. The mixture is said to be more effective than the pure cerous compound. The application of the oxides of the rare earth elements to the same process has also been proposed. These proposals do not, however, appear to be of much practical value.[5] Cerium nitride is said to hasten catalytically the union of nitrogen and hydrogen, and its use in the production of synthetic ammonia has been patented.[6]

Cerous sulphate is said to form an excellent catalyst for use in the oxidation of aniline to aniline black.[7]

It may also be mentioned that ceria has been proposed as a suitable substitute for platinised asbestos in Dennstedt's method for the combustion of organic compounds.[8]

Oxidation of Organic Compounds.—Since ceric salts are readily reduced to the cerous state, they may be utilised as oxidising agents. It is

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[1] Garelli, *Atti R. Accad. Lincei*, 1907, [v.], **16**, i. 582; *Collegium*, 1912, p. 418; *J. Soc. Chem. Ind.*, 1912, **31**, 830; Parenzo, *Collegium*, 1910, p. 121; *J. Soc. Chem. Ind.*, 1910, **29**, 579; Eitner, *Gerber*, 1911, **37**, 199, 213; *J. Soc. Chem. Ind.*, 1911, **30**, 1128.

[2] Lumière, *Bull. Soc. franç. Photog.*, 1900, **16**, 103; Lumière Bros. and Seyewetz, *Moniteur Scient.*, 1901, **15**, 169. See also *Brit. J. Photog.*, 1900, **47**, 184; 1901, **48**, 594; and *Eng. Pat.*, 470 (1900).

[3] Gateau, *Fr. Pat.*, 380,188 (1907); *Eng. Pat.*, 20,740 (1907).

[4] See Witt, *Chem. Ind.*, 1896, **19**, 156; *J. Soc. Chem. Ind.*, 1896, **15**, 580; Matschak, *ibid.*, 1898, **17**, 150; Gnehm, *ibid.*, 1898, **17**, 577.

[5] See *Eng. Pat.*, 1385 (1901); *Fr. Pat.*, 326, 321 (1903); and Plüddemann, *Inaugural Dissertation* (Berlin, 1907).

[6] Kunheim & Co., *D.R.P.*, 276,986 (1913).

[7] Kruis, *Dingl. poly. J.*, 1874, **212**, 347; Bührig, *ibid.*, 1879, **231**, 77; but *cf.* Witt, *loc. cit.*

[8] Bekk, *Ber.*, 1913, **46**, 2574; Miss M. Reimer, *J. Amer. Chem. Soc.*, 1915, **37**, 1636.

said, for instance, that crude ceric sulphate, in the presence of sulphuric acid, is an efficient oxidiser of aromatic hydrocarbons, converting them into aldehydes, quinones, etc., *e.g.* toluene into benzaldehyde, anthracene into anthraquinone, etc.[1]

Medicinal Uses.—Cerium is used to a limited extent in therapeutics in the form of cerous nitrate, cerous oxalate, and other organic salts. It acts like bismuth as a sedative and is said to be of value in the treatment of sea-sickness, pregnancy-sickness, dyspepsia, and gastric ulcer. The medicinal use of cerium salts is not, however, in very great favour.[2]

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[1] See *D.R.P.*, 158,609 (1905).

[2] See *Eng. Pat.*, 5328 (1884); *J. Soc. Chem. Ind.*, 1889, 8, 304; and Cushny, *Text-book of Pharmacology and Therapeutics* (Churchill, 5th ed., 1910); *Brit. Pharmaceutical Codex*, 1911.

CHAPTER XI.

THE RARE EARTH ELEMENTS (*continued*).

Separation and Purification. Homogeneity.
Detection and Estimation.

Choice of Material.—Monazite in the form of monazite sand is the most abundant of the rare earth minerals. Very large quantities of this material are worked up annually in connection with the gas-mantle industry. For the manufacture of mantles the thorium present in the sand is its most valuable constituent, very little of the cerium and "didymium" present being required. Accordingly, even when the residual salts of cerium, lanthanum, etc., are worked up for the production of pyrophoric alloys, etc., large quantities of them are left over, and when it is possible to obtain them in bulk they constitute the most convenient source of the rare earths from the point of view of the scientific investigator. Since, however, monazite sand seldom contains more than one or two per cent. of crude yttria, and frequently contains less than one per cent., it is obvious that very considerable quantities of monazite residues are necessary to obtain a reasonable supply of the earths of the yttrium group, but when they are available they constitute an excellent source of samarium, gadolinium, europium, terbium, dysprosium, and holmium.[1] In smaller quantities they constitute the cheapest and most convenient source of cerium, lanthanum, praseodymium, and neodymium. Commercial cerium oxalate and "cerium oxalicum medicinale" are essentially monazite residues, and when calcined yield mixtures of oxides containing about fifty per cent. of ceria.[2]

With regard to the other rare earth minerals it may be said that the crude "erbia" of the early chemists[3] is most abundant in xenotime, euxenite, samarskite, and certain Norwegian columbates, while different samples of gadolinite vary considerably in their "erbia" content;[4] that samarskite is comparatively rich in the earths of the terbium group; that the gadolinite earths are rich in yttria and "ytterbia"; and that the element celtium, concerning which very little is known, occurs in gadolinite but not in xenotime.[5]

Extraction of the Rare Earths from Minerals.—The rare earth elements are readily separated from the other elements with which they are associated in nature by taking advantage of the fact that their oxalates are practically insoluble in dilute mineral acids. It is only necessary to obtain the rare earths in solution as the sulphates, nitrates, or chlorides in the

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[1] James, *J. Amer. Chem. Soc.*, 1913, **35**, 235; James and Grant, *ibid.*, 1916, **38**, 41.

[2] Böhm, *Zeitsch. angew. Chem.*, 1902, **15**, 372.

[3] *I.e.* prior to 1878. See the historical section in the preceding chapter (p. 221).

[4] James, *J. Amer. Chem. Soc.*, 1911, **33**, 1332.

[5] Urbain, *Compt. rend.*, 1911, **152**, 141.

presence of a slight excess of mineral acid, and then, after saturating the solution with hydrogen sulphide, if necessary, and removing the precipitated sulphides, to add a slight excess of oxalic acid. The precipitated oxalates separate at first in an amorphous form and "ball up," so that warm solutions should be used and the first portion of the precipitate vigorously shaken until it assumes the crystalline form before the remainder is precipitated. The amorphous precipitate rapidly becomes crystalline and may then be filtered and washed very readily. On ignition, the oxalates leave a residue of oxides, *i.e.* the rare earths themselves.

Most rare earth minerals contain *thorium*, and frequently *zirconium* is also present. The former is precipitated as oxalate with the rare earth oxalates, but the latter remains in solution, since its oxalate is soluble in oxalic acid and in mineral acids.

The precipitated oxalates are liable to be contaminated with small quantities of iron, aluminium and calcium oxalates, etc., and, when monazite or xenotime has been employed, with small amounts of phosphates. Accordingly, the oxides derived from them by ignition or the hydroxides obtained by boiling them with sodium hydroxide should be dissolved in a slight excess of nitric or hydrochloric acid, and the precipitation with oxalic acid repeated. The alkali and alkaline earth metals may be eliminated by precipitating the rare earths as hydroxides with ammonia, but this is not very convenient on a large scale.

Any remaining impurities usually concentrate in the most soluble fractions, when the rare earths are subsequently separated by fractional crystallisation. Being then concentrated into a small portion of the initial rare earth material, their complete removal offers no difficulty.

The methods that may be employed for opening up rare earth minerals are as follows.

(i.) *Decomposition with Concentrated Sulphuric Acid.*—This answers well with the minerals cerite, gadolinite, orthite, monazite, and æschynite. *Cerite* is finely powdered, moistened with water, stirred up into a paste with about two-thirds its weight of concentrated sulphuric acid and heated. The temperature is gradually raised until finally at a dull red heat there is left a residue of anhydrous sulphates. The residue is cooled, pulverised, and slowly added to ice-cold water. The other silicates *orthite* and *gadolinite* may be similarly treated, though gadolinite is usually decomposed by heating it with concentrated hydrochloric acid or aqua regia.

Monazite sand requires rather different treatment. It is treated with twice its weight of sulphuric acid, and only heated to 200°–300°. It is necessary to leave a certain minimum amount of sulphuric acid in the residue in order that when it is added to water the phosphates of the rare earth elements may be kept in solution. The mixed phosphates dissolve readily when the residue is stirred slowly into an excess of water, which need not be cooled below the ordinary temperature.

Æschynite[1] is very finely ground and heated with sulphuric acid until excess of the latter has been expelled. The residue is dissolved in ice-cold water and, after twenty-four hours, the liquid is decanted from the residual titanic, columbic, and tantalic acids, etc.

The liquid is treated with excess of ammonia to eliminate the considerable quantity of calcium present. The washed precipitate is dissolved in excess

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[1] Urbain, *Ann. Chim. Phys.*, 1900, [vii.], 19, 206.

of concentrated nitric acid and the solution boiled for several days, more acid being added from time to time to replace that lost by evaporation. The liquid is then evaporated to a syrup and the residue taken up with water. After several days the clear liquid is decanted from the residue, which contains the last traces of titanic, columbic, and tantalic acids, and is extremely difficult to remove by filtration.

Euxenite,[1] like æschynite, is a columbo-tantalate. In order that it may be decomposed by sulphuric acid it must be very finely ground. According to James, the nitric acid process just described for eliminating the last traces of the earth-acids may be omitted.

(ii.) *Fusion with Potassium Hydrogen Sulphate.*—This method was formerly employed to a considerable extent for decomposing rare earth minerals containing columbium, tantalum, etc., but it is a troublesome process. *Samarskite, æschynite, euxenite,* and *fergusonite* may be treated in this manner. The residue after fusion is dissolved in water and treated as already described in connection with æschynite.[2]

(iii.) *Fusion with Sodium Hydroxide.*[3]—Various *columbates* may be decomposed by fusion with twice their weight of sodium hydroxide. The product is cooled, broken up, and allowed to disintegrate in water. It is then acidified with hydrochloric acid, heated, and the columbic acid, etc., removed by filtration.

Xenotime (ytterspar) may also be decomposed by this method. The product is boiled with water and filtered. The residue is then dissolved in hydrochloric acid.[4]

(iv.) *Decomposition with Hydrofluoric Acid.*[5]—This is an excellent, but rather expensive, method for the decomposition of columbates and tantalates, e.g. *samarskite, fergusonite, euxenite, æschynite,* etc. The mineral is powdered and warmed with aqueous hydrofluoric acid. Columbium, tantalum, titanium, zirconium, tungsten, etc., pass into solution and the rare earths are converted into insoluble fluorides. The latter are filtered off and converted into the neutral sulphates by heating with sulphuric acid;[6] the oxalates are then obtained in the usual manner.

(v.) *Decomposition by Disulphur Dichloride.*[7]—Those rare earth minerals that contain columbic, tantalic, titanic acids, etc., as their acid components are readily decomposed when heated in a stream of the vapour of disulphur dichloride, S_2Cl_2. The chlorides of the rare earth metals, etc., remain behind, and the volatile chlorides or oxychlorides of columbium, tantalum, titanium, tungsten, etc., distil over with the excess of disulphur dichloride. The method works excellently with *samarskite, fergusonite, æschynite,* and *euxenite.*

Separation of Thoria from the Rare Earths.—It was mentioned in the preceding section that the rare earth oxalates extracted from a mineral

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[1] James, *J. Amer. Chem. Soc.*, 1911, **33**, 1335.

[2] See Nilson, *Ber.*, 1880, **13**, 1430; Krüss and Nilson, *Ber.*, 1887, **20**, 1676; James, *J. Amer. Chem. Soc.*, 1911, **33**, 1336.

[3] James, *J. Amer. Chem. Soc.*, 1911, **33**, 1336.

[4] A somewhat similar procedure, viz. fusion with sodium carbonate, is recommended by Urbain (*Ann. Chim. Phys.*, 1900, [vii.], **19**, 202) for the decomposition of *monazite.*

[5] Roscoe, *Ber.*, 1882, **15**, 1274; Lawrence Smith, *Chem. News*, 1883, **48**, 13, 29; 1885, **51**, 289, 304; James, *loc. cit.*; *cf.* Wolcott Gibbs, *Amer. J. Sci.*, 1864, [ii.], **37**, 355.

[6] Uranium, when present, *e.g.* in samarskite, accompanies the rare earths up to this point.

[7] W. B. Hicks, *J. Amer. Chem. Soc.*, 1911, **33**, 1492; *cf.* Barlot and Chauvenet, *Compt. rend.*, 1913, **157**, 1153, for a similar method, using carbonylchloride, $COCl_2$, as reagent.

frequently contain more or less thorium oxalate.[1] It is therefore necessary to discuss the methods by which the thorium may be eliminated.[2]

(i.) *The Hydrogen Peroxide Method* (Method of Wyrouboff and Verneuil).[3]—This method is based upon the fact that from a neutral or slightly acid solution of the nitrates of thorium and the rare earth metals, thorium is completely precipitated by hydrogen peroxide in excess. The precipitate is white and voluminous, and has a composition expressed by the formula $Th_2O_7.N_2O_5.xH_2O$. The precipitation should take place in a solution containing not more than two parts of thoria per 100 of solution; the solution should be heated for a few minutes to 85°, the precipitate allowed to settle, filtered, and washed with hot water.

When little thorium is present, associated with much cerium, etc., the precipitation of the thorium is complete, but a little cerium peroxide is co-precipitated. On the other hand, when the thorium is in excess, the precipitate is not contaminated with cerium, but a trace of thorium remains in solution.

In applying the peroxide method on a large scale, it is advisable, first, to effect an initial concentration of the thorium; next, to remove the thorium by hydrogen peroxide; and, finally, to unite the rare earths in the filtrate from the peroxide precipitate with those left over in initially concentrating the thorium. The procedure recommended by Wyrouboff and Verneuil is as follows:—

The precipitated oxalates[4] are washed, heated with 10 per cent. sodium carbonate to convert them into carbonates, and sodium hydroxide added to precipitate all the thorium that passes into solution. The washed precipitate is dissolved in the minimum of hydrochloric acid, and a suspension of barium peroxide is stirred into the solution a little at a time until a sample of the clear liquid no longer gives a precipitate with pure hydrogen peroxide. The filtered liquid contains the bulk of the rare earths, free from thorium; the precipitate contains all the thorium, contaminated with 20 to 30 per cent. of other earths. The precipitate is washed, dissolved in cold hydrochloric acid, and the barium removed by a slight excess of sulphuric acid. The filtered solution, which should not contain more than 15 per cent. of free acid, is treated with oxalic acid, the precipitated oxalates thoroughly washed, and then treated with a very concentrated solution of ammonium carbonate (to which sufficient ammonia has been added to secure a solution of the normal carbonate). The thorium oxalate passes into solution completely, together with about 7 per cent. of its weight of rare earth oxalates. The residual oxalates are free from thorium. To obtain the rare earths still associated with the thorium, the cold filtered solution is decomposed by the addition of sodium hydroxide, the precipitate thoroughly washed by decantation, and dissolved in the minimum excess of cold nitric acid. The solution is diluted and the thorium removed by treatment with excess of hydrogen peroxide.

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[1] See also the section on "Occurrence" in Chap. X.

[2] No attempt will be made to discuss the purification of thoria; for that the reader is referred to Vol. V.

[3] Wyrouboff and Verneuil, *Bull. Soc. chim.*, 1897, [iii.], **17**, 679; 1898, **19**, 219; *Compt. rend.*, 1898, **126**, 340; **127**, 412; *Ann. Chim. Phys.*, 1905, [viii.], **6**, 484; *cf.* Cleve, *Bull Soc. chim.*, 1885, [ii.], **43**, 53; Lecoq de Boisbaudran, *Compt. rend.*, 1885, **100**, 605.

[4] In working up cerium minerals containing a few per cent. of thorium, the latter is completely precipitated when sufficient oxalic acid is gradually added to the well-stirred acid solution of the sulphates to precipitate one-half of the rare earths present.

All the filtrates containing rare earths devoid of thorium are united, and the rare earths precipitated with oxalic acid in a slightly acid solution.

(ii.) *The Ammonium Oxalate Method* (Bahr's Method).[1]—The mixed oxalates are treated with a hot concentrated solution of ammonium oxalate, in which thorium oxalate is readily soluble. The separation of a little thorium oxalate from excess of rare earth oxalate in this manner requires several repetitions of the treatment, and is not a sharp separation, for notable quantities of the rare earth oxalates dissolve, particularly the oxalates of the yttrium group. This method has been employed commercially.

(iii.) *The Thiosulphate Method* (Method of Chydenius).[2]—A dilute, neutral (or slightly acid) solution of the chlorides is boiled with an excess of sodium thiosulphate, when basic thorium thiosulphate is precipitated. This method is frequently employed in the separation of small amounts, *e.g.* in analytical chemistry (see later, p. 371).

(iv.) *The Sebacic Acid Method.*[3]—A slight excess of a hot, concentrated solution of sebacic acid is added to a boiling, neutral or faintly acid solution of the mixed nitrates. Thorium sebacate is precipitated, filtered, and washed with hot water.

Sebacic acid may be prepared from castor oil.

(v.) *The Lead Carbonate Method.*[4]—A dilute and nearly neutral solution of the nitrates is prepared, and an excess of pure, moist, precipitated lead carbonate is stirred into the solution. The solution is allowed to stand for some hours, with occasional shaking. The thorium is completely precipitated, together with zirconium and any cerium present as ceric nitrate.[5]

(vi.) *Other Methods.*—It has been proposed to precipitate the thorium present by means of sodium azide,[6] or as the fumarate,[7] meta-nitrobenzoate,[8] pyrotartrate,[9] iodate,[10] pyrophosphate,[11] hypophosphate,[12] etc.[13]

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[1] Bahr, *Annalen*, 1864, **132**, 227; Bunsen, *Pogg. Annalen*, 1875, **155**, 380; Glaser, *J. Amer. Chem. Soc.*, 1896, **18**, 782; Hintz and Weber, *Zeitsch. anal. Chem.*, 1897, **36**, 27, 213, 676; Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184.

[2] Chydenius, *Pogg. Annalen*, 1863, **119**, 46; Hermann, *J. prakt. Chem.*, 1864, **93**, 106; Drossbach, *Zeitsch. angew. Chem.*, 1901, **14**, 655; Hauser and Wirth, *ibid.*, 1909, **22**, 484; Hintz and Weber, *loc. cit.*; Glaser, *loc. cit.*, and *Chem. Zeit.*, 1896, **20**, 612; Johnstone, *J. Soc. Chem. Ind.*, 1914, **33**, 55.

[3] T. O. Smith and C. James, *J. Amer. Chem. Soc.*, 1912, **34**, 281. See also Knöfler, *D.R.P.*, 266,459 (1912).

[4] Giles, *Chem. News*, 1905, **92**, 1.

[5] Hence, if it is not desired that any cerium should be precipitated, care must be taken to ensure the absence of ceric nitrate. For this purpose the dilute solution may be saturated with hydrogen sulphide, and the excess of gas removed by boiling, or sulphurous acid may be used.

[6] Dennis and Kortright, *Amer. Chem. J.*, 1894, **16**, 79; Dennis, *J. Amer. Chem. Soc.*, 1896, **18**, 947; Wyrouboff and Verneuil, *loc. cit.*

[7] Metzger, *J. Amer. Chem. Soc.*, 1902, **24**, 901.

[8] Neish, *ibid.*, 1904, **26**, 780; Kolb and Ahrle, *Zeitsch. angew. Chem.*, 1905, **18**, 92.

[9] Smith and James, *J. Amer. Chem. Soc.*, 1912, **34**, 281.

[10] R. J. Meyer and Speter, *Chem. Zeit.*, 1910, **34**, 306; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1911, **71**, 65.

[11] Carney and Campbell, *J. Amer. Chem. Soc.*, 1914, **36**, 1134; and *D.R.P.*, 286,087 (1914).

[12] Koss, *Chem. Zeit.*, 1912, **36**, 686; Rosenheim, *ibid.*, 1912, **36**, 821; Wirth, *ibid.*, 1913, **37**, 773; *D.R.P.*, 268,866.

[13] Lecoq de Boisbaudran, *Compt. rend.*, 1884, **99**, 525; Urbain, *Bull. Soc. chim.*, 1896, **15**, 338, 347; *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184; Schützenberger and Boudouard, *Compt. rend.*, 1897, **124**, 481; Chavastelon, *ibid.*, 1900, **130**, 781; Grossmann, *Zeitsch. anorg. Chem.*, 1905, **44**, 229; Batěk, *ibid.*, 1905, **45**, 87; Muthmann and Baur, *Ber.*, 1900, **332**, 2028; Miss Jefferson, *J. Amer. Chem. Soc.*, 1902, **24**, 540; Hartwell, *ibid.*, 1903, **25**, 1128; Smith and James, *ibid.*, 1912, **34**, 281.

Should any trace of thorium be left with the rare earths after one of the preceding methods has been used to effect its removal, it will be subsequently found in the most soluble fractions of the yttrium group if the separation of the earths is commenced by the double sulphate method, using sodium sulphate as precipitant, and the general procedures given later are followed (see p. 357).

SEPARATION OF THE RARE EARTH ELEMENTS FROM ONE ANOTHER. METHODS AVAILABLE. FRACTIONATION. CONTROL OF FRACTIONATION.

The preparation of pure ceria from a mixture of rare earths is a comparatively simple operation that may be carried out by methods closely resembling the ordinary analytical methods of separation. The preparation of any other rare earth, however, is a tedious process, the ordinary methods of separation being unavailable. In the following account the nature of the separation processes is first outlined, and an indication given of the manner in which they are applied in practice. The actual processes are then enumerated and the application of the more useful of them briefly outlined.

Methods Available.—In ordinary analytical chemistry the problem of separating the metals present in a mixture is accomplished by converting each in turn into an insoluble or volatile compound to the exclusion of those accompanying it. Each separation may thus be effected completely, or almost completely, in a single operation. In the case of the rare earth elements, however, the most that can be done in one such operation is to effect a partial separation, *i.e.* to divide the primitive mixture into two parts containing the rare earths in different proportions. These two parts have then to be further subdivided, and the process of subdivision carried on for a very long time, portions similar in composition being united at appropriate intervals. Such a method of separation is spoken of as a **fractionation**, and the various parts into which the initial mixture is divided are termed **fractions.**

The methods of fractionation, which most closely resemble the methods of ordinary analytical chemistry, are as follows:—

(i.) Fractional **volatilisation.**

(ii.) Fractional **decomposition** of salts by heat.

(iii.) Fractional **precipitation.**

Fractional volatilisation has so far only been employed in effecting the partial separation of ytterbium and lutecium, and need not be further discussed.

The methods of fractional decomposition and precipitation were much employed by the early workers on the rare earths. The former is of little value except in one instance, the decomposition of the nitrates of the yttrium group. Both exploit the fact that the rare earths, although all fairly strong bases, exhibit slight differences in their strengths. In the case of fractional precipitation the results obtained also depend upon the relative solubilities of the sparingly soluble compounds that are precipitated; in most cases, however, the solubilities of these compounds do not differ widely among themselves, so that the influence of solubility is of very little account. The weakest base precipitates first and the strongest last. This holds good whether the rare earths are separated by precipitating the hydroxides, basic salts or normal salts; for example, the yttrium compound is the last to precipitate, whether the yttrium group is precipitated as hydroxides, ferrocyanides, iodates, stearates, or basic nitrites. A knowledge of the relative strength of the rare earths is therefore of importance for fractional decomposition or precipitation; the relative strengths have been already discussed (p. 257).

The method to be pursued in effecting fractional decomposition or precipitation will be evident after reading the description of fractional crystallisation, given below, and the short account of the "decomposition of the nitrates," given later (p. 353). There is little doubt that the precipitates obtained in fractionating by precipitation are usually solid solutions or mixed crystals.

Fractionation involves the frequent repetition of the same operations. It is accordingly very desirable that the technique of the process should be as simple as possible, in order to economise time, minimise the risk of accidents, and prevent the continual loss of small quantities of material. Methods of fractionation that involve filtrations, ignitions, and tedious evaporations should therefore only be employed in special cases; "fractional precipitation to be of value must be very rapid."[1] In general, it is much better to resort to a method of separation which finds no counterpart in ordinary analytical procedure, namely, fractional **crystallisation** of corresponding isomorphous salts from a suitable solvent. The salts should preferably be very soluble in the hot solvent and separate on cooling in compact crystalline masses. The most convenient solvent is water. The only operations involved consist in dissolving crystals in mother liquors, occasionally concentrating the solutions, and decanting mother liquors from crystals.

Fractional Crystallisation.—The utility of this method for separating the rare earth elements is due to the fact that the corresponding salts of these elements are usually isomorphous and capable of forming mixed crystals. If two salts are not isomorphous, then fractional crystallisation only permits, according to circumstances, of the isolation of the least soluble or most abundant of them from a mixture. With isomorphous salts, however, it is possible, by a series of skilfully conducted crystallisations, to separate them in a state of purity, step by step, in the order of their solubilities. The experimental procedure may be varied somewhat to suit a particular case, but in general is as follows:—

The initial mixture of salts (1) is crystallised from the solvent, about half the mixture being left in solution. Crystals (2) and mother liquor (3) are thus obtained and separated. Each in turn is crystallised. The crystals (2) give place to crystals (4) and mother liquor (5); the mother liquor (3) becomes divided into crystals (6) and mother liquor (7). Liquor (5) and crystals (6) are united into one fraction, and this, together with crystals (4) and liquor (7), constitute the three fractions into which the material is now divided. By further crystallisation, crystals (4) yield crystals (8) and liquor (9); fraction (5, 6) gives crystals (10) and liquor (11); and liquor (7) supplies crystals (12) and liquor (13). The following combinations are then effected: (9) with (10), (11) with (12); the method being to pour liquor (13) into a fresh vessel, then pour liquor (11) on to crystals (12), and finally to pour liquor (9) on to crystals (10). Resolution into four fractions is thus accomplished. The subsequent operations, as well as those just described, are sufficiently indicated in the accompanying diagram (fig. 34). In this

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[1] James, *J. Amer. Chem. Soc.*, 1908, 30, 184.

diagram even numbers represent crystals and odd numbers denote mother liquors; the arrows indicate how each fraction is subdivided, and the juxtaposition of two numbers represents the combination of two fractions into one.

The method of proceeding with the work of subdivision should now be clear. By this process the initial mixture is resolved into some twenty or thirty fractions, according to the nature of the mixture. The first stage of the fractionation is then finished.

During the second stage of the process the number of fractions is maintained constant. Suppose, for instance, that twenty fractions have been obtained. They are numbered from (1) to (20), beginning with the least and ending with the most soluble fraction. Each is crystallised (with readily soluble substances it is usually best to allow the greater part of the solid to separate out, say, three-fourths of the whole). The mother liquor from (20) is poured into a new vessel (21), the liquor from (19) poured into (20), that from (18) into (19), and so on until the liquor from (1) is poured into (2). From (2) to (20) the vessels are heated until the crystals dissolve in the liquids, and are then allowed to cool slowly. Fresh solvent is added to (1) for the crystallisation, but (21) is left alone. After crystallisation has occurred, the previous process of decantation is gone through, commencing as before by pouring the liquor from (20) into (21). For the next crystallisation a further quantity of solvent is added to (1), but fraction (21) is still untouched.

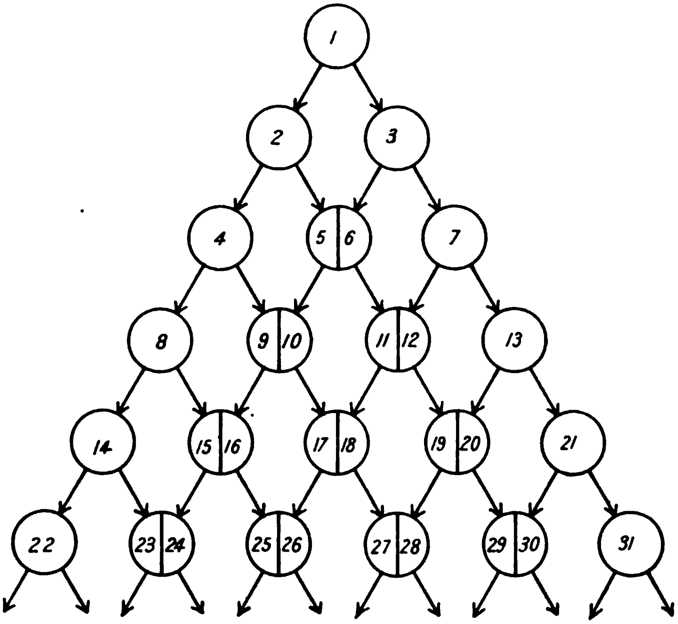

FIG. 34.—To illustrate fractional crystallisation.

After one or two more series of crystallisations, fraction (1) has dwindled to a very small amount. It therefore misses the next crystallisation. After the decantation of mother liquors has been performed, fraction (1) is then added to the crystals in (2), which thus becomes the new "head" fraction. By this time, however, the accumulation of mother liquors in (21) has produced a new fraction equal in size to the others, and from this time onwards it becomes the new "tail" fraction and takes part in the crystallisations.

By operating in the preceding manner, the fractions (2), (3), (4), etc., disappear in turn, and new fractions (22), (23), (24), etc., are successively added; throughout the entire process, therefore, the number of fractions remains constant. It is generally desirable to maintain the fractions equal in size throughout the series of crystallisations, and, in effecting this, some little skill is required to counteract the tendency of the middle fractions to grow at the expense of those at the two ends. Care should also be taken to exclude dust, etc., and if the crystallisations are carried out in Jena glass flasks, as recommended by Urbain, the flasks must not be more than half filled, otherwise expansion of the crystals not infrequently leads to breakages.[1]

Serial Order of the Rare Earth Elements.—Fractional crystallisation of salts of the rare earth elements usually amounts to the separation of the components of a mixture of isomorphous salts. Consider the case of three such salts, A, B, and C, the solubilities of which increase in the order specified. The prolonged fractional crystallisation of a mixture of these salts leads in general to the following result:—The first few "head" fractions consist of pure A; the next fractions in order consist of mixtures of A and B, the percentage of B increasing as the most soluble fractions are approached; then follows a series of fractions consisting of practically pure B; the next series of fractions contain both B and C, the percentage of C increasing in the direction of the more soluble fractions; and, finally, a number of fractions of pure C are obtained.[2] In short, the salts are spread out and separated in the order of their solubilities, a number of mixtures or intermediate fractions being interposed between each two consecutive salts.

The separation of two rare earth salts by an assigned method requires the presence of a certain number of intermediate fractions. The efficiencies of different methods of separation may be regarded as inversely proportional to the number of intermediate fractions they necessitate. In order to continue with the separation of the salts contained in a series of intermediate fractions, it is necessary to increase their number by the usual method of subdivision and then to continue the fractionation. The intermediate fractions may thus be diminished in quantity, but not in number.

In the case discussed it happens that while A has only to be separated from more soluble, and C from less soluble impurities, B has to be separated from a less soluble and also a more soluble impurity. In such a case as that of B it is often more difficult to eliminate the less soluble impurity than the more soluble one. The way out of this difficulty, however, is fairly obvious; after C has been eliminated as completely as possible, the still impure salt B is converted into a new salt B′ so that the order of increasing solubility

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[1] For further information on fractional crystallisation, see Urbain, *J. Chim. phys.*, 1906, 4, 36; Auer von Welsbach, *Monatsh.*, 1885, 6, 477.

[2] This assumes that none of the salts is very scarce in comparison with the others. There is usually no advantage gained by increasing the number of fractions beyond twenty or thirty, and if, say, the salt B constitutes only one-hundredth of the mixture, the state of affairs mentioned in the text obviously cannot be realised. The salt B, however, accumulates in the middle fractions of the series, so that after fractionation has been proceeded with for a sufficient length of time end fractions of pure A and C may be removed. The intermediate fractions may now be increased in number, and further quantities of A and C removed, until eventually B forms a considerable proportion of the fractions left.

is now C′, B′, A′. Further fractionation of B′ then eliminates A′ in the "tail" fractions.[1]

Similar considerations to the preceding apply when the mixtures to be fractionated contain not merely three, but a considerably greater number of salts. In separating complex mixtures, however, the procedure adopted is first to effect a preliminary separation into groups of salts, and then to treat each group apart from the others.[2]

From a study of the various salts that have been utilised for the purpose of fractional crystallisation it has been found that *the order of separation, or* **serial order,** *of the rare earth elements is usually as follows* :—[3]

La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Tm, Yb, Lu (Ct).

Hence, for example, a neodymium salt that has been freed by fractional crystallisation from all but the last traces of praseodymium and samarium salts, its neighbours in the series, will be even more free from lanthanum, europium, gadolinium, etc.

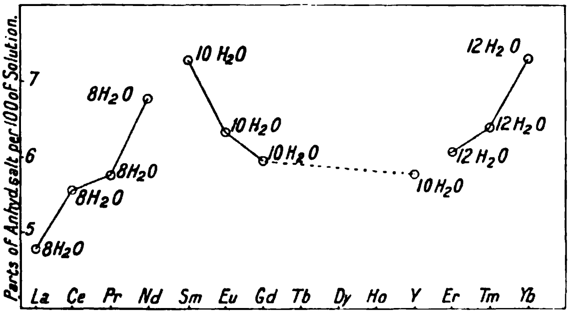

FIG. 35.—Solubilities of the 1 : 4 : 2—bromonitrobenzenesulphonates of the rare earth metals at 25°.

It is generally assumed that the serial order represents not only the order in which the rare earth salts separate, but also the order of solubility of the salts. It is not certain, however, that the separations always do occur in the order of the solubilities of the salts, although this usually appears to be the case.[4] It is noteworthy that with the exception of yttrium the *serial order of the elements is the order of increasing atomic weights*, and thus ranges the terbium group between the cerium and yttrium groups. In the majority of cases the lanthanum salt is the least soluble of the series; occasionally, however, it is the most soluble.

The separation of the rare earth salts by crystallisation does not always follow the serial order. It is, perhaps, not to be expected that this order

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[1] Urbain, *Ann. Chim. Phys.*, 1900, [vii.], 19, 227-29; Baxter and Chapin, *J. Amer. Chem. Soc.*, 1911, 33, 1.

[2] This often involves changing the method of fractionation, and in doing so each fraction should be separately converted into the new salt if the order of separation remains the same; otherwise much of the advantage of the previous separation is lost.

[3] Urbain and Lacombe, *Chem. News*, 1904, 90, 319; Urbain, *J. Chim. phys.*, 1906, 4, 64; *Chem. News*, 1909, 100, 73; *Seventh Int. Cong. Appl. Chem.*, 1909, Sect. X., p. 94.

[4] Thus, praseodymium bromate is rather more soluble in water than yttrium bromate, and yet when the mixed bromates of yttrium, praseodymium, erbium, and thulium are fractionated, the praseodymium salt rapidly accumulates in the head fractions in advance of the yttrium (James, *J. Amer. Chem. Soc.*, 1911, 33, 1341). See also the data on p. 269.

would be followed when the salts are not isomorphous and of the same type. The 1 : 4 : 2—*bromonitrobenzenesulphonates*[1] are a case in point, as they fall into three groups according to their degrees of hydration. The solubilities have been already given (p. 281); they are plotted against the serial order in fig. 35. It is clear that fractional crystallisation of a complex mixture of these rare earth salts will not effect their separation in serial order. Even when the salts are isomorphous, however, there are cases in which the serial order is not observed. The *ethylsulphates* (p. 278) afford one such instance, the solubilities diminishing from lanthanum to neodymium, and thereafter increasing. The *bromates* (p. 256) and *nitrates* (p. 267) are analogous to the ethylsulphates; in the case of the bromates the europium salt is the least soluble, and in the case of the nitrates, which crystallise from nitric acid as the pentahydrates, the least soluble nitrate is the salt of gadolinium.

Separating Elements.—In discussing the atomic weights of the rare earth elements it was pointed out that a number of *bismuth* salts are isomorphous with the corresponding salts of the rare earth elements (p. 234). If, then, a quantity of the bismuth salt is added to a suitable mixture of rare earth salts, and the whole submitted to fractional crystallisation, the bismuth salt eventually separates out at a definite point in the series, between two of the salts of the rare earth elements. If the crystallisation is continued until a number of fractions of chemically pure bismuth salt have been obtained, a quantitative separation of the rare earths has been achieved. This ingenious method of using bismuth as a separating element is due to Urbain and Lacombe.[2]

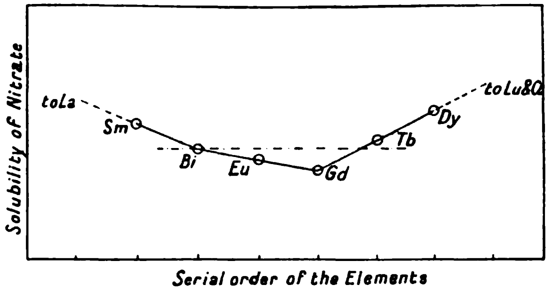

FIG. 36.—Solubilities of the nitrates of the rare earth elements.

Bismuth occupies a definite position in the serial order, namely, between *samarium* and *europium*; and hence, with mixtures conforming with the law of serial order, it is only possible to produce a quantitative separation at this one point in the rare earth series. When the mixture does not separate in that manner, however, a different point of separation becomes possible. Only one instance has yet been worked out, namely, the case of the *nitrates*, $M(NO_3)_3.5H_2O$. When the solubilities of these salts are plotted against the serial order of the elements, the result is somewhat as shown in fig. 36. It will be clear that not only may a quantitative separation be made between samarium and europium if the rare earth elements from lanthanum to

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[1] Katz and James, *J. Amer. Chem. Soc.*, 1913, **35**, 872.

[2] Urbain and Lacombe, *Compt. rend.*, 1903, **137**, 792; 1904, **138**, 84, 627, 1166; *Chem. News*, 1903, **88**, 295; 1904, **89**, 52, 277; Urbain, *J. Chim. phys.*, 1906, **4**, 40, 105.

gadolinium only are present, but a similar separation may be made between *gadolinium* and *terbium* in mixtures that contain the elements from gadolinium to celtium in the series.[1]

The application of bismuth as a separating element, when made in connection with the fractionation of the *double magnesium nitrates*, results in the quantitative separation of samarium from europium, *i.e.* the complete elimination of intermediate Sm-Eu fractions. This is not, however, the only beneficial result that is achieved. The samarium and bismuth salts are miscible to a considerable extent in the solid state; but the neodymium compound is only taken up to a very slight extent, and the praseodymium, cerium, and lanthanum compounds not at all by the bismuth salt. Accordingly, after the bulk of the lanthanum, cerium, praseodymium, and neodymium has been removed in the ordinary way (and this may readily and quickly be effected), the application of the bismuth process leads to the rapid elimination of the remainder of these elements from the samarium, intermediate Nd-Sm fractions being reduced to a very small amount. In a somewhat similar manner the separation of europium and gadolinium is greatly facilitated, although in this case each salt is readily miscible with the salt of bismuth; four intermediate Eu-Gd fractions only are necessary, instead of eighteen when the bismuth salt is omitted (see p. 349).[2]

When the simple *nitrates* of gadolinium, terbium, dysprosium, etc., are fractionated in the presence of bismuth nitrate, the intermediate Gd-Tb fractions may be reduced practically to zero, and the intermediate Tb-Dy fractions to a small amount.

Bismuth may be employed as a separating element in a different manner from the preceding. In fractionating the rare earths, mixtures are sometimes obtained comparatively rich in samarium, and especially in gadolinium, but containing so much of the yttrium group that the samarium and gadolinium cannot be removed from them by crystallisation as the double magnesium nitrates. Now the members of the yttrium group do not form double magnesium nitrates. If, then, bismuth magnesium nitrate is added in sufficient amount to allow the crystallisation to commence, and more added from time to time to the most soluble fraction, the bismuth salt accumulates quite rapidly in the "head" fractions, carrying with it practically the whole of the samarium and gadolinium salts.[3]

The great value of bismuth for the preceding purposes lies in the fact that when the necessary rare earth separations have been effected by its aid, it may be rapidly and completely eliminated by simple analytical processes. Unfortunately, in its isomorphism with the rare earth metals bismuth appears to be unique among the common elements. Occasionally, however, one rare earth element may be used as a separating element for two others.

As an example, the separation of lanthanum, praseodymium, and neodymium by the crystallisation of the double ammonium nitrates from nitric acid may be discussed. In this process the lanthanum salt separates in the

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[1] Urbain, *Compt. rend.*, 1909, 149, 37.

[2] From the results of Eberhard's investigations of the arc spectra of Urbain and Lacombe's Sm-Eu-Gd fractions it may be stated that (i.) the separation of Sm and Eu is quantitative, (ii.) pure Eu may be obtained, (iii.) Sa may be completely freed from Eu, and (iv.) Gd may be obtained quite free from Sm but containing traces of Eu (Eberhard, *Zeitsch. anorg. Chem.*, 1905, 45, 374).

[3] Urbain and Lacombe, *Compt. rend.*, 1904, 138, 84: *Chem. News*, 1904, 89, 52; Urbain, *J. Chim. phys.*, 1906, 4, 121.

"head" fractions fairly readily, before the praseodymium and neodymium have separated to any considerable extent, and once the bulk of the lanthanum has been thus eliminated, the separation of the other two elements proceeds extremely slowly and it is difficult to induce crystallisation. Further separation of the praseodymium and neodymium may, however, be brought about more rapidly if part of the separated lanthanum is returned to the final mother liquor and again crystallised through the series of fractions.[1] It is better, however, to add cerous ammonium nitrate, since the subsequent elimination of cerium is much easier than the removal of the lanthanum.[2] In a somewhat similar manner, James has utilised praseodymium bromate in effecting the separation of the bromates of erbium and thulium.[3]

In the preceding example, the use of lanthanum or cerium resembles the use of bismuth in facilitating the separation of europium and gadolinium. It should be possible, however, to realise the quantitative separation of two rare earth elements by a third in the same way that bismuth effects the separation of samarium and europium. Thus, suppose a mixture of the salts of three rare earth elements A, B, C be fractionated, the solubilities of the salts increasing in the order A, B, C and the salt of B being in excess of the others, until several consecutive middle fractions consist of practically pure salt of B. The less soluble fractions will then be A-B mixtures practically free from C, and the more soluble fractions will be B-C mixtures free from A. Now, by a proper choice of salts the solubilities of which do *not* follow the serial order from lanthanum to celtium, it may be possible to separate quantitatively each of the binary mixtures A-B and B-C by the bismuth magnesium nitrate method, and, if so, the separation of A from C will have been accomplished quantitatively by the aid of B. James and Bissel[4] have obtained good evidence that neodymium may be used in this manner in effecting a quantitative separation of gadolinium and terbium bromates; in this case A, B, C are gadolinium, neodymium, and terbium respectively, and the A-B and B-C mixtures may be quantitatively separated by the bismuth method.

Control of Fractionation.—It is necessary from time to time to follow the progress of the fractionation. The methods utilised for this purpose are (i.) measurement of chemical equivalents, (ii.) measurement of magnetic susceptibilities, and (iii.) observations of various types of spectra.

(i.) *The "Chemical Equivalent" Method.*—It is possible to give a perfectly definite meaning to the term "equivalent" when applied to a mixture of rare earths, viz., the number of parts by weight of the mixture that react with one equivalent of an acid, and the experimental determination of the equivalent may be carried out by any of the methods that have been previously described for the determination of the atomic weights of the rare earth elements (p. 239). It is usual, however, to express the result of the measurement, not in terms of an equivalent, but rather as the fictitious "atomic weight" corresponding to it.

Suppose, now, that a rare earth mixture has been resolved into a number

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[1] Auer von Welsbach, *Monatsh.*, 1885, 6, 477; Schottländer, *Ber.*, 1892, 25, 378, 569.

[2] Von Scheele, *Zeitsch. anorg. Chem.*, 1898, 17, 310; *cf.* Feit and Przibylla, *Zeitsch. anorg. Chem.*, 1905, 43, 202, and Erdmann and Wirth, *Annalen*, 1908, 361, 190, who use cerous magnesium nitrate to assist in the separation of the double magnesium nitrates of lanthanum, praseodymium, and neodymium.

[3] James, *J. Amer. Chem. Soc.*, 1911, 33, 1341.

[4] James and Bissel, *J. Amer. Chem. Soc.*, 1914, 36, 2060.

of fractions. Frequently, the order of separation of the rare earth elements corresponds with the order of their atomic weights. If, then, the extreme atomic weights of the elements in a mixture are W_α and W_ω, the fictitious "atomic weights" of the two end fractions continually approximate to the values W_α and W_ω, and the "atomic weights" of the intermediate fractions vary regularly from the one extreme to the other. The manner in which these "atomic weights" vary as fractionation proceeds may be described most simply, perhaps, in terms of a graphical construction, in which the numbers of the fractions are plotted as ordinates and the corresponding "atomic weights" as abscissæ, a curve being then drawn through the points. The curve has at first an upward or downward trend throughout its entire length, but as fractionation proceeds, indications of horizontal portions appear in the curve and gradually become more and more pronounced. As a rule, each horizontal region corresponds to a series of fractions of a pure rare earth compound; so that the atomic weights W_α, W_β, W_γ . . . W_ω, corresponding to the horizontal portions of the curve, are the atomic weights of the rare earth elements present in the mixture. Occasionally, however, a horizontal region corresponds to the isolation of a mixture that cannot be resolved by the particular process that is being employed.

Even when the rare earth elements do not separate in the order of their atomic weights the final curve will consist of a number of horizontal regions joined together by intermediate curved portions; its evolution, however, from a simple starting-curve cannot be followed in the preceding manner. This is the case, for instance, when the yttrium earths are fractionated by crystallisation, the atomic weight of yttrium being much less than that of any other rare earth element.

In any case, however, the "atomic weight" method of control is used in conjunction with the spectroscopic method. Valuable information may be obtained by it, but, owing to the fact that the atomic weights of any two successive elements in the serial order are very close together,[1] the method is not very sensitive.[2]

(ii.) *The Magnetic Susceptibility Method.*—The rare earths differ very much among themselves in the values of their magnetic susceptibilities. For instance, the values for gadolinia and europia are in the ratio of 5 to 1. Determinations of magnetic susceptibilities therefore provide a much more sensitive means of controlling the course of a fractionation than measurements of chemical equivalents. Moreover, by means of Curie and Cheneveau's magnetic balance it is possible to determine a magnetic susceptibility in a few minutes; the method is therefore extremely practical. Its utility was pointed out by Urbain and Jantsch.[3]

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[1] Yttrium being excluded.

[2] The oxalate method of p. 242 is, perhaps, the one that has been most frequently employed in determining the "atomic weights" corresponding to the various fractions. Like practically all the other methods, the "weight of oxide" is one term of the ratio measured. Since, then, ceria is a dioxide, it is necessary to eliminate cerium before commencing the fractionation, or else with each "atomic weight" measurement to determine the percentage of ceria in the oxide. Similar difficulties are likewise encountered owing to the fact that the oxalates of praseodymium and terbium give peroxides when calcined and not sesquioxides; either the peroxides may be reduced in hydrogen or their peroxide oxygen determined iodimetrically. The "atomic weight" method is accordingly of very little value so far as the cerium group is concerned.

[3] Urbain, *Compt. rend.*, 1908, **146**, 406, 922; Urbain and Jantsch, *ibid.*, 1908, **147**, 1286; Urbain, *ibid.*, 1909, **149**, 37; 1910, **150**, 913; 1911, **152**, 141; Blumenfeld and Urbain, *ibid.*, 1914, **159**, 323.

In putting this method into practice the oxalates should be precipitated from the fractions and calcined to oxides just previous to the actual measurements of the susceptibilities. The numerical data for the pure earths are given on p. 257.[1]

(iii.) *The Spectroscopic Method.*—The salts of nine of the rare earth elements give *absorption* spectra in the visible region, and those of one other give a well-defined ultraviolet spectrum. The frequent observation of the absorption spectra of the fractions therefore affords a rapid and extremely valuable method for following the progress of fractionation. Throughout the early stages of the separation, observations with a good pocket spectroscope are sufficient for the purpose; subsequently, however, more precise measurements are necessary. The comparison of the spectra of different fractions must be effected under conditions which are the same for each fraction, or erroneous conclusions may easily be drawn.[2]

When a series of consecutive fractions have identical absorption spectra, it is usually, but not invariably, the case that a pure rare earth salt has been obtained. It is not enough to compare the visible absorption spectra; the ultraviolet regions must also be examined, preferably by the photographic method.

The separation of the elements in the colourless fractions should be followed by studying the *spark* spectra, which are not so sensitive as the *arc* spectra and involve no sensible loss of material in their examination. The study of the spark spectra of the coloured fractions is also extremely valuable. These spectra should not be examined, however, until very considerable progress has been made in the fractionation, since the spark spectra of rare earth mixtures are exceedingly rich in lines. The constancy of absorption and spark spectra throughout several consecutive fractions is the best criterion of the isolation of a pure rare earth compound, but it is not infallible. When this constancy of spectral characteristics is attained, accurate atomic weight measurements should be made, in order to obtain additional confirmation.

Finally, observations of the *arc* and *phosphorescence* spectra may be made in order to determine the degree of purity of the rare earth salt that has been isolated.

The various spectra of the rare earth elements and their compounds are described in some detail in the preceding chapter (pp. 282–312).

It may generally be assumed that a pure rare earth compound has been isolated in the course of fractionation when a number of consecutive fractions are obtained, identical in all respects; that is to say, when all the fractions correspond to the same atomic weight, yield rare earths identical in their physical properties, particularly their magnetic susceptibilities, and possess identical spectral characteristics, quantitatively as well as qualitatively. When, in addition, the fractionation of such a series of fractions is continued by other methods with negative results, the assumption that a pure rare earth compound has been isolated becomes practically certain. The rare earth thus isolated conforms, in fact, to the experimental definition of a pure substance.

In controlling the course of fractionation one other point should be noted. As has been already pointed out, between each two consecutive series of

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[1] On the measurement of magnetic susceptibilities, see Curie, *Ann. Chim. Phys.*, 1895, [vii.], 5, 289; Meslin, *ibid.*, 1906, [viii.], 7, 145; Curie and Chenevenau, *J. de physique*, 1903, [iv.], 2, 796; Poynting and Thomson, *Electricity and Magnetism* (Griffin & Co., 1914).

[2] See pp. 283–7.

fractions of pure rare earth salts there exists a series of intermediate fractions. It is of importance (i.) that these should be expanded into a larger number of smaller fractions, and the process of separation continued until eventually the intermediate portions are insignificant in comparison with the pure salts; and (ii.) that confirmation can be obtained that the spectral and other characteristics of these intermediate fractions are in harmony, both qualitatively and quantitatively, with the assumption that they are mixtures of the two pure compounds in varying proportions. Without such confirmation, there is always the possibility that the intermediate fractions contain another earth, rare in comparison with those that have been isolated.

SEPARATION OF CERIUM FROM THE OTHER RARE EARTH ELEMENTS.

The comparative ease with which cerium may be separated by chemical means from the other rare earth elements is due to the fact that cerium, unlike the others, forms two definite series of salts, one derived from a strongly basic hydroxide, $Ce(OH)_3$, the other from a feebly basic hydroxide, $Ce(OH)_4$. The latter hydroxide resembles thorium hydroxide, $Th(OH)_4$, in strength. Accordingly, when cerium is separated from the rare earths by any of the usual procedures, the thorium, unless previously removed, accompanies it.

A mixture of rare earths containing not more than 50 per cent. of ceria dissolves completely in hydrochloric or nitric acid; in the latter case the cerium passes into solution almost entirely as ceric nitrate. If, however, a mixture of rare earths contains more than 50 per cent. of ceria, it cannot be completely dissolved in either hydrochloric or nitric acid; but it can be completely converted into a mixture of sulphates by heating with excess of concentrated acid. In this manner the ceria is converted into ceric sulphate, insoluble in the excess of sulphuric acid, and if the mixed sulphates are dissolved in cold dilute nitric acid and boiled with excess of alkali hydroxide, the precipitated hydroxides contain the cerium, mainly as ceric hydroxide. This precipitate dissolves readily in nitric acid, forming ceric nitrate, etc.

A rare earth mixture containing more than 50 per cent. of ceria can be dissolved by heating it with nitric acid if hydrogen peroxide is added from time to time.[1] The ceria then passes into solution as cerous nitrate. The mixture may also be dissolved in concentrated hydrochloric acid if ammonium or potassium iodide is also added. Iodine is liberated and the cerium is transformed into cerous chloride.[2] Ceric chloride is not known.

Natural mixtures of rare earths rich in ceria, *e.g.* those extracted from monazite and cerite, do not as a rule contain more than 50 per cent. of ceria.

(i.) **The Basic Nitrate-Sulphate Method.**[3]—This method is based upon the fact that ceric nitrate and sulphate readily hydrolyse in aqueous

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[1] Wyrouboff and Verneuil, *loc. cit.*

[2] Bunsen, *Annalen*, 1858, **105**, 40, 45.

[3] Brauner, *Trans. Chem. Soc.*, 1885, **47**, 879; *Monatsh.*, 1885, **6**, 785; *Zeitsch. anorg. Chem.*, 1903, **34**, 207; Brauner and Batěk, *ibid.*, 1903, **34**, 103; Wyrouboff and Verneuil, *Bull. Soc. chim.*, 1897, [iii.], **17**, 679; 1898, [iii.], **19**. 219; *Compt. rend.*, 1897, **124**, 1230; **125**, 950; 1899, **128**, 1331; *Ann. Chim. Phys.*, 1906, [viii.], **9**, 333; Sterba, *ibid.*, 1904, [viii.], **2**, 193; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1903, **37**, 378. *Cf.* the following early memoirs: Hermann, *J. prakt. Chem.*, 1843, **30**, 184; Marignac, *Ann. Chim. Phys.*, 1849, [iii.], **27**, 212; Bunsen, *Annalen*, 1858, **105**, 40, 45; *Pogg. Annalen*, 1875, **155**, 230, 366; Holzmann, *J. prakt. Chem.*, 1858, **75**, 321; *Jahresber.*, 1862, p. 136; Czudnowicz, *ibid.*, 1860, **80**, 16; W. Gibbs, *Amer. J. Sci.*, 1864, [ii.], **37**, 352; Erk, *Zeitsch. für Chem.*, 1870, [ii.], **7**, 100; *Jahresber.*, 1870, p. 319.

solution, producing precipitates of basic salts that may be readily filtered and washed. The necessary procedure is here described on the assumption that the mixed earths contain less than 50 per cent. of ceria; the details are essentially those of Wyrouboff and Verneuil, as modified slightly by Sterba.

The rare earth elements are precipitated as oxalates, and the latter washed, dried, and calcined to oxides. The mixed oxides are added gradually to four times their weight of cold, concentrated nitric acid, the mixture being warmed towards the end of the operation to 50° or 60°. The dark red solution is allowed to stand for twenty-four hours, and then decanted from any slight insoluble residue. The solution is evaporated on the water-bath until it is of the consistency of a thick syrup and solidifies completely when cooled. The syrup is dissolved in a quantity of water equal to thirty[1] times the weight of the oxides used, 1 gram of ammonium sulphate added for every litre of solution, the liquid heated to the boiling-point and boiled for about fifteen minutes. A pale yellow precipitate with a faint greenish tint is thus obtained; it consists of basic ceric nitrate and sulphate. The precipitate is filtered off and thoroughly washed with a solution containing 50 grams of ammonium nitrate and 10 grams of ammonium sulphate per litre of water; hot water will serve, but the preceding solution is better. Provided the initial evaporation of the nitric acid solution was continued to the right point, the precipitate contains practically all the cerium that was present in the liquid as ceric nitrate. A little ceric nitrate and some cerous nitrate, however, still remain in the filtrate.

Wyrouboff and Verneuil give two methods for eliminating the remainder of the cerium from the filtrate. (*a*) The liquid is vigorously stirred and a mixture of ammonia and pure hydrogen peroxide is slowly added. The cerium is thus precipitated as peroxide, accompanied by more or less of the other earths. When the filtered liquid only gives a bluish-white precipitate, the addition of ammonia and peroxide is stopped. The precipitate is washed, dissolved in nitric acid, and precipitated by oxalic acid. The oxalates are ignited to oxides, and the procedure already described in the preceding paragraph is followed with the oxides. There is thus obtained, by these two treatments, (*α*) 99 per cent. of the cerium in a nearly pure state, (*β*) about 90 per cent. of the other earths free from cerium, and (*γ*) a small fraction consisting of other earths contaminated with a trace of cerium. (*b*) An excess of sodium acetate is added and the liquid boiled, while ammonium persulphate is added little by little. In this manner all the cerium may be precipitated as basic ceric sulphate, and there is thus obtained three fractions: (*α*) the original precipitate containing 85 to 90 per cent. of the cerium in a nearly pure state; (*β*) about 99 per cent. of the other earths quite free from cerium; and (*γ*) about 10 to 15 per cent. of the cerium (from the persulphate precipitate) containing a few per cent. of foreign earths. The fraction (*γ*) may be dissolved in nitric acid, evaporated to a syrup, diluted with water, and boiled, when the cerium it contains is precipitated almost completely and practically free from other substances.

The great advantages of the basic nitrate-sulphate method are that in one operation it separates about three-fourths of the total cerium in an almost pure state, and the precipitate may be purified in the same manner as that by which it was produced (p. 337).

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[1] When operating on large quantities of material, this may be reduced to ten.

When the initial mixture is such that the cerium is most conveniently brought into solution as a cerous salt, a mixture of the nitrates is prepared. The following procedures are then available:—

(*a*) The concentrated solution of the nitrates, slightly acidified with nitric acid, is electrolysed in a large platinum dish which serves as the anode. The current density should be 0·5-0·7 ampères per sq. dcm. of anode surface. About 70-80 per cent. of the cerium may be thus converted into ceric nitrate. The solution is treated with dilute ammonia until a permanent turbidity is first produced, when the procedure already outlined may be followed.[1]

(*b*) The nitrates are converted into double ammonium nitrates and the latter dissolved in water (2 litres per 100 grams of double nitrates). The solution is boiled, stirred with steam, and a solution of magnesium acetate and hydrogen peroxide added drop by drop (50 grams magnesium acetate dissolved in 500 c.c. of 2·5 per cent. peroxide per 100 grams of double nitrates), until a filtered sample no longer gives the orange-yellow cerium precipitate. The precipitate contains all the cerium (as basic perceric acetate), but is contaminated with about 4 per cent. of other earths. It is filtered off and washed with boiling water.[2]

The precipitate is dried at 120° in order to convert it into basic ceric acetate. It is then dissolved in excess of concentrated nitric acid and the solution evaporated on the steam bath till the free acid is almost entirely expelled and the residue has the consistency of a very thick syrup. The cerium is then precipitated as basic ceric nitrate-sulphate by the method already described.

There are thus obtained three fractions: (α) nearly pure basic ceric nitrate-sulphate, containing the greater part of the cerium; (β) the filtrate from (α) containing part of the cerium and a little lanthanum, etc.; and (γ) the filtrate from the basic perceric acetate, free from cerium, and containing the greater part of the lanthanum, etc.

(*c*) Wyrouboff and Verneuil's procedure (*b*) above, using ammonium persulphate and sodium acetate, may be employed. Witt and Thiel[3] replace the sodium acetate by precipitated calcium carbonate.

(ii.) **The Bromate Method.**[4]—Potassium bromate may be used to oxidise cerous to ceric salts, and, provided that the solution is kept almost neutral, the ceric salt hydrolyses and basic ceric salt is precipitated.

As the starting material, a nearly neutral, concentrated solution of the nitrates is required. The solution is heated to boiling, and potassium bromate added. As soon as red fumes of bromine make their appearance, two or three lumps of marble are added and the liquid boiled for one or two hours. As soon as the peroxide test (p. 367) on a sample of the filtered liquid indicates that very little cerium is left in solution, the boiling is discontinued, the marble removed, and the precipitate allowed to settle. The liquid is syphoned off and the precipitate washed with 5 per cent. ammonium nitrate solution. The precipitate thus obtained from a concentrated solution is dense, settles readily, washes easily, and contains very little impurity. It consists

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[1] Sterba, *loc. cit.*

[2] R. J. Meyer and Koss, *Ber.*, 1902, **35**, 672; *cf.* Popp, *Annalen*, 1864, **131**, 359; Erk, *Zeitsch. für Chem.*, 1870, [ii.], **7**, 100. According to Wyrouboff and Verneuil, magnesium acetate offers no advantages over sodium acetate.

[3] Witt and Thiel, *Ber.*, 1900, **33**, 1315.

[4] James and Pratt, *J. Amer. Chem. Soc.*, 1911, **33**, 1326.

mainly of basic ceric nitrate when only a slight excess of bromate is employed, and mainly of basic ceric bromate when excess of bromate is used.

The filtrate is boiled with a little more potassium bromate and marble until the liquid is quite free from cerium. The precipitate thus obtained contains a little of the other rare earths, and is dissolved in nitric acid and added to the next lot of starting material. The filtrate contains the other rare earths, free from cerium.

(iii.) **The Permanganate Method.**[1]—When potassium permanganate is added to a hot, neutral solution of cerous nitrate, it is immediately bleached, and a brown precipitate appears, consisting of a mixture of ceric hydroxide and hydrated manganese dioxide. After a certain quantity of permanganate has been added, the colour is no longer discharged. The solution is then found to give an acid reaction with litmus and to contain cerium in solution. The addition of a little alkali leads to the bleaching of the permanganate and the precipitation of more cerium, and if the liquid be kept neutral by the addition of alkali, the permanganate colour only ceases to be bleached when all the cerium is precipitated. In putting this method for the precipitation of cerium into practice, zinc oxide, magnesia, calcium carbonate, and sodium carbonate have all been used as neutralising agents. Of these, the last is probably the best to employ:—

$$3Ce(NO_3)_3 + KMnO_4 + 4Na_2CO_3 + 8H_2O$$
$$= 3Ce(OH)_4 + MnO_2.2H_2O + 8NaNO_3 + KNO_3 + 4CO_2.$$

In order to use this method for the separation of cerium from the rare earths, a neutral solution of the rare earth nitrates should be prepared, containing the cerium as cerous nitrate. The solution is heated to boiling, and potassium permanganate solution added in small quantities at a time until the red colour just begins to be permanent. At this point the precipitant is changed for a solution of permanganate to which has been added sodium carbonate in the exact ratio $KMnO_4 : 4Na_2CO_3$. This solution is added very slowly to the nearly boiling nitrate solution. A faint colour of permanganate should be maintained all the time, a little pure permanganate being added if at any time the colour is bleached. When the cerium is nearly all precipitated, the colour disappears more slowly after each addition of precipitant, and the effervescence is less noticeable. The acidity of the solution is then tested from time to time with litmus paper, and small amounts of the permanganate-carbonate mixture or pure carbonate are added until the solution is nearly neutral to litmus and still pink with permanganate. The whole is heated, stirred for ten minutes and filtered hot, the precipitate being washed thoroughly with boiling water. The precipitate is practically free from other rare earths, but it should be dissolved in hot concentrated hydrochloric acid, diluted and precipitated with oxalic acid, the cerium oxalate converted into cerous nitrate, and the entire process repeated. The cerium is then free from other rare earths, but must be separated from manganese.[2]

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[1] Winkler, *J. prakt. Chem.*, 1865, 95, 410; Stolba, *Jahresber.*, 1878, p. 1059; Drossbach, *Ber.*, 1896, 29, 2452; *D.R.P.*, 143,106 (1903); Muthmann and Rölig, *Ber.*, 1898, 31, 1718; Muthmann and Weiss, *Annalen*, 1904, 331, 1; Böhm, *Zeitsch. angew. Chem.*, 1903, 16, 1129; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1903, 37, 378; R. J. Meyer and Schweitzer, *Zeitsch. anorg. Chem.*, 1907, 54, 104; Esposito, *Proc. Chem. Soc.*, 1907, 23, 64; James, *J. Amer. Chem. Soc.*, 1908, 30, 982; Roberts, *Amer. J. Sci.*, 1911, [iv.], 31, 350; *Chem. News*, 1911, 103, 303.

[2] The procedure here described is due to Roberts (*loc. cit.*).

The filtrate from the cerium precipitate contains a trace of cerium unless it has been made quite neutral. This trace may be removed, together with a little of the other earths, by heating with a little permanganate-carbonate solution containing more than four molecular proportions of carbonate per molecule of permanganate.

(iv.) **Mosander's Chlorine Method.**[1]—In this process the mixed chlorides are precipitated as hydroxides, the latter suspended in excess of sodium hydroxide, and a stream of chlorine passed into the cold suspension until the liquid is saturated. Cerium is left as insoluble ceric hydroxide; the other rare earths pass into solution as chlorides, the solution of the lanthana being effected much more rapidly than that of the "didymia."[2] The precipitate is thoroughly washed, dissolved in hydrochloric acid, and the process repeated. Six or seven repetitions of the alkali and chlorine treatment are required, so that the process is very tedious, and, unless the liquid is boiled for some minutes at the end of each chlorine treatment, a little cerium is found in the solution. Instead of chlorine, excess of bromine may be added and the whole heated until the excess has been removed (Browning and Roberts).

Owing to the difficulty of removing the last traces of impurities from the cerium by this method, it is advisable to use it for the isolation of nearly pure ceric hydroxide and continue the purification by other methods, *e.g.* (i.) or (v.).

(v.) **The Ceric Ammonium Nitrate Method.**[3]—Ceric nitrate forms with ammonium nitrate an orange-yellow beautifully crystalline double salt, $Ce(NO_3)_4.2(NH_4)NO_3$, which is only sparingly soluble in nitric acid. It is of a different type from, and is not isomorphous with, the double ammonium nitrates of the other rare earth elements. Owing to the nature of this salt, it is easy to remove the bulk of the cerium from a mixture of crude cerium earths as ceric ammonium nitrate, and to continue the purification of the cerium salt thus obtained. The following procedure is perhaps the most convenient for commencing to work up large quantities of crude cerium earths in the laboratory, since it allows the greater part of the cerium to be separated rapidly in a small volume of solution.

The mixed oxalates are calcined and the oxides obtained dissolved in two or three times their weight of concentrated nitric acid. Assuming that ceria constitutes one-half of the oxides, the requisite amount of ammonium nitrate to form ceric ammonium nitrate is added. The finely-divided ammonium salt may be stirred into a hot solution of the nitrates or added in the form of a concentrated aqueous solution. On cooling, the bulk of the

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[1] Mosander, *Phil. Mag.*, 1843, [iii.], **23**, 241; *Ann. Chim. Phys.*, 1844, [ii.], **11**, 464; *Pogg. Annalen*, 1843, **60**, 297; Watts, *Quart. J. Chem. Soc.*, 1850, **2**, 140; Jolin, *Bull. Soc. chim.*, 1874, [ii.], **21**, 533; Hartley, *Trans. Chem. Soc.*, 1882, **41**, 202; Dennis and Magee, *J. Amer. Chem. Soc.*, 1894, **16**, 649; Mengel, *Zeitsch. anorg. Chem.*, 1899, **19**, 67; Pollok and Leonard, *Sci. Proc. Roy. Dubl. Soc.*, 1908, **11**, 257; Hauser and Wirth, *Zeitsch. anal. Chem.*, 1909, **48**, 679; Neish, *J. Amer. Chem. Soc.*, 1909, **31**, 517; Browning and Roberts, *Amer. J. Sci.*, 1910, [iv.], **29**, 45; *cf.* Popp, *Annalen*, 1864, **131**, 359; Erk, *Zeitsch. für Chem.*, 1870, [ii.], **7**, 100.

[2] See Hauser and Wirth, *loc. cit.*; Browning, *Compt. rend.*, 1914, **158**, 1679; *Chem. News*, 1914, **110**, 49. The fact that the hydroxide of lanthanum passes into solution more rapidly than the hydroxide of "didymium" is of some practical interest.

[3] Auer von Welsbach, *Monatsh.*, 1884, **5**, 508; *Sitzungsber. K. Akad. Wiss. Wien*, 1884, **90**, ii., 337; Schottländer, *Ber.*, 1892, **25**, 378; see also Meyer and Marckwald, *Ber.*, 1900, **33**, 3003; Muthmann and Rölig, *Ber.*, 1898, **31**, 1718; Job, *Ann. Chim. Phys.*, 1900; [vii.], **20**, 205; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1903, **37**, 378; Böhm, *Zeitsch. angew. Chem.*, 1902, **15**, 372; Drossbach, *Ber.*, 1900, **33**, 3506.

cerium crystallises out from the solution. The precipitated salt is collected on an asbestos filter and washed with concentrated nitric acid.

The crude ceric ammonium nitrate may contain some five per cent. of impurities. It is divided into several batches; the first is recrystallised from hot nitric acid (3 of acid to 2 of water), the second recrystallised from the mother liquor from the first, and so on. Several crops of nearly pure ceric ammonium nitrate are thus obtained.[1]

(vi.) **Miscellaneous.**—Several other methods have been proposed for separating cerium from the other rare earth elements, *e.g.* precipitation as ceric valerianate,[2] fractional solution of the oxides in dilute nitric acid[3] or boiling aqueous ammonium chloride,[4] fusion of the nitrates with excess of potassium nitrate[5] at 330–350°, fractional decomposition of the chromates,[6] solubility of ceric oxalate in ammonium oxalate,[7] etc.[8]

The Preparation of Pure Ceria.—(i.) *From Basic Ceric Nitrate-Sulphate.*—The washed precipitate is dissolved in concentrated nitric acid, the solution evaporated on the steam-bath to the consistency of a very thick syrup, cooled, dissolved in cold water, and the liquid boiled for 10–15 minutes —that is to say, the precipitate is purified by a process identical with that by which it was produced (p. 333), the addition of ammonium sulphate, however, being unnecessary. According to Sterba, four precipitations as basic nitrate-sulphate are sufficient to eliminate the last traces of other rare earths from ceria, starting with the crude monazite or cerite earths from which thoria has been removed.

The preceding method also serves for the elimination of the impurities from basic ceric sulphate obtained by the persulphate method. It will, moreover, answer for the purification of ceria obtained by the permanganate method (p. 335), for which purpose the ceric hydroxide is dissolved out of the precipitate by strong nitric acid, which leaves the hydrated manganese dioxide undissolved. In the first precipitation of the basic ceric nitrate-sulphate, however, the requisite ammonium sulphate must be added.

With careful working, the preceding method of purification gives an excellent yield of pure product.

(ii.) *From Ceric Ammonium Nitrate.*—The salt is recrystallised from nitric acid four or five times. The method already outlined is a very economical one for the purpose.

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[1] The combined filtrates may be treated in various ways. A convenient method is to evaporate them on the steam bath to a thick syrup and precipitate the remaining ceric salt as basic ceric nitrate-sulphate (p. 332). Little cerium then remains in the filtrate; it may be removed by the permanganate method (p. 335), or by any other convenient process (see, *e.g.*, Böhm, *Zeitsch. angew. Chem.*, 1902, **15**, 372).

[2] Buonaparte, *Compt. rend.*, 1843, **16**, 1008.

[3] Mosander, *Phil. Mag.*, 1843, [iii.], **23**, 241; Scheerer, *Pogg. Annalen*, 1842, **56**, 482; Marignac, *Ann. Chim. Phys.*, 1849, [iii.], **27**, 209; Zschiesche, *J. prakt. Chem.*, 1869, **107**, 65; Frerichs and Smith, *Annalen*, 1878, **191**, 331; *cf.* Gibbs, *Amer. J. Sci.*, 1864, [ii.], **37**, 352.

[4] Watts, *Q. J. Chem. Soc.*, 1849, **2**, 140; Esposito, *Proc. Chem. Soc.*, 1906, **22**, 20.

[5] Debray's Method: Debray, *Compt. rend.*, 1883, **96**, 828, *Chem. News*, 1883, **47**, 199; Dennis and Magee, *J. Amer. Chem. Soc.*, 1894, **16**, 649; Schützenberger, *Compt. rend.*, 1895, **120**, 663, 962; Schützenberger and Boudouard, *ibid.*, 1897, **124**, 481; Boudouard, *ibid.*, 1897, **125**, 772, 1096; Wyrouboff and Verneuil, *loc. cit.*; Esposito, *Proc. Chem. Soc.*, 1906, **22**, 20; *cf.* Czudnowicz, *J. prakt. Chem.*, 1860, **80**, 16; Gibbs, *loc. cit.*

[6] Pattison and Clarke, *Chem. News*, 1867, **16**, 259; *cf.* Esposito, *loc. cit.*

[7] Orloff, *Chem. Zeit.*, 1906, **30**, 733; 1907, **31**, 562.

[8] Koppel, *Zeitsch. anorg. Chem.*, 1898, **18**, 305; Drossbach, *Ber.*, 1900, **33**, 3506; Chavastelon, *Compt. rend.*, 1900, **130**, 781.

This method is also an excellent one for preparing pure ceria, and may obviously be applied to the purification of the precipitates obtained by Mosander's and the permanganate method.

(iii.) *From Basic Ceric Nitrate-bromate.*—The precipitate is dissolved in concentrated nitric acid by the aid of a *very little* alcohol, the solution diluted with water and boiled after the introduction of some lump marble. The precipitate is washed with ammonium nitrate, converted into anhydrous cerous sulphate, and the latter dissolved in ice-cold water. Hydrated cerous sulphate is then crystallised out by warming the solution to 30°–40°. Traces of other rare earth sulphates may readily be eliminated in this manner, since cerous sulphate is not isomorphous with them.

Traces of thorium may be eliminated by the recrystallisation of cerous sulphate, but where a solution of ceric nitrate or ceric ammonium nitrate is available, it is preferable to reduce with hydrogen peroxide to the cerous state and eliminate the thorium with hydrogen peroxide from a hot, neutral (or feebly acid) solution (p. 320).

A cerous salt in concentrated aqueous solution should show no trace of the absorption spectrum of "didymium" when examined through a very thick layer (10–20 cms.), and the residual oxide obtained by the ignition of the oxalate, nitrate, double nitrate, or sulphate (at a white heat), should have a pale yellow colour when cold, entirely free from any suggestion of a salmon, red or brown tint.[1]

PRELIMINARY SEPARATION OF THE RARE EARTH ELEMENTS INTO GROUPS.

In commencing the fractionation of the rare earths obtained from a mineral, the procedure employed depends upon the relative amounts of the rare earths present. Two cases present themselves—(i.) the *cerium group* is present to a much greater extent than the *yttrium group*, and (ii.) vice versa. In the first case the predominating element is *cerium*; in the second it is *yttrium*. The *terbium group* never seems to predominate.

Potassium sulphate is the classic reagent for effecting a *separation of the cerium and yttrium groups.*[2] The double sulphates of potassium and the rare earth elements may be classified according to their solubility in a cold saturated solution of potassium sulphate as follows:—

(*a*) Those practically insoluble (La, Ce, Pr, Nd).

(*b*) Those sparingly soluble (Sm, Eu, Gd, Tb).

(*c*) Those more readily soluble in that solution than in pure water (Dy, Y, Er, Tm, Yb, Lu, Ct).

It might therefore be anticipated that a sharp separation of the cerium and yttrium groups could be effected by shaking a cold solution of the sulphates with potassium sulphate in excess; and that the bulk of the terbium group would accompany the cerium group. Such, however, is not the case. The precipitated double sulphates are found to be contaminated with a certain quantity of the yttrium group. Further, the filtrate is found

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[1] On the preparation of pure ceria, see especially Sterba, *Ann. Chim. Phys.*, 1904, [viii.], **2**, 193; Wyrouboff and Verneuil, *ibid.*, 1906 [viii.], **9**, 333; Drossbach, *Ber.*, 1900, **33**, 3506; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1903, **37**, 378; Brauner and Batěk, *ibid.*, 1903, **34**, 103; Brauner, *ibid.*, 1903, **34**, 207; Neish, *J. Amer. Chem. Soc.*, 1909, **31**, 517.

[2] Klaproth, *Ann. Chim.*, 1803, [i.], **49**, 256; Berzelius and Hisinger, *ibid.*, 1803, [i.], **50**, 245; Berzelius and Gahn, *Schweigger's J.*, 1814, **16**, 250, 404; Berlin, *Pogg. Annalen*, 1834, **43**, 105; Mosander, *Phil. Mag.*, 1843, [iii.], **25**, 241.

to retain a considerable portion of the terbium and appreciable quantities of the cerium group, particularly neodymium[1] and samarium salts; for the double sulphates of the latter elements are appreciably soluble in the presence of much yttrium sulphate, and, in addition to the solubilities of the double sulphates of the terbium group being augmented, these double salts are only slowly formed.

The double sulphate separation, then, can only be regarded as a process of fractionation. It may conveniently be carried out by adding finely-divided potassium sulphate continuously to a cold dilute solution of the nitrates, chlorides, or sulphates contained in a tall vessel and vigorously stirred by a water-turbine;[2] or a hot saturated solution of potassium sulphate may be stirred into a cold solution of the rare earth salts.[3] The whole is allowed to stand, with occasional shaking, until the presence of "didymium" in the liquid (as indicated by its absorption-spectrum) can scarcely be detected. The precipitate is then filtered off and washed with a cold saturated solution of potassium sulphate. The earths in the filtrate are then precipitated either as hydroxides or oxalates.

Instead of using potassium sulphate, the more soluble **sodium sulphate** has been used, and, indeed, is said to be preferable.[4] The finely-powdered solid is stirred into a ten per cent. solution of the rare earth chlorides, nitrates, or sulphates. Care must be taken, however, not to add an unduly large excess of sodium sulphate owing to the possibility of thereby precipitating yttrium as the double sulphate.[5]

The preceding method is not very satisfactory when the cerium group predominates very largely over the yttrium group, *e.g.* with the monazite earths, and one of the following alternative processes may be adopted: (*a*) The potassium sulphate method is used, but the precipitant is added slowly, and in quantity insufficient to precipitate all the cerium group. By leaving a considerable amount of the neodymium in the solution, practically none of the metals of the terbium and yttrium groups are precipitated. The earths in the filtrate are precipitated as oxalates, converted into double magnesium nitrates, and fractionated from dilute nitric acid until the final mother liquor refuses to crystallise. The crystals contain the cerium group up to neodymium; the mother liquor contains samarium and the terbium and yttrium groups. The further treatment of this liquor may be carried out according to the procedure described later for working up the final fractions (δ) of the double magnesium nitrates (see p. 349).[6] (*b*) The entire material may be fractionated by the double magnesium nitrate method, the terbium and yttrium groups rapidly concentrating in the most soluble fractions. (*c*) A solution of the sulphates is prepared, a considerable excess of sulphuric acid added, and the liquid warmed slightly. The bulk of the cerium group is thus precipitated as sulphates. The filtrate is partly

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[1] Boudouard, *Compt. rend.*, 1898, **126**, 900; *Bull. Soc. chim.*, 1898, [iii.], **19**, 382; Urbain, *Bull. Soc. chim.*, 1898, [iii.], **19**, 381; *Ann. Chim. Phys.*, 1900, [vii.], **19**, 251.

[2] Dennis and Chamot, *J. Amer. Chem. Soc.*, 1897, **19**, 799.

[3] For modifications of the process, see Bettendorf, *Annalen*, 1891, **263**, 164; Marignac, *Ann. Chim. Phys.*, 1880, [v.], **20**, 535; Muthmann and Rölig, *Ber.*, 1898, **31**, 1718; Lecoq de Boisbaudran, *Compt. rend.*, 1886, **102**, 902, 1003.

[4] Gibbs, *Amer. J. Sci.*, 1864, [ii.], **37**, 354; Delafontaine, *Compt. rend.*, 1881, **93**, 63; Smith, *Amer. Chem. J.*, 1883, **5**, 44, 73; Drossbach, *Ber.*, 1896, **29**, 2452; 1900, **33**, 3506; James, *J. Amer. Chem. Soc.*, 1908, **30**, 979; 1912, **34**, 757.

[5] See p. 433 and fig. 42.

[6] James, *J. Amer. Chem. Soc.*, 1913, **35**, 235.

neutralised with sodium hydroxide. The remainder of the cerium and part of the terbium group are thereby separated as double sulphates.[1] (*d*) The double carbonate method given later (p. 342) is applied in order to precipitate the bulk of the cerium group, the yttrium and terbium groups remaining in solution.[2]

When the yttrium group largely predominates in a mixture of rare earths, as, for example, in the earths extracted from xenotime or gadolinite, Urbain strongly recommends the fractionation of the **ethylsulphates** as being the best method for commencing the separation.[3] The ethylsulphates should be methodically separated into twenty fractions and then submitted to sixty series of crystallisations. The separation does not occur in serial order. The neodymium salt separates first. The lanthanum salt, the most soluble in the cerium group, is approximately equal in solubility to the gadolinium salt. From gadolinium onwards the serial order holds good. Accordingly, after the fractionation has been carried to the degree just mentioned, the head fractions are examined for lanthanum,[4] and all fractions containing that element are removed. They contain the cerium group, europium, gadolinium, and terbium, and their subsequent fractionation is commenced by the double magnesium nitrate method. The remaining fractions consist essentially of yttrium ethylsulphate, the least soluble containing in addition terbium, dysprosium, and holmium, and the most soluble erbium, thulium, ytterbium, and lutecium.

According to Urbain, the preceding method of fractionation also constitutes the best as yet available for effecting the *separation of the terbium and yttrium groups.* For this purpose the ethylsulphate fractions remaining after the removal of those containing lanthanum are submitted to further series of fractionations. The more soluble fractions may be set aside as soon as the rare earths extracted from them exhibit a pure white or pale pink tint entirely free from any trace of an orange tint. In this manner the yttrium group may be completely freed from the terbium group.[5] An excellent alternative is the fractional crystallisation of the **bromates** (see pp. 348, 351, 355–6).

There are two methods, resembling one another closely, whereby a reasonably sharp separation of lanthanum, cerium, praseodymium, and neodymium from samarium, europium, gadolinium, etc., can be quickly effected. The first consists in fractionally crystallising the **double magnesium nitrates** of the type $2M(NO_3)_3.3Mg(NO_3)_2.24H_2O$ from nitric acid of density 1·3, and

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[1] Drossbach, *Ber.*, 1896, **29**, 2452; *Chem. News*, 1896, **74**, 274.

[2] Drossbach, *Ber.*, 1900, **33**, 3506.

[3] Urbain, *Compt. rend.*, 1898, **126**, 835; *Bull. Soc. chim.*, 1898, [iii.], **19**, 376; *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184; 1909, [viii.], **18**, 274; *J. Chim. phys.*, 1906, **4**, 55.

[4] By means of their spark spectra.

[5] The preparation of the ethylsulphates is described elsewhere (p. 278). It is extremely important that the solutions should be free from acid. In fractionating, the solutions should never be heated any more than is necessary, since the salts are liable to hydrolyse to a considerable extent—an occurrence which may be recognised by solutions originally neutral becoming acid. The small amounts of sulphates that may thus be produced in solution are easily reconverted into ethylsulphates by double decomposition with barium ethylsulphate. The crystals formed in one fraction are dissolved in the mother liquor from the preceding fraction by vigorous shaking, and heat is only applied when very little solid remains undissolved. The crystals deposited in any operation of crystallisation should occupy about one-third the total volume of crystals plus liquid. The final mother liquors should be allowed to evaporate spontaneously in a shallow vessel. By keeping to these conditions it is never necessary to raise the temperature above 60° (Urbain, *J. Chim. phys.*, 1906, **4**, 58).

is known as *Demarçay's Method*;[1] the second, due to Lacombe, consists in fractionally crystallising the **double manganese nitrates** in a similar manner.[2] These double salts separate in serial order, and it will be seen from an inspection of the table of solubilities (p. 269) that in passing from neodymium to samarium there is a large increase in solubility. By either of the preceding methods samarium, europium, etc., rapidly concentrate in the most soluble fractions, which acquire an orange colour and show the principal absorption bands of samarium.

The methods of Demarçay and Lacombe may be regarded as methods for *separating the cerium and terbium groups*, although samarium, which is always classed with cerium, accompanies the terbium group of elements; they have other uses, however, as will be seen later.[3]

THE SEPARATION OF LANTHANUM, PRASEODYMIUM, AND NEODYMIUM.

In order to accomplish this separation, recourse must be had to methods of fractional crystallisation. The separation of praseodymia from neodymia by methods depending on differences of basicity seems to be almost impossible to effect.

The method by which lanthanum and "didymium" were first separated was a crystallisation process, utilising the sulphates for the purpose, but the early workers never carried out the separation in a sufficiently prolonged and systematic manner to resolve the "didymium" into its components. Subsequently, the method gave place to a basic one, namely, fractional precipitation with ammonia, and thus it happened that the separation of samarium from "didymium" preceded by some six years the discovery of praseodymium and neodymium.

A. **Separation by Fractional Crystallisation.**—The following salts have been utilised for the purpose:—

(i.) Nitrates,[4] $M(NO_3)_3.5H_2O$.
(ii.) Double ammonium nitrates,[5] $M(NO_3)_3.2(NH_4)NO_3.4H_2O$.
(iii.) Double sodium nitrates,[6] $M(NO_3)_3.2NaNO_3.xH_2O$.
(iv.) Double magnesium nitrates,[7] $2M(NO_3)_2.3Mg(NO_3)_2.24H_2O$.
(v.) Double manganese nitrates,[8] $2M(NO_3)_3.3Mn(NO_3)_2.24H_2O$.
(vi.) Chlorides,[9] $MCl_3.6$ or $7H_2O$.

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[1] Demarçay, *Compt. rend.*, 1900, 130, 1019, 1185.

[2] Lacombe, *Bull. Soc. chim.*, 1904, [iii.], 31, 570; *Chem. News*, 1904, 89, 277.

[3] For the utility of the **dimethylphosphates**, see J. C. Morgan and C. James, *J. Amer. Chem. Soc.*, 1914, 36, 10. Fractional precipitation of the **formates** and **lactates** in acetone solution has been suggested by Barnebey, *ibid.*, 1912, 34, 1174.

[4] Demarçay, *Compt. rend.*, 1896, 122, 728; 1900, 130, 1019; Feit and Przibylla, *Zeitsch. anorg. Chem.*, 1905, 43, 202; Baxter and Chapin, *J. Amer. Chem. Soc.*, 1911, 33, 1.

[5] Mendeléeff, *J. Russ. Chem. Soc.*, 1873; *Annalen*, 1873, 168, 45; Auer von Welsbach, *Monatsh.*, 1885, 6, 477: *Sitzungsber. K. Akad. Wiss. Wien*, 1903, 112, ii., A, 1037; von Scheele, *Ber.*, 1899, 32, 409; Dennis and Chamot, *J. Amer. Chem. Soc.*, 1897, 19, 799; Baxter and Chapin, *ibid.*, 1911, 33, 1; Baxter and Stewart, *ibid.*, 1915, 37, 516; Schottländer, *Ber.*, 1892, 25, 378, 569.

[6] Auer von Welsbach, *loc. cit.*; von Scheele, *loc. cit.*

[7] Demarçay, *Compt. rend.*, 1900, 130, 1019, 1185; Drossbach, *Ber.*, 1902, 35, 2826; Muthmann and Weiss, *Annalen*, 1904, 331, 1; Feit and Przibylla, *Zeitsch. anorg. Chem.*, 1905, 43, 202.

[8] Lacombe, *Bull. Soc. chim.*, 1904, [iii.], 31, 570; *Chem. News*, 1904, 89, 277.

[9] Baskerville and Stevenson, *J. Amer. Chem. Soc.*, 1904, 26, 54.

(vii.) Sulphates,[1] $M_2(SO_4)_3.xH_2O$.
(viii.) Ethylsulphates,[2] $M(C_2H_5.SO_4)_3.9H_2O$.
(ix.) Bromates,[3] $M(Bro_3)_3.9H_2O$.
(x.) Oxalates,[4] $M_2(C_2O_4)_3.xH_2O$.
(xi.) Metanitrobenzenesulphonates,[5] $M[C_6H_4(NO_2)SO_3]_3.6H_2O$.
(xii.) Double potassium carbonates,[6] $K_2CO_3.M_2(CO_3)_3.12H_2O$.
(xiii.) Picrates,[7] $M[C_6H_2(NO_2)_3O]_3$.

The double nitrates, sulphates, ethylsulphates, bromates, picrates, and metanitrobenzenesulphonates may be crystallised from water, but the double ammonium, sodium, and manganese nitrates are best crystallised from strong nitric acid, in which they are much less soluble than in water. The chlorides are crystallised from concentrated hydrochloric acid, the oxalates from dilute nitric acid, and the double carbonates from aqueous potassium carbonate.

The sulphates must be dehydrated, dissolved in ice-cold water, and crystallised by warming the solution to 30°–40°. The double carbonate method is carried out as follows:—A 20 per cent. solution of the chlorides is poured drop by drop into excess of 50 per cent. potassium carbonate, whereby a solution of the double carbonates in potassium carbonate is obtained.[8] The double salts are fractionally precipitated by successive additions of water; they separate slowly, and readily form supersaturated solutions. The oxalates may be suspended in water, the latter heated to boiling, and nitric acid added with vigorous shaking until complete solution is effected. The liquid is then rapidly cooled, being agitated throughout the process. Another method is to acidify strongly a solution of the nitrates with nitric acid, and drop oxalic acid solution into the nearly boiling nitrate solution until the precipitate that first forms no longer redissolves. The liquid is then cooled as before.

The order of separation is as follows, the least soluble being placed first:—

Double nitrates	La, (Ce), Pr, Nd ;	Metanitrobenzenesulphonates	La, (Ce), Pr, Nd.
Ethylsulphates	Nd, Pr, La ;	Oxalates	"Di," La.
Bromates	Nd, Pr, La ;	Sulphates	La, Nd, Pr.
Nitrates	Nd, Pr, (Ce), La ;	Double carbonates	La, Pr, (Ce), Nd.

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[1] Muthmann and Rölig, *Ber.*, 1898, **31**, 1718 ; *cf.* Mosander, *Phil. Mag.*, 1843, [iii.], **23**, 241 ; *Ann. Chim. Phys.*, 1844, [iii.], **11**, 464 ; *Pogg. Annalen*, 1843, **60**, 297 ; Marignac, *Ann. Chim. Phys.*, 1849, [iii.], **27**, 209; 1853, [iii.], **38**, 148; Watts, *Q. J. Chem. Soc.*, 1850, **2**, 140 ; Holzmann, *J. prakt. Chem.*, 1858, **75**, 321 ; Czudnowicz, *ibid.*, 1860, **80**, 31 ; Bunsen, *Pogg. Annalen*, 1875, **155**, 230, 366 ; Hillebrand and Norton, *ibid.*, 1875, **156**, 466 ; Frerichs, *Ber.*, 1874, **7**, 798 ; Frerichs and Smith, *Annalen*, 1878, **191**, 331.

[2] Urbain, *Compt. rend.*, 1898, **126**, 835 ; *Bull. Soc. chim.*, 1898, [iii.], **19**, 376 ; *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184.

[3] James, *J. Amer. Chem. Soc.*, 1908, **30**, 182, 979 ; 1909, **31**, 913 ; 1912, **34**, 757.

[4] Mosander, *loc. cit.*; Marignac, *loc. cit.*; Bunsen, *loc. cit.*; Zschiesche, *J. prakt. Chem.*, 1869, **107**, 65 ; Brauner, *Trans. Chem. Soc.*, 1882, **41**, 68 ; 1898, **73**, 951 ; *Monatsh.*, 1882, **3**, 1 ; Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 226.

[5] Holmberg, *Zeitsch. anorg. Chem.*, 1907, **53**, 83 ; *Bihang K. Svenska Vet.-Akad. Handl.*, 1902–3, **28**, ii., No. 5 ; Garnier, *Arch. Sci. phys. nat.*, 1915, [vi.], **40**, 93, 199.

[6] Hiller, *Inaugural Dissertation* (Berlin, 1904) ; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1904, **41**, 97 ; *cf.* Drossbach, *Ber.*, 1900, **33**, 3506.

[7] Dennis and Rhodes, *J. Amer. Chem. Soc.*, 1915, **37**, 807 ; *cf.* Dennis and Bennett, *ibid.*, 1912, **34**, 7.

[8] One hundred grams of rare earths require about 1250 grams of the carbonate solution.

B. **Other Methods of Separation.** — The following are among the more important of these processes:—

(i.) *Fractional Precipitation with Ammonia,*[1] *Sodium Hydroxide,*[2] *or Magnesia.*[3]—By the gradual addition of magnesia to a boiling solution of the nitrates until the filtrate no longer exhibits the absorption spectrum of "didymium," a solution can be rapidly obtained containing lanthanum quite free from "didymium." The yield, however, is very poor.

(ii.) *Auer von Welsbach's Oxide Method.*—By this process a fairly rapid separation of lanthanum and "didymium" is obtained. It is founded on the fact that lanthana is a stronger base than "didymia." One hundred grms. of mixed oxides are dissolved in the minimum of nitric acid, and the solution diluted to 800 c.c.; another 100 grms. of oxide are stirred up with 100 c.c. of water and poured into the nitrate solution. Chemical change soon commences and the mass becomes warm; it is then heated on the steam-bath, with frequent shaking and stirring for some time, diluted to 1400 c.c., and allowed to stand for twelve hours. The precipitate is filtered and washed with water. It contains the greater part of the "didymium," most of the lanthanum being in the filtrate. In subsequent fractionation more than half the earths should be left as nitrates at the lanthanum end and less than half at the "didymium" end.[4]

(iii.) *Decomposition of the Nitrates.*[5]—The mixed nitrates are mixed with excess of potassium and sodium nitrates, and heated to 420°–460° until part of the rare earth nitrates have been decomposed. The mass is then extracted with water, when a residue of basic "didymium" nitrate, practically free from lanthanum, is obtained. If the aqueous extract is pink, it is evaporated to dryness and the fusion repeated, until eventually a practically colourless filtrate is obtained. Separation into crude lanthana and crude "didymia" may be rapidly effected in this manner, but pure lanthana cannot be thus obtained.

(iv.) *Fractional Precipitation of the Chromates.*[6]—The oxides are dissolved in chromic acid and precipitated in dilute boiling solution with potassium chromate. The order of precipitation is Ce, La, Pr, Nd, Sm.

(v.) *Electrolysis of Aqueous Salt Solutions.*[7]—When an aqueous solution of the chlorides or nitrates of the rare earth elements is electrolysed, a precipitate of mixed hydroxides appears at the cathode. By removing this precipitate from time to time, a fractionation of the rare earths in the order of their basic strengths may be effected, the weakest base precipitating first.

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[1] Marignac, *Ann. Chim. Phys.*, 1853, [iii.], **38**, 148; Hermann, *J. prakt. Chem.*, 1861, **82**, 385; Erk, *Jahresber.*, 1870, p. 319; Cleve, *Bull. Soc. chim.*, 1874, [ii.], **21**, 196, 246; 1883, [ii.], **39**, 151, 289; 1885, [ii.], **43**, 359; Brauner, *Monatsh.*, 1882, **3**, 1, 486; *Trans. Chem. Soc.*, 1882, **41**, 68; 1883, **43**, 278; Frerichs and Smith, *Annalen*, 1878, **191**, 331.

[2] Drossbach, *Ber.*, 1896, **29**, 2452; *Chem. News*, 1896, **74**, 274; Brauner and Pavlíček, *Trans. Chem. Soc.*, 1902, **81**, 1243.

[3] Muthmann and Rölig, *Ber.*, 1898, **31**, 1718; R. J. Meyer and Marckwald, *Ber.*, 1900, **33**, 3003.

[4] Auer von Welsbach, *Monatsh* , 1883, **4**, 630; 1884, **5**, 1, 508; Schottländer, *Ber.*, 1892, **25**, 378, 569.

[5] Damour and Deville, *Compt. rend.*, 1864, **59**, 270; *Bull. Soc. chim.*, 1864, [ii.], **2**, 339; Bettendorf, *Annalen*, 1890, **256**, 159; Schützenberger, *Compt. rend.*, 1895, **120**, 1143; Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 225; Brauner and Pavlíček, *loc. cit.*

[6] Böhm, *Zeitsch. angew. Chem.*, 1902, **15**, 1282.

[7] Dennis and Lemon, *J. Amer. Chem. Soc.*, 1915, **37**, 131; Dennis, *U.S.A. Pat.*, No. 1,115,513.

This method gives a rapid separation of lanthanum from praseodymium or "didymium." It is convenient to use a solution of the nitrates contained in a tall jar, at the bottom of which a layer of mercury, kept in constant agitation by means of a stream of air, serves as the cathode; a platinum wire may be used as anode. The current should be adjusted so as to obtain a suitable rate of precipitation.

(vi.) *Miscellaneous.*[1]

C. **General Method of Procedure.**—The separation of lanthanum, praseodymium, and neodymium is best effected in a series of stages by the fractionation of the double nitrates. The procedures recommended by Urbain and by James are practically identical.[2] Thoria and ceria should have been eliminated, and also the greater part of the earths of the yttrium group. The earths to be fractionated (prepared from the oxalates by ignition) are dissolved in the minimum of nitric acid, an equal amount of nitric acid is neutralised by magnesia, the two solutions mixed and evaporated until small crystals form when a current of cold air is blown on the surface. A little water is sprayed on the surface, and the whole allowed to stand for twenty-four hours. An initial separation into crystals and mother liquor is thus effected. The further fractionation is then carried on, using water for solvent, as has been previously described (p. 323).

The most soluble fractions rapidly undergo change, developing a yellow colour and showing the absorption spectrum of samarium. All the erbium and yttrium salts present also concentrate into these soluble fractions. The fractionation of the double magnesium salts is continued until spectroscopic examination indicates that the soluble samarium fractions are nearly free from neodymium; a result that is brought about comparatively rapidly. After fractionation has been carried out for some time, it usually happens that the final mother liquors crystallise with great difficulty, owing to the accumulation of soluble impurities in them. The solutions are then diluted, the rare earths precipitated with oxalic acid, washed, reconverted into the double magnesium nitrates, and the fractionation continued. When the purified, very soluble, double nitrates again refuse to crystallise, it is due to the accumulation of the simple nitrates of the yttrium group in the final liquors. The further treatment of these soluble fractions is described later (p. 349).

In a comparatively short time a practically complete separation of neodymium from samarium may be effected, and the fractions classified according to their composition into four groups, which, commencing with the least soluble, are as follows:—(α) Crude lanthanum and praseodymium salts, the separation of lanthanum from praseodymium not having proceeded very far; (β) praseodymium and neodymium salts (*i.e.* "didymium" salts); (γ) crude neodymium salt; and (δ) samarium, europium, and gadolinium magnesium nitrates together with the simple nitrates of terbium, dysprosium,

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[1] See Marignac, *Ann. Chim. Phys.*, 1849, [iii.], **27**, 209; 1853, [iii.], **38**, 148; Rammelsberg, *Pogg. Annalen*, 1859, **107**, 631; Berlin, *Inaugural Dissertation* (Göttingen, 1864); Frerichs, *Ber.*, 1874, **7**, 798; Frerichs and Smith, *Annalen*, 1878, **191**, 331; Brauner, *loc. cit.*; Pettersson, *Zeitsch. anorg. Chem.*, 1893, **4**, 1; von Scheele, *ibid.*, 1898, **17**, 310; Drossbach, *Ber.*, 1902, **35**, 2826; Browning, *Chem. News*, 1914, **110**, 49; *Compt. rend.*, 1914, **158**, 1679; Stoddart and Hill, *J. Amer. Chem. Soc.*, 1911, **33**, 1076; Baskerville and Turrentine, *ibid.*, 1904, **26**, 46.

[2] James, *J. Amer. Chem. Soc.*, 1912, **34**, 757; *cf. ibid.*, 1908, **30**, 979; Urbain, *J. Chim. phys.*, 1906, **4**, 57.

holmium, yttrium. Of the rare earth elements in (δ), all but yttrium are rare in comparison with lanthanum, praseodymium, and neodymium; samarium and gadolinium are the most abundant.

The fractions (α) are now fractionated by Auer von Welsbach's method, for which purpose they are converted into double ammonium nitrates and dissolved in water containing one-tenth their weight of nitric acid. The double nitrates are then methodically fractionated; in each case, after decanting mother liquor from one fraction to the next, the crystals are washed with a little concentrated nitric acid and the washings also added to the next fraction. This is the best general procedure for the preparation of pure **lanthanum** and **praseodymium** material. Fractionation may be carried out from aqueous solution simply, but proceeds more rapidly in the presence of nitric acid.[1]

Each of the fractions (β) is converted into the double manganese nitrates, and the fractionation continued from nitric acid of density 1·3. The greater part of the salt present in a fraction should be separated at each crystallisation, so that each mother liquor is small in volume compared with the volume of the crystals. This procedure is the most rapid yet known for the separation of **praseodymium** from **neodymium**, and enables the fractionation to be continued and pure salts separated at each end until the intermediate fractions are practically insignificant.

The neodymium fractions (γ) are fractionated still further for the preparation of pure **neodymium** salt, any praseodymium still present passing into the least soluble, and any samarium, etc., into the most soluble portions. According to Demarçay, the elimination of samarium from neodymium by this method requires only a few days' work on four fractions. It is even more rapid, for the elimination of both praseodymium and samarium, to convert each of the (γ) fractions into the double manganese nitrates, as with (β).

The further treatment of fractions (δ) is described later (p. 349).[2]

D. **Purification of Lanthanum, Praseodymium, and Neodymium.**—Lanthanum ammonium nitrate may be obtained in a high state of purity by prolonged fractional crystallisation, the last traces of praseodymium salt concentrating in the most soluble fractions. The most rapid method for the elimination of a little praseodymium from a nearly pure lanthanum preparation is said by R. J. Meyer to be the double carbonate method. The following process is recommended by James for the final purification.[3]

The double ammonium nitrate is dissolved in water and precipitated with oxalic acid. The oxalate is heated with concentrated sulphuric acid and thereby converted into the neutral, anhydrous sulphate. The powdered salt is slowly added to ice-cold water till a saturated solution is obtained, after which it is filtered and heated to 32°. The hydrated salt which separates out is washed with hot water, dehydrated, and the crystallisation repeated. The rapid elimination of traces of praseodymium by this method

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[1] This method was the first by means of which praseodymium and neodymium were separated. It is not, however, the best method for that purpose.

[2] Muthmann and Weiss have separated lanthanum, praseodymium, and neodymium very satisfactorily merely by prolonging the fractionation of the double magnesium nitrates; Feit and Przibylla also recommend this process, and propose the addition of cerous magnesium nitrate from time to time to the most soluble fractions, to aid in the separation (*cf.* p. 329).

[3] James, *J. Amer. Chem. Soc.*, 1908, **30**, 979; 1912, **34**, 757.

is due to the fact that lanthanum and praseodymium sulphates are not isomorphous. A pure lanthanum salt yields a pure white oxide, and when converted into the nitrate or chloride and examined through a thick layer of concentrated solution exhibits no trace of the praseodymium absorption bands.

Praseodymium material may be contaminated with lanthanum and neodymium. The last traces of lanthanum are best removed by a process in which they accumulate in the most soluble fractions, *e.g.* crystallisation of the ethylsulphates, bromates, or the simple nitrates.[1] Crystallisation of the oxalates from nitric acid is also a very expeditious method. According to Brauner,[2] pure praseodymium tetroxide, Pr_2O_4, separates when the nitrate is fused with nitre at 400°. The last traces of neodymium may be removed by the prolonged crystallisation of the double ammonium, magnesium or manganese nitrate, or by the double carbonate method (p. 342).

According to Baskerville and Turrentine, pure praseodymium material is readily obtained in one operation from an impure material containing not more than 10 per cent. of lanthanum. The hydroxides are precipitated with ammonia, thoroughly washed till free from ammonia, dissolved in an ice-cold, saturated solution of citric acid, and the solution filtered and heated to 100°. Normal praseodymium citrate separates as an amorphous green powder, which is filtered off and washed with hot water.[3]

Neodymium material is liable to contain praseodymium and samarium. The latter, however, may be eliminated very easily by the crystallisation of the double ammonium, magnesium, or, best of all, manganese nitrates. The complete elimination of praseodymium is a very tedious operation; one of the best methods consists in the fractional crystallisation of the nitrate from concentrated nitric acid, which concentrates the praseodymium salt in the most soluble fractions.[4] Crystallisation of the bromate likewise eliminates the praseodymium in the most soluble fractions. Baskerville and Stevenson recommend fractional precipitation of the chloride from acid solution (by saturation with hydrogen chloride) as a ready means of eliminating lanthanum and praseodymium chlorides[5]; while Holmberg and Garnier purify neodymium material by fractionating the metanitrobenzoate. Strongly ignited neodymium oxide has a beautiful blue colour; several tenths of one per cent. of praseodymia, however, do not affect the colour. The absorption bands in the blue are sharply defined when a neodymium nitrate or chloride solution is free from samarium and praseodymium salt, but are somewhat hazy in the presence of these impurities.

SEPARATION OF SAMARIUM, EUROPIUM, GADOLINIUM, AND TERBIUM.

The double potassium (sodium) sulphates of these elements are slightly, but appreciably, soluble in a saturated solution of potassium (sodium) sulphate, and hence divide themselves between the precipitate and the filtrate when

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[1] From nitric acid; Feit and Przibylla, *Zeitsch. anorg. Chem.*, 1905, **43**, 202.

[2] Brauner, *Proc. Chem. Soc.*, 1898, **14**, 70; 1901, **17**, 66.

[3] Baskerville and Turrentine, *J. Amer. Chem. Soc.*, 1904, **26**, 46; Baskerville, *Zeitsch. anorg. Chem.*, 1905, **45**, 86. The method is adversely criticised by R. J. Meyer (*ibid.*, 1904, **41**, 97). For another method of eliminating La, see Orloff, *Chem. Zeit.*, 1907, **31**, 115.

[4] Baxter and Chapin, *J. Amer. Chem. Soc.*, 1911, **33**, 1.

[5] Baskerville and Stevenson, *J. Amer. Chem. Soc.*, 1904, **26**, 54.

the potassium (sodium) sulphate method is used to effect a separation of the cerium from the yttrium earths. If the sulphate method be applied in such a manner as to separate the cerium double salts in a series of fractions, samarium, europium, gadolinium, and terbium may be concentrated in the final fractions. It was by operating in this manner that Lecoq de Boisbaudran, the discoverer of samarium, was able to concentrate samarium with "didymium," and afterwards separate them by various processes; and a similar method of experimenting led Marignac to the discovery and isolation of gadolinium.[1]

The methods which have been applied to effect the separation of samarium, europium, gadolinium, and terbium from one another or from the elements of the cerium and yttrium groups are as follows:—

A. **Fractional Crystallisation.**—The following salts have been utilised:—

(i.) Formates,[2] $M(O.OC.H)_3.xH_2O$, from water.
(ii.) Oxalates,[3] $M_2(C_2O_4)_3.xH_2O$, from dilute nitric acid.
(iii.) Ethylsulphates,[4] $M(C_2H_5.SO_4)_3.9H_2O$, from water (p. 340).
(iv.) Nitrates,[5] $M(NO_3)_3.5H_2O$, from nitric acid of density 1·3.
(v.) Double magnesium nitrates,[6] $2M(NO_3)_3.3Mg(NO_3)_2.24H_2O$, from nitric acid (1·3).
(vi.) Double manganese nitrates,[7] $2M(NO_3)_3.3Mn(NO_3)_2.24H_2O$, from nitric acid (1·3).
(vii.) Double nickel nitrates,[8] $2M(NO_3)_2.3Ni(NO_3)_2.24H_2O$, from nitric acid (1·3).
(viii.) Picrates,[9] $M[O.C_6H_2(NO_2)_3]_3.xH_2O$, from water.
(ix.) Metanitrobenzenesulphonates,[10] $M[C_6H_4(NO_2).SO_3]_3.xH_2O$, from water.

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[1] Lecoq de Boisbaudran, *Compt. rend.*, 1879, **88**, 322; 1879, **89**, 212; Marignac, *Arch. Sci. phys. nat.*, 1880, [iii.], **3**, 413; *Compt. rend.*, 1880, **90**, 899; *Ann. Chim. Phys.*, 1880, [v.], **20**, 535.

[2] Delafontaine, *Arch. Sci. phys. nat.*, 1877, **59**, 176; 1878, **61**, 273; *Ann. Chim. Phys.*, 1878, [v.], **14**, 238; Marignac, *loc. cit.*; Krüss and Hofmann, *Zeitsch. anorg. Chem.*, 1893, **4**, 27; Feit, *ibid.*, 1905, **43**, 267; Bettendorf, *Annalen*, 1907, **352**, 88; Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184.

[3] Delafontaine, *Arch. Sci. phys. nat.*, 1865, **22**, 30, 38; 1878, **61**, 273; *Ann. Chim. Phys.*, 1878, [v.], **14**, 238; Marignac, *Arch. Sci. phys. nat.*, 1878, **61**, 283; *Ann. Chim. Phys.*, 1878, [v.], **14**, 247.

[4] Urbain, *Bull. Soc. chim.*, 1898, [iii.], **19**, 376; *Compt. rend.*, 1898, **126**, 835; 1904, **139**, 736; 1906, **142**, 785; *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184; *J. Chim. phys.*, 1906, **4**, 334.

[5] Demarçay, *Compt. rend.*, 1896, **122**, 728; 1900, **130**, 1019; Benedicks, *Zeitsch. anorg. Chem.*, 1900, **22**, 393; Urbain, *Compt. rend.*, 1904, **139**, 736; 1909, **149**, 37; Feit and Przibylla, *Zeitsch. anorg. Chem.*, 1905, **43**, 202.

[6] Demarçay, *Compt. rend.*, 1900, **130**, 1019, 1185, 1469; **131**, 343; 1901, **132**, 1484; Urbain and Lacombe, *ibid.*, 1903, **137**, 792; 1904, **138**, 84, 627, 1166; Urbain, *J. Chim. phys.*, 1906, **4**, 31, 105; Muthmann and Weiss, *Annalen*, 1904, **331**, 1; Feit and Przibylla, *loc. cit.*; James and Robinson, *J. Amer. Chem. Soc.*, 1911, **33**, 1363; Holmberg, *vide infra.*

[7] Lacombe, *Bull. Soc. chim.*, 1904, [iii.], **31**, 570; *Chem. News*, 1904, **89**, 277.

[8] Urbain, *Compt. rend.*, 1904, **139**, 736; 1905, **141**, 521; *J. Chim. phys.*, 1906, **4**, 324.

[9] Holmberg, *Bihang K. Svenska Vet.-Akad. Handl.*, 1902–3, **28**, ii., No. 5; *Zeitsch. anorg. Chem.*, 1907, **53**, 83; Dennis and Bennett, *J. Amer. Chem. Soc.*, 1912, **34**, 7; Dennis and Rhodes, *ibid.*, 1915, **37**, 807.

[10] Holmberg, *loc. cit.*

(x.) Bromates,[1] $M(BrO_3)_3.9H_2O$, from water.
(xi.) Dimethylphosphates,[2] $M[(CH_3)_2PO_4]_3.xH_2O$, from water.
(xii.) Chlorides,[3] $MCl_3.6H_2O$, from hydrochloric acid.

The solubilities of corresponding salts of samarium, europium, gadolinium, and terbium usually increase in the order Sm, Eu, Gd, Tb. With the dimethylphosphates the reverse holds good; with the simple nitrates the solubilities diminish in the order Sm, Eu, Gd, but the solubility of the terbium salt exceeds that of the gadolinium. In fact, from gadolinium to lutecium and celtium the "serial order" holds good (see p. 327).

B. **Fractional Precipitation.**—The following compounds may be fractionally precipitated:—

(i.) The double sulphates.[4]
(ii.) The hydroxides or basic salts, by ammonia.[5]
(iii.) The stearates.[6]

The hydroxides of terbium, samarium, and gadolinium are precipitated in the order Tb, Sm, Gd by ammonia; europium hydroxide precipitates before the hydroxide of samarium.

C. **General Method of Procedure.**—When the earths extracted from a mineral contain very little of the yttrium group and the fractionation is commenced by the double magnesium nitrate method without previously eliminating the yttrium group, the whole of the samarium, europium, gadolinium, etc., finds its way into the soluble fractions (δ) previously mentioned (p. 344). If, however, the earths extracted from a mineral have been initially submitted to the double sulphate separation process, the crude double sulphates of the cerium group contain probably the greater part, but not all of the samarium, europium, and gadolinium, and very little of the terbium, while the filtrate contains the remainder of these elements as sulphates. From a mixture of crude yttrium earths the elements samarium, europium, gadolinium, and terbium may be eliminated in the least soluble fractions by fractionally crystallising the ethylsulphates or bromates, as has been previously mentioned (p. 340).

In outlining the procedures best adapted to the separation of samarium, europium, gadolinium, and terbium, it is only necessary to describe the method of working up the extremely soluble fractions (δ) from the double magnesium nitrate fractionation of the cerium group (p. 344). Head fractions obtained from crude yttrium earths by the ethylsulphate or bromate method may be converted into double magnesium nitrates and treated in a similar manner.[7]

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[1] James and Bissel, *J. Amer. Chem. Soc.*, 1914, **36**, 2060.

[2] J. C. Morgan and C. James, *J. Amer. Chem. Soc.*, 1914, **36**, 10.

[3] James and Bissel, *J. Amer. Chem. Soc.*, 1914, **36**, 2065.

[4] Marignac, *Arch. Sci. phys. nat.*, 1880, [iii.], **3**, 413; *Compt. rend.*, 1880, **90**, 899; *Ann. Chim. Phys.*, 1880, [v.], **20**, 535; Lecoq de Boisbaudran, *Compt. rend.*, 1879, **88**, 322; 1879, **89**, 212; 1883, **97**, 1463; Delafontaine, *Arch. Sci. phys. nat.*, 1878, **61**, 273; Bettendorf, *Annalen*, 1892, **270**, 376; 1907, **352**, 88.

[5] Lecoq de Boisbaudran, *Compt. rend.*, 1879, **88**, 322; **89**, 212; 1890, **111**, 394; Urbain, *ibid.*, 1905, **141**, 521; Bettendorf, *Annalen*, 1892, **270**, 376; Benedicks, *loc. cit.*; Holmberg, *loc. cit.*

[6] Stoddart and Hill, *J. Amer. Chem. Soc.*, 1911, **33**, 1076.

[7] For more complete descriptions, see Urbain, *J. Chim. phys.*, 1906, **4**, 31, 105 (general); *Compt. rend.*, 1909, **149**, 37 (Tb); James, *J. Amer. Chem. Soc.*, 1908, **30**, 979; 1912, **34**, 757 (general).

The fractionation of the double magnesium nitrates (δ) is continued from nitric acid of density 1·3, as recommended by Demarçay. This is the best method for separating samarium, europium, and gadolinium. The fractionation should be continued until a considerable quantity of the **samarium** has been eliminated in the head fractions, free from europium.[1] Throughout the course of this fractionation great care must be taken to prevent the deposition of crystals of magnesium nitrate, which are apt to separate out, since that salt is less soluble than the double nitrates. The solutions should therefore be allowed to cool down and form supersaturated solutions, and then seeded either with tiny crystals saved for the purpose, or, better, with bismuth magnesium nitrate.[2]

After as much europium-free samarium as possible has been removed, considerable quantities of *bismuth magnesium nitrate* are continually added to the final mother liquors as the fractionation proceeds. The material should be separated into about 20 fractions and fractionation carried on daily for about six months. After each crystallisation the volume of the mother liquor should be about one-tenth of the total volume. By working in this manner on 611 grams of rare earths, which consisted almost entirely of samaria and gadolinia, Urbain and Lacombe (p. 327), the originators of this method, added in all about 5 kilos. of bismuth magnesium nitrate. They eliminated the head fractions as soon as it was clear that they were free from europium. Finally, after nearly six months' fractionation, the two head fractions were found to be practically devoid of samarium and europium, *i.e.* they were practically pure bismuth magnesium nitrate. The remaining fractions contained much bismuth salt and the following amounts of rare earths (head fraction was No. 12):—

No. of fraction .	14	15	16	17	18	19	20	21	22	etc.
Wt. of oxides .	0·537	1·01	1·50	1·74	1·50	1·80	2·7	12·7	29·0	grams.

Numbers 14 to 19 were free from gadolinium, and numbers 23 onwards were free from europium. Thus the earths extracted from fractions 14 to 19 consisted of pure **europia**, and the intermediate fractions between pure europia and pure gadolinia had been reduced to three (numbers 20, 21, and 22).[3]

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[1] By examining the absorption spectrum of the double nitrates, melted in their water of crystallisation, through a thickness of about 12 cms. (the diameter of a litre flask), and rejecting fractions which do not show the two bands 5337 and 5251 due to europium, considerable amounts of samarium but practically no europium may be eliminated.

[2] It has been already mentioned (see p. 344) that considerable trouble may be experienced in crystallising the most soluble part of the (δ) fractions owing to the fact that all the yttrium earths left in the crude cerium earths become concentrated in them. The following means are available for eliminating the yttrium earth from these uncrystallisable fractions:—

(i.) Convert into sulphates and apply the *double sulphate* method.

(ii.) Convert into the simple *nitrates* and fractionally crystallise from nitric acid of density 1·3. This excellent method was strongly recommended by Demarçay (*Compt. rend.*, 1900, **130**, 1019), and has also been employed by James (*J. Amer. Chem. Soc.*, 1913, **35**, 235). The nitric acid should not have a greater density than 1·3, or yttrium nitrate trihydrate, $Y(NO_3)_3.3H_2O$, may separate and cause trouble.

(iii.) Add a large quantity of *bismuth magnesium nitrate* and fractionally crystallise from nitric acid (Urbain and Lacombe, *Compt. rend.*, 1904, **138**, 84 ; *J. Chim. phys.*, 1906, **4**, 121).

[3] Without the addition of the isomorphous bismuth salt, the separation of europium from gadolinium requires 18 intermediate fractions (Demarçay, see p. 347). The work of Urbain and Lacombe has been repeated and verified by James and Robinson (p. 347), who worked on a larger scale than the French chemists.

From the preceding description it will be seen that the separation of samarium and europium by Urbain and Lacombe's method is quantitative. For the purification of samarium it is necessary to eliminate the last traces of neodymium. This may be accomplished (i.) by the fractional crystallisation of a mixture of equal weights of the double nitrate of samarium and magnesium and the double nitrate of bismuth and magnesium, when the neodymium is eventually found in the head fraction;[1] (ii.) by the fractional crystallisation of samarium dimethylphosphate, when the neodymium is rapidly expelled in the most soluble fractions;[2] or (iii.) by the fractional crystallisation of samarium manganese nitrate from nitric acid.[3]

The elimination of terbium from **gadolinium** is more tedious than the elimination of europium. The fractions following those which contain the europium are suitably treated to extract the rare earths and to convert them into the simple nitrates. The nitrates are then fractionated from nitric acid of density 1·3 in the presence of a large excess of *bismuth nitrate*, $Bi(NO_3)_3.5H_2O$. The order of separation is Gd, Bi, Tb, (Dy), and a practically quantitative separation of gadolinium and terbium can be brought about by prolonging the fractionation for a sufficient length of time. The separation proceeds very slowly, but it is certain.

The purification of **terbium** is completed when both gadolinium and dysprosium have been eliminated from it. The elimination of the gadolinium has just been described; at the same time that the separation of gadolinium and terbium is proceeding in the least soluble fractions, a very good, but not quantitative, separation of terbium and dysprosium simultaneously takes place in the more soluble fractions, and, owing to the presence of the excess of bismuth salt, the intermediate terbium-dysprosium fractions are reduced to a very small amount.

The great objection to the method of the fractional crystallisation of the nitrates for separating gadolinium, terbium, and dysprosium is the extreme slowness with which it effects the separation. A much more rapid and convenient process is the fractional crystallisation of the *bromates*, which separates gadolinium and terbium particularly well. Moreover, it is very probable that the separation can be conducted quantitatively in the presence of neodymium bromate.

The best alternatives to the methods outlined in the preceding paragraphs for the isolation of gadolinium and terbium are: (i.) the fractionation of the *double nickel nitrates* to eliminate terbium from gadolinium, and vice versa; (ii.) the fractional precipitation of the *hydroxides* with ammonia to eliminate the last traces of gadolinium from terbium prepared by method (i.); (iii.) the fractionation of the *ethylsulphates* to eliminate dysprosium from terbium;[4] and (iv.) the fractionation of the *dimethylphosphates*, which rapidly eliminates terbium from gadolinium.

The Separation of the Yttrium Group.

The metals of this group are distinguished from those of the cerium and terbium groups by the solubility of their double potassium sulphates in a

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[1] Urbain and Lacombe, *Compt. rend.*, 1904, 138, 1166; Urbain, *J. Chim. phys.*, 1906, 4, 119.

[2] J. C. Morgan and C. James, *J. Amer. Chem. Soc.*, 1914, 36, 10.

[3] Lacombe, *Bull. Soc. chim.*, 1904, [iii.], 31, 570; *Chem. News*, 1904, 89, 277

[4] For references, see p. 351.

saturated solution of potassium sulphate, and by the inability of their nitrates to form double salts with the alkali nitrates or the nitrates of magnesium, zinc, nickel, etc.

The separation of the elements of the yttrium group from one another has, as yet, not been effected so satisfactorily as the separation of the elements of the other groups. Practically all the methods that have been tried are mentioned in the following paragraphs, and an outline of the experimental procedure is given in the cases of the more valuable methods.

A. **Fractional Crystallisation.**—The following salts have been employed:—

(i.) The *ethylsulphates*, from water.[1] The utility of this valuable method is discussed later (pp. 355–6).

(ii.) The *bromates*, from water.[2] The utility of this method is also discussed later (pp. 355–6).

(iii.) The *acetates*, from acetic acid.[3]

(iv.) The *metanitrobenzoates*, from water.[4]

(v.) The *nitrates*, from strong nitric acid.[5] The utility of this valuable method is discussed later (pp. 356–7).

(vi.) The *double ammonium oxalates*.[6] The wet oxalates are dissolved in a boiling, concentrated, slightly ammoniacal solution of ammonium oxalate, and the solution cooled in successive stages, the crystals separating at each stage being collected before proceeding to the next.[7]

(vii.) The *acetylacetonates*, from alcohol and benzene.[8]

(viii.) The *picrates*, from water.[9] This is an efficient method for removing small amounts of the earths of the erbium and yttrium groups from those of the cerium group and for separating yttrium from erbium and holmium.

(ix.) The *chlorides*, from concentrated hydrochloric acid.[10]

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[1] Urbain, *Bull. Soc. chim.*, 1898, [iii.], **19**, 376; *Compt. rend.*, 1898, **126**, 835; 1906, **142**, 785; *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184; G. and E. Urbain, *Compt. rend.*, 1901, **132**, 136; R. J. Meyer and Wuorinen, *Zeitsch. anorg. Chem.*, 1913, **80**, 7.

[2] James, *J. Amer. Chem. Soc.*, 1908, **30**, 182, 979; 1910, **32**, 517; 1911, **33**, 1332; 1912, **34**, 757; 1913, **35**, 235; Holden and James, *ibid.*, 1914, **36**, 638; James and Bissel, *ibid.*, 1914, **36**, 2065. In the first of these papers, James mentions that the fractionation of the bromates is superior to the fractionation of any of the following salts:—Sulphites, succinates, xanthates, methylsulphates, propylsulphates, camphorates, iodates, thiocyanates, monochloracetates, monobromosuccinates, and oleates.

[3] Postius, *Inaugural Dissertation* (Munich Tech. Inst., 1902).

[4] Holmberg, *Arkiv Kem. Min. Geol.*, 1911, **4**, Nos. 2, 10; *Zeitsch. anorg. Chem.*, 1911, **71**, 226.

[5] Demarçay, *Compt. rend.*, 1896, **122**, 728; 1900, **130**, 1019; Urbain, *ibid.*, 1907, **145**, 759; 1908, **146**, 406; *Bull. Soc. chim.*, 1905, [iii.], **33**, 739; Blumenfeld and Urbain, *Compt. rend.*, 1914, **159**, 323; Holmberg, *loc. cit.*

[6] Auer von Welsbach, *Monatsh.*, 1906, **27**, 935; 1908, **29**, 181; 1911, **32**, 373; *Chem. News*, 1907, **95**, 197; 1908, **98**, 223; Holmberg, *loc. cit.*; Hofmann and Burger, *Ber.*, 1908, **41**, 308.

[7] For other methods of fractionating by means of oxalates, see Mosander, *Phil. Mag.*, 1843, [iii.], **23**, 241; Delafontaine, *Arch. Sci. phys. nat.*, 1864, **21**, 97; *Annalen*, 1864, **134**, 99; Cleve, *Compt. rend.*, 1879, **89**, 419; Lecoq de Boisbaudran, *ibid.*, 1879, **88**, 322; 1886, **103**, 627; Krüss, *Annalen*, 1891, **265**, 1; Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184; Marc, *Ber.*, 1902, **35**, 2382; Dennis and Dales, *J. Amer. Chem. Soc.*, 1902, **24**, 401.

[8] Urbain and Budischovsky, *Compt. rend.*, 1897, **124**, 618; Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184.

[9] Holmberg, *Zeitsch. anorg. Chem.*, 1907, **53**, 83; Dennis and Bennett, *J. Amer. Chem. Soc.*, 1912, **34**, 7; Dennis and Rhodes, *ibid.*, 1915, **37**, 807; James, *ibid.*, 1911, **33**, 1332.

[10] Dennis and Dales, *J. Amer. Chem. Soc.*, 1902, **24**, 401; Langlet, *Arkiv Kem. Min. Geol.*, 1907, **2**, No. 32; James and Bissel, *J. Amer. Chem. Soc.*, 1914, **36**, 2065.

(x.) The *dimethylphosphates*, from water.[1] This separation appears to be a very rapid one, and deserves further study.

B. **Fractional Precipitation.** — The following compounds may be fractionally precipitated :—

(i.) The *hydroxides* or *basic salts*, by the addition of ammonia,[2] sodium hydroxide,[3] aniline,[4] or magnesia.[5] These processes are very tedious. The magnesia method is useful in removing small amounts of impurities from yttrium, for which purpose the magnesia is stirred up into a "cream" with water, and added gradually to a concentrated, boiling solution of the rare earth nitrates.

(ii.) The *chromates*.[6] For this purpose the rare earths (*i.e.* the oxides) are mixed with the calculated amount of chromic acid, and water then added. A violent reaction ensues and an aqueous solution of the dichromates is produced.[7] The liquid is diluted (about 1 litre per 50 grams of oxides) and 10 per cent. potassium chromate added until a permanent turbidity is produced. The liquid is heated to boiling, and while heating by a burner is still carried on, a vigorous current of steam is blown through the liquid. By this means a constant volume may be maintained throughout the fractionation, which is effected by adding 10 per cent. potassium chromate, drop by drop, from a tap-funnel. The precipitate is collected in a series of fractions.

The method is an excellent one for the rapid preparation of practically pure yttrium material from a starting material composed of the crude yttrium earths from which the cerium group, and preferably the terbium group, has been eliminated. Unfortunately it does not seem to have any other practical use.

(iii.) The *ferrocyanides*.[8] This method, like the preceding, enables pure yttrium material to be obtained, but the yields are very poor.

(iv.) The *succinates*.[9] A solution of ammonium or sodium succinate is added, drop by drop, to a 2 or 3 per cent. boiling solution of the nitrates, and the precipitate collected in fractions.

(v.) The *stearates*.[10] A 50 per cent. hot alcoholic solution of potassium

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[1] J. C. Morgan and C. James, *J. Amer. Chem. Soc.*, 1914, **36**, 10.

[2] Mosander, *Phil. Mag.*, 1843, [iii.], **23**, 251 ; Lecoq de Boisbaudran, *Compt. rend.*, 1886, **102**, 1003, 1005 ; Krüss, *Annalen*, 1891, **265**, 1 ; Muthmann and Baur, *Ber.*, 1900, **33**, 1748 ; Marc, *ibid.*, 1902, **35**, 2382 ; Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184 ; G. and E. Urbain, *loc. cit.* ; Postius, *loc. cit.* ; Dennis and Dales, *loc. cit.* ; Bettendorf, *Annalen*, 1907, **352**, 88 ; Holmberg, *loc. cit.*

[3] Holden and James, *J. Amer. Chem. Soc.*, 1914, **36**, 638.

[4] Krüss, *Annalen*, 1891, **265**, 1 ; *Zeitsch. anorg. Chem.*, 1893, **3**, 108, 353 ; K. A. Hofmann and Krüss, *ibid.*, 1893, **3**, 407 ; **4**, 27.

[5] Muthmann and Rölig, *Ber.*, 1898, **31**, 1718 ; Drossbach, *Ber.*, 1896, **29**, 2452 ; Dennis and Dales, *loc. cit.* ; James, *J. Amer. Chem. Soc.*, 1907, **29**, 495.

[6] Krüss and Loose, *Zeitsch. anorg. Chem.*, 1893, **3**, 92 ; Moissan and Étard, *Compt. rend.*, 1896, **122**, 573 ; Muthmann and Böhm, *Ber.*, 1900, **33**, 42 ; Böhm, *Zeitsch. angew. Chem.*, 1902, **15**, 1282 ; Dennis and Dales, *loc. cit.* ; R. J. Meyer and Wuorinen, *Zeitsch. anorg. Chem.*, 1913, **80**, 7 ; Egan and Balke, *J. Amer. Chem. Soc.*, 1913, **35**, 365 ; Holden and James, *ibid.*, 1914, **36**, 638.

[7] Instead of using a solution of the dichromates, a neutral solution of the nitrates may be used and potassium dichromate added (James, *J. Amer. Chem. Soc.*, 1912, **34**, 769).

[8] Rowland, *Johns Hopkins Univ. Circular*, 1894, **112**, 73 ; *Chem. News*, 1894, **70**, 68 ; Jones, *Amer. Chem. J.*, 1895, **17**, 154 ; Crookes, *Chem. News*, 1894, **70**, 81 ; Bettendorf, *Annalen*, 1907, **352**, 88 ; R. J. Meyer and Wuorinen, *loc. cit.*

[9] Lenher, *J. Amer. Chem. Soc.*, 1908, **30**, 572 ; Benner, *ibid.*, 1911, **33**, 50.

[10] Stoddart and C. W. Hill, *J. Amer. Chem. Soc.*, 1911, **33**, 1076.

stearate is added, drop by drop, to a cold, vigorously stirred solution of the neutral nitrates, and the precipitate removed in fractions. This is said to be a rapid method for preparing pure yttria.

(vi.) The *iodates.*[1] A solution of potassium iodate is added, drop by drop, to a hot solution of the nitrates, slightly acidified with nitric acid. The method is of value in the purification of yttrium, which separates last.

(vii.) The *cobalticyanides.*[2] This affords a rapid method for the separation of pure yttrium.

(viii.) The *tartrates.* A solution of tartaric acid in acetone is added to one of the rare earth nitrates in the same solvent, and the precipitate removed in fractions.[3]

(ix.) Other salts. The *azides,*[6] *hypophosphites,*[7] *phosphites,*[7] *phosphates,*[7] *arsenates,*[7] *sulphites,*[2] *tungstates,*[2] *sebacates,*[2] *citrates,*[2] *tartrates,*[2] *cacodylates,*[4] *glycollates,*[5] *mono-* and *di-methylphosphates,*[7] *phenoxyacetates,*[2] *camphorates,*[2] *m-nitrobenzoates,*[2] and *azobenzenesulphonates*[2] have all been examined.

C. **Other Methods.**—These include the following:—

(i.) *Fractional Decomposition of the Nitrates by Heat.*[8]—For this purpose, the hydroxides are dissolved in nitric acid, the solution evaporated to dryness, and the residual nitrates heated. The evolution of red fumes is allowed to proceed until the surface acquires a peculiarly steely appearance, but should not be allowed to continue until the mass becomes creamy. The fused mass is then poured very carefully into cold water, and the liquid heated to boiling. If yttrium predominates very largely over the other rare earth metals present, the entire mass generally passes into solution, and, on cooling, basic nitrates separate out in the crystalline form; otherwise an insoluble residue is left, in which case it must be well agitated by vigorous boiling before the liquid is cooled. After cooling, the residue is separated by filtration, dissolved in nitric acid, and again partially decomposed, while the filtrate is evaporated to dryness, and the residue also subjected to the same treatment, and so on, the filtrate from one fraction being combined with the basic salts separated from the next.

This is one of the classic methods for the fractionation of the rare earths. It has been of great service to past investigators, scandium, ytterbium, thulium, and holmium having, in fact, been discovered as the result of the application of this method to the fractionation of the yttrium earths. At the present time it still remains one of the best methods, at least on a large scale, for eliminating erbium from yttrium.

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[1] R. J. Meyer and Wuorinen, *Zeitsch. anorg. Chem.*, 1913, **80**, 7; Holden and James, *J. Amer. Chem. Soc.*, 1914, **36**, 638.

[2] Bonardi and James, *J. Amer. Chem. Soc.*, 1915, **37**, 2642.

[3] Barnebey, *J. Amer. Chem. Soc.*, 1912, **34**, 1174.

[4] Whittemore and James, *J. Amer. Chem. Soc.*, 1913, **35**, 127; Holden and James, *loc. cit.*

[5] Jantsch and Grünkraut, *Zeitsch. anorg. Chem.*, 1912, **79**, 305.

[6] Dennis and Dales, *J. Amer. Chem. Soc.*, 1902, **24**, 401.

[7] Holden and James, *J. Amer. Chem. Soc.*, 1914, **36**, 638.

[8] The older references are: Berlin, *Forhandl. Scand. Naturf. Kjöbenhavn*, 1860, **8**, 448; Bahr and Bunsen, *Annalen*, 1866, **137**, 1; Cleve and Hoglund, *Bihang K. Svenska Vet.-Akad. Handl.*, 1873, **1**, No. 8; *Bull. Soc. chim.*, 1873, [ii.], **18**, 193, 289; Marignac, *Arch. Sci. phys. nat.*, 1878, [ii.], **64**, 97; *Compt. rend.*, 1878, **87**, 578; *Ann. Chim. Phys.*, 1878, [v.], **14**, 247; Nilson, *Compt. rend.*, 1879, **88**, 645; Cleve, *ibid.*, 1880, **91**, 381. Modern references are: G. and E. Urbain, *Compt. rend.*, 1901, **132**, 136; Dennis and Dales, *J. Amer. Chem. Soc.*, 1902, **24**, 401; James and Pratt, *ibid.*, 1910, **32**, 87; Holden and James, *ibid.*, 1914, **36**, 638. See also Barnebey, *loc. cit.*

Before applying this method to the fractionation of the yttrium earths, it is important the europium, gadolinium, terbium, dysprosium, and holmium should as far as possible be eliminated (and, of course, the cerium group). Serious errors have been made owing to the fact that this initial step was not taken (see pp. 355, 363).

(ii.) *Auer von Welsbach's Oxide Method.*[1]—The manner in which this method is carried out has been already described (p. 343).

(iii.) *Hydrolysis of the Phthalates.*[2]—A cold solution of the phthalates is slowly heated and the precipitated basic salts removed in fractions. The yttrium precipitates last.

(iv.) *The Ammonium Carbonate and Acetic Acid Method.*[3]—The hydroxides of the rare earth elements of the yttrium group are soluble in ammonium carbonate.[4] Fractionation may be effected by dissolving the hydroxides in ammonium carbonate, adding concentrated acetic acid till the liquid becomes turbid, and then adding dilute acetic acid, drop by drop, to the well-stirred liquid until the earths are partially precipitated.

Terbium and yttrium rapidly concentrate in the first fractions, erbium and "ytterbium" in the last, and holmium, thulium, and dysprosium in the middle fractions.

(v.) *The Oxalate-Carbonate Method.*[5]—The oxalates are dissolved in a warm saturated solution of normal ammonium carbonate and then heated to 100°. The precipitate that forms is collected in fractions. The elements separate in the following order: (Tb, Y), (Dy, Ho), Er, Tm, (Yb, Lu). The separation of erbium from holmium, terbium, and dysprosium is very rapid.

(vi.) *The Basic Nitrite Method.*[6]—A neutral solution of the nitrites is boiled and stirred by a current of steam, while concentrated sodium nitrite solution is slowly added to the liquid. The precipitate of basic nitrites (?) is removed in fractions as usual.

The separation of all the members of the yttrium group appears to be effected by the method, but at present it has only been studied in any detail so far as the separation of yttrium and erbium is concerned. For this separation it is the most rapid method known. Unfortunately, however, the precipitates are at times obtained in a colloidal form, and when this occurs no appreciable separation can be effected. The formation of the colloidal precipitates is connected with the presence of excess of sodium nitrate, but the necessary conditions for successful fractionation still require to be discovered.

(vii.) *Fractional Sublimation of the Chlorides.*[7]—This method is of use in separating small quantities of lutecium from ytterbium (neoytterbium), the lutecium chloride being the more volatile. Scandium and thorium are liable to be present when crude "ytterbium" is isolated; their chlorides are much more volatile than lutecium chloride.

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[1] Auer von Welsbach, *Monatsh.*, 1883, **4**, 630; 1906, **27**, 935; *Chem. News*, 1907, **95**, 197; Bettendorf, *Annalen*, 1907, **352**, 88; *cf.* Drossbach, *Ber.*, 1902, **35**, 2826.

[2] R. J. Meyer and Wuorinen, *Zeitsch. anorg. Chem.*, 1913, **80**, 7.

[3] Dennis and Dales, *J. Amer. Chem. Soc.*, 1902, **24**, 401.

[4] Mosander, *Annalen*, 1843, **48**, 219; *Phil. Mag.*, 1843, [iii.], **23**, 251; Krüss, *Annalen*, 1891, **265**, 1.

[5] James, *J. Amer. Chem. Soc.*, 1907, **29**, 495; *Chem. News*, 1907, **95**, 181.

[6] Holden and James, *J. Amer. Chem. Soc.*, 1914, **36**, 1418.

[7] Urbain, Bourion, and Maillard, *Compt. rend.*, 1909, **149**, 127; *cf.* Pettersson, *Zeitsch. anorg. Chem.*, 1893, **4**, 1.

(viii.) *Electrolysis of Aqueous Salt Solutions.*[1]—The procedure necessary has been already described (see p. 343). By this method yttria may be separated from the erbia earths with considerable rapidity.

(ix.) *Fractional Decomposition of the Sulphates by Heat.*[2]

D. **General Procedure.**—In nearly all cases in which the yttrium group is separated by fractional crystallisation, the elements separate in "serial order," with dysprosium in the least and lutecium and celtium in the most soluble fractions. The reverse order of solubilities, however, holds for the dimethylphosphates.

Separation methods which depend on differences of basicity, particularly the precipitation with ammonia, decomposition of the nitrates, and crystallisation of the oxalates from nitric acid, received considerable attention in the early days of rare earth chemistry. In all such methods as these, yttria acts as the strongest base present; erbia, thulia, ytterbia, and lutecia as much weaker bases; and dysprosia and holmia as bases intermediate in strength. Accordingly, by applying method (C. i.), the fractional decomposition of the nitrates by heat, yttria may be largely separated from the other earths. It is separated, however, in an impure state, being contaminated more especially with holmia and dysprosia, and also with terbia and gadolinia if these earths are present. Impure yttria thus obtained from a mixture of yttrium earths resists fractionation in a very extraordinary fashion, so much so that in 1896 Schützenberger and Boudouard, as the result of their experiments on the nitrate method, were inclined to believe that among the elements of the yttrium group there is one, of atomic weight 97, that had previously been overlooked. The oxide of this new "element," however, as Urbain showed in 1900, was merely yttria contaminated with terbia, gadolinia, dysprosia, and holmia, in spite of the fact that it could not be fractionated by the partial decomposition of the nitrates, or the fractional crystallisation of the sulphates, acetylacetonates, etc.[3]

From the preceding remarks it will be seen that it is desirable to eliminate the terbium group, dysprosium and holmium, before endeavouring to fractionate the remaining earths of the yttrium group. It is therefore the best plan to commence by fractional crystallisation, and for this purpose the ethylsulphates or bromates should be selected. The method of procedure in the case of the ethylsulphates has been already described (p. 340), and the fractionation of the bromates may be carried out in a similar manner. The ethylsulphate and bromate methods may to a certain extent be looked upon as effecting a separation into three sub-groups: (α) the least soluble fractions, in which dysprosium, holmium, and yttrium separate in the order named; (β) the middle fractions, constituting the greater part of the material and consisting essentially of yttrium salt, contaminated chiefly with dysprosium and holmium in the least soluble, and with erbium in the most soluble, fractions; and (γ) the most soluble fractions, in which erbium, thulium,

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[1] Krüss, *Zeitsch. anorg. Chem.*, 1893, **3**, 60; Dennis and Dales, *J. Amer. Chem. Soc.*, 1902, **24**, 401; Dennis and Lemon, *ibid.*, 1915, **37**, 131; Dennis and van der Meulen, *ibid.*, 1915, **37**, 1963; Dennis, *U.S.A. Pat.*, No. 1,115,513.

[2] Hofmann and Burger, *Ber.*, 1908, **41**, 308.

[3] Schützenberger and Boudouard, *Compt. rend.*, 1896, **122**, 697; 1896, **123**, 782; *Bull. Soc. chim.*, 1898, [iii.], **19**, 227, 236; Boudouard, *Compt. rend.*, 1898, **126**, 1648; *Bull. Soc. chim.*, 1898, [iii.], **19**, 603; Urbain and Budischovsky, *Compt. rend.*, 1897, **124**, 618; *Bull. Soc. chim.*, 1897, [iii.], **17**, 98; Urbain, *Ann. Chim. Phys.*, 1900, [vii.], **19**, 184; Drossbach, *Ber.*, 1896, **29**, 2452.

yttrium, and lutecium separate in the order named. The terbium group fractions, if any, precede the (α) fractions.

The (α) fractions serve for the preparation of dysprosium and holmium. To isolate **dysprosium** in a state of purity it is necessary to prolong the fractional crystallisation of the ethylsulphates containing dysprosium until the degree of hydrolysis becomes too great for further progress to be made. By this means terbium may be satisfactorily eliminated in the least soluble fractions. For further purification each fraction may be separately converted into the nitrate and the fractionation continued from concentrated nitric acid. This method allows a very slow but sure separation of dysprosium from holmium to be accomplished.[1] At the same time it eliminates terbium, if present, in the least soluble fractions, and this may be greatly facilitated if a large quantity of bismuth nitrate is added (see p. 328).

The separation of **holmium** from both dysprosium and yttrium is an extremely difficult task. Urbain found that the fractional crystallisation of the ethylsulphates enables erbium, thulium, etc., to be separated from holmium very satisfactorily, and also brings about a considerable separation between holmium and dysprosium; and that the subsequent crystallisation of the nitrates brings about the elimination of the remaining dysprosium, but not the yttrium. He suggested that the most satisfactory methods for freeing holmium from yttrium would be the partial decomposition of the nitrates by heat, or fractional precipitation of the hydroxides with ammonia,[2] and by employing the latter method, Holmberg has succeeded in obtaining practically pure holmia.[3]

The (β) fractions consist almost entirely of yttrium bromate or ethylsulphate and serve for the isolation of **yttrium**. For this purpose the fractional decomposition of the nitrates (p. 353), the fractional precipitation of the chromates (p. 352), and the fractional precipitation of the basic nitrites (p. 354) are suitable methods; they may be cheaply employed on a large scale, and the first method introduces no volatile reagent. For the final purification Lecoq de Boisbaudran had recourse to fractional precipitation with ammonia, and Cleve to fractional crystallisation of the oxalate from nitric acid; R. J. Meyer and Wuorinen recommend the fractional precipitation of the iodate in nitric acid solution.[4]

The (γ) fractions (p. 355) contain yttrium, erbium, thulium, ytterbium, and lutecium. They may be treated by either of the following methods: (i.) crystallisation of the bromates, or (ii.) crystallisation of the nitrates from nitric acid of density 1·3. The former method is difficult to carry out with the ytterbium and lutecium fractions owing to their great solubility, and the temperature should not exceed 15°, but it may nevertheless be prolonged for a sufficient length of time to enable **thulium** to be isolated in a state of purity.[5] The fractions preceding thulium bromate consist of yttrium and erbium bromates, which do not separate appreciably. From them **erbium**

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[1] Urbain, *Compt. rend.*, 1906, **142**, 785; 1909, **149**, 37.

[2] Urbain, *J. Chim. phys.*, 1906, **4**, 61-2; *Ann. Chim. Phys.*, 1909, [viii.], **18**, 278.

[3] Holmberg, *Arkiv Kem. Min. Geol.*, 1911, 4, Nos. 2, 10; *Zeitsch. anorg. Chem.*, 1911, **71**, 226.

[4] Lecoq de Boisbaudran, *Compt. rend.*, 1886, **103**, 627; Cleve, *ibid.*, 1882, **95**, 1225; G. and E. Urbain, *ibid.*, 1901, **132**, 136; James and Pratt, *J. Amer. Chem. Soc.*, 1910, **32**, 873; Egan and Balke, *ibid.*, 1913, **35**, 365; R. J. Meyer and Wuorinen, *Zeitsch. anorg. Chem.*, 1913, **80**, 7.

[5] James, *J. Amer. Chem. Soc.*, 1910, **32**, 517; 1911, **33**, 1332.

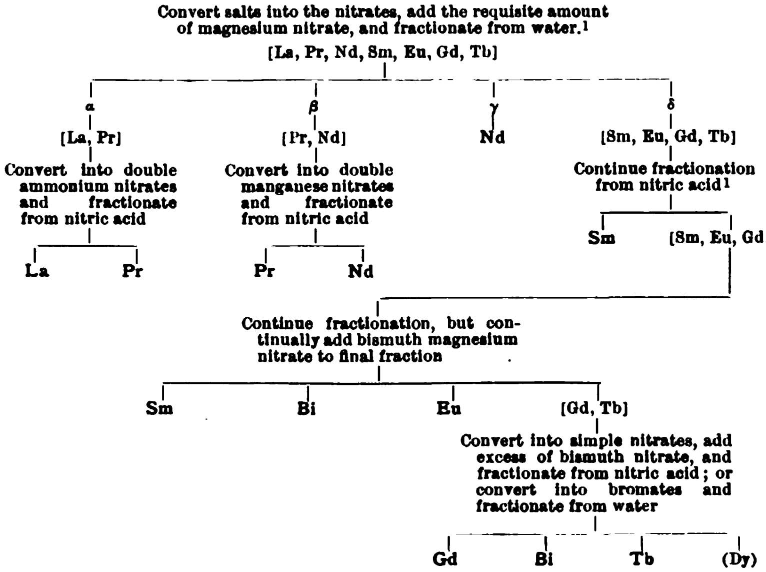
is best obtained by the fractional decomposition of the nitrates (p. 353), the fractional precipitation of the basic nitrites (p. 354), or fractional precipitation with ammonia (p. 352). Pure erbia has not yet been obtained.

The crystallisation of the simple nitrates has been studied by Urbain; it effects the separation of erbium, thulium, ytterbium, and lutecium slowly, but very satisfactorily;[1] but up to the present only one of these elements has been thus obtained as a pure salt, namely, **ytterbium** (*i.e.* neoytterbium).[2] Pure **lutecium** and **celtium** salts have yet to be obtained.

It remains to be mentioned that small quantities of scandium and thorium may occasionally be present in the more soluble of the yttrium group fractions, the latter element being present owing to its incomplete removal at the commencement. They may be readily eliminated by fractional sublimation of the chlorides,[3] but it is simpler to eliminate the scandium by R. J. Meyer's silicofluoride method, which is described in connection with scandium (Chap. IX.). Any remaining thorium may then be eliminated by the hydrogen peroxide method (p. 320). It is still simpler to eliminate the scandium and thorium together as basic thiosulphates (p. 207).

Tabular Summary of General Procedures.—The following tabular outlines may be of service in helping the reader to follow the preceding descriptions[4]:—

A. *Treatment of double sulphates insoluble in sodium or potassium sulphate solution* (cerium is supposed to have been removed)—



1 If the most soluble portion refuses to crystallise, see pp. 344, 349 for method to adopt.

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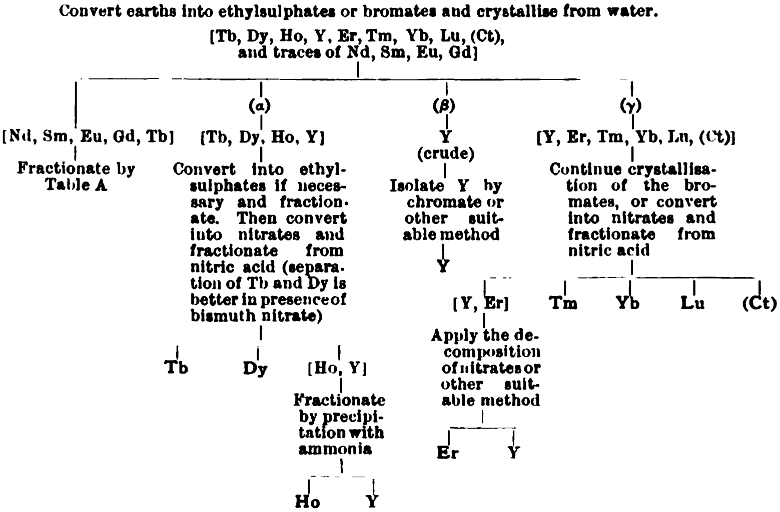
[1] Urbain, *J. Chim. phys.*, 1906, 4, 63; *Ann. Chim. Phys.*, 1909, [viii.], 18, 278; *Compt. rend.*, 1907, 145, 759; 1908, 146, 406.

[2] Blumenfeld and Urbain, *Compt. rend.*, 1914, 159, 323.

[3] Urbain, Bourion and Maillard, *Compt. rend.*, 1909, 149, 127.

[4] Compare James, *J. Amer. Chem. Soc.*, 1908, 30, 979; 1912, 34, 757.

B. *Treatment of crude yttrium earths left in solution from double sulphate treatment*—



Convert earths into ethylsulphates or bromates and crystallise from water.

[Tb, Dy, Ho, Y, Er, Tm, Yb, Lu, (Ct), and traces of Nd, Sm, Eu, Gd]

[Nd, Sm, Eu, Gd, Tb]
Fractionate by Table A

(α) [Tb, Dy, Ho, Y]
Convert into ethylsulphates if necessary and fractionate. Then convert into nitrates and fractionate from nitric acid (separation of Tb and Dy is better in presence of bismuth nitrate)
Tb Dy [Ho, Y]
Fractionate by precipitation with ammonia
Ho Y

(β) Y (crude)
Isolate Y by chromate or other suitable method
Y
[Y, Er]
Apply the decomposition of nitrates or other suitable method
Er Y

(γ) [Y, Er, Tm, Yb, Lu, (Ct)]
Continue crystallisation of the bromates, or convert into nitrates and fractionate from nitric acid
Tm Yb Lu (Ct)

HOMOGENEITY OF THE RARE EARTH ELEMENTS.

Cerium.—The homogeneity of cerium was first doubted by Wolf in 1868.[1] In 1885 Brauner also concluded that cerium was probably complex, stating that "under certain conditions 'cerium' may consist of a mixture. The nature of this admixture must be ascertained by further experiments."[2] Ten years later, Brauner stated that further work had substantiated his previous conclusion, and he announced the existence of ordinary cerium (Ce = 140·2), giving a nearly white dioxide, and *metacerium*, having a higher atomic weight than cerium and forming a dark salmon-coloured oxide. He also mentioned seven methods by which metacerium may be separated more or less completely from cerium.[3]

In 1895 Schützenberger announced that cerium was complex, and in 1897, in association with Boudouard, he declared that cerium from cerite was different from the cerium contained in monazite.[4] These results, however, were shown to be erroneous by Wyrouboff and Verneuil, who, in the course of their work on the purification of ceria, proved the insufficiency of Schützenberger and Boudouard's methods for separating cerium from thorium and the yttrium group, and established the identity of ceria from cerite with ceria from monazite.[5]

In 1900 Drossbach made a prolonged series of crystallisations of ceric

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[1] Wolf, *Amer. J. Sci.*, 1868, [ii.], **45**, 53. Wolf died before his investigations were completed.

[2] Brauner, *Trans. Chem. Soc.*, 1885, **47**, 879; *Monatsh.*, 1885, **6**, 785.

[3] Brauner, *Chem. News*, 1895, **71**, 283.

[4] Schützenberger, *Compt. rend.*, 1895, **120**, 663, 962; Schützenberger and Boudouard, *ibid.*, 1897, **124**, 481; Boudouard, *ibid.*, 1897, **125**, 772, 1096. See also Brauner, *Proc. Chem. Soc.*, 1898, **14**, 69.

[5] Wyrouboff and Verneuil, *Compt. rend.*, 1897, **124**, 1230, 1300; **125**, 950, 1180.

ammonium nitrate prepared from 250 kilos. of crude cerous carbonate, but was unable to find any differences among his cerium fractions.[1] Since this method was given by Brauner as one by which metacerium could be separated, Drossbach's results throw considerable doubt upon the work of Brauner. The latter chemist returned again in 1903 to the question of the purification of ceria, in an important research on the atomic weight of cerium. No reference was made, however, to the nature of metacerium.[2]

At the present time, therefore, it must be admitted that the existence of metacerium is very problematical.

Lanthanum, Praseodymium, Neodymium, and Samarium.—It is generally considered that when the cerium has been removed from the cerium group, four metals remain, namely, lanthanum, praseodymium, neodymium, and samarium. These elements may be quantitatively separated from europium, gadolinium, etc., by the bismuth magnesium nitrate method of Urbain and Lacombe (pp. 327, 349).

The homogeneity of each of the elements praseodymium, neodymium, and samarium was disputed by a number of chemists very soon after Welsbach's discovery of the complexity of "didymium" was announced;[3] and in later years others have also denied the elementary character of these substances.[4] Their opinions have been based, however, almost exclusively upon observations of the absorption spectra, and there is little doubt that they are unjustified.[5]

Demarçay devoted considerable attention to the question of the homogeneity of neodymium and samarium. By fractionating the double ammonium nitrates he isolated a large quantity of the neodymium salt containing only a trace of praseodymium. This material was submitted to a prolonged series of crystallisations. A little praseodymium and considerable quantities of samarium were thus removed, and more than twenty consecutive neodymium fractions obtained which presented complete identity from every point of view. Demarçay found that neodymium thus isolated was the same whether its source was cerite, samarskite, or mosandrite, and that other methods of fractionation led to the same conclusions. Later he discovered in the fractional crystallisation of the double magnesium nitrates a rapid method for the separation of neodymium and samarium, and separated several kilograms of the salts of these elements from one another, reducing the intermediate fractions to less than 20 grams. The intermediate fractions showed only the superposed spectra of neodymium and samarium, and prolonged fractionation of the samarium salt failed to resolve it into dissimilar parts.[6]

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[1] Drossbach, *Ber.*, 1900, **33**, 3506.

[2] Brauner and Batěk, *Zeitsch. anorg. Chem.*, 1903, **34**, 103; Brauner, *ibid.*, 1903, **34**, 207.

[3] Krüss and Nilson, *Ber.*, 1887, **20**, 1676, 2134, 3067; 1888, **21**, 585, 2019; Crookes, *Chem. News*, 1886, **54**, 27; C. M. Thompson, *ibid.*, 1887, **55**, 227; Bettendorf, *Annalen*, 1890, **256**, 159; 1891, **263**, 164; Becquerel, *Ann. Chim. Phys.*, 1888, [vi.], **14**, 170, 257.

[4] Dennis and Chamot, *J. Amer. Chem. Soc.*, 1897, **19**, 799; Brauner, *Proc. Chem. Soc.*, 1898, **14**, 71; Böhm, *Die Zerlegbarkeit des Praseodyms u. Darst. selt. Erd. mit Hilfe einer neuen Trennungsmethode* (Halle, 1900); *Zeitsch. angew. Chem.*, 1903, **16**, 1220; Baskerville and Turrentine, *J. Amer. Chem. Soc.*, 1904, **26**, 46; Baskerville and Stevenson, *ibid.*, 1904, **26**, 54. Although Baskerville and his co-workers speak in a very positive manner of the complexity of praseodymium and neodymium, none of their attempts succeeded in affording any evidence in favour of this view.

[5] See, *e.g.*, Demarçay, *Compt. rend.*, 1898, **126**, 1039 (Nd); Stahl, *Le Radium*, 1909, 6, 215 (Nd, Pr); also pp. 283-7.

[6] Demarçay, *Compt. rend.*, 1898, **126**, 1039; 1900, **130**, 1185.

Demarçay's work shows clearly that the ordinary sources of the rare earths contain no significant amount of an element intermediate between neodymium and samarium, and argues strongly for the homogeneity of these elements. The subsequent work of various other investigators[1] affords corroborative evidence in favour of Demarçay's conclusions. The homogeneity of praseodymium, however, cannot be so definitely affirmed, though modern work has not yielded any satisfactory evidence for regarding it as complex;[2] moreover, definite information with respect to elements intermediate between praseodymium and neodymium is lacking, although here again modern work points strongly to their non-existence.

Lanthana may be defined as the most strongly basic of the ceria earths, a colourless oxide that gives rise to salts devoid of absorption spectra. The question of its homogeneity has been studied by Brauner, by Cleve, by Schützenberger, and by Brauner and Pavlíček. In 1882 Brauner[3] announced the existence of a new earth, intermediate in its equivalent weight and in its basicity between lanthana proper and "didymia." In the same year, Cleve[4] thought he had obtained evidence of the existence of a similar new earth, which he provisionally named oxide of Diβ; a few months later, however,[5] he discovered that the spark line $\lambda 4333{\cdot}5$, characteristic of Diβ, really belongs to the lanthanum spectrum, the previous measurement of its wave-length by Thalen having been erroneous, and in the following year,[6] in the course of an important research on the atomic weights of lanthanum and "didymium," he definitely declared against the existence of an intermediate element. In 1902 Brauner, in conjunction with Pavlíček, returned to the subject and maintained the correctness of his earlier work.[7] According to Brauner, when lanthana is fractionated by the "basic" method, the least basic fractions contain "a small quantity of an element with a higher atomic weight than that of lanthanum," and the new element "gives to the oxide a very pale buff tint." As other considerations point to the incorrectness of these conclusions, it is desirable that further work on the homogeneity of lanthanum should be undertaken.[8]

Europium, Gadolinium, Terbium, and Dysprosium.—Europia and gadolinia were first isolated in an almost pure state by Demarçay. He was not satisfied, however, that europia was a homogeneous substance, chiefly owing to the fact that it gave rise to salts which exhibited, in his opinion,

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[1] See, *e.g.*, Muthmann and Weiss, *Annalen*, 1904, **331**, 1; Feit and Przibylla, *Zeitsch. anorg. Chem.*, 1905, **43**, 202; 1906, **50**, 249; Welsbach, *Sitzungsber. K. Akad. Wiss. Wien*, 1903, **112**, II. A, 1037; Urbain and Lacombe, *Compt. rend.*, 1904, **138**, 1166; Urbain, *J. Chim. phys.*. 1906, **4**, 119; Eberhard, *Zeitsch. anorg. Chem.*, 1905, **45**, 374; Rech, *Zeitsch. wiss. Photochem.*, 1905, **3**, 411; Holmberg, *Zeitsch. anorg. Chem.*, 1907, **53**, 83; Baxter and Chapin, *J. Amer. Chem. Soc.*, 1911, **33**, 1; Baskerville and Stevenson, *loc. cit.*

[2] See, *e.g.*, von Scheele, *Zeitsch. anorg. Chem.*, 1898, **17**, 310; *Ber.*, 1899, **32**, 409; Welsbach, *loc. cit.*; Lacombe, *Bull. Soc. chim.*, 1904, [iii.], **31**, 570; *Chem. News*, 1904, **89**, 277; Muthmann and Weiss, *loc. cit.*; Feit and Przibylla, *loc. cit.*; Rech, *loc. cit.*; Baxter and Stewart, *J. Amer. Chem. Soc.*, 1915, **37**, 516.

[3] Brauner, *Monatsh.*, 1882, **3**, 486.

[4] Cleve, *Compt. rend.*, 1882, **94**, 1528.

[5] Cleve, *ibid.*, 1882, **95**, 33.

[6] Cleve, *Bull. Soc. chim.*, 1883, [ii.], **39**, 151, 289.

[7] Brauner and Pavlíček, *Trans. Chem. Soc.*, 1902, **81**, 1243.

[8] In 1895 Schützenberger (*Compt. rend.*, 1895, **120**, 1143) declared that by a modification of the method of decomposition of the nitrates, lanthana could be resolved into dissimilar parts, the atomic weight of lanthanum varying in the different fractions from 135 to 138. Brauner and Pavlíček (*loc. cit.*) have shown, however, that lanthana prepared by Schützenberger's method is contaminated with small quantities of yttria.

abnormally weak absorption spectra.[1] The question of the homogeneity of europia and gadolinia was subsequently studied with great care by Urbain, who succeeded, moreover, in isolating terbia and dysprosia and including these earths also within the scope of his researches.[2]

The methods employed by Urbain in effecting the separation of europia, gadolinia, terbia, and dysprosia were in nearly all cases crystallisation methods which separate these earths in serial order, *i.e.* the order in which they have been mentioned. In each case, the isolation of a pure earth was shown by the constancy of the spark spectrum, absorption spectrum (visible and ultraviolet), and atomic weight throughout a series of fractions, even after further fractionation had been attempted. Moreover, the intermediate fractions were reduced to as small amounts as possible in comparison with the quantities of pure earths isolated, and examined for indications of either the presence of other earths or the decomposition of the presumably pure earths obtained. The results were entirely negative.

In the case of europia, Urbain showed that the earth can be freed entirely from samaria and gadolinia, but cannot be resolved into dissimilar parts by prolonged fractionation of the double magnesium nitrate in the presence of excess of the corresponding salt of bismuth; that europia isolated by the "bismuth" method from monazite is identical with the earth isolated in the same manner from gadolinite, xenotime, or pitchblende, and that europia thus prepared is identical with that isolated by Demarçay's process (p. 341) without the addition of the bismuth salt.

In the case of gadolinia, Urbain found that when this earth has been isolated by the "bismuth" method, and shown spectroscopically and by its colour to be free from all but traces of europia and terbia, further prolonged fractionation of the double nickel nitrates fails to resolve it, but merely accumulates the europia and terbia in the head and tail fractions respectively; moreover, that gadolinia extracted from gadolinite is identical in its properties with gadolinia obtained from xenotime or pitchblende.

The spectral characteristics of terbium were found by Urbain to indicate no signs whatever of the complexity of that element when its separation from gadolinium and dysprosium is effected by any of the following processes: fractional crystallisation of the nitrates or double nickel nitrates from nitric acid and of the ethylsulphates from water or alcohol, fractional precipitation with ammonia, and fractional decomposition of the nitrates by heat. Further, terbia isolated by the ammonia method, after the preliminary application of the ethylsulphate and double nickel nitrate processes, is identical with that obtained by crystallising the simple nitrates in the presence of excess of bismuth nitrate.

Lastly, Urbain found that when dysprosia has been freed as far as possible from impurities by crystallisation of the ethylsulphates, subsequent fractionation of the nitrates, while slowly removing the holmia and more rapidly eliminating the terbia, fails to indicate that any resolution of the dysprosia occurs. In fact, forty consecutive dysprosium fractions were obtained by this method of preparation, which were practically identical in all their properties.

A very careful examination of the arc spectra of a number of Urbain's

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[1] Demarçay, *Compt. rend.*, 1896, **122**, 728; 1900, **130**, 1469; 1901, **132**, 1484 (Eu); *ibid.*, 1900, **131**, 343 (Gd).

[2] See particularly, Urbain, *J. Chim. phys.*, 1906, 4, 31, 105, 232, 321; *Ann. Chim. Phys.*, 1909, [viii.], **18**, 222; *Compt. rend.*, 1906, **142**, 785; 1909, **149**, 37.

preparations has been made by Eberhard,[1] who concludes that there is no evidence for the complexity of europium, gadolinium, and terbium, or for the existence of intermediate elements.

From the work of Urbain, then, it would seem legitimate to conclude that europium, gadolinium, terbium, and dysprosium are all well-defined elements. The homogeneity of terbium, however, has been disputed by Auer von Welsbach,[2] who, in fractionating the yttria and terbia earths by his double ammonium oxalate method (p. 351), obtained indications of its complexity. Welsbach considers terbium to be probably a mixture of three elements, TbI., TbII., and TbIII. His conclusions, however, must be regarded with considerable suspicion in view of the work of James and Bissel.[3] These experimenters found in the fractional crystallisation of the bromates an extremely efficient method for the separation of gadolinium, terbium, and dysprosium, and, on putting this method into practice, isolated only one element from the fractions intermediate between gadolinium and dysprosium. This element exhibited no signs of being complex and answered to the description of terbium as given by Urbain. The balance of evidence is therefore decidedly in favour of the elementary nature of terbium.

The Yttrium Group.—Apart from dysprosium, which has been discussed, the following members of this group receive official recognition in the 1916 table of the International Committee on Atomic Weights: holmium, yttrium, erbium, thulium, ytterbium, and lutecium. The existence of Urbain's celtium awaits confirmation.

In the present imperfect state of chemical knowledge concerning this group, it is difficult to form any definite conclusions as to the homogeneity of the above-mentioned elements. By the upholders of the "one band—one element" theory (p. 287), holmium, erbium, and thulium were regarded as complex, and a number of later experimenters have also expressed the opinion that these elements are really composite, basing their conclusions upon a study of the absorption spectra.[4] These conclusions, however, are most probably erroneous, the comparisons of various absorption spectra not having been made under identical conditions.[5] In the case of thulium, however, Welsbach[6] has given the wave-lengths of the spark lines characteristic of each of the three elements, TmI., TmII., and TmIII., into which he considers thulium can be resolved, and briefly described the three new earths; the homogeneity of thulium is therefore questionable. According to James, the method of fractionation employed by Welsbach is decidedly inferior to the bromate method for the isolation of thulium, being more difficult to operate, involving many more fractions, and effecting the separation more slowly; and yet a prolonged fractionation of thulium bromate, involving 15,000 crystallisations, failed to

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[1] Eberhard, *Zeitsch. anorg. Chem.*, 1905, **45**, 374; *Sitzungsber. K. Akad. Wiss. Berlin*, 1906, p. 384; *Zeitsch. wiss. Photochem.*, 1906, **4**, 137.

[2] Auer von Welsbach, *Chem. Zeit.*, 1912, **35**, 658.

[3] James and Bissel, *J. Amer. Chem. Soc.*, 1914, **36**, 2060.

[4] Forsling (*Bihang K. Svenska Vet.-Akad. Handl.*, 1902-3, **28**, II., No. 1) denies the elementary nature of holmium. Muthmann and Weiss (*Annalen*, 1904, **331**, 1), Welsbach (*Monatsh.*, 1906, **27**, 935), and James (*J. Amer. Chem. Soc.*, 1907, **29**, 498) consider erbium to be complex. Marc (*Ber.*, 1902, **35**, 2382; *Chem. News*, 1902, **86**, 73) denies the existence of thulium, a conclusion that is unquestionably erroneous.

[5] Thus Langlet (*Arkiv Kem. Min. Geol.*, 1907, **2**, No. 32) contradicts Forsling's conclusions as to the nature of holmium, and James (private communication) no longer maintains that erbium is complex.

[6] Welsbach, *Monatsh.*, 1911, **32**, 373; *Zeitsch. anorg. Chem.*, 1911, **71**, 439.

resolve it into dissimilar parts. He accordingly maintains that thulium is really an element.[1] Further work upon thulium is therefore necessary.[2]

It is at present (1916) impossible to state definitely whether there exists any element intermediate between thulium and ytterbium, but according to Blumenfeld and Urbain[3] this is extremely unlikely.

There is little or no doubt as to the homogeneity of yttrium. At one time, however, it was supposed that yttrium is accompanied by another element of atomic weight approximately 97. This supposition was finally disproved by Urbain in 1900, as has been already mentioned,[4] but, while the nature of this supposed element was in doubt, an enterprising firm interested in the manufacture of incandescent gas mantles was enabled to "discover" a new element *lucium* and to patent methods for the preparation of its salts. The new "element," however, had but a brief existence, its true nature being ascertained by Crookes.[5]

The Cathodic Phosphorescence Spectra and their Bearing on the Homogeneity of the Rare Earth Elements.—The cathodic phosphorescence spectra of the rare earth compounds have been discussed at some length in the preceding chapter (see p. 294). From the account there given it will be seen that the study of these spectra clearly indicates that lanthana, praseodymia, neodymia, samaria, europia, gadolinia, terbia, dysprosia, and yttria are substances of the same degree of complexity, and comparable in this respect with alumina, lime, chromium sesquioxide, and other oxides the metallic constituents of which are recognised without question as elementary substances. The homogeneity of terbium thus receives additional confirmation. Further, the study of these spectra affords valuable evidence as to the non-existence of any elements between samarium and holmium other than europium, gadolinium, terbium, and dysprosium.

The X-Ray Spectra and their Bearing on the Homogeneity of the Rare Earth Elements.—The nature of these spectra has already been briefly indicated (see p. 312).

In fig. 37[6] the X-ray spectra of the elements are arranged on horizontal lines spaced at equal distances. The order chosen for the elements is the order of increasing atomic weights, except in the cases of A and K, Ni and Co, I and Te, where this order clashes with that required by the Periodic Classification. Further, vacancies have been left, as required by that classification, between molybdenum and ruthenium and between tungsten and osmium, and, in addition, one vacancy has been left between neodymium and samarium and four vacancies between erbium and tantalum. This

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[1] James, *J. Amer. Chem. Soc.*, 1911, **33**, 1332.

[2] It may be remarked that in 1909 Urbain stated that he had obtained thulium sufficiently pure for its principal characteristics to be determined with accuracy, although the fractions still contained a little erbium or ytterbium according to their position. No mention was made of any indications of its complexity; Urbain's method of preparation, namely, fractional crystallisation of the nitrates, differs from the methods of Welsbach and James (see Urbain, *Ann. Chim. Phys.*, 1909, [viii.], **18**, 279).

[3] Blumenfeld and Urbain, *Compt. rend.*, 1914, **159**, 323.

[4] For further information on this point, and references to the literature, see p. 355.

[5] See Barrière, *Chem. News*, 1896, **74**, 159, 212; Crookes, *ibid.*, 1896, **74**, 259; R. Fresenius, *ibid.*, 1896, **74**, 269; Shapleigh, *ibid.*, 1897, **76**, 41.

The "elements" *kosmium* and *neokosmium* (Kosmann, *Zeitsch. Elektrochem.*, 1896-7, p. 279 : *cf.* Winkler, *Ber.*, 1897, **30**, 13) were of a similar nature to lucium.

[6] This diagram represents the results given by Moseley, *Phil. Mag.*, 1914, [vi.], **27**, 709.

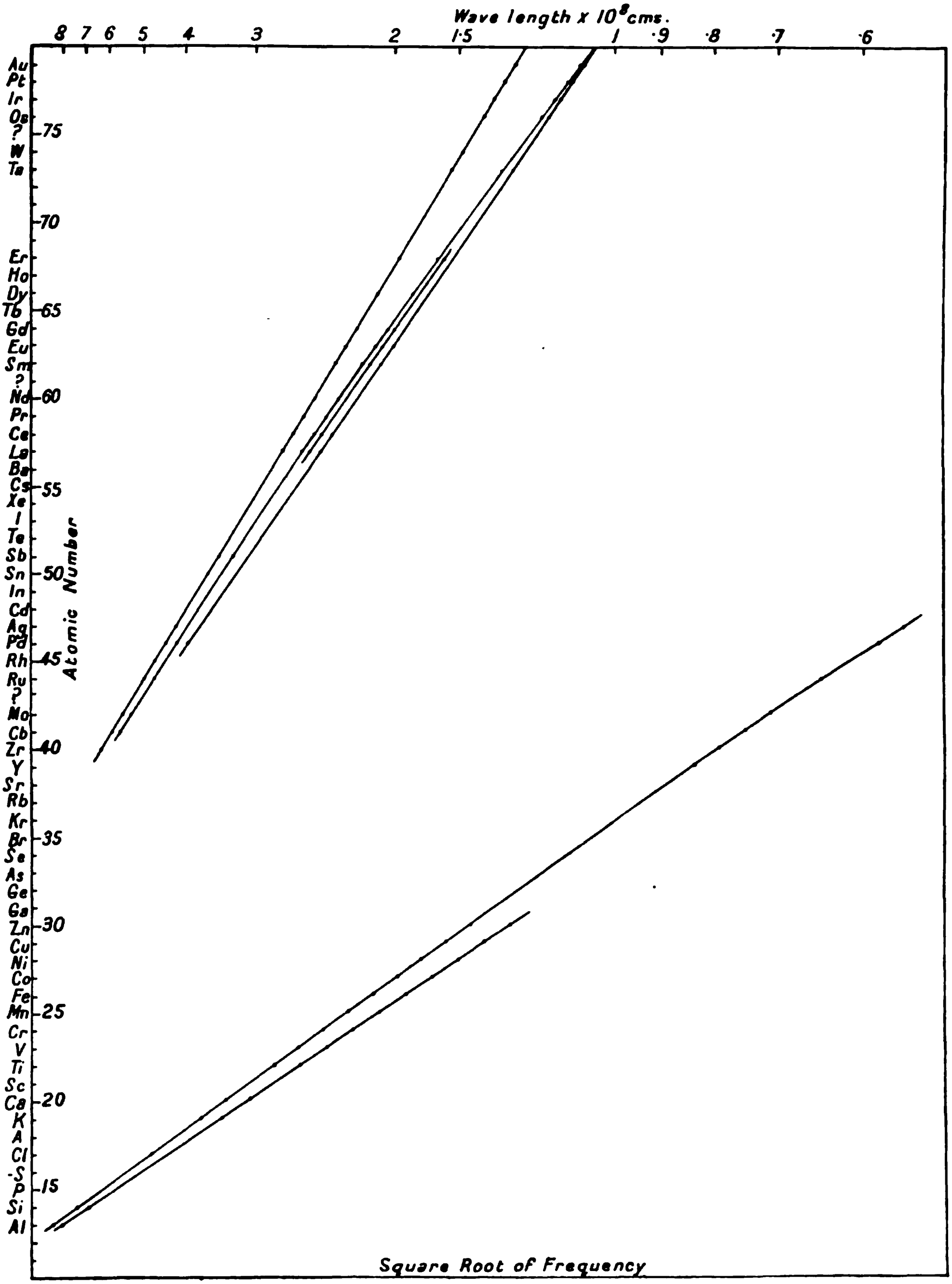

FIG. 37.—High-frequency spectra of the elements (Moseley).

arrangement of the elements is equivalent to assigning to successive elements a series of successive characteristic integers. The integer N for Al, the thirteenth element, has been taken as thirteen. The corresponding integers for the other elements are indicated in the diagram and are spoken of as their atomic numbers. As abscissæ, the square roots of the frequencies (ν) of the lines have been plotted.

It is clear from the diagram that when the values of N are plotted against those of $\nu^{\frac{1}{2}}$, the points lie on a series of smooth curves which approximate closely to straight lines. Such a remarkable relationship between the X-ray spectra of the elements cannot be regarded as accidental; it is undoubtedly of great theoretical importance. The deductions that may be drawn from it in connection with the rare earths are as follows: (i.) an element, presumably intermediate in atomic weight between Nd (144·3) and Sm (150·4), has yet to be discovered, (ii.) terbium and holmium must be regarded as elementary substances, and (iii.) four rare earth elements come between erbium (167·7) and tantalum (181·5). With regard to (iii.), it follows that thulium cannot be a mixture of *three* elements, as Welsbach maintains, since ytterbium and lutecium must account for *two* of the available places; if, on the other hand, thulium is really elementary, the existence of celtium becomes very probable, the four blanks being presumably filled in order by thulium, ytterbium, lutecium, and celtium.

Granting, then, the existence of celtium, it would appear that all the rare earth elements at present recognised are really elementary substances,[1] and that only one other remains to be discovered. That this unknown element should come between neodymium and samarium is, however, surprising in view of the negative result obtained by Demarçay in his search for such an element (p. 359). It may be that the missing element is extremely rare, and occurs in some rare earth minerals but not in others, as celtium appears to do; with this possibility in view, search is now being made for it by James.[2]

Further work on the X-ray spectra of the rare earth elements will be awaited with considerable interest.

Detection and Estimation of the Rare Earths.[3]

Qualitative Analysis.—The analytical reactions of the rare earth elements are summarised in the accompanying table, in which the reactions of scandium, titanium, zirconium, and thorium have been included for purposes of comparison. A number of special tests for cerium are known, but characteristic reactions for the other rare earth elements are lacking; the formation of a blue adsorption compound of basic lanthanum acetate and iodine, for instance, which has been proposed as a test for lanthanum, is not

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[1] That is to say, they have as much right to the title of "element" as have the substances ordinarily recognised as elements.

[2] Prof. James; private communication to the author. It may be mentioned here that in working up the rare earths from certain minerals, Prof. James has observed that small quantities of a radioactive substance concentrate in the samarium fractions. Further work on this point is in progress.

[3] For further information on this subject, see R. J. Meyer and O. Hauser, *Die Analyse der seltenen Erden und der Erdsäuren* (Enke, Stuttgart, 1912); Mellor, *A Treatise on Quantitative Analysis* (C. Griffin & Co., Ltd., 1913). On the analysis of cerium alloys see also Arnold, *Zeitsch. anal. Chem.*, 1914, **53**, 496, 678; Bellucci, *Ann. Chim. Applicata*, 1914, **2**, 366.

REACTIONS OF THE RARE EARTH ELEMENTS COMPARED WITH THOSE OF SCANDIUM, TITANIUM, ZIRCONIUM, AND THORIUM.[1]

	Reagent.	Cerium Group, including Ce^{III}.	Quadrivalent Cerium Ce^{IV}.	Yttrium Group.	Scandium.	Titanium.	Zirconium.	Thorium.
1	Ammonium, sodium, or potassium hydroxide.	Hydroxide precipitated.[2]	Hydroxide precipitated.	Hydroxide precipitated.	Hydroxide precipitated.	Hydroxide precipitated.	Hydroxide precipitated.	Hydroxide precipitated.
2	Sodium, potassium, or ammonium *carbonate.*	Carbonate precipitated, slightly *soluble in excess of* reagent.[3]	Excess of reagent produces a clear *solution.*	Carbonate precipitated, fairly *easily soluble in* excess of reagent.	Same as yttrium.	Hydroxide precipitated.	Hydroxide precipitated, soluble *in ammonium carbonate.*	Basic salt precipitated, soluble *in excess of reagent.*
3	Precipitated lead carbonate.	No precipitate.	Hydroxide precipitated.	No precipitate.	?	Hydroxide precipitated.	Hydroxide precipitated.	Hydroxide precipitated.
4	Sodium, potassium, or ammonium sulphate (excess of saturated solution).	Double sulphates precipitated.	Precipitate only with K salt.	No precipitate.	Precipitate only with K salt.	No precipitate.	Precipitate only with K salt.	Precipitate only with K salt.
5	Sodium acetate (boiling solution).	No precipitate.	Basic acetate precipitated.	No precipitate.	Basic acetate precipitated.	Hydroxide precipitated.	Hydroxide precipitated.	Basic acetate precipitated.
6	Sodium thiosulphate (boiling solution).	No precipitate.	Hydroxide precipitated.	No precipitate.	Basic thiosulphate precipitated.	Hydroxide precipitated.	Same as scandium.	Hydroxide precipitated.
7	Hydrogen peroxide in neutral or slightly acid solution.	No precipitate.	Reduced to Ce^{III}.	No precipitate.	No precipitate.	Yellowish - red coloration.	Hydrated peroxide precipitated.[4]	Hydrated peroxide precipitated.
8	Oxalic acid or ammoniumoxalate.	Oxalate precipitated, slightly soluble in mineral acids or excess of ammonium oxalate.	Reduced to Ce^{III}, which see.	Oxalate precipitated, rather more soluble in acids or ammonium oxalate than Ce^{III}.	Oxalate precipitated, sparingly soluble in acids, readily in ammonium oxalate.	No precipitate.	Basic oxalate precipitated, readily soluble in oxalic acid, ammonium oxalate, or mineral acids.	Same as scandium.
9	Tartaric acid.	No precipitate, and precipitation with ammonia inhibited.	Reduced to Ce^{III}.	No precipitate, but with ammonia precipitates double tartrates.	Same as yttrium.	Same as Ce^{III}.	Same as Ce^{III}.	Same as Ce^{III}.
10	Hydrofluoric acid.	Fluoride precipitated, insoluble in alkali fluorides. Appreciably soluble in hot mineral acids.	..	Same as Ce^{III}.	Fluoride precipitated, soluble in alkali fluorides. Much less soluble in mineral acids than the Ce^{III} and Y salts.	No precipitate.	No precipitate.	Same as scandium.
11	Iodic acid.	Iodate precipitated, readily soluble in nitric acid.	Iodate precipitated, sparingly soluble in nitric acid.	Same as Ce^{III}.	Iodate precipitated, fairly easily soluble in nitric acid.	Incomplete hydrolysis.	Iodate precipitated, practically insoluble in nitric acid plus iodic acid.	Same as zirconium.

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[1] See also L. Haber, *Monatsh.*, 1897, **18**, 687.

[2] Cerous hydroxide oxidises to ceric hydroxide on exposure to air (p. 382).

[3] The cerous solution oxidises in air, forming an alkali perceric carbonate (p. 401).

[4] From zirconyl chloride solution, but not from nitrate or sulphate solutions unless ammonia is also added.

a specific reaction of that element, for it is given by praseodymium and possibly by other rare earth elements (see pp. 410 and 416).[1]

Special reactions of **cerium** salts are as follows:—

(i.) To a slightly acid or neutral solution of a cerous salt, hydrogen peroxide and an excess of ammonium acetate are added, and the mixture warmed to 40°–60°. A yellowish-brown precipitate of basic perceric acetate is produced even when only 1 part of cerium is present in 10,000 of solution (Hartley's reaction).[2]

(ii.) Very dilute ammonia is added, drop by drop, to a solution of a cerous salt until a permanent precipitate just commences to form. A few drops of hydrogen peroxide are added and the mixture well shaken. A yellow precipitate or coloration is produced even when only traces of ceria are present and other rare earths present in quantity.[3]

(iii.) A solution of a cerous salt is warmed with very concentrated potassium carbonate solution, and a little hydrogen peroxide added to the clear solution; the solution turns yellow even when only a trace of cerium is present.[4]

(iv.) A solution of a cerous salt is boiled with an ammoniacal solution of ammonium tartrate; it turns dark brown owing to oxidation. When traces of cerium are sought, the oxidation may be accomplished by means of hydrogen peroxide.[5]

(vi.) The lead peroxide, sodium bismuthate, and ammonium persulphate methods mentioned later in connection with quantitative analysis (p. 373) may be utilised as qualitative tests for cerium.

(vii.) Ammoniacal silver nitrate is added to a neutral solution of a cerous salt and the mixture warmed; a brown coloration or black precipitate is produced according to the amount of cerium present.[6]

(viii.) The cerium solution is made alkaline with sodium hydroxide, evaporated to dryness, and a drop of a solution of strychnine in excess of sulphuric acid added. The solution turns blue or violet in colour and then becomes red.[7]

The usual methods for separating the rare earth elements from other metals in the course of analysis utilise the insolubility of (i.) the hydroxides in ammonia, (ii.) the fluorides in dilute hydrofluoric acid, and (iii.) the oxalates in dilute mineral acids. The following process may be employed. The metals that form insoluble chlorides and sulphides insoluble in dilute hydrochloric acid are removed, hydrogen sulphide expelled from the filtrate, and ammonium chloride and ammonia then added. The precipitate is dissolved in hydrochloric acid, the solution evaporated to dryness, a decided

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[1] Praseodymium gives a yellowish-green *borax bead* in the oxidising, and a green bead in the reducing flame; neodymium gives a violet bead in the reducing flame. The colours are seen only with cold beads (Milbauer, *Zeitsch. anal. Chem.*, 1907, **46**, 657). On the *microchemical tests* for the rare earths, see Pozzi-Escot and Couquet, *Compt. rend.*, 1900, **130**, 1136; Behrens, *Arch. Néerland.*, 1901, [ii.], **6**, 67; *Rec. trav. chim.*, 1905, **23**, 413; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1902, **33**, 113.

[2] Hartley, *Trans. Chem. Soc.*, 1882, **41**, 202; Dennis and Magee, *J. Amer. Chem. Soc.*, 1894, **16**, 649.

[3] Lecoq de Boisbaudran, *Compt. rend.*, 1885, **100**, 605; Cleve, *Bull. Soc. chim.*, 1885, [ii.], **43**, 57; Dennis and Magee, *loc. cit.*; Marc, *Ber.*, 1902, **35**, 2370.

[4] Job, *Compt. rend.*, 1898, **126**, 246; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1904, **41**, 94.

[5] Wirth, *Chem. Zeit.*, 1913, **37**, 773.

[6] W. Biltz and Zimmermann, *Ber.*, 1907, **40**, 4979.

[7] Sonnenschein, *Ber.*, 1870, **3**, 631; *Bull. Soc. chim.*, 1870, [ii.], **14**, 201; Plugge, *Arch. Pharm.*, 1891, **229**, 558; Dennis and Magee, *loc. cit.*

excess of hydrofluoric acid added to the residue, and the liquid boiled for a minute or two. The residue of fluorides is filtered off, heated with concentrated sulphuric acid, the sulphates dissolved in water, and any barium, strontium, or calcium sulphate removed by filtration. The rare earth elements are then precipitated from the filtrate by the addition of ammonia. They are free from titanium and zirconium, but contain any scandium and thorium originally present.[1]

For the qualitative separation of the rare earths themselves, so far as this is usually attempted, the methods given for their quantitative separation may be followed.

Quantitative Analysis.—In the absence of other elements, a rare earth element is usually estimated by precipitation as *oxalate*, followed by ignition to the *oxide*. Precipitation is preferably made from a boiling, dilute nitrate solution, slightly acidified with nitric acid, by the addition of oxalic acid;[2] the oxide finally obtained from a chloride solution is very liable to contain traces of basic chloride, presumably derived from oxalochloride co-precipitated with the oxalate.[3] The oxalate precipitate should be allowed to stand for several hours (preferably overnight) before it is filtered. The oxide finally obtained should be strongly ignited; ceria, for instance, as obtained from cerous oxalate by heating over a Bunsen burner, loses 0·5–0·7 per cent. of its weight when ignited over the blowpipe.[4] In all but three cases, the oxide obtained is the sesquioxide, M_2O_3; cerium, however, leaves the dioxide, CeO_2, and praseodymium and terbium are obtained as peroxides which may be assumed[5] to have the composition M_4O_7; as alternatives, their peroxidic oxygen may be determined iodimetrically, or the peroxides may be reduced to sesquioxides by heating in hydrogen. In weighing the sesquioxides it should be borne in mind that they take up moisture and carbon dioxide from the air fairly rapidly.

The use of an alkali oxalate as precipitant instead of oxalic acid has been carefully studied by Baxter, Griffin, and Daudt,[6] who have found that, in neutral solution, co-precipitation of alkali oxalate occurs to a very appreciable extent, except with sodium oxalate, which is only carried down in small amounts. The contamination increases with rise of temperature, but may usually be greatly diminished if precipitation is conducted in the presence of a quantity of a strong acid considerably more than equivalent to the oxalate added. Contamination with ammonium oxalate is, of course, unimportant for the gravimetric determination of the rare earth, but is as serious as contamination with any other oxalate when it is desired to carry out the estimation volumetrically by titrating the rare earth oxalate.[7]

A convenient alternative to the precipitation as oxalate is the precipitation as *sebacate*, effected by adding ammonium sebacate to a boiling, neutral solution of the nitrate.[8] Precipitation as *hydroxide* is also satisfactory when

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[1] See A. A. Noyes, Bray, and Spear, *J. Amer. Chem. Soc.*, 1908, 30, 481.

[2] See, *e.g.*, Lenher, *J. Amer. Chem. Soc.*, 1908, 30, 577.

[3] See, *e.g.*, Job, *Compt. rend.*, 1898, 126, 246; Matignon, *Ann. Chim. Phys.*, 1906, [viii.], 8, 245.

[4] Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [viii.], 9, 297.

[5] Welsbach, *Monatsh.*, 1885, 6, 477; Baxter and Griffin, *J. Amer. Chem. Soc.*, 1906, 28, 1684; Urbain and Jantsch, *Compt. rend.*, 1908, 146, 127.

[6] Baxter and Griffin, *J. Amer. Chem. Soc.*, 1906, 28, 1684; Baxter and Daudt, *ibid.*, 1908, 30, 563.

[7] For the titration, see the references cited on p. 242.

[8] Whittemore and James, *J. Amer. Chem. Soc.*, 1912, 34, 772; 1913, 35, 129.

precipitation is made by means of ammonia from a nitrate solution. Co-precipitation of basic chloride when the chloride is used leads to results that are slightly high; on the other hand, adsorption of alkali leads to very high results if sodium or potassium hydroxide is used as precipitant.[1] Matignon has recommended the determination of the rare earths by weighing them as the anhydrous *sulphates*.[2]

Separation of the Rare Earth Elements from other Metals.—It might be anticipated that the separation of the rare earth elements from sodium or potassium could readily be accomplished by precipitation with ammonia or oxalic acid. Such, however, is not the case, for appreciable quantities of alkali compounds are co-precipitated. A satisfactory separation is afforded, however, by precipitation with ammonium sebacate from a boiling, neutral solution of the nitrate.[3] The fluoride method also appears to be satisfactory. A quantitative separation from lithium may be effected with oxalic acid if the precipitation is made in a cold solution in the presence of ammonium chloride.[4]

The first steps taken in effecting the quantitative separation of the rare earth elements are usually the same as those followed in qualitative work; metals which form chlorides or sulphides insoluble in dilute hydrochloric acid are removed in the usual manner, the filtrate freed from hydrogen sulphide, and the rare earth elements then precipitated as hydroxides by the addition of ammonium chloride and ammonia. Iron, aluminium, chromium, glucinum, zirconium, thorium, uranium, and titanium may be co-precipitated, while an almost complete separation from zinc, manganese, nickel, cobalt, magnesium, and the alkali and alkaline-earth metals is obtained. The separation may be rendered more efficient, if necessary, by solution of the precipitate in acid and reprecipitation with ammonia. In rare earth mineral analysis, chromium, zinc, nickel, cobalt, barium, strontium, and the alkali metals are seldom encountered, while titanium is usually removed at the commencement.

The rare earth elements are separated from the other metals contained in the ammonia precipitate by means of oxalic acid. When the cerium group predominates, the following conditions are most suitable.[5] The precipitate is dissolved in hydrochloric acid, the concentration of the acid being adjusted so as to be between 0·25N and 0·5N, and 60 c.c. of acid being used for a gram of mixed earths. Precipitation is then effected by the addition of sufficient oxalic acid for the final liquid to contain 3 grams of oxalic acid per 100 c.c., and the whole maintained at about 60° for twelve hours. The best conditions when the yttrium group predominates require to be investigated.

The rare earth elements are thus separated as oxalates, but still in association with thorium. With respect to the separation from the other metals, it has been observed that the rare earth oxalates are appreciably soluble in solutions of uranyl salts,[6] and also, though to a less extent, in ferric and aluminium salts,[7] complex uranyloxalates, etc., being produced; hence a considerable excess of oxalic acid has to be added to effect a quantita-

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[1] T. O. Smith and James, *J. Amer. Chem. Soc*, 1914, 36, 909; *Chem. News*, 1914, 109, 219.

[2] Matignon, *Ann. Chim. Phys.*, 1906, [viii.], 8, 247.

[3] Whittemore and James, *J. Amer. Chem. Soc.*, 1912, 34, 772 (Y); 1913, 35, 129 (La, Ce, Nd). In the case of Y—K mixtures, double precipitation is necessary.

[4] Whittemore and James, *ibid.*, 1912, 34, 772 (Y).

[5] Hauser and Wirth, *Zeitsch. anal. Chem.*, 1908, 47, 389.

[6] Hauser, *Zeitsch. anal. Chem.*, 1908, 47, 677.

[7] Dittrich, *Ber.*, 1908, 41, 4373.

tive precipitation, and the determination of small amounts of rare earths in uranium minerals is rendered very difficult.[1]

The separation of the rare earth elements from thorium is most conveniently dealt with in a separate section, but at this point the methods for opening up rare earth minerals for analysis may be mentioned. As a matter of fact they have already been enumerated at the beginning of this chapter (see p. 318). *Silicates* may, if necessary, be fused with sodium carbonate, but as a rule they may be completely decomposed by evaporation with aqua regia. *Phosphates*, such as monazite and xenotime, may also be decomposed by fusion with sodium carbonate or fusion mixture, and removal of the alkali phosphate produced by extracting with dilute sodium hydroxide,[2] although monazite is usually treated with sulphuric acid or sodium bisulphate.[3] The *columbo-tantalates* and related minerals may be attacked by one of three methods. (i.) The mineral is fused with an excess of sodium bisulphate. The mass is extracted with water, the solution largely diluted, and boiled for several hours in a flask fitted with a reflux condenser. If titanium can then be detected in the liquid, the free acid present is partially neutralised with ammonia and the boiling continued until the titanium is entirely precipitated. The liquid is then filtered; it contains all the rare earth elements, thorium, zirconium (part), uranium, etc., while the residue may contain columbic, tantalic, titanic, tungstic,[4] stannic, and silicic acids, zirconium (part), iron (part), and sparingly soluble sulphates or basic sulphates such as those of lead, mercury, bismuth, etc. (ii.) The finely powdered mineral is decomposed by means of hydrofluoric acid (see p. 319). (iii.) The mineral, contained in a porcelain or silica boat, is placed in a combustion tube and heated to dull redness in a stream of the vapour of disulphur dichloride. Columbium, tantalum, titanium, and tungsten are thus removed as volatile chlorides or oxychlorides, and collected in dilute nitric acid, together with some or all of the volatile chlorides of iron and aluminium. When decomposition is complete, the residual chlorides in the boat are cooled in a stream of hydrogen chloride and their analysis effected in the manner already described.[5]

Traces of rare earths are occasionally found in *silicate rocks*, and may be determined as follows. The powdered rock is partially evaporated with hydrofluoric acid several times, the insoluble fluorides or silicofluorides separated by filtration and converted into sulphates by means of concentrated sulphuric acid. The filtered solution of the sulphates in dilute hydrochloric acid is precipitated with ammonia, the precipitate dissolved in hydrochloric acid, and the rare earths precipitated as oxalates.[6]

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[1] According to Whittemore and James (*J. Amer. Chem. Soc.*, 1912, **34**, 772), yttrium is satisfactorily separated from iron, aluminium, and magnesium by precipitation with oxalic acid in a cold solution to which ammonium chloride has been added. Smith and James (*ibid.*, 1913, **35**, 563) have shown that precipitation with oxalic acid in a slightly acid solution gives a satisfactory separation of neodymium from titanium, uranium, glucinum, zirconium, and barium.

[2] See, *e.g.*, Chesneau, *Compt. rend.*, 1911, **153**, 429.

[3] See, *e.g.*, Glaser, *J. Amer. Chem. Soc.*, 1896, **18**, 782; *Chem. Zeit.*, 1896, **20**, 612; Fresenius and Hintz, *Zeitsch. anal. Chem.*, 1896, **35**, 525; Hintz and Weber, *ibid.*, 1897, **36**, 27, 676; Benz, *Zeitsch. angew. Chem.*, 1902, **15**, 297; Johnstone, *J. Soc. Chem. Ind.*, 1914, **33**, 55. For another method of attacking phosphates, see Barlot and Chauvenet, *Compt. rend.*, 1913, **157**, 1153.

[4] On the separation from tungsten, see also Wunder and Schapria, *Ann. Chim. anal.*, 1913, **18**, 257.

[5] Hicks, *J. Amer. Chem. Soc.*, 1911, **33**, 1492.

[6] W. F. Hillebrand, *The Analysis of Silicate and Carbonate Rocks* ("Bull. U.S. Geol. Survey," 1910, No. **422**), p. 143, where an alternative procedure will also be found.

Separation of Thorium from the Rare Earth Elements.—The mixed oxalates of the rare earth elements and thorium are converted into the nitrates by heating on the steam-bath with a mixture of ordinary concentrated nitric acid and the fuming acid.[1] The liquid is evaporated to dryness and the residue dissolved in 100 c.c. of 10 per cent. ammonium nitrate. The solution is warmed to 60°–80° C., and the thorium precipitated by the addition of pure 3 per cent. hydrogen peroxide. The precipitate is filtered, washed with hot dilute ammonium nitrate, ignited wet in a platinum crucible, and weighed as thoria, ThO_2. This method gives very good results;[2] for great accuracy, the moist precipitate may be dissolved in nitric acid and the thorium reprecipitated as peroxide.[3]

Alternative methods are the thiosulphate, iodate, pyrophosphate, hypophosphate, fumarate, meta-nitrobenzoate, lead carbonate and sebacate processes mentioned earlier in this chapter (see p. 321, where references to the literature will be found), precipitation as basic thorium acetate,[4] precipitation of the thorium as hydroxide by certain weak organic bases,[5] volatilisation of the thorium as the chloride,[6] etc. The thiosulphate method is the oldest and one of the most convenient. It is rather tedious to carry out when results of a high degree of accuracy are required,[7] but for many purposes the procedure may be simplified. Precipitation should be effected from a dilute solution of the mixed chlorides after having evaporated it to dryness or added ammonia to expel or neutralise free acids, and the sodium thiosulphate added should be at least equivalent to the total rare earths present. After boiling for fifteen minutes only a trace of thorium remains in solution; but, unless the thoria constitutes some 90 per cent. or more of the total earths, the precipitate contains small amounts of earths other than thoria, which must be removed by a second precipitation. A third precipitation is seldom necessary.

Separation of the Rare Earth Elements from One Another.—A general solution of this problem is not yet known. As a rule the cerium is determined and an approximate separation of the remaining elements into the cerium and yttrium groups effected. Two methods of procedure are available: (i.) the cerium is separated first by a suitable gravimetric method, and (ii.) the separation into the cerium and yttrium groups is carried out first, and the cerium subsequently estimated either gravimetrically or volumetrically.[8]

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[1] *Cf.* Borelli, *Gazzetta*, 1909, **39**, i. 425.

[2] According to R. C. Wells (*J. Soc. Chem. Ind.*, 1910, **29**, 1304), this results from the balancing of slight positive and negative errors.

[3] Wyrouboff and Verneuil, *Bull. Soc. chim.*, 1897, [iii.]. **17**, 679; 1898, **19**, 219; *Compt. rend.*, 1898, **126**, 340; **127**, 412; *Ann. Chim. Phys.*, 1905, [viii.], **6**, 489; Benz, *Zeitsch. angew. Chem.*, 1902, **15**, 297.

[4] Mingaye, *Records Geol. Survey N.S. Wales*, 1909, **8**, 276.

[5] Miss Jefferson, *J. Amer. Chem. Soc.*, 1902, **24**, 540; Hartwell, *ibid.*, 1903, **25**, 1128.

[6] Bourion, *Ann. Chim. Phys.*, 1910, [viii.], **21**, 109.

[7] For the necessary procedure, see White, *Lecture on Thorium and its Compounds* (The Institute of Chemistry, 1912); *cf.* Johnstone, *J. Soc. Chem. Ind.*, 1914, **33**, 55, and the references cited on p. 321.

[8] When procedure (ii.) is employed and the cerium determined volumetrically, the volumetric analysis is made after the weight of the total rare earths of the cerium group, including the ceria, has been ascertained; the ceria earths other than ceria may then be calculated. This latter result, however, will be slightly in excess of the true value owing to the presence of praseodymium dioxide in the oxides weighed.

The error caused by the praseodymium may be eliminated by heating the oxides to redness in hydrogen, but only when ceria has been previously removed, for ceria loses in weight when heated in hydrogen.

Separation of the Cerium.—Assuming the thorium to have been removed by the peroxide method, the filtrate is treated in a dish with excess of ammonia and hydrogen peroxide, the liquid boiled, and then the whole is evaporated to dryness on the steam-bath. The residue is carefully heated until ammonium nitrate commences to decompose, or else dried at 110°; the perceric hydroxide is thus converted into ceric hydroxide. The residue is dissolved in strong nitric acid and the cerium separated as basic ceric nitrate-sulphate as described on p. 333, about 0·1 gram of ammonium sulphate being used to 0·5 gram of mixed rare earths. The precipitate is filtered off and washed with hot dilute ammonium nitrate. To the filtrate 0·5 gram of sodium acetate and about 0·5 gram of ammonium persulphate are added, and the liquid boiled. The remaining cerium is thus precipitated, together with traces of the other elements. The two precipitates are ignited together at a white heat, and the cerium weighed as ceria, CeO_2.[1] In mineral analysis the result is then calculated to cerous oxide, Ce_2O_3, since the cerium minerals are cerous compounds.

In addition to the preceding process the bromate method described on p. 334, and Mosander's chlorine method, outlined on p. 336, may be employed.[2]

Separation of the Cerium and Yttrium Groups.—This separation is usually effected by the double sulphate method. The rare earth elements, having been freed from thorium, are suitably treated to obtain a very concentrated and nearly neutral solution of the chlorides. A large excess of a saturated solution of potassium sulphate is added, together with a few grams of the powdered salt, and the whole allowed to stand for twelve hours, with occasional agitation. The crystalline precipitate is washed with saturated potassium sulphate solution, reconverted into the chloride, and the separation repeated. From the combined filtrates the yttria earths are precipitated as hydroxides, and then converted successively into nitrates, oxalates, and oxides. The total ceria earths are extracted from the precipitated double sulphates in a similar manner. The weights of the mixed oxides give approximately the amount of ceria and yttria earths present.[3] Sodium sulphate is not so satisfactory a precipitant as the potassium salt.

An alternative method has been proposed by James and Smith.[4] A solution of the mixed nitrates is first prepared. This is evaporated to dryness, treated with 25 c.c. of concentrated nitric acid saturated with bismuth magnesium nitrate, and then a further 10 grams of bismuth magnesium nitrate and 1 gram of magnesium nitrate added. The whole is warmed and stirred until most of the salt has dissolved; it is then set aside for twenty-four hours. The precipitate is collected in a Gooch crucible and washed with nitric acid saturated with bismuth magnesium nitrate.

In this method the metals of the yttrium group remain in solution, while those of the cerium group are precipitated almost quantitatively.[5]

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[1] Wyrouboff and Verneuil, *Compt. rend.*, 1899, **128**, 1331; *Ann. Chim. Phys.*, 1906, [viii.], **9**, 345.

[2] For details of the former, see James and Pratt, *J. Amer. Chem. Soc.*, 1911, **33**, 1326; for details of the latter, see Johnstone, *J. Soc. Chem. Ind.*, 1914, **33**, 55; Hauser and Wirth, *Zeitsch. anal. Chem.*, 1909, **48**, 679; Browning and Roberts, *Amer. J. Sci.*, 1910, [iv.], **29**, 45.

[3] See, *e.g.*, Johnstone, *loc. cit.*, and *cf.* footnote 8 on p. 371.

[4] James and T. O. Smith, *J. Amer. Chem. Soc.*, 1912, **34**, 1171.

[5] Precisely how samarium, europium, gadolinium, terbium, dysprosium, and holmium behave is not known.

Volumetric Estimation of Cerium.—Several volumetric methods are available whereby cerium may be accurately determined in the presence of the other rare earth elements. They are all based upon the conversion of cerous into ceric salts or *vice versâ.*

(i.) The mixed nitrates, in cold, concentrated nitric acid solution, are treated with an excess of lead peroxide and shaken until oxidation of the cerous salt is complete. In the filtered solution the ceric salt is titrated with standard hydrogen peroxide until the colour of the ceric salt just vanishes :—[1]

$$2Ce(NO_3)_4 + H_2O_2 = 2Ce(NO_3)_3 + 2HNO_3 + O_2.$$

(ii.) The lead peroxide of method (i.) is replaced by bismuth tetroxide, oxidation being effected in cold nitric acid (1 vol. of acid to 1 of water). The solution is diluted, filtered through asbestos, excess of standard hydrogen peroxide added, and the excess titrated with standard potassium permanganate.[2]

(iii.) The oxidising agent used is sodium bismuthate, and oxidation effected in boiling, dilute sulphuric acid (1 of acid to 4 of water) in the presence of a gram or two of ammonium sulphate. The filtered solution is reduced with standard ferrous sulphate, excess of which is titrated with potassium permanganate.[3]

(iv.) Oxidation to the ceric state is effected in boiling, dilute sulphuric acid by means of ammonium persulphate; the titration is then effected in the cold liquid by the use of hydrogen peroxide and potassium permanganate.[4]

This method is largely employed. It gives good results, but requires careful attention to points of detail.

(v.) The oxidation is effected by means of potassium ferricyanide in the presence of alkali hydroxide :—

$$Ce_2(SO_4)_3 + 2K_3Fe(CN)_6 + 8KOH = 2Ce(OH)_4 + 2K_4Fe(CN)_6 + 3K_2SO_4.$$

The ceric hydroxide is removed by filtration and the potassium ferrocyanide in the filtrate titrated with potassium permanganate in the presence of sulphuric acid.[5]

(vi.) The neutral solution, containing the cerium as cerous salt, is added, with constant shaking, to a definite volume of hot, standard potassium permanganate containing excess of magnesia in suspension, until the permanganate is decolorised :—[6]

$$\begin{aligned}3Ce(NO_3)_3 + KMnO_4 + 4MgO + 8H_2O \\ = 3Ce(OH)_4 + MnO_2 . 2H_2O + 4Mg(NO_3)_2 + KNO_3.\end{aligned}$$

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[1] Job, *Compt. rend.*, 1899, **128**, 101; *Ann. Chim. Phys.*, 1900, [vii.], **20**, 205; Chesneau, *Compt. rend.*, 1911, **153**, 429; *cf.* Gibbs, *Amer. J. Sci.*, 1864, [ii.], **37**, 354; Bührig, *J. prakt. Chem.*, 1875, [ii.], **12**, 231.

[2] Waegner and Müller, *Ber.*, 1903, **36**, 282, 1732; *cf.* Gibbs, *Amer. Chem. J.*, 1893, **15**, 546.

[3] Metzger, *J. Amer. Chem. Soc.*, 1909, **31**, 523; Metzger and Heidelberger, *ibid.*, 1910, **32**, 642.

[4] Von Knorre, *Zeitsch. angew. Chem.*, 1897, **10**, 685, 717; *Ber.*, 1900, **33**, 1924; Power and Shedden, *J. Soc. Chem. Ind.*, 1900, **19**, 636. Strohbach (*Mitt. Techn. Versuchsamtes*, 1912, **1**, 45; *J. Soc. Chem. Ind.*, 1913, **32**, 139) oxidises with chloric acid.

[5] Browning and Palmer, *Amer. J. Sci.*, 1908, [iv.], **26**, 83; *Chem. News*, 1908, **98**, 106; *Zeitsch. anorg. Chem.*, 1908, **59**, 71.

[6] R. J. Meyer and Schweitzer, *Zeitsch. anorg. Chem.*, 1907, **54**, 104; *cf.* Brauner, *Chem. News*, 1895, **71**, 283; Lenher and Meloche, *J. Amer. Chem. Soc.*, 1916, **38**, 66.

(vii.) When ceria is digested in an atmosphere of carbon dioxide with a warm solution of potassium iodide in concentrated hydrochloric acid, it is quantitatively reduced to the cerous state and the liberated iodine may be titrated with sodium thiosulphate :—[1]

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

This reaction, however, is of no practical value for the estimation of ceria in mixtures of earths.[2]

(viii.) Small quantities of ceria present in thoria may be determined colorimetrically.[3]

Quantitative Analysis by Spectroscopic Methods.—(i.) *Spark Spectra.*—When the relative degrees of persistency of the lines in the spark spectrum of, say, lanthanum chloride solution, are known, it is clear that the results may be utilised to advantage for the purposes of quantitative analysis. A dilute chloride solution of the substance containing lanthanum is prepared, of known concentration, and its spark spectrum examined. A first approximation to the lanthanum content of the solution being thus obtained, closer and closer approximations to the true value may then be obtained in successive trial experiments. The feasibility of such a method of analysis was demonstrated as long ago as 1884 by Hartley;[4] at the present time, though, the necessary data for the spark spectra of the rare earth elements are almost entirely lacking.[5]

(ii.) *Absorption Spectra.*—Two general methods may here be employed for the estimation of those rare earth elements that give rise to absorption spectra.

In the first method, the absorption produced by the element in the substance to be analysed is recorded photographically and compared with a series of photographs of the absorption produced by the element at a series of known concentrations and under the same conditions of experiment.

In the second method, the amount of absorption exerted by the substance is measured quantitatively at those regions of the spectrum where its absorption is most characteristic. The necessary photometric measurements are effected by the use of a spectrophotometer, for a description of which the reader must be referred elsewhere. The method of calculation may, however, be briefly outlined.

Suppose that a layer of absorbing medium is used of thickness d, the layer being bounded in part by two parallel faces, on to one of which homogeneous light[6] of intensity I_0 falls normally. If the light emerges from the opposite face with intensity I, then

$$I/I_0 = a^d,$$

where a is a constant (the absorption coefficient) the value of which depends upon the nature of the medium and the wave-length of the light. If d' is

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[1] Bunsen, *Annalen*, 1853, 86, 265; 1858, 105, 49; Browning, *Amer. J. Sci.*, 1899, [iv.], 8, 451; *Chem. News*, 1900, 81, 30, 41; *Zeitsch. anorg. Chem.*, 1899, 22, 297; Brauner, *ibid.*, 1903, 34, 207.

[2] Marc, *Ber.*, 1902, 35, 2370; R. J. Meyer and Koss, *Ber.*, 1902, 35, 3740; Mengel, *Zeitsch. anorg. Chem.*, 1899, 19, 71.

[3] Benz, *Zeitsch. angew. Chem.*, 1902, 15, 300.

[4] Hartley, *Phil. Trans.*, 1884, 175, 49, 325.

[5] For La, Ce, and Y, see Pollok and Leonard, *Sci. Proc. Roy. Dubl. Soc.*, 1908, 11, 257, and the table of wave-lengths given on p. 307.

[6] *I.e.* light of one wave-length.

the particular value of d for which $I/I_0 = 1/10$, then $1/d'$ is called the "extinction coefficient" and denoted by α. It follows that $a = 10^{-\alpha}$ and

$$-\log_{10}(I/I_0) = \alpha d.$$

In accordance with Beer's Law, if $c', c'', c''' \ldots$ be the concentrations of the absorbing substance, and the corresponding thicknesses of absorbing layer for the light intensity to fall from I_0 to I be $d', d'', d''' \ldots$, then $c'd' = c''d'' = c'''d''' = \ldots$ If, then, the extinction coefficients of the solutions be $\alpha', \alpha'', \alpha''' \ldots$, it follows that

$$c'/\alpha' = c''/\alpha'' = c'''/\alpha''' = \ldots = A,$$

or, in general terms,

$$c = \alpha A,$$

where A, called the "absorption ratio," is a constant that may be determined once for all for any particular absorbing substance in a given solvent.

Suppose, now, that the concentration (c) of neodymium in an aqueous solution of rare earth chlorides is required: the extinction coefficient (α) is measured by the spectrophotometer at a particular part of the spectrum where the absorption ratio (A) for aqueous neodymium chloride is known. From the relationship $c = \alpha A$ the required concentration can then be immediately calculated.

It has been already pointed out in the preceding chapter that the absorption exerted by a rare earth salt is modified by the presence of a salt of another rare earth element, even though the second salt gives no absorption spectrum. Hence measurements of concentrations effected by observations upon absorption spectra only give approximate results when mixtures are examined, *i.e.* in the only cases where one need resort to the process at all.[1]

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[1] For further information, see Bahr and Bunsen, *Annalen*, 1866, **137**, 30; Muthmann and Stützel, *Ber.*, 1899, **32**, 2653; G. and H. Krüss, *Kolorimetrie und quantitative Spektralanalyse* (Voss, Leipzig, 2nd ed., 1909); Thorpe, *A Dictionary of Applied Chemistry* (Longmans, 1912–1913), vol. v., article "Spectrum Analysis"; Meyer and Hauser, *Die Analyse der seltenen Erden und der Erdsäuren* (Enke, Stuttgart, 1912).

CHAPTER XII.

THE RARE EARTH ELEMENTS (*continued*).

THE CERIUM GROUP.

The rare earth elements included in this group are five in number, namely, lanthanum, cerium, praesodymium, neodymium, and samarium. The chemistry of these elements is fairly well known, the commercial treatment of monazite sand for thorium having enabled large quantities of the earths of the cerium group to be placed at the disposal of scientific investigators.

The isolation of ceria from the mixed ceria earths is a comparatively simple operation. The separation of the remaining members of the group is most conveniently effected by the fractional crystallisation of the double ammonium, magnesium, or manganese nitrates, as described in the preceding chapter.

The points of difference between the cerium and yttrium groups have been already stated (see p. 249).

In the following account of the cerium elements and their compounds cerium itself is dealt with first, the other elements being then taken in their serial order.

CERIUM.

Symbol, Ce. Atomic weight, 140·25 (O = 16).

Cerium is the most abundant of the rare earth elements. Its occurrence, history, atomic weight, homogeneity, and analytical chemistry have already been discussed in Chapters X. and XI.

The separation of ceria from the other rare earths and its purification have been discussed in some detail in Chapter X. (see p. 332). On a commercial scale pure cerium salts are obtained by (i.) the permanganate method (p. 335), (ii.) the basic nitrate method (p. 332), or (iii.) the ceric ammonium nitrate method (p. 336), the procedures already outlined being suitably modified for technical work. Only a small proportion of the cerium available (in monazite residues) is worked up into pure cerium salts.

Metallic cerium is obtained by the electrolytic methods previously described (p. 230).

Cerium[1] is a metal which resembles steel in appearance and takes a high polish. Its density is 6·92 at 25°. It is malleable and highly ductile,

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[1] The properties of cerium as here given are substantially those stated by Hirsch, *J. Ind. Eng. Chem.*, 1911, **3**, 880; 1912, **4**, 65; *Trans. Amer. Electrochem. Soc.*, 1911, **29**, 57. See also Muthmann and Kraft, *Annalen*, 1902, **325**, 261; Muthmann and Weiss, *Annalen*, 1904, **331**, 1; Hillebrand and Norton, *Pogg. Annalen*, 1875, **155**, 633; **156**, 466.

may be readily cut with a knife, and can be machined fairly well, although there is a tendency to buckle. Its ultimate strength is 9 kilos. per square mm. The metal is paramagnetic, its magnetic susceptibility at 18° being 15×10^{-6} c.g.s. units per gram.[1] Cerium is a fairly good conductor of heat, but a poor conductor of electricity, its resistance being 71·6 micro-ohms per cm. cube at the ordinary temperature. The following values have been obtained for the specific heat:—[2]

Mendeléeff .	?	spec. ht. = 0·05	atomic ht. = 7·01
Hillebrand .	0°–100°	„ = 0·0448	„ = 6·28
Hirsch . .	20°–100°	„ = 0·05112	„ = 7·17

Hirsch's value was obtained by using the differential steam calorimeter and operating with 70 grams of cerium. The atomic heat of cerium thus appears to be unusually high. Cerium melts at 635° (Hirsch), 623° (Muthmann and Weiss).

Cerium takes fire in air at 160°, burning with even greater brilliancy than magnesium and evolving much heat. A shower of sparks is produced by striking the metal with a flint. When a lump of cerium is kept warm in a closed bottle, a black powder slowly forms on the surface, and when the bottle is opened the powder inflames spontaneously. Cerium burns brilliantly in chlorine at 210°–215°, and in bromine at 215°–220°; it also combines directly with hydrogen, nitrogen, iodine, sulphur, selenium, tellurium, arsenic, antimony, etc. It reduces carbon monoxide and carbon dioxide with the separation of carbon.

Cerium preserves its lustre in dry, but tarnishes in moist air. It is very slightly attacked by cold water, but in boiling water a slow evolution of hydrogen occurs. At the ordinary temperature ethyl and amyl alcohols, chloroform, carbon tetrachloride, and concentrated solutions of sulphuric acid, sodium and ammonium hydroxides have no action on cerium; dilute hydrogen peroxide, ammonium and potassium chloride slowly attack it, and the action of hydrochloric or nitric acid, both dilute and concentrated, and dilute sulphuric acid is moderately vigorous. At boiling temperatures the mineral acids, dilute or concentrated, attack the metal rapidly, except concentrated sulphuric acid.

According to Hirsch, cerium is best purified by heating it with boiling mercury in a long iron pipe. The cerium amalgamates with the mercury, and the impurities may be skimmed off from the molten amalgam. The amalgam is placed in a magnesia vessel, the whole placed inside a larger quartz vessel, and the amalgam heated very strongly *in vacuo* to drive off the mercury.

Alloys.—Cerium alloys readily with a large number of metals. Many of the alloys thus obtained are hard and brittle, differing therefore from pure cerium, which is soft and malleable. Accordingly, small particles are easily detached from the alloys by friction, and when the alloys are rich in cerium the heat produced is more than sufficient to raise the temperature of the particles above 160°, the ignition-point of cerium. Hence numerous alloys rich in cerium are pyrophoric. Some of them, *e.g.* iron-cerium alloys, are of

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[1] M. Owen, *Ann. Physik*, 1912, [iv.], 37, 657; *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 637.

[2] Mendeléeff, *Bull. Acad. Sci. Petrograd*, 1870, p. 445; Hillebrand, *Pogg. Annalen*, 1876, 158, 71; Hirsch, *loc. cit.*

commercial importance owing to this property, being utilised in the manufacture of automatic lighters, etc.[1] The alloy of cerium, lanthanum, etc., known as "Mischmetall," is a valuable reducing agent (see p. 230).

Sodium alloys with cerium quietly, forming a hard and somewhat pyrophoric alloy that oxidises on exposure to air. *Silver* and *gold* alloy readily with cerium; the silver alloys are hard and brittle, but the gold alloys are fairly soft.[2] The *copper* alloys have been systematically examined[3] and four compounds discovered, viz. Cu_6Ce (m.p. 935°), Cu_4Ce, Cu_2Ce (m.p. 820°), and

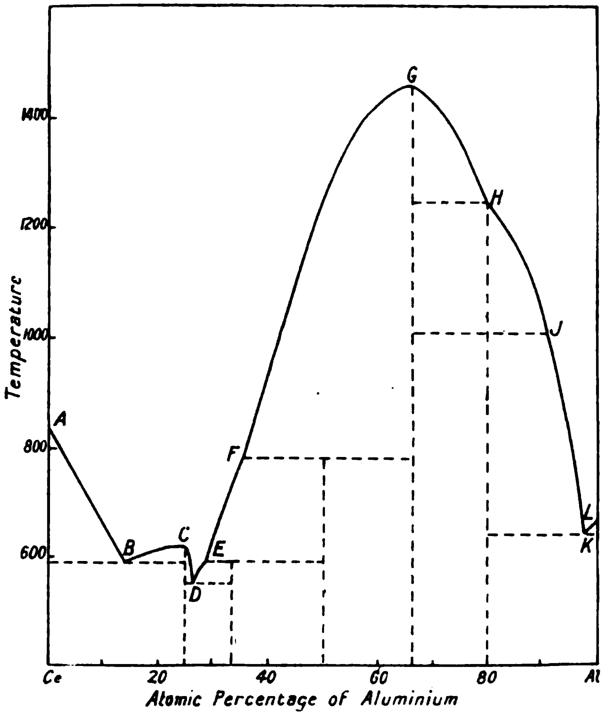

FIG. 38.—The system cerium-aluminium equilibrium diagram (Vogel). Solid phases; Ce along AB, Ce_3Al along BCD, Ce_2Al along DE, CeAl along EF, $CeAl_2$ along FGH, $\beta CeAl_4$ along HJ, $\alpha CeAl_4$ along JK, Al along KL.

CuCe. Between 55 and 85 per cent. Ce the alloys are pyrophoric, and with more than 30 per cent. Ce they soon disintegrate.

Calcium and cerium alloys are white and very hard; they are stable in air, do not disintegrate, and emit brilliant sparks when struck. They may be prepared from the metals, or by reducing cerous fluoride with calcium.[4]

Magnesium and cerium alloys are white in colour and extremely brittle.

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[1] See Kellermann, *Die Ceritmetalle und ihre pyrophoren Legierungen* (Knapp, Halle, 1912).

[2] Hirsch, *loc. cit.*

[3] Hanaman, *Intern. Zeitsch. Metallographie*, 1915, 7, 174.

[4] Moldenhauer, *Chem. Zeit.*, 1914, 38, 147.

The alloys rich in cerium form excellent flashlight powders. Those containing 60–75 per cent. of cerium may be finely powdered, and form excellent reducing agents, *e.g.* for preparing vanadium from its oxide. Alloys containing more than 75 per cent. of cerium are difficult to powder without catching fire. The alloys have been systematically examined by Vogel,[1] who has described the compounds Ce_4Mg (m.p. 632°), CeMg (m.p. 738°), $CeMg_3$ (m.p. 780°), and $CeMg_9$. The compound Ce_4Mg breaks up into Ce and CeMg at 497°; the compounds CeMg and $CeMg_3$ form solid solutions with one another. *Zinc* alloys with cerium almost explosively. The alloy is hard, brittle, and pyrophoric, but oxidises in the air. *Cadmium* behaves similarly to zinc. *Mercury* readily alloys with cerium. The amalgams, which are liquid at ordinary temperatures when only 1 or 2 per cent. of cerium is present, decompose water with the evolution of hydrogen and oxidise quickly in the air, spontaneous combustion readily occurring when 8–10 per cent. of cerium is present.[2]

Aluminium and cerium alloys have been studied by the thermal and microscopic methods. The equilibrium diagram, due to Vogel, is shown in fig. 38.[3] No solid solutions are formed. Five compounds exist, two only being stable at the melting-point: Ce_3Al (m.p. 614°), Ce_2Al, CeAl, $CeAl_2$ (m.p. 1460°), and $CeAl_4$. The compound $CeAl_4$ exists in two forms, the transition-point being 1005°. The form stable at ordinary temperatures is probably rhombic. Its density is 4·193.[4] The cerium-aluminium alloys are stable to air and water unless the cerium is more than 75 per cent. The maximum hardness is 6, corresponding to $CeAl_2$. This compound is very resistant towards acids, but burns brilliantly.

For other cerium alloys, see the subsequent volumes of this series.

Thermochemistry of Cerium.—The following results have been recorded:—[5]

$$\begin{array}{lll}
[Ce] + (O_2) & = [CeO_2] \quad . \quad . \quad . \quad . \quad . & +224{\cdot}6 \text{ Cals.} \\
[Ce] + 4[Al] & = [CeAl_4] \quad . \quad . \quad . \quad . & +124{\cdot}4 \quad ,, \\
[Ce(OH)_4] + H_2SO_4aq. & = Ce(SO_4)_2aq. \quad . \quad . \quad . \quad . & + \quad 0{\cdot}90 \quad ,, \\
2[Ce(OH)_3.O.OH] + 3H_2SO_4aq. & = Ce_2(SO_4)_3aq. + H_2O_2aq. + (O_2) & + \quad 29{\cdot}95 \quad ,, \\
2Ce(SO_4)_2aq. + H_2O_2aq. & = Ce_2(SO_4)_3aq. + H_2SO_4aq. + (O_2) & + \quad 33{\cdot}58 \quad ,, \\
[Ce(OH)_3.O.OH] & = [Ce(OH)_4)] + (O) \quad . \quad . \quad . & + \quad 20{\cdot}39 \quad ,,
\end{array}$$

CEROUS COMPOUNDS.

The cerous salts are derived from the basic oxide Ce_2O_3 and, if derived from colourless acids, are themselves colourless. Their aqueous solutions are devoid of absorption spectra.

In chemical properties the cerous salts resemble the salts of lanthanum very closely, except for the fact that they may be oxidised to ceric salts. The equivalent conductivities, λ, of cerous salts are in harmony with the view that

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[1] Vogel, *Zeitsch. anorg. Chem.*, 1915, 91, 277.

[2] Muthmann and Beck, *Annalen*, 1904, 331, 46; Hirsch, *loc. cit.*

[3] R. Vogel, *Zeitsch. anorg. Chem.*, 1912, 75, 41.

[4] Muthmann and Beck, *loc. cit.*

[5] Muthmann and Weiss, *Annalen*, 1904, 331, 1 (Ce, O_2); Muthmann and Beck, *ibid.*, 1904, 331, 46 (Ce, Al_4); Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1900, 32, 609. The data given for ceric and perceric hydroxides refer to the hydroxides as ordinarily precipitated.

they are derived from a fairly strong triacid base. The following data hold for a temperature of 25° (v = dilution in litres per gram-equivalent) :—[1]

$CeCl_3$	$v=$	31·43	62·86	125·72	251·44	502·88	1005·76
	$\lambda=$	107·5	114·2	121·2	126·7	131·0	136·0
$Ce_2(SO_4)_3$	$v=$	33	66	132	264	528	1056
	$\lambda=$	45·66	53·71	63·63	74·09	87·17	100·90

Numerous cerous salts have been described by Jolin[2] and others. The methods for the conversion of cerous into ceric compounds and *vice versâ* are discussed later (p. 391).

CERIUM AND HYDROGEN.

Cerous hydride, CeH_3, has been described (see p. 251). The combination of cerium and hydrogen proceeds readily even at 310°, but is best effected at 450°, at which temperature the dissociation pressure of the hydride does not exceed 1 mm.[3] The hydride is spontaneously inflammable.[4]

CERIUM AND THE FLUORINE GROUP.

Cerous fluoride, CeF_3, is said by Brauner to be obtained by carefully heating ceric fluoride to dull redness.[5] The hemihydrate, $2CeF_3.H_2O$, is obtained by double decomposition.[6] Cerous fluoride forms no compound with potassium fluoride.[7]

Cerous chloride, $CeCl_3$.—The methods of preparation and properties of the anhydrous salt are described on p. 252. Bourion's sulphur chloride method, starting with ceric oxide, is very convenient. The chloride is a white, crystalline, hygroscopic solid, readily soluble in water.

Anhydrous cerous chloride readily absorbs ammonia. The following compounds have been prepared, and their dissociation pressures measured :—[8]

$CeCl_3.20NH_3$
$CeCl_3.12NH_3$
$CeCl_3.8NH_3$
$CeCl_34.NH_3$
$CeCl_3.2NH_3$

An aqueous solution of cerous chloride may be prepared by heating ceric hydroxide with concentrated hydrochloric acid, chlorine being evolved. On saturating the cold solution with hydrogen chloride, orthorhombic crystals ($a : b : c = 0{\cdot}8083 : 1 : 1{\cdot}4419$) of the heptahydrate, $CeCl_3.7H_2O$, separate.[9] A triclinic salt ($a : b : c = 1{\cdot}1580 : 1 : 0{\cdot}8635$; $\alpha = 91° 3'$, $\beta = 114° 9'$, $\gamma = 88° 12'$) has also been described, isomorphous with lanthanum chloride heptahydrate, but it is said to be the hexahydrate, $CeCl_3.6H_2O$.[10]

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[1] Aufrecht, *Inaugural Dissertation* (Berlin, 1904); *cf.* Holmberg, *Arkiv Kem. Min. Geol.*, 1903, **1**, 1.

[2] Jolin, *Bull. Soc. chim.*, 1874, [ii.], **21**, 533.

[3] Zhukov, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 2073.

[4] Dafert and Miklauz, *Monatsh.*, 1912, **33**, 911.

[5] Brauner, *Ber.*, 1881, **11**, 1944 ; *Trans. Chem. Soc.*, 1882, **41**, 68. See also p. 393.

[6] Jolin, *Bull. Soc. chim.*, 1874, [ii.], **21**, 533.

[7] Puchin and Baskov, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 82.

[8] Barre, *Compt. rend.*, 1913, **156**, 1017.

[9] Dennis and Magee, *J. Amer. Chem. Soc.*, 1894, **16**, 649 ; *Zeitsch. anorg. Chem.*, 1894, **7**, 250 ; *cf.* Jolin, *Bull. Soc. chim.*, 1874, [ii.], **21**, 533 ; Lange, *J. prakt. Chem.*, 1861, **82**, 129 ; R. J. Meyer and Koss, *Ber.*, 1902, **35**, 3740.

[10] Fock, *Zeitsch. Kryst. Min.*, 1894, **22**, 32.

The following double salts are known, in addition to those containing metals of Groups IV. and V. and organic bases :—

$CeCl_3.4HgCl_2.10H_2O$;[1] $CeCl_3.3Hg(CN)_2.8H_2O$.[2]
$CeCl_3.AuCl_3.13H_2O$.[1, 4]
$CeCl_3.2PtCl_2.10H_2O$;[7] $CeCl_3.PtCl_4.12H_2O$.[1, 3, 5, 6, 7]

Cerous oxychloride, CeOCl (?) has been described by several chemists.[8]

Cerous bromide, $CeBr_3$.—The anhydrous salt, a white, hygroscopic mass, has been prepared.[9] A hydrate and an *auribromide*, $CeBr_3.AuBr_3.8H_2O$ (Jolin), are known.

Cerous iodide, CeI_3.—The hydrate, $CeI_3.9H_2O$, forms colourless crystals which turn brown in the air.[10]

Cerous perchlorate, $Ce(ClO_4)_3.8H_2O$ or $9H_2O$ (?), is a deliquescent, crystalline salt, which may be prepared from cerous sulphate and barium perchlorate.[11]

Cerous bromate, $Ce(BrO_3)_3.9H_2O$, must be crystallised from aqueous solution by concentrating *in vacuo* at 35° and then cooling. It melts at 49°, and decomposes at slightly higher temperatures. Further, it slightly decomposes in aqueous solution.[12]

Cerous iodate, $Ce(IO_3)_3.2H_2O$, is readily obtained by double decomposition as a white, amorphous, sparingly soluble precipitate.[13] At 25°, one litre of saturated solution contains 1·64 grams of the anhydrous salt.[14]

CERIUM AND THE OXYGEN GROUP.

Cerium sesquioxide or **cerous oxide,** Ce_2O_3, so readily oxidises to form cerium dioxide that cerous salts of volatile oxyacids yield ceria when ignited in the air. The sesquioxide can be prepared by the reduction of the dioxide with hydrogen at 150 atmos. pressure and at a temperature of about 2000° C. (*cf.* p. 393).[15] In small quantities and mixed with much ceria and a little carbon, it is produced by the ignition of cerous oxalate *in vacuo* or in hydrogen.[16] It is also produced in poor yield by heating ceria

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[1] Jolin, *loc. cit.*

[2] Alén, *Oefvers. Svenska Vet.-Akad. Förhandl.*, 1876, **33**, Nos. 8, 9 ; *Bull. Soc. chim.*, 1876, [ii.], **27**, 365.

[3] Holzmann, *J. prakt. Chem.*, 1861, **84**, 76.

[4] Holzmann, *Jahresber.*, 1862, p. 135.

[5] Marignac, *Ann. Chim. Phys.*, 1873, [iv.], **30**, 67.

[6] Cleve, *Bull. Soc. chim.*, 1874, [ii.], **21**, 196.

[7] Nilson, *Ber.*, 1876, **9**, 1056. See also p. 254.

[8] Wöhler, *Annalen*, 1867, **144**, 251; Erk, *Jahresber.*, 1870, p. 319; Didier, *Compt. rend.*, 1885, **101**, 882.

[9] See p. 255 ; also Robinson, *Proc. Roy. Soc.*, 1884, **37**, 150.

[10] Lange, *J. prakt. Chem.*, 1861, **82**, 129.

[11] Jolin, *loc. cit.*; Morgan and Cahen, *Trans. Chem. Soc.*, 1907, **91**, 475.

[12] See p. 256, and Rammelsberg, *Pogg. Annalen*, 1842, **52**, 84.

[13] Rammelsberg, *Pogg. Annalen*, 1838, **44**, 557 ; Holzmann, *J. prakt. Chem.*, 1858, **75**, 321 ; Jolin, *loc. cit.*

[14] Rimbach and Schubert, *Zeitsch. physikal. Chem.*, 1909, **67**, 183.

[15] Newbery and Pring, *Proc. Roy. Soc.*, 1916, **A**, **92**, 276. According to Guertler (*Zeitsch. anorg. Chem.*, 1904, **40**, 247), cerium dioxide is quantitatively reduced to the sesquioxide when heated to a white heat in the reducing atmosphere of a petroleum injector-furnace.

[16] Mosander, *Phil. Mag.*, 1843, [iii.], **23**, 241 ; Delafontaine, *Arch. Sci. phys. nat.*, 1865, **22**, 38 ; Bührig, *J. prakt. Chem.*, 1875, [ii.], **12**, 209 ; Popp, *Annalen*, 1864, **131**, 359 ; Sterba, *Ann. Chim. Phys.*, 1904, [viii.], **2**, 209. See also Beringer, *Annalen*, 1842, **42**, 138 ; Rammelsberg, *Pogg. Annalen*, 1859, **108**, 40 ; Winkler, *Ber.*, 1891, **24**, 873.

with zinc at the boiling-point of the metal, but it cannot be separated from the other products of the reaction.[1] The simplest method yet known for its preparation consists in heating ceria with metallic calcium and dissolving out the lime and excess of calcium in aqueous ammonium chloride at − 10° C. The sesquioxide is thus obtained as a yellowish-green powder which readily absorbs oxygen even at ordinary temperatures and burns easily when gently heated.[2]

Cerous hydroxide, $Ce(OH)_3$, is obtained as a white precipitate by the addition of ammonia or alkali hydroxide to a solution of a cerous salt, or by the action of water on cerium carbide, CeC_2. It may be dried without losing its white colour if air is completely excluded.[3] It cannot, however, be further dehydrated to cerous oxide, for the latter, as it is produced, attacks the water present and oxidises.

Cerous hydroxide, like the other hydroxides of the rare earth elements, is a strong base. It readily oxidises in the air, becoming first violet (p. 393) and finally yellow, owing to its conversion into ceric hydroxide. Oxidising agents effect the change more rapidly (p. 396). Owing to the ease with which it is oxidised, cerous hydroxide is a strong reducing agent, reducing cupric salts to cuprous, mercuric salts to mercurous, etc.[4]

Cerous sulphide, Ce_2S_3, may be prepared by heating ceric oxide to bright redness in a stream of dry hydrogen sulphide, the oxide, contained in a porcelain boat inserted in a porcelain tube, being heated until its weight ceases to alter (see p. 259). An alternative method is to use cerous sulphate instead of ceric oxide and heat to 750°–800° in hydrogen sulphide.[5]

Cerous sulphide is a dark reddish-purple solid of density 5·02 at 11° (Muthmann and Stützel). When heated in the air it roasts to cerous sulphate and ceric oxide, but in hydrogen or nitrogen it is stable till 1400°–1500°, when it melts and decomposes.

Cerium persulphide, Ce_2S_4, is prepared by heating cerous sulphate to 580°–600° in a stream of dry hydrogen sulphide, the preparation being followed by weighing from time to time. The persulphide is a dark yellowish-brown, crystalline powder, moderately stable in air and cold water. It dissolves in cold hydrochloric acid, an odour of hydrogen persulphide being first noticed and subsequently a precipitation of sulphur. The compound therefore appears to be a polysulphide. At 720° it decomposes into the sesquisulphide and sulphur; it may be reduced to the sesquisulphide by heating in hydrogen at 400°.[6]

Cerous oxysulphide, Ce_2O_2S, may be prepared by heating cerium dioxide to redness in a current of wet hydrogen sulphide. It is a golden-yellow solid which has not been obtained quite free from impurities.[7]

Cerous sulphite, $Ce_2(SO_3)_3$.—Hydrates of this salt with $3H_2O$ and $9H_2O$ are known.[8]

Cerous sulphate, $Ce_2(So_4)_3$.—The preparation and general properties of the anhydrous sulphate are given on p. 260. In 100 parts of ice-cold water

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[1] Sterba, *loc. cit.*

[2] Burger, *Ber.*, 1907, 40, 1652.

[3] Dennis and Magee, *J. Amer. Chem. Soc.*, 1894, 16, 649; Damiens, *Compt. rend.*, 1913, 157, 214.

[4] W. Biltz and Zimmermann, *Ber.*, 1907, 40, 4979; Barbieri, *Atti R. Accad. Lincei*, 1907, [v.], 16, i. 395.

[5] See p. 259; also W. Biltz, *Ber.*, 1908, 41, 3341.

[6] W. Biltz, *loc. cit.*

[7] Sterba, *Ann. Chim. Phys.*, 1904, [viii.], 2, 193.

[8] See p. 260; and Batěk, *Zeitsch. anorg. Chem.*, 1905, 47, 87.

40 parts of cerous sulphate can be dissolved.[1] The specific heat (0° to 100°) of the anhydrous sulphate is 0·1168.[2]

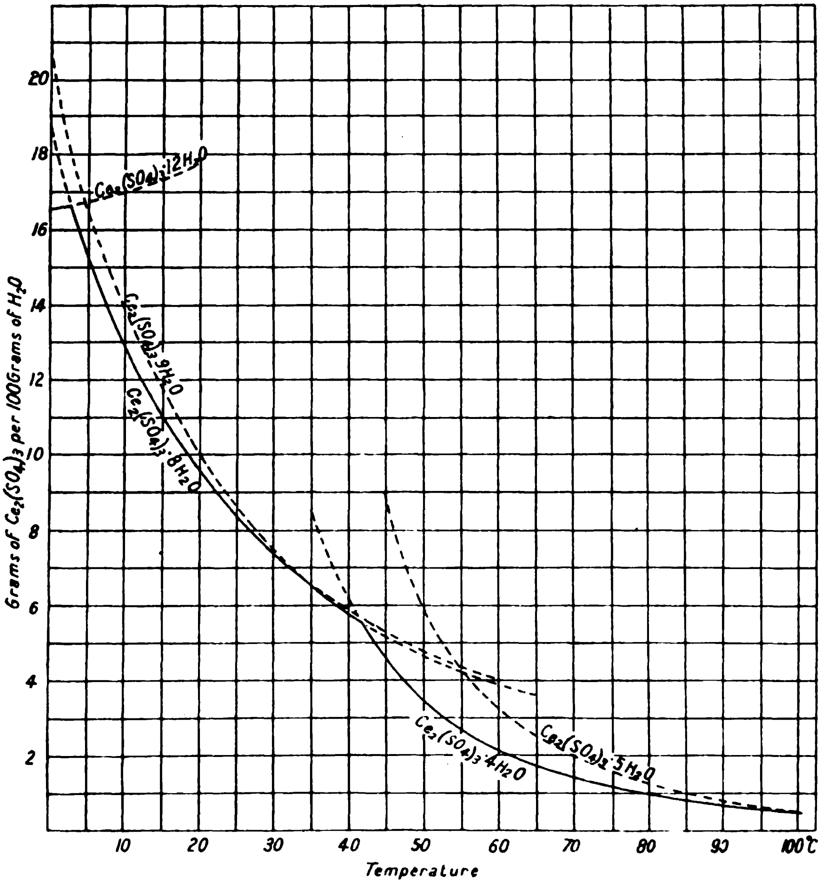

Fig. 39.—Solubility of the hydrates of cerous sulphate in water.

Cerous sulphate forms numerous hydrates. The existence of hydrates with $4H_2O$, $5H_2O$, $8H_2O$, $9H_2O$, and $12H_2O$ is definitely established, but the existence of the hydrate with $6H_2O$ is very doubtful.[3]

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[1] Muthmann and Rölig, *Zeitsch. anorg. Chem.*, 1898, **16**, 450. On the densities of aqueous solutions of cerous sulphate, see Brauner, *Trans. Chem. Soc.*, 1888, **53**, 257.

[2] Nilson and Pettersson, *Ber.*, 1880, **13**, 1459; *Compt. rend.*, 1880, **91**, 232.

[3] The hydrates of cerous sulphate have been studied in detail by Koppel (*Zeitsch. anorg. Chem.*, 1904, **41**, 377), who gives a critical review of earlier work on the subject. The other references are as follows: Otto, *Pogg. Annalen*, 1837, **40**, 404; Marignac, *Mém. Sci. phys. nat.*, 1855, **14**, 201; *Ann. Chim. Phys.*, 1873, [iv.], **30**, 56; Czudnowicz, *J. prakt. Chem.*, 1860, **80**, 16; Hermann, *ibid.*, 1843, **30**, 184; 1864, **92**, 113; Wolf, *Amer. J. Sci.*, 1868, [ii.], **45**, 53; Wing, *ibid.*, 1870, [ii.], **46**, 356; Jolin, *Bull. Soc. chim.*, 1874, [ii.], **21**, 533; Muthmann and Rölig, *loc. cit.*; Wyrouboff, *Bull. Soc. chim.*, 1901, [iii.], **25**, 105; *Bull. Soc. franç. Min.*, 1901, **24**, 105; Kraus, *Zeitsch. Kryst. Min.*, 1901, **34**, 307.

The various hydrates may be obtained as follows:—The dodecahydrate, $Ce_2(SO_4)_3.12H_2O$, separates from a concentrated solution of cerous sulphate over sulphuric acid at 0° C. in the form of tiny needles. The enneahydrate, $Ce_2(SO_4)_3.9H_2O$, is prepared by evaporating the aqueous solution at 40°–45°, and forms hexagonal prisms. The octahydrate, $Ce_2(SO_4)_3.8H_2O$, is best prepared by warming to 45°–50° a solution of the sulphate that was saturated at 0° C. The pentahydrate, $Ce_2(SO_4)_3.5H_2O$, is obtained by preparing a cold saturated solution and heating it to 70°–100°, and forms monoclinic prisms. The tetrahydrate, $Ce_3(SO_4)_3.4H_2O$, is conveniently prepared by agitating the enneahydrate with a little water at 70° for 48 hours, and drying the mass at the same temperature. For densities, see p. 260.

The crystals of the penta- and enneahydrates have been already described (p. 261). The octahydrate has been generally regarded as crystallising in the orthorhombic system; but according to Wyrouboff, whose view is adopted by Groth, the crystals are triclinic and devoid of all elements of symmetry ($a:b:c = 1{\cdot}0650:1:1{\cdot}1144, \alpha = 90°\,52', \beta = 90°\,40', \gamma = 91°\,45'$). Rammelsberg has described a monoclinic octahydrate, isomorphous with the octahydrates of the other metals.[1]

The solubilities of the various hydrates, in grams of anhydrous sulphate per 100 grams of water, are given in the accompanying table (Koppel) and represented graphically in fig. 39, from which the stable hydrate at any temperature is readily seen. It will be noticed that solubilities have been determined even where the hydrates are metastable in contact with the solution:—

t° C.	0°	18·8°	19·2°					
$12H_2O$	16·56	17·52	17·70					
t° C.	0°	15°	30°	45°	50°	60°	65°	
$9H_2O$	20·98	11·87	7·35	5·13	4·67	3·88	3·60	
t° C.	0°	15°	20·5°	30°	40°	50°	60°	
$8H_2O$	19·09	11·06	9·53	7·39	5·95	4·79	4·06	
t° C.	45°	60°	70°	80°	90°	100·5°		
$5H_2O$	8·83	3·25	1·93	1·21	0·84	0·47		
t° C.	35°	40°	50°	57°	65°	70°	82°	100·5°
$4H_2O$	8·50	6·04	3·43	2·34	1·88	1·38	1·01	0·43

The acid *sulphate*, $Ce(HSO_4)_3$, is known (see p. 263).

The following double salts with *alkali sulphates* have been described:—

$Ce_2(SO_4)_3.K_2SO_4.2H_2O$;[6] $2Ce_2(SO_4)_3.3K_2SO_4$,[2, 3] and with $8H_2O$;[6] $Ce_2(SO_4)_3.2K_2SO_4.2H_2O$;[4] $Ce_2(SO_4)_3.3K_2SO_4$;[2, 3] $Ce_2(SO_4)_3.5K_2SO_4$.[6]

$Ce_2(SO_4)_3.Na_2SO_4.2H_2O$.[5, 6]

$Ce_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$,[3, 4, 6] and anhydrous;[4, 7] $Ce_2(SO_4)_3.5(NH_4)_2SO_4$.[6]

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[1] For crystal measurements, see Marignac, *loc. cit.*; Wyrouboff, *loc. cit.*; Kraus, *loc. cit.*; Descloiseaux, *Mém. l'Institut*, 1858, p. 111; Vrba, *Zeitsch. anorg. Chem.*, 1904, **39**, 283; Groth, *Chemische Krystallograpie* (Leipzig, 1906–10), vol. ii.; Rammelsberg, cited by Groth, *op. cit.*

[2] Hermann, *loc. cit.*

[3] Czudnowicz, *loc. cit.*

[4] Jolin, *loc. cit.*

[5] Beringer, *Annalen*, 1842, **42**, 138.

[6] Barre, *Compt. rend.*, 1910, **151**, 871.

[7] Wolff, *Zeitsch. anorg. Chem.*, 1905, **45**, 89.

They are sparingly soluble in water and practically insoluble in saturated solutions of the corresponding alkali sulphates.

The diminution in the solubility of cerous sulphate in water, caused by the presence of various alkali sulphates, is as follows (data represent grams of anhydrous salt present in solution per 100 grams of water):—[1]

Temp. 16° C.		Temp. 19° C.		Temp. 16° C.	
K_2SO_4.	$Ce_2(SO_4)_3$.	Na_2SO_4.	$Ce_2(SO_4)_3$.	$(NH_4)_2SO_4$.	$Ce_2(SO_4)_3$.
0·00	10·75	0·00	9·65	0 00	10 75
0·18	0·96	0·33	0·64	3·46	1·03
0·51	0·43	1·09	0·09	9·32	0·78
0·73	0·25	1·39	0·06	19·24	0·75
1·29	0·04	1·70	0·03	45·62	0·50
2·50	0·00	3·59	0·01	72·84	0·04

Cerous ammonium sulphate, $Ce_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$, is a monoclinic salt (see p. 263) of density 2·523. It loses $6H_2O$ at 100°, and the remaining $2H_2O$ at 150°. The solubility, in grams of $Ce_2(SO_4)_3.(NH_4)_2SO_4$ per 100 grams of water, is as follows (Wolff):—[2]

Temp. ° C.	22·3°	35·1°	45·2°
Grains of $Ce_2(SO_4)_3.(NH_4)_2SO_4$	5·33	5·18	4·99

Above 45° the anhydrous double salt is the stable phase in contact with the solution, and its solubility is as follows (Wolff):—[2]

Temp. ° C.	45°	55·3°	75·4°	82·2°
Grams of $Ce_2(SO_4)_3.(NH_4)_2SO_4$	2·99	2·24	1·48	1·18

The sulphates of *hydrazine* and *hydroxylamine* combine with cerous sulphate.[3]

Cerous thallous sulphate, $Ce_2(SO_4)_3.Tl_2SO_4.4H_2O$, crystallises in monoclinic prisms ($a:b:c = 1·1309:1:0·7059$, $\beta = 91° 53'$).[4] The salt $Ce_2(SO_4)_3.3Tl_2SO_4.H_2O$ has also been described.

Cerous cadmium sulphate, $Ce_2(SO_4)_3.CdSO_4.6H_2O$, crystallises in the orthorhombic system ($a:b:c = 1·1336:1:0·7535$).[5]

Cerous nitratosulphate, $Ce(NO_3)(SO_4).H_2O$, crystallises out when a solution of cerous sulphate in concentrated nitric acid is evaporated on the steam-bath.[6]

Cerous dithionate, $Ce_2(S_2O_6)_3.24H_2O$, is extremely soluble in water (Jolin). The hydrate with $15H_2O$ separates from solution at 15°–17° in triclinic crystals ($a:b:c = 0·5917:1:1·1912$; $\alpha = 81° 26'$, $\beta = 105° 21'$, $\gamma = 86° 38'$) of density 2·288; the hydrate with $3H_2O$ separates above 20°, in triclinic

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[1] Barre, *loc. cit.* Solid phases not specified.

[2] Wolff, *Zeitsch. anorg. Chem*, 1905, 45, 89.

[3] Kolb, *Zeitsch anorg. Chem.*, 1908, 60, 123

[4] Wyrouboff, *Bull. Soc franç. Min.*, 1891, 14, 83

[5] Wyrouboff, *loc. cit.*

[6] Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [viii.], 9, 290.

crystals ($a : b : c = 0{\cdot}5807 : 1 : 1{\cdot}2030$; $\alpha = 89° 25'$, $\beta = 96° 9'$, $\gamma = 96° 18'$) of density 2·631.[1] A hydrate with $12H_2O$ is also known.[2]

Cerous selenite, $Ce_2(SeO_3)_3.12H_2O$, is precipitated from cerous acetate and selenious acid, and loses $9H_2O$ over sulphuric acid. The *acid selenites*, $Ce_2(SeO_3)_3.H_2SeO_3.4H_2O$ (or $5H_2O$) and $Ce_2(SeO_3)_3.3H_2SeO_3.2H_2O$, have also been described.[3]

Cerous selenate, $Ce_2(SeO_4)_3$, and hydrates with 4, 5, 7, 8, 10, 11, and $12H_2O$ have been described by Cingolani, while Jolin has described hydrates with 6 and $9H_2O$. The hydrates are less soluble in hot than in cold water.[4] The following double salts have been prepared by Jolin :—

$Ce_2(SeO_4)_3.5K_2SeO_4$

$Ce_2(SeO_4)_3.Na_2SeO_4.5H_2O$

$Ce_2(SeO_4)_3.(NH_4)_2SeO_4.9H_2O$

Cerous chromate.—Potassium chromate or dichromate gives with a solution of a cerous salt a yellow precipitate of a basic salt.[5]

Cerous molybdate, $Ce_2(MoO_4)_3$, forms yellow crystals of density 4·56.[6]

Cerous tungstate, $Ce_2(WO_4)_3$, forms sulphur-yellow crystals of density 6·514 and specific heat 0·0821.[7] It melts at 1089°.[8] For paratungstates, double and complex tungstates, see p. 265.

Cerous silicotungstate, $Ce_4(W_{12}SiO_{40})_3$. See p. 266.

CERIUM AND THE NITROGEN GROUP.

Cerous nitride, CeN.—The preparation of this compound has been described (p. 267). Gas is violently evolved when a little water is added to the nitride :—

$$CeN + 2H_2O = CeO_2 + NH_3 + H.$$

It dissolves in acids, producing cerous and ammonium salts, *e.g.* :—

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

Cerous azide (*hydrazoate, trinitride*) is an explosive salt.[9]

Cerous nitrite, $Ce(NO_2)_3.xH_2O$, is extremely soluble in water, from which it separates in transparent, amber-yellow crystals. The solid salt is very unstable, and its aqueous solution also readily decomposes when warmed, so that the salt has not been obtained in a state of purity.[10]

Cerous nitrate, $Ce(NO_3)_3.6H_2O$, forms very deliquescent, triclinic crystals.[11] A solution of the salt may be prepared from cerous sulphate and barium nitrate, by heating ceric hydroxide or oxide with nitric acid and a reducing agent, *e.g.* hydrogen peroxide, or by heating cerous oxalate with

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[1] Wyrouboff, *Bull. Soc. franç. Min.*, 1891, **14**, 83.

[2] Morgan and Cahen, *Trans. Chem. Soc.*, 1907, **91**, 475.

[3] Jolin, *loc. cit.*; Nilson, *Nova Acta Soc. Upsala*, 1875, [iii.], **9**, No. 7; *Ber.*, 1875, **8**, 655; *Bull. Soc. chim.*, 1875, [ii.], **23**, 494.

[4] Cingolani, *Gazzetta*, 1908, **38**, i. 292; *Atti R. Accad. Lincei*, 1908, [v.], **17**, i. 254; Jolin, *loc. cit.*

[5] Beringer, *Annalen*, 1842, **42**, 138.

[6] See p. 265; also Didier, *Compt. rend.*, 1886, **102**, 823.

[7] See p. 265; also Didier, *loc. cit.*

[8] Zambonini, *Atti R. Accad. Lincei*, 1913, [v.], **22**, i. 519.

[9] Curtius and Darapsky, *J. prakt. Chem.*, 1900, [ii.], **61**, 408.

[10] Morgan and Cahen, *Trans. Chem. Soc.*, 1907, **91**, 475.

[11] Marignac, *Ann. Chim. Phys.*, 1873, [iv.], **30**, 56. See p. 268.

concentrated nitric acid.[1] The crystals lose $3H_2O$ at 100°, and begin to decompose at 200°.

Cerous ammonium nitrate, $Ce(NO_3)_3.2(NH_4)NO_3.4H_2O$, described on p. 268, has been prepared by numerous chemists.[2] Its solubility, in grams of $Ce(NO_3)_3.2(NH_4)NO_3$ per 100 of water, is as follows (Wolff):—

Temp. ° C.	8·8°	25°	45°	60°	65·1°
Grams of $Ce(NO_3)_3.2(NH_4)NO_3$	235·5	296·8	410·2	681·2	817·4

The *salt* $2Ce(NO_3)_3.3(NH_4)NO_3.12H_2O$ separates from aqueous solution of 0°.[3]

Cerous cæsium nitrate, $Ce(NO_3)_3.2CsNO_3.2H_2O$, crystallises in the monoclinic system ($a:b:c = 1·2052:1:0·9816$; $\beta = 103° 41'$).[4]

Cerous rubidium nitrate, $Ce(NO_3)_3.2RbNO_3.4H_2O$, has been described (p. 268).

Cerous potassium nitrate, $Ce(NO_3)_3.2KNO_3.2H_2O$, crystallises in the orthorhombic system (hemimorphic; $a:b:c = 0·5227:1:0·5704$).[5]

Cerous sodium nitrate, $Ce(NO_3)_3.2NaNO_3.H_2O$, forms hygroscopic crystals of density 2·65 at 0°.[6]

Cerous thallous nitrate, $Ce(NO_3)_3.2TlNO_3.4H_2O$, has been described (p. 268).

The double salts of cerous nitrate and the nitrates of bivalent metals, $2Ce(NO_3)_3 3M^{II}(NO_3)_2.24H_2O$, have been already described.[7]

Cerous hypophosphite, $Ce(H_2PO_2)_3.H_2O$, crystallises in thin, prismatic crystals.[8]

Cerous orthophosphate, $CePO_4$.—The dihydrate, $CePO_4.2H_2O$, is obtained by double decomposition between a cerous salt and phosphoric acid or an alkali phosphate.[9] When dried it forms a white, amorphous powder, from which orthorhombic crystals of density 5·09, closely resembling the mineral *monazite*, may be obtained by heating to redness with excess of fused cerous chloride. The phosphate dissolves in the molten chloride and crystallises out on cooling.[10]

The *double phosphates*, $K_3PO_4.2CePO_4$, and $Na_3PO_4.2CePO_4$, have been obtained by Ouvrard.

Cerous pyrophosphate, $Ce_4(P_2O_7)_3.12H_2O$, *cerous hydrogen pyrophosphate*, $CeHP_2O_7$, and *cerous sodium pyrophosphate*, $CeNaP_2O_7$, have been described, and likewise *cerous metaphosphate*, $Ce(PO_3)_3$.[11] Cerous pyrophosphate is readily soluble in dilute mineral acids.

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[1] Jolin, *Bull. Soc. chim.*, 1874, [ii.], **21**, 533; Lange, *J. prakt. Chem.*, 1861, **82**, 129.

[2] Marignac, *loc. cit.*; Fock, *Zeitsch. Kryst. Min.*, 1894, **22**, 37; Kraus, *ibid.*, 1901, **34**, 307; Wolff, *Zeitsch. anorg. Chem.*, 1905, **45**, 89.

[3] Holzmann, *J. prakt. Chem.*, 1861, **84**, 76.

[4] Wyrouboff, *Bull. Soc. franç. Min.*, 1907, **30**, 299; Jautsch and Wigdorow, *Zeitsch. anorg. Chem.*, 1911, **69**, 221.

[5] Lange, *loc. cit.*; Fock, *loc. cit.*; Wyrouboff, *loc. cit.*

[6] Jantsch and Wigdorow, *loc. cit.*

[7] See p. 269; also Holzmann, *loc. cit.*; Lange, *loc. cit.*; Zschiesche, *J. prakt. Chem.*, 1869, **107**, 65; Rammelsberg, *Pogg. Annalen*, 1859, **108**, 435.

[8] Rammelsberg, *Ber.*, 1872, **5**, 492.

[9] Jolin, *loc. cit.*; Hartley, *Trans. Chem. Soc.*, 1882, **41**, 202.

[10] Radominski, *Compt. rend.*, 1875, **80**, 304. See also Ouvrard, *ibid.*, 1888, **107**, 37; Grandeau, *Ann. Chim. Phys.*, 1886, [vi.], **8**, 193; Holm, *Inaugural Dissertation* (Munich, 1902).

[11] Rosenheim and Triantaphyllides, *Ber.*, 1915, **48**, 582 ($Ce_4(P_2O_7)_3.12H_2O$); Jolin, *loc. cit.* ($CeHP_2O_7$); Wallroth, *Bull. Soc. chim.*, 1883, [ii.], **39**, 316 ($CeNaP_2O_7$); Rammelsberg, *loc. cit.* ($Ce(PO_3)_3$). See also Johnston, *Ber.*, 1889, **22**, 976.

Cerous vanadate, $CeVO_4$, may be obtained in dark-red, dichroic needles by fusing sodium orthovanadate with cerous chloride. The compound $Ce_2O_3.5V_2O_5.27H_2O$ is also known.

CERIUM AND THE CARBON GROUP.

Cerium carbide, CeC_2, is prepared by reducing ceric oxide with carbon in the electric furnace. It has been already described.[1] The reduction of ceria by carbon probably proceeds in three stages:—

$$\begin{aligned} 2CeO_2 + C &= Ce_2O_3 + CO \\ Ce_2O_3 + 9C &= 2CeC_3 + 3CO \\ CeC_3 &= CeC_2 + C \end{aligned}$$

and red crystals of the carbide CeC_3 may be isolated under suitable conditions. They are decomposed by water with the evolution of acetylene:—[2]

$$2CeC_3 + 6H_2O = 2Ce(OH)_3 + 3C_2H_2.$$

Cerium silicide, $CeSi_2$, is prepared by heating ceric oxide with silicon in the electric furnace. It forms small, lustrous crystals of density 5·67. It is decomposed by fluorine in the cold and by the other halogens when heated. It burns in oxygen at a red heat. Unlike the carbide, cerium silicide is scarcely affected by water or dilute alkalies, even when boiling; and although it dissolves in dilute hydrochloric and sulphuric acids, the gas evolved is pure hydrogen.[3]

Cerous carbonate, $Ce_2(CO_3)_3.5H_3O$, is known,[4] and also the following double carbonates:—[5]

$Ce_2(CO_3)_3.K_2CO_3.3H_2O$ (and $12H_2O$)
$Ce_2(CO_3)_3.2Na_2CO_3.2H_2O$
$2Ce_2(CO_3)_3.3Na_2CO_3.24H_2O$
$Ce_2(CO_3)_3.(NH_4)_2CO_3.6H_2O$

For preparation and properties, see p. 271.

Cerous thiocyanate, $Ce(CNS)_3.7H_2O$, and the *double salt*, $Ce(CNS)_3.3Hg(CN)_2.12H_2O$, are known. (Jolin; see p. 272.)

Cerous platinocyanide, $2Ce(CN)_3.3Pt(CN)_2.18H_2O$, crystallises in yellow prisms (sp. gr. 2·657) having a blue reflex.[6]

Cerous ethylsulphate, $Ce(C_2H_5.SO_4)_3.9H_2O$, has been described (p. 278).

Cerous acetylacetonate, $Ce(CH_3.CO.CH.CO.CH_3)_3$, has also been described (p. 279).

Cerous oxalate, $Ce_2(C_2O_4)_3.10H_2O$, may readily be obtained by double decomposition as a white, crystalline powder. The oxalate when air-dried has the above composition, but crystalline hydrates containing $3H_2O$, $9H_2O$,

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[1] See p. 270; also Sterba, *Compt. rend.*, 1902, **134**, 1056; *Ann. Chim. Phys.*, 1904, [viii.], **2**, 223.

[2] Damiens, *Compt. rend.*, 1913, **157**, 335.

[3] Sterba, *Compt. rend.*, 1902, **135**, 170; *Ann. Chim. Phys.*, 1904, [viii.], **2**, 229.

[4] Beringer, *Annalen*, 1842, **42**, 138; Jolin, *Bull. Soc. chim.*, 1874, [ii.], **21**, 533; Czudnowicz, *J. prakt. Chem.*, 1861, **82**, 277.

[5] Jolin, *loc. cit.*; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1904, **41**, 97; K. A. Hofmann and Höschele, *Ber.*, 1915, **48**, 20 (Ce – NH_4).

[6] Czudnowicz, *J. prakt. Chem.*, 1860, **80**, 16; Lange, *ibid.*, 1861, **82**, 129. See also p. 272.

and $11H_2O$ have also been prepared.[1] For the solubility of cerous oxalate in water and acids, see p. 273.

Cerous oxalate is transformed into a crystalline oxalochloride when it is dissolved in hot, concentrated hydrochloric acid, and the solution allowed to cool.[2]

Cerous salts of other organic acids.—The following salts have been described:—

Cerous *formate*,[3, 7] *acetate*,[3, 4, 5, 6] *propionate*,[6] *butyrate*,[6] *isobutyrate*,[6] *monochlor-*,[6] *dichlor-*[17] *and trichlor-acetate*,[6] *succinate*,[5] *citrate*,[5, 14] *tartrate*,[5, 13, 14] *glycollate*,[12, 15] *dimethylphosphate*,[10] *crotonate*,[12] *malate* [12] and *acid malate*,[12] *maleate* [12] and *acid maleate*,[12] *fumarate* [12] and *acid fumarate*,[12] *malonate* [11, 12, 14] and *acid malonate*,[12] *benzoate*,[5] *salicylate*,[7] *phthalate* [12] and *acid phthalate*,[12] *hippurate*,[5] *phenoxyacetate*,[8] *sulphanilate*,[17] *benzenesulphonate*,[17] *m-nitrobenzenesulphonate*,[14] *p-dibromobenzenesulphonate*,[16] 1 : 4 : 2-*bromonitrobenzenesulphonate*,[9] *phenol-p-sulphonate*,[17] *naphthionate*,[17] *β-naphthol*-6-*sulphonate*,[17] *camphor-β-sulphonate*,[17] *chromotropate*,[18] *anthraquinonesulphonate* [18] and numerous *naphthalenesulphonates*.[18]

Cerous silicate, $Ce_2(SiO_3)_3$, may be obtained in prismatic crystals by fusing together cerous chloride or oxychloride, silica and sodium or calcium chloride.[19]

CERIUM AND BORON.

Cerous metaborate, $Ce(BO_2)_3$, has been described.[20]

CERIC COMPOUNDS.[21]

Ceric salts are derived from the feebly basic oxide CeO_2, and are yellow, orange, or red in colour. Being salts derived from a weak base, they are considerably hydrolysed in aqueous solution, and normal ceric salts of weak acids are not known. Further, the normal chloride and nitrate are only known in combination as double, or possibly complex, salts. Aqueous solutions

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[1] Holzmann, *J. prakt. Chem.*, 1861, **84**, 76; Jolin, *Bull. Soc. chim.*, 1874, [ii.], **21**, 533; Erk, *Jahresber.*, 1870, p. 319; Power and Shedden, *J. Soc. Chem. Ind.*, 1900, **19**, 636; Wyrouboff, *Bull. Soc. franç. Min.*, 1901, **24**, 105; Hauser and Wirth, *Zeitsch. anal. Chem.*, 1908, **47**, 389; Wirth, *Zeitsch. anorg. Chem.*, 1912, **76**, 174. See also p. 273.

[2] Job, *Compt. rend.*, 1898, **126**, 246.

[3] Jolin, *Bull. Soc. chim.*, 1874, [ii.], **21**, 533.

[4] Lange, *J. prakt. Chem.*, 1861, **82**, 129.

[5] Czudnowicz, *ibid.*, 1861, **82**, 277.

[6] Wolff, *Zeitsch. anorg. Chem.*, 1905, **45**, 89.

[7] Behrens, *Arch. Néerland.*, 1901, [ii.], **6**, 67.

[8] Pratt and James, *J. Amer. Chem. Soc.*, 1911, **33**, 1330.

[9] Katz and James, *ibid.*, 1913, **35**, 872.

[10] Morgan and James, *ibid.*, 1914, **36**, 10.

[11] Erdmann and Wirth, *Annalen*, 1908, **361**, 190.

[12] Rimbach and Kilian, *ibid.*, 1909, **368**, 110.

[13] Rimbach and Schubert, *Zeitsch. physikal. Chem.*, 1909, **67**, 183.

[14] Holmberg, *Zeitsch. anorg. Chem.*, 1907, **53**, 83.

[15] Jantsch and Grünkraut, *ibid.*, 1913, **79**, 305.

[16] Armstrong and Rodd, *Proc. Roy. Soc.*, 1912, **A**, **87**, 204.

[17] G. T. Morgan and Cahen, *Trans. Chem. Soc.*, 1907, **91**, 475.

[18] Erdmann and Nieszytka, *Annalen*, 1908, **361**, 166.

[19] Didier, *Compt. rend.*, 1885, **100**, 1461; **101**, 882.

[20] See p. 282, and *cf.* Ceric Borate on p. 404.

[21] **Ceroceric** and **perceric** compounds are also included in this section.

of ceric salts, owing to hydrolysis, react strongly acid. The solutions are very unstable and are easily reduced to the cerous state. On the ionic hypothesis, the instability is attributed to the ceric ion, $Ce^{\cdot\cdot\cdot\cdot}$, the oxidation potential of which is greater than that of oxygen; acid solutions of ceric salts accordingly behave as if they were supersaturated with oxygen.[1] In alkaline media, however, ceric compounds are not readily reduced to the cerous state, while the converse change is very easy to effect.

Hydrolysis of Ceric Salts.—The hydrolysis of a ceric salt in cold, aqueous solution proceeds for a long time after the solution has been prepared, and the colour fades away very perceptibly; the hydrolysis may be hastened and increased by raising the temperature. A freshly prepared solution of a ceric salt immediately darkens in colour when a mineral acid is added, since the degree of hydrolysis is thereby diminished; with an old solution, however, the deepening of the colour takes place very slowly. Again, a fresh solution is immediately decolorised by hydrogen peroxide, with the formation of a cerous salt and oxygen, but an old solution first turns dark red in colour when similarly treated, and is only slowly reduced.[2] By the hydrolysis of ceric salts basic ceric salts are produced, which, under suitable circumstances, may be utilised for the separation of ceria from the other rare earths (see p. 332).

Colloidal Ceric Compounds.—A cold solution of ceric nitrate in which hydrolysis has proceeded to a considerable extent, either by long standing or by heating, contains a colloidal hydrosol, which coagulates when nitric acid is added and is almost quantitatively precipitated if 12 cubic centimetres of concentrated nitric acid are added for every 100 cubic centimetres of dilute ceric solution present. The hydrogel thus obtained, when dried over potassium hydroxide, forms an amber-coloured, horny, translucent solid of the composition $4CeO_2.N_2O_5.5H_2O$. It easily changes back into the hydrosol in contact with water, giving a greenish, limpid solution unless it is very concentrated, when a faint opalescence is observable. Submitted to dialysis, the solution loses nitric acid; the whole of the acid present in the hydrosol, however, cannot be thus removed, the decomposition ceasing when the ratio $28CeO_2 : 1N_2O_5$ is reached.

When the solution of the basic nitrate hydrosol is treated with one-fifth its volume of concentrated hydrochloric acid, the cerium is almost quantitatively precipitated as a hydrogel which has the composition $4CeO_2.2HCl.34H_2O$ and is very similar in properties to the basic nitrate; in solutions of both of these compounds one-half of the acid present may be neutralised with sodium hydroxide before ceric hydroxide begins to be precipitated. When, however, a dilute solution of a dibasic acid (or, better, its ammonium salt) is added to the basic nitrate hydrosol, a hydrogel is precipitated which does not dissolve in water. The basic sulphate, $4CeO_2.SO_3.5H_2O$, for instance, which resembles the chloride and nitrate in appearance, loses half its sulphuric acid when washed with warm water, but does not dissolve to any appreciable extent.

The addition of ammonia to the basic nitrate hydrogel converts the latter into a hydroxide which has the composition $8CeO_2.11H_2O$ when dried over potassium hydroxide, and the same horny appearance as the basic nitrate.

Colloidal compounds similar in properties to the preceding may be prepared containing lanthanum, praseodymium, etc., in addition to cerium.

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[1] Baur and Glaessner, *Zeitsch. Elektrochem.*, 1903, **9**, 534.

[2] R. J. Meyer and Jacoby, *Ber.*, 1900, **33**, 2135; *Zeitsch. anorg. Chem.*, 1901, **27**, 359.

Concerning the constitution of these colloidal substances, little can be said beyond the statement that they do not appear to be basic salts of the ordinary type. Wyrouboff and Verneuil regard them as derivatives of polymerised or "condensed" ceric hydroxides, such as $Ce_{24}O_{15}(OH)_{60}(OH)_6$, in which only part of the hydroxyl (the $(OH)_6$ of the preceding formula, for example) is capable of reacting with acids; they speak of the compounds as being derived from certain *metaoxides* or mixed metaoxides,[1] the term "meta-" being used as in naming "condensed" acids, *e.g.* metastannic and metatungstic acids. There is very little evidence, however, for the molecular formulæ ascribed to these compounds by the French chemists.[2]

Colloidal basic ceric compounds of another type have also been prepared by Wyrouboff and Verneuil, who speak of them as derivatives of a *paraoxide*. A description of the basic nitrate may be given. When cerous oxalate is calcined in air at the lowest possible temperature, a canary-yellow residue of ceria is obtained containing 2·9 per cent. of water. It is quite indifferent towards concentrated nitric acid, but is transformed into a white, gelatinous substance when heated to 100° with 3 per cent. nitric acid for several hours. This substance, when separated from the dilute acid by decantation, may be dissolved in water. The solution has a decidedly milky appearance; the hydrosol it contains may be completely precipitated by the addition of nitric acid (2 per cent.) or ammonium nitrate, and dries at 100° to a very pale-coloured, horny, translucent mass, soluble in water. Wyrouboff and Verneuil propose the molecular formula $20CeO_2.N_2O_5.5H_2O$ for the substance; basic chlorides, sulphates, etc., and another modification of ceric hydroxide may be prepared from it as in the case of the meta-nitrate. Moreover, the French chemists state that when cerous hydroxide, precipitated from a cerous salt by means of ammonia, is oxidised to ceric hydroxide by a current of air, the product is almost entirely insoluble in boiling concentrated nitric acid, and that the insoluble portion is colloidal, dissolving in water to form a solution of the para-hydroxide.

Further work upon these interesting substances is very desirable.

Conversion of Cerous into Ceric Compounds.—Owing to the great instability of ceric chloride, this transformation cannot be effected in solutions acidified with hydrochloric acid.

(i.) *Oxidation in nitric acid solution.*—A solution of cerous nitrate in concentrated nitric acid may be oxidised to ceric nitrate to the extent of 6–8 per cent. by evaporation at 100°.[3] In the presence of the requisite amount of alkali nitrate, some 30 per cent. or more of the cerous salt may be oxidised, a result that is attributed to the transformation of the ceric ions $Ce^{\cdot\cdot\cdot\cdot}$, as they are produced, into the complex ion $Ce(NO_3)_6''$, the probable existence of which has been shown by Meyer and Jacoby (see p. 400).[4] Provided that (i.) a cerous salt is readily soluble, and the corresponding ceric salt only sparingly soluble in concentrated nitric acid, and (ii.) the acid from which the cerous salt is derived is not attacked by nitric acid, *e.g.* iodic, phosphoric, and arsenic acids, the oxidation of the cerous to the ceric salt may be readily accomplished by boiling it with concentrated nitric acid.[5]

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[1] It would be more correct to say metahydroxides.

[2] Wyrouboff and Verneuil, *Compt. rend.*, 1898, **127**, 863; 1899, **128**, 501; *Bull. Soc. chim.*, 1899, [iii.], **21**, 118; *Ann. Chim. Phys.*, 1906, [viii.], **9**, 289.

[3] Giles, *Chem. News*, 1905, **92**, 1; Barbieri, *Atti R. Accad. Lincei*, 1907, [v.], **16**, i. 395.

[4] Barbieri, *loc. cit.*

[5] Barbieri, *ibid.*, 1907, [v.], **16**, i. 644; *Ber.*, 1910, **43**, 2214.

Oxidation in nitric acid solution may be effected by the use of various oxidising agents, *e.g.* lead peroxide and bismuth tetroxide; the processes are useful in connection with the analytical chemistry of cerium.[1]

(ii.) *Oxidation in sulphuric acid solution.*—This may be accomplished by means of ammonium persulphate or sodium bismuthate. The processes are useful for analytical purposes (see p. 373), and the former may also be utilised for the preparation of pure ceria (see p. 333).

(iii.) *Electrolytic oxidation.*—The electrolysis of cerous nitrate or sulphate between platinum electrodes in neutral or slightly acid solution leads to the separation of ceric hydroxide or basic ceric salt at the anode; but in the presence of sufficient mineral acid, ceric salt is produced in solution. As much as 95 per cent. of the cerium may be oxidised under suitable conditions.[2]

(iv.) *Oxidation in alkaline media.*—Cerous hydroxide is readily oxidised to ceric hydroxide by alkali hypochlorite or hypobromite. Cerous salts are also readily converted into ceric hydroxide by potassium permanganate in the presence of a base, *e.g.* sodium hydroxide or magnesia. These reactions are of considerable value both in preparation work (see pp. 335, 336) and in analytical chemistry (see p. 373). A solution of cerous carbonate in potassium carbonate is easily oxidised by oxygen or hydrogen peroxide (see p. 401).

In alkaline or acetic acid solution, cerous compounds may be oxidised to perceric compounds by means of hydrogen peroxide (see pp. 401–3).

Conversion of Ceric into Cerous Compounds.—In acid solution ceric salts may be reduced to the cerous state with great ease by numerous reducing agents, *e.g.* hydrogen peroxide, sulphurous acid, hydrochloric, hydrobromic, and hydriodic acids, oxalic acid, stannous chloride, ferrous sulphate, etc. The neatest method is that involving the use of hydrogen peroxide, but on a large scale it is rather expensive. The transformation from ceric nitrate or sulphate into cerous oxalate is readily effected in warm, acid solution by the addition of oxalic acid.

The conversion of cerium dioxide into cerous salts is worthy of special notice, inasmuch as the dioxide is insoluble in hot, concentrated hydrochloric or nitric acid. The conversion into cerous nitrate may be accomplished very neatly by warming the oxide with moderately concentrated nitric acid and adding hydrogen peroxide from time to time. The conversion into cerous sulphate or chloride may be brought about by heating the oxide with hydroquinone and an excess of the requisite acid in aqueous solution, the hydroquinone being converted into benzoquinone and quinhydrone.[3] Ceria may also be converted into cerous sulphate by heating it with concentrated sulphuric acid until it has been converted into ceric sulphate and reducing its aqueous solution with sulphurous acid; while it may be converted into anhydrous cerous chloride by heating in the vapour of disulphur dichloride (p. 252), and into a solution of cerous chloride (plus alkali chloride) by heating with concentrated hydrochloric acid and an alkali iodide (p. 332).

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[1] See p. 373. For the use of the lead peroxide method in preparing pure ceria, see Robinson, *Proc. Roy. Soc.*, 1884, **37**, 150; *Chem. News*, 1884, **50**, 251.

[2] Erk, *Jahresber.*, 1870, p. 319; Smith, *Ber.*, 1880, **13**, 754; Bricout, *Compt. rend.*, 1894, **118**, 145; Kölle, *Inaugural Dissertation* (Zurich, 1898); von Knorre, *Zeitsch. angew. Chem.*, 1897, **10**, 685, 717; Job, *Compt. rend.*, 1899, **128**, 101; Sterba, *ibid.*, 1901, **133**, 221; *Ann. Chim. Phys.*, 1904, [viii.], **2**, 193; Muhlbach, *Inaugural Dissertation* (Munich, Tech. Hochschule, 1903); Krilitschewski, *Inaugural Dissertation* (Geissen, 1904); Plancher and Barbieri, *Atti R. Accad. Lincei*, 1904, [v.], **14**, i. 119. See also p. 334.

[3] Marino, *Gazzetta*, 1907, **37**, i. 51.

Cerium and the Fluorine Group.

Ceric fluoride, $CeF_4.H_2O$, is obtained as a brown powder, insoluble in water, by acting upon ceric hydroxide with hydrogen fluoride and drying the residue at 100°. When heated, water, hydrogen fluoride, and possibly fluorine, are evolved.[1] According to Brauner, the double salt $2CeF_4.3KF.2H_2O$ is produced by the action of potassium hydrogen fluoride on ceric hydroxide. Rimbach and Kilian [2] could not obtain this salt, but have prepared a series of double salts of the type $2CeF_4.MF_2.7H_2O$, where $M = Cd$, Cu, Co, Ni, or Mn. They are decomposed by water.

Ceric chloride, $CeCl_4$.—This salt has not been isolated. It can be obtained in solution, but the solution cannot be kept without decomposing. Thus, ceric hydroxide dissolves in cold concentrated hydrochloric acid with the production of a dark red solution; chlorine, however, is slowly evolved, and ultimately a solution of cerous chloride remains. The decomposition proceeds rapidly in hot solutions.

By preparing a solution of ceric chloride in methylalcoholic hydrogen chloride and adding an organic base, crystalline double chlorides may be prepared. The *pyridine*, *quinoline*, and *triethylamine* salts have thus been made,[3] and ascribed the formulæ $CeCl_4.2(C_5H_5N.HCl)$, $CeCl_4.2(C_9H_7N.HCl)$, and $CeCl_4.2[(C_2H_5)_3N.HCl]$. The compositions of these compounds, however, vary with the amounts of the reacting salts.[4]

Ceric iodate, $Ce(IO_3)^4$, may be prepared by heating together cerous nitrate, iodic acid, and concentrated nitric acid. It is a yellow crystalline salt, very sparingly soluble even in boiling nitric acid, and hydrolysed somewhat by water.[5]

Cerium and the Oxygen Group.

Ceroceric oxide, Ce_4O_7 or Ce_7O_{12} (?).—When cerium dioxide is heated to a red heat in a current of dry hydrogen free from air, it is partially reduced and loses in weight by about 2 per cent. The reduction proceeds most rapidly with an oxide that has not previously been intensely ignited, but such an oxide is liable to have retained a little water; accordingly it is difficult to obtain reliable analytical data concerning the product formed by the reduction. The lower oxide is considered to correspond to the violet ceroceric hydroxide (described below) and to the acid salt known as ceroceric hydrosulphate (p. 397); hence Meyer regards it as Ce_4O_7, and Wyrouboff and Verneuil as Ce_7O_{12}. It is a blue or bluish-black solid which readily absorbs oxygen and is sometimes pyrophoric.[6]

Ceroceric hydroxide, $Ce(OH)_3.Ce(OH)_4$ or $4Ce(OH)_3.3Ce(OH)_4$ (?).—When white cerous hydroxide is exposed to air or oxygen, it absorbs oxygen and is eventually converted into yellow ceric hydroxide, but the initial product

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[1] Brauner, *Trans. Chem. Soc.*, 1882, 41, 68.

[2] Rimbach and Kilian, *Annalen*, 1909, 368, 101.

[3] Koppel, *Zeitsch. anorg. Chem.*, 1898, 18, 305.

[4] Grant and James, *J. Amer. Chem. Soc.*, 1915, 37, 2652.

[5] Barbieri, *Atti R. Accad. Lincei*, 1907, [v.], 16, i. 644.

[6] Sterba, *Compt. rend.*, 1901, 133, 221; *Ann. Chim. Phys.*, 1904, [viii.], 2, 210; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1903, 37, 378; Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [viii.], 9, 289. The early workers obtained erroneous results; see Beringer, *Annalen*, 1842, 42, 138; Bunsen, *ibid.*, 1858, 105, 40, 45; Rammelsberg, *Pogg. Annalen*, 1859, 108, 40; Winkler, *Ber.*, 1891, 24, 873.

of oxidation has a violet or purple tint. A precipitate of the same violet colour is obtained by adding an alkali hydroxide to a solution of a mixture of a cerous and a ceric salt, and the colour attains a maximum intensity when the ratio Ce^{III} Ce^{IV} has a certain definite value, which, however, can only be approximately estimated. Wyrouboff and Verneuil consider that this intermediate hydroxide is obtained in a pure state by precipitating ceroceric hydrosulphate with alkali, and, if this is the case, its composition is probably expressed by one or other of the alternative formulæ given above. The violet hydroxide becomes bluish-black in colour when dried *in vacuo*, but a slight oxidation to ceria is always observed.[1]

Ceric oxide, cerium dioxide, or **ceria,** CeO_2, may be prepared by the ignition of cerous or ceric hydroxide, nitrate, sulphate, etc., or by the ignition of the cerous salt of any volatile oxyacid; it is perhaps most commonly prepared by the ignition of cerous oxalate.

Ceria is an amorphous powder of specific gravity 6·405 at 17° when prepared from the oxalate, and 6·99 when obtained from the nitrate (Sterba); its specific heat is 0·0877 (0°–100°).[2] There has been a great deal of discussion over the question of the colour of ceria. It might be anticipated that ceria, like zirconia and thoria, would be white. Most experimenters agree that pure ceria[3] has a pale yellow colour. The depth of colour depends upon the temperature at which the oxide has been calcined and the salt from which it has been prepared. When prepared by the prolonged ignition of cerous sulphate at a white heat, its tint is so slight that it may almost be said that the ceria is white,[4] but when obtained at a lower temperature by the ignition of cerous oxalate or ceric ammonium nitrate it has a more pronounced tint, usually described as that of pale chamois. On the other hand, Spencer claims that when ceric sulphate is heated for a prolonged period at temperatures below a red heat, cerium dioxide is formed, which is pure white; further, that when the ceria is heated above a red heat it shrinks in volume and becomes pale yellow in colour. Ceria darkens in colour very markedly when heated, but returns (practically) to its original colour when cooled.[5] When ceria is contaminated with a little of the other earths of the cerium group, it is salmon-coloured, reddish-brown, or brown, according to the extent of contamination and the temperatnre of ignition. The coloration is attributed mainly to the presence of praseodymia, or rather, its peroxide.

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[1] Dennis and Magee, *J. Amer. Chem. Soc.*, 1894, **16**, 662; Wyrouboff and Verneuil, *loc. cit.*; Rammelsberg, *Pogg Annalen*, 1859, **108**, 45.

[2] Nilson and Pettersson, *Compt. rend.*, 1880, **91**, 232; *Ber.*, 1880, **13**, 1459.

[3] For the preparation of which see p. 337.

[4] In this sense of the term, ceria is said to be white by Wyrouboff and Verneuil (*Compt. rend.*, 1897, **124**, 1300; *Ann. Chim. Phys.*, 1906, [viii.], **9**, 356), who consider that it is possible to distinguish different kinds of white, and that the colour of ceria prepared from cerous sulphate by ignition is not definite enough to be described as anything but a particular kind of white.

[5] Sterba (*Compt. rend.*, 1901, **133**, 221; *Ann. Chim. Phys.*, 1904, [viii.], **2**, 193) has prepared ceria devoid of any yellow tint, but Brauner has shown that the ceria so prepared contains traces of impurities. Other chemists (*e.g.* Wolf, *Amer. J. Sci.*, 1868, [ii.], **46**, 53; Moissan, *Compt. rend.*, 1897, **124**, 1233) have also described ceria as being white. Sterba, after preparing ceria in various ways, concluded that it could be white or pale citron yellow in colour, and that the yellow colour, which could not be attributed to iron, platinum, or other rare earth elements, might possibly be due to the presence of traces of a higher oxide than the dioxide. Spencer's results appear to lend support to this view. On the question of the colour of pure ceria. see Sterba, *loc. cit.*; Wyrouboff and Verneuil, *loc. cit.*; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1903, **37**, 378; Brauner, *ibid.*, 1903, **34**, 207; Neish, *J. Amer. Chem. Soc.*, 1909, **31**, 517; J. F. Spencer, *Trans. Chem. Soc.*, 1915, **107**, 1265.

Ceria is readily obtained in the crystalline form by adding anhydrous cerous sulphate to molten magnesium chloride, allowing to cool slowly, and extracting the mass with hydrochloric acid. The crystals belong to the regular system and exhibit faces of the cube and octahedron. They are practically colourless, very hard and very brilliant, the refractive index being high (about 1·9); they have a density of 7·3.[1] If small quantities of another rare earth sulphate are added in the preparation, *e.g.* neodymium, praseodymium or erbium sulphate, beautiful coloured crystals may be obtained.[2]

Ceria does not melt at *c.* 1900°, but it volatilises *in vacuo* quite rapidly at that temperature.[3] It readily melts in the electric furnace and attacks the containing vessel.

Ceria is a very stable oxide, but it can be reduced to the metallic state by heating it with aluminium [4] or magnesium.[5] By neither of these methods, however, has a regulus of the metal been obtained. The action of other reducing agents is discussed in connection with cerous oxide and ceroceric oxide.

Crystalline ceria is very resistant towards acids and alkalis. The amorphous substance after ignition is insoluble in hydrochloric or nitric acid, except in the presence of a suitable reducing agent, *e.g.* hydrogen peroxide, hydriodic acid, or stannous chloride, when it passes into solution as a cerous salt. Concentrated sulphuric acid converts it into ceric sulphate, while moderately concentrated acid causes partial reduction to cerous sulphate and dilute acid has no perceptible action.

Ceria acts as an oxygen-carrier towards other substances, in a manner that is not at present understood.[6] It may therefore be employed as the catalyst in Dennstedt's method for the combustion of organic compounds.[7]

Ceria is a very weakly basic oxide; it is possible that it can also act as a feebly acidic oxide. It has been pointed out in describing the preparation of ceria (p. 332) that rare earth mixtures obtained by the ignition of the mixed oxalates are completely soluble in nitric or hydrochloric acid, provided that the ceria does not exceed 45 to 50 per cent. of the mixture; pure ceria, however, is insoluble in these acids. The usual explanation of these results is that the ceria acts as a feeble acid and combines with the other strong bases present to form salts; these salts are decomposed by a strong acid with the liberation of ceric acid, *i.e.* ceric hydroxide, which is soluble, as a base, in the excess of strong acid present. If such is the case, the salts must apparently be of the type $M_2O_3.2CeO_2$ or $2M_2O_3.3CeO_2$ in order to account for the 45–50 per cent. limit to the solubility of the ceria.

Ceria combines with uranium dioxide. When a dry mixture of cerous and uranyl sulphates is heated with molten magnesium chloride in a covered crucible for fifteen hours, deep blue cubic crystals are produced which can be separated from the accompanying substances by reason of the relative stability

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[1] The higher the temperature of formation the higher the density of the crystals. Thus, ceria crystallised from sodium chloride, borax, and potassium sulphate respectively has been found to possess the following densities (Sterba): 7·314, 7·415, and 7·995.

[2] K. A. Hofmann and Höschele, *Ber.*, 1914, 47, 238. For other methods of crystallising ceria, see Nordenskiöld, *Pogg. Annalen*, 1861, 114, 612; Didier, *Ann. Sci. Ecole norm.*, 1887, p. 65; Grandeau, *Compt. rend.*, 1885, 100, 1134; Sterba, *Compt. rend.*, 1901, 133, 221, 294; *Ann. Chim. Phys.*, 1904, [viii.], 2, 193.

[3] Tiede and Birnbräuer, *Zeitsch. anorg. Chem.*, 1914, 87, 160.

[4] Schiffer, *Inaugural Dissertation* (Munich, 1900); Muthmann and Weiss, *Annalen*, 1904, 331, 1.

[5] Winkler, *Ber.*, 1891, 24, 873; Holm, *Inaugural Dissertation* (Munich, 1902).

[6] Marc, *Ber.*, 1902, 35, 2370; R. J. Meyer and Koss, *Ber.*, 1902, 35, 3740.

[7] Bekk, *Ber.*, 1913, 46, 2574; Miss Reimer, *J. Amer. Chem. Soc.*, 1915, 37, 1636.

towards dilute acids. The composition of the crystals approximates to that required by the compound $UO_2.2CeO_2$. A similar deep blue compound may be obtained by precipitating an aqueous solution of uranyl and cerous nitrates with excess of ammonium hydroxide or dilute potassium hydroxide solution; the precipitate is at first yellow, but soon changes to a denser blue solid.[1]

Ceric hydroxide, $Ce(OH)_4$.—The normal hydroxide is not known. When ammonia or an alkali hydroxide is added to a solution of a ceric salt, a yellow, gelatinous precipitate of ceric hydroxide is obtained, insoluble in excess of precipitant; it is usually contaminated with basic salt and adsorbed alkali hydroxide. A pure hydroxide may be prepared from ceric ammonium nitrate by precipitation with ammonia from a cold solution, the precipitate being washed, allowed to become nearly dry at a low temperature, and again washed with cold water to remove ammonium nitrate. When dried over potassium hydroxide, its composition corresponds with the formula $Ce_2O(OH)_6$ or $2CeO_2.3H_2O$.[2]

Ceric hydroxide may be conveniently prepared by the oxidation of cerous hydroxide. For this purpose excess of alkali hypochlorite or hypobromite may be added to a cerous salt, or, what amounts to the same thing, precipitation may be effected by alkali hydroxide and the oxidation then accomplished by the use of chlorine or bromine.[3] Ceric hydroxide may also be prepared by heating hydrated perceric hydroxide to 120° or boiling its aqueous suspension until decomposition of the peroxide has been completed.

Ceric hydroxide dissolves in nitric or sulphuric acid with the production of a ceric salt,[4] but reduction to the cerous state usually occurs to a slight extent. According to Brauner, the reduction is complete if the hydroxide has been prepared from perceric hydroxide and its solution in sulphuric acid is effected in a platinum dish,[5] but this is denied by Barbieri.[6] Ceric hydroxide reacts with hydrochloric acid to produce cerous chloride, chlorine, and water.

Colloidal ceric hydroxide may be prepared by dialysing a 10 per cent. aqueous solution of ceric ammonium nitrate for four or five days. The hydrosol thus obtained is very readily coagulated; when evaporated, it leaves a gummy residue, soluble in hot water. The hydroxide is positively charged.[7]

Perceric hydroxide, $CeO_3.xH_2O$ or $Ce(OH)_3.O.OH$.—When a cerous salt is treated with a mixture of ammonia and hydrogen peroxide, a reddish-brown, gelatinous precipitate of perceric hydroxide is obtained, which has the composition of a hydrated trioxide, $CeO_3.xH_2O$.[8] According to Pissarjewsky,[9] the precipitate is produced as follows:—

$$Ce(OH)_4 + HO.OH = Ce(OH)_3.O.OH + H_2O.$$

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[1] K. A. Hofmann and Höschele, *Ber.*, 1915, **48**, 20.

[2] Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [viii.], **9**, 310; Rammelsberg (*Pogg. Annalen*, 1859, **108**, 40) and Erk (*Zeitsch. für Chem.*, 1870, [ii.], **7**, 100) give the same formula, but *cf.* Carnelley and Walker, *Trans. Chem. Soc.*, 1888, **53**, 59.

[3] Mosander, *Phil. Mag.*, 1843, [iii.], **23**, 241; Popp, *Annalen*, 1864, **131**, 359; Hermann, *J. prakt. Chem.*, 1843, **30**, 184; 1864, **92**, 113; Stapff, *ibid.*, 1860, **79**, 257; Rammelsberg, *loc. cit.*

[4] *Cf.* p. 391.

[5] Brauner, *Zeitsch. anorg. Chem.*, 1904, **39**, 261.

[6] Barbieri, *Atti R. Accad. Lincei*, 1907, [v.], **16**, i. 525.

[7] W. Biltz, *Ber.*, 1902, **35**, 4431; 1904, **37**, 1095.

[8] Hermann, *J. prakt. Chem.*, 1843, **30**, 184; Cleve, *Bull. Soc. chim.*, 1885, [ii.], **43**, 53; Lecoq de Boisbaudran, *Compt. rend.*, 1885, **100**, 605; *cf.* von Knorre, *Zeitsch. angew. Chem.*, 1897, p. 723; Mengel, *Zeitsch. anorg. Chem.*, 1899, **19**, 71; Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [viii.], **9**, 313.

[9] Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 609; *Zeitsch. anorg. Chem.*, 1902, **31**, 359.

It is an unstable compound, losing oxygen fairly quickly even at the ordinary temperature. It is rapidly converted into ceric hydroxide when heated with boiling water or when dried at 120°. It dissolves in dilute mineral acids, producing a cerous salt, hydrogen peroxide, and oxygen, *e.g.* :—

$$2Ce(OH)_3.O.OH + 3H_2SO_4 = Ce_2(SO_4)_3 + H_2O_2 + O_2 + 6H_2O.$$

Ceroceric hydrosulphate.—When ceric oxide or hydroxide is heated with fairly concentrated sulphuric acid it is not quantitatively converted into ceric sulphate ; oxygen is evolved and part of the ceric salt reduced to the cerous state. From the acid solution a beautiful red hexagonal crystalline salt may be readily obtained, and from the mother liquor normal ceric sulphate, $Ce(SO_4)_2.4H_2O$, may then be separated in pale yellow crystals.

In addition to the preceding method of preparation, the red crystals may be obtained by mixing cerous sulphate with an excess of ceric sulphate and crystallising from fairly concentrated sulphuric acid.

The hexagonal crystals appear dark orange-coloured when large crystals are viewed in the direction of the principal axis, and orange-yellow when fine needles are similarly examined. Viewed parallel to the basal plane, the crystals appear to have a beautiful red colour. They may be heated to 230° without losing anything but their water of crystallisation.

The composition of these hexagonal crystals has been a matter of dispute for many years ; the formulæ that have been assigned to the substance are given in the appended table :—

Formula.	Authority.	Date.
$Ce_4O_9.9SO_3.27H_2O$	Hermann[1]	1843
$3Ce(SO_4)_2.Ce_2(SO_4)_3.27H_2O$	Rammelsberg[2]	1859
$3Ce(SO_4)_2.Ce_2(SO_4)_3.27H_2O$	Czudnowicz[3]	1860
$2Ce(SO_4)_2.Ce_2(SO_4)_3.2H_2SO_4.25H_2O$ . . .	Hermann[4]	1864
$2Ce(SO_4)_2.1\frac{1}{3}Ce_2(SO_4)_3.H_2SO_4.26H_2O$ . . .	Zschiesche[5]	1869
$3Ce(SO_4)_2.Ce_2(SO_4)_3.31\frac{1}{2}H_2O$	Rammelsberg[6]	1873
$2Ce(SO_4)_2.Ce_2(SO_4)_3.24H_2O$	Mendeléeff[7]	1873
$3Ce(SO_4)_2.Ce_2(SO_4)_3.31H_2O$	Jolin[8]	1874
$2Ce(SO_4)_2.Ce_2(SO_4)_3.24H_2O$	Brauner[9]	1895
$2Ce(SO_4)_2.Ce_2(SO_4)_3.1\frac{1}{2}H_2SO_4.26H_2O$ . . .	Brauner[10]	1895
$2Ce(SO_4)_2.Ce_2(SO_4)_3.20H_2O$	Muthmann and Stützel[11]	1900
$2Ce(SO_4)_2.Ce_2(SO_4)_3.H_2SO_4.26H_2O$ . . .	Meyer and Aufrecht[12]	1904
$2Ce(SO_4)_2.Ce_2(SO_4)_3.H_2SO_4.24H_2O$ . . .	Brauner[13]	1904
$3Ce(SO_4)_2.2Ce_2(SO_4)_3.1\frac{1}{2}H_2SO_4.42H_2O$ . .	Wyrouboff and Verneuil[14]	1906

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[1] Hermann, *J. prakt. Chem.*, 1843, **30**, 184.

[2] Rammelsberg, *Pogg. Annalen*, 1859, **108**, 40.

[3] Czudnowicz, *J. prakt. Chem.*, 1860, **80**, 16.

[4] Hermann, *J. prakt. Chem.*, 1864, **92**, 113.

[5] Zschiesche, *J. prakt. Chem.*, 1869, **107**, 65.

[6] Rammelsberg, *Ber.*, 1873, **6**, 84.

[7] Mendeléeff, *Ber.*, 1873, **6**, 558 ; *Annalen*, 1873, **168**, 45.

[8] Jolin, *Bull. Soc. chim.*, 1874, [ii.], **21**, 533.

[9] Brauner, *Chem. News*, 1895, **71**, 283.

[10] Brauner, *Bull. Intern. Acad. Sci. de l'Empereur François Joseph I.*, 1895.

[11] Muthmann and Stützel, *Ber.*, 1900, **33**, 1763.

[12] R. J. Meyer and Aufrecht, *Ber.*, 1904, **37**, 140.

[13] Brauner, *Zeitsch. anorg. Chem.*, 1904, **39**, 261.

[14] Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [viii.], **9**, 293.

The substance contains both cerous and ceric sulphates as well as sulphuric acid, and the latter cannot be eliminated at 130° *in vacuo*. It may therefore be described as a *ceroceric hydrosulphate*. The *cerous* sulphate may be replaced by the sulphates of the other rare earth elements, and Brauner has prepared the *lanthanum*, *praseodymium*, and *neodymium* salts. They are hexagonal, and isomorphous with one another and with the cerous salt. According to Brauner, they are acid salts of a complex *cerisulphuric acid*, $H_4.Ce^{IV}(SO_4)_4.12H_2O$, of the type $HM^{III}.Ce^{IV}(SO_4)_4.12H_2O$ (M^{III} = Ce, La, Pr, or Nd).[1]

It will be noticed that the formula assigned to ceroceric hydrosulphate by Meyer and Aufrecht only differs from Brauner's formula (1904) in the amount of water of crystallisation present. Too much significance should not, however, be attached to this agreement, for the analytical data upon which the formulæ are based are of slender value, and at the present time the composition and constitution of this interesting compound must be regarded as undetermined.[2]

Ceric sulphate,[3] $Ce(SO_4)_2$.—Ceria is quantitatively converted into ceric sulphate when heated on a sand-bath with concentrated sulphuric acid. The salt, which is insoluble in the excess of acid, may be washed with glacial acetic acid and dried over potash, when it is obtained as a deep yellow, crystalline powder. When heated in the air, slight loss of weight is observed

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[1] It may be remarked that the acid sulphate of thorium has the composition $Th(SO_4)_2.H_2SO_4$ or $H_2Th(SO_4)_3$, and not $H_4Th(SO_4)_4$. On the other hand, the acid sulphates of the rare earth elements have formulæ of the type $M^{III}_2(SO_4)_3.3H_2SO_4$ or $H_3[M^{III}(SO_4)_3]$, the ceric salt of which would be $Ce^{IV}_3[M^{III}(SO_4)_3]_4$ or $3Ce^{IV}(SO_4)_2.2M^{III}_2(SO_4)_3$, in harmony with the formula of Wyrouboff and Verneuil; it is then difficult, however, to account for the extra sulphuric acid present in the molecule.

If ceroceric hydrosulphate is a "complex" salt, it is not a very stable complex, for the addition of alkali leads to the initial precipitation of the violet ceroceric hydroxide.

[2] Thus, even the atomic ratio $Ce^{IV} : Ce^{III}$ is uncertain. The analytical data given by Wyrouboff and Verneuil agree very well with the result $Ce^{IV} : Ce^{III} : : 3 : 4$, and the data given by Meyer and Aufrecht and by Brauner agree at least as well with this ratio as with the ratio 1 : 1, which they adopt. Brauner's analyses of the lanthanum, praseodymium, and neodymium salts are also unsatisfactory, as Wyrouboff and Verneuil have justly remarked.

It is, perhaps, worth while to point out that the formula $3Ce(SO_4)_2.2Ce_2(SO_4)_3.2H_2SO_4.42H_2O$ agrees with the analytical data given by Brauner and by Wyrouboff and Verneuil at least as well as do their own formulæ. This is readily seen from the following table of results:—

Per cent. of	Calculated from the Formula of			Found by		
	Brauner.	W. and V.	H.F.V.L.	Brauner.		W. and V.
Ce_2O_3 . .	37·25	37·75	37·27	36·57	36·15	37·57
Active oxygen .	0·91	0·79	0·78	0·82	0·84	0·79
SO_3 . . .	36·31	35·63	36·29	...	36·78	36·16
H_2O . . .	25·53	25·83	25·66	26·08	26·13	25·51

which serves to illustrate the difficulties attaching to the investigation of the composition of ceroceric hydrosulphate.

Finally, it may be mentioned that Brauner has described a *ceroceric sulphate*, $Ce^{III}_4[Ce^{IV}(SO_4)_4]_3.44H_2O$, and the corresponding *lanthanoceric* salt.

[3] Rammelsberg, *Ber.*, 1873, **6**, 84; Mendeléeff, *Annalen*, 1873, **168**, 45; *Ber.*, 1873, **6**, 558; Muthmann and Stützel, *Ber.*, 1900, **33**, 1763; R. J. Meyer and Aufrecht, *Ber.*, 1904, **37**, 140; Brauner, *Zeitsch. anorg. Chem.*, 1904, **39**, 261; Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [viii.], **9**, 311; Barbieri, *Atti R. Accad. Lincei*, 1907, [v.], **16**, i. 525.

at 155°, and when heated to constant weight at 195° the basic sulphate $3CeO_2.4SO_3$ is produced. On raising the temperature, further loss of sulphur trioxide occurs at 250°, and at 300° the loss in weight is continuous until cerium dioxide is left.[1]

Ceric sulphate is very soluble in water, in which it forms a yellowish-brown, unstable solution. A concentrated solution of the salt in dilute sulphuric acid may be prepared either by dissolving the anhydrous salt in dilute sulphuric acid or by carefully dissolving ceric hydroxide in the same medium. When concentrated over sulphuric acid, sulphur-yellow, orthorhombic[2] crystals of the tetrahydrate,[3] $Ce(SO_4)_2.4H_2O$, are obtained (bipyramidal; $a : b : c = 0{\cdot}717 : 1 : 0{\cdot}471$).

Ceric sulphate in solution readily hydrolyses, and, according to Wyrouboff and Verneuil, when diluted largely or warmed, a crystalline basic salt of the composition $2CeO_2.2SO_3.5H_2O$ is obtained;[4] from a dilute ice-cold solution the compound $4CeO_2.3SO_3.12H_2O$ has been prepared, and from a saturated solution at 0° C. the compound $2CeO_2.3SO_3.4H_2O$.[5] A physicochemical study of the hydrolysis has been made by Spencer, who could only prepare and characterise one basic salt at 25° C., viz. $CeO_2.SO_3.2H_2O$.[6]

Ceric potassium sulphate, $Ce(SO_4)_2.2K_2SO_4.2H_2O$, is obtained in orange-yellow, monoclinic crystals ($a : b : c = 1{\cdot}216 : 1 : 2{\cdot}093$; $\beta = 100° 40'$),[7] scarcely soluble in water, by adding a solution of potassium sulphate to an acid solution of ceric sulphate.[8]

Ceric ammonium sulphate, $Ce(SO_4)_2.2(NH_4)_2SO_4.2H_2O$, separates in yellow crystals when an acid solution of the mixed sulphates is evaporated: it is followed by orange-red crystals of the monoclinic ($a : b : c = 0{\cdot}6638 : 1 : 0{\cdot}7838$; $\beta = 96° 44'$)[9] double salt $Ce(SO_4)_2.3(NH_4)_2SO_4.2H_2O$.[10]

Ceric silver sulphate, $5Ce(SO_4)_2.3Ag_2SO_4$, is obtained as an orange-yellow, crystalline precipitate by adding silver nitrate to a strongly acid solution of ceric sulphate. The salt slowly combines with $2H_2O$, and is decomposed by boiling water.[11]

Ceric selenite, $Ce(SeO_3)_2$, may be prepared by heating cerous nitrate and selenious acid with boiling concentrated nitric acid. It is an orange-yellow powder, insoluble in water but slightly soluble in nitric acid.[12]

Ceric chromate, $Ce(CrO_4)_2.2H_2O$, is obtained by heating ceric hydroxide with aqueous chromic acid. It is a bright scarlet crystalline salt that cannot be heated above 180° without decomposing. It is decomposed by water, losing chromic acid and turning orange in colour.[13]

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[1] J. F. Spencer, *Trans. Chem. Soc.*, 1915, **107**, 1265.

[2] Slavik, *Zeitsch. anorg. Chem.*, 1904, **39**, 290.

[3] According to Wyrouboff and Verneuil (*Ann. Chim. Phys.*, 1906, [viii.], **9**, 312), the formula is $2Ce(SO_4)_2.7H_2O$.

[4] Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [viii.], **9**, 312.

[5] Hauser and Wirth, *Zeitsch. anorg. Chem.*, 1908, **60**, 242.

[6] J. F. Spencer, *Trans. Chem. Soc.*, 1915, **107**, 1265.

[7] Marignac, *Ann. Min.*, 1859, [v.], **15**, 221.

[8] Scheerer, *Pogg. Annalen*, 1842, **56**, 482; Hermann, *J. prakt. Chem.*, 1843, **30**, 184; Rammelsberg, *Pogg. Annalen*, 1859, **108**, 40; Marignac, *loc. cit.*

[9] Geipel, *Zeitsch. Kryst. Min.*, 1902, **35**, 608.

[10] Rammelsberg, *Pogg. Annalen*, 1859, **108**, 40; *Ber.*, 1873, **6**, 84; Mendeléeff, *Annalen*, 1873, **168**, 45; Geipel, *loc. cit.*

[11] Pozzi-Escot, *Compt. rend.*, 1913, **156**, 1074.

[12] Barbieri and Calzolari, *Ber.*, 1910, **43**, 2214.

[13] Browning and Flora, *Amer. J. Sci.*, 1903, [iv.], **15**, 177; *cf.* Bricout, *Compt. rend.*, 1894, **118**, 145; Böhm, *Zeitsch. angew. Chem.*, 1902, **15**, 372, 1282.

Ceric molybdate.—A number of salts of a *cerimolybdic* acid have been prepared, analogous to the complex molybdates of zirconium and thorium.[1] *Ammonium cerimolybdate*, $(NH_4)_8[Ce(Mo_2O_7)_6].8H_2O$, is a yellow crystalline substance, yielding yellow solutions which are stable towards hydrogen peroxide and give a precipitate with oxalic acid only after prolonged boiling. The *acid ammonium* salt $(NH_4)_6H_2[Ce(Mo_2O_7)_6].10H_2O$, the *silver* salt, $Ag_8[Ce(Mo_2O_7)_6]$, and the *acid aniline* salt are also known.

CERIUM AND THE NITROGEN GROUP.

Ceric nitrate, $Ce(NO_3)_4$, has not been isolated. By evaporating a solution of ceric hydroxide in concentrated nitric acid, in the presence of a considerable quantity of calcium nitrate, red monoclinic crystals ($a:b:c=1·7834:1:1·0465$; $\beta=90°\ 48'$)[2] of *basic ceric nitrate*, $2Ce(OH)(NO_3)_3.9H_2O$, can be obtained. The aqueous solution of the salt readily undergoes hydrolysis (p. 332).[3]

Ceric nitrate forms an isomorphous series of double nitrates with the nitrates of *potassium*, *rubidium*, *cæsium*, and *ammonium*. They are of the type $Ce(NO_3)_4.2MNO_3$, and form anhydrous,[4] orange-red, monoclinic crystals:—[5]

	a		*b*		*c*		*β*
$Ce(NO_3)_4.2KNO_3$	1·2455	:	1	:	1·9170	;	91° 12′
$Ce(NO_3)_4.2(NH_4)NO_3$	1·1690	:	1	:	1·9260	;	90° 21′

The salts are readily soluble in water and alcohol, but much less soluble in fairly concentrated nitric acid. In aqueous solution they are hydrolysed in a similar manner to ceric nitrate. It is probable that the solutions contain not only the ions $Ce^{\cdot\cdot\cdot\cdot}$, $M^{\cdot}$, and NO_3', but also the complex ion $Ce(NO_3)_6''$; indeed, in alcoholic solution it has been shown by migration experiments that a coloured cation is present.[6]

Ceric ammonium nitrate, $Ce(NO_3)_4.2(NH_4)NO_3$, is of considerable practical importance for the preparation of pure ceria (see p. 336). Indeed, from the practical point of view, it is the most important of the ceric salts. Its solubility in water is as follows (in grams of salt per 100 grams of solution):—[7]

Temp. ° C.	25°	35·2°	45·3°	64·5°	85·6°
Grams of $Ce(NO_3)_4.2(NH_4)NO_3$	58·5	62·8	64·5	66·8	69·4

At temperatures above 60° partial reduction to cerous nitrate takes place in the aqueous solution.

It may readily be prepared by the electrolytic oxidation of cerous ammonium nitrate in a divided cell.[8]

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[1] Barbieri, *Atti R. Accad. Lincei*, 1914, [v.], 23, i. 805.

[2] von Lang and Haitinger, *Annalen*, 1907, 351, 450.

[3] R. J. Meyer and Jacoby, *Ber.*, 1900, 33, 2135; *Zeitsch. anorg. Chem.*, 1901, 27, 359; these authors give the water of crystallisation as $3H_2O$ and not $4\frac{1}{2}H_2O$.

[4] Meyer and Jacoby, *loc. cit.*; Wolff, *Zeitsch. anorg. Chem.*, 1905, 45, 89; *cf.* Holzmann, *J. prakt. Chem.*, 1858, 75, 321; Muthmann and Rölig, *Zeitsch. anorg. Chem.*, 1898, 16, 450.

[5] Sachs, *Zeitsch. Kryst. Min.*, 1901, 34, 162.

[6] Meyer and Jacoby, *loc. cit.* See also Barbieri, *Atti R. Accad. Lincei*, 1907, [v.], 16, i. 395.

[7] Wolff, *loc. cit.*

[8] Plancher and Barbieri, *Atti R. Accad. Lincei*, 1904, [v.], 14, i. 119.

Ceric nitrate also forms an isomorphous series of double salts with the nitrates of the bivalent metals *magnesium*, *zinc*, *nickel*, *cobalt*, and *manganese*; they are of the type $Ce(NO_3)_4.M(NO_3)_2.8H_2O$, and must be crystallised from concentrated nitric acid.[1] The crystals are monoclinic and isomorphous with the corresponding double thorium nitrates:—[2]

	a		*b*		*c*		*β*
$Ce(NO_3)_4.Mg(NO_3)_2.8H_2O$	1·032	:	1	:	1·586	;	96° 43′
$Ce(NO_3)_4.Zn(NO_3)_2.8H_2O$	0·978	:	1	:	1·339	;	100° 0′

Ceric orthophosphate.—When sodium phosphate is added to a slightly acid solution of a ceric salt, a yellow precipitate is obtained. According to Hartley, the composition of this precipitate (dried *in vacuo* over sulphuric acid) is in accordance with the formula $2Ce^{IV}_2H(PO_4)_3.25H_2O$, but this cannot be considered as definitely established.[3] *Ceric pyrophosphate*, $CeP_2O_7.xH_2O$(?), like the corresponding thorium salt, is practically insoluble in dilute mineral acids. It is obtained as a yellow precipitate by warming a solution of cerous pyrophosphate in hydrochloric acid with bromine.[4]

Ceric dihydrogen arsenate, $Ce(H_2AsO_4)_4.4H_2O$, may be prepared by heating cerous nitrate (1 mol.) and arsenic acid (4 mols.) with concentrated nitric acid for several hours, distilling off most of the nitric acid, and allowing the liquid to crystallise. The salt separates in white needles. When it is dissolved in the minimum quantity of concentrated nitric acid and the cold solution diluted with water, a white, crystalline precipitate of **ceric monohydrogen arsenate,** $Ce(HAsO_4)_2.6H_2O$, is obtained.[5]

CERIUM AND THE CARBON GROUP.

Ceric carbonate.—A yellow, gelatinous precipitate, presumably of a *basic ceric carbonate*, is obtained by double decomposition between a ceric salt and an alkali carbonate. The precipitate dissolves readily in concentrated potassium carbonate solution, forming a yellow solution that is stable in the air but which may be oxidised with hydrogen peroxide.[6] The basic ceric carbonates, $2CeO_2.3CO_2$ and $2CeO_2.CO_2$, are obtained (combined with potassium carbonate)? by heating perceric potassium carbonate to 240° and 360° respectively.[7]

Perceric carbonate.—Cerous carbonate dissolves to a considerable extent in concentrated potassium carbonate solution.[8] When hydrogen peroxide is added to the solution, the latter turns blood-red in colour owing to oxidation, and the colour darkens with the addition of hydrogen peroxide up to a certain point; beyond this, the addition of more peroxide lightens the colour and throws down an orange-yellow precipitate, and by the addition of sufficient reagent all the cerium is precipitated.

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[1] Bunsen and Jegel, *Annalen*, 1858, **105**, 40, 45; Holzmann, *loc. cit.*; Meyer and Jacoby, *loc. cit.*

[2] Geipel, *Zeitsch. Kryst. Min.*, 1902, **35**, 608.

[3] Hartley, *Trans. Chem. Soc.*, 1882, **41**, 202.

[4] Carney and Campbell, *J. Amer. Chem. Soc.*, 1914, **36**, 1134; Rosenheim and Triantaphyllides, *Ber.*, 1915, **48**, 582.

[5] Barbieri and Calzolari, *Ber.*, 1910, **43**, 2214.

[6] Job, *Ann. Chim. Phys.*, 1900, [vii.], **20**, 205.

[7] Job, *loc. cit.*

[8] It is much less soluble in sodium or ammonium carbonate.

When the colour reaches its maximum intensity, all the cerium is present in solution as perceric carbonate. The solution of perceric carbonate in potassium carbonate may be prepared from ceric carbonate as well as from cerous carbonate, by oxidation with hydrogen peroxide. By a suitable process of crystallisation, Job obtained **perceric potassium carbonate,** $Ce_2(CO_3)_3O_3.4K_2CO_3.12H_2O$, from this solution in dark-red, triclinic crystals.

This curious double salt is remarkably stable. It may be dehydrated at 110°, but withstands a temperature of 200° for several hours without decomposition being perceptible. At 240°, however, it loses oxygen, leaving a residue of a basic ceric carbonate.[1]

By modifying Job's method of preparation in certain particulars, Meloche[2] has prepared a crystalline perceric potassium carbonate of the composition $Ce_2O_4(CO_3)_2.4K_2CO_3.12H_2O$. This compound readily loses part of its water when exposed to dry air, and may be almost completely dehydrated at 110°–120° without loss of available oxygen.

As already mentioned, the addition of hydrogen peroxide to perceric potassium carbonate solution causes all the cerium to be thrown out of solution as an orange-yellow precipitate. This precipitate appears to be a derivative of CeO_4, and is very unstable. When covered with a concentrated solution of potassium carbonate it slowly evolves oxygen, and beautiful red crystals of a perceric potassium carbonate are formed. According to Job, this is the best method for preparing the double salt; according to Baur, however, the crystals formed are rather different in composition from those described by Job, and have the formula $Ce_2O_4(CO_3)_2.4K_2CO_3.10H_2O$.[3]

In alkaline solution the perceric potassium carbonates have three atoms of available oxygen per two atoms of cerium. In acid solution, however, only one-third of this oxygen is available, the remainder being set free in the gaseous state, *e.g.*:—

$$\begin{aligned}&Ce_2O_4(CO_3)_2.4K_2CO_3.12H_2O + 7H_2SO_4\\ &\qquad = Ce_2(SO_4)_3 + O_2 + H_2O_2 + 4K_2SO_4 + 6CO_2 + 18H_2O.\end{aligned}$$

A solution of ceric carbonate in potassium carbonate is quite stable towards air or oxygen. On the other hand, the corresponding cerous solution readily absorbs oxygen, passing into perceric and not into ceric carbonate. Simultaneously with this reaction another change occurs, namely, the interaction of the perceric carbonate produced with the unchanged cerous carbonate to produce ceric carbonate; and by varying the conditions of experiment the relative speeds of these two reactions may, within certain limits, be altered at will. This auto-oxidation of cerous carbonate may be used to affect the oxidation of various substances by the air, a small quantity of cerous salt acting as the oxygen-carrier. It is only necessary for this purpose that the "acceptor" shall be able to reduce both ceric and perceric carbonates to the cerous state; glucose is one such substance. When, however, the "acceptor" can only reduce perceric carbonate to the ceric state, the cerous salt soon becomes quantitatively transformed into ceric salt, when the auto-oxidation ceases. According to Engler, the auto-oxidation of cerous carbonate takes place in two stages, as follows:—

$$\begin{aligned}&\text{(i.)}\quad Ce_2(CO_3)_3 + 2H_2O + O_2 = Ce_2(CO_3)_3(OH)_2 + H_2O_2\\ &\text{(ii.)}\quad Ce_2(CO_3)_3(OH)_2 + 2H_2O_2 = Ce_2(CO_3)_3O_3 + 3H_2O\end{aligned}$$

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[1] Job, *Ann. Chim. Phys.*, 1900, [vii.], 20, 205.

[2] Meloche, *J. Amer. Chem. Soc.*, 1915, 37, 2338, 2645.

[3] Baur, *Zeitsch. anorg. Chem.*, 1902, 30, 256.

the initial products of oxidation being basic ceric carbonate and hydrogen peroxide, which then interact to produce the perceric compound.[1]

Ceric acetate.—The normal salt is not known. A weakly acid solution of a ceric salt is completely precipitated as yellow *basic ceric acetate* when heated to boiling with excess of an alkali acetate. An aqueous solution of cerous acetate is said to be oxidised to ceric acetate by ozone.[2]

Basic perceric acetate is obtained as an orange-brown precipitate when hydrogen peroxide and an alkali acetate are added to a solution of a cerous salt. The precipitate thus obtained is apparently a derivative of a peroxide ($Ce(OH)_2.O_2H$) analogous to the peroxides of the other rare earth elements, since the atomic ratio of cerium to active oxygen (*i.e.* oxygen in excess of that required for a cerous salt) is Ce : O.[3] The formation of basic perceric acetate may be used as a test for cerium or as a means of separating cerium from the other rare earth elements.[4] The precipitate is converted into basic ceric acetate when dried at 120°.

Ceric oxalate, $Ce(C_2O_4)_2.7H_2O$ (?).—Ceric oxalate is obtained as an orange-yellow gelatinous precipitate when cold, aqueous solutions of ceric ammonium nitrate and ammonium oxalate are mixed. The precipitate is difficult to filter and wash, and when attempts are made to dry it on a porous plate, considerable decomposition occurs; apparently a mixture of cerous oxalate, $Ce_2(C_2O_4)_3.10H_2O$, and ceric oxalate, $Ce(C_2O_4)_2.7H_2O$, is produced, from which ceric oxalate may be extracted with aqueous ammonium oxalate.[5]

Cerous oxalate is a very unstable salt, readily losing carbon dioxide and becoming converted into cerous oxalate:—

$$2Ce(C_2O_4)_2 = Ce_2(C_2O_4)_3 + CO_2.$$

It is readily soluble in ammonium oxalate solution, thereby resembling thorium oxalate. The orange-yellow solution deposits cerous oxalate on standing, the decomposition being rapid when the solution is warmed. The cerium may be rapidly and quantitatively precipitated from the solution by the addition of sulphurous acid.[6]

Ceric acetylacetonate, $Ce(CH_3.CO.CH.CO.CH_3)_4$, may be prepared by shaking a suspension of ceric hydroxide in water with excess of acetylacetone for several days. Deep red needles of the hydrated compound ($11H_2O$) are thus formed. They are dried *in vacuo* and crystallised from carbon tetrachloride, when black, lustrous crystals of the anhydrous substance separate out, m.p. 171–172°. The acetylacetonate is slightly soluble in water, which hydrolyses it slightly; hydrolysis may be repressed by the addition of a little acetylacetone. The compound dissolves in most organic media, forming deep red solutions that are readily reduced.[7]

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[1] For further information on the auto-oxidation of cerous salts, see Job, *Compt. rend.*, 1898, **126**, 246; 1899, **128**, 178, 1098; 1902, **134**, 1052; 1903, **135**, 45; *Ann. Chim. Phys.*, 1900, [vii.], **20**, 205; Baur, *Zeitsch. anorg. Chem.*, 1902, **30**, 251; *Ber.*, 1903, **36**, 3038, 1904, **37**, 795; Engler and Wöhler, *Zeitsch. anorg. Chem.*, 1902, **29**, 1; Engler, *Ber.*, 1903, **36**, 2642; 1904, **37**, 49, 3268; Engler and Weissberg, *Kritische Studien über die Vorgänge der Auto-oxydation* (Vieweg, Brunswick, 1904).

[2] Job, *Compt. rend.*, 1903, **136**, 45.

[3] Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [viii.], **9**, 314; *cf.* Meloche, *loc. cit.*

[4] Popp, *Annalen*, 1864, **131**, 359; R. J. Meyer and Koss, *Ber.*, 1902, **35**, 672.

[5] Brady and Little; unpublished experiments.

[6] See Orloff, *Chem. Zeit.*, 1906, **30**, 733; 1907, **31**, 562.

[7] Job and Goissedet, *Compt. rend.*, 1913, **157**, 50.

CERIUM AND BORON.

Ceric borate, $CeO_2.B_2O_3$, may be prepared, according to Holm, by heating ceria with an excess of boric anhydride in a petroleum injector-furnace and extracting the mass with water; it is described as a yellow powder, insoluble in water and dilute mineral acids.[1] Guertler,[2] however, states that this method of preparation only yields *cerous metaborate*, $Ce(BO_2)_3$.

LANTHANUM.

Symbol, La. Atomic weight, 139·0 (O = 16).

Lanthanum is one of the most abundant of the rare earth elements. Its occurrence, history, preparation, atomic weight, and homogeneity have been already discussed in Chapters X. and XI.

Lanthanum[3] is a tin-white metal of density 6·155. It is malleable, but not ductile. Its specific and atomic heats (0°–100°) are 0·0449 and 6·23 respectively;[4] its melting-point is 810°. Measurements made with material of doubtful purity indicate that lanthanum is feebly paramagnetic,[5] but this is questionable.[6]

Lanthanum tarnishes rapidly, even in dry air. It burns in air at 440°–460°. The chemical properties of the metal, so far as they are known, are very similar to those of cerium.

Alloys.—Little is known of the alloys of lanthanum. Lanthanum alloys with aluminium, and if excess of the latter is taken, and subsequently removed with sodium hydroxide, the compound $LaAl_4$ is obtained. Its density is 3·923 and its heat of formation 97·8 Cals.; it resembles the corresponding cerium compound.[7]

COMPOUNDS OF LANTHANUM.

The salts of lanthanum are derived from the colourless basic oxide La_2O_3, and, if derived from colourless acids, are themselves colourless. Their aqueous solutions are devoid of absorption spectra.

The following values for the equivalent conductivities λ of a number of lanthanum salts at 25° are in harmony with the view that the salts are derived from a fairly strong triacid base (v = dilution in litres per gram-equivalent):—[8]

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[1] Holm, *Inaugural Dissertation* (Munich, 1902).

[2] Guertler, *Zeitsch. anorg. Chem.*, 1904, 40, 225.

[3] See pp. 229–230. Hillebrand and Norton, *Pogg. Annalen*, 1875, 155, 633; 156, 466; Muthmann and Kraft, *Annalen*, 1902, 325, 261; Muthmann and Weiss, *ibid.*, 1904, 331, 1; Muthmann and Scheidmandel, *ibid.*, 1907, 355, 116.

[4] Hillebrand, *Pogg. Annalen*, 1876, 158, 71.

[5] Owen, *Ann. Physik*, 1912, [iv.], 37, 657; *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 637.

[6] Pure lanthana is diamagnetic (p. 257).

[7] Muthmann and Beck, *Annalen*, 1904, 331, 46.

[8] Aufrecht, *Inaugural Dissertation* (Berlin, 1904); Muthmann, *Ber.*, 1898, 31, 1829; Ley, *Zeitsch. physikal. Chem.*, 1899, 30, 193; Holmberg, *Arkiv Kem. Min. Geol.*, 1903, 1, 1; A. A. Noyes and J. Johnston, *J. Amer. Chem. Soc.*, 1909, 31, 987; A. Heydweiller, *Zeitsch. physikal. Chem.*, 1915, 89, 281.

$LaCl_3$	$v =$	21·3	42·6	85·2	170·6	341·1	682·2	1364·5
	$\lambda =$	101·7	108·6	114·9	122·3	126·5	131·9	136·4
$La(NO_3)_3$	$v =$	32	64	128	256	512	1024	
	$\lambda =$	98·6	105·4	112·8	118·1	124·1	126·5	
$La_2(SO_4)_3$	$v =$	33·86	67·72	135·44	270·88	541·76	1083·52	
	$\lambda =$	43·58	50·30	58·49	68·89	80·93	96·26	

Noyes and Johnston have measured the equivalent conductivities of dilute solutions of lanthanum nitrate and sulphate over a wide range of temperature, and Johnston[1] has calculated from the results that the ionic conductivity of the lanthanum ion varies with the temperature as follows:—

Temp. °C.	0°	18°	25°	50°	75°	100°	128°	156°
$\frac{1}{3}$ $La^{\cdots}$	35	61	72	119	173	235	312	388

At 25° the percentage dissociation of the nitrate and sulphate is as follows (Noyes and Johnston):—

v . .	∞	500·0	80·00	20·00	10·00	5·00
1000η .	0	0·002	0·0125	0·050	0·100	0·200
$La(NO_3)_3$	100	90·4	80·4	70·0	64·4	58·6
$La_2(SO_4)_3$	100	45·0	27·8	19·0	15·8	13·2

Numerous compounds of lanthanum have been prepared and described by Cleve,[2] and by Frerichs and Smith.[3]

Thermochemistry of Lanthanum.—The following results have been obtained:—[4]

$2[La] + 3(O) = [La_2O_3]$ . . . . . + 444·7 Cals.
$[La] + 4[Al] = [LaAl_4]$ . . . . . + 97·8 „
$[La_2O_3] + 6HClaq. = 2LaCl_3aq. + 3H_2O$ . . . . + 114·6 „
$[La_2O_3] + 6(HCl) = 2[LaCl_3] + 3[H_2O]$ . . . . + 160·6 „
$[La] + 3(Cl) = [LaCl_3]$ . . . . . + 263·0 „
$[LaCl_3] + Aq. = LaCl_3aq.$ . . . . . + 31·3 „
$[La_2O_3] + 3[H_2SO_4] = [La_2(SO_4)_3] + 3[H_2O]$ . . . + 138·2 „
$La_2(SO_4)_3 + Aq. = La_2(SO_4)_3aq.$ . . . . . + 34·6 „

Lanthanum hydride, LaH_3, has been described (p. 251).

LANTHANUM AND THE FLUORINE GROUP.

Lanthanum fluoride, LaF_3.—See p. 252. The hemihydrate, $2LaF_3.H_2O$, and the *acid fluoride*, $2LaF_3.3HF$, have been described (Cleve; Frerichs and Smith).

Lanthanum chloride,[5] $LaCl_3$.—For methods of preparation and

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[1] Johnston, *J. Amer. Chem. Soc.*, 1909, **31**, 1010.

[2] Cleve, *Bihang K. Svenska Vet.-Akad. Handl.*, 1872, **2**, No. 7; *Bull. Soc. chim.*, 1874, [ii.], **21**, 196; 1878, [ii.], **29**, 492.

[3] Frerichs and Smith, *Annalen*, 1878, **191**, 331.

[4] Matignon, *Ann. Chim. Phys.*, 1906, [viii.], **8**, 426; *Compt. rend.*, 1906, **142**, 276; Muthmann and Weiss, *Annalen*, 1904, **331**, 1 (2La + 3O); Biltz, *Zeitsch. anorg. Chem.*, 1911, **71**, 434.

[5] Matignon, *Ann. Chim. Phys.*, 1906, [viii.], **8**, 426; Bourion, *ibid.*, 1910, [viii.], **21**, 49.

properties of the anhydrous salt, see p. 252. It is a white, crystalline, hygroscopic solid, readily soluble in water.

From an aqueous solution of the chloride, large triclinic crystals ($a : b : c = 1·1593 : 1 : 0·8659$; $\alpha = 91° \ 3'$, $\beta = 114° \ 28'$, $\gamma = 88° \ 12'$) of the heptahydrate, $LaCl_3.7H_2O$, may be obtained.[1] The double salts listed below have been prepared, in addition to those containing metals of Groups IV. and V.:—

$LaCl_3.3CsCl.4H_2O(?5H_2O)$
$2LaCl_3.9HgCl_2.24H_2O$ [2]
$LaCl_3.3Hg(CN)_2.8H_2O$ [3]
$LaCl_3.AuCl_3.10H_2O$ [4]
$2LaCl_3.3AuCl_3.21H_2O(?)$ [5]
$2LaCl_3.3PtCl_2.18H_2O$ [6]
$LaCl_3.PtCl_4.13H_2O$ [4]
$2LaCl_3.3PtCl_4.24H_2O$ [5]

Lanthanum oxychloride, $LaOCl$, has been described.[7]

Lanthanum bromide, $LaBr_3$.—The anhydrous salt has been prepared (p. 255) and also the heptahydrate, $LaBr_3.7H_2O$ (Cleve), the *auribromide*, $LaBr_3.AuBr_3.9H_2O$ (Cleve), and *lanthanum zinc bromide*, $2LaBr_3.3ZnBr_2.39H_2O$(?) (Frerichs and Smith).

Lanthanum iodide, LaI_3, is not known, but *lanthanum zinc iodide*, $2LaI_3.3ZnI_2.27H_2O$, has been described (Frerichs and Smith).

Lanthanum perchlorate, $La(ClO_4)_3$, forms deliquescent needles, soluble in alcohol (Cleve).

Lanthanum bromate, $La(BrO_3)_3.9H_2O$.—See p. 256. When dried at 100°, this salt loses water and is converted into the dihydrate, $La(BrO_3)_3.2H_2O$. At 150° the anhydrous salt is obtained, and at high temperatures it readily decomposes.

Lanthanum iodate, $2La(IO_3)_3.3H_2O$, obtained by double decomposition,[8] is sparingly soluble in water, one litre of a saturated solution at 25° containing 1·87 grams of anhydrous iodate.[9]

Lanthanum periodate, $LaIO_5.2H_2O$, is obtained as a white, microcrystalline precipitate when aqueous solutions of lanthanum acetate and periodic acid are mixed (Cleve).

LANTHANUM AND THE OXYGEN GROUP.

Lanthanum sesquioxide, or **lanthana**, La_2O_3, is obtained as a white powder by the ignition of the hydroxide, carbonate, nitrate, oxalate, etc. The strongly ignited oxide has a density of 6·53 at 17° (Cleve), 5·94

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[1] Marignac, *Mem. Sci. phys. nat.*, 1855, **14**, 201; *Œuvres Complètes* (Geneva, 1902), vol. i. p. 362; Cleve, *Bull. Soc. chim.*, 1874, [ii.], **21**, 196; Zschiesche, *J. prakt. Chem.*, 1869, **107**, 65; R. J. Meyer and Koss, *Ber.*, 1902, **35**, 2622.

[2] Marignac, *Œuvres Complètes* (Geneva, 1902), vol. i. p. 640.

[3] Alén, *Oefvers. Svenska Vet.-Akad. Förhandl.*, 1876, **33**, Nos. 8, 9; *Bull. Soc. chim.*, 1876, [ii.], **27**, 365.

[4] Cleve, *loc. cit.*

[5] Frerichs and Smith, *Annalen*, 1878, **191**, 331.

[6] Nilson, *Ber.*, 1876, **9**, 1056, 1142.

[7] See p. 255, and Hermann, *J. prakt. Chem.*, 1861, **82**, 385; Frerichs, *Ber.*, 1874, **7**, 798.

[8] Holzmann, *J. prakt. Chem.*, 1858, **75**, 321; Hermann, *ibid.*, 1861, **82**, 385.

[9] Rimbach and Schubert, *Zeitsch. physikal. Chem.*, 1909, **67**, 183.

(Hermann).[1] It is slightly diamagnetic (see p. 257); the specific heat between 0° and 100° is 0·0749. The powder rapidly absorbs water, with the evolution of heat, and it also combines readily with carbon dioxide. The oxide crystallises in the form of hexagonal bipyramids of density 5·30 when dissolved in borax at a white heat and slowly cooled[2]; the crystals are not affected by water.

Lanthana, even after intense ignition, is readily soluble in acids.

Lanthanum hydroxide, $La(OH)_3$, is produced by the direct union of lanthana and water, and may be obtained as a white, gelatinous precipitate by the addition of an excess of ammonia or alkali hydroxide to a solution of a lanthanum salt. The precipitate is sufficiently soluble in water to turn red litmus blue; it easily absorbs carbon dioxide from the air and sets free ammonia from ammonium salts. Lanthanum hydroxide is, in fact, the strongest base of all the rare earth hydroxides, being comparable with calcium hydroxide in its strength, and on this account the claim of Baskerville and Catlett[3] to have prepared metallic *lanthanates*, in which lanthana acts as an acid, cannot be accepted until independent confirmation of their results is forthcoming.

Lanthanum peroxide.—An oxide of lanthanum higher than La_2O_3 cannot be prepared in the dry way, but indications of the existence of such an oxide have been obtained.[4]

When a mixture of ammonia and hydrogen peroxide is added to a solution of a lanthanum salt, a gelatinous, hydrated peroxide, $La_2O_5.xH_2O$, is obtained, to which the constitution $(OH)_2La(O.OH)$ has been ascribed.[5] Dilute sulphuric acid and carbonic acid set free hydrogen peroxide from the precipitate, and concentrated sulphuric acid decomposes it with the liberation of ozonised oxygen.

Lanthanum sulphide, La_2S_3, the preparation and properties of which are given on p. 259, is a yellow solid of density 4·911 at 11° (Muthmann and Stützel).

Lanthanum persulphide, La_2S_4, is prepared by heating lanthanum sulphate to 580°–600° in hydrogen sulphide, and resembles the corresponding cerium compound in properties, decomposing into the sesquisulphide and sulphur at 650°.[6]

Lanthanum sulphite, $La_2(SO_3)_3$.—A tetrahydrate of this salt has been described by Cleve, and a trihydrate by Grossmann (see p. 260).

Lanthanum sulphate, $La_2(SO_4)_3$.—See p. 260 for general properties. Of all the rare earth sulphates, this is the most difficult to decompose completely by heat. Its specific heat (0°–100°) is 0·1182.[7]

One part of the anhydrous sulphate dissolves in 6 parts of ice-cold water; from the solution at 0° C. a hydrate, $La_2(SO_4)_3.16H_2O$, may be crystallised.[8]

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[1] Hermann, *J. prakt. Chem.*, 1861, **82**, 385.

[2] Nordenskiöld, *Pogg. Annalen*, 1861, **114**, 612; *J. prakt. Chem.*, 1861, **85**, 431.

[3] Baskerville and Catlett, *J. Amer. Chem. Soc.*, 1904, **26**, 75.

[4] Marc, *Ber.*, 1902, **35**, 2370; *cf.* Hermann, *J. prakt. Chem.*, 1861, **82**, 385; Zschiesche, *ibid.*, 1869, **107**, 65.

[5] Cleve, *Bull. Soc. chim.*, 1885, [ii.], **43**, 53; Melikoff and Pissarjewsky, *Zeitsch. anorg. Chem.*, 1899, **21**, 70. See also Job, *Compt. rend.*, 1903, **136**, 45.

[6] W. Biltz, *Zeitsch. anorg. Chem.*, 1911, **71**, 427.

[7] Nilson and Pettersson, *Ber.*, 1880, **13**, 1459; *Compt. rend.*, 1880, **91**, 232.

[8] Brauner and Pavlíček, *Trans. Chem. Soc.*, 1902, **81**, 1243.

The hexagonal[1] enneahydrate, $La_2(SO_4)_3.9H_2O$, is the only hydrate stable in contact with the solution between 0° and 100°. It is readily prepared by warming a 15 per cent. ice-cold solution of lanthanum sulphate to 30°. The solubility diminishes with the temperature as follows :—[2]

Temp. ° C . .	0°	14°	18°	30°	50°	75°	100°
Grams of $La_2(SO_4)_3$.	3·0	2·6	2·1	1·9	1·6	1·0	0·7

The figures represent grams of anhydrous salt per 100 grams of water.

A hexahydrate, $La_2(SO_4)_3.6H_2O$, is said to crystallise from a solution in aqueous sulphuric acid (Frerichs and Smith).

The *acid sulphate*, $La(HSO_4)_3$, and the *basic sulphate*, $La_2O_3.SO_3$, are known (p. 263). The following *double salts* have been described :—

$La_2(SO_4)_3.Cs_2SO_4.2H_2O$;[6] $3La_2(SO_4)_3.2Cs_2SO_4$.[6]
$La_2(SO_4)_3.Rb_2SO_4.2H_2O$;[6] $La_2(SO_4)_3.Rb_2SO_4$;[6] $3La_2(SO_4)_3.2Rb_2SO_4$.[6]
$La_2(SO_4)_3.K_2SO_4.2H_2O$;[7] $La_2(SO_4)_3.3K_2SO_4$.[3, 4]
$La_2(SO_4)_3.5K_2SO_4$.[7]
$La_2(SO_4)_3.Na_2SO_4.2H_2O$.[4, 7]
$La_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$;[4, 5] with $2H_2O$, see Barre.[7]
$2La_2(SO_4)_3.5(NH_4)_2SO_4$;[7] $La_2(SO_4)_35(NH_4)_2SO_4$.[7]

Lanthanum sulphate also combines with *hydrazine* sulphate.[8]

The diminution in solubility of lanthanum sulphate brought about by the addition of *potassium*, *sodium*, or *ammonium* sulphate will be seen from the following data, given by Barre, and denoting grams of anhydrous salts present in solution per 100 grams of water (solid phases not stated by Barre) :—

Temperature 16·5°.		Temperature 18°.		Temperature 18°.	
K_2SO_4.	$La_2(SO_4)_3$.	Na_2SO_4.	$La_2(SO_4)_3$.	$(NH_4)_2SO_4$.	$La_2(SO_4)_3$.
0·00	2·21	0·00	2·13	0·00	2·13
0·25	0·73	0·40	1·00	4·01	0·39
0·50	0·27	0·69	0·35	8·73	0·28
0·85	0·19	0·77	0·30	18·24	0·25
1·03	0·05	1·14	0·13	27·89	0·48
1·16	0·02	2·48	0·04	36·11	0·28
2·50	0·00	3·80	0·02	47·49	0·14
...	...	5·55	0·02	65·29	0·01

Lanthanum dithionate, $La_2(S_2O_6)_3.24H_2O$, is readily soluble in water and crystallises in six-sided plates (Cleve).

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[1] Kraus, *Zeitsch. Kryst. Min.*, 1901, **34**, 307. See p. 261.
[2] Muthmann and Rölig, *Ber.*, 1898, **31**, 1718 ; Barre, *vide infra.*
[3] Hermann, *J. prakt. Chem.*, 1861, **82**, 385.
[4] Cleve, *Bull. Soc. chim.*, 1874, [ii.], **21**, 196.
[5] Marignac, *Mem. Soc. phys. nat.*, 1855, **14**, 201.
[6] Baskerville and Moss, *J. Amer. Chem Soc.*, 1904, **26**, 67.
[7] Barre, *Compt. rend.*, 1910, **151**, 871.
[8] Kolb, *Zeitsch. anorg. Chem.*, 1908, **60**, 123.

Lanthanum selenite, $La_2(SeO_3)_3$.—Hydrates of this salt with $9H_2O$ and $12H_2O$ have been described, and also the acid salts, $La_2(SeO_3)_3.2H_2SeO_3.4H_2O$ and $La_2(SeO_3)_3.3H_2SeO_3.2H_2O$.[1]

Lanthanum selenate, $La_2(SeO_4)_3$.—Hydrates with $6H_2O$ and $10H_2O$ have been described by Cleve, and also the following double salts :—

$La_2(SeO_4)_3.K_2SeO_4.9H_2O$
$La_2(SeO_4)_3.Na_2SeO_4.4H_2O$
$La_2(SeO_4)_3.(NH_4)_2SeO_4.9H_2O$

Lanthanum chromate, $La_2(CrO_4)_3.8H_2O$, may be obtained by double decomposition as a sparingly soluble, yellow, crystalline precipitate (Cleve).

Lanthanum molybdate, $La_2(MoO_4)_3$, has been prepared (p. 265).

Lanthanum tungstate, $La_2(WO_4)_3$, the metatungstate, double and complex tungstates have been described (p. 265).

Lanthanum silicotungstate, $La_4(W_{12}SiO_{40})_3$.—See p. 266.

LANTHANUM AND THE NITROGEN GROUP.

Lanthanum nitride, LaN, has been described (p. 267).

Lanthanum azide (*hydrazoate, trinitride*).—The basic salt $2La(N_3)_2(OH).3H_2O$ is known and is very explosive.[2]

Lanthanum nitrate, $La(NO_3)_3.6H_2O$, forms deliquescent, triclinic crystals[3] which lose $5H_2O$ over sulphuric acid.[4] At 25° a saturated aqueous solution of the hexahydrate contains 151·1 parts of anhydrous salt per 100 of water.[5] Lanthanum nitrate is isodimorphous with bismuth nitrate (see p. 234).

Lanthanum ammonium nitrate, $La(NO_3)_3.2(NH_4)NO_3.4H_2O$, has already been described.[6]

Lanthanum cæsium nitrate, $La(NO_3)_3.2CsNO_3.2H_2O$, forms monoclinic crystals ($a : b : c = 1\cdot3052 : 1 : 0\cdot9663$; $\beta = 103° 26'$).[7]

Lanthanum rubidium nitrate, $La(NO_3)_3.2RbNO_3.4H_2O$, has been described (p. 268).

Lanthanum potassium nitrate, $La(NO_3)_3.2KNO_3.2H_2O$, forms orthorhombic crystals (hemimorphic ; $a : b : c = 0\cdot5306 : 1 : 0\cdot5696$)[8] of density 2·54 at 0° C.

Lanthanum sodium nitrate, $La(NO_3)_3.2NaNO_3.H_2O$, forms monoclinic crystals ($a : b : c = 1\cdot9970 : 1 : 0\cdot7678$; $\beta = 90° 32'$) of density 2·63 at 0° C.[9]

Lanthanum thallium nitrate, $La(NO_3)_3.2TlNO_3.4H_2O$, has been described (p. 268).

Acid lanthanum rubidium nitrate, $La(NO_3)_3.RbNO_3.HNO_3.6H_2O$, has been prepared by Jantsch and Wigdorow. When heated to 120° it loses nitric acid and water, leaving the salt $La(NO_3)_3.RbNO_3.H_2O$.

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[1] Cleve, *loc. cit.* ; Nilson, *Nova Acta Soc. Upsala*, 1875, [iii.], 9, No. 7 ; *Bull. Soc. chim.*, 1875, [ii.], 23, 494 ; *Ber.*, 1875, 8, 655.

[2] Curtius and Darapsky, *J. prakt. Chem.*, 1900, [ii.], 61, 408.

[3] See p. 268 ; and Marignac, *Ann. Chim. Phys.*, 1873, [iv.], 30, 56.

[4] Mosander, *Phil. Mag.*, 1843, [iii.], 23, 241 ; Cleve, *Bull. Soc. chim.*, 1874, [ii.], 21, 196 ; Hermann, *J. prakt. Chem.*, 1861, 82, 385 ; Zschiesche, *ibid.*, 1869, 107, 65.

[5] James and Whittemore, *J. Amer. Chem. Soc.*, 1912, 34, 1168.

[6] See p. 268 ; Marignac, *loc. cit.* ; Dufet, *Bull. Soc. franç. Min.*, 1888, 11, 143, 215 ; Kraus, *Zeitsch. Kryst. Min.*, 1901, 34, 307.

[7] Wyrouboff, *Bull. Soc. franç. Min.*, 1907, 30, 299 ; Jantsch and Wigdorow, *Zeitsch anorg. Chem.*, 1911, 69, 221.

[8] Fock, *Zeitsch. Kryst. Min.*, 1894, 22, 37 ; Wyrouboff, *Bull. Soc. franç. Min.*, 1907, 30, 299 ; Jantsch and Wigdorow, *loc. cit.*

[9] Wyrouboff, *loc. cit.* ; Jantsch and Wigdorow, *loc. cit.*

For the double nitrates of lanthanum and bivalent metals, $3M^{II}(NO_3)_2.2La(NO_3)_3.24H_2O$, see p. 269.[1]

Lanthanum phosphite, $La_2(HPO_3)_3$. has been described by Frerichs and Smith.

Lanthanum orthophosphate, $LaPO_4$, is obtained as a white, amorphous precipitate by adding phosphoric acid or sodium orthophosphate to a solution of a lanthanum salt (Cleve). It may be obtained in the crystalline form by heating lanthana with molten potassium metaphosphate.[2] The *double salt* $2LaPO_4.K_3PO_4$ may be prepared by saturating molten potassium pyro- or ortho-phosphate with lanthana.

Lanthanum hydrogen pyrophosphate, $LaHP_2O_7.3H_2O$.—From a solution of a lanthanum salt sodium pyrophosphate throws down a white precipitate which then redissolves. On allowing the solution to stand, the acid pyrophosphate crystallises out in needles (Cleve).

The *double salt* $LaNaP_2O_7$ may be obtained in crystals by fusing together sodium metaphosphate and lanthana.[3]

Lanthanum metaphosphate, $La(PO_3)_3$, and the compound $La_2O_3.5P_2O_5$ have been prepared.[4]

Lanthanum arsenite, $La_2(HAsO_3)_3$, and **lanthanum arsenate,** $La_2(HAsO_4)_3$, have also been described (Frerichs and Smith).

LANTHANUM AND THE CARBON GROUP.

Lanthanum carbide, LaC_2, has been described (p. 270).

Lanthanum carbonate, $La_2(CO_3)_3.8H_2O$, loses $7H_2O$ at 100°. The octahydrate occurs in nature as the orthorhombic mineral *lanthanite* ($a : b : c = 0·9528 : 1 : 0·9023$). The following double salts are known :—[5]

$La_2(CO_3)_3.K_2CO_3.12H_2O$

$2La_2(CO_3)_3.3Na_2CO_3.20H_2O$

$La_2(CO_3)_3.(NH_4)_2CO_3.4H_2O$

Lanthanum thiocyanate, $La(CNS)_3.7H_2O$, and the *double salt*, $La(CNS)_3.3Hg(CN)_2.12H_2O$, are known (Cleve; see p. 272).

Lanthanum platinocyanide, $2La(CN)_3.3Pt(CN_2.18H_2O$, forms yellow prisms having a blue reflex (Cleve; see p. 272).

Lanthanum acetate, $2La(C_2H_3O_2)_3.3H_2O$, crystallises from its aqueous solution in thin prisms.[6]

When a cold aqueous solution of lanthanum acetate is made ammoniacal, a colloidal basic acetate is precipitated; if a little solid iodine be added to the precipitate a blue adsorption compound is produced, similar in appearance to the familiar "starch-iodide" precipitate.[7] The blue substance may conveniently be prepared by adding a solution of iodine in potassium iodide

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[1] Also Holzmann, *J. prakt. Chem.*, 1858, **75**, 321; Carius, *ibid.*, 1858, **75**, 352; Grant and James, *J. Amer. Chem. Soc.*, 1915, **37**, 2652 (Fe).

[2] Ouvrard, *Compt. rend.*, 1888, **107**, 37; Grandeau, *Ann. Chim. Phys.*, 1886, [vi.], **8**, 193.

[3] Wallroth, *Bull. Soc. chim.*, 1883, [ii.], **39**, 316.

[4] Frerichs and Smith, *loc. cit.*; Johnson, *Ber.*, 1889, **22**, 976.

[5] R. J. Meyer, *Zeitsch. anorg. Chem.*, 1904, **41**, 97; see p. 271.

[6] Czudnowicz, *J. prakt. Chem.*, 1860, **80**, 31; Cleve, *Bull. Soc. chim.*, 1874, [ii.], **21**, 196; Behrens, *Arch. Néerland.*, 1901, [ii.], **6**, 67.

[7] Damour, *Compt. rend.*, 1856, **43**, 976.

to a cold solution of lanthanum acetate (or nitrate acidified with acetic acid), adding ammonia cautiously until very little iodine is left unchanged, and then warming the mixture very gently.[1]

Lanthanum ethylsulphate, $La(C_2H_5.SO_4)_3.9H_2O$. See p. 278.

Lanthanum acetylacetonate, $La(CH_3.CO.CH.CO.CH_3)_3$, has also been described (p. 279).

Lanthanum oxalate, $La_2(C_2O_4)_3.9(10 \text{ or } 11)H_2O$,[2] may be obtained by double decomposition as a white, crystalline precipitate. According to the temperature at which precipitation occurs and the temperature of the wash water, the precipitate appears to contain 9, 10, or $11H_2O$. Most experimenters give $10H_2O$ as being present in the hydrate in equilibrium with its aqueous solution at 25°.

Lanthanum oxalate is appreciably soluble in a solution of lanthanum nitrate, but no crystalline oxalonitrate can be isolated at 25°. The only hydrates of lanthanum oxalate that are stable at 25° in contact with aqueous solutions of lanthanum nitrate of the appropriate concentrations are those containing $3H_2O$, $5H_2O$, and $8H_2O$.[3] A hydrate containing $7H_2O$ may be crystallised from dilute sulphuric acid.[4]

A solution of lanthanum oxalate in hot, concentrated hydrochloric acid deposits crystals of *lanthanum oxalochloride*, $2La(C_2O_4)Cl.5H_2O$, when cooled. The salt is decomposed by water.[5]

For further details concerning lanthanum oxalate, see p. 273.

Lanthanum salts of organic acids.—The following salts have been described:—

Lanthanum *formate*,[6] *succinate*,[6, 7, 8, 9] *tartrate*,[6, 7, 10, 12] *citrate*,[7, 12] *sebacate*,[17] *glycollate*,[13] *malonate*,[11, 12] *dimethylphosphate*,[19] *benzoate*,[7] *phenylacetate*,[13] *hippurate*,[7] *phenoxyacetate*,[16] *benzenesulphonate*,[12] *m-nitro-*, *m-chloro-*, and *m-bromobenzenesulphonate*,[12] *p-dichlorobenzenesulphonate*,[15] *p-dibromobenzenesulphonate*,[14] 6 : 3 : 1-*chloronitrobenzenesulphonate*,[12] 1 : 4 : 2-*bromonitrobenzenesulphonate*,[18] 8-*hydroxynaphthalene*-1-*sulphonate*,[11] *a-naphthalenesulphonate*,[12] 1 : 5-, 1 : 6-, 1 : 7-*nitronaphthalenesulphonate*[12] and *pyromucate*.[20]

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[1] W. Biltz, *Ber.*, 1904, **37**, 719.

[2] $9H_2O$; Czudnowicz, *J. prakt. Chem.*, 1860, **80**, 31; Cleve, *Bull. Soc. chim.*, 1874, [ii.], **21**, 196. $10H_2O$; Power and Shedden, *J. Soc. Chem. Ind.*, 1900, **19**, 636; Hauser and Wirth, *Zeitsch. anal. Chem.*, 1908, **47**, 389; Wirth, *Zeitsch. anorg. Chem.*, 1912, **76**, 174. $11H_2O$; Wyrouboff, *Bull. Soc. franç. Min.*, 1901, **24**, 105; Brauner and Pavlíček, *Trans. Chem. Soc.*, 1902, **81**, 1243.

[3] Whittemore and James, *J. Amer. Chem. Soc.*, 1912, **34**, 1168.

[4] See Wirth, *Zeitsch. anorg. Chem.*, 1908, **58**, 213.

[5] Job, *Compt. rend.*, 1898, **126**, 246.

[6] Cleve, *Bull. Soc. chim.*, 1874, [ii.], **21**, 196.

[7] Czudnowicz, *J. prakt. Chem.*, 1860, **80**, 31.

[8] Behrens, *Arch. Néerland.*, 1901, [ii.], **6**, 67.

[9] R. J. Meyer, *Zeitsch. anorg. Chem.*, 1902, **33**, 113.

[10] Rimbach and Schubert, *Zeitsch. physikal. Chem.*, 1909, **67**, 183.

[11] Erdmann and Wirth, *Annalen*, 1908, **361**, 190.

[12] Holmberg, *Zeitsch. anorg. Chem.*, 1907, **53**, 83.

[13] Jantsch and Grünkraut, *ibid.*, 1913, **79**, 305.

[14] Armstrong and Rodd, *Proc. Roy. Soc.*, 1912, **A**, **87**, 204.

[15] Rodd, *ibid.*, 1913, **A**, **89**, 292.

[16] Pratt and James, *J. Amer. Chem. Soc.*, 1911, **33**, 1330.

[17] Whittemore and James, *ibid.*, 1913, **35**, 127.

[18] Katz and James, *ibid.*, 1913, **35**, 872

[19] Morgan and James, *ibid.*, 1914, **36**, 10.

[20] Grant and James, *ibid.*, 1915, **37**, 2652.

LANTHANUM AND BORON.

Lanthanum metaborate, $La(BO_2)_3$, has been described (p. 282).

PRASEODYMIUM.

Symbol, Pr. Atomic weight, 140·92[1] (O = 16).

Praseodymium is one of the most abundant of the rare earth elements, but it is decidedly less plentiful than lanthanum or neodymium. The relative proportions of praseodymium and neodymium in different minerals do not vary very much, the ratio praseodymium to neodymium being approximately 1 to 2.[2]

The occurrence, history, preparation, atomic weight, and homogeneity of praseodymium have been already discussed in Chapters X. and XI.

Praseodymium[3] is a yellow metal of density 6·475. It melts at 940° and is strongly paramagnetic, the magnetic susceptibility at 18° being about 25×10^{-6} c.g.s. units per gram.[4] Very little else is known of the properties of the metal.

COMPOUNDS OF PRASEODYMIUM.

The salts of praseodymium are derived from the basic oxide Pr_2O_3. They are leek-green in colour, and their reflection spectra or the absorption spectra of their solutions exhibit characteristic absorption bands. The conductivities of praseodymium salts in aqueous solution are in harmony with the view that the salts are derived from a fairly strong triacid base. The following results, for example, refer to the chloride at 25° (v = dilution in litres per gram equivalent):—[5]

$PrCl_3$						
$v =$	31·3	62·6	125·2	250·4	500·8	1001·6
$\lambda =$	105·3	112·25	120·1	125·1	130·4	135·7

Praseodymium is of interest in that it forms a *dioxide*, PrO_2. According to Brauner, the dioxide is a weak base, and gives rise to a *basic sulphate*, $2Pr_2O_4.SO_3 + 2\frac{1}{2}H_2O$, and a *basic acetate*, $(CH_3.CO)_3.\overset{\text{IV}}{Pr}O.\overset{\text{IV}}{Pr}(OH)_3$ or $(CH_3.CO)_2.\overset{\text{III}}{Pr_2}O_2(OH)(CO.CH_3) + H_2O$.[6] The same authority also mentions an acetate of the constitution $(CH_3.CO)_2\overset{\text{III}}{Pr}.O.O.O.\overset{\text{III}}{Pr}(OH)(CH_3.CO) + H_2O$.[7]

Numerous compounds of praseodymium have been described by von Schéele.[8]

Thermochemistry of Praseodymium.—The following results have been obtained:—[9]

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[1] Baxter and O. J. Stewart, *J. Amer. Chem. Soc.*, 1915, **37**, 516.

[2] Muthmann and Stützel, *Ber.*, 1899, **32**, 2653.

[3] Muthmann and Weiss, *Annalen*, 1904, **331**, 1. See also pp. 229–230.

[4] Owen, *Ann. Physik*, 1912, [iv.], **37**, 657.

[5] Aufrecht, *Inaugural Dissertation* (Berlin, 1904); see also Jones and Reese, *Amer. Chem. J.*, 1898, **20**, 606.

[6] Brauner, *Proc. Chem. Soc.*, 1898, **14**, 70.

[7] Brauner, *Proc. Chem. Soc.*, 1901, **17**, 66.

[8] Von Schéele, *Zeitsch. anorg. Chem.*, 1898, **17**, 310; **18**, 352.

[9] Muthmann and Weiss, *Annalen*, 1904, **331**, 1 (2Pr + 3O); Matignon, *Ann. Chim. Phys.*, 1906, [viii.], **8**, 386; *Compt. rend.*, 1906, **142**, 276.

$2[Pr]+3(O) = Pr_2O_3$ . . . . $+412{\cdot}4$ Cals.
$[Pr_2O_3]+6HClaq. = 2PrCl_3aq.+3H_2O$ . . . . $+106{\cdot}2$ „
$[Pr_2O_3]+6(HCl) = 2[PrCl_3]+3[H_2O]$ . . . . $+147{\cdot}8$ „
$[Pr_2O_3]+3[H_2SO_4] = [Pr_2(SO_4)_3]+3[H_2O]$ . . $+125{\cdot}7$ „
$[PrCl_3]+Aq. = PrCl_3aq.$ . . . . . . $+\ 33{\cdot}5$ „
$[PrCl_3.H_2O]+Aq. = PrCl_3aq.$ . . . . . $+\ 28{\cdot}9$ „
$[PrCl_3.7H_2O]+Aq. = PrCl_3Aq.$ . . . . . $+\ \ 5{\cdot}3$ „
$[Pr_2(SO_4)_3]+Aq. = Pr_2(SO_4)_3aq.$ . . . . . $+\ 36{\cdot}0$ „

Praseodymium hydride, PrH_3, has been described (p. 251).

PRASEODYMIUM AND THE FLUORINE GROUP.

Praseodymium fluoride, PrF_3, prepared from aqueous praseodymium sulphate and hydrofluoric acid, is a yellow precipitate. When dried, it forms glittering yellow crystals which appear green by reflection.[1]

Praseodymium chloride,[2] $PrCl_3$.—The methods of preparation and properties of the anhydrous salt are given on p. 252. It is a green, hygroscopic solid which fuses to a green liquid. The density is 4·020 at 25° C. (Baxter and Stewart).

From aqueous solution the heptahydrate, $PrCl_3.7H_2O$, separates in large, green crystals of density 2·25 at 15° (Schéele). The crystals melt at 111° C. (Baxter and Stewart). When dried over sulphuric acid, the heptahydrate rapidly passes into the hexahydrate, $PrCl_3.6H_2O$, which is slowly dehydrated to the trihydrate, $PrCl_3.3H_2O$. The monohydrate is also known (p. 254). At 13·8°, 100 parts of water dissolve 103·9 parts of anhydrous chloride or 334·2 of the heptahydrate, the solution being in equilibrium with the heptahydrate (Matignon). The concentrated aqueous solution dissolves considerable quantities of rare earth oxalates.

Praseodymium aurichloride, $PrCl_3.AuCl_3.10H_2O$, forms yellow crystals of specific gravity 2·60 and is readily soluble in water. The *chloroplatinate*, $PrCl_3.PtCl_4.12H_2O$, is also a yellow crystalline salt, of density 2·41 at 16°.

Praseodymium oxychloride, $PrOCl$, has been prepared (p. 255).

Praseodymium bromide, $PrBr_3$.—The anhydrous salt has been prepared, and closely resembles the chloride (p. 255). The hexahydrate, $PrBr_3.6H_2O$, crystallises from aqueous solution (von Schéele).

Praseodymium iodide, PrI_3, has been prepared by Matignon (see p. 255).

Praseodymium bromate, $Pr(BrO_3)_3.9H_2O$, forms green hexagonal prisms (p. 256). It is converted into the dihydrate, $Pr(BrO_3)_3.2H_2O$, at 100° and the anhydrous salt at 130°, while it decomposes at 150°.

PRASEODYMIUM AND THE OXYGEN GROUP.

Praseodymium sesquioxide, or **praseodymia,** Pr_2O_3, is obtained by reducing the dioxide at a red heat in a stream of hydrogen. It is a yellowish-green powder of density 6·88[3] (or 7·07[4]) at 15°. When heated in the air it absorbs oxygen and becomes brown in colour.

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[1] Popovici, *Ber.*, 1908, 41, 634.

[2] Matignon, *Compt. rend.*, 1902, 134, 427; *Ann. Chim. Phys.*, 1906, [viii.], 8, 364; Bourion, *ibid.*, 1910, [viii.], 21, 49; *cf.* R. J. Meyer and Koss, *Ber.*, 1902, 35, 2622; Baxter and Stewart, *J. Amer. Chem. Soc.*, 1915, 37, 516.

[3] Von Schéele, *Zeitsch. anorg. Chem.*, 1898, 17, 310.

[4] Brauner, *Proc. Chem. Soc.*, 1901, 17, 66.

Praseodymium hydroxide, $Pr(OH)_3$, may be obtained by double decomposition as a bright green, gelatinous precipitate. In the presence of hydrogen peroxide, ammonia produces with praseodymium salts a precipitate of *hydrated praseodymium peroxide,* $Pr_2O_5.xH_2O$ or $(OH)_2Pr.O.OH$. The peroxide closely resembles the lanthanum compound in its properties.[1]

Praseodymium dioxide, PrO_2, may be prepared by heating the nitrate to 440° or by fusing the nitrate with nitre at 400° until decomposition is complete.[2] It is a black solid of density 5·978 at 20°. According to Brauner, the pure oxide is not of the hydrogen peroxide type, but contains quadrivalent praseodymium. It sets free chlorine from hydrochloric acid, iodine from hydriodic acid, and ozonised oxygen with oxyacids:[3] it oxidises cerous salts from ceric, manganous salts to permanganic acid, and gives a violet coloration with a solution of strychnine in sulphuric acid. It is reduced by hydrogen peroxide in acid solution. It oxidises ferrous and stannous salts, but a part of the available oxygen is always lost (von Schéele).

When praseodymium hydroxide, carbonate, nitrate, oxalate, etc., are heated, dark brown oxide residues are obtained which are intermediate in composition between Pr_2O_3 and PrO_2, and which contain less oxygen in proportion as the temperature at which they are produced increases.[4] Intermediate oxides of the formulæ Pr_4O_7,[5] Pr_5O_9,[6] and Pr_6O_{11}[7] have been described, but their individuality is doubtful. Brauner considers the oxide Pr_5O_9 to be a complex oxide formed by the combination of Pr_2O_3 with PrO_2 ($Pr_5O_9 = Pr_2O_3.3PrO_2$).

The formation of praseodymium dioxide in a mixture of cerium earths is favourably influenced by the presence of ceria, which probably acts as an oxygen-carrier, but is adversely affected by the presence of lanthana or neodymia.[8]

Praseodymium sulphide, Pr_2S_3, cannot be prepared by the usual methods (see p. 259) if entirely free from cerium; the sulphate, when heated in hydrogen sulphide, giving only *praseodymium oxysulphide,* Pr_2O_2S. If, however, the praseodymium sulphate contains a little cerous sulphate, the *trisulphide,* Pr_2S_3, and *persulphide,* Pr_2S_4, may be obtained as in the cases of cerium and lanthanum. The trisulphide is chocolate-brown in colour and has a density of 5·042 at 11° (Muthmann and Stützel). The persulphide begins to lose sulphur at about 650°.[9]

Praseodymium sulphate, $Pr_2(SO_4)_3$.—For preparation and general properties, see p. 260. At 0°, 23·6 parts, and at 20°, 17·7 parts of the anhydrous sulphate can be dissolved in 100 of water.

The monoclinic[10] octahydrate, $Pr_2(SO_4)_3.8H_2O$, is the only hydrate stable in

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[1] Melikoff and Klimenko, *J. Russ. Phys. Chem. Soc.*, 1901, 33, 663.

[2] Brauner, *Proc. Chem. Soc.*, 1898, 14, 70; 1901, 17, 66.

[3] See, however, Melikoff and Klimenko, *J. Russ. Phys. Chem. Soc.*, 1901, 33, 739.

[4] Von Schéele, *loc. cit.*

[5] Auer von Welsbach, *Monatsh.*, 1885, 6, 477.

[6] Brauner, *Proc. Chem. Soc.*, 1898, 14, 70; 1901, 17, 66.

[7] Schottländer, *Ber.*, 1892, 25, 569; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1904, 41, 97.

[8] Brauner, *Monatsh.*, 1882, 3, 1; Marc, *Ber.*, 1902, 35, 2370; R. J. Meyer and Koss, *Ber.*, 1902, 35, 3740.

[9] W. Biltz, *Zeitsch. anorg. Chem.*, 1911, 71, 427.

[10] Kraus, *Zeitsch. Kryst. Min.*, 1901, 34, 307; Dufet, *Chem. Zentr.*, 1902, i. 452. See p. 261.

contact with the solution from 0°–75° ;[1] its solubility, in grams of anhydrous salt per 100 grams of water, is as follows:—

Temp. °C.	0°	18°	35°	55°	75°
Grams of $Pr_2(SO_4)_3$	19·80	14·05	10·40	7·02	4·20

The monoclinic[2] pentahydrate, $Pr_2(SO_4)_3.5H_2O$, separates from the aqueous solution at 90°–100°. Its solubility, in grams of anhydrous sulphate per 100 grams of water, is as follows (Muthmann and Rölig):—

Temp. °C.	85°	90°	95°
Grams of $Pr_2(SO_4)_3$	1·60	1·35	1·00

The transition-point (from octa- to penta-hydrate) is about 75°. Two labile hydrates, $Pr_2(SO_4)_3.15\frac{1}{2}H_2O$ and $Pr_2(SO_4)_3.12H_2O$, have been isolated at low temperatures by von Schéele and by Muthmann and Rölig respectively; Brauner mentions a hexahydrate.[3]

For *acid* and *basic* sulphates, $Pr(HSO_4)_3$ and $Pr_2O_3.SO_3$ respectively, see p. 263.

The following *double sulphates* have been described:—

$Pr_2(SO_4)_3.Cs_2SO_4.2H_2O$ [5] and $Pr_2(SO_4)_3.Cs_2SO_4.4H_2O$ [5]
$Pr_2(SO_4)_3.K_2SO_4.4H_2O$,[5] $Pr_2(SO_4)_3.3K_2SO_4.H_2O$,[4] density 3·29
$Pr_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$,[4] density 2·53

Praseodymium dithionate, $Pr_2(S_2O_6)_3.12H_2O$, is extremely soluble in water (von Schéele).

Praseodymium selenite.—The basic salt precipitated by sodium selenite from praseodymium sulphate solution is converted into the *acid selenite*, $Pr_2(SeO_3)_3.H_2SeO_3.3H_2O$, by heating with aqueous selenious acid (von Schéele).

Praseodymium selenate, $Pr_2(SeO_4)_3$.—The octahydrate, $Pr_2(SeO_4)_3.8H_2O$, crystallises from cold aqueous solutions, and the pentahydrate, $Pr_2(SeO_4)_3.5H_2O$, from hot solutions. The double salt *praseodymium potassium selenate*, $Pr_2(SeO_4)_3.3K_2SeO_4.4H_2O$, is somewhat more soluble than the double sulphate (von Schéele).

Praseodymium molybdate, $Pr_2(MoO_4)_3$.—See p. 265.

Praseodymium tungstate, $Pr_2(WO_4)_3$, and complex tungstates have been already mentioned (p. 265).

Praseodymium silicotungstate, $Pr_4(W_{12}SiO_{40})_3$.—See p. 266.

PRASEODYMIUM AND THE NITROGEN GROUP.

Praseodymium nitride, PrN, has been described (p. 267).

Praseodymium nitrate, $Pr(NO_3)_3.6H_2O$, crystallises in large, green needles. The following double salts are known: $Pr(NO_3)_3.2(NH_4)NO_3.4H_2O$; $Pr(NO_3)_3.2RbNO_3.4H_2O$; $Pr(NO_3)_3.2NaNO_3.H_2O$ (von Schéele): and the double salts with the nitrates of bivalent metals, $3M^{II}(NO_3)_2.2Pr(NO_3)_3.24H_2O$ (see p. 268).

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[1] Muthmann and Rölig, *Ber.*, 1898, **31**, 1718.
[2] Kraus, *loc. cit.* See p. 261.
[3] Brauner, *Proc. Chem. Soc.*, 1898, **14**, 70.
[4] Von Schéele, *loc. cit.*
[5] Baskerville and Holland, *J. Amer. Chem. Soc.*, 1904, **26**, 71.

Praseodymium and the Carbon Group.

Praseodymium carbide, PrC_2, has been described (p. 270).

Praseodymium carbonate, $Pr_2(CO_3)_3.8H_2O$, has been prepared by von Schéele. The following double salts are known:—[1]

$Pr_2(CO_3)_3.K_2CO_3.12H_2O$ $2Pr_2(CO_3)_3.3Na_2CO_3.22H_2O$
$Pr_2(CO_3)_3.(NH_4)_2CO_3.4H_2O$

Praseodymium ethylsulphate, $Pr(C_2H_5.SO_4)_3.9H_2O$, has been described (p. 278).

Praseodymium acetylacetonate, $Pr(CH_3.CO.CH.CO.CH_3)_3$, has also been described (p. 279).

Praseodymium oxalate, $Pr_2(C_2O_4)_3.10H_2O$, may be obtained by double decomposition as a green, crystalline precipitate. For its solubility in water and acids, see p. 273.

Praseodymium salts of organic acids. The following salts have been described:—

Praseodymium *acetate*,[2] *propionate*,[2] *malonate*,[10] *citrate*,[5] *succinate*,[3, 4] *sebacate*,[7] *glycollate*,[12] *cacodylate*,[7] *dimethylphosphate*,[9] *phenoxyacetate*,[6] *benzenesulphonate*,[11] *m-nitrobenzenesulphonate*,[11] *m-chlorobenzenesulphonate*,[11] 6 : 3 : 1-*chloronitrobenzenesulphonate*,[11] 1 : 4 : 2-*bromonitrobenzenesulphonate*,[8] *p-dichlorobenzenesulphonate*,[14] *p-dibromobenzenesulphonate*,[13] *a-naphthalenesulphonate*,[11] 1 : 5-, 1 : 6-, and 1 : 7-*nitronaphthalenesulphonate*,[11] 8-*hydroxynaphthalene*-1-*sulphonate*.[10]

Basic praseodymium acetate gives rise to a violet-blue absorption compound with iodine in a similar manner to the lanthanum compound (p. 410).[15]

NEODYMIUM.

Symbol, Nd. Atomic weight, 144·3 (O = 16).

Neodymium is one of the most abundant of the rare earth elements, being about twice as plentiful as praseodymium (p. 412). Its occurrence, history, preparation, atomic weight, and homogeneity have been already discussed in Chapters X. and XI.

Neodymium[16] is a pale yellow metal of density 6·956. It melts at 840°. Neodymium is decidedly paramagnetic, the magnetic susceptibility at 18° being about 36×10^{-6} c.g.s. units per gram.[17]

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[1] R. J. Meyer, *Zeitsch. anorg. Chem.*, 1904, **41**, 97 ; see p. 271.

[2] Von Schéele, *Zeitsch. anorg. Chem.*, 1898, **17**, 310 ; **18**, 352.

[3] Behrens, *Arch. Néerland.*, 1901, [ii.], **6**, 67.

[4] R. J. Meyer, *Zeitsch. anorg. Chem.*, 1902, **33**, 113.

[5] Baskerville and Turrentine, *J. Amer. Chem. Soc.*, 1904, **26**, 46.

[6] Pratt and James, *ibid.*, 1911, **33**, 1330.

[7] Whittemore and James, *ibid.*, 1913, **35**, 127.

[8] Katz and James, *ibid.*, 1913, **35**, 872.

[9] Morgan and James, *ibid.*, 1914, **36**, 10.

[10] Erdmann and Wirth, *Annalen*, 1908, **361**, 190.

[11] Holmberg, *Zeitsch. anorg. Chem.*, 1907, **53**, 83.

[12] Jantsch and Grünkraut, *ibid.*, 1913, **79**, 305.

[13] Armstrong and Rodd, *Proc. Roy. Soc.*, 1912, **A**, **87**, 204.

[14] Rodd, *ibid.*, 1913, **A**, **89**, 292.

[15] Orloff, *Chem. Zeit.*, 1907, **31**, 45.

[16] Muthmann, Hofer, and Weiss, *Annalen*, 1902, **320**, 231; Muthmann and Weiss, *ibid.*, 1904, **331**, 1; Muthmann and Scheidmandel, *ibid.*, 1907, **355**, 116. See pp. 229-230.

[17] Owen, *Ann. Physik*, 1912, [iv.], **37**, 657.

COMPOUNDS OF NEODYMIUM.

The salts of neodymium are rose-red or reddish-violet in colour, and the absorption spectra of their aqueous solutions show characteristic absorption bands. The following equivalent conductivity determinations (λ), effected at 25°, show that the salts are derived from a fairly strong triacid base (v = dilution in litres per gram equivalent) :—[1]

$NdCl_3$	$v=$	29·28	58·56	117·12	234·24	468·48	936·96
	$\lambda=$	103·0	110·9	118·85	124·1	128·7	133·4
$Nd_2(SO_4)_3$	$v=$	33·47	66·94	133·88	267·76	535·52	1071·04
	$\lambda=$	40·61	48·15	47·12(?)	62·23	80·21	95·95
$Nd(C_2H_3O_2)_3$	$v=$	33·81	67·62	135·24	270·48	540·96	1081·92
	$\lambda=$	42·43	50·28	58·55	67·66	76·81	86·89

Thermochemistry of Neodymium.—The following results have been recorded :—[2]

$2[Nd]+3(O)=[Nd_2O_3]$ . . . . +435·1 Cals.
$2[Nd]+3[S]=[Nd_2S_3]$ . . . . +285·9 „
$[Nd]+3(Cl)=[NdCl_3]$ . . +249·5 „
$[Nd]+3[I]=[NdI_3]$ . . . . +157·7 „
$2[Nd]+3[S]+6(O_2)=[Nd_2(SO_4)_3]$ . . +928·2 „
$2[Nd]+3[S]+6(O_2)+8[H_2O]=[Nd_2(SO_4)_3 8H_2O]$. +946·8 „
$[NdCl_3]+Aq.=NdCl_3aq.$ . . . . + 35·4 „
$[NdCl_3.6H_2O]+Aq.=NdCl_3aq.$ . . . . + 7·6 „
$[NdI_3]+Aq.=NdI_3aq.$ . . . . + 48·9 „
$[Nd_2(SO_4)_3]+Aq=Nd_2(SO_4)_3aq.$ . . . + 36·5 „
$[Nd_2(SO_4)_3.5H_2O]+Aq.=Nd_2(SO_4)_3aq.$ . . . + 8·3 „
$[Nd_2(SO_4)_3.8H_2O]+Aq.=Nd_2(SO_4)_3aq.$ . . . + 6·7 „
$[NdCl_3]+\text{alcohol}=NdCl_3$ in alc. soln. . + 21·5 „
$[Nd_2O_3]+6HClaq.=2NdCl_3aq.+3H_2O$. +105·5 „
$[Nd_2O_3]+6HIaq=2NdI_3aq.+3H_2O$. +106·1 „
$[Nd_2O_3]+3[H_2SO_4]=Nd_2(SO_4)_3]+3[H_2O]$. +125·1 „
$[Nd_2O_3]+3H_2SO_4aq.=Nd_2(SO_4)_3aq.+3H_2O$. +106·4 „

NEODYMIUM AND HYDROGEN.

Neodymium hydride, NdH_2, has been already described (p. 251).

NEODYMIUM AND THE FLUORINE GROUP.

Neodymium fluoride, NdF_3, from aqueous neodymium sulphate and hydrofluoric acid, is deposited on warming as a pale lilac-coloured crystalline powder, insoluble in water.[3]

Neodymium chloride,[4] $NdCl_3$.—For the preparation and properties of the anhydrous salt, see p. 252. It is a hygroscopic, rose-coloured, crystalline mass of density 4·134 at 25° (Baxter and Chapin).

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[1] Aufrecht, *Inaugural Dissertation* (Berlin, 1904).

[2] Matignon, *Compt. rend.*, 1906, **142**, 276; *Ann. Chim. Phys.*, 1906, [viii.], **8**, 243; 1907, [viii.], **10**, 104; Muthmann and Weiss, *Annalen*, 1904, **331**, 1 (2Nd+3O).

[3] Popovici, *Ber.*, 1908, **41**, 634.

[4] Matignon, *Compt. rend.*, 1901, **133**, 289; 1905, **140**, 1637; *Ann. Chim. Phys.*, 1906, [viii.], **8**, 243; Bourion, *ibid.*, 1910, [viii.], **21**, 49; *cf.* R. J. Meyer and Koss, *Ber.*, 1902, **35**, 2622.

From aqueous solution the hexahydrate, $NdCl_3.6H_2O$, crystallises out in rose-coloured, monoclinic crystals of density 2·282 at 16·5°. The hexahydrate melts at 124°. One hundred parts of water dissolve 98·7 parts at 13°, 140·0 parts at 100° of the anhydrous chloride, the solution being in equilibrium with the hexahydrate. The concentrated aqueous solution dissolves neodymium oxalate on warming, and a *neodymium oxalochloride* crystallises out when the solution is cooled.

The monohydrate, $NdCl_3.H_2O$, is also known (p. 254).

The anhydrous chloride forms the following compounds with *ammonia*, the dissociation temperature being given with each formula:—[1]

$NdCl_3.NH_3$	360° C.	$NdCl_3.8NH_3$	79° C.
$NdCl_3.2NH_3$	255°	$NdCl_3.11NH_3$	26°
$NdCl_3.4NH_3$	157°	$NdCl_3.12NH_3$	-10°
$NdCl_3.5NH_3$	117°		

Neodymium oxychloride, NdOCl, has been prepared (p. 255).

Neodymium bromide, $NdBr_3$, resembles the chloride. See p. 255.

Neodymium iodide, NdI_3, also resembles the chloride. See p. 255.

Neodymium bromate, $Nd(BrO_3)_3.9H_2O$, forms pink hexagonal prisms. At 100° the dihydrate, $Nd(BrO_3)_3.2H_2O$, and at 150° the anhydrous salt is obtained; at higher temperatures decomposition takes place. See p. 256.

Neodymium and the Oxygen Group.

Neodymium sesquioxide, or neodymia, Nd_2O_3, may be prepared by igniting the hydroxide, carbonate, nitrate, oxalate, etc. The oxide obtained by igniting the oxalate strongly has a pure sky-blue colour. It dissolves readily in acids.

As regards the existence of higher oxides of neodymium, the evidence is conflicting. Auer von Welsbach, Jones, and R. J. Meyer and Koss deny that a higher oxide may be prepared in the dry way, but Marc maintains that neodymia may be peroxidised in the presence of cerium and praseodymium. Waegner also affirms the existence of a higher oxide, Nd_4O_7, and even describes its reflection spectrum, but Joye and Garnier have shown that this spectrum is due to a hydrated oxide, $Nd_2O_3.H_2O$. Brauner states (without any details) that the oxides Nd_2O_4 and Nd_2O_5 both exist. By the latter Brauner presumably means a hydrated peroxide, $Nd_2O_5\,xH_2O$ or $(OH)_2Nd^{III}.O.OH$, corresponding to the known lanthanum and praseodymium peroxides. The same authority also mentions the existence of an acetate of the constitution $(CH_3.CO)_2Nd^{III}.O.O.O.Nd^{III}(OH)(CO.CH_3) + H_2O$, analogous to the praseodymium compound.[2]

Neodymium hydroxide, $Nd(OH)_3$, is obtained as a blue precipitate when an alkali hydroxide is added in excess to a solution of a neodymium salt. When dried at 300° it leaves the hydrate $2Nd_2O_3.3H_2O$; this, when heated to 525°, is converted into the hydrate $Nd_2O_3.H_2O$; and the latter at a bright red heat is converted into neodymia.[3]

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[1] Matignon and Trannoy, *Compt. rend.*, 1906, **142**, 1042.

[2] Jones, *Amer. Chem. J.*, 1898, **20**, 345; Meyer and Koss, *Ber.*, 1902, **35**, 3740; Marc, *Ber.*, 1902, **35**, 2370; Waegner, *Zeitsch. anorg. Chem.*, 1904, **42**, 118; Joye and Garnier, *Compt. rend.*, 1912, **154**, 510; Joye, *Arch. Sci. phys. nat.*, 1913, [iv.], **36**, 41; Brauner, *Proc. Chem. Soc.*, 1898, **14**, 72; 1901, **17**, 66; *Zeitsch. anorg. Chem.*, 1902, **32**, 1.

[3] Joye and Garnier, *Compt. rend.*, 1912, **154**, 510; Joye, *Arch. Sci. phys. nat.*, 1913, [iv.], **36**, 41.

Neodymium sulphide, Nd_2S_3, the preparation and properties of which have been described (p. 259), is an olive-green powder of density 5·179 at 11° (Muthmann and Stützel).

Neodymium sulphate, $Nd_2(SO_4)_3$. — For preparation and general properties, see p. 260. The only hydrate known[1] is the monoclinic[2] octahydrate, $Nd_2(SO_4)_3.8H_2O$, the solubility of which, in grams of anhydrous sulphate per 100 grams of water, is as follows :—[3]

Temp. °C.	0°	16°	30°	50°	80°	100°
Grams of $Nd_2(SO_4)_3$ . .	9·5	7·1	5·1	3·6	2·7	2·25

For *acid* and *basic* sulphates, $Nd(HSO_4)_3$ and $Nd_2O_3.SO_3$ respectively, see p. 263. *Neodymium cæsium sulphate*, $Nd_2(SO_4)_3.Cs_2SO_4.3H_2O$, forms lavender-blue crystals.[4]

Neodymium molybdate, $Nd_2(MoO_4)_3$.—See p. 265.

Neodymium tungstate, $Nd_2(WO_4)_3$, and complex tungstates have been mentioned (p. 265).

Neodymium silicotungstate, $Nd_4(W_{12}SiO_{40})_3$.—See p. 266.

Neodymium uranate, $Nd_2(U_3O_{10})_3.18H_2O$, is obtained as a yellow, crystalline solid by heating neodymium hydroxide with aqueous uranyl acetate.[5]

NEODYMIUM AND THE NITROGEN GROUP.

Neodymium nitride, NdN, has been described (p. 267).

Neodymium nitrate, $Nd(NO_3)_3.6H_2O$.—A saturated solution of this salt in water at 25° contains 152·9 grams of anhydrous nitrate per 100 grams of water.[6] Neodymium nitrate is isodimorphous with bismuth nitrate (see p. 234). The double salts $Nd(NO_3)_3.2(NH_4)NO_3.4H_2O$,[7] $Nd(NO_3)_3.2RbNO_3.4H_2O$,[8] and the double salts of the type $2Nd(NO_3)_3.3M(NO_3)_2.24H_2O$ are known (see p. 268).

NEODYMIUM AND THE CARBON GROUP.

Neodymium carbide, NdC_2, has been described (p. 270).

Neodymium carbonate, $Nd_2(CO_3)_3.xH_2O$, has not been analysed. The following double salts are known :—[9]

$Nd_2(CO_3)_3.K_2CO_3.12H_2O$ $2Nd_2(CO_3)_3.3Na_2CO_3.22H_2O$
$Nd_2(CO_3)_3.(NH_4)_2CO_3.4H_2O$

Neodymium ethylsulphate, $Nd(C_2H_5.SO_4)_3.9H_2O$, has been described (p. 278).

Neodymium acetylacetonate, $Nd(CH_3.CO.CH.CO.CH_3)_3$, has also been described (p. 279).

Neodymium oxalate, $Nd_2(C_2O_4)_3.10H_2O$, is obtained by double decomposition as a pale rose-red crystalline powder. For its solubility in water and

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[1] Matignon (*Ann. Chim. Phys.*, 1907, [viii.], **10**, 110) mentions the existence of a pentahydrate, $Nd_2(SO_4)_3.5H_2O$, but does not describe its preparation.

[2] Kraus, *Zeitsch. Kryst. Min.*, 1901, **34**, 307 ; Dufet, *Chem. Zentr.*, 1902, i. 452.

[3] Muthmann and Rölig, *Ber.*, 1898, **31**, 1718.

[4] Baskerville and Holland, *J. Amer. Chem. Soc.*, 1904, **26**, 71.

[5] Orloff, *Chem. Zeit.*, 1907, **31**, 1119.

[6] James and Robinson, *J. Amer. Chem. Soc.*, 1913, **35**, 754.

[7] Auer von Welsbach, *Monatsh.*, 1885, **6**, 477.

[8] Jantsch and Wigdorow, *Zeitsch. anorg. Chem.*, 1911, **69**, 221.

[9] R. J. Meyer, *Zeitsch. anorg. Chem.*, 1904, **41**, 97 ; see p. 271.

acids, see p. 273. According to James and Robinson,[1] the only stable hydrate in contact with water or aqueous neodymium nitrate at 25° has the composition $Nd_2(C_2O_4)_3.11H_2O$. The oxalate dissolves perceptibly in aqueous neodymium nitrate, and under certain conditions *neodymium oxalonitrate* $Nd_2(C_2O_4)_3.4Nd(NO_3)_3.xH_2O$ or perhaps $Nd_2(C_2O_4)_3.5Nd(NO_3)_3.xH_2O$, is produced. The solubility curve for a temperature of 25° is shown in fig. 40. The oxalate also dissolves in an aqueous solution of the chloride, and a *neodymium oxalochloride* exists.

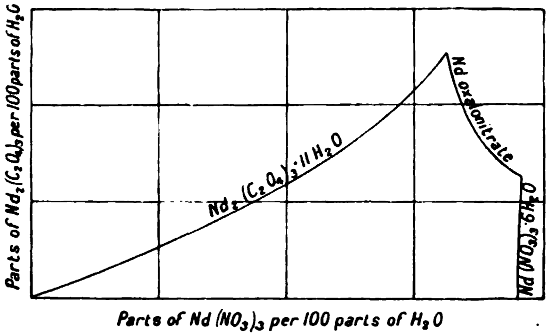

FIG. 40.—The system $Nd_2(C_2O_4)_3$—$Nd(NO_3)_3$—H_2O at 25°. Solubility diagram.

Neodymium salts of organic acids.—The following salts have been described:—

Neodymium *acetate, malonate,*[7] *sebacate,*[4] *glycollate,*[9] *cacodylate,*[4] *dimethylphosphate,*[6] *methyl-, ethyl-, propyl-,* and *isobutyl-sulphonates,*[3] *methanetrisulphonate,*[3] *ethanedisulphonate,*[3] *quinate,*[3] *anisate,*[3] *oxanilate,*[3] *phenoxyacetate,*[2] *m-nitrobenzenesulphonate,*[8] *p-dibromobenzenesulphonate,*[10] *p-dichlorobenzenesulphonate,*[11] 1 : 4 : *2-bromonitrobenzenesulphonate,*[5] 1 : 3 : *4-metaxylenesulphonate,*[3] *m-sulphobenzoate,*[3] *camphorsulphonate,*[3] *8-hydroxynaphthalene-1-sulphonate.*[7]

SAMARIUM.

Symbol, Sm.[12] Atomic weight, 150·4 (O = 16).

Samarium is one of the less common of the rare earth elements, being on the one hand much less abundant than the other elements of the cerium group, and on the other hand much more abundant than europium, terbium, and thulium. It is about as plentiful as gadolinium.

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[1] James and Robinson, *J. Amer. Chem. Soc.*, 1913, **35**, 754.

[2] Pratt and James, *J. Amer. Chem. Soc.*, 1911, **33**, 1330.

[3] James, Hoben, and Robinson, *ibid.*, 1912, **34**, 276.

[4] Whittemore and James, *ibid.*, 1913, **35**, 127.

[5] Katz and James, *ibid.*, 1913, **35**, 872.

[6] Morgan and James, *ibid.*, 1914, **36**, 10.

[7] Erdmann and Wirth, *Annalen*, 1908, **361**, 190.

[8] Holmberg, *Zeitsch. anorg. Chem.*, 1907, **53**, 83.

[9] Jantsch and Grünkraut, *ibid.*, 1913, **79**, 305.

[10] Armstrong and Rodd, *Proc. Roy. Soc.*, 1912, **A**, **87**, 204.

[11] Rodd, *ibid.*, 1913, **A**, **89**, 292.

[12] Two symbols are in common use for samarium, viz., Sm and Sa. In this book the former has been adopted, since it is the symbol that was assigned to the element by its discoverer, Lecoq de Boisbaudran.

The occurrence, history, preparation, atomic weight, and homogeneity of samarium have been already discussed in Chapters X. and XI.

Another method for the separation of samarium from lanthanum, praseodymium, and neodymium may conveniently be mentioned here; its theoretical value has been pointed out by Matignon and Cazes,[1] but its practical value does not appear to have been determined. The mixed oxides are converted into the mixed anhydrous chlorides by the method of Bourion or some other suitable process (p. 252), and heated to redness in a stream of dry hydrogen. The samarium is thus converted into the lower chloride $SmCl_2$, which may be isolated from the mixture by extracting the other chlorides with alcohol. If, on the other hand, the mixed chlorides are dissolved in a large quantity of water, about one-third of the samarium separates as hydroxide and the washed precipitate may be freed from small quantities of oxychlorides by dissolving it in cold, dilute hydrochloric acid, in which the oxychlorides are insoluble.

Samarium[2] is a yellow metal of density 7·7–7·8. It is as hard as steel and melts at 1300°–1400°. The metal quickly tarnishes in the air.

COMPOUNDS OF SAMARIUM.

The majority of the known compounds of samarium are salts derived from the basic oxide Sm_2O_3. They are pale yellow in colour and the absorption spectra of their solutions exhibit characteristic bands in the blue and violet. Two compounds of the type SmX_2, however, are known, viz., the chloride and iodide.

The equivalent conductivities (λ) of samarium chloride and sulphate solutions at 25° C. indicate that the salts are derived from a fairly strong triacid base (v = litres per gram-equivalent):—[3]

$SmCl_3$	$v =$	32·59	65·18	130·36	260·72	521·44	1042·9
	$\lambda =$	107·2	112·5	120·8	126·1	131·3	135·9
$Sm_2(SO_4)_3$	$v =$	31·35	62·70	125·40	250·80	501·60	1003·2
	$\lambda =$	31·17	43·49	51·59	61·39	72·76	89·24

The compounds of samarium have been described mainly by Cleve, whose samaria was contaminated with a little europia.[4]

Thermochemistry of Samarium.—The following results have been obtained:—[5]

$[Sm_2O_3] + 6HClaq. = 2SmCl_3aq. + 3H_2O$ . . . $+ 94·63$ Cals.
$[Sm_2O_3] + 6(HCl) = 2[SmCl_3] + 3[H_2O]$ . . . $+128·4$ „
$[Sm_2O_3] + 3[H_2SO_4] = [Sm_2(SO_4)_3] + 3[H_2O]$ . . $+113·8$ „
$[SmCl_3] + Aq. = SmCl_3aq.$ . . . . . $+ 37·4$ „
$[Sm_2(SO_4)_3] + Aq. = Sm_2(SO_4)_3aq.$ . . . . $+ 38·8$ „

and

$[SmCl_3,NH_3] = +20·7$ Cals.,
$[SmCl_3,2NH_3] = +37·1$ „
$[SmCl_3,3NH_3] = +52·2$ „
$[SmCl_3,4NH_3] = +65·9$ „
$[SmCl_3,5NH_3] = + 78·0$ Cals.
$[SmCl_3,8NH_3] = +111·6$ „
$[SmCl_3,9·5NH_3] = +126·6$ „
$[SmCl_3,11·5NH_3] = +145·0$ „

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[1] Matignon and Cazes, *Ann. Chim. Phys.*, 1906, [viii.], **10**, 424.

[2] Muthmann and Weiss, *Annalen*, 1904, **331**, 1; see pp. 229–230.

[3] Aufrecht, *Inaugural Dissertation* (Berlin, 1904); Heydweiller, *Zeitsch. physikal. Chem.*, 1915, **89**, 281.

[4] Cleve, *Chem. News*, 1886, **53**, 30, etc.; see also Cleve, *Compt. rend.*, 1883, **97**, 94; *Bull. Soc. chim.*, 1885, [ii.], **43**, 162; *Chem. News*, 1883, **48**, 39, 74; 1885, **51**, 145; *Trans. Chem. Soc.*, 1883, **43**, 362; *Oefvers. Svenska Vet.-Akad. Forhandl.*, 1883, **40**, No. 7.

[5] Matignon, *Compt. rend.*, 1906, **142**, 276; *Ann. Chim. Phys.*, 1906, [viii.], **8**, 402.

SAMARIUM AND THE FLUORINE GROUP.

Samarium fluoride, $SmF_3.H_2O$, is obtained by double decomposition (Cleve).

Samarium chloride,[1] $SmCl_3$, is a very pale yellow, hygroscopic, crystalline solid which darkens when heated and melts to a brown liquid. For its preparation and properties, see p. 252.

From aqueous solution the hexahydrate, $SmCl_3.6H_2O$, separates in large, yellow tablets of density 2·383 (Cleve). The monohydrate, $SmCl_3.H_2O$, is also known (p. 254). *Samarium aurichloride*, $SmCl_3.AuCl_3.10H_2O$, crystallises in orange prisms; the *chloroplatinate* has the formula $2(SmCl_3.PtCl_4)21H_2O$.

Anhydrous samarium chloride absorbs ammonia. The following compounds are known, their dissociation pressures being 760 mm. at the temperatures given opposite the formulæ:—[2]

$SmCl_3.NH_3$	375° C.	$SmCl_3.5NH_3$	105° C.
$SmCl_3.2NH_3$	240°	$SmCl_3.8NH_3$	76°
$SmCl_3.3NH_3$	200°	$SmCl_3.9{\cdot}5NH_3$	40°
$SmCl_3.4NH_3$	155°	$SmCl_3.11{\cdot}5NH_3$	15°

Curiously enough, a compound with $6NH_3$ does not appear to exist.

Samarium oxychloride, $SmOCL$, is known (p. 255).

Samarium subchloride, $SmCl_2$, is prepared by strongly heating samarium chloride in a current of pure, dry hydrogen or ammonia. It is a dark brown, crystalline solid of density 3·69 at 22°, insoluble in alcohol, pyridine, carbon disulphide, chloroform, or benzene. It dissolves readily in water, giving a dark reddish-brown solution. The colour slowly disappears, hydrogen being evolved and samarium hydroxide precipitated. The rapidity with which the colour disappears is greatly enhanced by shaking the solution in air:—[3]

$$6SmCl_2 + 6H_2O = 4SmCl_3 + 2Sm(OH)_3 + 3H_2$$
$$12SmCl_2 + 6H_2O + 3O_2 = 8SmCl_3 + 4Sm(OH)_3$$

Samarium bromide, $SmBr_3$.—See p. 255. The hexahydrate, $SmBr_3.6H_2O$, separates from aqueous solution in prismatic crystals of density 2·97, and forms an *auribromide*, $SmBr_3.AuBr_3.10H_2O$ (Cleve).

Samarium iodide, SmI_3, has been prepared by Matignon (p. 255).

Samarium subiodide, SmI_2, has been prepared by reducing the heated tri-iodide in a current of dry hydrogen.[3]

Samarium bromate, $Sm(BrO_3)_3.9H_2O$. — See p. 256. This salt crystallises in yellow, hexagonal prisms, is converted into the dihydrate, $Sm(BrO_3)_3.2H_2O$, at 100°, the anhydrous salt at 150°, and decomposes at higher temperatures.

Samarium iodate, $Sm(IO_3)_3.6H_2O$, forms a voluminous, white, amorphous precipitate (Cleve).

Samarium periodate, $SmIO_5.4H_2O$, may be obtained as an amorphous precipitate which becomes crystalline on standing (Cleve).

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[1] Matignon, *Compt. rend.*, 1902, **134**, 1308; *Ann. Chim. Phys.*, 1906, [viii.], **8**, 403; Bourion, *ibid.*, 1910, [viii.], **21**, 49.

[2] Matignon and Traunoy, *Compt. rend.*, 1905, **140**, 141; *Ann. Chim. Phys.*, 1906, [viii.], **8**, 407.

[3] Matignon and Cazes, *Compt. rend.*, 1906, **142**, 83: *Ann. Chim. Phys.*, 1906, [viii.], **8**, 417.

SAMARIUM AND THE OXYGEN GROUP.

Samarium sesquioxide, or **samaria,** Sm_2O_3, may be prepared by the ignition of the hydroxide, carbonate, nitrate, oxalate, etc. It is an almost white powder with a faint yellow tinge, and its density is 8·347. It dissolves readily in acids. The corresponding *hydroxide* is a gelatinous precipitate that absorbs carbon dioxide from the air. The addition of ammoniacal hydrogen peroxide to a solution of a samarium salt causes the precipitation of a hydrated *peroxide*, $Sm_4O_9.xH_2O$ or probably $Sm_2O_5xH_2O$.[1]

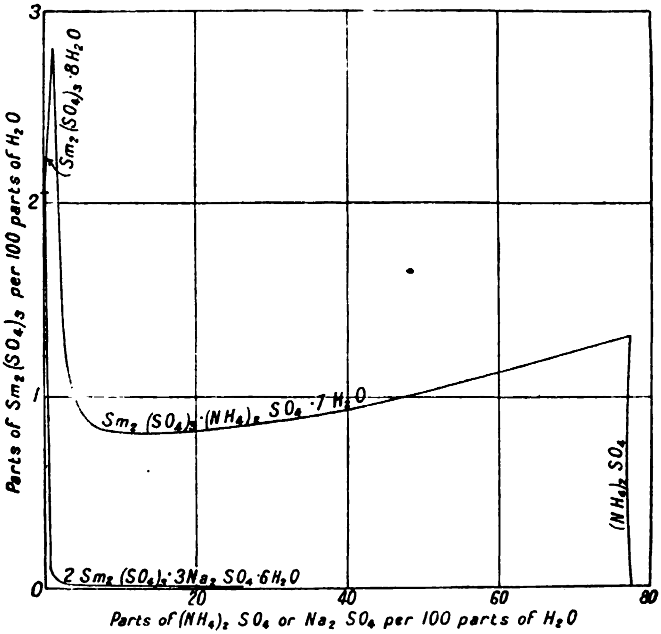

FIG. 41.—The systems $Sm_2(SO_4)_3$—Na_2SO_4—H_2O and $Sm_2(SO_4)_3$—$(NH_4)_2SO_4$—H_2O at 25°. Solubility diagrams.

Samarium sulphide, Sm_2S_3, is a yellow solid of density 3·70.[2]

Samarium sulphite, $Sm_2(SO_3)_3.3H_2O$, has been obtained by Cleve as a white, amorphous powder (see p. 260).

Samarium sulphate, $Sm_2(SO_4)_3$.—For preparation and general properties, see p. 260. The monoclinic[3] octahydrate, $Sm_2(SO_4)_3.8H_2O$, is the only hydrate known. The *acid sulphate*, $Sm(HSO_4)_3$, and the *basic sulphate*, $Sm_2O_3.SO_3$, are known (p. 263). The following double sulphates have been described by Cleve:—

$2Sm_2(SO_4)_3.9K_2SO_4.3H_2O$
$Sm_2(SO_4)_3.Na_2SO_4.2H_2O$
$Sm_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$

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[1] Cleve, *Bull. Soc. chim.*, 1885, [ii.], 43, 53.

[2] Erdmann and Wirth, *Annalen*, 1908, 361, 190; *cf.* Moissan, *Compt. rend.*, 1900, 131, 924. See p. 259.

[3] Fock, *Zeitsch. Kryst. Min.*, 1900, 32, 250; Dufet, *Chem. Zentr.*, 1902, i. 452. See p. 261.

According to Keyes and James,[1] the only double sodium and ammonium sulphates that exist at 25° have the formulæ $2Sm_2(SO_4)_3.3Na_2SO_4.6H_2O$ and $Sm_2(SO_4)_3.(NH_4)_2SO_4.7H_2O$. The results of their solubility measurements are shown graphically in fig. 41.

Samarium selenite.—Sodium selenite gives with samarium sulphate a precipitate of a basic selenite. *Acid samarium selenite*, $Sm_2(SeO_3)_3.H_2SeO_3.4H_2O$, is precipitated when aqueous solutions of samarium acetate and selenious acid are mixed (Cleve).

Samarium selenate, $Sm_2(SeO_4)_3$.—The octahydrate, $Sm_2(SeO_4)_3.8H_2O$, crystallises from aqueous solution at ordinary temperatures. Below 10°, the dodecahydrate, $Sm_2(SeO_4)_3.12H_2O$, separates in shining, prismatic crystals. The following double salts are readily soluble in water (Cleve):—

$Sm_2(SeO_4)_3.K_2SeO_4.6H_2O$ $Sm_2(SeO_4)_3.(NH_4)_2SeO_4.6H_2O$

Samarium chromate.—Potassium dichromate gives no precipitate with samarium nitrate, but potassium chromate gives a yellow, crystalline precipitate of *samarium potassium chromate*, $Sm_2(CrO_4)_3.K_2CrO_4.6H_2O$ (Cleve).

Samarium molybdate, $Sm_2(MoO_4)_3$, forms small, lustrous crystals of density approximately 5·95. The *double salt*, $SmNa(MoO_4)_2$, has also been made (Cleve).

Samarium tungstate.—The *metatungstate*, $Sm_2(W_4O_{13})_3.35H_2O$, forms readily soluble, topaz-yellow crystals of density 3·994. A *sodium samarium tungstate* is also known (see p. 265).

Samarium silicotungstate, $Sm_4(W_{12}SiO_{40})_3$.—See p. 266.

SAMARIUM AND THE NITROGEN GROUP.

Samarium nitride.—See p. 267.

Samarium nitrate, $Sm(NO_3)_3.6H_2O$, crystallises in extremely soluble, yellow needles, melting at 78°–79° (Cleve). The double salts are described on p. 268.[2]

Samarium orthophosphate, $SmPO_4$, is obtained in the crystalline form by fusing sodium metaphosphate with samaria, allowing to cool, and extracting the mass with water. It is a crystalline powder of density 5·83 at 17·5°, insoluble in water (Cleve).

Samarium hydrogen pyrophosphate, $2SmHP_2O_7.7H_2O$, may be prepared by adding samarium hydroxide to aqueous pyrophosphoric acid (Cleve). The compound $Sm_2O_3.5P_2O_5$ is also known.

Samarium vanadates.—Two hydrates of the salt $Sm_2O_3.5V_2O_5$ have been prepared by Cleve, namely, red crystals of $Sm_2O_3.5V_2O_5.28H_2O$ and yellow crystals of $Sm_2O_3.5V_2O_5.24H_2O$.

SAMARIUM AND THE CARBON GROUP.

Samarium carbide, SmC_2, has been described (p. 270).

Samarium carbonate, $Sm_2(CO_3)_3.3H_2O$, loses $1H_2O$ at 100°. The following double salts are known (Cleve):—

$Sm_2(CO_3)_3.K_2CO_3.12H_2O$ $Sm_2(CO_3)_3.(NH_4)_2CO_3.4H_2O$
$Sm_2(CO_3)_3.Na_2CO_3.16H_2O$

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[1] Keyes and James, *J. Amer. Chem. Soc.*, 1914, **36**, 634.

[2] See also Demarçay, *Compt. rend.*, 1900, **130**, 1185.

Samarium platinocyanide, $2Sm(CN)_3.3Pt(CN)_2.18H_2O$, crystallises in yellow prisms having a blue reflex (*cf.* p. 272).

Samarium thiocyanate, $Sm(CNS)_3.6H_2O$, forms prismatic crystals easily soluble in water. The *double salt,* $Sm(CNS)_3.3Hg(CN)_2.12H_2O$, is also known (Cleve).

Samarium ethylsulphate, $Sm(C_2H_5.SO_4)_3.9H_2O$, has been described (p. 278).

Samarium acetylacetonate, $Sm(CH_3.CO.CH.CO.CH_3)_3$, has also been described (p. 279).

Samarium oxalate, $Sm_2(C_2O_4)_3.10H_2O$, is obtained as a yellow, crystalline precipitate by adding a solution of oxalic acid to one of a samarium salt. For its solubility in water and acids, see p. 273. When potassium oxalate is used as precipitant, *samarium potassium oxalate,* $Sm_2(C_2O_4)_3.K_2C_2O_4.5H_2O$, is obtained (Cleve).

Samarium salts of organic acids.—The following salts have been described :—

Samarium *formate,*[1] *acetate,*[1] *propionate,*[1] *thioacetate,*[3] *glycollate,*[3, 9] *succinate,*[1] *citrate,*[1] *tartrate,*[1] *malonate,*[7] *citraconate,*[3] *sebacate,*[4] *dimethylphosphate,*[6] *cacodylate,*[3, 4] *ethylglycollate,*[3] *methylsulphonate,*[3] *ethylsulphonate,*[3] *propylsulphonate,*[3] *isobutylsulphonate,*[3] *methanetrisulphonate,*[3] *ethanedisulphonate,*[3] *phenoxyacetate,*[2] *m - nitrobenzenesulphonate,*[8] *p - dibromobenzenesulphonate,*[10] 1 : 4 : 2-*bromonitrobenzenesulphonate,*[5] 1 : 3 : 4-*metaxylenesulphonate,*[3] *camphorsulphonate,*[3] and 8-*hydroxynaphthalene*-1-*sulphonate.*[7]

SAMARIUM AND BORON.

Samarium orthoborate, $SmBO_3$, is produced when samaria is dissolved in molten borax at a white heat. It crystallises in very thin micaceous scales, which may be extracted from the mass, after cooling, by careful treatment with cold, dilute hydrochloric acid (Cleve).

Samarium metaborate, $Sm(BO_2)_3$, has been described (p. 282).

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[1] Cleve, *Chem. News*, 1883, 53, 30.
[2] Pratt and James, *J. Amer. Chem. Soc.*, 1911, 33, 1330.
[3] James, Hoben, and Robinson, *ibid.*, 1912, 34, 276.
[4] Whittemore and James, *ibid.*, 1913, 35, 127.
[5] Katz and James, *ibid.*, 1913, 35, 872.
[6] Morgan and James, *ibid.*, 1914, 36, 10.
[7] Erdmann and Wirth, *Annalen*, 1908, 361, 190.
[8] Holmberg, *Zeitsch. anorg. Chem.*, 1907, 53, 83.
[9] Jantsch and Grünkraut, *ibid.*, 1913, 79, 305.
[10] Armstrong and Rodd, *Proc. Roy. Soc.*, 1912, 87, 204.

CHAPTER XIII.

THE RARE EARTH ELEMENTS (*continued*).

THE TERBIUM GROUP.

THE rare earth elements included in this group are only three in number, namely, europium, gadolinium, and terbium. Europium and terbium are rare in comparison with gadolinium, itself not one of the most abundant of the rare earth elements.

By utilising bismuth as a separating element it is possible to effect a quantitative separation of the cerium and terbium groups by the crystallisation of the double magnesium nitrates. At the same time a very good separation of europium and gadolinium is obtained. The most rapid method for eliminating terbium from gadolinium consists in fractionally crystallising the bromates. A summary of the various processes for the separation of the terbium group is given in Chapter XI.

Few compounds of europium and terbium have been described.

EUROPIUM.

Symbol, Eu. Atomic weight, 152·0 ($O = 16$).

Europium (Z_ϵ, Z_ζ, Σ, and S_δ) is one of the least abundant of the rare earth elements. Monazite sand contains about 0·002 per cent. of europia.[1] Europium has been detected spectroscopically in the chromosphere of the sun and in the stars α-Boötis and β-Geminorum.[2]

Europium compounds are pale pink in colour. Europia was isolated by Demarçay, and prepared in a state of purity by Urbain and Lacombe in 1904. Subsequently it has been prepared by James and Robinson.[3] The methods employed have been already described (p. 348).

Europium chloride, $EuCl_3$, has been prepared by Bourion (p. 252).

Europous chloride, $EuCl_2$, is prepared by heating the anhydrous trichloride to 400°–450° in a current of dry hydrogen. It is a colourless, amorphous solid, which dissolves in cold water, forming a neutral solution. The aqueous solution oxidises on boiling:—[4]

$$12EuCl_2 + 3O_2 + 6H_2O = 8EuCl_3 + 4Eu(OH)_3.$$

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[1] Urbain and Lacombe, *Compt. rend.*, 1904, **138**, 627.

[2] Lunt, *Proc. Roy. Soc.*, 1907, **A**, **79**, 118.

[3] Demarçay, *Compt. rend.*, 1900, **130**, 1019, 1469; 1901, **132**, 1484; Urbain and Lacombe, *ibid.*, 1903, **137**, 792; 1904, **138**, 84, 627; *J. Chim. phys.*, 1906, **4**, 31, 105; James and Robinson, *J. Amer. Chem. Soc.*, 1911, **33**, 1363. See also Stoddart and Hill, *ibid.*, 1911, **33**, 1076.

[4] Urbain and Bourion, *Compt. rend.*, 1911, **153**, 1155.

Europium sesquioxide, or **europia,** Eu_2O_3, produced by igniting the oxalate or sulphate, is a pale pink powder.

Europium sulphate, $Eu_2(SO_4)_3$, is obtained by heating the octahydrate, $Eu_2(SO_4)_3.8H_2O$, to 375°. It is completely decomposed at 1600°.[1]

Europium ethylsulphate, $Eu(C_2H_5.SO_4)_3.9H_2O$, has been described (p. 278).

Other organic salts.—The *formate*,[2] *quinate*,[2] *pyromucate*,[2] *m-nitrobenzenesulphonate*,[2] and 1 : 4 : 2-*bromonitrobenzenesulphonate*[3] have been prepared.

GADOLINIUM.

Symbol, Gd. Atomic weight, 157·3 (O = 16).

Gadolinum (Y_α and victorium) is, like samarium, neither one of the most nor one of the least abundant of the rare earth elements. It forms a colourless oxide and a series of colourless salts, which exhibit no selective absorption in the visible region of the spectrum, but show an ultraviolet absorption spectrum. Gadolinia was doubtless one of the main constituents of the "terbia" obtained by the earlier workers in the field of rare earth chemistry.

Since gadolinium was discovered by Marignac and examined by Lecoq de Boisbaudran, the isolation of pure gadolinia has been studied by Bettendorf, Benedicks, Demarçay, Marc, and by Urbain and Lacombe.[4]

The salts of gadolinium have been described mainly by Benedicks.[5]

Gadolinium fluoride, GdF_3, prepared from aqueous gadolinium sulphate and hydrofluoric acid, is a colourless, gelatinous precipitate which becomes granular when warmed.[6]

Gadolinium chloride, $GdCl_3$, is a white, hygroscopic crystalline mass (p. 252). It forms a hexahydrate, $GdCl_3.6H_2O$, of density 2·42. *Gadolinium aurichloride*, $GdCl_3.AuCl_3.10H_2O$, crystallises in yellow tables of specific gravity 2·71. *Gadolinium platinichloride*, $GdCl_2.PtCl_4.10H_2O$, forms orange-red crystals of density 2·72.

Gadolinium oxychloride, GdOCl, has been prepared (p. 255).

Gadolinium bromide, $GdBr_3$, is known (p. 256), and also the hexahydrate, $GdBr_3.6H_2O$, which crystallises in rhombic tables of density 2·84.

Gadolinium oxide, or **gadolinia,** Gd_2O_3, is a white powder of density 7·407 at 15°. It is hygroscopic, absorbs carbon dioxide, and is readily soluble in acids. The gelatinous *hydroxide*, $Gd(OH)_3$, also absorbs carbon dioxide rapidly.

Gadolinium sulphide, Gd_2S_3, is a hygroscopic, yellow solid of density 3·8. It is slowly decomposed by water, quickly by acids.[7]

Gadolinium sulphate, $Gd_2(SO_4)_3$.—The octahydrate, $Gd_2(SO_4)_3.8H_2O$, is

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[1] See Jantsch, *Compt. rend.*, 1908, **146**, 473.

[2] James and Robinson, *J. Amer. Chem. Soc.*, 1913, **35**, 754.

[3] Katz and James, *ibid.*, 1913, **35**, 872.

[4] Marignac, *Arch. Sci. phys. nat.*, 1880, [iii.], **3**, 413; *Ann. Chim. Phys.*, 1880, [v.], **20**, 535; Lecoq de Boisbaudran, *Compt. rend.*, 1890, **111**, 394; Bettendorf, *Annalen*, 1892, **270**, 376; Benedicks, *Zeitsch. anorg. Chem.*, 1900, **22**, 393; Demarçay, *Compt. rend.*, 1900, **131**, 343: Marc, *Zeitsch. anorg. Chem.*, 1904, **38**, 121; Urbain and Lacombe, *Compt. rend.*, 1903, **137**, 792; 1904, **138**, 84, 627; Urbain, *Compt. rend.*, 1904, **139**, 736; 1905, **140**, 583; *J. Chim. phys.*, 1906, **4**, 31, 105, 321.

[5] Benedicks, *loc. cit.*

[6] Popovici, *Ber.*, 1908, **41**, 634.

[7] Erdmann and Wirth, *Annalen*, 1908, **361**, 190.

the only hydrate known, and forms monoclinic crystals (p. 261). The solubility (in parts of anhydrous salt per 100 of water) is as follows :—

0°	10°	14°	25°	34·4°
3·98	3·33	2·80	2·40	2·26

The solubility in a saturated solution of sodium sulphate is such that at 25° C. the solution contains 0·6 gram of anhydrous gadolinium sulphate per litre, *gadolinium sodium sulphate*, $Gd_2(SO_4)_3.Na_2SO_4.2H_2O$, being the stable solid phase.[1] The corresponding potassium salt is also known (Benedicks).

Gadolinium acid selenite, $Gd_2(SeO_3)_3.H_2SeO_3.6H_2O$, obtained from gadolinium acetate and selenic acid, is an amorphous precipitate which becomes crystalline on standing.

Gadolinium selenate, $Gd_2(SeO_4)_3$, and the octa- and deca-hydrates are known (p. 264). The octahydrate separates from aqueous solution at 100°, the decahydrate at the ordinary temperature. The double salt, *gadolinium potassium selenate*, $Gd_2(SeO_4)_3.3K_2SeO_4.4H_2O$, is also known.

Gadolinium silicotungstate, $Gd_4(W_{12}SiO_{40})_3$. See p. 266.

Gadolinium nitrate, $Gd(NO_3)_3.6H_2O$, separates from aqueous solution in large, triclinic crystals of density 2·33, and melts at 91°.[2] From concentrated nitric acid the pentahydrate, $Gd(NO_3)_3.5H_2O$, crystallises out in prisms of density 2·41. Of all the rare earth nitrates, this salt is the least soluble in nitric acid. It melts at 92°.

Gadolinium ammonium nitrate, $Gd(NO_3)_3.2(NH_4)NO_3.xH_2O$, is an extremely soluble, deliquescent salt. For other double nitrates, see p. 269.

Gadolinium vanadate, $GdV_5O_{14}.13H_2O$, crystallises in yellow, triclinic prisms of density 2·66.

Gadolinium carbonate, $Gd_2(CO_3)_3.13H_2O$(?), is obtained by passing a current of carbon dioxide for a long time through an aqueous suspension of gadolinium hydroxide. The *basic carbonate*, $Gd(OH)CO_3.H_2O$, is also known.

Gadolinium platinocyanide, $2Gd(CN)_3.3Pt(CN)_2.21H_2O$, forms rhombic crystals isomorphous with the yttrium salt.

Gadolinium oxalate, $Gd_2(C_2O_4)_3.10H_2O$, is obtained by precipitation as a white, microcrystalline powder. It separates from concentrated nitric acid in monoclinic crystals. For its solubility in sulphuric acid, see p. 273. The decahydrate loses $6H_2O$ at 100°.

Gadolinium ethylsulphate, $Gd(C_2H_5.SO_4)_3.9H_2O$. See p. 278.

Gadolinium acetate, $Gd(C_2H_3O_2)_3.4H_2O$, forms soluble triclinic crystals of density 1·611. The *propionate*,[3] *glycollate*,[5] *malonate*,[6] *dimethylphosphate*,[10] 1 : 4 : 2 *bromonitrobenzenesulphonate*,[9] *m-nitrobenzenesulphonate*,[4] *p-dichlorobenzenesulphonate*,[8] and *p-dibromobenzenesulphonate* [7, 8] have also been described.

Gadolinium metaborate, $Gd(BO_2)_3$, has been described (p. 282).

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[1] Bissel and James, *J. Amer. Chem. Soc.*, 1916, **38**, 873.

[2] Demarçay, *loc. cit.*; von Lang and Haitinger, *Annalen*, 1907, **351**, 450. See p. 268.

[3] Benedicks, *Zeitsch. anorg. Chem.*, 1900, **22**, 393.

[4] Holmberg, *ibid.*, 1907, **53**, 83.

[5] Jantsch and Grünkraut, *ibid.*, 1913, **79**, 305.

[6] Erdmann and Wirth, *Annalen*, 1908, **361**, 190.

[7] Armstrong and Rodd, *Proc. Roy. Soc.*, 1912, **A**, **87**, 204.

[8] Rodd, *ibid.*, 1913, **A**, **89**, 292.

[9] Katz and James, *J. Amer. Chem. Soc.*, 1913, **35**, 872.

[10] Morgan and James, *ibid.*, 1914, **36**, 10.

TERBIUM.

Symbol, Tb. Atomic weight, 159·2 (O=16).

Terbium (Z_β, Z_δ, Γ, ionium, and incognitum), notwithstanding the fact that its existence was foretold by Mosander in 1843, is one of the least abundant of the rare earth elements. Its curious history, and also the processes by which pure terbia may be isolated, have been already given in Chapters X. and XI. The preparation of pure terbia was first accomplished by Urbain.[1]

Terbia is white and the salts of terbium are colourless. The most interesting compound of terbium is the peroxide. Only a few terbium compounds have been described.[2]

Terbium chloride, $TbCl_3$, prepared by Bourion (p. 252), crystallises in colourless needles which melt to a colourless liquid. The hexahydrate, $TbCl_3.6H_2O$, forms hygroscopic, colourless, prismatic crystals.

Terbium bromide, $TbBr_3$.—See p. 255.

Terbium sesquioxide, or **terbia,** Tb_2O_3, is a white solid obtained by heating the peroxide in hydrogen.

Terbium peroxide, Tb_4O_7, is produced by calcining the terbium salts of volatile acids in air. Prepared by the ignition of the oxalate in a muffle furnace, it is a dark brown powder, but when obtained from the sulphate at a white heat it is black. The strongly calcined peroxide is not attacked by cold mineral acids and is only slowly acted upon by hot, dilute acids.

Owing to the ready formation of this peroxide and its intense colouring power, the presence of even traces of terbia in europia, gadolinia, dysprosia, and yttria is easily detected.

Terbium may be estimated quantitatively by igniting the oxalate and weighing the residual peroxide.

Terbium sulphate, $Tb_2(SO_4)_3$, is prepared by dehydrating the octahydrate, $Tb_2(SO_4)_3.8H_2O$, at 360°.

Terbium silicotungstate, $Tb_4(W_{12}SiO_{40})_3$.—See p. 266.

Terbium nitrate, $Tb(NO_3)_3.6H_2O$, forms colourless, monoclinic needles, m.p. 89·3°.

The *propionate*,[3] *pyromucate*,[3] and 1 : 4 : 2-*bromonitrobenzenesulphonate*[3] have also been described.

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[1] Urbain, *Compt. rend.*, 1904, **139**, 736; 1905, **141**, 521; 1909, **149**, 37; *J. Chim. phys.*, 1906, **4**, 334. See also James and Bissel, *J. Amer. Chem. Soc.*, 1914, **36**, 2060, and *cf.* Marc, *Ber.*, 1902, **35**, 2382; Feit, *Zeitsch. anorg. Chem.*, 1905, **43**, 267; Potratz, *Chem. News*, 1905, **92**, 3.

[2] Urbain, *loc. cit.*, and *Compt. rend.*, 1906, **142**, 957; Urbain and Jantsch, *ibid.*, 1908, **146**, 127.

[3] Grant and James, *J. Amer. Chem. Soc.*, 1915, **37**, 2652.

CHAPTER XIV.

THE RARE EARTH ELEMENTS (*concluded*).

THE YTTRIUM GROUP.

THE elements of this group are dysprosium, holmium, yttrium, erbium, thulium, ytterbium, lutecium, and celtium. All are rare in comparison with yttrium itself, ytterbium being perhaps the most abundant. Erbium is much less abundant than is commonly supposed.

The compounds of the elements of this group have received little attention at the hands of chemists. Attention has been directed mainly towards the problem of separating the actual earths of the group from one another; the results, however, still leave much to be desired, and considerable work still remains to be done in connection with the yttria earths.

In the following brief account the elements are discussed in their serial order.

DYSPROSIUM.

Symbol, Dy. Atomic weight, 162·5 ($O=16$).

Dysprosium (Z_α, Z_γ, Δ, and demonium [1]) is one of the least abundant of the rare earth elements. Its salts were isolated in a pure state by Urbain in 1906. They are yellow or greenish-yellow in colour. Only a few dysprosium compounds have been described.[2]

Dysprosium chloride, $DyCl_3$, crystallises in pale yellow, pearly spangles, and melts to a colourless liquid. It has been prepared by Bourion (p. 252). The chloride forms a hexahydrate, $DyCl_3.6H_2O$.

Dysprosium oxychloride, $DyOCl$, is also known (p. 255).

Dypsrosium bromide, $DyBr_3$.—See p. 255.

Dysprosium bromate, $Dy(BrO_3)_3.9H_2O$, forms shining, pale yellow, hexagonal needles, m.p. 78°. By prolonged heating at 110°, the trihydrate, $Dy(BrO_3)_3.3H_2O$, is obtained.[3]

Dysprosium sesquioxide, or **dysprosia,** Dy_2O_3, is a white, highly paramagnetic solid (p. 256). No peroxide is known.

Dysprosium sulphate, $Dy_2(SO_4)_3$, may be obtained by dehydrating the octahydrate, $Dy_2(SO_4)_3.8H_2O$, at 360°. The latter forms brilliant yellow crystals, stable at 110°.

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[1] Rowland's element *demonium* was characterised by the spectrum line λ4000·6, which belongs to *dysprosium* (see p. 308). See Rowland, *Chem. News*, 1894, **70**, 68.

[2] Urbain, *Compt. rend.*, 1906, **142**, 785; 1908, **146**, 922; Urbain and Demenitroux, *ibid.*, 1906, **143**, 598; Urbain and Jantsch, *ibid.*, 1908, **146**, 127; Jantsch and Ohl, *Ber.*, 1911, **44**, 1274.

[3] Jantsch and Ohl, *loc. cit.*

Dysprosium selenate, $Dy_2(SeO_4)_3$, may be obtained by dehydrating the yellow, crystalline octahydrate, $Dy_2(SeO_4)_3.8H_2O$, at 200°.[1]

Dysprosium chromate, $Dy_2(CrO_4)_3.10H_2O$, obtained by double decomposition, is a greenish-yellow, microcrystalline powder. At 150° it loses $3{\cdot}5H_2O$, and above that temperature decomposition occurs. A saturated solution of the decahydrate at 25° contains 10 grams of the salt per litre.[1]

Dysprosium nitrate, $Dy(NO_3)_3.5H_2O$, melts at 88·6° and resembles the corresponding bismuth salt.

Dysprosium phosphate, $DyPO_4.5H_2O$, a gelatinous precipitate which slowly turns crystalline, is a pale yellow solid which may be dehydrated at 200°.[1]

Dysprosium carbonate, $Dy_2(CO_3)_3.4H_2O$, an insoluble powder formed by treating an aqueous suspension of dysprosium hydroxide with a current of carbon dioxide, loses $3H_2O$ at ordinary temperatures. In contact with saturated aqueous ammonium carbonate, it is slowly converted into sparingly soluble, crystalline *dysprosium ammonium carbonate,* $(NH_4)_3Dy(CO_3)_3.H_2O$, which begins to lose ammonia at 60°.[1]

Dysprosium oxalate, $Dy_2(C_2O_4)_3.10H_2O$, is precipitated as microscopic prisms, insoluble in water. One litre of normal sulphuric acid at 20° dissolves 1·893 grams of the oxalate (anhydrous). *Dysprosium potassium oxalate,* $KDy(C_2O_4)_2.3H_2O$, precipitated when solutions of dysprosium nitrate and potassium oxalate are mixed, is readily soluble in dilute acids.[1]

Dysprosium platinocyanide,[1] $2Dy(CN)_3.3Pt(CN)_2.21H_2O$, forms cinnabar-red crystals with a green reflex (*cf.* p. 272). The *formate*[1] and *acetate*[1] are also known.

HOLMIUM.[2]

Symbol, Ho. Atomic weight, 163·5 (O=16).

Holmium is one of the least abundant of the rare earth elements. The isolation of pure holmia has been a task of great difficulty. The methods that have been used are described elsewhere (p. 356). The best holmia yet obtained (1916) was extracted from the mineral euxenite by Holmberg. It contained traces of erbia and dysprosia.

Holmia, Ho_2O_3, is a pale yellow, highly paramagnetic powder. The salts of holmium are yellow with an orange tinge.[3]

YTTRIUM.

Symbol,[4] Y. Atomic weight, 88·7 (O=16).

Yttrium is the most abundant of the rare earth elements of the yttrium group. Since, however, minerals rich in this group are much less abundant than minerals rich in the cerium group, and the latter minerals are usually

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[1] Jantsch and Ohl, *loc. cit.*

[2] Sometimes called **neoholmium,** the original "holmium" being neoholmium plus dysprosium.

[3] Holmberg, *Arkiv Chem. Min. Geol.*, 1911, 4, Nos. 2 and 10; *Zeitsch. anorg. Chem.*, 1911, 71, 226.

[4] Two symbols are in use for yttrium, viz., Y and Yt. The symbol Y, used by Berzelius and by all the early workers on the rare earths, has been adopted here.

very poor in yttrium, it is doubtful whether yttrium is as abundant as any of the cerium metals, samarium excepted.

The occurrence, history, preparation, atomic weight, and homogeneity of yttrium have been already discussed in Chapters X. and XI.

Yttrium.—The metal has not yet been prepared in quantity in the massive form. One or two chemists have prepared it as a grey, metallic powder, the chemical properties of which were similar to those of cerium and lanthanum ; but they did not work with pure yttrium compounds.[1]

COMPOUNDS OF YTTRIUM.

The compounds of yttrium have been described mainly by Cleve and Höglund.[2] Those derived from colourless acids are themselves colourless and exhibit no selective absorption.

YTTRIUM AND THE FLUORINE GROUP.

Yttrium fluoride, YF_3.—See p. 252. The hemihydrate, $2YF_3.H_2O$, is obtained by double decomposition (Cleve).

Yttrium chloride,[3] YCl_3.—For the preparation and properties of the anhydrous salt, see p. 252. It is a hygroscopic, colourless, crystalline solid, perceptibly volatile at a bright red heat.

The hexahydrate, $YCl_3.6H_2O$, crystallises in colourless, monoclinic prisms and melts at 156° to 160°. The monohydrate, $YCl_3.H_2O$, is also known (p. 254).

Yttrium aurichloride, $YCl_3.2AuCl_3.16H_2O$ (Cleve), and *yttrium mercuric chloride*,[4] $YCl_3.3HgCl_2.9H_2O$, are known.

Yttrium bromide, YBr_3, crystallises from aqueous solution as the *hydrate*, $YBr_3.9H_2O$ (Cleve).

Yttrium chlorate, $Y(ClO_3)_3.9H_2O$, obtained by double decomposition between yttrium sulphate and barium chlorate, crystallises from water in colourless needles (Cleve).

Yttrium perchlorate, $Y(ClO_4)_3.9H_2O$, is a very hygroscopic salt, soluble in water and alcohol (Cleve).

Yttrium bromate, $Y(BrO_3)_3.9H_2O$, forms colourless, hexagonal prisms. At 100° the trihydrate, $Y(BrO_3)_3.3H_2O$, is produced (see p. 256).

Yttrium iodate, $Y(IO_3)_3.3H_2O$, is obtained from yttrium nitrate and iodic acid as a white precipitate (Cleve).

Yttrium per-iodate.—Two per-iodates have been prepared by Cleve, $Y_2O_3.I_2O_7.8H_2O$ and $3Y_2O_3.2I_2O_7.6H_2O$.

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[1] For references, see pp. 229-230. S. Meyer (*Monatsh.*, 1899, **20**, 793) gives the density of yttrium (powder) as 3·80 at 15°. Owen (*Ann. Physik*, 1912, [iv.], **37**, 657) says that yttrium is paramagnetic. Pure yttria, however, is diamagnetic.

On the preparation of yttrium alloys, see Siemens and Halske, *D.R.P.*, No. 146,503.

[2] Cleve and Höglund, *Bihang K. Svenska Vet.-Akad. Handl.*, 1873, **2** ; *Bull. Soc. chim.*, 1873, [ii.], **18**, 193, 289 ; *Ber.*, 1873, **6**, 1467 ; Cleve, *Bihang K. Svenska Vet.-Akad. Handl.*, 1874, **2**, No. 12 ; *Bull. Soc. chim.*, 1874, [ii.], **21**, 344 ; *cf.* Popp, *Annalen*, 1864, **131**, 197.

[3] Matignon, *Compt. rend.*, 1902, **134**, 1308 ; *Ann. Chim. Phys.*, 1906, [viii.], **8**, 433 ; Bourion, *ibid.*, 1910, [viii.], **21**, 49.

[4] Popp, *Annalen*, 1864, **131**, 197.

YTTRIUM AND THE OXYGEN GROUP.

Yttrium sesquioxide, or **yttria,** Y_2O_3, is a pure white powder of density 4·84 at 15° C.[1] It is feebly diamagnetic (p. 257).

Yttria absorbs carbon dioxide from the air, liberates ammonia from ammonium salts, and dissolves readily in acids.

When dissolved in molten calcium chloride and cooled, yttria assumes the crystalline state, crystallising in trapezohedra.[2] For further information concerning yttria, see p. 256.

Yttrium hydroxide, $Y(OH)_3$, is obtained as a gelatinous precipitate from solutions of yttrium salts by the addition of excess of a soluble hydroxide. It readily absorbs carbon dioxide. When the precipitant is a mixture of ammonia and hydrogen peroxide, hydrated *yttrium peroxide*, $Y_4O_9.xH_2O$ or perhaps $Y_2O_5.xH_2O$, is produced.[3]

Yttrium sulphide, Y_2S_3, is a yellow solid which resembles the other rare earth sulphides.[4] A green, crystalline, insoluble *double sulphide*, $Y_2S_3.Na_2S$, is obtained by heating a mixture of yttria and sodium chloride to 1000° in a stream of hydrogen sulphide, and washing the product with cold water.[5]

Yttrium sulphite, $Y_2(SO_3)_3.3H_2O$, has been prepared (p. 260).

Yttrium sulphate, $Y_2(SO_4)_3$.—For preparation and general properties, see p. 260. The specific heat of the anhydrous sulphate between 0° and 100° is 0·1319.[6]

The monoclinic[7] octahydrate, $Y_2(SO_4)_3.8H_2O$, is the only hydrate known. At 25° the saturated solution contains 5·38 grams of anhydrous sulphate per 100 grams of water.[8] Its solubility diminishes with rise of temperature.

For *acid* and *basic sulphates*, see p. 263. The following *double sulphates* are known (Cleve):—

$2Y_2(SO_4)_3.3K_2SO_4$

$Y_2(SO_4)_3.4K_2SO_4$

$Y_2(SO_4)_3.Na_2SO_4.2H_2O$

$Y_2(SO_4)_3.(NH_4)_2SO_4.9H_2O$

The addition of sodium sulphate increases the solubility of yttrium sulphate at first, and then causes the solubility to diminish rapidly. With diminution in solubility is associated a change in solid phase, from hydrated yttrium sulphate to double salt. Solutions supersaturated with respect to the double salt may remain in the metastable state for several months. The solubility curve for a temperature of 25° is shown in fig. 42.[8]

Yttrium dithionate, $Y_2(S_2O_6)_3.18H_2O$, is a very soluble salt (Cleve).

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[1] R. J. Meyer and Wuorinen, *Zeitsch. anorg. Chem.*, 1913, **80**, 7. Previous results are 5·03 (Cleve), 5·05 (Nilson and Pettersson), 4·84 (Muthmann and Böhm), and 5·32 to 5·38 (Tanatar and Voljansky, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 96). They suggest very strongly that the yttria used by Cleve, by Nilson and Pettersson, and by Tanatar and Voljansky, was impure.

[2] Duboin, *Compt. rend.*, 1888, **107**, 99.

[3] Cleve, *Bull. Soc. chim.*, 1885, [ii.], **43**, 53.

[4] See p. 259; also Cleve, *Bull. Soc. chim.*, 1874, [ii.], **21**, 344.

[5] Duboin, *Compt. rend.*, 1888, **107**, 243.

[6] Nilson and Pettersson, *Compt. rend.*, 1880, **91**, 232; *Ber.*, 1880, **13**, 1459.

[7] Kraus, *Zeitsch. Kryst. Min.*, 1901, **34**, 307; see p. 261.

[8] James and Holden, *J. Amer. Chem. Soc.*, 1913, **35**, 559.

Yttrium selenite, $Y_2(SeO_3)_3.12H_2O$, is obtained as a white precipitate by adding sodium selenite to a solution of yttrium sulphate, and is converted by warming with aqueous selenious acid into the acid selenite, $Y_2(SeO_3)_3.H_2SeO_3.4H_2O$ (Cleve).

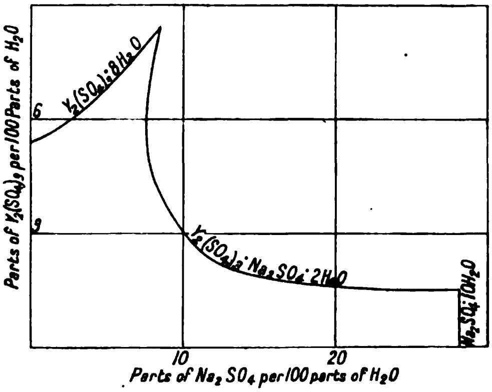

FIG. 42.—The system $Y_2(SO_4)_3$—Na_2SO_4—H_2O at 25° C. Solubility diagram.

Yttrium selenate, $Y_2(SeO_4)_3$.—The monoclinic octahydrate, $Y_2(SeO_4)_3.8H_2O$, and the orthorhombic decahydrate, $Y_2(SeO_4)_3.10H_2O$, are known (see p. 264); also the following *double sulphates*:—

$Y_2(SeO_4)_3.K_2SeO_4.6H_2O$ $\qquad$ $Y_2(SeO_4)_3.(NH_4)_2SeO_4.6H_2O$

which are readily soluble in water.

Yttrium tungstate, $Y_2(WO_4)_3$.—See p. 265.

Yttrium silicotungstate, $Y_4(W_{12}SiO_{40})_3$.—See p. 266.

YTTRIUM AND THE NITROGEN GROUP.

Yttrium nitrate, $Y(NO_8)_3.6H_2O$, forms deliquescent, triclinic crystals[1] and loses $3H_2O$ at 100°. The trinitrate, $Y(NO_3)_3.3H_2O$, crystallises from very concentrated nitric acid.[2] A dihydrate has also been described.[3] When heated, yttrium nitrate first forms basic nitrate and subsequently at very high temperatures leaves a residue of yttria. Yttrium nitrate is isodimorphous with bismuth nitrate (see p. 234).

A saturated aqueous solution of the nitrate at 25° has a specific gravity (25°/25°) of 1·7446 and contains 141·6 grams of anhydrous nitrate per 100 grams of water.[4]

The only *basic yttrium nitrate* that exists at 25° has the composition $3Y_2O_3.4N_2O_5.20H_2O$. It is stable in air and in the presence of a solution of yttrium nitrate containing one-fourth its weight or more of anhydrous

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[1] Von Lang and Haitinger, *Annalen*, 1907, **351**, 450.

[2] Demarçay, *Compt. rend.*, 1900, **130**, 1019.

[3] Tanatar and Voljansky, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 586.

[4] James and Pratt, *J. Amer. Chem. Soc.*, 1910, **32**, 873.

nitrate, and from such a solution it can be recrystallised (see fig. 43). It is not affected by absolute alcohol, but is decomposed by water.[1]

Yttrium orthophosphate, YPO_4, occurs in nature as the mineral *xenotime.* An ammoniacal solution of ammonium orthophosphate when added to yttrium nitrate precipitates a white dihydrate, $YPO_4.2H_2O$. The amorphous phosphate may be crystallised from molten yttrium chloride.[2]

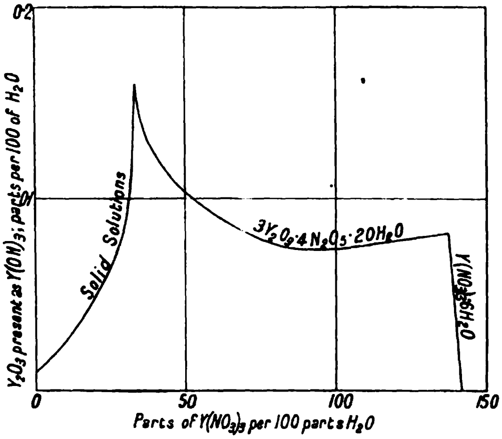

Fig. 43.—The system Y_2O_3—N_2O_5—H_2O at 25° C. Solubility diagram.

Acid yttrium orthophosphate, $Y_2(HPO_4)_3$, may be obtained as an amorphous precipitate by adding disodium orthophosphate to a solution of a yttrium salt (Cleve).

Yttrium hydrogen pyrophosphate, $2YHP_2O_7.7H_2O$, has been prepared by Cleve. The following compounds have also been described :—[3]

$2Y_2O_3.3P_2O_5$	$Y_2O_3.K_2O.2P_2O_5$	$5Y_2O_3.3K_2O.6P_2O_5$
$Y_2O_3.Na_2O.2P_2O_5$	$Y_2O_3.3K_2O.2P_2O_5$	$Y_2O_3.3Na_2O.2P_2O_5$

Yttrium metaphosphate, $Y(PO_3)_3$, is obtained by heating yttria with molten metaphosphoric acid and removing excess of acid with water (Cleve).

Yttrium and the Carbon Group.

Yttrium carbide, YC_2, has been described (p. 270).

Yttrium carbonate, $Y_2(CO_3)_3.3H_2O$, and the following double salts are known (see p. 271) :—

$Y_2(CO_3)_3.Na_2CO_3.4H_2O$ $\qquad$ $Y_2(CO_3)_3.(NH_4)_2CO_3.2H_2O$

Yttrium platinocyanide, $2Y(CN)_3.3Pt(CN)_2.21H_2O$ forms red crystals having a green reflex (see p. 272).

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[1] James and Pratt, *J. Amer. Chem. Soc.*, 1910, **32**, 873.

[2] Radominsky, *Compt. rend.*, 1875, **80**, 304.

[3] Johnson, *Ber.*, 1889, **22**, 976 ; Wallroth, *Bull. Soc. chim.*, 1883, [ii.], **39**, 316 ; Duboin, *Compt. rend.*, 1888, **107**, 622.

Yttrium thiocyanate, $Y(CNS)_3.H_2O$, and likewise the *double salt*, $Y(CNS)_3.3Hg(CN)_2.12H_2O$, are known (see p. 272).

Yttrium oxalate, $Y_2(C_2O_4)_3.9H_2O$, is obtained by double decomposition as a white, crystalline precipitate. For its properties, see p. 273.

The only stable *yttrium potassium oxalate* at 25° has the formula $Y_2(C_2O_4)_3.4K_2SO_4.12H_2O$, and is decomposed by water. Fig. 44 shows the solubility diagram, as determined by Pratt and James.[1]

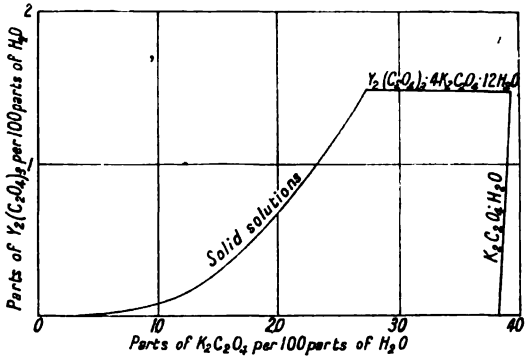

FIG. 44.—The system $Y_2(C_2O_4)_3—K_2C_2O_4—H_2O$ at 25° C. Solubility diagram.

Yttrium ethylsulphate, $Y(C_2H_5.SO_4)_3.9H_2O$, is known (p. 278).

Yttrium acetylacetonate, $Y(CH_3.CO.CH.CO.CH_3)_3$.—See p. 279.

Other organic salts.—The following salts are known :—

Yttrium *formate*,[2, 3] *acetate*,[2, 3] *propionate*,[11] *isobutyrate*,[11] *succinate*,[2, 3, 4] *tartrate*,[2, 3, 10] *glycollate*,[5, 9] *citrate*,[10] *lactate*,[11] *cacodylate*,[6] *sebacate*,[6] *malonate*,[3, 10] *fumarate*,[11] *methylsulphonate*[5] *ethylsulphonate*,[5] *methanedisulphonate*,[5] *methanetrisulphonate*,[5] *crotonate*,[11] *malate*,[11] *citraconate*,[11] *benzoate*,[11] *phenylacetate*,[5] *phenoxyacetate*,[5] *salicylate*,[5] *phthalate*,[5, 11] *benzenesulphonate*,[10] *m-nitrobenzenesulphonate*,[10] 1 : 4 : 2-*bromonitrobenzenesulphonate*,[7] *camphorsulphonate*,[5] 8-*hydroxynaphthalene*-1-*sulphonate*[8] and *pyromucate*.[13]

Yttrium silicate.—By heating a mixture of yttria (3 parts), silica (1 part), and calcium chloride (30 parts) for two hours in a wind furnace and extracting the mass with water, Duboin[12] obtained monoclinic crystals of yttrium silicate, $Y_2O_3.SiO_2$, which in crystalline form and optical properties closely resembled the mineral *gadolinite*.

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[1] Pratt and James, *J. Amer. Chem. Soc.*, 1911, **33**, 488.

[2] Cleve and Höglund, *Bull. Soc. chim.*, 1873, [ii.], **18**, 193, 289.

[3] Cleve, *ibid.*, 1874, [ii.], **21**, 344.

[4] Benner, *J. Amer. Chem. Soc.*, 1911, **33**, 50.

[5] Pratt and James, *ibid.*, 1911, **33**, 1330.

[6] Whittemore and James, *ibid.*, 1913, **35**, 127.

[7] Katz and James, *ibid.*, 1913, **35**, 872.

[8] Erdmann and Wirth, *Annalen*, 1908, **361**, 190.

[9] Jantsch and Grünkraut, *Zeitsch. anorg. Chem.*, 1913, **79**, 305.

[10] Holmberg, *ibid.*, 1907, **53**, 83.

[11] Tanatar and Voljansky, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 586.

[12] Duboin, *Compt. rend.*, 1888, **107**, 99.

[13] Grant and James, *J. Amer. Chem. Soc.*, 1915, **37**, 2652.

ERBIUM.[1]

Symbol, Er. Atomic weight, 167·7 (O=16).

Erbium has been found in certain titanium minerals[2] and is one of the least abundant of the rare earth elements.[3] Erbium salts are pink or rose-red in colour, have a sweet, astringent taste, and exhibit characteristic absorption spectra. Certain erbium preparations have been found to exhibit signs of radioactivity.[4]

The few known compounds of erbium have been described mainly by Cleve.[5]

Erbium has been described as a dark grey, metallic powder of density 4·77 at 15°.[6] The material was probably impure.

Erbium sesquioxide, or **erbia,** Er_2O_3, is a rose-coloured powder of density 8·64 and specific heat (between 0° and 100°) 0·065.[7] It does not combine directly with water. A hydrated *peroxide* also exists.

Erbium sulphate, $Er_2(SO_4)_3$, is described on p. 260, together with the octahydrate, $Er_2(SO_4)_3.8H_2O$, which forms monoclinic crystals.[8] The *double sulphates*, $Er_2(SO_4)_3.K_2SO_4.4H_2O$ and $Er_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$, are readily soluble in water.

Erbium acid selenite, $Er_2O_3.4SeO_2.5H_2O$, is known.

Erbium tungstate.—See p. 265.

Erbium silicotungstate.—See p. 266.

Erbium nitrate, $Er(NO_3)_3.5H_2O$, forms large red crystals, stable in air.

Erbium platinocyanide, $2Er(CN)_3.3Pt(CN)_2.21H_2O$, is isomorphous with the yttrium salt.

Erbium oxalate, $Er_2(C_2O_4)_3.xH_2O$, is a red, microcrystalline powder (p. 273). Hydrates with 3, 9, 10, and 14 H_2O have been described.[9]

Erbium *formate*,[10] *malonate*,[11] *dimethylphosphate*,[12] 8-*hydroxy-naphthalene*-1-*sulphonate*,[11] and 1:4:2-*bromonitrobenzenesulphonate*[13] have also been described.

THULIUM.

Symbol, Tm. Atomic weight, *c.* 168·5 (O=16).

Thulium is one of the least abundant of the rare earth elements. Pure thulia was isolated by James in 1911, by a method that has been already

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[1] Sometimes known as **neo-erbium,** since the old "erbium" contained "ytterbium," holmium, dysprosium, and thulium.

[2] K. A. Hofmann, *Ber.*, 1910, **43**, 2631.

[3] According to Cleve (*vide infra*) the greater part of the "erbium" of Bahr and Bunsen consisted of "ytterbium."

[4] Strong, *Amer. Chem. J.*, 1909, **42**, 147.

[5] Cleve, *Compt. rend.*, 1880, **91**, 381; *cf.* Cleve and Höglund, *Bull. Soc. chim.*, 1873, [ii.], **18**, 193, 289; see also Hofmann, *loc. cit.*; Hofmann and Burger, *Ber.*, 1908, **41**, 308; Hofmann and Bugge, *Ber.*, 1908, **41**, 3783; Hofmann and Kirmreuther, *Zeitsch. physikal. Chem.*, 1910, **71**, 312.

[6] S. Meyer, *Monatsh.*, 1899, **20**, 793.

[7] Nilson and Pettersson, *Compt. rend.*, 1880, **91**, 232; *Ber.*, 1880, **13**, 1459.

[8] Kraus, *Zeitsch. Kryst. Min.*, 1901, **34**, 307.

[9] Cleve, *loc. cit.* ($9H_2O$); Hofmann, *Ber.*, 1910, **43**, 2631 ($3H_2O$ and $10H_2O$); Wirth, *Zeitsch. anorg. Chem.*, 1912, **76**, 174 ($14H_2O$).

[10] Cleve, *loc. cit.*

[11] Erdmann and Wirth, *Annalen*, 1908, **361**, 190.

[12] Morgan and James, *J. Amer. Chem. Soc.*, 1914, **36**, 10.

[13] Katz and James, *ibid.*, 1913, **35**, 872.

described (p. 356). A few compounds of thulium have been described. They are pale green in the solid state and in solution. As the amount of erbium salt present as impurity increases from a trace upwards, the colour of the aqueous solution becomes successively yellowish-green, yellow, colourless, and pink.[1]

Thulium chloride, $TmCl_3.7H_2O$, is extremely soluble in water and alcohol.

Thulium bromate, $Tm(BrO_3)_3.9H_2O$, crystallises in pale, bluish-green, hexagonal prisms.

Thulium sesquioxide, or **thulia,** Tm_2O_3, has a faint green tint. When carefully made to incandesce, it emits a carmine glow. The oxide dissolves slowly in concentrated acids.

Thulium sulphate, $Tm_2(SO_4)_3$, and the octahydrate, $Tm_2(SO_4)_3.8H_2O$, have been prepared.

Thulium nitrate, $Tm(NO_3)_3.4H_2O$, is deliquescent and very soluble in water. It may be crystallised from nitric acid. In its water content it resembles "ytterbium" nitrate.

Thulium oxalate, $Tm_2(C_2O_4)_3.6H_2O$, is soluble in aqueous alkali oxalates, with which it forms double oxalates.

Thulium acetylacetonate, $[(CH_3.CO)_2CH]_3Tm.H_2O$, has been prepared. It is not volatile *in vacuo.*

Thulium *phenoxyacetate,*[2] *cacodylate,*[3] and 1 : 4 : 2-*bromonitrobenzenesulphonate*[4] have also been described.

YTTERBIUM.

Symbol, Yb. Atomic weight, 173·5[5] (O = 16).

The name *ytterbium* it now adopted by the International Committee on Atomic Weights to indicate the main constituent of the old "ytterbium" discovered by Marignac. Urbain uses the name *neoytterbium,* and Auer von Welsbach adopts *aldebaranium.*[6]

From the data given by Auer von Welsbach[7] it appears that 80 to 90 per cent. of the old "ytterbium" consists of the new ytterbium. It may be separated from the accompanying element lutecium (or cassiopëium) by fractional crystallisation of the nitrates, double ammonium oxalates, or

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[1] James, *J. Amer. Chem. Soc.*, 1910, **32**, 517 ; 1911, **33**, 1332.

[2] James, *J. Amer. Chem. Soc.*, 1911, **33**, 1332.

[3] Whittemore and James, *ibid.*, 1913, **35**, 127.

[4] Katz and James, *ibid.*, 1913, **35**, 872.

[5] This value is due to Urbain and Blumenfeld, and was obtained with material free from all but the merest traces of thulium and lutecium. Auer von Welsbach obtained the value 173·0 in 1913. The atomic weight of lutecium exceeds that of the new ytterbium. It is therefore a matter of surprise that the determinations of the atomic weight of old "ytterbium," made by Nilson (*vide infra*) and A. Cleve (*vide infra*), should have given the value 173·1, unless the result obtained by Urbain and Blumenfeld is too high. From the chemical point of view, however, the results of the last-named chemists merit the most confidence.

[6] Auer von Welsbach, *Anzeiger K. Akad. Wiss. Wien*, 1905, No. 10 ; *Annalen*, 1907, **351**, 464 ; *Monatsh.*, 1906, **27**, 935 ; 1908, **29**, 181 ; 1909, **30**, 695 ; *Sitzungsber. K. Akad. Wiss. Wien*, 1906, **115**, II.B, 737 ; 1907, **116**, II.B, 1425 ; 1909, **118**, II.B, 507 ; Urbain, *Compt. rend.*, 1907, **145**, 759 ; 1908, **146**, 406 ; Urbain, Bourion, and Maillard, *ibid.*, 1909, **149**, 127.

[7] Auer von Welsbach, *Monatsh.*, 1913, **34**, 1713.

bromates,[1] the ytterbium salt being in each case less soluble than the other. By the nitrate method, Urbain and Blumenfeld[2] isolated eight successive fractions which furnished specimens of rare earth practically identical with respect to their magnetic susceptibilities and arc spectra. According to these experimenters, Auer von Welsbach's aldebaranium contains some thulium.

Ytterbia, or *neoytterbia*, Yb_2O_3, is a colourless oxide the magnetic susceptibility of which is $33{\cdot}6 \times 10^{-6}$ c.g.s. units per unit mass. Its salts with colourless acids exhibit no selective absorption. The **sulphate** forms an octahydrate, $Yb_2(SO_4)_3.8H_2O$.

The salts of old "ytterbium" have been examined in detail by Astrid Cleve, but will not be described here.[3]

LUTECIUM.

Symbol, Lu. Atomic weight, 175·0[4] (O = 16).

The name *lutecium* is adopted by the International Committee on Atomic Weights to indicate the constituent of old "ytterbium" that has a higher atomic weight and is less abundant than the new ytterbium. The name lutecium is due to Urbain; Auer von Welsbach adopts the name *cassiopëium*.

Pure lutecia has perhaps been isolated by Auer von Welsbach (1913). It is a colourless oxide, much less paramagnetic than ytterbia.[5] Its salts with colourless acids are themselves colourless and exhibit no selective absorption. The anhydrous chloride is more volatile than ytterbium chloride. The **sulphate** forms an octahydrate, $Lu_2(SO_4)_3.8H_2O$.[6]

CELTIUM.

Symbol, Ct. Atomic weight, (?).

In endeavouring to isolate lutecium from a large quantity of the mineral gadolinite, Urbain obtained a final noncrystallisable mother liquor in the course of fractionating the mixed nitrates of ytterbium and lutecium. From this liquor he isolated the rare earth present and purified it from all but lutecium and negligible traces of scandium, calcium, and magnesium.

The earth was quite white. Its magnetic susceptibility was only one-fourth that of nearly pure lutecia obtained from xenotime, and its arc

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[1] See Chapter XI.

[2] Urbain and Blumenfeld, *Compt rend.*, 1914, **159**, 328.

[3] Astrid Cleve, *Zeitsch. anorg. Chem.*, 1902, **32**, 129; *Chem. News*, 1902, **86**, 248; see also Marignac, *Arch. Sci. phys. nat.*, 1878, **64**, 97; *Compt. rend.*, 1878, **87**, 578; Nilson, *ibid.*, 1879, **88**, 642; 1880, **91**, 56, 118; *Ber.*, 1879, **12**, 551; 1880, **13**, 1430, 1439; Matignon, *Ann. Chim. Phys.*, 1906, [viii.], **8**, 440; Bourion, *ibid.*, 1910, [viii.], **20**, 547; **21**, 49; *Compt. rend.*, 1907, **145**, 243; Katz and James, *J. Amer. Chem. Soc.*, 1913, **35**, 872; Morgan and James, *ibid.*, 1914, **36**, 10; Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1095.

[4] Auer von Welsbach's value (1913) for cassiopëium.

[5] Neoytterbia is four to five times as paramagnetic as lutecia (Urbain, *Compt. rend.*, 1908, **146**, 406; S. Meyer, *Monatsh.*, 1908, **29**, 1017).

[6] Auer von Welsbach, *Anzeiger K. Akad. Wiss. Wien*, 1905, No. 10; *Annalen*, 1907, **351**, 464; *Monatsh.*, 1906, **27**, 935; 1908, **29**, 181; 1909, **30**, 695; 1913, **34**, 1713; Urbain, *Compt. rend.*, 1907, **145**, 759; 1908, **146**, 406; Urbain, Bourion, and Maillard, *ibid.*, 1909, **149**, 127; Urbain and Blumenfeld, *ibid.*, 1914, **159**, 323; Bourion, *Ann. Chim. Phys.*, 1910, [viii.], **20**, 547; **21**, 49.

spectrum showed, besides the lines of lutecium, a number of new lines, several of which were very intense (see p. 307).

It thus appears extremely probable that gadolinite contains a new rare earth element that is not present in xenotime. To this element, defined by the arc spectrum given on p. 307, Urbain has given the name *celtium*.

Anhydrous celtium chloride is more volatile than lutecium chloride, but less so than scandium chloride. Celtium hydroxide is a weaker base than lutecium hydroxide, but is stronger than the hydroxide of scandium. In other respects celtium is also intermediate between lutecium and scandium.[1]

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[1] Urbain, *Compt. rend.*, 1911, **152**, 141.

CHAPTER XV.

ACTINIUM AND ITS DISINTEGRATION PRODUCTS.[1]

Occurrence.—Actinium is a constant constituent of uranium minerals. According to Boltwood,[2] in uranium minerals in which radioactive equilibrium has been established the total α-ray ionisation due to the uranium-radium series of products is 4·36 times as great as that due to the uranium itself, whilst there is an additional activity, equal to 0·28 times that of the uranium, due to actinium and its products. It follows that actinium is very scarce even in comparison with radium.[3]

History.—In 1899, shortly after the discovery of radium and polonium in pitchblende, Debierne discovered a third radioactive element in the same mineral. In 1900 he named this element **actinium.**[4] Debierne found that in working up pitchblende residues, the actinium, which was not precipitated by hydrogen sulphide in acid solution, separated with iron and the rare earth elements in the ammonia precipitate, and his final actinium preparations consisted mainly of thorium. For several years no more work on actinium was published by Debierne, and meanwhile Giesel[5] announced the discovery in pitchblende of a new radioactive element *emanium*, characterised by the fact that it gave rise to an emanation which rapidly decayed. Giesel obtained the new element free from thorium, but mixed with the cerium group of rare earth elements. In 1903 and 1904 Debierne[6] gave further details concerning actinium, described the emanation to which it gave rise, and declared that emanium and actinium were identical. This identity, at first disputed,[7] was confirmed by Hahn and Sackur[8] in 1905. With the subsequent discovery of the radio-element ionium, it was seen that both Debierne's and Giesel's actinium preparations must have been contaminated with that element.[9]

Preparation.—The element actinium has not been isolated; neither have actinium salts been obtained in anything approaching a pure state.

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[1] For further information, see Rutherford, *Radioactive Substances and their Radiations* (Cambridge University Press, 1912); Soddy, *The Chemistry of the Radio-elements* (Longmans & Co., pt. i., 2nd ed., 1914; pt. ii., 1914); and the sections on *Radioactivity* in the Chemical Society's Annual Reports from 1904 onwards.

[2] Boltwood, *Amer. J. Sci.*, 1908, [iv.], **25**, 269.

[3] On the occurrence of actinium products in the atmosphere, see Kurz, *Abh. K. Akad. Wiss. München*, 1909, **25**, 5.

[4] Debierne, *Compt. rend.*, 1899, **129**, 593; 1900, **130**, 906.

[5] Giesel, *Ber.*, 1902, **35**, 3608; 1903, **36**, 342; 1904, **37**, 1696.

[6] Debierne, *Compt. rend.*, 1903, **136**, 446, 671; 1904, **138**, 411; **139**, 538.

[7] Giesel, *Ber.*, 1904, **37**, 3963; 1905, **38**, 775; W. Marckwald, *Ber.*, 1905, **38**, 2264; *cf.* Debierne, *Physikal. Zeitsch.*, 1906, **7**, 14.

[8] Hahn and Sackur, *Ber.*, 1905, **38**, 1943.

[9] Boltwood, *Amer. J. Sci.*, 1908, [iv.], **25**, 365.

Actinium preparations consist for the most part of compounds of the rare earth elements containing unweighable amounts of actinium. Since, moreover, the reactions of actinium are not very well known, strongly active actinium preparations are difficult to prepare and in consequence are extremely expensive. Their preparation from pitchblende, carnotite, and the complex Olary ores (S. Australia) may be indicated.[1]

(i.) In working up *pitchblende*[2] for uranium and radioactive preparations, it has usually been the custom to roast the crushed ore with sodium carbonate and then to extract the mass first with water and then with dilute sulphuric acid. The insoluble residue consists of silica and the sulphates of lead, bismuth, calcium, barium, rare earth elements, etc. It is heated with a boiling solution of caustic soda, washed and treated with hydrochloric acid. The radium is then found in the insoluble residue and the polonium and actinium in the solution. (ii.) Numerous processes have been devised for working up the mineral *carnotite* for uranium and vanadium. These have been examined by Plum[3] to see which are suitable for extracting also the radio-elements it contains. Working with the concentrates from a Colorado carnotite ($U = 4·27$, $V = 5·5$ per cent.) he finally preferred to mix ten parts of carnotite with four parts of anhydrous sodium carbonate and twenty parts of water, heat to boiling for several hours, stirring frequently and adding more water as the mass thickened, and then while hot to filter under suction, wash the residue with hot water and boil it for eight hours with about five and a half parts by weight of concentrated hydrochloric acid diluted with ten parts of water. The filtered solution contains the greater part of the radium, polonium, and actinium present in the carnotite. (iii.) The Olary uranium ore[4] occurs in a lode formation of magnetic titaniferous iron, magnetite, and quartz, in association with biotite. The ore is crushed and then concentrated magnetically. The concentrates amount to 30 per cent. of the ore and have the following composition :—

CaO.	PbO.	Fe_2O_3.	FeO.	MnO.	$\underbrace{ThO_2, Ce_2O_3, (La, Di, Y)_2O_3}$.	Cr_2O_3.	U_3O_8.	V_2O_5.	TiO_2.	SiO_2.
0·55	0·16	17·4	16·9	trace	3·27	0·85	1·6	0·86	45·85	12·70

It is only necessary to decompose about half the ore, by fusion with sodium hydrogen sulphate (salt cake), to secure a practically complete yield of the radioactive contents. The fused product is crushed, agitated with water, and the finely divided silica and lead, barium and radium sulphates separated from the coarser, unchanged ore by elutriation. The turbid liquid is allowed to stand and the "slime" of crude sulphates and silica separated from the clear liquid, which is treated for uranium. The uranium liquor contains part

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[1] In consequence of the rayless nature of the initial change of actinium, it often happens that actinium preparations when separated from minerals are scarcely radioactive; their activity and emanating power, however, increase enormously during the next few months. It is thus easy to overlook the presence of actinium; hence, in seeking to obtain actinium preparations no material should ever be thrown away in a hurry.

[2] Debierne, *Compt. rend.*, 1899, **129**, 593; 1900, **130**, 906; Mme. Curie, *Thesis* (Paris, 1903), or translation in *Chem. News*, 1903, **88**; Haitinger and Ulrich, *Sitzungsber. K. Akad. Wiss. Wien*, 1908, **117**, ii. *a*, 619; *Monatsh.*, 1908, **29**, 485; Auer von Welsbach, *Sitzungsber. K. Akad. Wiss. Wien*, 1910, **119**, ii. *a*, 1; *Monatsh.*, 1910, **31**, 1159; *Zeitsch. anorg. Chem.*, 1911, **69**, 353; *J. Soc. Chem. Ind.*, 1911, **30**, 535; Boltwood, *Proc. Roy. Soc.*, 1911, **A**, **85**, 77; *Le Radium*, 1911, **8**, 104.

[3] Plum, *J. Amer. Chem. Soc.*, 1915, **37**, 1797.

[4] Radcliff, *J. Roy. Soc. New South Wales*, 1913, **47**, 145; 1914, **48**, 408; *Mining Sci.*, 1914, **69**, 37; *J. Soc. Chem. Ind.*, 1914, **33**, 229; *Chem. News*, 1915, **111**, 59.

of the rare earths originally present in the ore, but practically none of the actinium, which is found, along with the remainder of the rare earths, in the "slime."

It will be seen that pitchblende residues and Olary ore "slimes" are somewhat similar in composition. Radcliff originally worked up the latter in the following manner. The "slimes" are treated with sulphuric acid, filtered, and boiled with excess of an aqueous solution of sodium carbonate. Insoluble sulphates are converted into carbonates and much silica is dissolved. The washed carbonates are dissolved in hydrochloric acid and the sulphates again precipitated. The crude sulphates thus obtained are fused with sodium carbonate in graphite pots and the product digested with hot water. The insoluble residue, after picking out the metallic lead, is dissolved in hydrochloric acid and the solution evaporated to dryness to dehydrate the silica. The chlorides are dissolved in dilute hydrochloric acid, filtered to remove silica, and the solution is then saturated with hydrogen chloride. Barium and radium chlorides are quantitatively precipitated, nearly free from other elements, whilst the actinium remains in solution with the rare earths. This method has subsequently been modified as follows. The crude mixture of sulphates is fused in an iron crucible with excess of caustic soda and a little sodium carbonate. The melt is repeatedly extracted with hot water, whereby most of the lead is dissolved, and the insoluble residue is digested with sodium carbonate solution under a pressure of 90 lbs. per square inch. The carbonate residue is washed, converted into chlorides, freed from silica, and the barium and radium separated as before.[1]

Properties.—Little is known of the chemical properties of actinium. It has been known since its discovery that actinium resembles the rare earth elements. Debierne was in error, however, in regarding it as analogous to thorium;[2] it is most similar in properties to the tervalent rare earth elements of the cerium group,[3] particularly lanthanum. When these actiniferous rare earth elements are fractionated as the double magnesium nitrates the actinium concentrates in the neodymium and samarium fractions.[4]

Actinium is not precipitated by hydrogen sulphide in dilute acid solution (separation from polonium and radio-lead), but is precipitated as hydroxide by ammonia (separation from radium). This precipitation, however, is very uncertain, and in the presence of considerable quantities of ammonium salts is by no means complete.[5] Plum,[6] who studied the precipitation of actinium by ammonia in the presence of a little aluminium salt, found it impossible to separate all the actinium from radiferous and actiniferous barium chloride in

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[1] According to Radcliff (*loc. cit.*), ten tons of Olary ore concentrates yield only forty kilograms of crude sulphates of the following composition :—

$PbSO_4$.	$BaSO_4$.	Fe_2O_3.	SiO_2.	TiO_2.	Rare Earths.
69·2	12·5	2·2	10·8	3·0	3·0 per cent.

[2] Debierne, *Compt. rend.*, 1899, **129**, 593; 1900, **130**, 906.

[3] See Giesel, *Ber.*, 1907, **40**, 3011; Strömholm and Svedberg, *Zeitsch. anorg. Chem.*, 1909, **63**, 197.

[4] Debierne, *Compt. rend.*, 1904, **139**, 538.

[5] Levin, *Phil. Mag.*, 1906, [vi.], **12**, 177; *Physikal. Zeitsch.*, 1907, 8, 129; Hahn, *Phil. Mag.*, 1906, [vi.], **12**, 244; 1907, [vi.], **13**, 165; Boltwood, *Amer. J. Sci.*, 1908, [iv.], **25**, 292; *Proc. Roy. Soc.*, 1911, A, **85**, 77; Auer von Welsbach, *loc. cit.* To remove ammonium salts, evaporate to dryness and heat the residue with boiling nitric acid or aqua regia; then remove excess of acid by evaporation.

[6] Plum, *J. Amer. Chem. Soc.*, 1915, **37**, 1797.

one operation. Actinium is not precipitated from its chloride solution by boiling with sodium thiosulphate, nor from its nitrate solution by the addition of hydrogen peroxide (separation from thorium and ionium). It is precipitated as oxalate by oxalic acid or ammonium oxalate; in this precipitation the concentration of free mineral acid should be reduced to a minimum, since actinium oxalate, like lanthanum oxalate, is decidedly soluble in mineral acids. The fluoride of actinium, like the fluorides of the rare earth elements, is insoluble in water and aqueous hydrofluoric acid (separation from zirconium and titanium). When a little barium salt is added to an actinium solution and the barium precipitated as sulphate, the precipitate adsorbs the actinium. This property, observed by Debierne, is utilised in separating actinium from pitchblende and Olary ore. Actinium is readily separated with manganese when that element is precipitated from basic solutions as a manganite.[1] Auer von Welsbach describes actinium as being intermediate in chemical properties between lanthanum and calcium.

Actinium is an *unstable* element, and, like thorium and uranium, it is constantly breaking down at a slow but definite rate, and so giving rise to a series of *radioactive disintegration products.* When in equilibrium with these products, α-, β-, and γ-rays are emitted by actinium preparations. The α-rays are very powerful; preparations 100,000 times as active as uranium oxide have been obtained. The β-rays have a relatively small penetrating power, and the γ-rays are feeble both in activity and in penetrating power. The most striking feature of an actinium preparation is its emanating power (p. 449). In the course of the radioactive transformations occurring in actinium preparations helium is evolved, and aqueous solutions of the preparations slowly evolve hydrogen and oxygen.[2]

THE DISINTEGRATION PRODUCTS OF ACTINIUM.

History.—It was early known that actinium produced a rapidly decaying **emanation**, which gave rise to radioactive deposits upon surrounding objects. The modern theory of the atomic disintegration of radioactive elements was put forward in 1903. In terms of this theory, Rutherford, in the Bakerian Lecture for 1904, gave the actinium series as follows:—[3]

$$\begin{array}{lccccccccccc}
 & & & & \overset{\alpha}{\nearrow} & & \overset{\alpha}{\nearrow} & & & & \overset{\alpha}{\nearrow} & \\
\text{Element}\ \ .\ \ . & \text{Ac} & \rightarrow & \text{AcX(?)} & \rightarrow & \text{AcEm} & \rightarrow & \text{AcA} & \rightarrow & \text{AcB} & \rightarrow & \text{AcC(end)} \\
\text{Half-period}\ \ .\ \ . & & & & & \text{3·7 secs.} & & \text{41 mins.} & & \text{1·5 mins.} & &
\end{array}$$

The existence of *actinium-X* was assumed by analogy with the uranium and thorium series. The assumption that the emanation gave rise to an active deposit, **actinium-A,** which was transformed into another element, **actinium-B,** and that this in turn was transformed into a non-radioactive and stable element, **actinium-C,** was based upon Miss Brooks' study of the actinium active deposit.[4]

With the publication of the disintegration theory, the view arose that the α-particles emitted in radioactive changes are charged atoms of helium. Although this view was not definitely established until 1908, its probability

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[1] Auer von Welsbach, *loc. cit.*

[2] Debierne, *Compt. rend.*, 1905, **141**, 383; *Ann. Chim.*, 1914, [ix.]. 2, 97, 428.

[3] Rutherford, *Phil. Trans.*, 1905, **A**, **204**, 169.

[4] Miss Brooks, *Phil. Mag.*, 1904, [vi.], **8**, 373.

was quickly recognised when in 1903 Ramsay and Soddy demonstrated the continuous production of helium from radium. The growth of helium from actinium was observed by Debierne[1] in 1905 and confirmed by Giesel[2] in 1907.

In 1905 Godlewski[3] and Giesel[4] independently discovered the missing element **actinium-X** (half-period = 10·2 days). Godlewski's results indicated that the change from actinium to actinium-X is a rayless one. In the following year, however, Hahn[5] discovered that the rayless change is from actinium to a new element **radioactinium** (half-period = 19·5 days), which expels α-rays and passes into actinium-X.

In 1908 Hahn and Meitner[6] discovered that the transformations of the active deposit produced by the decay of actinium emanation are more complex than had been hitherto supposed. Their views on the degradation of the deposit may be thus summarised :—

$$\begin{array}{llllllll} & \overset{\beta}{\nearrow} & & \overset{\alpha}{\nearrow} & & \overset{\beta}{\nearrow} & & \\ \text{Element} \;.\;.\;. & \text{AcA} & \rightarrow & \text{AcB} & \rightarrow & \text{AcC} & \rightarrow & \text{AcD(end)} \\ \text{Half-period} \;.\;.\;. & \text{36 mins.} & & \text{2·15 mins.} & & \text{5·1 mins.} & & \end{array}$$

The active deposit, however, has proved to be still more complex, for in the same year Bronson[7] discovered that the emanation produces in its decay twice as many α-particles as does the active deposit it produces. In accordance with the preceding scheme for the degradation of actinium-A, this means that each atom of emanation evolves two α-particles in its decomposition. This fact was confirmed by Geiger and Marsden[8] in 1910. The explanation was supplied by Geiger[9] in 1911. The emanation breaks down with the loss of one α-particle per atom decomposed into a new solid element which decays with extraordinary rapidity, also losing one α-particle per atom decomposing, and becoming transformed into the element previously known as actinium-A. Geiger determined the half-period of the new element to be only 0·002 second, and Moseley and Fajans,[10] who developed a highly accurate method for measuring such a short period, obtained exactly the same result. The new element was called **actinium-A,** the elements previously known as actinium-A, B, C, and D respectively being renamed **actinium-B, C, D,** and **E.**

The foregoing, however, does not completely describe the transformations of the active deposit. In 1909 Mlle. Blanquies[11] concluded that actinium-C (then called AcB) gave rise to two kinds of α-rays. Her experimental results have not been confirmed,[12] but the experiments of Marsden and others leave little doubt that actinium-C is complex. The α-rays it emits have been found

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[1] Debierne, *Compt. rend.*, 1905, **141**, 383. For full experimental details, see Debierne, *Ann. Phys.*, 1914, [ix.], **2**, 428.

[2] Giesel, *Ber.*, 1907, **40**, 3011.

[3] Godlewski, *Phil. Mag.*, 1905, [vi.], **10**, 35, 375 ; *Bull. Acad. Sci. Cracow*, 1905, p. 265.

[4] Giesel, *Jahrb. Radioaktiv. Elektronik*, 1904, i. 358.

[5] O. Hahn, *Ber.*, 1906, **39**, 1605 ; *Phil. Mag.*, 1906, [vi.], **12**, 244 ; 1907, [vi.], **13**, 165 ; *cf.* Levin, *ibid.*, 1906, [vi.], **12**, 177.

[6] Hahn and Meitner, *Physikal. Zeitsch.*, 1908, **9**, 649, 697 ; Hahn, *ibid.*, 1909, **10**, 81.

[7] Bronson, *Phil. Mag.*, 1908, [vi.], **16**, 291.

[8] Geiger and Marsden, *Physikal. Zeitsch.*, 1910, **11**, 7.

[9] Geiger, *Phil. Mag.*, 1911, [vi.], **22**, 201.

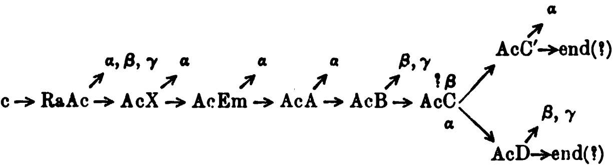
[10] Moseley and Fajans, *ibid.*, 1911, [vi.], **22**, 629.

[11] Mlle. Blanquies, *Compt. rend.*, 1909, **148**, 1753; 1910, **151**, 57 ; *Le Radium*, 1909, **6**, 230 ; 1910, **7**, 159.

[12] See, *e.g.*, Moseley and Fajans, *loc. cit.* ; Varder and Marsden, *vide infra.*

to be of two kinds, their ranges in air being 5·4 and 6·45 cms.; the latter only arise from 0·15 to 0·20 per cent. of the atoms undergoing change.[1] The explanation is as follows:—Actinium-C breaks down in two different ways, in one of which an α-particle of range 5·4 cms. is evolved and actinium-D produced, while in the other and slower method a β-particle is evolved and a new element, **actinium-C′**, is produced. The relative amounts of AcD and AcC′ produced are as 99·83 is to 0·17, and the new element decays at almost exactly the same rate as actinium-A, with the emission of α-rays of range 6·45 cms.

In 1912 Chadwick and Russell[2] announced the existence of an element intermediate between radioactinium and actinium-X. This was denied by Hahn and Meitner,[3] and subsequently Chadwick and Russell[4] withdrew their claim. The actinium series, as it is at present known, is accordingly as indicated in the following scheme, in which the nature of the radiation from each product is also shown:—



The α-, β-, and γ-radiations.—Actinium, when carefully freed from its products, is found to emit no detectable β- and γ-rays, and to emit α-rays to so slight an extent that the phenomenon is presumably due to traces of its products. In other words, the change from actinium to radioactinium is a rayless one.[5] Six actinium products, viz. radioactinium, actinium-X, actinium emanation, actinium-A, actinium-C, and actinium-C′, decay with the emission of **α-rays**, one α-particle being expelled per atom decomposed. The *ranges* (in cms.) of these α-rays in air at N.T.P. are given as follows by various experimenters:—[6]

	RaAc.	AcX.	AcEm.	AcA.	AcC.	AcC′.
Geiger and Nuttall[7]	4·36	4·17	5·40	6·16	5·12	...
Meyer, Hess, and Paneth[8]	4·0 and 4·37	4·04	5·28	5·94	4·88	...
Varder and Marsden[9]	...	...	...	...	5·12	6·11
M'Coy and Leman[10]	4·17	...	...	...	...	...

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[1] Marsden and Wilson, *Nature*, 1913, **92**, 29; Marsden and Perkins, *Phil. Mag.*, 1914, [vi.], **27**, 690; Varder and Marsden, *ibid.*, 1914, [vi.], **28**, 818.

[2] Chadwick and Russell, *Nature*, 1912, **90**, 463.

[3] Hahn and Meitner, *Physikal. Zeitsch.*, 1913, **14**, 752.

[4] Russell and Chadwick, *Phil. Mag.*, 1914, [vi.], **27**, 112.

[5] Hahn, *Ber.*, 1906, **39**, 1605; *Phil. Mag.*, 1907, [vi.], **13**, 165; Levin, *ibid.*, 1906, [vi.], **12**, 177; Hahn and Rothenbach, *Physikal. Zeitsch.*, 1913, **14**, 409. According to S. Meyer, Hess, and Paneth (*vide infra*), however, actinium emits α-rays of range 3·38 cms. in air at N.T.P.

[6] The range in air is directly proportional to the absolute temperature and inversely proportional to the pressure.

[7] Geiger and Nuttall, *Phil. Mag.*, 1912, [vi.], **24**, 647.

[8] S. Meyer, Hess, and Paneth, *Sitzungsber. K. Akad. Wiss. Wien*, 1914, **123**, ii. *a*. 1459.

[9] Varder and Marsden, *Phil. Mag.*, 1914, [vi.], **28**, 818.

[10] M'Coy and Leman, *Phys. Review*, 1914, [ii.], **4**, 409.

Three members of the series, viz. radioactinium, actinium-B, and actinium-D, emit **β-rays**. The nature of these rays has been studied by various physicists;[1] those emitted by radioactinium and actinium-B have very little penetrating power. Associated with the β-rays are **γ-rays**. Radioactinium and actinium-D emit very penetrating γ-rays, and actinium-B likewise emits fairly powerful γ-rays. Radioactinium and actinium-B also emit fairly weak γ-rays, while in addition to this actinium-B emits very feeble γ-rays.[2]

It will be observed that radioactinium emits both α- and β-rays. Only one other radio-element is known to do this, viz. radium.

Rates of Decay.—The various members of the actinium series differ greatly in stability, the half-periods varying from years with actinium itself to 18·88 days in the case of radioactinium, and to 0·002 second in the case of actinium-A. The precise rate of change of actinium itself is unknown. According to Soddy, however, its period of average life probably does not exceed a hundred years, and Mme. Curie[3] has made observations which point to a period of only thirty years. It should therefore be possible to observe the growth of actinium. The fact that this has never been done suggests the existence of an intermediate long-lived product between actinium and radioactinium. The matter, however, is still obscure.

The *radioactive constant* (λ), *half-period* (T), and *period of average life* (P) of each of the members of the actinium series are given in the following table ($P = 1/\lambda = 1{\cdot}443T$):—

Element.	λ(sec.)$^{-1}$.	T.	P.	Element.	λ(sec.)$^{-1}$.	T.	P.
Radioactinium[4]	$4{\cdot}25 \times 10^{-7}$	18·88 days	27·24 days	Actinium-B[8] .	$3{\cdot}21 \times 10^{-4}$	36·0 mins.	51·9 mins.
Actinium-X[5] .	$7{\cdot}07 \times 10^{-7}$	11·35 days	16·38 days	Actinium-C[9] .	$5{\cdot}38 \times 10^{-3}$	2·15 mins.	3·1 mins.
Emanation[6] .	$1{\cdot}77 \times 10^{-1}$	3·920 secs.	5·656 secs.	Actinium-D[10] .	$2{\cdot}45 \times 10^{-3}$	4·71 mins.	6·80 mins.
Actinium-A[7] .	346	0·002 sec.	0·003 sec.				

In the uranium and thorium series the following empirical relationship has been discovered: the longer the period of the element the shorter the

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[1] See Hahn and Meitner, *Physikal. Zeitsch.*, 1908, **9**, 649, 697; O. von Baeyer, Hahn, and Meitner, *ibid.*, 1913, **14**, 321; *cf.* Godlewski, *Phil. Mag.*, 1905, [vi.], **10**, 35, 375; Levin, *ibid.*, 1906, [vi.], **12**, 177.

[2] See Rutherford and Richardson, *Phil. Mag.*, 1913, [vi.], **26**, 937; F. and W. M. Soddy and Russell, *ibid.*, 1910, [vi.], **19**, 725; Russell and F. Soddy, *ibid.*, 1911, [vi.], **21**, 130; Russell and Chadwick, *ibid.*, 1914, [vi.], **27**, 112.

[3] Mme. Curie, *Le Radium*, 1911, **8**, 353.

[4] M'Coy and Leman, *Phys. Review*, 1914, [ii.], **4**, 409; *cf.* Hahn, *Phil. Mag.*, 1907, [vi.], **13**, 165; Hahn and Rothenbach, *Physikal. Zeitsch.*, 1913, **14**, 409.

[5] M'Coy and Leman, *Physikal. Zeitsch.*, 1913, **14**, 1280, and *loc. cit.*; *cf.* Godlewski, *Phil. Mag.*, 1905, [vi.], **10**, 35; Geisel, *Ber.*, 1907, **40**, 3011; Hahn and Rothenbach, *loc. cit.*

[6] P. B. Perkins, *Phil. Mag.*, 1914, [vi.], **27**, 720; *cf.* Debierne, *Compt. rend.*, 1904, **138**, 411; Hahn and Sackur, *Ber.*, 1905, **38**, 1943; Miss M. Leslie, *Phil. Mag.*, 1912, [vi.], **24**, 637.

[7] Moseley and Fajans, *Phil. Mag.*, 1911, [vi.], **22**, 629; Geiger, *ibid.*, 1911, [vi.], **22**, 201.

[8] Hahn and Meitner, *Physikal. Zeitsch.*, 1908, **9**, 649; *cf.* Miss Brooks, *Phil. Mag.*, 1904, [vi.], **8**, 373; Hess, *Sitzungsber. K. Akad. Wiss. Wien*, 1907, **116**, ii. *a*, 1121; S. Meyer and von Schweidler, *ibid.*, 1905, **114**, ii. *a*, 1147; Bronson, *Amer. J. Sci.*, 1905, [iv.], **19**, 185.

[9] Hahn and Meitner, *loc. cit.*; *cf.* Miss Brooks, *loc. cit.*

[10] Kovářík, *Physikal. Zeitsch.*, 1911, **12**, 83; *cf.* Hahn and Meitner, *loc. cit.*

range of its α-particles at N.T.P., and if the logarithms of the ranges are plotted against the logarithms of the radioactive constants or periods the points lie on straight lines in each series (the Geiger-Nuttall Law). To this rule in the actinium series radioactinium constitutes an exception if Geiger and Nuttall's values for the ranges are accurate; according to M'Coy and Leman, however, their value for radioactinium is too high, while Meyer, Hess, and Paneth state that this element gives α-rays of two different ranges, an indication that the actinium series is more complicated than it is at present thought to be. Applied to actinium-C′, the rule indicates that the values of λ, T, and P must be almost identical with those for actinium-A.

From the periods here given it is possible to calculate the manner in which the α- and β-ray activities of actinium, radioactinium, and actinium-X, initially free from any other radioactive elements, vary with the time, provided the radioactive preparations lose none of their radioactive products through loss of gaseous emanation; experimental and calculated results are in good agreement. The α-ray activity of actinium, initially zero, develops as the preparation is kept, slowly at first, then more rapidly, and finally more slowly again, reaching a limiting value after four months, when the actinium and its products are in radioactive equilibrium.[1] With radioactinium, the α-ray activity rises to a maximum of about 2·25 times the initial value in seventeen days and then diminishes, the rate of decay soon approximating to the exponential value for radioactinium and being practically complete in four months. The β-ray activity varies similarly, its maximum being reached in about twenty days.[1, 2, 5] The α- and β-activities of pure actinium-X rise to their maximum values in about four hours, and then decay at a rate which ultimately becomes exponential with the period of actinium-X.[2, 3, 4]

Separation of the Members of the Actinium Series.—*Radioactinium* may be separated from its parent and its products by adding a little thorium salt to an acid solution of the actinium preparation and boiling with an excess of sodium thiosulphate. The precipitated thorium basic thiosulphate carries with it the radioactinium.[6] Hahn,[7] who originated this thiosulphate method, added no thorium salt, and he described the separation as uncertain; probably his actinium contained a little thorium. To ensure the purity of the radioactinium, the precipitate may be dissolved in hydrochloric acid and reprecipitated by sodium thiosulphate. Instead of adopting the thiosulphate method for separating the thorium and radioactinium, the hydrogen peroxide method (p. 320) may be used.[6, 8] If the addition of thorium is undesirable, a little zirconium may be added and the thiosulphate method employed.[9] By fractionally precipitating an actinium solution with ammonia, radioactinium concentrates in the first fractions.[7]

Actinium-X may be separated from a solution of an actinium preparation by precipitation with ammonia, which leaves the actinium-X in the filtrate.[10]

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[1] Hahn, *Phil. Mag.*, 1907, [vi.], **13**, 165.

[2] Hahn and Rothenbach, *Physikal. Zeitsch.*, 1913, **14**, 409.

[3] M'Coy and Leman, *ibid.*, 1913, **14**, 1280.

[4] Levin, *Phil. Mag.*, 1906, [vi.], **12**, 177.

[5] M'Coy and Leman, *Phys. Review*, 1914, [ii.], **4**, 409.

[6] Fleck, *Trans. Chem. Soc.*, 1913, **103**, 381.

[7] Hahn, *Ber.*, 1906, **39**, 1605; *Physikal. Zeitsch.*, 1906, **7**, 855; *Phil. Mag.*, 1907, [vi.], **13**, 165.

[8] M'Coy and Leman, *Physikal. Zeitsch.*, 1913, **14**, 1280.

[9] Hahn and Rothenbach, *ibid.*, 1913, **14**, 409.

[10] Godlewski, *Phil. Mag.*, 1905, [vi.], **10**, 35.

To ensure the removal of actinium and radioactinium the filtrate may be acidified and reprecipitated by ammonia after the addition of a little ferric salt.[1] The filtrate is then evaporated to dryness and the residue ignited to expel the actinium "active deposit," or the actinium-X is removed from solution by co-precipitation with barium sulphate.[2] Freedom from actinium is probably best ensured by growing the actinium-X from pure radioactinium, and after a suitable interval of time removing the residual radioactinium as has been previously described.[3]

Actinium emanation may be removed from actinium solutions by passing a rapid stream of air or other gas through it. The emanation is also evolved with great facility from most solid actinium preparations, particularly the hydroxides. The remarkably rapid rate of decay of the emanation and the readiness with which it is evolved make it easy to demonstrate the emanating power of an actinium preparation by merely holding it over a large zinc sulphide screen in the dark. The emanation streams away and illuminates the screen, and as the currents in the air blow the emanation about so the screen becomes illuminated in different places.

Actinium active deposit.—In view of the excessively brief life of actinium-A, it cannot be isolated and studied like an ordinary radio-element. In all ordinary work, actinium emanation and actinium-A act together as one product. By their decay, actinium B, C, C′, D, and the end products arise. Collectively they are termed the "active deposit," since they are produced on all objects with which the emanation comes into contact. To separate the active deposit a current of air laden with emanation may be passed through a metal cylinder provided with a metal electrode held axially in position and insulated from the cylinder by rubber stoppers. A potential difference of about 50 volts is maintained between the central electrode and the cylinder, the latter being positive to the former. The active deposit then collects on the negative electrode. The yield is never more than 95 per cent.[4]

The manner in which the α-ray activity of the "active deposit" varies with the time depends upon how long is taken to collect the deposit. If this does not exceed ten seconds, the activity increases slightly with the time, reaches a maximum in seven minutes, and then decreases, the decay soon becoming exponential with the period of actinium-B, the longest-lived element in the deposit. If the time taken to collect the deposit exceeds ten seconds the initial rise in its α-ray activity cannot be observed.[5]

Actinium-B is more volatile than actinium-C. When the active deposit is collected on a platinum wire and heated in air, actinium-B begins to volatilise at 400° C., and is completely volatilised in ten minutes at 750° C., in four minutes at 900° C., or in about half a minute in the blowpipe flame, when actinium-D is also volatilised. Actinium-C is not perceptibly volatile below 700° C.[6] After having been volatilised in air, actinium-B becomes

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[1] Hahn and Rothenbach, *Physikal. Zeitsch.*, 1913, **14**, 409.

[2] M'Coy and Leman, *Phys. Review*, 1914, [ii.], **4**, 409.

[3] M'Coy and Leman, *Physikal. Zeitsch.*, 1913, **14**, 1280.

[4] On the behaviour of the active deposit in an electric field, see Miss Brooks, *Phil. Mag.*, 1904, [vi.], **8**, 373; Russ, *ibid.*, 1908, [vi.], **15**, 601, 737; Kennedy, *ibid.*, 1909, [vi.], **18**, 744; M'Lennan, *ibid.*, 1912, [vi.], **24**, 370; Walmsley, *ibid.*, 1913, [vi.], **26**, 381; Lucian, *ibid.*, 1914, [vi.], **28**, 761; *Amer. J. Sci.*, 1914, [iv.], **38**, 539.

[5] Miss Brooks, *Phil. Mag.*, 1904, [vi.], **8**, 373.

[6] S. Meyer and von Schweidler, *Sitzungsber. K. Akad. Wiss. Wien*, 1905, **114**, ii. *a*, 1147; Levin, *Physikal. Zeitsch.*, 1906, **7**, 812; Hahn and Meitner, *ibid.*, 1908, **9**, 649; Schrader, *Phil. Mag.*, 1912, [vi.], **24**, 125.

much less volatile and may be condensed on a surface at 1000° C.; this is presumably due to oxidation of the element, since the phenomenon is not observed in an atmosphere of hydrogen.[1] Exposure of the active deposit for ten to fifteen minutes to bromine vapour increases the volatility of actinium-B, as also does exposure to chlorine or hydrogen iodide. The last two gases, however, cause actinium-C to become more volatile; in fact, after treatment with hydrogen iodide, actinium-C is more volatile than actinium-B. Exposure to hydrogen chloride does not affect the volatilities, but if the active deposit be then treated with water, nearly all the actinium-B is dissolved, but no actinium-C. Actinium-B is very readily dissolved by dilute acids; immersion of the active deposit for one minute in 0·001N hydrochloric or sulphuric acid causes 80 to 95 per cent. of the actinium-B to be dissolved and practically none of the actinium-C.[1]

The actinium active deposit may be dissolved in boiling hydrochloric acid. By electrolysing this solution between platinum electrodes, part of the actinium-C may be deposited on the cathode.[2] A much better and simpler method of separating the actinium-C from this solution is to have it nearly neutral, heat it to boiling and immerse a piece of sheet nickel in it for a few minutes. The actinium-C is deposited on the nickel.[3] Actinium-D may be withdrawn from the solution by shaking with animal charcoal, in which it is adsorbed.[4] It is best prepared, however, by the method of radioactive recoil.

An atom of actinium-C, of mass 210, loses an α-particle, *i.e.* a charged atom of helium, of mass 4, when it disintegrates. The helium atom is expelled with a velocity of $1{\cdot}89 \times 10^9$ cms. per second, and in accordance with the second law of motion the residual atom of actinium-D, of mass 206, must recoil (just like a gun recoils when it discharges a projectile) with a velocity of $(4 \times 1{\cdot}89 \times 10^9)/206$ or $3{\cdot}67 \times 10^7$ cms. per second. The actinium-D as it is produced has accordingly a kind of "nascent" volatility and feeble penetrating power. Since the α-particles are discharged in all possible directions, so also do the atoms of actinium-D recoil in all directions, and if an excessively thin layer of active deposit is collected on a smooth, carefully polished metal surface, 50 per cent. of the actinium-D atoms produced in its decay may be expected to recoil normal to and away from the plate. The recoiling particles carry positive charges and deposit preferentially on a negatively charged surface. Accordingly, by placing the metal plate carrying the active deposit opposite the surface on which the actinium-D is to be collected, both being contained in an evacuated vessel, and establishing a suitable potential difference between active deposit and receiving surface, it is possible under good conditions to collect almost the theoretical yield of actinium-D.[5]

Physical Properties of Actinium Emanation.—Actinium emanation is a gas which so far as is known does not enter into any chemical combination. At − 120° C. it begins to condense, and condensation is

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[1] Schrader, *loc. cit.*

[2] Miss Brooks, *Phil. Mag.*, 1904, [vi.], **8**, 373.

[3] Meitner, *Physikal. Zeitsch.*, 1911, **12**, 1094.

[4] Hahn and Meitner, *ibid.*, 1908, **9**, 649.

[5] Hahn and Meitner, *loc. cit.*; Kovářik, *Phil. Mag.*, 1912, [vi.], **24**, 722; Wood, *ibid.*, 1913, [vi.], **26**, 586; Fleck, *Trans. Chem. Soc.*, 1913, **103**, 1052. The recoil method is a general one for preparing the products of α-ray changes. Some curious early observations on the decay of actinium active deposit (S. Meyer and von Schweidler, *Sitzungsber. K. Akad. Wiss. Wien*, 1905, **114**, ii. *a*, 1147; 1907, **116**, ii. *a*, 315) were ultimately traced to contamination with actinium-X which had recoiled at the moment of its formation (Hahn *Physikal. Zeitsch.*, 1909, **10**, 81).

complete at −150° C., agreeing in these respects extremely closely with thorium emanation.[1] It is twice as soluble in water as thorium emanation, and six times as soluble as radium emanation. The following, as solvents for actinium emanation, are arranged in increasing order of absorbing power: saturated potassium chloride solution, water, sulphuric acid, alcohol, ammonia, acetone, benzaldehyde, benzene, toluene, petroleum, and carbon disulphide. The emanation is strongly adsorbed by cocoanut charcoal at the ordinary temperature.[2]

The rate of diffusion of the emanation in various gases has been determined by several observers with results of doubtful value from the point of view of calculating the molecular weight of the emanation.[3] It is very improbable that the ordinary laws of gaseous diffusion can be applied to the case of an excessively minute amount of emanation diffusing into a relatively enormous amount of another gas. From comparative experiments on the actinium and thorium emanations (in the carrying out of which various sources of possible error in the work of previous experimenters were detected), Miss Leslie[4] concluded that these two emanations have molecular weights that are nearly equal, and it is known that the value for thorium emanation is 220·2. Marsden and Wood[5] have determined the molecular weight of actinium emanation by a new diffusion method in which gas other than the emanation is present only in minute amounts. Their experiments lead to a value of about 230 for the molecular weight, and this result is probably fairly accurate, since Debierne[6] has devised a method which is based upon the same theoretical principles as that of Marsden and Wood, and by its use obtained a value of 221 for the molecular weight of radium emanation, the correct value being otherwise known to be 222.

Chemical Properties of the Members of the Actinium Series.— The account already given of the preparation and properties of actinium leaves little doubt as to the tervalency of that element. In 1909 Strömholm and Svedberg[7] examined the chemical nature of various radio-elements by crystallising salts from their solutions and seeing whether the radio-elements separated with the crystals or not. In this manner they found that actinium was isomorphous with lanthanum, actinium-X with the alkaline earth metals, and radioactinium with thorium. A physico-chemical method for determining the valencies of the radio-elements was devised in 1913 by von Hevesy[8] who found that actinium is tervalent and actinium-X is bivalent.

The chemical properties of actinium and several of its products have been carefully examined by Fleck,[9] with the following results. Actinium is so similar to mesothorium-2 that when once mixed, chemical means fail to effect any separation of one from the other. Similarly, radio-actinium is chemically indistinguishable from thorium, and actinium-B, actinium-C, and actinium D are identical in chemical properties with lead, bismuth, and thallium respectively.

The chemical identity of two elements having different atomic weights is

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[1] Kinoshita, *Phil. Mag.*, 1908, [vi.], **16**, 121; *cf.* Henriot, *Le Radium*, 1908, **5**, 41.
[2] Von Hevesy, *Physikal. Zeitsch.*, 1911, **12**, 1214.
[3] Debierne, *Le Radium*, 1907, **4**, 213; Bruhat, *ibid.*, 1909, **6**, 67; *Compt. rend.*, 1909, **148**, 628; Russ, *Phil. Mag.*, 1909, [vi.], **17**, 412.
[4] Miss Leslie, *Phil. Mag.*, 1912, [vi.], **24**, 637.
[5] Marsden and Wood, *Phil. Mag.*, 1913, [vi.], **26**, 948.
[6] Debierne, *Ann. Phys.*, 1915, [ix.], **3**, 62.
[7] Strömholm and Svedberg, *Zeitsch. anorg. Chem.*, 1909, **61**, 338; **63**, 197.
[8] Von Hevesy, *Phil. Mag.*, 1913, [vi.], **25**, 390; 1914, [vi.], **27**, 586.
[9] Fleck, *Trans. Chem. Soc.*, 1913, **103**, 381 (Ac, RaAc, AcB, AcC), 1052 (AcD).

a very startling discovery. The preceding results are only a few of those that have been experimentally investigated. A group of elements which are chemically identical is called a group of *isotopes* or *isotopic* elements. The isotopic groups, so far as they have been experimentally examined and relate to members of the actinium series, are as follows:—[1]

(i.) Radioactinium, thorium, radiothorium, ionium, and uranium-X.
(ii.) Actinium and mesothorium-2.
(iii.) Actinium-X, radium, mesothorium-1, and thorium-X.
(iv.) Actinium emanation and the emanations of radium and thorium.
(v.) Actinium-B, lead, radium-B, thorium-B, and radium-D.
(vi.) Actinium-C, bismuth, radium-C, thorium-C, and radium-E.
(vii.) Actinium-D, thallium, and thorium-D.

The identity of isotopes extends to their electro-chemical behaviour. Actinium-B and actinium-C, for instance, are electro-chemically identical with the B and C members of the thorium and radium series.[2]

With the recognition of isotopism it became possible to assign the radio-elements positions in the Periodic Table, for it was seen that two general rules could be framed. (i.) An element formed in an α-ray change (*i.e.* a mass change) differs in valency from its parent by two, and so occupies a position two places behind its parent (*i.e.* in the direction of diminishing mass). (ii.) An element formed in a β-ray change (*i.e.* no change in mass) differs in valency from its parent by one, the valency increasing in the change; the product accordingly occupies a position one in advance of its parent. By these rules the members of the uranium and thorium series may be placed in position since the starting-points for thorium and uranium are known, and it is found that a group of isotopes occupies one space in the Periodic Table. In the absence of definite knowledge concerning the origin and atomic weight of actinium, the actinium series must be placed in position in accordance with the principle of isotopy, and it must further be assumed that the rayless change Ac→RaC follows the β-ray rule.[3] The actinium series then falls into Mendeléeff's table as follows:—[4]

→ Group.	0	1	2	3	4	5	6	7
Fourth long period (Odd series)	...	Au	Hg	Tl AcD	Pb AcE	Bi AcC	AcA AcC′	...
Fifth long period (Even series)	Nt AcEm	...	Ra AcX	... Ac	Th RaAc	...	U	...

Origin of Actinium.—Actinium is a constant constituent of uranium minerals, and it occurs in them in amounts proportional to their uranium contents.[5] It is therefore hard to resist the conclusion that actinium is

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[1] Soddy, *The Chemistry of the Radio-elements* (Longmans & Co., 1914), pt. ii., p. 14.

[2] Von Hevesy, *Phil. Mag.*, 1912, [vi.], **23**, 628.

[3] This has also to be assumed for the rayless change MsThI→MsThII.

[4] A short account of modern work on the theory of atomic structure and its bearing on the periodic classification and the positions of the radio-elements is given in this series, Vol. I. pt. i., pp. 276–282. For a fuller account, see Soddy, *opus cit.*

[5] Boltwood, *Phys. Review*, 1906, **22**, 320; *Amer. J. Sci.*, 1906, [iv.], **22**, 537; 1908, [iv.], **25**, 269; M'Coy, *Phil. Mag.*, 1906, [vi.], **11**, 177; M'Coy and Ross, *J. Amer. Chem. Soc.*, 1907, **29**, 1698.

derived from uranium. The α-ray activity of the actinium products is, however, very small in comparison with that of the uranium-radium series of products in the same mineral (p. 441). Rutherford[1] accordingly suggested that some member of the uranium-radium series undergoes disintegration in two ways, so that from that member onwards the uranium disintegration series branches into two such series, one of which contains actinium and its products. It would suffice to account for the observed results if about 8 per cent. of the disintegrated uranium followed the actinium branch series.[2]

Passing over the earlier suggestions as to the precise point at which this branching of the uranium series occurs,[3] and viewing the problem in the light of modern knowledge, it is seen that if formed by an α-ray change, actinium is derived from a homologue of tantalum, and if formed by a β-ray change, it is derived from radium or an isotope of that element.[4] The production of actinium from radium has been disproved.[5] No isotope of radium derived from uranium is known. Such an element would exist if ionium broke down in two ways and α-rays were emitted in each. However, no actinium could be detected in a concentrated ionium preparation four years after it had been made.[6] So far as a radioactive homologue of tantalum is concerned, the element brevium or uranium-X_2 is the only one known, but its short life and absence of α-radiation completely negative the view that it is the parent of actinium. If, then, actinium is formed in an α-ray change, there is an isotope of brevium still to be discovered. It has been sought in pitchblende, with negative results, but there is no certainty that the chemical methods used would have isolated it.[7] The missing element might arise from uranium-X_1[8] or ionium by a β-ray change, but the latter is unlikely in view of the failure to produce actinium from ionium. Another alternative has been proposed, and meets with most favour at the present time (1916). Uranium-I or uranium-II breaks down in two ways, each of the α-ray type, producing uranium-X_1 or ionium on the one hand, and uranium-Y on the other. Uranium-Y, by a β-ray change, passes into the missing homologue of tantalum. The existence of uranium-Y was announced by Antonov in 1911, and is now fairly well established.[9] Assuming the branching to start from uranium-II, the uranium series will then be as follows:—

$$\begin{tikzcd}
 & & & & \alpha & \alpha & & \\
 & & & & \mathrm{Io} \arrow[u] \arrow[r] & \mathrm{Ra} \arrow[u] \arrow[r] & \mathrm{etc.} & \\
\alpha & \beta & \beta & & & & & \\
\mathrm{UrI} \arrow[u] \arrow[r] & \mathrm{UrX_1} \arrow[u] \arrow[r] & \mathrm{UrX_2} \arrow[u] \arrow[r] & \mathrm{UrII} \arrow[uur, "\alpha", "92\%"'] \arrow[ddr, "8\%", "\alpha"'] & & & & \\
 & & & & \beta & \alpha & & \\
 & & & & \mathrm{UrY} \arrow[u] \arrow[r] & {[?]} \arrow[u] \arrow[r] & \mathrm{Ac} \arrow[r] & \mathrm{etc.}
\end{tikzcd}$$

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[1] Rutherford, *Radioactive Transformations* (Constable, 1906), p. 177.

[2] Rutherford, *Radioactive Substances and their Radiations* (Cambridge Univ. Press, 1912), p. 523.

[3] M'Coy and Ross, *loc. cit.*; Soddy, *Phil. Mag.*, 1909, [vi.], **18**, 739; *cf.* Nicholson, *Nature*, 1911, **87**, 515.

[4] Soddy, *Chem. News*, 1913, **107**, 97; *Jahrb. Radioaktiv. Elektronik*, 1913, **10**, 188; Fajans, *Le Radium*, 1913, **10**, 61, 171; *Ber.*, 1913, **46**, 422.

[5] Soddy, *Nature*. 1913, **91**, 634.

[6] Göhring, *Physikal. Zeitsch.*, 1914, **15**, 642.

[7] Göhring, *loc. cit.*

[8] Hahn and Meitner, *Physikal. Zeitsch.*, 1913, **14**, 752.

[9] Antonov, *Phil. Mag.*, 1911, [vi.], **22**, 419; 1913, [vi.], **26**, 1058; Fleck, *ibid.*, 1913, [vi.], **25**, 710; Soddy, *ibid.*, 1914, [vi.], **27**, 215; Hahn and Meitner, *Physikal. Zeitsch.*, 1914, **15**, 236.

There is reason to believe that the branching proceeds from uranium-II rather than from uranium-I. The two alternatives lead to the respective values 226 and 230 for the atomic weight of actinium. Now for a group of isotopic elements it is the rule that for α-ray giving members the stability increases with increase in atomic weight, while for β-ray giving members the reverse is true. The actinium series falls in with this rule (to which, however, there are one or two exceptions) much better if Ac = 226 than if Ac = 230.[1]

Atomic Weights of Actinium and its Products.—Until pure actinium salts are prepared the chemical equivalent of actinium cannot be directly measured, and until more accurate measurements of the molecular weight of actinium emanation are obtained, the accurate atomic weight of actinium cannot be calculated from that of the emanation. If actinium arises from uranium-II, as has been supposed, it should clearly have the same atomic weight as radium, viz. 226·0 (or 226·2 if calculated from U = 238·2 and He = 4·00); on the other hand, if it arises from uranium-I, the atomic weight should be 230·0 (or 230·2). Assuming the origin of actinium from uranium-II, the atomic weights in the actinium series will be as follows:—

Element . .	Ac	RaAc	AcX	AcEm	AcA	AcB	AcC	AcC′	AcD
Atomic weight .	226	226	222	218	214	210	210	210	206

End Products in the Actinium Series.—The nature of the product arising from AcC′ by the expulsion of α-rays is quite unknown, but it should be an isotope of lead. This product, however, only arises from 0·2 per cent. of the parent actinium, the remainder of which ultimately passes *viâ* AcC by an α-ray change into AcD, thence by a β ray change into another isotope of lead. The nature of this product, AcE say, is also quite unknown, since it emits no detectable radiation. It is of great interest to determine whether AcE is stable or not. Its most probable atomic weight, as has already been explained, is 206 or 206·2, say 206·1, the next alternative being 210·1.

Now the ultimate end product of uranium through the radium series is a stable isotope of lead of calculated atomic weight 206·2 (from U = 238·2) or 206·1 (from Ra = 226·0), say 206·1. The atomic weight of "lead" extracted from uranium minerals practically free from thorium is always less than 207·2, the atomic weight of lead derived from non-radioactive sources,[2] and in the cases of (i.) a crystalline specimen of uraninite from Africa and (ii.) a crystalline sample of bröggerite from Norway, Hönigschmid and Mlle. St. Horovitz[3] have found Pb = 206·04 and 206·06 respectively, *i.e.* the value for the end product of the uranium-radium series. But if about 8 per cent. of this "lead" came from the actinium side-branch, and AcE = 210·1, the "lead" should have an "atomic weight" of 206·42. Hence, if AcE = 210·1, it is an unstable element, and disintegrates while the end product of the

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[1] Fajans, *Le Radium*, 1913, 10, 171; *Physikal. Zeitsch.*, 1913, 14, 951; *cf.*, however, Richardson, *Phil. Mag.*, 1914, [vi.], 27, 252. According to S. Meyer, Hess, and Paneth (*Sitzungsber. K. Akad. Wiss. Wien*, 1914, 123, ii. *a*, 1459), when the logarithms of the radioactive constants (λ) are plotted against the logarithms of the ranges of the α-rays at N.T.P. the points lie on a straight line which cuts the corresponding line for the uranium series at UII, indicating the genesis of actinium from that element.

[2] Richards and Lembert, *J. Amer. Chem. Soc.*, 1914, 36, 1329; Maurice Curie, *Compt. rend.*, 1914, 158, 1676; Hönigschmid and Mlle. St. Horovitz, *ibid.*, 1914, 158, 1796.

[3] Hönigschmid and Mlle. St. Horovitz, *Monatsh.*, 1915, 36, 355.

	Act	D.
Symbol		
Atomic weight		
Radioactive constant $\lambda(\text{sec.})^{-1}$ . . .		-3
Period of half-change (T)		.
Period of average life (P)		.
Radiation	N	
Range of α-rays in cms. at N.T.P. . .		
Absorption coefficients of β-rays, $\mu(\text{cm.})^{-1}$.		
Absorption coefficients of γ-rays, $\mu(\text{cm.})^{-1}$.		, Pb)
Parent		
Disintegration product	E	
Chemical properties	Inte betw of la and	

* Probably 22

‡ Theoreticall

uranium-radium series accumulates. If, on the other hand, AcE = 206·1, no conclusion as to its stability can be drawn from this line of argument.

Should AcE slowly decay and emit β-rays it would pass into an isotope of bismuth, and if this were stable, the atomic weight of bismuth extracted from uranium minerals would not be 208, but would approach, probably, either 206 or 210. This is a matter that is deserving of experimental study.[1]

Detection and Estimation of Actinium.—For these topics the reader must be referred to the literature.[2]

Summary.—The properties of actinium and its disintegration products are summarised in the accompanying table.

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[1] Holmes and Lawson, *Phil. Mag.*, 1915, [vi.], **29**, 673.

[2] See, *e.g.*, Boltwood, *Amer. J. Sci.*, 1908, [iv.], **25**, 269; Meitner, *Physikal. Zeitsch.*, 1911, **12**, 1094; von Hevesy, *ibid.*, 1911, **12**, 1213; Ramsauer, *Le Radium*, 1914, **11**, 100.

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